The Development and Evaluation of Novel Techniques For the Study of Polymerisation and Degradation Reactions

by

Geoffrey John Sutton

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Summary

The work described in this thesis has been divided into two sections, designated I and II.

Section I deals with the feasibility of utilising the known chemistry of cationically initiated olefinic polymerisation reactions in a metal coating application. The ultimate aim of this work is to harness reactions of this type, which are potentially very fast, to obtain a polymer system capable of undergoing rapid cross linking reactions in thin film. The development and application of a novel technique is described by means of which rapid rates of polymerisation and cross linking can be measured in thin film. In addition the results of synthetic work are presented showing how the more promising homopolymerisation systems based on cyclic dienes can be utilised in cross linking reactions.

Section II describes the development and application of equipment, incorporating some novel features, for use in thermal degradation studies of polymers. The technique combines thermogravimetric, gas evolution and gas liquid chromatographic analyses, the latter being coupled to in-line filament and Curie point pyrolysis techniques. A further technique is incorporated which enables rheological studies of residual polymer in the melt state to be carried out during degradation processes. The potential applicability of the above equipment to the study of the thermal degradation of cross linked polymers in the context of work described in Section I is referred to. In order to demonstrate the scope of

application of the equipment the detailed study of the thermal degradation of a series of poly-α-esters in the melt state is described.

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I hereby declare that this thesis has not been submitted for any other award and that no part of the work described was done in collaboration except where specifically stated.

G. J. Sutton.

G.J. Sutton

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S.I. Units

Experimental results presented in Section II are, for convenience, expressed in c.g.s. units to facilitate direct comparison with results given in the series of papers included at the rear of the thesis.

Conversion to the appropriate S.I. Units can be carried out as necessary using the following relationship:

1 Calorie $\equiv$ 4.184 Joules.

Location of Plates

SECTION I

The Development and Evaluation of Rapid Cross Linking Systems: A Preliminary Study

CHAPTER 1

Introduction

The work presented in this section is concerned with the feasibility of utilising the known chemistry of cationically initiated olefin polymerisation reactions in a metal coating application. The particular feature of interest in this respect is the potentially high speed of polymerisation of such systems and the possibility of harnessing this to obtain a material capable of undergoing rapid crosslinking reactions in thin film. This is in effect a feasability study and was commissioned by the Metal Box Company.

The ultimate aim of the work presented in this section was therefore, to develop and apply a technique capable of studying the rates of polymerisation and polymer crosslinking reactions in thin film. Because no suitable technique was available a large section of work was taken with the development of such a technique the need for which was established as a matter of prime importance during the initial stages of work concerned as it was with the development of fast curing systems.

The application of fast curing systems to a conventional metal coatings process would enable industrial equipment used in these areas at present to operate at higher throughput or under more economical conditions in a manner illustrated as follows.

Equipment which uses conventional coating systems generally operates as a sheet line which consists of two main sections:-

a) a roller coating device which rapidly coats the sheet metal with a suitable resin system, and

b) a tunnel oven in which the resin system is cured under optimum conditions.

The tunnel ovens are generally operated within the temperature range of 150-200°C, conventional coating systems having typical stoving times of between 5 and 10 minutes under these conditions, so that for an economically viable sheet line a coating line 95 feet in length would be required. For a strip (i.e. continuous metal) line, assuming equivalent throughput cure times in the order of 5 to 10 seconds would be necessary to obviate the need for an impossibly long oven.

If cure times of coating systems can be reduced to around 10 seconds existing sheet lines could be run at higher throughput under present operating conditions or alternatively these lines could be converted to the somewhat more convenient striplines operated at an equivalent throughput to the sheet lines used at present. If the cure times of coatings systems could be reduced below the 5-10 second range the throughput of strip lines could be increased to a level beyond that of the present sheet lines thus affording the dual advantage of high throughput and convenience of operation.

The ultimate goal would be achieved with the development of fast curing room temperature coating systems which would yield the advantages of higher throughput, convenience of operation and lowering of operating temperature.

The effective development of fast curing systems for the type of application outlined above depends initially on the successful development of a suitable laboratory technique which is capable of quantitatively distinguishing between the reactivity of systems in terms of their rates of polymerisation or cross linking in thin film. The constraints placed on the development of such a technique, for example, choice of measuring system, sample environment, sample geometry etc. together with the constraints placed on the nature and extent of literature survey work were established in the light of the type of chemical system ultimately chosen for this study together with the basic approach decided upon for the development of a fast curing system.

Conclusions based on extensive discussions concerning the type of system which should be investigated and the general approach needed for the solution of the problem, reinforced the validity of two important proposals which form the basis on which work presented in this section was carried out. These proposals can be summarised as follows:-

i) that the cationic type of polymerisation should be the type of reaction which will be investigated, and

ii) that the basic approach to the problem of developing fast curing systems should be based in the first instance on acquiring a fast cationic homopolymerisation system through original development or through discovery of existing reactive systems within the available literature. This stage of the work would be followed in the second instance by an investigation into the applicability and performance of such systems in cross linking reactions carried out in conjunction with formed backbones. These could be of the epoxy or polyester type and would contain suitable, reactive cross linking sites within or pendant to the backbone.

The reasoning behind the feasability of proposal i) outlined above stems from the fact that although individual propagating steps involving cationic species and monomer are generally slower than corresponding reactions involving free radicals the fact that a higher concentration of active species can be built up in cationic systems, without increasing the rate of bimolecular termination reactions, a much faster rate of conversion to polymer can ultimately be obtained.

Both proposals establish the basis firstly for carrying out a literature survey (discussed in detail in Chapters 2.1 and 2.2) and secondly for establishing the constraints necessary for the development of a suitable laboratory technique (referred to above and discussed in detail in Chapter 3.1). The second part of proposal ii) intimates the synthetic work which would necessarily follow from the successful development of a fast homopolymerisation system. Such work entails the grafting of suitable reactive sites onto formed backbones (e.g. an epoxy or polyester chain) or alternatively developing purpose synthesised backbones, which as stated in the proposal, would contain reactive sites within or pendant to the backbone. These sites would as far as possible be structurally identical to those monomers which are found to be particularly reactive. By using such monomers as cross linking agents it was hoped that the above backbone structures could be rapidly cross linked and that these reactions would exhibit rates of the same order as the corresponding homopolymerisation reactions. This aspect of the work is discussed in detail in Chapters 6 and 7.

The use of cationic vinyl polymerisation as a cross linking reaction depends upon the incorporation of unsaturated monomer residues having the appropriate structure either in the backbone of the uncrosslinked main chain or pendant to it. Literature survey work presented in this chapter is accordingly divided into two main sections.

The first section (2.1) concentrates on the correlation of information contained in the literature on the relationship between monomer structure and reactivity.

Because of the obvious importance of balancing the reactivity of cross linking sites, in or pendant to the backbone, and the cross linking agent literature work has been extended to include a second section (2.2), summarising available information on the relevance of propagation rate constants and reactivity ratios to the development of a rapid cross linking system. Some reference is also made in this section to the importance of such parameters in assessing monomer reactivity.

Considerable attention has been paid in the literature to the preparation of polymers via the cationic polymerisation of various monomers and the subsequent evaluation of the properties of the polymers obtained. Although little really systematic work has been carried out on establishing the relationship between monomer structure and properties of the final polymer, a summary of the work carried out in this area has been included in a third section (2.3) which gives some idea of the nature and extent of such work and provides some predictive knowledge about the type of polymer certain monomers are likely to produce. This knowledge may be important in the later stages of the development of the rapid curing surface coating in which certain critical properties will be required particularly in terms of flexibility, chemical resistance and adhesion.

CHAPTER 2

Literature Survey

2.1 Literature Relating to Chemical Types and Reactivity in the Cationic Polymerisation of Vinyl Monomers

Introduction

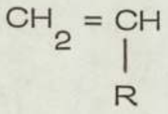
In order to determine to what extent particular cationic systems had been investigated in terms of the effect of the type and concentration of monomer, catalyst, co-catalyst and solvent on reaction rate, a literature survey was carried out on cationic vinyl polymerisation over the period 1960 to the present.

The monomer types which undergo cationic polymerisation and which may have potential application to this work can be conveniently summarised as follows,

1) Olefin monomers e.g. alkyl-1-substituted and alkoxy-1-substituted mono olefins.
2) Carbonyl monomers e.g. aldehydes, ketones, and substituted ketenes.
3) Cyclic ethers and related monomers, e.g. 3-, 4-, and 5 membered epoxy alkanes, e.g. epoxides, oxancyclobutane and tetrahydrofuran.
4) Cyclic esters and amide monomers, e.g. lactones, lactides (cyclic dimers of α hydroxy acids) and cyclic diesters of dibasic acids and glycols.
5) Miscellaneous monomers, e.g. cyclopropanes, diazoalkanes, cyclic dienes.

For a given cationic polymerisation system i.e. monomer, catalyst, co-catalyst and solvent, the rate of polymerisation can be drastically increased merely by increasing the concentration of catalyst or initiating species. Bearing in mind the types of catalyst generally used in these reactions, however, coupled with the likely end use to which any viable coatings system ultimately developed is likely to be put, this latter approach towards the development of a rapid curing system has obvious drawbacks. A survey which concentrates on the search for monomer types which are reactive primarily by virtue of their structure at low catalyst concentrations was therefore considered justifiable. Since variables such as the type of solvent together with the type and concentration of catalyst and co-catalyst can have a profound effect on the polymerisation rates, reference to such variables is also included where appropriate.

The field of cationic polymerisation has been so widely studied that it was decided to restrict the survey in the main to olefin monomer types, and mono α olefins of the general form I were taken as the basis on which to carry out this part of literature survey work.



$CH_2=CH(R)$

where R = alkyl,
alkoxy,
aryl,
substituted aryl.

I

Literature Survey

A general and basic account on cationic polymerisation is given by Plesch$^{(1,2)}$ and Lenz$^{(3)}$.

Absolute comparison of the reactivity of various monomer types dealt with in the literature was found to be an involved process. Propagation rate constants, k_p quoted for various systems were often determined under different sets of conditions and in this respect this field has been widely but unsystemmatically studied. In isolated instances k_p values have been quoted for the cationic polymerisation of a series of monomers under identical conditions thus the k_p values quoted for the polymerisation of a series of parasubstituted styrene monomers(4) indicate the following order of reactivity for the parasubstituents (see Table 3, p 35);

$OCH_3 > CH_3 > H > Cl$.

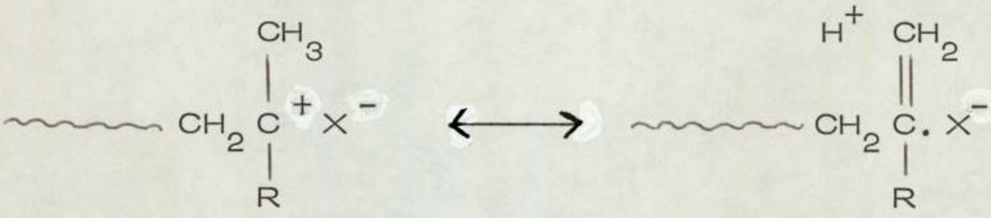
This order of reactivity imparted to styrene by these substituents also follows from the theoretical consideration of their electron releasing ability.

Ortho substituents reduce the rate of polymerisation irrespective of whether they exhibit favourable inductive resonance effects(5) indicating that for this type of substitution steric effects are the controlling factors.

An order of reactivity has been established employing localisation energy calculations for a series of common monomers(6) as follows;

Ethyl vinyl ether > isoprene > p-methoxystyrene > α-methyl styrene > isobutene > 1,3-butadiene > styrene > propylene > ethylene.

Resonance energy calculations indicate that although phenyl group conjugation is about as equally important in the case of carbon free radicals as it is for carbonium ions, the resonance stabilisation imparted to carbonium ions by methyl group conjugation (II) is considerably greater than that imparted to carbon free radicals:



$$\sim\sim\sim CH_2\overset{CH_3}{\underset{R}{C}}{}^{+}X^{-} \longleftrightarrow \sim\sim\sim CH_2\overset{H^{+}\;CH_2}{\underset{R}{C}}.\,X^{-}$$

II

Such theoretical predictions are not always supported by experimental observations as shown by the reactivity series (III) obtained for the acid catalysed addition reactions of methanol to a number of olefins.

α methylstyrene $>$ isobutene $>$ isoprene(7)

III

In anionic and free radical propagation reactions, copolymerisation studies indicate that the most reactive monomer is the one which forms the least reactive radical or anion because of resonance stabilisation. This relationship does not hold for the cationic polymerisation of a series of styrene derivatives listed in Table 3, p 35, where the order of reactivity of the respective carbonium ion derived from the monomers was found to be the same as that for the monomers themselves in the propagation step(4). In contrast, the normal inverse relationship, namely, the more reactive the monomer the less reactive its ion, held for the two vinyl ethers listed in Table 3. The abnormal behaviour exhibited by the styrene derivatives has been attributed to polarisation of the

π electrons of these structures which overrides any contribution to reactivity from resonance stabilisation of the incipient carbonium ion in the transition state(8).

Russian workers, Lyudvig et al(9) studied the copolymerisation of the following systems using stannic chloride as the catalyst

a) β-methyl styrene-styrene,

b) isobutylene-styrene,

c) vinyl butyl ether-styrene.

The copolymerisation constants determined for the systems a) and b) were as follows:

a) r_1 (styrene) = 0.05, r_2 (β methyl styrene) 2.90

b) r_1 (styrene) = 0.17, r_2 (isobutylene) 1.60.

Induction periods were found to be inversely proportional to the concentration of stannic chloride and to the concentration of the more reactive component and independent of the initial concentration of styrene. Temperature and dielectric constant and polarity of solvent all affected induction periods. Water and hydrogen chloride were found to form a complex with stannic chloride which resulted in a lowering of polymerisation rates.

These workers also studied(9) the mechanism of the elementary reactions which occur in cationic polymerisation. They copolymerised styrene with small quantities of α-methyl styrene, isobutylene, isoprene and butadiene, and showed that the ease with which these monomers formed complexes with the catalyst was as indicated below:

α methyl styrene $>$ isobutylene $>$ isoprene $>$ butadiene, styrene

The sharp increase in the rate of initiation observed in the polymerisation of styrene when small amounts of more active monomer were added at $0^{o}C$ or when pure styrene was used at $40^{o}C$, was thought to be caused by the formation of a double π complex from a monocomplex consisting of a catalyst molecule and a monomer molecule containing solely one substituent at one carbon atom of the double bond. It was considered feasible that such a double bond complex could be formed either by attaching a molecule of the same monomer at elevated temperatures or a molecule of the more active monomer to the monocomplex. The formation of a double complex between a catalyst molecule and two molecules of a monomer containing two substituents on one carbon atom of the double bond was found to be difficult due to steric hindrance.

A series of cationic polymerisation catalysts (IV) whose catalytic activity was studied by Scholven(10) for the polymerisation of ethylene, propylene and 4 methyl 1 pentene.

$Ti(OPr)_2$, $VOCl_3$, Et_2AlCl, $(isoBu)_2AlF$, Et_3Al, Pr_3Al and Bu_3Al

IV

These catalysts were found to possess higher activity than known catalysts containing boron trifluoride.

A catalyst has been prepared from antimony pentafluoride (1 mole) in trichloro trifluoro ethane to which 5 moles of propylene oxide had been added. This catalyst(11) was found to give polymerisation rates in the order of two hundred times greater than for tetrafluoroborate catalysts when used for the cationic polymerisation of monomers of the general form V.

$$CH_2 : CHOR \text{ , where } R = \text{alkyl}.$$

V

A patent submitted by Doi(12), describes the preparation of rapid hardening phenol formaldehyde resins. The title resins were prepared by treating trihydric phenols with formaldehyde in the molar ratio 1:0.7-0.9 respectively, in the presence of non ortho oriented catalyst at a pH of less than 3. When more than 60% of the formaldehyde had been consumed, 5% w/w, based on the amount of reactants of ortho oriented catalyst was added. The novolak resin thus produced was mixed with hexamine in the ratio 100:12 respectively. This system gave a gel time of 30 seconds at 150°C.

The effect of pressure on the rate of cationic polymerisation of some vinyl ethers has been studied by Hamann and co workers(13). They examined polymerisation reactions with and without solvent (ether) at pressures of $\leqslant$ 10,000 atmospheres using iodine as catalyst. They observed an increase in the rate of initiating reactions at higher pressures.

Schriesheim(14) studied the base catalysed proton migration rates of a series of terminal olefins of varying structure in a homogeneous system using potassium tert-butoxide/dimethyl sulphoxide between 35 and 55°C. He studied a considerable number of acyclic olefin structures of the type (VI) together with cyclic structures

$$CH_2 = CR_1CHR_2R_3$$

VI

Schriesheim found that methylene cyclobutane and methylene cyclopentane give higher proton migration rates than the acyclic olefin,2-ethyl 1 butene but established that methylene cyclohexane is thirty times less reactive in this respect than 2 ethyl 1 butene.

Iwasaki(15) studied the catalytic activity of a series of magnesium halides in the cationic polymerisation of vinyl ethers. He used these halides in conjunction with dioxan (i), tetrahydrofuran (ii), and diethyl ether (iii). The molecular weight of polymers decreased as indicated below for the series of catalysts studied:

$$\mathrm{MgBr_2\,2(i)} > \mathrm{MgF_2.HF} > \mathrm{MgCl_2} > \mathrm{MgBr_2 2(ii)} >$$

$$\mathrm{Mg_2 2\ (iii)}$$

The reactivity of a series of substituted vinyl ethers was also established (VII) using $\mathrm{MgBr_2 3(ii)}$ as catalyst;

isopropyl > ethyl > isobutyl > methyl vinyl ether

VII

Neels(16) determined the copolymerisation parameters for glycidyl ether/vinyl monomer systems using boron trifluoride etherate as catalyst in dioxan at temperatures between 40 and 50°C. On copolymerisation with styrene, the respective parameters were found to be 1.8 for methyl glycidyl ether, 0.75 for ethyl glycidyl ether and 4.9 for propyl glycidyl ether. For the system methyl glycidyl ether/isobutyl vinyl ether, the parameters were found to be 1.03 and 7.3 respectively.

Kanoh(17) presented the relationship between the reactivity of monomer and corresponding propagating species under steady state conditions for cationic polymerisation reactions. Theoretical considerations(18) were developed with respect to the mechanism of the propagation reaction involved and a two step process was postulated as indicated below; (a and b),

a) the formation of a covalent bond between polymer cation and β carbon atom of attacking monomer, and

b) chain formation stemming from the interaction between the ion pair of the propagating species and monomer.

Further studies by Japanese workers include work on evaluating the effect of solvent on k_p values(19). Styrene derivatives were polymerised using iodine as catalyst in various solvents and k_p values were found to increase markedly as the polarity of solvent was increased. The solvating power of a monomer was found to be an important factor in cationic copolymerisation reactions where the copolymer formed was found to contain a higher proportion of the monomer with the minimum solvating power. The dissociation of the gegenion, formed from growing chain ends (or monomer) and initiator, by the attacking monomer was thought to be the rate determining step in the propagation reaction particularly when weak Lewis acids such as iodine were used as initiators.

Some of the more systematic work on monomer structure/reactivity relationships in cationic polymerisation was carried out by Okamura and co workers in their studies of αβ disubstituted olefins(20). The behaviour of this type of monomer in cationic polymerisation reactions was discussed under the following headings;

a) the steric hindrance of the β substituent,

b) the electronic effect of the β substituent on monomer reactivity.

c) the reactivity of geometric isomers of a monomer.

d) the stereospecific polymerisation of geometric isomers.

They found, for example, that the cis isomer of propenyl butyl ether is both 1.5 times more reactive than the trans isomer and produces highly crystalline polymer, using a heterogeneous catalyst in inert solvent at room temperature.

Okamura(21) also studied the radical induced cationic polymerisation of cyclic ethers using benzoyl peroxide, γ and ultraviolet radiation. He polymerised the following monomers, trioxan (iv), tetroxane (v), 3,3 bis (chloromethyl)cycloxabutane (vi), diketene (vii), and β propiolactone (viii) which all readily formed polymers in the presence of ionising radiation provided the reactions were carried out in the solid state. Radiation induced polymerisation of (iv), (v), (vi) and (vii) took place in the presence of cationic catalysts, but did not occur in the absence of air or peroxy catalysts and was inhibited by hydroquinone and 1,1-diphenyl 2 picryl hydrazyl.

The copolymerisation of propenyl butyl ether (ix) and vinyl butyl ether (x) was also studied by the above workers(22). They showed that both isomers of (ix) were more reactive than (x) which is demonstrated by the monomer reactivity ratios they obtained for the respective comonomers. These values are summarised in Table 1 below.

Table 1

Monomer reactivity ratios (MRR) calculated from cationic copolymerisation studies on cis and trans propenyl butyl ether and vinyl butyl ethers in methylene chloride using BF_3 etherate as catalyst at $-78^{\circ}C$.

Comonomer M_2	MRR value for vinyl butyl ether, r_1	MRR value for the propenyl butyl ether r_2
cis propenyl butyl ether	0.5 ± 0.2	4.0 ± 1.0
trans propenyl butyl ether	0.8 ± 0.3	2.3 ± 1.0

From around 1967 onwards considerable activity from Japanese workers is evident in their studies on monomer structure/reactivity relationships in cationic polymerisation. Okuyama(13,24) in a series of papers on the structure and reactivity of α β unsaturated ethers looked at the cationic polymerisation of alkenyl alkyl ethers. Relative polymerisabilities of geometric isomers of various alkenyl alkyl ethers were established from copolymerisation studies. In accord with the findings of Okamura(20) copolymerisation studies at -78°C using methylene dichloride as the solvent with boron trifluoride etherate as catalyst, revealed that cis isomers were more reactive than corresponding trans isomers. Primary alkyl substituents in the β cis position in vinyl ethyl ethers were found to enhance monomer reactivity but substitution of bulky alkyl groups in the same position resulted in a lowering of monomer reactivity due to the steric hindrance effects of such groups. Monomers substituted with isobutyl or dimethyl groups in the β cis position showed little tendency to homopolymerise.

In heterogeneous polymerisation reactions it was found that a β methyl group on the vinyl ether, whether in the cis or trans position, greatly reduced monomer reactivity possibly because of the steric hindrance of such groups towards adsorption of monomer on the catalyst surface.

Eley(25) carried out the iodine catalysed polymerisation of butyl vinyl ether and studied the kinetics of the polymerisation in three different solvents ethylene dichloride, diethyl ether, and carbon tetrachloride using infra red and dilatometric techniques. He found that both methods gave similar results which corresponded to the third order equation (1).

$$R_p \simeq k[M][I]^2 \qquad \ldots\ldots \quad 1)$$

The rate constants k for reactions carried out in ethylene dichloride, diethyl ether and carbon tetrachloride were 10^5, 400, and 501^2 mole^{-2} sec^{-1} respectively showing that rate constants are markedly increased by increasing the polarity of the solvent.

Higashimura(26) compared the cationic polymerisabilities of t-butyl cis propenyl ether (xi) and t-butylvinyl ether (xii) in the presence of boron trifluoride etherate. In copolymerisation studies using these monomers (xi) was found to be more reactive than (xii) although (xi) gave both low polymerisation rates and low molecular weights in homopolymerisation reactions. The introduction of methyl groups into the β position of vinyl ethers already possessing such bulky alkoxy groups as t-butoxy groups, decreased monomer reactivity due to steric effects. Crystalline or amorphous polymers derived from (xi) were obtained by carrying out polymerisation reactions in toluene or methylene dichloride respectively.

Mizote and co workers(27) studied the effects on monomer reactivity of the β methyl group present in β methyl styrene and in monomers of the general form (VIII).

MeCH:CHOR

VIII.

They compared the monomer reactivity ratios of the above monomers and β unsubstituted monomers. The homopolymerisation rate of β substituted monomers (VIII) was depressed some 90–95% when compared with styrene due to steric repulsion of the β methyl group.

Higashimura(28) extended this study when he carried out the copolymerisation of propenyl alkyl ethers with vinyl ethers each having the same alkoxy groups. He found that in contrast to the behaviour of α methyl and β methyl styrene propenyl alkyl ethers with unbranched alkoxy groups (ethyl or butyl propenyl ethers) were more reactive than the corresponding vinyl ethers. Propenyl alkyl ethers with branched alkoxy groups at the α carbon (isopropyl or t-butyl) were however found to be less reactive than the corresponding vinyl ethers. In general cis isomers were observed to be more reactive than trans isomers regardless of the kind of alkoxy group and solvent used.

Higashimura(29) also studied the cationic polymerisation of butenyl ethers of the general form (IX) using boron trifluoride etherate as the catalyst.

$$\mathrm{EtCH{:}CHOR}$$

IX.

Low molecular weight polymers were easily produced from derivatives of IX where R = Et (xi), isoPr (xii) or Bu (xiii) despite the presence of the ethyl group in the β position. Copolymers of (xi), (xii) and (xiii) with their corresponding vinyl ethers were prepared when it was found that cis isomers of the former monomers were more reactive than the corresponding vinyl ethers while the trans isomers were less reactive than the vinyl ethers and also the cis isomers of (IX).

Further work was carried out by these workers when they studied the effect of alkoxy groups on the polymerisability of alkyl vinyl ethers (X)

$$CH_2 : CHOR$$

X.

Reactions were carried out at $-78^{o}C$ in toluene or methylene chloride using boron trifluoride etherate as catalyst. The relative reactivity of the series of vinyl ethers studied was calculated from the rate of monomer consumption as measured using gas chromatography. They found the following reactivity order for a series of R substituents irrespective of solvent used;

$$tBu > isoPr > Et > Bu > isoBu > Me.$$

The order of reactivity determined for the ethyl, butyl and isobutyl substituents was thought to be unrelated to the polarity of the resulting alkoxy group. The results suggest that steric as well as polarity effects influence the ultimate reactivity of a particular monomer.

Mamedov(30) studied the ionic polymerisation of the following monomers, 1-pentene (xiv), methyl-1-butene (xv) and 3-methyl-1-butene (xvi) using titanium tetrachloride/triethyl aluminium catalyst. The reactivity of these monomers was shown to be in the following order:

$$(xiv) > (xvi) > (xv).$$

The cationic polymerisation of ortho isopropyl styrene was carried out by Aso et al(31) using radical, anionic and cationic initiators. They found the ortho substituted styrene to be less reactive than the para substituted monomer and suggested that this was due to steric hindrance of the ortho substituent.

The study of the cationic polymerisation of α β substituted olefins was extended by Higashimura(32) in his work using 2 chloroethyl propenyl ether (xvii) and its geometric isomers and the corresponding vinyl ether. The rate of consumption of monomer (i.e. monomer reactivity) decreased as follows:

cis (vii) $>$ 2 chloroethyl vinyl ether $>$ trans(vii).

The polymerisation rates(33) of ortho, meta and para-hydroxystyrene determined in solution using boron trifluoride etherate catalyst were found to decrease in the order;

p hydroxystyrene $\gg$ o hydroxystyrene $>$ m hydroxystyrene.

Styrene itself has been polymerised in the presence of π electron acceptors using boron trifluoride etherate as catalyst(34). The polymerisation rate was found to increase as the efficiency of the electron acceptor improved. The activity of electron acceptors used in terms of their effect on polymerisation rate increased as indicated below:

1,3,5 trinitrobenzene $<$ chloranil $<$ tetracyano ethylene.

Polymerisation rates increased with higher concentrations of electron acceptor but a limit was reached when further addition of the latter caused a lowering of rate thought to be due to complex formation between the electron acceptor and monomer.

Okuyama(35) studied the cationic polymerisation of cis (xviii) and trans (xix) β chlorovinyl ether together with the copolymerisation of (xviii) with vinyl isobutyl ether (xx). Reactions were carried out in methylene chloride at $-78^{\circ}C$ using boron trifluoride etherate catalyst. Copolymerisation studies yielded monomer reactivity ratios of $\sim$ 1.39 and 0.28 for (xviii) and (xix) respectively. Monomer (xviii) was found to be less reactive than (xix) by a factor of $\sim$ 26. The low reactivity exhibited by (xviii) and (xix) was explained by the reduction of electron density on the β carbon atom by the inductive effect of the chlorine substituent.

The polymerisation of diolefins has been studied by Anzai(36) using catalyst systems based on Group VIII compounds and Lewis acids. In the polymerisation of mono-olefins and diolefins using a catalyst based on nickel carbonyl, $Ni(CO)_4$ and a Lewis acid, monomer reactivity was found to increase as -e values decreased.

The polymerisation kinetics for the cationic polymerisation of styrene, acenaphthylene and some epoxides, have been examined by Guisti et al(37). They review the polymerisation mechanisms for such reactions (25 references) and used the following catalyst types in their work; perchloric acid, sulphuric acid, iodine, boron trifluoride etherate, Ph_3 CS b CL_6 and $PhCH_2$ $SbCl_6$.

The polymerisation of α olefins using anionic catalyst systems has been reviewed(38). The following catalysts were included in the survey:

a) heterogeneous catalysts e.g. $TiCl_3$, Et_2AlCl, VCl_3, Et_2Zn and Et_3Al, and

b) homogeneous catalysts containing VCl_4 and vanadium acetyl acetonate.

A further review by Erusalimskii(39) summarises information on the mechanism of the cationic polymerisation of vinyl monomers for the period 1964 to 1966. The review deals mainly with initiation, chain propagation and isomerisation processes which constitute the overall polymerisation process.

Higashimura(40) carried out further studies on the cationic polymerisation of α β disubstituted olefins and attempted to elucidate the propagation mechanism for cationic polymerisation of vinyl ethers and β substituted vinyl ethers by extending Hückel's suggestions for the carbon-carbon double bond formation. Higashimura, therefore, proposed a model based on the electronic stabilisation energy arising from delocalisation of electrons from the occupied orbital of a monomer to the vacant orbital of a carbonium ion. This type of consideration effectively explained the relative reactivities of vinyl ethers and β substituted vinyl ethers observed in copolymerisation studies using boron trifluoride etherate as catalyst.

The use of triphenyl methylcycloheptatrienyl cations as initiators for cationic polymerisation reactions in establishing the absolute reactivity of free ions and ion pairs as propagating intermediates was studied by Ledwith(41) for the polymerisation of vinyl alkyl ethers, N vinyl carbazole and tetrahydrofuran. He found that free ions were much more reactive than ion pairs in most cases. The 'free ion' polymerisation of N vinyl carbazole in methylene dichloride was found to proceed 10^5 times faster than the corresponding polymerisation of isobutyl vinyl ether.

Anton(42) and Caillaud(43) compared the reactivities of the following monomers based on indene; 5 methyl, 6 methyl, 7 methyl, 5,7 dimethyl and 4,6,7 trimethyl indenes. They showed that 5 methyl and 6 methyl indene gave high molecular weight polymer and established the following reactivity order for the above series of monosubstituted indenes:

6 methyl indene $\gg$ 7 methyl indene $\simeq$ indene $>$ 5 methyl indene.

An extensive review containing 271 references has been carried out by Field and Lorenz(44) in which they discuss the synthesis, properties, purification chemical reactions and the polymerisation of vinyl ethers.

As early as 1926, the cationic polymerisation of cyclic-dienes was studied by Staudinger and Bruson(45) in their work on the polymerisation of cyclopentadiene (to be referred to as CPD). Imanishi(46) and Moniyama(47) revived interest in this area when they observed that the cationic polymerisation of CPD at -78°C using titanium tetrachloride/trichloroacetic acid catalyst was very fast. In this sense CPD appears to be a monomer type which could provide an important contribution in attaining the ultimate aim of this work.

Imanishi(46) and Moniyama(47) also reported on the effect of water on the final conversion of CPD to polymer. They found that as the concentration of water was increased conversion decreased and showed that this was due to two effects namely deactivation of catalyst and deactivation of growing chain ends both due to the presence of water.

The polymerisation of CPD is the subject of a patent submitted by Okamura and Higashimura(48).

Imanishi et al(49) carried out further studies on the CPD, stannic chloride/trichloroacetic acid system when they attempted to characterise factors which determined stationary or nonstationary conditions. They compared the polymerisation of the above system(46, 47) with the polymerisation of systems based on methyl cyclopentadiene (to be referred to as MCPD)(50) and systems based on cyclohexadiene (to be referred to as CHD)(51). Using titanium tetrachloride/trichloroacetic acid as the catalyst for the polymerisation of CPD and stannic chloride/trichloroacetic acid as the catalyst for the polymerisation of CHD, these workers found that the initiating reaction in each case was so fast that non stationary state conditions prevailed. CHD polymerised using boron trifluoride etherate as catalyst however, produced stationary state concentration of growing species.

Kinetic studies on the cationic polymerisation of MCPD were carried out in 1968 by Kohjiya et al(52) where they found that MCPD was generally about ten times more reactive than CPD. It was suggested by these workers that the high reactivity of MCPD and other reactive cyclic dienes is due to the high stability of the cycloalkyl cation derived from corresponding monomers.

Aso(53) studied the cationic polymerisation of 1,3 dimethyl cyclopentadiene and presented a general mechanism for the cationic polymerisation of cyclopentadiene derivatives.

Hara et al(54) established the order of reactivity for 1-vinyl cyclohexene and cis and trans 3 methyl 1,3 pentadiene, which was as follows:

1 vinylcyclohexene > trans 3 methyl 1,3 pentadiene >
cis 3 methyl 1,3 pentadiene.

The resonance stabilisation of these monomers was found to decrease in the same order indicated above so that monomer reactivity was thought to be related directly to the stability of the corresponding carbonium ion intermediate, the more stable the latter the more reactive the monomer.

Imanishi extended work on the study of cyclic dienes when he carried out the cationic polymerisation of 1,3 cyclohexadiene(55,56) (to be referred to as 1,3 CHD) and 1,3 cyclooctadiene(57) (to be referred to as 1,3 COD) and observed that both polymerisations produced non stationary state conditions. They established the order of reactivity(XI) for a series of monomers polymerised at 0°C in methylene chloride using boron trifluoride etherate or stannic chloride/trichloroacetic acid as catalysts.

1 vinylcyclohexene > 1,3 CHD > trans 3 methyl-1,3
pentadiene > cis 3 methyl-1,3 pentadiene

XI.

Recent work by Kohjiya et al(58) has established the propagation rate constant, k_p, for CPD in toluene using titanium tetrachloride/ trichloroacetic acid as the catalyst. The k_p value quoted for this system was found to be 350 l mole^{-1} sec^{-1}(Table 2 p. 34). Vairon and Sigwalt(82) obtained a k_p value of 2,190 l mole^{-1} sec^{-1} for the polymerisation of CPD in methyl chloride using $Cl_3TiOBu.H_2O$ as the catalyst. These values have been exceeded only by the k_p value (6,300 l mole^{-1} sec^{-1}) for the isobutylene, aluminium bromide/ titanium tetrachloride, n heptane system(59).

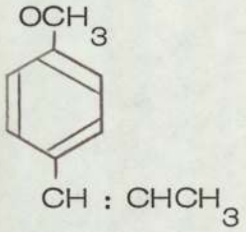
The technique generally used by the Japanese workers was based on the adiabatic calorimeter originally developed by Plesch(126).

Further recent work by the Japanese workers has included studies under the following headings:

a) The cationic polymerisation of α β unsaturated ethers e.g. 1,2 dimethoxy and 1,2 diethoxy ethylene(60).

b) The cationic polymerisation of α β disubstituted olefins, notably butenyl ethers and their stereospecific polymerisation using cationic catalysts.

c) Copolymerisation studies on anethole (XII)/p methoxystyrene and anethole/styrene systems(62).



XII

Monomer reactivity ratios obtained for the systems quoted in c) showed that trans anethole was more reactive than cis anethole when both monomers were separately copolymerised with p methoxystyrene or styrene. The trans isomer was, however, found to be less reactive than the cis isomer when the two geometric isomers were copolymerised together. It was concluded from these observations that the trans isomer reacted more readily with a less bulky, less sterically hindered growing chain end but less readily than the cis isomer with a more sterically hindered chain end. The behaviour of the geometric isomers of anethole was compared with results obtained for isomers of vinyl ethers where the cis isomer was always found to be the more reactive irrespective of the structure of the growing chain end.

The cationic copolymerisation of tetrahydrofuran with propylene oxide has been studied by Alvarez(63). The monomer reactivity ratios obtained for the reaction catalysed by antimony pentachloride, were as follows:

r_1 (propylene oxide) = 1.15 and r_2 tetrahydrofuran = 0.70. The cationic copolymerisation of tetrahydrofuran with other epoxides has been studied by Hammond(64,65).

Reference has previously been made to the main components (besides the monomer) used in cationic systems (p. 7 & 8) and the effect such components can have on the reactivity of a particular cationic system has been described in various parts of the foregoing survey. Few papers have been wholly devoted to the study of the effect of single components on the reactivity of cationic systems, a short summary, therefore, of some of the work which has been carried out on the effect of solvent type and cocatalyst on reactivity is included since such components can profoundly affect the latter. Further treatment of this topic is included in Chapter 2.21 (pages 35 to 49) in which literature relating to the effect of solvent, temperature, catalyst and cocatalyst on propagation rate constant k_p, is presented.

Two interesting papers which provide good background information on solvent properties and their effect on chemical reactivity have been presented by Dack(66) and Gutmann(67).

In studies on the cationic copolymerisation of cyclopentadiene and α methylstyrene, Imanishi(68) showed that solvent had little effect on the reactivity of a particular monomer even in copolymerisation between monomers of dissimilar structure, if the stabilities of the corresponding cations are similar. He also studied the copolymerisation of isobutene and styrene(69) in mixed solvents consisting of n hexane and methylene di chloride using titanium tetrachloride as catalyst, and observed a large variation in monomer reactivity ratios depending on the solvent composition used. In n hexane the monomer reactivity ratios were found to be of the following order: r_1 (isobutene) $<$ 1 and r_2 (styrene) $>$ 1, and in methylene di chloride $r_1 > 1$ and $r_2 \doteqdot 1$. In mixed solvent systems r_1 and r_2 were greater than unity. As the dielectric constant of the solvent was increased r_1 became larger. These findings were interpreted in terms of the effect of solvent on the stability of the growing ion pair.

An early and extensive study on solvent effects in cationic polymerisation and copolymerisation was carried out by Overberger(70).

A recent paper by Czechoslovakian workers Kucera, Svabik and Majerova(71) describes the influence of water on the rate of polymerisation of styrene initiated by stannic chloride. The dependence of the overall rate of polymerisation on the concentration of water present in different media of varying polarity for the systems studied was measured at various temperatures and concentrations of monomer and initiator respectively. The overall polymerisation rate was found to reach a maximum value with increasing concentration of water, the level of the latter, which corresponded to maximum polymerisation rate, varied with the polarity of the reaction medium and other reaction conditions. The cocatalytic interaction between the initiator and water was presented as being based on solvation leading to the activation of the initiator.

Okamura and Higashimura(72) studied the polymerisation of the styrene, benzene, stannic chloride/water system and observed maximum polymerisation rates when the ratio of water to stannic chloride was equal to one. Colclough and Dainton(73) observed maximum polymerisation rates, for a similar system using 1,2 dichloroethane as the solvent, when the latter ratio referred to was equal to two. Overberger, Ehrig and Marcus(74) found that maximum polymerisation rates for the styrene system could be observed at various water:stannic chloride ratios depending on the type of solvent used.

It is evident that the extent to which studies have been carried out in the field of cationic polymerisation is enormous and for the purposes of this study unsystemmatic. An attempt has been made, however, to sift from the desultory mass of material presented in the literature, a survey which summarises the more relevant work carried out on various systems particularly that involving an attempt at correlating monomer structure with reactivity.

The important practical conclusion to be drawn from the survey presented above is that of the monomers studied to date, vinyl ethers and cyclic dienes but particularly the latter, appear to be the most promising in terms of reactivity for the aims of this work.

2.2 The Relevance of Propagation Rate and Reactivity Ratio Studies to the Formation of a Rapid Cross Linking System

Introduction

A cross linking reaction utilising a cationic type of polymerisation process has been offered as a basis on which the development of a rapid cross linking system can be initiated (Chapters 1 and 2.1). The success of such development work depends firstly on the successful development or discovery within available literature of fast homopolymerising systems and secondly on the appropriate and careful choice and siting of reactive sites, based on monomer structures used in the above systems, within or pendant to a formed backbone thus producing polymer chains which are potentially capable of rapidly cross linking.

The evaluation of both propagation rate constants, k_p, and monomer reactivity ratios (MRR) provides information for the execution of the first stage of the development work described above. The evaluation of appropriate MRR values alone provides information for the second stage of development work described, since these values enable some prediction of the behaviour between reactive sites within or pendant to a formed backbone and cross linking agent employed as to whether for example homopolymerisation of the cross linking agent is likely to take place at the expense of cross linking reactions between the latter and the site of unsaturation associated with the backbone.

Some reference has already been made, Chapter 2.1 to MRR

Table 2

The Propagation Rate Constants k_p and Activation Energies E_R for the Cationic Polymerisation of Various Systems Studied over the last 10 years

Monomer	Initiator	rate constant k_p[l mol^{-1} sec^{-1}]	Solvent	Temp. [^oC]	Activation energy E_R[Kcal mol^{-1}]	Mechanism	Literature Reference
Styrene	$TiCl_4$	6	CH_2Cl_2	30	–	–	75
	$ReCl_5$	3.73 1.69	Benzene/ CH_2Cl_2 Benzene	20	$E_R = 11.8$	stationary	75
	H_2SO_4	1.6	CH_2Cl_2	25	$E_2 = 8.5$ $E_3 = 12.5$ $E_4 = 16$ $E_5 = 13.5$	non-stationary	76
	$HClO_4$	19.7 0.0012 17.0 0.70	97.5% CH_3Cl_2 95% CCl_4 95% CH_2Cl_2 95% CH_2Cl_2	20 " " -30	$E_2 = 8.3$ $E_3 = 11.6$ $E_4 = 13.5$	non-stationary without termination	77
Isobutylene	$AlBr_3.TiCl_4$	6,300	n-heptane	-14	–	non-stationary	78
Isobutyl-vinylether	$BF_3.EtOEt$	8.3	n-hexane/ toluene	-40	$E_R = 12.5$	non-stationary	79

Continued

Table 2 Continued

Monomer	Initiator	rate constant k_p [l mol^{-1} sec^{-1}]	Solvent	Temp. [^oC]	Activation energy E_R[Kcal mol^{-1}/	Mechanism	Literature Reference
Cyclo-pentadiene (CPD)	$HClO_4$	6.7	CH_2Cl_2	75	-	non-stationary	80
		0.83	Toluene				
	$TiCl_4$. TCA	350	Toluene	-75	-	non-stationary	81
	$Cl_3TiOBu.H_2O$	2190	CH_3Cl	-20	-	non-stationary	82

and k_p values quoted in the literature for various systems. In this section of literature work the use of such parameters in accomplishing the aims of this study is discussed in more detail.

2.21 The Assessment of the Reactivity of Systems Polymerising via a Cationic Mechanism in Terms of the Propagation Rate Constant k_p.

The propagation rate constants of some cationic polymerisation systems which have been studied over the past 10 years are summarised in Table 2 (p. 34) and absolute values of propagation rate constants for several monomers determined experimentally under identical conditions(8) are given in Table 3 below.

Table 3

The Propagation Rate Constants, k_p, for Several Monomers Cationically Polymerised with I_2 in 1,2 Dichloroethane at 30°C

Monomer	Propagation Rate Constant k_p (l. mole^{-1} sec^{-1})
p-Chlorostyrene	0.0021
Styrene	0.0037
p-Methylstyrene	0.095
p-Methoxystyrene	$\sim$ 6
2-Chloroethylvinyl ether	4.8
Isobutylvinyl ether	6.5

Direct comparison of many k_p values quoted in the literature for particular monomer types is often meaningless, difficult or unreliable since these values are so dependent on temperature, solvent and concentration and type of catalyst and cocatalyst. The enormous range of different reaction conditions created by this list of variables increases the order of complication encountered in any systematic study on the effect such variables individually have on propagation rate constant so that a great deal of unsystematic work presents itself in the literature in this respect.

In many cationic polymerisation systems initiation is considered to be a spontaneous process followed by a non-stationary polymerisation to which it is difficult to apply a simple model enabling kinetic treatment of results to be carried out in a meaningful fashion and values of k_p quoted for such processes must be treated with caution.

The Determination of k_p Values

As stated above steady state conditions are not achieved for many ionic polymerisations where reaction is virtually spontaneous and can be completed in a matter of minutes or seconds. The main features which characterise a polymerisation proceeding under non-stationary conditions have been observed by workers mentioned in Table 2, as follows:

a) At low $\frac{[C]_o}{[M]_o}$ ratios the yield of polymer is limited. If $[C]_o$ is below a critical value the polymerisation process stops before all of the monomer has been consumed, the degree of conversion of monomer to polymer depending on the amount of catalyst used.

b) The molecular weight of polymer achieved decreases with increasing catalyst concentration.

c) The overall rate decreases rapidly towards the end of the polymerisation.

Burton and Pepper(83) explained the above behaviour by the assumption that chain initiation is very rapid and faster than any of the other elementary processes which they represent as follows;

A) Initiation: $M + C \xrightarrow{k_1} M^+ \text{ or } P_1^+$

B) Propagation: $P_n^+ + M \xrightarrow{k_2} P_{n+1}^+$

C) Transfer Reactions:

i) Spontaneous: $P_x^+ \xrightarrow{k_3} P_x + C$

ii) To Monomer: $P_x^+ + M \xrightarrow{k_4} P_x + P_1^+$

D) Termination: $P_r^+ \xrightarrow{k_5} P_r$

If $k_1 << k_2$ the above scheme would lead according to Burton and Pepper to a conventional stationary state chain propagation. If $k_1 >> k_2$ there can be no stationary or steady concentration of active species and hence no steady rates. Instead there will be an initial rapid reaction which will decelerate as the concentration of chain carriers initially virtually equal that of the initiator species declines according to the kinetics of the termination process. The rate of polymerisation will approach zero before all monomer has been consumed giving a definite asymptotic yield which may approach but not reach unity according to the initiator concentration and the value of k_2 / k_5.

Much of the data presented in Table 2 was obtained using Pepper's model assuming that the number of polymer chains started is equal to the initial catalyst concentration. Pepper points out that the significant quantity to be observed and calculated is the average degree of polymerisation of the whole product which can be expressed in terms of the polymer yield and total number of chains started which can be evaluated from the initiator concentration together with the effects of any transfer reactions taking place.

Chmelir and Marek(78) who obtained using Pepper's model the value for k_p of 6300 l mole^{-1} sec^{-1} for the polymerisation of isobutylene considered that their data only held for a narrow range of concentration of aluminium tribromide where polymerisation stopped before exhaustion of monomer. It was only in this particular case that they could be sure that initial initiator concentration was that given by the amount of aluminium tribromide taken.

Varion and Sigwalt(82) obtained the value for k_p of 2.19×10^3 l mol^{-1} sec^{-1} for the polymerisation of cyclopentadiene using $Cl_3TiOBu.\ H_2O$ as the initiator. They determined the maximum percentage of catalyst consumed from the degree of polymerisation, the corresponding conversion at time t, together with the number of active centres which could be calculated from the following relationship (2),

$$[M_n^+]_t = \frac{1}{k_p + k} \cdot \frac{(R_p)_t}{[M]_t} \qquad \ldots\ldots\ldots \; 2)$$

The ratio $\frac{(R_p)_t}{[M]_t}$ starts as a maximum at the beginning of the polymerisation and decreases during the reaction whereas the consumption of the catalyst increases slowly (Fig. 1, p. 40).

They conclude that in this case the formation of the active species is a continuous process but that termination is a faster process than initiation. Kohjiya$^{(81)}$ introduced into his kinetic treatment of the polymerisation of cyclopentadiene with titanium tetrachloride/trichloracetic acid, a catalyst consuming reaction for the very fast initiation step in which inactive bicyclopentadienyl titanium chloride is formed as follows, (3 and 4),

$$C + M \xrightarrow{k_1} M^+ (= P_1^+) \qquad \ldots\ldots \; 3)$$

$$C + 2M \xrightarrow{k_1'} C^1 \text{ (inactive)} \qquad \ldots\ldots \; 4)$$

They claim that the following relationship (5) holds

$$[P_o^+] = \frac{k_1 [C_o]}{k_1 + k_1' [M_o]} \qquad \ldots\ldots \; 5)$$

The Effect of Solvent on the Propagation Rate Constant, k_p

The propagating species in cationic polymerisation not only consist of free carbonium ions but also of ion pairs which

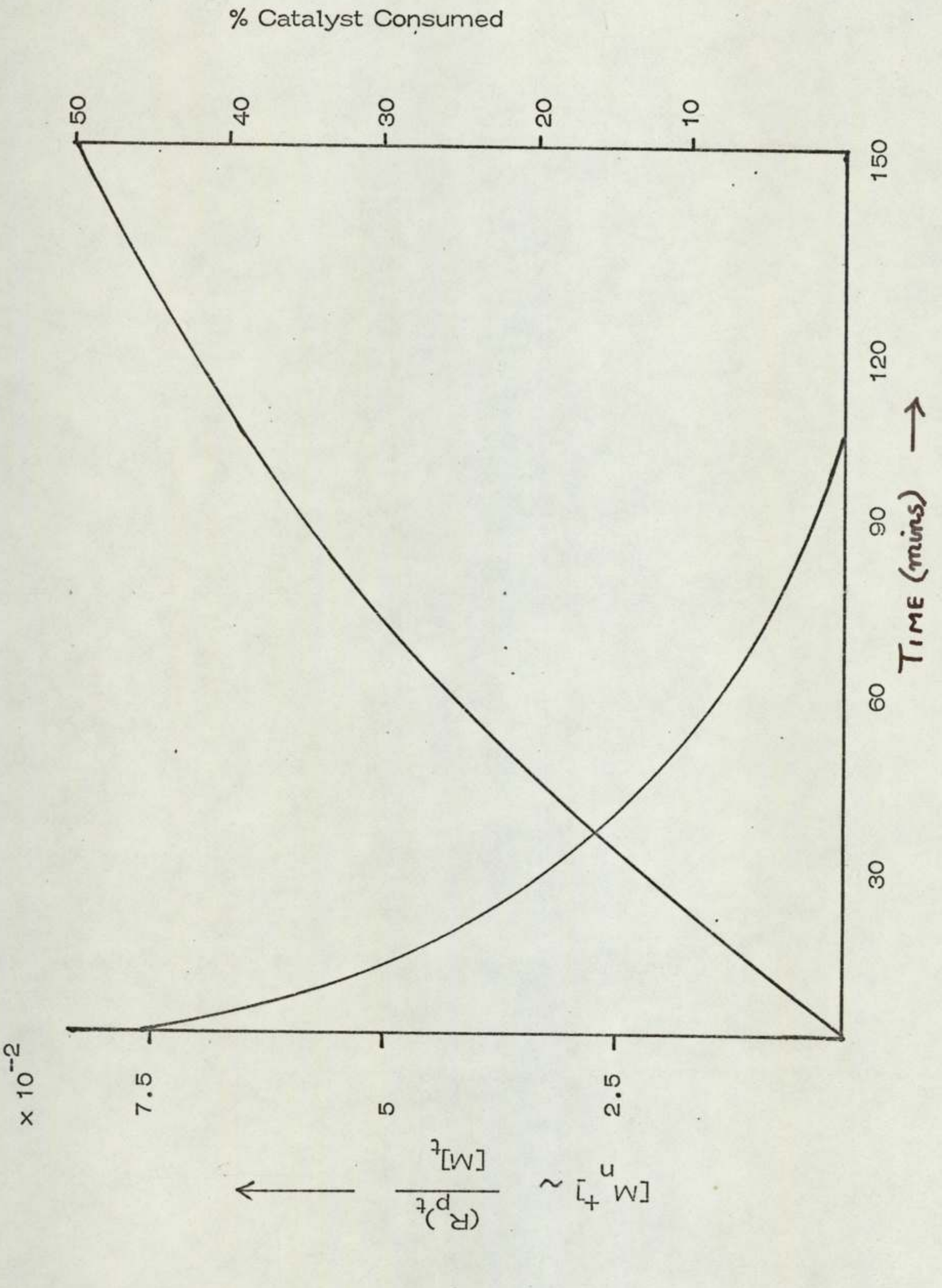
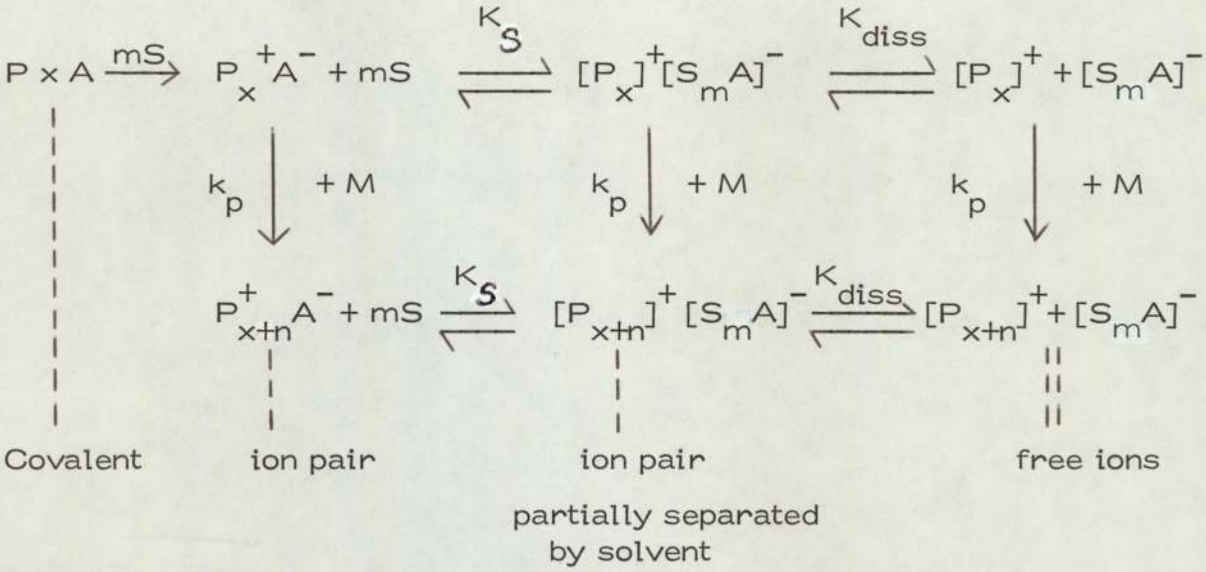

% Catalyst Consumed
50
40
30
20
10
30
60
90
120
150
TIME (mins) →
× 10^{-2}
7.5
5
2.5
$[M_n^+] \sim \frac{(R_p)_t}{[M]_t}$ →

FIGURE 1

can be more or less tightly bound depending upon the nature of the solvent as demonstrated below (XII).



XII

It is generally assumed⁽⁴¹⁾ that a free ion has the capacity to propagate a chain faster than the corresponding ion pair and that if the concentration of free ions can be increased by, for example, improving the solvating power of solvent used, an increase in k_p will ensue. This enhancement of reactivity is explained by the greater ease with which monomer insertion takes place as the separation of ion pairs is increased.

The dramatic effect a solvent can provide is demonstrated in the polymerisation of styrene by perchloric acid where a 5 fold increase in values of propagation rate constant can be induced in going from carbon tetrachloride (low dielectric constant) to 1,2-dichloroethane (high dielectric constant). (C.f. the study by Eley(25) of the polymerisation of butyl vinyl ether in the above solvents (p. 18).

The Effect of Temperature on The Propagation Rate Constant, k_p

Many polymerisation processes of the type listed in Table 2 (p.34) are studied at low temperatures and determination or prediction of the performance, especially in terms of k_p values, at room temperature and above is necessarily worthy of some consideration in our studies.

Values ranging from −5 to + 10 Kcal mole^{-1} have been observed for the activation energy E_R, of cationic polymerisations and systems having negative E_R values will exhibit decreasing polymerisation rates with increase in temperature.

The overall activation energy E_R (see equation 7) below) depends largely on the extent of the elementary reactions that can take place during the overall process of polymerisation. For systems conforming to stationary state conditions we have the following relationship (6):

$$R_p = \frac{k_i k_p}{k_t} [M] [C] [RH] \qquad \ldots\ldots \quad 6)$$

and $$E_R = E_i + E_p - E_t \qquad \ldots\ldots \quad 7)$$

Overall and detailed activation energies for some systems are listed in Table 2 (p.34). In the few cases where figures are available the detailed values for E do help in predicting the effect of temperature on rate of polymerisation. Thus where E values for termination and transfer reactions are high compared to E_p a negative energy of activation for the overall process would be expected. The handling of energetic data in this way can however be over-simplified leading to erroneous interpretation of results. Thus the establishment of equilibrium (K_s) between tight ion pairs and ion pairs partially separated by solvent can itself be temperature dependant so that should solvated ions predominate at low temperatures and ion pairs at high temperatures, polymerisation rates will by this token decrease with increase in temperature(84).

The overall activation energy for cationic systems can, as previously pointed out, vary dramatically from system to system. Hence the value reported for the polymerisation of cyclooctadiene with titanium tetrachloride between −20 and + 35°C was −10.1 Kcal mole^{-1} (85) whereas that reported for the polymerisation of isobutylene by aluminium tribromide was ~ O Kcal mole^{-1} (86). Both systems studied polymerise via a stationary state mechanism.

The Effect of the Catalyst and Co Catalyst on the Propagation Rate Constant, k_p

Initiators (or catalysts) for cationic polymerisation reactions have been classified into three general groups as follows,

1) Classical protonic acids, e.g., HCl, H_2SO_4, $HClO_4$, Cl_3COOH, H_3PO_4.
2) Lewis acids, e.g., BF_3, $AlCl_3$, $TiCl_4$, $SnBr_4$, $SbCl_3$, $BiCl_3$.
3) 'Other' cationic generators e.g. $tBuClO_4$, I_2, Ph_3CCl, ionizing radiation.

Perchloric acid is perhaps the most effective catalyst amongst the group of protonic acid initiators.

In general pure Lewis acids, MX_n, alone are not active initiators and a proton containing Lewis base, SH, capable of coordinating with the Lewis acid to form a complex protonic acid is required to generate activity as indicated below (8).

$$MX_n + SH \rightleftharpoons [SMX_n]^- \; H^+ \qquad \ldots\ldots \quad 8)$$

The Lewis base is termed the cocatalyst and can be a simple compound e.g. water but need not necessarily be a proton containing compound as indicated below (9)

$$MX_n + RX' \rightleftharpoons [RX'.MX_m] \rightleftharpoons R^+[X'MX_n]- \qquad \ldots\ldots \quad 9)$$

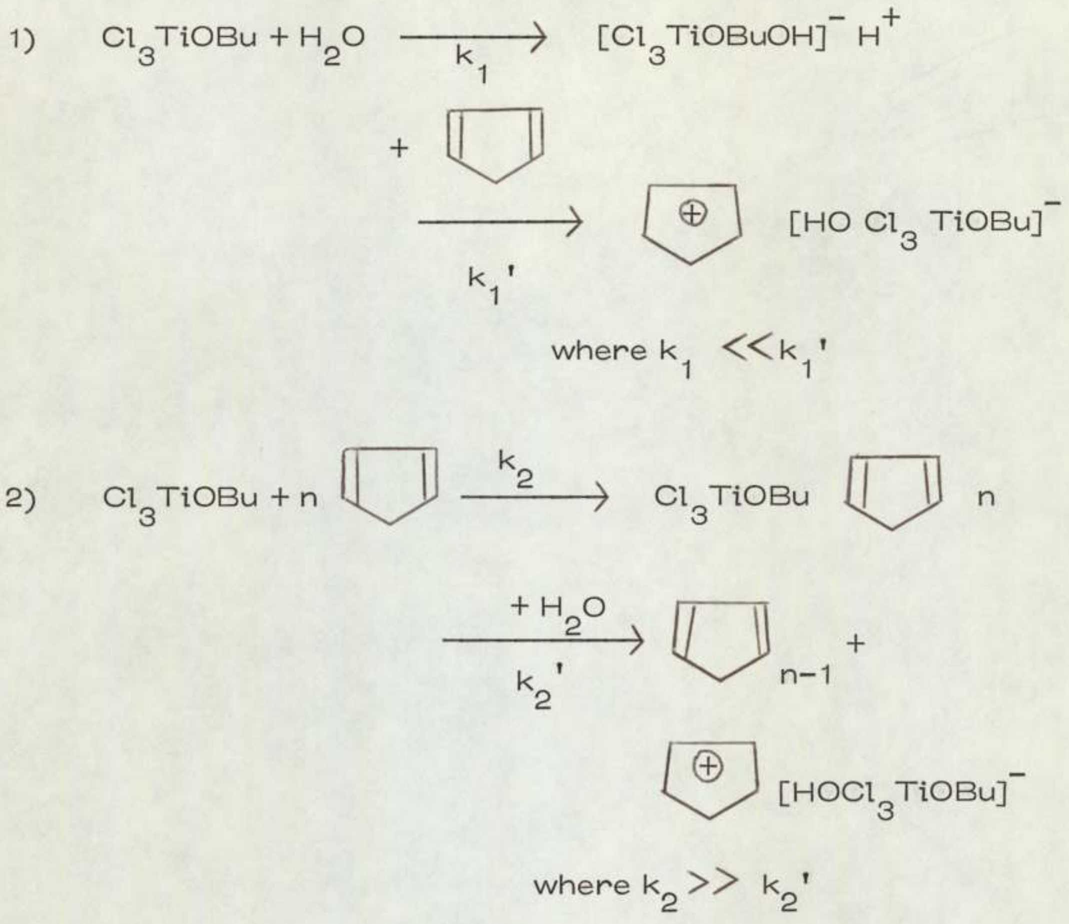
This group of initiators seem to be less active in general than the strong protonic acids (particularly perchloric acid) and for the polymerisation of styrene the efficiency of this former type decreases for the following series in the order $TiCL_4 > ReCl_5 > SnCl_4 > BF_3$. However the varieties of metal halides and co-catalysts which do or do not initiate cationic polymerisation reactions of different monomers are diverse and numerous and the problem of evaluating the reactivity of particular catalyst-cocatalyst combinations is a more complex one than that of evaluating a series of protonic acids where in general the stronger the acid, in the particular medium, the greater its activity as a catalyst. In general, however, where Lewis acids are employed catalyst activity can often be enhanced by the addition of appropriate quantities of a suitable co-catalyst. Thus in the polymerisation of isobutylene by aluminium tribromide higher catalyst activity can be achieved by addition of one of the following Lewis acids, the rate-enhancing power of a series of Lewis acids studied was found to decrease in the order indicated, $TiCl_4 > VCl_4 > SbCl_6 > SnCl_4 > TiBr_4 > BF_3 > BCl_3$(78). The aluminium tribromide and metal halide e.g. $TiCl_4$ seem to form a complex which produces cations which in turn react with monomer to form active species according to the following scheme (XIII):

$$TiCl_4 + AlBr_3 \rightleftharpoons TiCl_4.AlBr_3 \rightleftharpoons TiCl_3^{+} AlClBr_3^{-}$$

$$\xrightarrow[k_i]{+M} M^{+} \xrightarrow[k_p]{+M} \text{polymer.}$$

XIII.

Similarly Vairon and Sigwalt(82) studying the polymerisation of cyclopentadiene with Cl_3TiOBu in the absence of water observed only partial conversion. When water (or hydrochloric acid) was added, however, in the ratio $Cl_3TiOBu:H_2O$ (or HCl) = 1:1 then high conversions were obtained. The scheme shown below (XIV) summarises two possible explanations for this behaviour in terms of the formation of an initiator complex between catalyst and co-catalyst (or monomer) and subsequent formation of cations which allow propagation of the reaction.



XIV

Okamura and co workers(49) seem certain about the mechanism of initiation of cyclopentadiene, (CPD) in their polymerisation studies. They observed increasing catalyst efficiency for the following catalyst systems in the order indicated $BF_3OEt_2 < SnCl_4.TCA < TiCl_4.TCA$. They explained this series in terms of the ability of the complexed catalyst to initiate a non stationary polymerisation by the steps summarised in the following scheme (XIV A).

A) $$BF_3 + CPD \overset{k_1}{\rightleftharpoons} BF_3.CPD.$$

$$BF_3 + Et_2O \overset{k_2}{\rightleftharpoons} BF_3OEt_2 \xrightarrow[\text{slow}]{\text{CPD}} P_1^+ \quad \text{stationary state}$$

B) $$SnCl_4 + CPD \overset{k_3}{\rightleftharpoons} SnCl_4CPD \xrightarrow[\text{fast}]{\text{TCA}} P_1^+ \quad \text{non stationary state}$$

$$SnCl_4 + TCA \overset{k_4}{\rightleftharpoons} SnCl_4.TCA \xrightarrow[\text{slow}]{\text{CPD}} P_1^+ \quad \text{stationary state}$$

C) $$\begin{tikzcd} TiCl_4 + CPD \overset{k_5}{\rightleftharpoons} TiCl_4.CPD \arrow[r, "\text{TCA}", "\text{fast}"'] \arrow[dr, "\text{CPD}"'] & P_1^+ \text{ non stationary} \\ & TiCl_2(C_5H_5)_2 \text{ inactive catalyst} \end{tikzcd}$$

$$TiCl_4 + TCA \overset{k_6}{\rightleftharpoons} TiCl_4.TCA$$

XIVA

CPD was found to be very susceptible to forming complexes with metal halides, titanium tetrachloride being the most electrophilic and boron trifluoride the least electrophilic of the three metal halides studied.

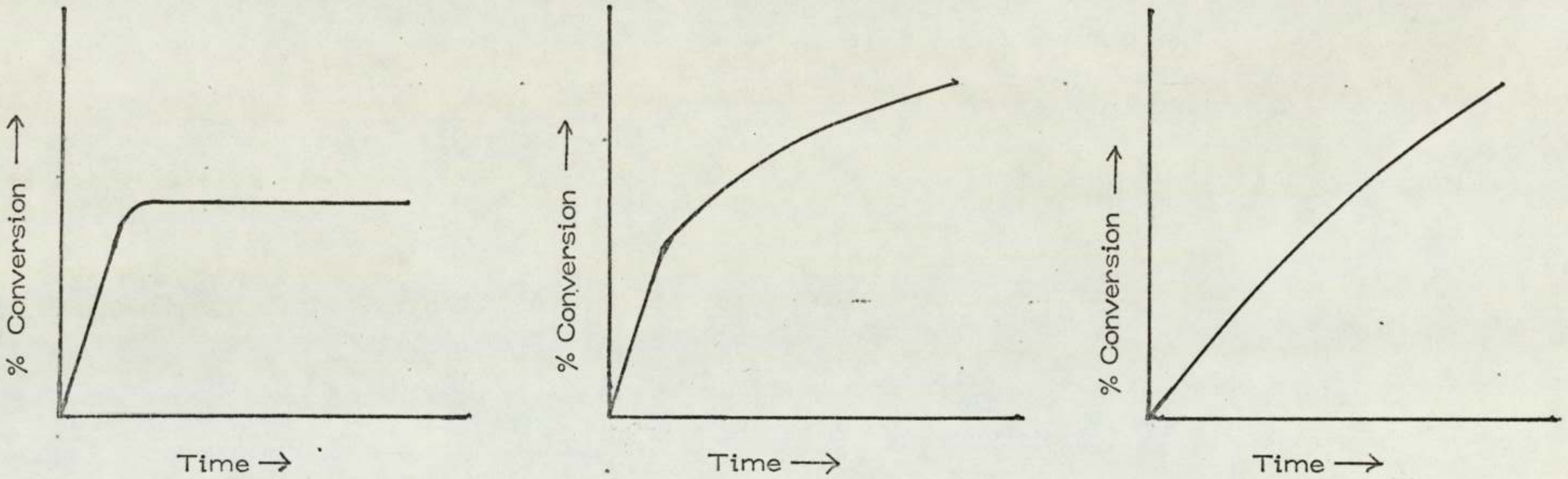
Referring to the above Scheme, (XIVA) and taking the reaction using BF_3 as catalyst first, it was found that $k_2 > k_1$ so that initiation proceeds entirely by reaction of the monomer with the BF_3OEt_2 complex. Ionisation of the monomer by this complex was found to be slow and the system assumed a stationary state character.

In the case of $TiCl_4$, it was found that $k_5 > k_6$ so that the initiation reaction proceeds almost solely via the reaction of TCA with $TiCl_4$CPD complex. The protonation of $TiCl_4$.CPD by TCA was found to be fast and thus non stationary state conditions emerge. Furthermore $TiCl_4$ is so electrophilic that the $TiCl_4$.CPD complex was observed to react with another molecule of CPD to give dicyclopentadiene a process competing with the initiation reaction, which leads to the phenomenon of inverse proportionality of final conversion to the initial concentration.

With $SnCl_4$ it was observed that k_3 competed with k_4 so that both initiation mechanisms are operative.

In the polymerisation of methylcyclopentadiene MCPD the same order of activity for the above catalysts was observed. MCPD is however more active than CPD and even in the case of BF_3OEt_2 a non-stationary state process was found to compete with the stationary state. Three basic types of shape were observed for the time - conversion curve depending on the catalyst and monomer used, these are shown in Figure 2 (p. 49).

A catalyst of possible interest has been reported by Kennedy(87). In the presence of $AlEt_2Cl$, olefins such as isobutylene, styrene, butadiene or isoprene and mixtures of these monomers in bulk or in solution could be mixed in the temperature range +30 to -100°C without reaction. Polymerisation commenced instantaneously when small amounts of hydrochloric, hydrobromic or other Brönsted acids were introduced as co-catalyst and depending on the amount of acid added a controlled or fast to explosive polymerisation could be induced.



1) A typical non stationary-state polymerisation (fast initiation and propagation with diminishing numbers of active species).

Typical examples of cationic systems exhibiting the above behaviour:

i) MCPD, $TiCl_4$— TCA
ii) MCPD, $SnCl_4$— TCA
iii) CPD , $TiCl_4$— TCA

2) A typical concomitant non-stationary- and stationary-state polymerisation.

Typical examples of cationic systems exhibiting the above behaviour:

i) MCPD, BF_3OEt_2
ii) CPD , $SnCl_4$— TCA

3) A typical near-stationary state polymerisation.

Typical example of cationic systems exhibiting the above behaviour:

i) CPD, $BF_3.OET_2$

FIGURE 2

2.22 The Assessment of Monomer Reactivity using Copolymerisation Studies

Monomer reactivity ratios for given copolymerisation reactions can be used to advantage in this work in two ways as follows:

a) They provide a means of assessing monomer reactivity under a given set of conditions.

b) They enable some assessment of the likelyhood and extent of reaction between monomers of different structures to be carried out. This information could in turn be used predictively in assessing the likelyhood of a crosslinking reaction taking place between a given crosslinking agent and a particular reactive site within the formed backbone, as against the likelyhood of homopolymerisation of the crosslinking agent taking place exclusively. The validity of this latter approach depends upon the accuracy with which one can relate the reactivity of a chemical structure when the latter is present in the form of isolated monomer units to that of the same structure present in the form of reactive sites within a backbone. A more ideal and less complex situation would be presented when a given chemical structure or reactive site is pendant to the main chain or backbone and one or two carbon atoms removed from it so that one would expect the reactivity of such a structure to be comparable to that of the corresponding monomer unit in isolation. If in this case the crosslinking agent and pendant group are identical in structure then one would expect a cross linking reaction to predominate.

The types of olefinic monomer which are likely to be the most reactive in cationic polymerisation have been previously discussed (Chapter 2.1) vinyl ethers and cyclic dienes having been presented as the more promisingly reactive monomer types, for use in this work.

Since the literature is somewhat unsystematic in its approach to the study of copolymerisation behaviour in cationic polymerisation only that literature relating to the more important monomer types will be discussed here.

Copolymerisation Studies of Cyclic Dienes

The monomers of this type which have commanded much attention are cyclopentadiene and methyl cyclopentadiene previously referred to in Chapter 2.1.

Cyclopentadiene (CPD) has been copolymerised with methylcyclopentadiene (MCPD(52) and dimethyl cyclopentadiene (DMCPD)(53) and some values obtained for monomer reactivity ratios are summarised in Table 4.

Table 4

Monomer Reactivity Ratios (MRR) for the Cationic Copolymerisation of Cyclopentadiene (CPD) with Methylcyclopentadiene (MCPD and Dimethyl cyclopentadiene (DMCPD) under Various Conditions.

Substituted CPD	Catalyst	Temperature °C	Solvent	r_1 Subst^{ed}CPD	r_2 CPD	r_1r_2
MCPD	$SnCl_4$/TCA	-78	Dichloromethane	14.3	0.42	5.25
MCPD	$SnCl_4$/TCA	-78	Toluene	8.5	0.36	3.05
DMCPD	BF_3OEt_2	-78	Toluene	6.85	0.50	2.05

It can be seen that a change in solvent has no dramatic effect on the MRR for the MCPD-CPD systems. The DMCPD-CPD toluene and MCPD-CPD toluene systems can not be directly compared since a different catalyst was used in each case.

The reactivity of CPD is substantially increased by the introduction of one methyl group (in MCPD) which is electron donating and thus improves the stability of the resultant cation. A further dramatic increase in reactivity was however not observed when a second methyl group was introduced as in DMCPD, where the beneficial electronic effects of this second group were found to be counterbalanced by adverse steric effects.

CPD and cyclohexadiene (CHD) are known to be the most reactive unsubstituted cyclic dienes but it is worth mentioning data available on the copolymerisation of another less reactive cyclic diene, cyclooctadiene (COD) with styrene and p-chlorostyrene in order to demonstrate the critical influence the catalyst system can have on MRR values(85) see Table 5 (p. 53).

A study of results presented in Table 5 shows that in the copolymerisation of p-chlorostyrene with COD using $TiCl_4$ as catalyst p-chlorostyrene is shown to be the more reactive monomer but when $SnCl_4$ is employed as the catalyst COD becomes the more active monomer.

It is of interest to note that CPD and MCPD have been incorporated into protective coatings as long ago as 1962(88) using copolymerisation processes. Various cyclic monomers were copolymerised with conjugated linseed, conjugated soybean, and

Table 5

MRR Values for the Cationic Copolymerisation of Cyclooctadiene (COD) with Styrene and p-Chlorostyrene using $TiCl_4.H_2O$ and $SnCl_4$ H_2O catalysts in Dichloromethane at 0°C and -20°C

Co-monomer	Initiator	Temp. °C	r_1; Octadiene	r_2; Styrene derivative	r_1 r_2
Styrene	$TiCl_4.H_2O$ 1:1	0	0.32	1.90	0.608
	$TiCl_4H_2O$ 1:1	-20	0.55	1.65	0.907
	$SnCl_4H_2O$ 1:1	0	0.52	1.62	0.84
	$SnCl_4H_2O$ 1:1	-20	0.47	1.61	0.75
p-Chloro styrene	$TiCl_4.H_2O$ 1:1	0	0.38	0.61	0.23
	$TiCl_4H_2O$ 1:1	-20	0.48	0.58	0.27
	$SnCl_4H_2O$ 1:1	0	0.70	0.46	0.32
	$SnCl_4H_2O$ 1:1	-20	0.85	0.36	0.31

non conjugated linseed vinyl ethers. All copolymers containing a cyclic comonomer gave baked films that were distinctly superior to unmodified drying oil or vinyl ether homopolymers in hardness and alkali resistance. Several of these copolymers air-dried overnight to moderately hard, wrinkle free films. The improvement in hardness and alkali resistance it was postulated may be caused by steric effects in which cyclic comonomers hold the fatty side chains apart thus increasing the proportion of intermolecular to intramolecular cross linking. Baked films were prepared by adding manganese drier to a 30% w/w solution of copolymer in toluene and films 1 mil thick were baked for 10 minutes at $200^{\circ}C$ and cured for 18 hrs at room temperature; air dried films being cast with lead-cobalt drier and dried for 18 hrs at room temperature. No study was made of the possible enhancement of curing rate under suitable conditions by the inclusion of these cyclic monomers into conventional systems used as surface coatings.

Copolymerisation Studies of Vinyl Ethers

Copolymerisation studies of vinyl ether derivatives have been widely carried out(60). The following reactivity series (XV) has been established for the polymerisation of some vinyl ethers under similar reaction conditions:

$$t-C_4H_9O > iC_3H_7O > iC_4H_9O > nC_4H_9O > C_2H_5O > CH_3O$$

XV

Alkenyl ethers of the form $R_1CH = CHOR_2$ are sensitive to cis-trans isomerism which can affect monomer reactivity, the cis isomer generally being the more reactive isomer. The reactivity of vinyl isobutyl ether (VIBE) is enhanced if the substituent R_1 is linear but less so if R_1 is a bulky secondary or tertiary group(24). Some values of MRR for the copolymerisation of alkenyl ethers and VIBE are summarised in Table 6 (p. 56). The introduction of a further alkoxy group significantly enhances the reactivity of vinyl ethers(60), the relative polymerisabilities of some monomers of this type are shown in Table 7 (p. 57).

The copolymerisation of vinyl ethers with styrene derivatives has been widely studied but due to a large difference in reactivity MRR values determined were found to be greater than unity. The copolymerisation of 2-chlorovinylether (CEVE), a less reactive vinyl ether, with styrene derivatives using $SnCl_4$. TCA as catalyst does however give MRR values approaching unity when α-methylstyrene is used as comonomer(89) at -78°C. Some MRR values for systems of the above type are summarised in Table 8 (p. 58) and show that CEVE is more reactive than p-methyl and α-methyl styrene but less reactive than p-methoxystyrene. The influence on monomer reactivity exercised by catalyst type is also demonstrated by these results where the content of styrene derivative in the copolymer increases in every system irrespective of monomer reactivity whenever $SnCl_4$. TCA is replaced by BF_3OEt_2, suggesting that BF_3OEt_2 is the more active catalyst for the polymerisation of styrene derivatives.

Table 6

MRR Values for the Cationic Copolymerisation of Some Alkenyl Ethers $R_1CH = CHOR_2$ (M_2) and Vinyl Isobutyl Ether (VIBE) in Methylene Chloride at -78°C using BF_3 Etherate Catalyst and n-Heptane as Internal Standard Except for Cases$^+$ where Toluene was used

Isomer used	R_1	R_2	Cat. concn. mmole/1	Polymn. time, min.	No. of runs	r_1	r_2	$1/r_1$	$r_1 r_2$
-	H	C_2H_5	3	1.5-3	5	0.92 ± 0.02	1.30 ± 0.02	1.09	1.20
cis	CH_3	"	5	0.5-1	6	0.23 ± 0.07	2.25 ± 0.10	4.35	0.52
trans	CH_3	"	5	0.5-1	7	0.56 ± 0.03	1.44 ± 0.02	1.79	0.81
cis	C_2H_5	"	12	15-30	7	0.26 ± 0.04	0.81 ± 0.03	3.85	0.21
trans	C_2H_5	"	12	10-20	6	0.68 ± 0.03	1.54 ± 0.14	1.47	1.05
cis	$i\text{-}C_3H_7$	"	5	10-30	6	1.71 ± 0.20	0.09 ± 0.04	0.58	0.15
trans	$i\text{-}C_3H_7$	"	5	30-100	5	14.44 ± 0.21	0.09 ± 0.01	0.07	1.30
trans	$t\text{-}C_4H_9$	"	10	10-20	7	ca. 100	ca. 0.01	ca. 0.01	
cis$^+$	$n\text{-}C_5H_{11}$	"	5	30-100	7	0.17 ± 0.05	0.46 ± 0.05	5.88	0.08
trans$^+$	$n\text{-}C_5H_{11}$	"	5	30-90	6	2.10 ± 0.21	0.59 ± 0.09	0.48	1.24
cis	$i\text{-}C_4H_9$	"	10	30-50	7	0.20 ± 0.10	0.032 ± 0.038	5.00	0.01
trans	$i\text{-}C_4H_9$	"	10	20-40	9	2.48 ± 0.10	0.33 ± 0.03	0.40	0.82
-	H	$i\text{-}C_3H_7$	5	3-5	4	0.22 ± 0.03	2.70 ± 0.11	4.55	0.81
trans	CH_3	$i\text{-}C_3H_7$	5	8-10	6	0.18 ± 0.08	2.37 ± 0.19	5.56	0.43
cis$^+$	C_2H_5	$i\text{-}C_3H_7$	5	10-60	10	0.32 ± 0.05	0.93 ± 0.06	3.13	0.30
trans$^+$	C_2H_5	$i\text{-}C_3H_7$	5	20-60	9	0.50 ± 0.06	0.90 ± 0.05	2.00	0.45
-	(CH_3)	C_2H_5	12	3-10	8	1.48 ± 0.03	0.00 ± 0.01	0.68	0.00

Table 7

The Relative Polymerisabilities of Dialkyloxyethylenes and Vinyl Alkyl Ethers in Methylene Chloride at $-70^{\circ}C$ using $BF_3.OEt_2$ as Catalyst

Ether	Relative Polymerisability [a]	
Vinyl ethyl ether	1.09	(1.00)
cis 1,2-diethoxyethylene	2.88	2.28
trans 1,2-diethoxyethylene	1.38	1.06
Vinyl methyl ether	0.55	0.41
cis 1,2-dimethoxyethylene	2.23	1.71
trans 1,2-dimethoxyethylene	0.57	0.44
Vinyl isobutyl ether	(1.00)	0.92

[a] Figures in parentheses show the reference reactivity.

Table 8

MRR Values for the Cationic Copolymerisation of 2-chlorovinylether (CEVE) with some Derivatives of Styrene using as catalysts BF_3OEt_2 or $SnCl_4TCA$ in Toluene and Dichloromethane at -78°C

Comonomer	Catalyst	Solvent	CEVE (r_1)	Styrene Derivatives (r_2)	$r_1 r_2$
p-Methoxy-Styrene	BF_3OEt_2	Toluene	2.81	4.37	12.3
	BF_3OEt_2	Dichloromethane	3.08	4.55	14.0
	$SnCl_4TCA$	Toluene	1.73	6.93	12.0
	$SnCl_4TCA$	Dichloromethane	1.56	7.80	12.0
p-Methyl-Styrene	BF_3OEt_2	Toluene	-	-	-
	BF_3OEt_2	Dichloromethane	8.80	0.40	3.52
	$SnCl_4TCA$	Toluene	10.1	0.50	5.05
	$SnCl_4TCA$	Dichloromethane	2.31	1.12	3.71
α-Methyl-Styrene	BF_3OEt_2	Toluene	5.72	0.31	1.77
	BF_3OEt_2	Dichloromethane	2.05	0.68	1.39
	$SnCl_4TCA$	Toluene	3.46	0.46	1.59
	$SnCl_4TCA$	Dichloromethane	1.02	1.0	1.00

The data summarised in Table 8 demonstrate also how solvent can affect a copolymerisation process and the trend shown in the results above support Overberger's theory(70) which postulates the solvation of propagating chain ends by a polar monomer when non polar media are employed. Hence for the copolymerisation of CEVE with α-methyl styrene or p-methyl styrene the content in the copolymer of the more polar CEVE increases when the reaction is carried out in toluene as opposed to dichloromethane. Overberger states that the propagating ion pair in non polar media requires considerable energy for dissociation to occur and in this situation he states, the ion pair is dissociated preferentially by the monomer with the larger solvating power hence the latter is included in the final copolymer to a greater extent than the less polar monomers present. Where such a copolymerisation is carried out in a polar solvent dissociation of the ion pair is facilitated and the monomer with weaker solvating power can now include itself more easily in the process. Hence should a copolymerisation be carried out in the absence of solvent the reactivity of the monomer is not only governed by the stability of active carbonium ions produced but also by the polarity or solvating power of the monomer.

Copolymerisation Studies of Styrene Derivatives

The copolymerisation of phenyl vinyl ether (m_1) with its p-CH_3O, mCH_3O, p CH_3, mCH_3, p Cl or m Cl derivatives reflects the effect these substituents have on the reactivity of the corresponding monomers(90). The polymerisability increases, as would be expected with the increase of electron donicity of the substituents which in turn results in increased stability of the corresponding cations formed. The results obtained for the above series of monomers are summarised in Table 9 below.

Table 9

MRR Values for the Cationic Copolymerisation of Phenyl Vinyl Ether with Various Substituted Phenyl Vinyl Ethers using $SnCl_4$ as catalyst in toluene at $-78^\circ C$

Substituent	Phenyl Vinyl Ether r_1	Substituted Phenyl Vinyl Ether r_2	$r_1 r_2$
$p-CH_3O$	0.42	2.1	0.88
$p-CH_3$	0.55	1.76	0.97
mCH_3	0.79	1.50	1.19
$m\ CH_3O$	0.71	1.1	0.78
p Cl	3.6	0.27	0.97
m Cl	4.6	0.18	0.97

The copolymerisation of styrene with isobutene has been studied^(69) and results for various systems are summarised in Table 10 (p. 61).

Table 10

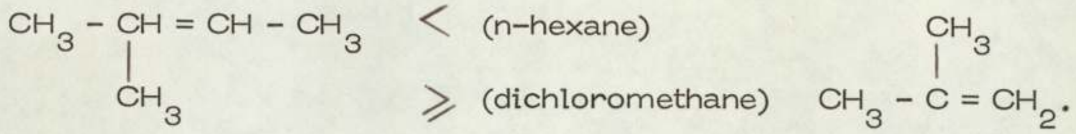
MRR Values for the Cationic Copolymerisation of Styrene with Isobutene using $TiCl_4$ as catalyst in n-Hexane/Dichloroethane Mixtures at $-78^{\circ}C$

×DIELECTRIC CONSTANT

Solvent Composition n-Hexane	 Dichloromethane	×ε	Isobutene r_1	Styrene r_2	r_1r_2
100	0	2.05	0.77	2.41	0.89
75	25	3.95	2.63	5.50	16.6
50	50	6.53	3.25	2.75	8.63
25	75	10.65	4.11	1.70	7.0
0	100	14.89	4.48	1.08	4.86

The effect that solvent can have on the copolymerisation process for the above system is demonstrated by the results shown in Table 10. When $TiCl_4$ was replaced by $SnCl_4$ as catalyst little or no effect was observed.

Isobutene has generally been considered to be a more reactive monomer in cationic processes than styrene. Imanishi(91) has shown that this is true for polymerisation in dichloromethane but not in n-hexane demonstrating again the importance of solvent choice. The same authors observed the same phenomenon in the co polymerisation of 2 methyl but-2-ene with isobutene as summarised in the following scheme (XVI).



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}=CH-CH_3 \quad \begin{array}{l} < \ (\text{n-hexane}) \\ \geqslant \ (\text{dichloromethane}) \end{array} \quad CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2.$$

XVI

Isoprene has been copolymerised with styrene in benzene solvent at room temperature (22^oC)$^{(92)}$ with a carefully prepared catalyst of the following composition.

Reagent	Volume (ml)
Dichloromethane	5.00
n-Heptane	1.50
Triethylaluminium	2.00
t.Butyl chloride	1.56
Water	0.26

The reactivity ratios for styrene and isoprene obtained were 0.46 and 0.50 respectively. The conversion of monomer to polymer being held below 12% in all runs.

In spite of some unexplained phenomena occurring e.g. phenyl groups were found in the polymer when benzene was used as solvent – it appeared likely to the authors that some type of alternation mechanism was occurring.

2.3 The Preparation and Evaluation of Polymers obtained via Cationic Polymerisation Reactions

In this section the range of properties obtained from the products of polymerisation reactions of the type under consideration are summarised. Although this information was not used in the selection of monomer/catalyst combinations for the research programme outlined herein it was felt that the information might be of some ultimate use in predicting changes in physical properties of networks resulting from the use of various monomer catalyst combinations in cross linking reactions.

Schildnecht(93) studied the properties and structures of polyvinyl isobutyl vinyl ethers prepared from vinyl isobutyl ether. He found that the latter yielded two types of polymer depending on the reaction conditions employed. Using boron trifluoride etherate as catalyst and carrying out the reaction in a controlled fashion, a well ordered polymer was obtained but rapid polymerisation using boron trifluoride as catalyst yielded an amorphous rubberlike polymer.

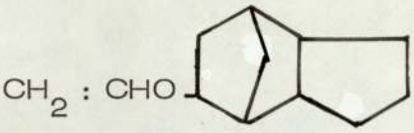
Okamura(94) studied the stereospecific polymerisation of isobutyl vinyl ether using homogeneous and heterogeneous catalysts and found that the latter catalyst types were not always the only types which yielded stereospecific polymers, thus methyl and propyl vinyl ethers gave stereospecific polymers when polymerised using boron trifluoride etherate as catalyst in the mixed solvents, n-hexane/toluene and n hexane/chloroform.

A large number of patents have been published which describe the preparation of polymers from novel systems in which a new monomer, catalyst or different polymerisation conditions are employed. Shearer(96) polymerised a series of mono α olefins, which included ethylene, propylene, 3 methyl-1-butene and 4 methyl-1-pentene, using germanium catalysts based on alkyl germanium compounds and halides of titanium, vanadium, chromium and molybdenum.

Price(97) prepared a series of heat resistant thermoplastic olefin copolymers from 3 methyl-1-butene and 3 methyl-1-pentene. The copolymers had melting points within the range 525 to 670°C. Catalysts based on titanium or vanadium halide complexes and aluminium alkyls were used in the work and reactions carried out in heptane in sealed bottles, at 160°F. He found that the polymer obtained from the system 3,5,5 trimethyl-1-hexane, heptane, alkyl aluminium/titanium tetrachloride catalyst, exhibited a high service temperature and melted around 422°C(98).

Crystalline poly (cis propenyl alkyl ethers) have been prepared by Heck(99) from the corresponding monomers using aluminium or titanium alkyls and sulphuric acid as catalysts at O and 25°C. High melting polymers which yielded useful fibres and films were obtained.

Tapas(100) polymerised dicyclopentyl vinyl ethers of the form (XVII) in toluene at -60°C using boron trifluoride etherate as catalyst. Materials obtained found application as pressure sensitive adhesives.



XVII.

Hagemeyer$^{(101)}$ polymerised the following series of substituted vinyl ethers; 2,2 dimethyl octyl, 2,2 dimethyl decyls, 2,2 dimethyl dodecyl and 2,2 dimethyl tetradecyl vinyl ethers. He prepared homopolymers in liquid propane using boron trifluoride etherate and in 1:1 toluene/propylene glycol using $Et_2Al\ Cl$ catalyst. Copolymers prepared were those derived from members of the series of vinyl ethers given above together with those derived from dimethyl butyl vinyl ether and vinyl chlorides, vinylidene chlorides, methyl methacrylate or acrylonitrile. The materials produced took the form of viscous liquids, rubbers, or film forming resins.

Edwards$^{(102)}$ prepared a series of amorphous elastomeric polyolefins containing the following unit (XVIII):

$-CH_2(CH_2)_aC\ Me\ R -$ where $R = $ alkyl and $a = 1, 2$ or 3.

XVIII

Some examples of monomers used in this work for the preparation of homopolymers, copolymers and terpolymers were 4-methyl-1-pentene, 3 methyl-1-pentene, 5 methyl-1-hexene. The catalyst employed for these reactions was aluminium trichloride at temperatures ranging from -150° to $0^{\circ}C$, in methylene dichloride as the solvent.

Duck(103) improved the efficiency of catalyst systems based on the $AlBr_3/(BuO)_3.VO/BuLi$ system which can be used as a catalyst for the copolymerisation of α-olefins with vinyl ethers. He effected this by premixing $AlBr_3$ with $(BuO)_3VO$ and the α olefin before adding the vinyl ether and BuLi. This prevented inactivation of the catalyst ($AlBr_3/(BuO)_3VO$) caused by polar monomers. Amongst the α olefins and vinyl ethers used were the following: ethylene, propylene, 1-hexene, methyl, isobutyl, and phenyl vinyl ethers.

In a study of vinyl ether polymerisation catalysts by the Japanese Yeon Co Ltd(104) vinyl ethers were polymerised to a high degree of conversion in high yields using catalysts based on the following: organoaluminium compound, an organic acid anhydride and Friedel Crafts halide.

Higashimura(105) polymerised lower members of the alkyl vinyl ether series at low temperatures using boron trifluoride etherate catalyst at -78°C and compared polymers obtained from isobutyl, butyl, isopropyl and ethyl vinyl ethers. In further studies on the cationic polymerisation of isobutyl and isopropyl vinyl ethers using boron trifluoride catalyst in the mixed solvents n hexane/chloroform or n hexane/toluene. Okamura and Higashimura (106) found that if the catalyst was added to the monomer/solvent mix a heterogeneous polymer was formed whereas if monomer was added to the catalyst/solvent mix a homogeneous polymer was formed.

Kodama(107) carried out further investigations into the low temperature cationic polymerisation of alkyl vinyl ethers in his study of the effect of polymerisation conditions on the properties of polyvinyl methyl and polyvinyl ethyl ethers. He found that the stereoregularity of polymers obtained decreased with increasing polymerisation temperature and dielectric constant of the solvent used. Okamura(108) polymerised tert-butyl vinyl ether using boron trifluoride etherate as catalyst at low temperatures and obtained stereoregular polymer.

Stereospecific polymerisation of racemic α-olefins using asymmetric catalysts to yield optically active vinyl polymers has been carried out by Ciardelli(109). He polymerised 3 methyl-1-pentene and 3,7-dimethyl-1-octene with a catalyst prepared from titanium tetrachloride and bis-(5) 2-methyl butyl zinc.

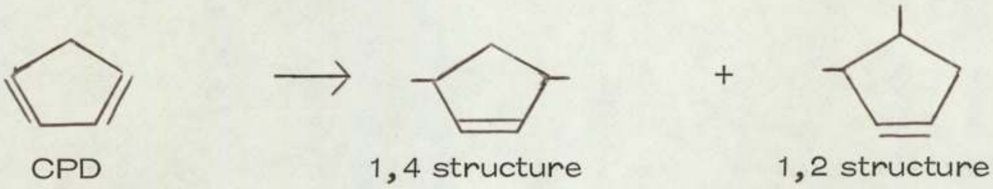
Ermakova(110) studied the bulk polymerisation reactions of 3 methyl 2 pentene using $EtAlCl_3$ and titanium tetrachloride catalysts at $60^\circ C$ in the presence of 0.002% moisture. He obtained equal quantities of the cis and trans form of the starting olefin, together with dimerisation and higher condensation products identified using I.R. and N.M.R. analyses.

Higashimura(111) studied the stereospecific polymerisation of propenyl alkyl ethers (methyl, ethyl, isopropyl, butyl and t butyl propenyl ethers) using a homogeneous catalyst (boron trifluoride etherate) or heterogeneous catalyst [$Al_2(SO_4)_3 . H_2SO_4$ complex]. The steric structure of polymers formed depended on the geometric structure of monomer together with the polymerisation conditions employed. Using boron trifluoride etherate catalyst at -78°C, trans isomers produced crystalline polymers and cis isomers produced amorphous ones with the exception of t-butyl propenyl ether. Using the heterogeneous catalyst the position was found to be reversed in that cis isomers gave rise to crystalline polymers and trans isomers gave amorphous polymers.

Fukuda(112) obtained highly crystalline polymers from boron trifluoride etherate catalysed polymerisation of the vinyl ethers of rosin derived alcohols prepared from Foral, a hydrogenated resin. Cationic copolymerisation of these vinyl ethers with isobutyl vinyl ether gave rubbery copolymers of high molecular weight in which the content of the resin derived vinyl ethers was less than 20% w/w.

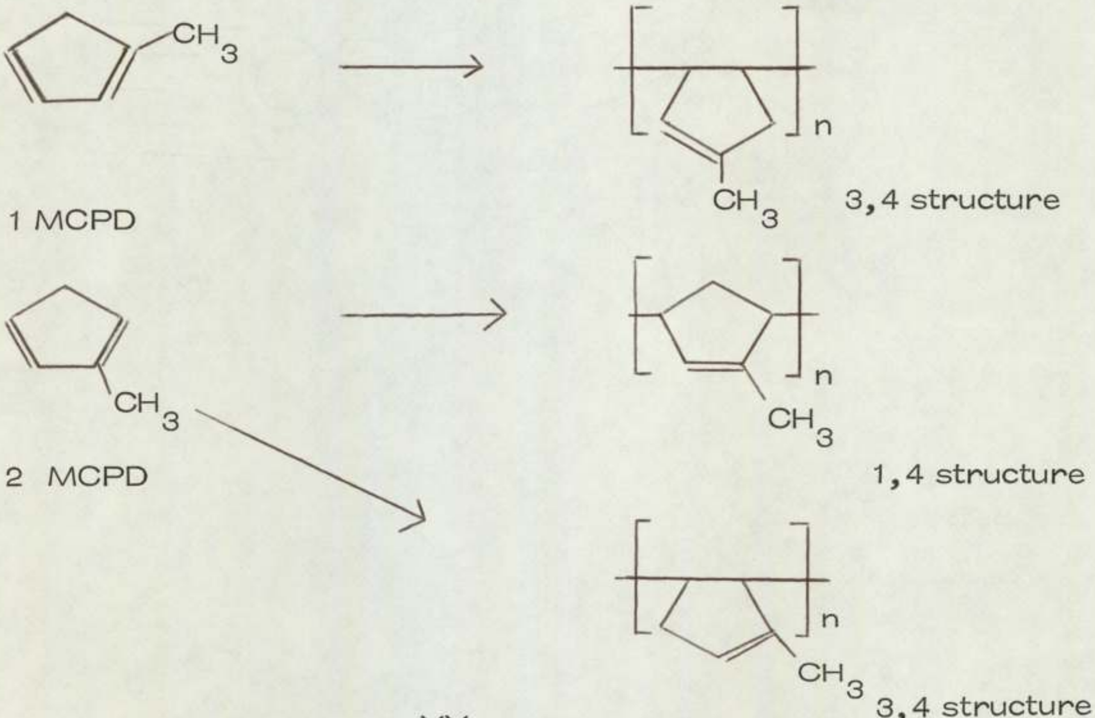
The cationic polymerisation of some 1,1 dialkyl olefins was studied by Lohuizen(113) 2 methyl-1-butene, 2 methyl-1-pentene, 2,3 dimethyl-1-butene were homopolymerised using aluminium trichloride or aluminium tribromide catalysts in ethyl chloride or ethyl chloride/vinyl chloride mixtures at around -175°C. Tg values of amorphous polymers were found to be -5, 27 and 37°C for polymers derived from the respective monomers listed above. The highest molecular weights of 200,000 to 350,000 were obtained at lowest polymerisation temperatures using monomer to catalyst molar ratios of 1,000:1 and over. 2,3,3, trimethyl-1-butene, 2,4,4, trimethyl-1-pentene and 2 ethyl-1-butene yielded only small amounts of liquid oligomers under the above conditions.

In addition to the work carried out by Dufek(88) on the incorporation of CPD and MCPD into protective coatings using copolymerisation reactions, Aso has evaluated the structures of the homopolymers derived from CPD(114, 115) and MCPD(116). He found that polycyclopentadiene obtained with Friedel-Crafts catalysts at low temperatures was composed mainly of the 1,4 and 1,2 structures (XIX)



XIX

The monomer used in studies of the polymerisation of MCPD contained 1 methyl and 2-methylisomers only. Aso found that most of the 1-methylcyclopentadiene units were incorporated as the 3,4 structure, 70-95% of the 2-methylcyclopentadiene units as the 1,4 structure and the residual part as the 3,4 structure as shown below (XX).



XX

CHAPTER 3

The Development of a Stopped Flow Rotational Viscometer for the Measurement of Homopolymerisation and Cross Linking Rates in Thin Film

As an extension to the literature survey presented in Chapter 2, a review of literature relating to established techniques available for measuring polymerisation rates was carried out. This revealed a number of techniques listed below:

1) Dilatometry,(117)
2) Conductimetry,(118,119)
3) Infra-red Analysis,(120)
4) U.V. Analysis,(121)
5) Adiabatic Calorimetry(121,122).

A detailed examination of these techniques showed that none could be applied to the area of work presented here and reinforced the importance of developing a novel technique for use in this work.

It has been established that the more promising systems in terms of reactivity are those which polymerise via a cationic mechanism and the literature survey (Chapter 2) has revealed some particularly reactive homopolymerisation systems based on cyclic dienes and vinyl ethers; although only one reference(12) described a rapid cross linking reaction.

Any novel technique envisaged for use in the study of reactions similar to those described above must of necessity be capable of differentiating between the polymerisation and cross linking rates of cationic systems whether they are highly reactive or not. With reference to the industrial background of this work it was also thought essential that some comparison of reactivity should be carried out for various systems in thin film.

The proposed experimental programme which forms the background to the development of the above technique can conveniently be summarised at this point. The programme was divided into four major sections as follows:

1) The acquisition (via established work) or synthesis, and evaluation of monomer structures which are capable of high rates of polymerisation.
2) The acquisition or synthesis of polymer backbones which can rapidly cross link. These could be one of two types, either,

   a) a structure containing cationically reactive cross linking sites within the chain. Such sites could be structurally similar to the more promising monomers selected from 1), or

   b) a structure containing cationically reactive sites pendant to the chain; such sites could be structurally identical to monomers selected from 1).
3) The selection of suitable cross linking monomers which can be used in conjunction with the backbone structures outlined in 2).
4) The development and evaluation of rapid cross linking systems using information gained from 1) to 3).

The development of a technique which forms an essential part of the experimental areas outlined above, is presented in two sections. The first section describes the development of prototype equipment (Apparatus Design I) and a second section describes the apparatus as it stands in its final form (Apparatus Design II).

3.1 The Development of Apparatus Design I

In the light of literature work carried out in Chapter 2 and the proposals put forward at the start of this study, four main considerations were taken into account in the initial stages of the development of the apparatus:-

1) The order of polymerisation rates which the apparatus must be capable of measuring accurately.
2) The choice of property of a polymerising and cross linking system which can be utilised for the measurement of polymerisation or cross linking rates.
3) The sample geometry to be used.
4) The sample environment in which meaningful measurements can be taken.

It was decided at the outset to use viscosity/time characteristics of a polymerising system as a basis for comparison of reactivity levels. A rotational viscometer known as the Rheomat 15 and marketed by Contraves Industrial Products Ltd. was known to be capable of measuring and recording the viscosity/time characteristics of fluids in thin film using a cone and plate measuring system. The instrument, which is described in detail later (p. 74) and in the literature by van Wazer(123), was considered unsuitable as it stood for immediate use in these studies for two main reasons. Firstly because presentation of samples to the instrument cannot be virtually instantaneous so that very reactive systems could not be studied, and secondly no provision existed for carrying out measurements in controlled environments. It, therefore, became apparent that although the Rheomat 15 could form the basis on which a technique relevent to this work could be developed extensive modifications to the instrument would be necessary to fulfil all the desirable requirements of such a technique, which can be summarised as follows:

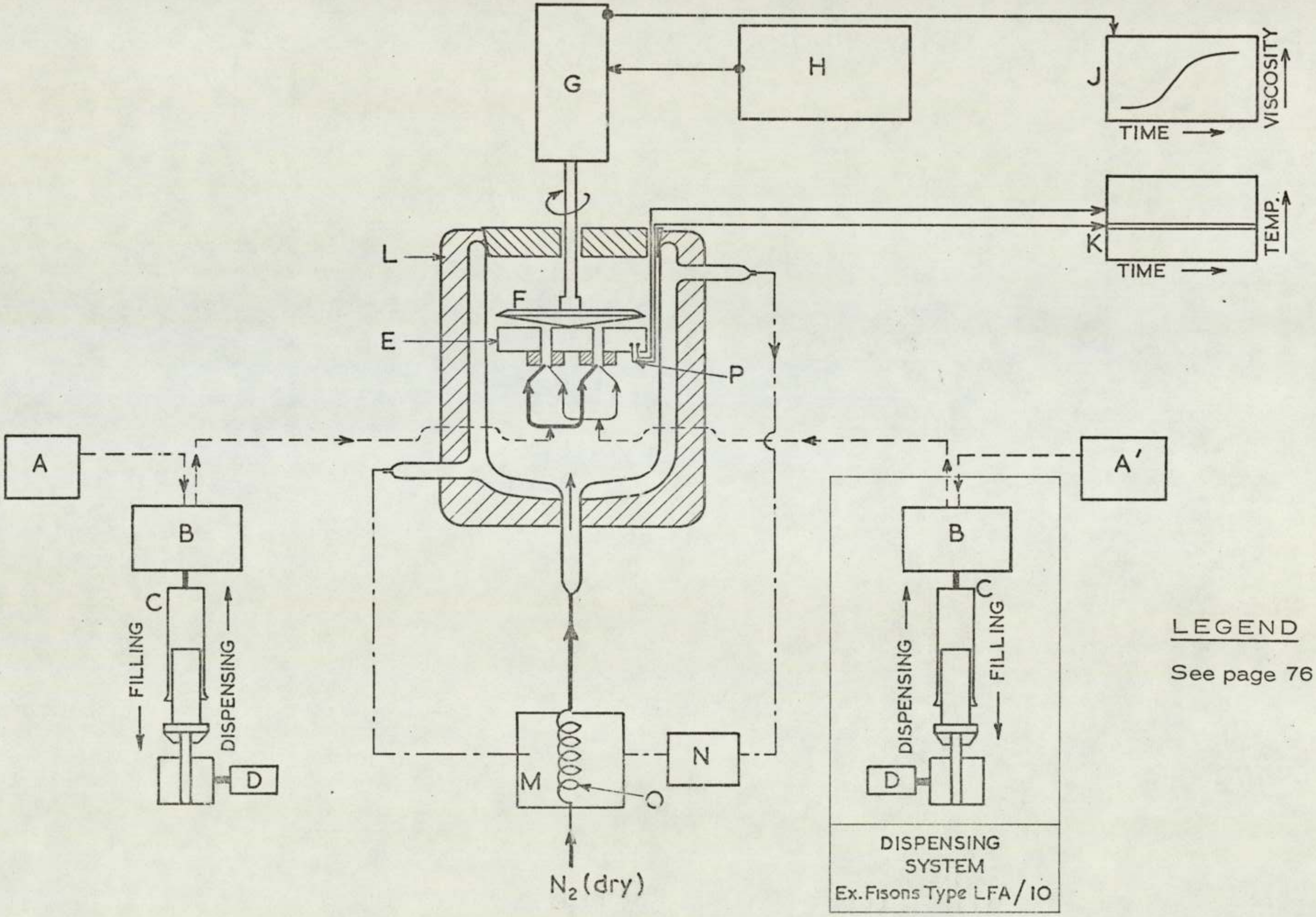
1) Provision for the instantaneous measurement and recording of the viscosity/time characteristics of polymerising and cross linking systems together with appropriate moisture and temperature levels in and around the sample being studied.
2) Provision for the rapid homogeneous mixing of the appropriate components of a polymerising or cross linking system followed by the rapid delivery of the mixed material to the sample cavity of the apparatus, and
3) Provision for the control of sample environment in terms of temperature and moisture levels.

The development work associated with these areas will be discussed separately for each requirement in turn as listed above.

1) The development of a measuring and recording system

The basic requirements of such a system are summarised above and the Rheomat 15 has been suggested as a suitable instrument for measuring the viscosity/time characteristics of polymerising or cross linking systems. The viscometer is presented schematically in Figure 3 p. 75 (which shows the first design of the apparatus as a whole). The viscometer is shown to consist of three basic com-

Based on the Rheomat 15 (Contraves Industrial Products Ltd)



LEGEND

See page 76.

LEGEND - to stopped flow rotational viscometer diagram (Figure 3)

A	Monomer/solvent reservoir
A′	Catalyst/solvent reservoir
B	Two way valves (P.T.F.E.)
C	Glass syringes. (5-20 ml. capacity)
D	Synchronous motor
E	Stainless steel plate Measuring system MS KP-1 ex Contraves. Modified to take fluid lines from automatic dispensing systems
F	Stainless steel cone Measuring system MS KP-1 ex Contraves. Angle between cone and plate 31' 54"
G	Rotational rheometer
H	Frequency generator
J	Recorder (Viscosity/time)
K	Recorder (Temperature/time)
L	Insulated Glass Jacket
M	Reservoir containing circulant at +80°C to -70°C
N	Circulating pump unit (Stewart-Turner)
O	Copper coil (cooling nitrogen gas flow to L)
P	Thermocouples
— — —	Circulating Fluid lines (to and from L)
- - - - - -	Monomer/solvent; catalyst/solvent lines
————	Electrical signal lines

ponents as follows:

a) A rheometer (G) which is connected via a coupling to the measuring system.

b) A frequency generator (H) with switching elements for the control of rheometer speeds.

c) A measuring system which consists of a stainless steel cone (F) and base plate (E).

The rheometer consists of an electric motor which drives the cone, and is controlled from the frequency generator (H) so that 15 different angular velocities of the cone can be selected. When a sample is introduced into the sample cavity created by the cone and plate, any resultant viscous drag on the rotating cone is detected by the motor in the form of a reaction which is offset by a precision spring and a torque reading is indicated by a pointer and dial which is calibrated in single divisions from 0–100. Absolute values of viscosity are read off calibration tables using dial reading and respective angular velocity.

When the viscosity of a sample is changing very rapidly with time manual recording of data becomes impractible so that the installation of an automatic recording system is essential. This took the form of a potentiometer incorporated in the rheometer (G) having a linear resistance of 200 ohms. A constant voltage of 6 volts supplied by a transformer (Philips Power Supply Unit Type PE 1507) was applied across the potentiometer and the pointer, which gives a visual indication of scale reading, was connected to the wiper of the potentiometer so that as an increase in viscosity was detected by the pointer a signal of between one and six volts could be detected in the potentiometer output using a suitable recorder.

The recorder selected for this purpose was a Watanabe Multicorder (Model MC611, European Agents: Environmental Equipments Ltd, Wokingham). The recorder was equipped with three channels, two of which had a 1 mV full scale maximum sensitivity and the third a maximum sensitivity of 10 mV full scale. The maximum response time of this instrument is 0.5 seconds (full scale) and chart speeds of 1200, 600 and 300 mm per hour and 1200, 600 and 300 mm per minute are provided.

One channel of the instrument was used to record the output from the viscometer and the two remaining channels to record thermocouple outputs. Thermocouples (chromel/alumel, Saxonia Products, London) were positioned at various points within and around the cone and plate measuring system. E.m.f. outputs from these thermocouples were measured against cold junctions maintained at $0^{o}C$, thus enabling standard e.m.f. (mV) versus temperature conversion tables to be used. The measuring capacity of the temperature measuring system was improved considerably by incorporating an eleven position thermocouple switch (Type SP2, Cropico, Hampton Road, Croydon) in the circuitry of the recorder channels, which therefore enabled up to eleven thermocouple outputs to be monitored separately as required.

Direct measurement of sample temperature proved difficult and reliance was placed on temperature levels indicated by the two thermocouples positioned in the base plate of the cone and plate system, (P, Figure 3) since the thermal capacity of the measuring system is high so that rapid thermal equilibration of samples within the sample cavity would be expected.

As indicated previously any valid study of cationic polymerisation reactions must include provision for the measurement of moisture levels both within reagents used and in the immediate environment of the experimental sample. These levels were monitored using an automatic moisture meter (Shaw Moisture Meters, Rawson Road, Bradford) which consists of two parts:

a) A direct reading meter, and

b) A sensing element.

The sensing element is an idealised hygroscopic system a few microns thick which contains pores equivalent in size to a water molecule. A dynamic equilibrium is set up between water contained within the element and that outside, and results in the development of a capacitance which varies with the water content of the environment around the element and which is monitored by the direct reading meter either as a scale reading or Dewpoint °C value via a Wheatstone bridge arrangement.

Various types of element are available for measuring levels of moisture in gases or liquids. The gas elements which give outputs measured in terms of scale reading on the meter are supplied with a calibration chart where scale readings can be converted to dewpoint values. These in turn are converted to moisture content in parts per million by consulting calibration tables supplied with the instrument. A wide range of moisture contents can be covered by using more than one element. A range of 7,729 ppM to 0.33 ppM could be covered using two elements ("gold spot") one of Dewpoint+10 to $-50^{o}C$ (7,729 ppM to 24 ppM) and a second element of Dewpoint -20 to $-80^{o}C$ (635 ppM to 0.33 ppM).

The operation of the elements ("liquid" elements) used to measure water contents of liquids was found to be far less convenient than in the case of gas elements. "Liquid" elements depend for their operation on knowing the saturated water content of the liquid, whose moisture content is required. This value corresponds to the full scale reading (100) of the meter, so that subsequent readings taken to determine unknown moisture levels in the same solvent can be related directly and simply to the saturated water content of the solvent. The two major drawbacks of this situation are firstly that saturated water content values have been reported for comparatively few solvents so that such values have to be determined separately via the Karl Fischer Method, and secondly that the elements can not be used for water miscible solvents.

2) The development of a rapid mixing and delivery system

The development of techniques suitable for use in the study of the kinetics and mechanisms of fast reactions has understandably received a great deal of attention over the past fifty years. The first major achievement in the development of such a technique came with the introduction by Hartridge and Roughton of a continuous flow method(124) in 1923. This method involved the rapid mixing of the system under study by passing the appropriate components through a simple T piece mixing head. The system could then be continuously delivered to the measuring cell of a spectrometer and finally to waste. The time constant of the apparatus could be varied by altering the distance between the mixing heads and measuring cell or the flow rate of the mixed system through the apparatus so that the kinetics of fast reactions could be measured.

A large number of techniques have been developed since 1923 based on various concepts and incorporating various designs of integral parts(125) of the apparatus such as the mixing head, the dispensing system etc.

One such technique, the stopped flow technique(125), has been established for a number of years and is at present used as the sample handling component of the Durrum Rapid Kinetics Spectrophotometer Systems (Series D-100). The technique is similar to the continuous flow method described above in that rapid mixing of a system is carried out followed by delivery to the measuring cell of an appropriate sensing instrument. In a stopped flow system however as the name implies, once the measuring cell has been filled with sample, flow of material is stopped. This effectively traps a sample of the rapidly mixed system in the measuring cell enabling appropriate measurements to be carried out. In practice the measuring cell is usually flushed with about twenty times its own volume of sample before the flow of material is stopped to ensure adequate removal of contaminant present in the cell and fluid lines leading to it.

The stopped flow technique has two major advantages when considered for use in these studies firstly it requires relatively small volumes of sample and secondly measurements can be taken virtually from the instant of mixing (t = 0), particularly when the volume of the sample cavity is small and flow rates are high. For these reasons coupled with the fact that the technique enabled rapid mixing and delivery of samples to be carried out in a reasonably contaminant free manner, the stopped flow technique was chosen for incorporation into the envisaged stopped flow rotational viscometer.

The technique consists of two systems, a dispensing system and a mixing system which will be described separately.

A dispensing system was required which could dispense reagents at a high, constant flow rate in a contaminant free manner. The most appropriate commercial instrument available for this purpose was found to be a dispenser (Type LFA/10) marketed by Fisons of Loughborough. The instrument is presented diagrammatically in detail-Figure 4, p. 83 and is also shown in Figure 3, p. 75. It consists of a specially designed P.T.F.E. twist valve, into which the syringe is fitted, operated by a synchronous motor. This same motor also drives a rack on which is mounted a bracket to hold the end of the syringe plunger. The syringe barrel is held

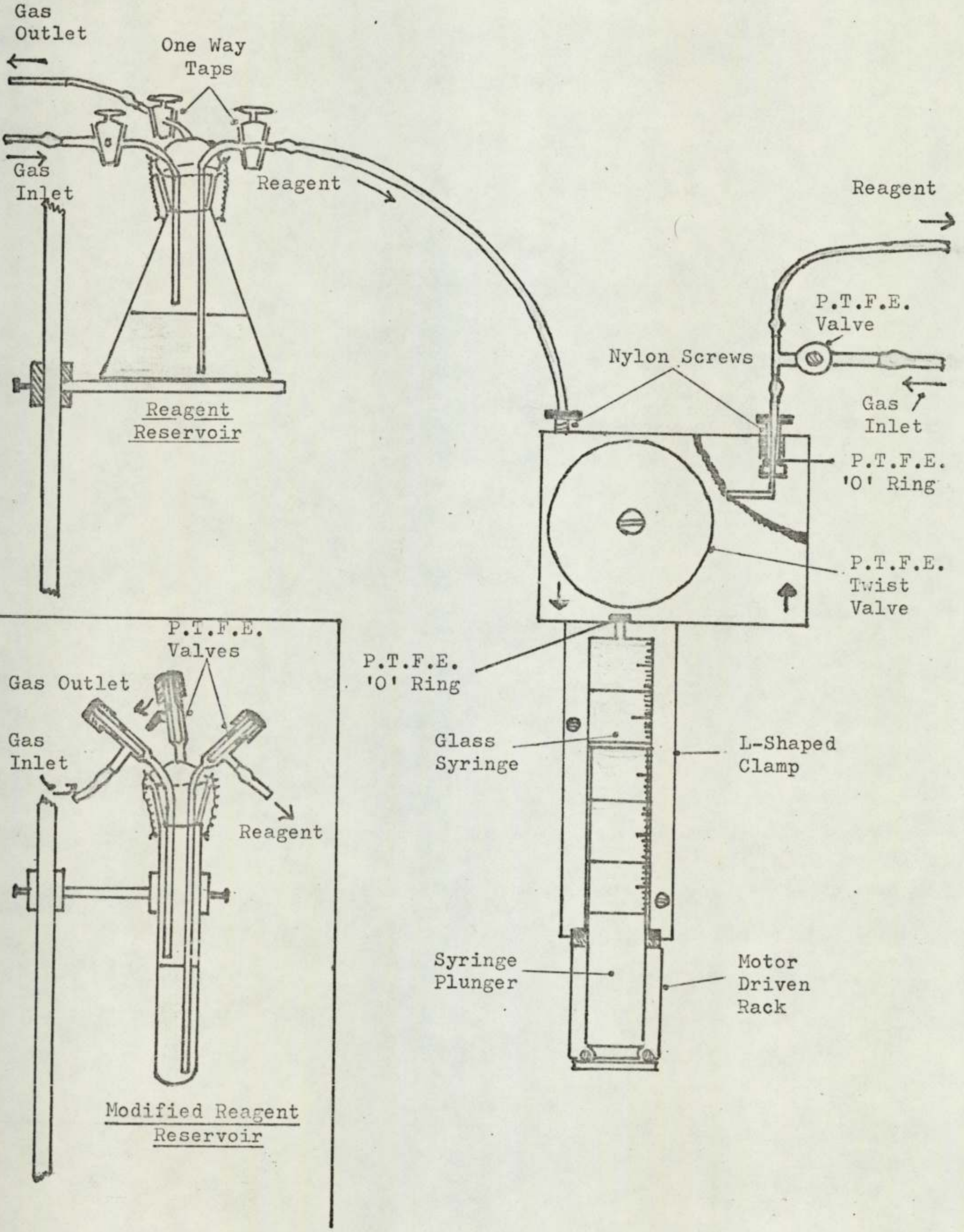

Gas Outlet
One Way Taps
Gas Inlet
Reagent
Reagent Reservoir
Reagent
P.T.F.E. Valve
Nylon Screws
Gas Inlet
P.T.F.E. 'O' Ring
P.T.F.E. Twist Valve
P.T.F.E. Valves
Gas Outlet
Gas Inlet
Reagent
P.T.F.E. 'O' Ring
Glass Syringe
L-Shaped Clamp
Syringe Plunger
Motor Driven Rack
Modified Reagent Reservoir

FIGURE 4

firmly against the twist valve by an L shaped clamp. As the rack moves backwards and forwards, so the plunger moves up and down the barrel sucking up and dispensing liquid, the inlet of the dispenser being connected to the reagent reservoir and the outlet to the mixing head. Various flow rates could be achieved depending upon the size of the syringe used, since the rack operates at a constant speed the larger the syringe used so the higher the flow rate. Table 11 presents the flow rates obtainable using three standard syringe sizes.

Table 11

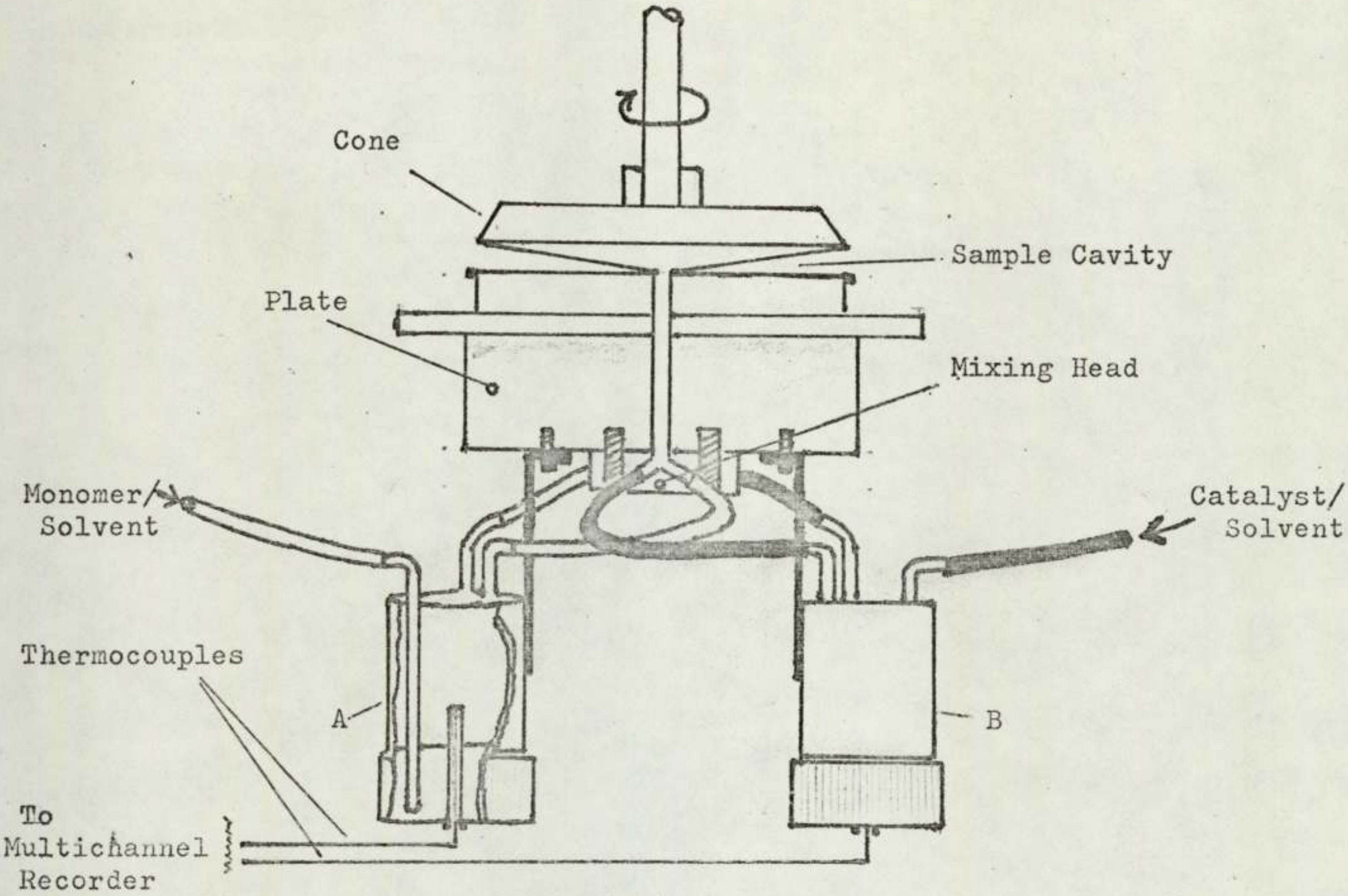
Flow rates achieved with the Fisons Automatic Dispenser (Type LFA/10) using three standard syringe sizes

Syringe Volume in ccs.	Time taken for Full stroke (i.e. half cycle) in secs.	Flow rate in ccs. sec^{-1}
5	5	1
10	6	1.7
20	6	3.3

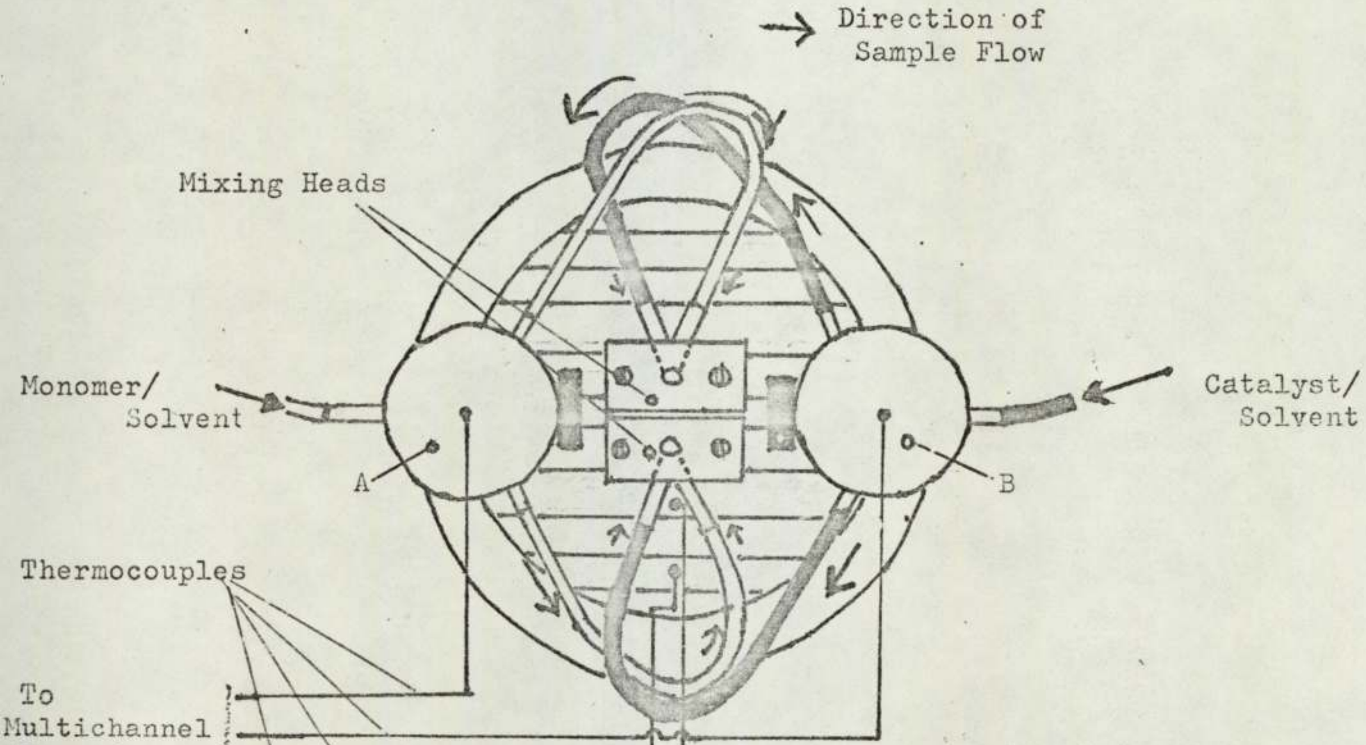
Since monomer/solvent and catalyst/solvent mixtures need to be dispensed separately two dispensing systems were installed, as shown in Figure 3, p. 75, which could be operated simultaneously via a common switch. This enabled a high degree of control over the system and ensured that the composition of the sample trapped in the sample cavity can be accurately deduced from the composition of components employed.

As indicated in Figure 3, the outlets from the two dispensers are connected to the inlets of the mixing system which is presented diagrammatically in detail in Figure 5, p. 86, where a side view and view from below are shown. The mixing system forms an integral part of the base plate of the measuring system described above. Reagents, monomer/solvent and catalyst/solvent, are delivered separately from the two dispensers so that the two reservoirs A and B located beneath the base plate are just filled to capacity. The reagents are then allowed to remain in the reservoirs until they attain the temperature at which a particular run is to be carried out. The preheated (or precooled) reagents are then forced through two mixing heads into the sample cavity by restarting the dispensers. A sample of the rapidly mixed system is then trapped within the sample cavity by simultaneously stopping the dispensers when measurements of viscosity versus time for a particular system can be initiated. The volume of material flushed through the sample cavity is equal to the volume of reservoir A and B (10 mls) and since the volume of the cavity is 0.36 mls, the latter is always purged therefore with 25 times its own volume of a particular system before measurements are initiated.

The outlets from the reservoirs A and B are each split into two streams which lead to the mixing heads as shown in Figure 5, p. 86 so that the two inlets to each mixing head comprise one monomer/solvent and one catalyst/solvent inlet, the outlets leading directly to the sample cavity.



SIDE VIEW



VIEW FROM BELOW

FIGURE 5

Earlier work had shown that the use of one mixing head, necessarily positioned off centre in the base plate was unsatisfactory and led to incomplete and unreproducible filling of the sample cavity. As sample was forced into the cavity the cone was displaced upwards and was tilted by the thrust of material as it entered the cavity, so that when delivery of the sample was stopped and the cone regained its normal or standing position the cavity remained underfilled. The provision of a second mixing head and entry port diametrically opposed to the first meant that material now entered the cavity in two sample streams which collided with the cone at two opposite points equidistant from its centre with equal force. Under these conditions the cone was displaced upwards with no tilting which resulted in complete and reproducible filling of the sample cavity.

The design of the mixing heads themselves was based on T piece heads used in early work by Hartridge and Roughton(124). They consist simply of two sample lines which merge into one, the two components to be mixed are pumped separately along the two lines and mixing occurs at the point where the lines merge. The efficiency of mixing of such systems can be evaluated by a number of tests(125). The test applied to the above system involved the mixing of 0.1 M solution of tris (hydroxymethyl amino methane) at pH 7.4 with a 0.02 to 0.05M solution of sodium hydroxide containing 0.25 g of phenolphthalein. These solutions were dispensed separately and passed through the mixing heads where in poorly mixed regions pink streaks would be observed. Other tests carried out involved the use of dyed and undyed solvents in a similar fashion. All tests carried out indicated that the system effected adequate mixing as it stood although a number of other mixing head designs are reported in the literature which are reputed to be very much more efficient than the T piece mixer(125).

The risk of contamination of reagents by atmospheric contaminants notably moisture was reduced in the following ways. Provision was made for purging dead space within the system with oxygen free nitrogen previously dried by passing through a drying train containing molecular sieve (Type 5A, B.D.H.). The dead space within the reagent reservoir and within fluid lines leading through to the sample cavity was therefore purged thoroughly prior to each run. Reagent solutions which had been previously dried over molecular sieve were always prepared and transferred to reagent reservoirs in a dry box which is described fully later (p. 109) and is shown in Plate X, p. 109a.

The commercial dispensers used in the system were originally supplied with 'Viton' or 'Neoprene' 'O' rings which effectively formed the seals at the fluid line P.T.F.E. twist valve junction and between the syringe and twist valve. Since the above materials showed little resistance to solvents such as acetone, methylene dichloride and even some hydrocarbon solvents serious leakages invariably occurred shortly after such solvents had been introduced. To enable virtually any solvent to be used in both the dispensing system and mixing system all component parts were fabricated from P.T.F.E., glass or stainless steel. Thus P.T.F.E. 'O' rings were cut from 1/8" diameter P.T.F.E. tubing and worked admirably when used in conjunction with 1/16" diameter fluid lines.

The other main difficulties which came to light during the operation of the system in its early stages can be summarised as follows:-

a) Interdiffusion of components in the fluid lines connecting the mixing heads to the dispensers, and

b) Solvent evaporation from material in the sample cavity.

These points are discussed separately.

a) Bearing in mind the sensitivity to moisture and other contaminants of systems likely to be studied using this technique, it had been hoped during the early stages of apparatus construction that a technique could be developed which could handle a number of consecutive runs before dismantling of the apparatus became necessary which would result in the possible introduction of contaminants. The concentration of a component in the system arriving at the sample cavity could be controlled in situ for example by varying the flow rate of that component to the sample cavity using variable speed dispensers. A study of the effect of concentration of a given component on a particular reaction system could then be effected by carrying out a series of runs in which the mixed components are consecutively injected into the sample cavity under similar conditions and the increase in viscosity with time measured for various flow rates of one component. Such a procedure can only be successfully carried out if sample residues from preceeding runs left in the sample cavity and fluid lines can be effectively flushed out in situ. Obvious problems would ensue if solid polymer were to be deposited particularly in the fluid lines.

A number of runs carried out using prototype equipment indicated that reliable continuous operation of the apparatus would not be possible due to the occurrence of an interdiffusion effect whereby polymerisation processes were seen to occur in the feed lines to the mixing heads. When high monomer concentrations were used polymerisation reactions were particularly severe and caused complete blockage of the fluid lines. This inferred that complete dismantling of the system would be necessary after such runs since cleansing of the system by flushing in situ with a suitable solvent was out of the question.

Because of the likely occurrence of the above processes it was decided to accept the fact that in many cases it would be possible to carry out only single runs and design the system in such a way that dismantling and cleaning could be carried out quickly and easily rather than attempt difficult mechanical solutions which would, for example, involve the incorporation of non return valves within the mixing heads preventing back flow of material from the sample cavity.

A further solution to this problem would be to ensure that any polymer formed during a run, stayed in solution, by adjusting, for example, the concentration of monomer and type of solvent employed. This line of approach was found in practice to be unreliable for the apparatus being used here with the particular monomer/polymer systems employed although it may be satisfactory in other cases.

b) This second problem became apparent from the start since the sample cavity of the measuring system Figure 5, p. 86, is open to the surrounding environment, volatile solvents placed in it were naturally lost by evaporation. Systems which incorporate such highly volatile solvents as methylene chloride could not therefore be studied effectively since solvent loss in these cases was complete within ten minutes at room temperature. The problem was simply avoided by choosing less volatile solvents.

The rapid mixing and delivery system finally developed is shown in Plate I, p. 91a, where the rheometer, the cone and plate measuring system, the mixing system and the two dispensers are included. A diagrammatic representation of the system is shown in Figure 3, p. 75. The system enabled only single runs to be carried out before dismantling and cleaning of the system was necessary.

3) <u>The development of a suitably controlled environment for housing the measuring system</u>

The requirements for such an environment are two fold: namely the accurate control of temperature within the range

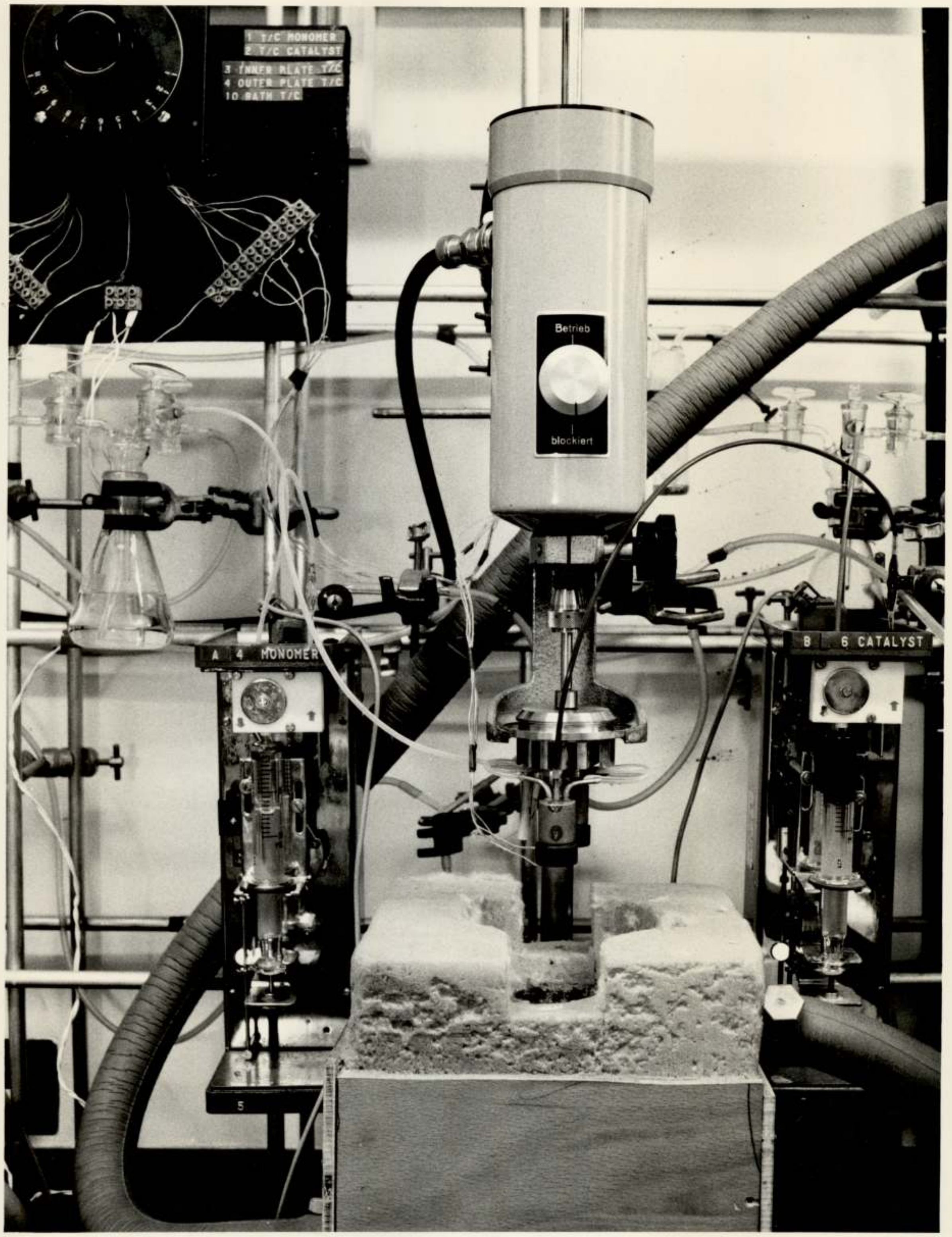

1 T/C MONOMER
2 T/C CATALYST
3 INNER PLATE T/C
4 OUTER PLATE T/C
10 BATH T/C
Betrieb
blockiert
A 4 MONOMER
B 6 CATALYST
5

PLATE I

specified, together with the accurate control of moisture and ideally other contaminant levels.

It was decided that the temperature range over which rate studies should be carried out would be −70 to +80°C. A number of cationic systems have been studied over this range of temperature where some have been found to be more reactive at low temperatures when they exhibit negative activation energies. A study of a particular system over the entire temperature range quoted would therefore enable a critical appraisal of its comparative reactivity to be carried out. The upper limit to the range could be relatively easily extended if necessary.

The temperature range was provided by two separate insulated jackets of the form (L) shown in Figure 3, p. 75. The lower end of the temperature range −70 to 0°C was covered, by circulating acetone at these temperatures through a jacket from a low temperature bath (−70°C Bath, Townsend and Mercer) using a circulating pump (Stuart Turner) suitably insulated. The pump was fitted with natural rubber seals and flow lines, the latter being insulated with expanded rubber tubing.

The higher end of the temperature range 0° to 80°C was covered by circulating water at these temperatures from a reservoir through an insulated jacket using a unit called a circotherm (Shandon) which both circulated the water and controlled its temperature over the range required.

The circulating jackets were each fitted with a gas inlet at their base through which dry oxygen free nitrogen could be passed

(Figure 3, p. 75), so that a relatively moisture free atmosphere could be maintained within the jacket. It was found impossible, however, to measure the levels of moisture present during a run due to restriction of space in the jacket prohibiting the insertion without risk of damage of the sensing element of the moisture meter together with the cone and plate measuring system and its accessories. Some assessment of prevailing moisture levels was carried out by taking moisture readings in the cavity immediately prior to a run.

The low temperature jacket positioned for a run is shown in Plate II, p. 93a.

The operation of the apparatus as a whole can be conveniently summarised with reference to Figure 3, p. 75 at this point. Samples of monomer/solvent (A) and catalyst/solvent (A') are dispensed separately at high constant flow rates using automatic dispensers. Rapid mixing of A and A' is carried out by passing the solutions through T piece mixing heads. The mixed sample passes from the mixing heads into the sample cavity of a cone and plate measuring system E, F and subsequently to waste. Simultaneous stopping of the two dispensers effectively traps a homogeneous sample of monomer/catalyst/solvent solution in the sample cavity. Since the viscometer is operating during sample delivery values of viscosity with time can be observed from virtually t = 0, particularly since filling of the sample cavity is rapid, volume of the cavity is small (0.36 mls) and recording of viscosity levels is automatic via a recorder J. The cone and plate

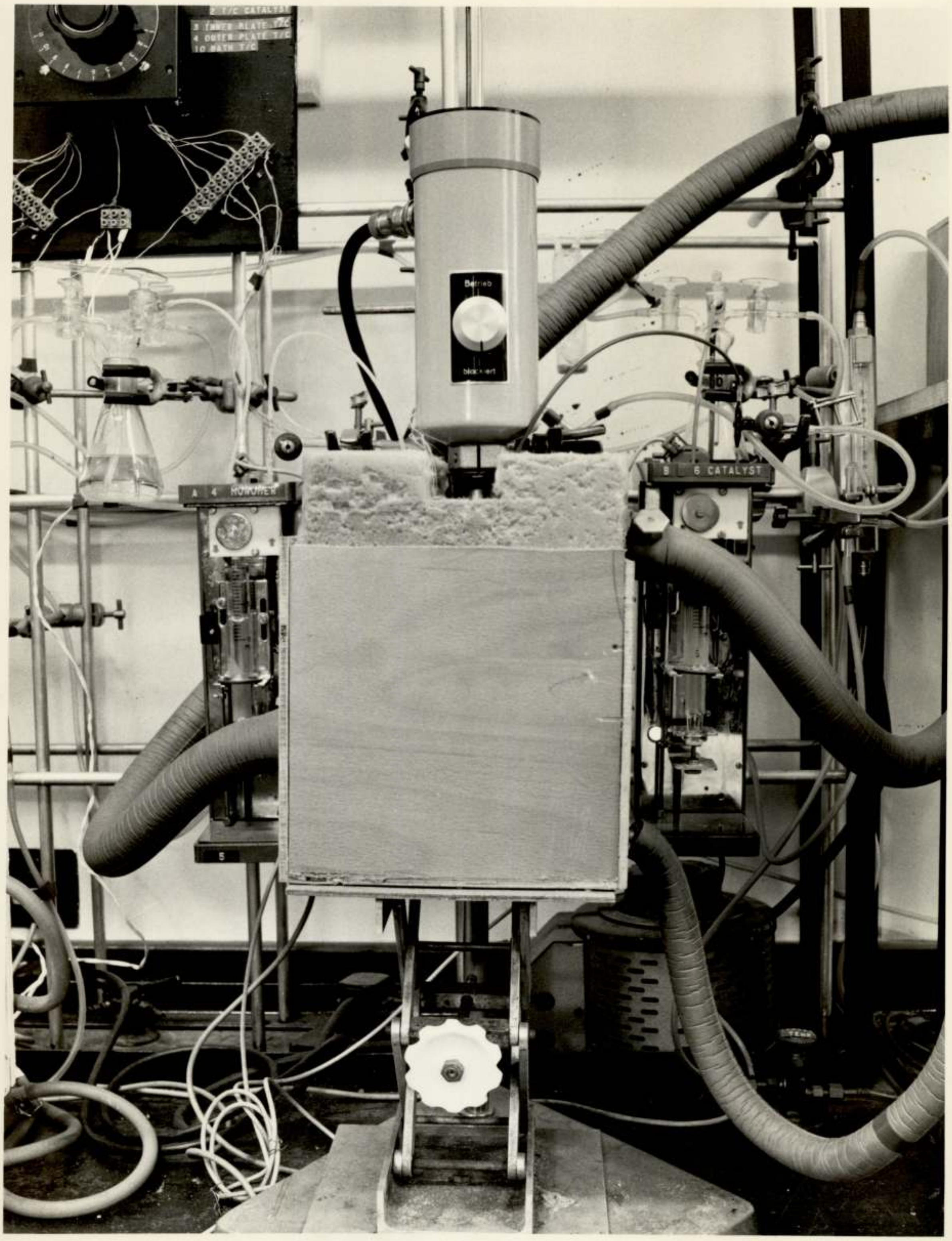

2 T/C CATALYST
3 INNER PLATE T/C
4 OUTER PLATE T/C
10 BATH T/C
Betrieb
A 4 MONOMER
B 6 CATALYST
5

PLATE II

measuring system is housed in a controlled environment (L) enabling runs to be carried out over the temperature range −70 to 80°C in a virtually moisture free atmosphere.

3.2 Apparatus Design I: Operating Procedure

A general view of the apparatus is shown in Plate III, p. 95a. The operating procedure for the equipment can be summarised as follows:-

1) Set up the appropriate circulating jacket.
2) Purge all gas lines thoroughly with dry oxygen free nitrogen, including the circulating jacket.
3) Purge all fluid lines with acetone followed by dry nitrogen to remove the solvent.
4) Detach monomer/solvent and catalyst/solvent reservoirs together with the syringes from the two dispensers and wash thoroughly with clean acetone. Remove old stopcock grease and replace using high temperature silicone grease. Place the reservoirs and syringes in an oven at 100°C for one hour.
5) Remove reagent reservoirs and syringes for dispensers from the oven and place in the dry box. Allow to cool to room temperature.
6) Prepare the appropriate monomer/solvent and catalyst/solvent solutions in the dry box and introduce these into their respective reservoirs. Assemble each reservoir.
7) Remove the two syringes from the dry box and quickly assemble in their respective dispensers.
8) Remove the charged reservoirs from the dry box and connect to the appropriate dispenser.
9) Connect the dispenser to the measuring system.

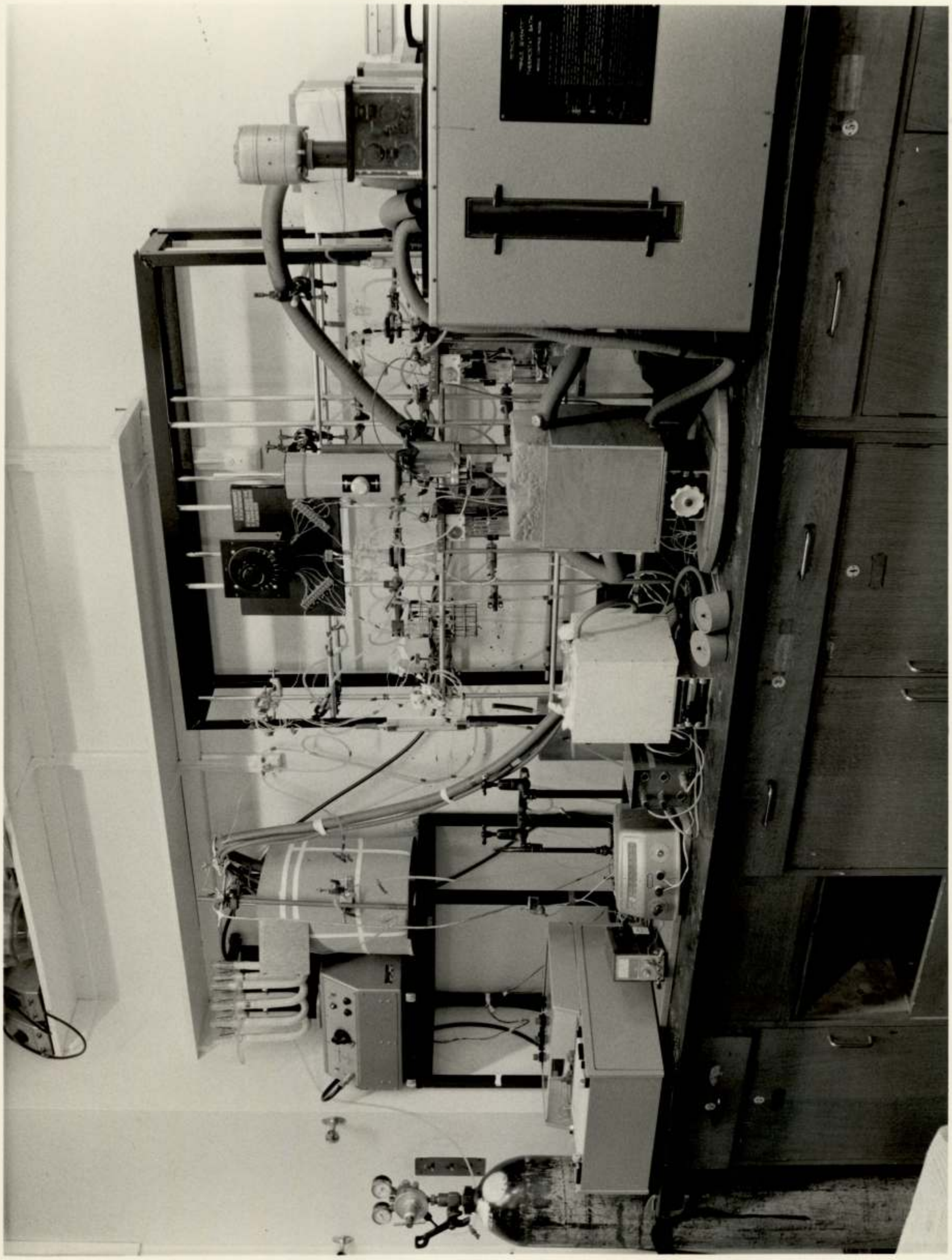


PLATE III

10) Purge the mixing system, fluid lines, reservoirs, and sample cavity with dry nitrogen.

11) Set the reservoir and fluid line taps in such a way that the reservoirs, A and B, Figure 5, p. 86, can be filled with their respective solutions.

12) Allow the solutions to attain the temperature at which the run is to be carried out.

13) Allow the base plate to attain the temperature at which the run is to be carried out and check the temperature at other parts of the system using the thermo-couple switch.

14) Set the chart recorder to the appropriate chart speed and range setting.

15) Set the rotational speed of the rheomat to the appropriate value and verify that the input voltage to the potentiometer of the rheomat is set correctly on the transformer.

16) Switch on chart recorder and viscometer.

17) Operate the dispensing cycle of the automatic dispensers.

18) Instantaneously stop the dispensers when around ten mililitres of fluid have been injected through the measuring system.

19) Confirm that an acceptable recorder trace is being produced thus indicating that the apparatus is operating satisfactorily.

20) Readjust recorder sensitivity, chart speed and rheomat speed as necessary during a run.

21) Allow the recorder trace to reach a plateau, indicating

completion of reaction and shut down the recorder and rheomat.

22) Dismantle the cone and plate system removing all thermocouples and removing the mixing heads and reservoirs A and B (Figure 5).

23) Dismantle the dispensers, removing reagent reservoirs and syringes.

24) Clean all the above components thoroughly with acetone and place in an oven at 100°C for one hour.

25) Clean all syringes and vessels used for transfer and measuring of liquids with acetone and place in an oven at 100°C for one hour.

26) Remove all apparatus placed in the oven and allow to cool in the dry box.

27) Assemble the cone and plate measuring system locating the mixing heads and reservoirs.

28) Connect the inlets of the mixing system to the outlets of the appropriate dispensers.

29) Locate all thermocouples in their respective positions.

30) Assemble the appropriate circulating jacket.

31) Purge all gas lines thoroughly with dry oxygen free nitrogen.

32) Purge all fluid lines thoroughly with dry oxygen free nitrogen including the circulating jacket.

33) For subsequent runs repeat operations 6) to 32).

Initial work, using the apparatus in the above form, was involved in the study of the polymerisation of a cationic system which consisted of styrene (50 parts), toluene (40 parts) and boron trifluoride etherate (10 parts). The reaction was carried out at 33°C in an environment containing a low level of moisture.

Many of the runs carried out using the above system were completely unreproducible although some runs indicated an acceptable level of reproducibility. Figures 6 and 7, p. 99 and 100 represent two reproducible runs, Figure 6 showing the first two and a half seconds of reaction, the reaction up to three hundred seconds being shown in Figure 7.

Figure 8, p. 101 shows the form of a typical unreproducible run for the same system reacted under similar conditions to the runs shown above. The main features of the run shown in Figure 8 which distinguish it from ideal runs of the type shown in Figures 6 and 7 are

i) a slower initial rate of viscosity increase followed by,

ii) subsequent oscillatory fall and rise in viscosity.

The slower initial rate of viscosity increase observed could be due to the effects of contamination from three possible sources as follows:

a) moisture contained in the air space surrounding the cone and plate system,

b) moisture (or contaminant) levels of the various reagents used,

c) the use of greased joints in the apparatus.

Viscosity versus Time Plots (△, □) for a Styrene/Toluene/BF_3 Etherate System Polymerising in Thin Film at 33°C (composition of system 50/40/10 parts by volume respectively)

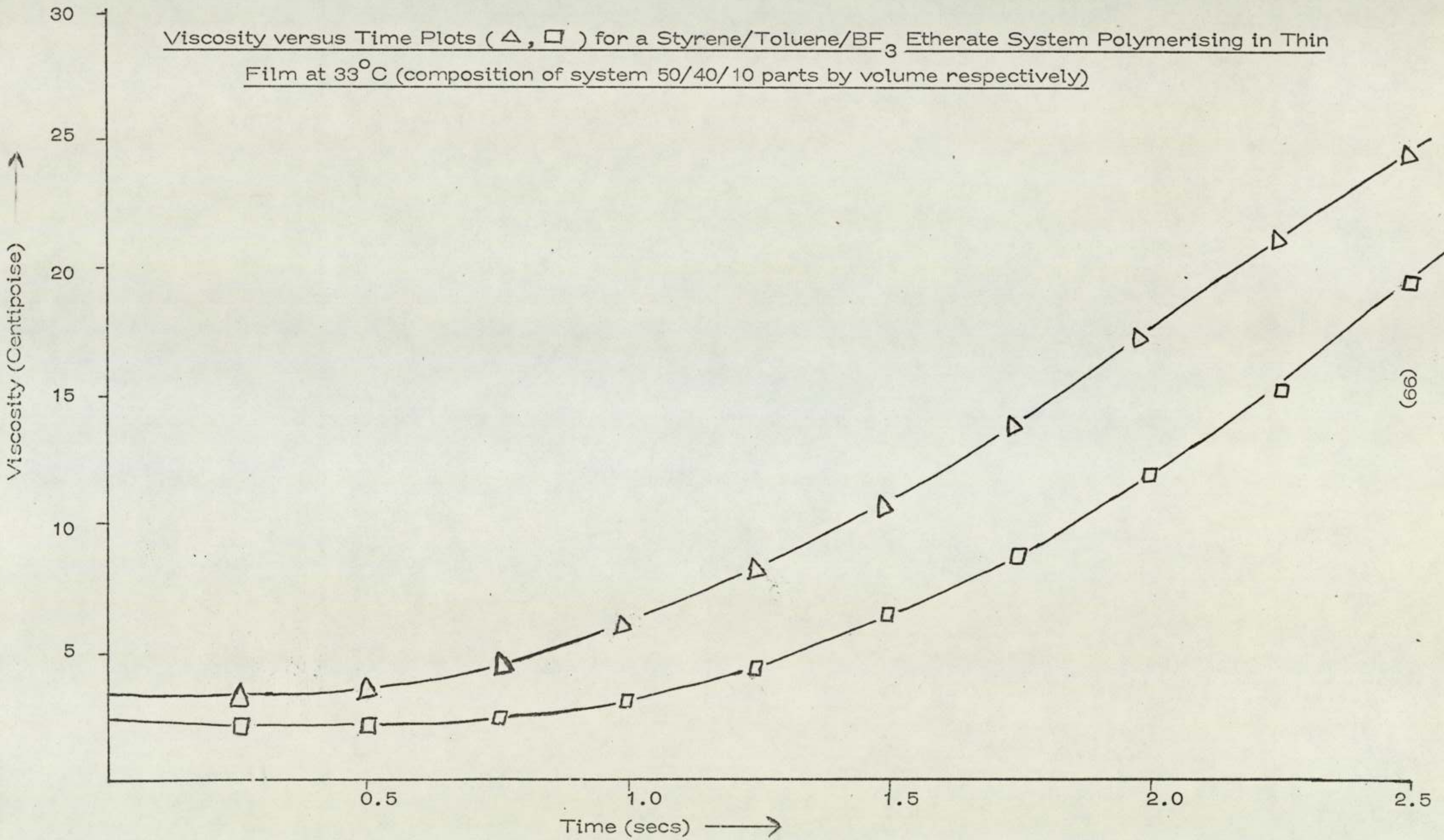
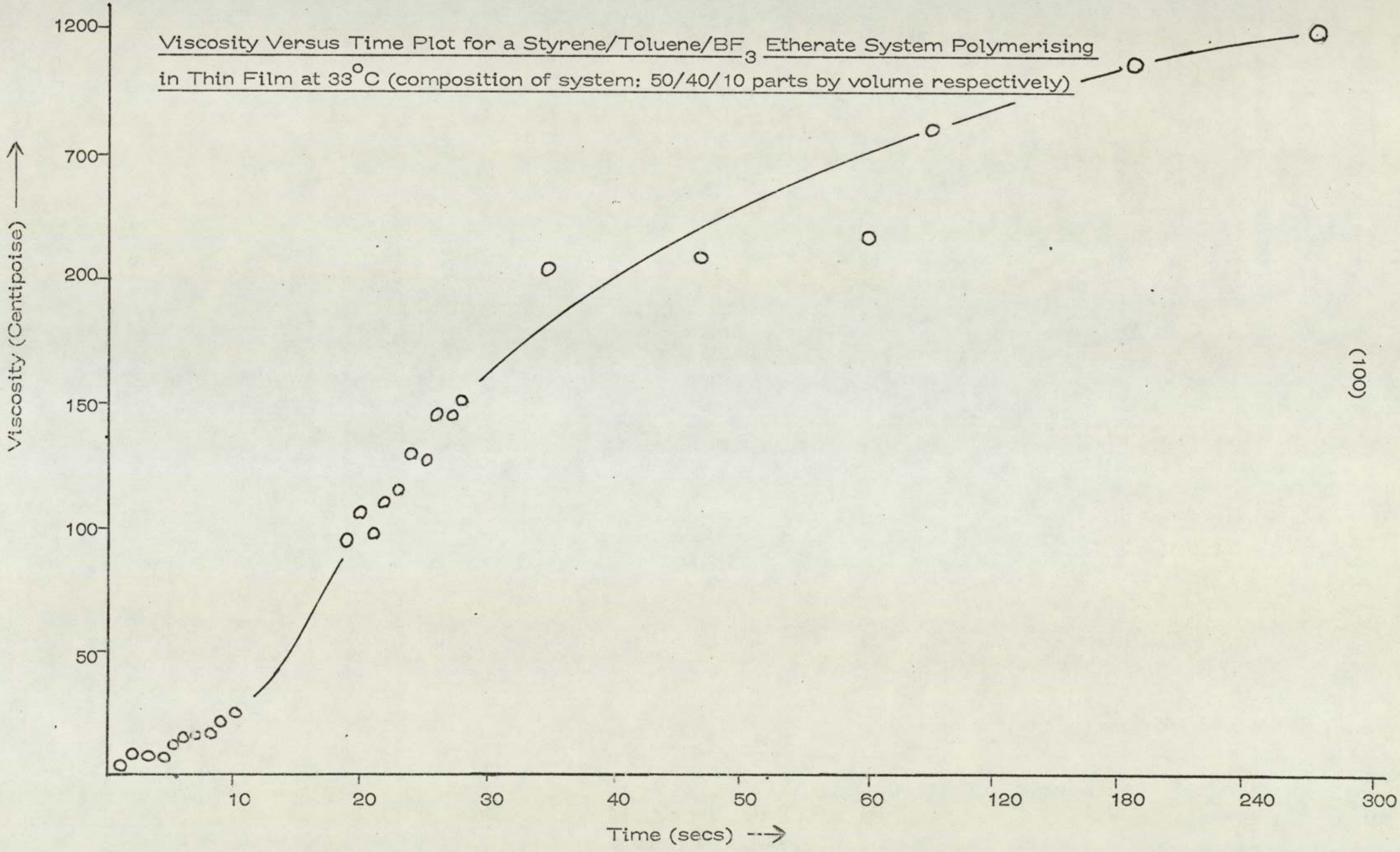
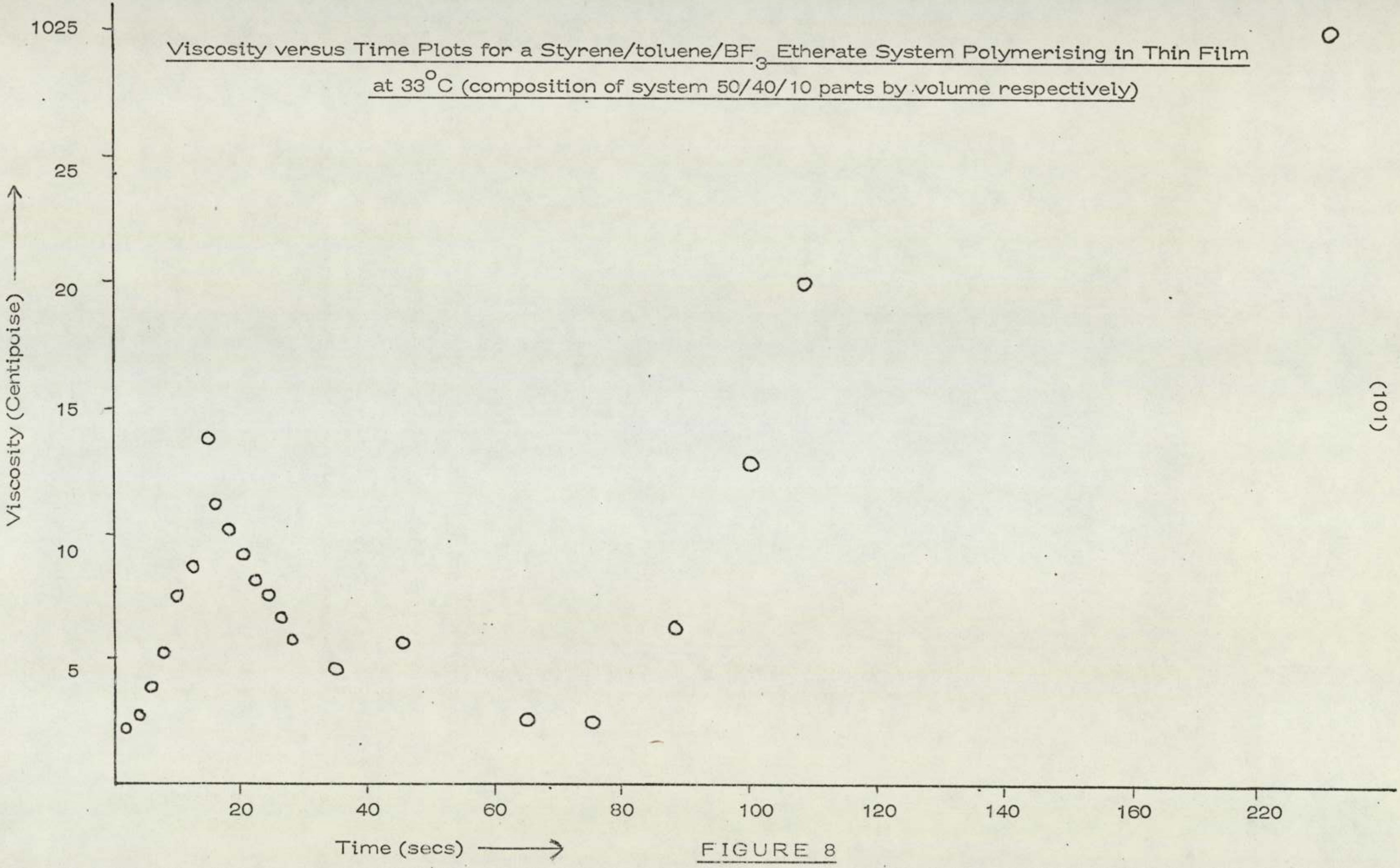


FIGURE 6



Viscosity Versus Time Plot for a Styrene/Toluene/BF_3 Etherate System Polymerising in Thin Film at 33°C (composition of system: 50/40/10 parts by volume respectively)



Viscosity versus Time Plots for a Styrene/toluene/BF_3 Etherate System Polymerising in Thin Film at 33°C (composition of system 50/40/10 parts by volume respectively)

FIGURE 8

The oscillatory effect observed could possibly be caused by contamination resulting in the formation of pockets of solid polymer in the sample cavity which would foul the cone. Such formation could, also be due to poor mixing of the system, poor solvent action, or the use of too high a concentration of monomer.

3.3 Final Modifications to the Apparatus (Design II)

In an attempt to overcome the problems outlined above (p. 98) for Apparatus Design I, modifications to the latter were implemented in a second design of apparatus which is depicted in its final form in Plate IV, p. 103a.

The major modifications proposed for the apparatus were

a) more effective control of the environment surrounding the cone and plate, particularly in terms of moisture content, and

b) the replacement of all greased joints in the system by P.T.F.E. valves.

a) The circulating jackets described above were replaced by an environmental test chamber which was specially commissioned from Montford Instruments, London.

The cone and plate measuring system is housed in the cavity of the chamber, which is 1 cubic foot in volume. The system is sited by means of a specially designed stainless steel clamp inserted through an aperature at the top of the chamber which enables it to be removed as required. Plate V, p. 104a shows the cavity with the cone and plate system in place together with the sensing element of the moisture meter and the various thermocouples.

The chamber shown in Plate VI, p.105a with the Rheomat and moisture meter in position is capable of achieving a temperature range of -50° to $+500^\circ$C with considerable accuracy ($\pm$ 0.1°C throughout the cavity). The low temperature levels (-50° to ambient) are achieved by using an indirect cooling system in which liquid

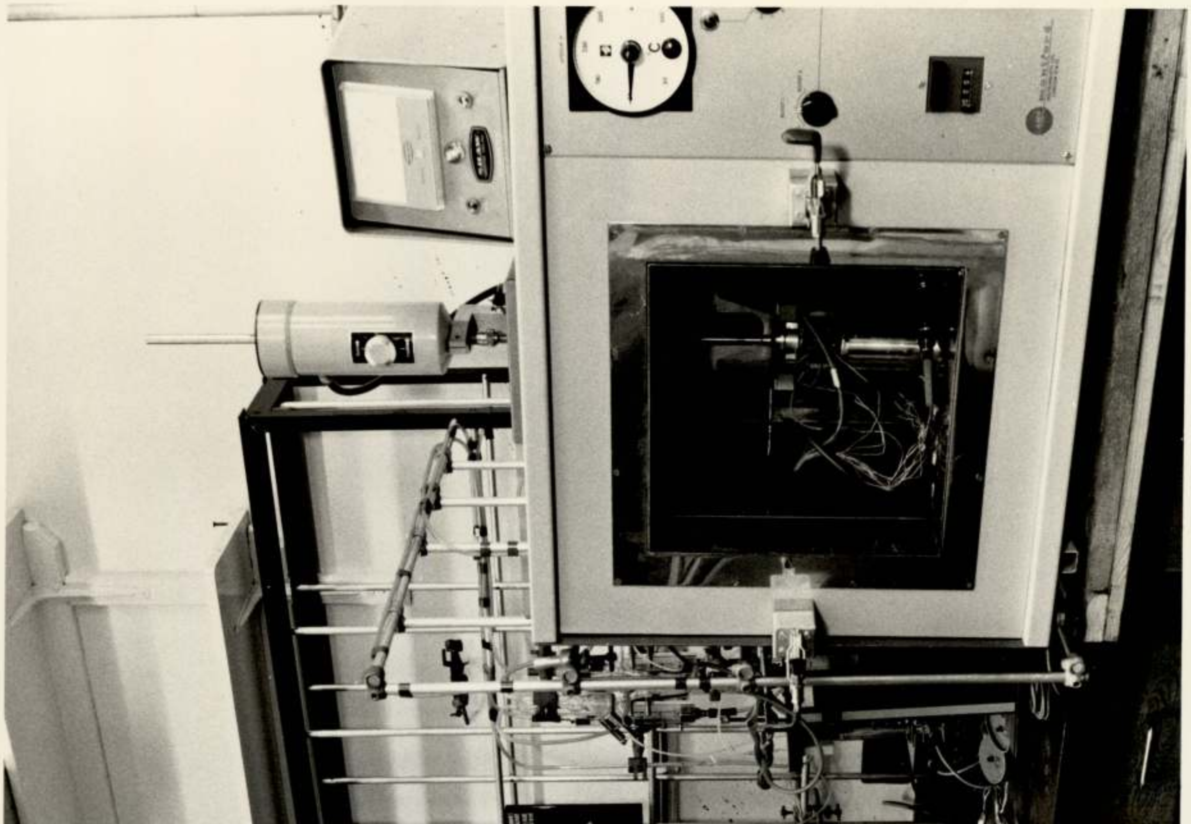


PLATE IV

carbon dioxide is injected through control valves into a heat exchange unit situated behind the back wall of the chamber cavity. Other methods of cooling involved the direct injection of liquid carbon dioxide or other suitable coolant into the chamber cavity. Although this form of cooling is more efficient than the former it could not be used since the gas coming into direct contact with the sample would contaminate and subsequently affect cationic systems being studied.

Low moisture levels (ca. 200 ppM) could only be achieved within the chamber cavity as it stood by purging with a very high flow rate of dry nitrogen which entailed obvious disadvantages. A glass vessel was, therefore, designed which would encase the cone and plate system and facilitate the efficient purging of the air space immediately surrounding the measuring system, which now only required a relatively low flow rate of dry gas. Plate VII, p. 106a shows the vessel in position in the chamber cavity. A seal is formed against the ceiling of the cavity by clamping the vessel tightly against a sealing gasket suitably positioned.

The accurate measurement of moisture levels in the vessel during the course of a run was again found difficult without risk of damage to the sensing element by its likely contact with the samples used. The same procedure was, therefore, followed as was used for Apparatus Design I. This entailed purging the glass vessel with the cone and plate in position, with known flow rates of dry nitrogen and measuring the resulting moisture levels in the

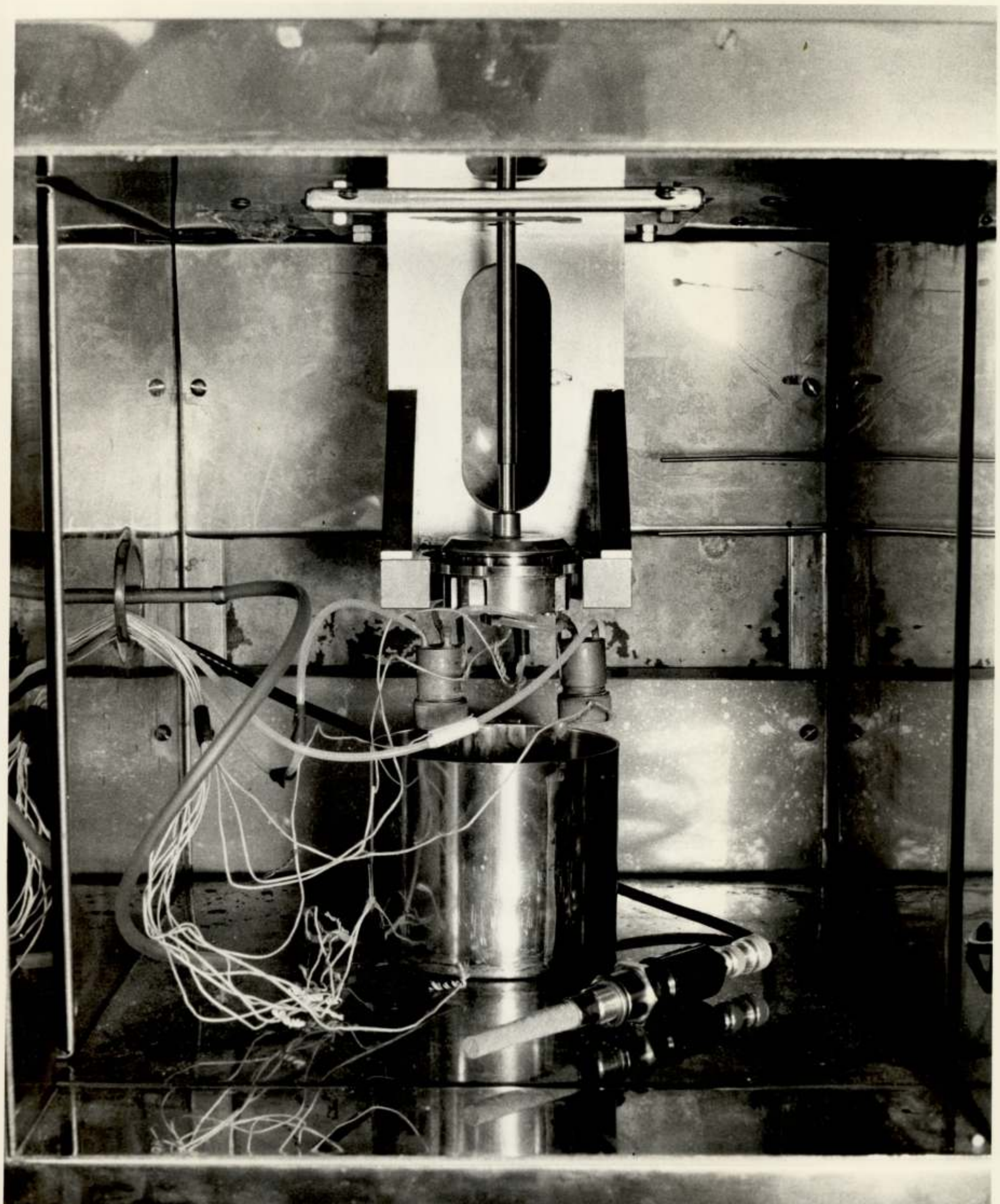


PLATE V

vessel with time using the moisture meter. A calibration graph could then be drawn showing the variation of moisture levels with time for a given flow rate of dry gas. Using exactly the same procedure during actual runs and periodically checking the calibration graph, particularly when high atmospheric relative humidities prevailed, a fairly accurate assessment of moisture levels present in the cavity during runs could be obtained. Figure 9, p. 106, shows a typical calibration graph of moisture levels versus time for conditions specified as determined immediately prior to a run.

The direct measurement of moisture levels in gases can not be carried out at temperatures greatly removed from ambient using the sensing element positioned in the cavity due to the sensitivity of the element to temperature. Accurate measurement of moisture under these conditions can only be achieved by circulating the gas in question through an external temperature control unit set at 25°C into which the sensing element is fitted. Since it was not possible to instal such a unit the sensing elements were used directly so that at least some indication of moisture levels created under such conditions could be obtained.

b) The modified reagent reservoir in which greased taps are replaced by P.T.F.E. valves are shown in Figure 4, p. 83 and Plate VIII, p. 107a which shows the resited dispensing system.

The experimental procedure for the operation of the above apparatus is essentially the same as that described for apparatus

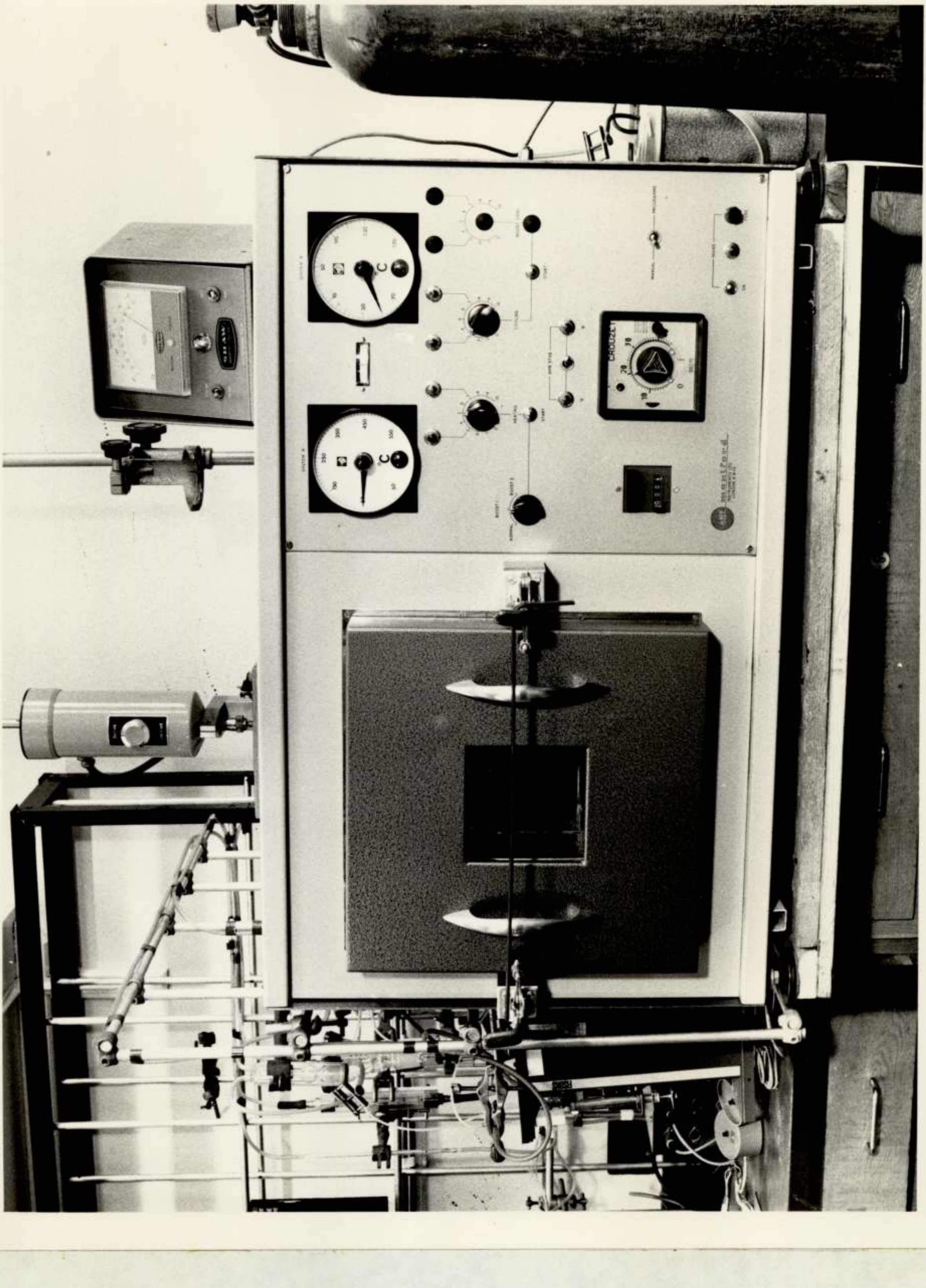
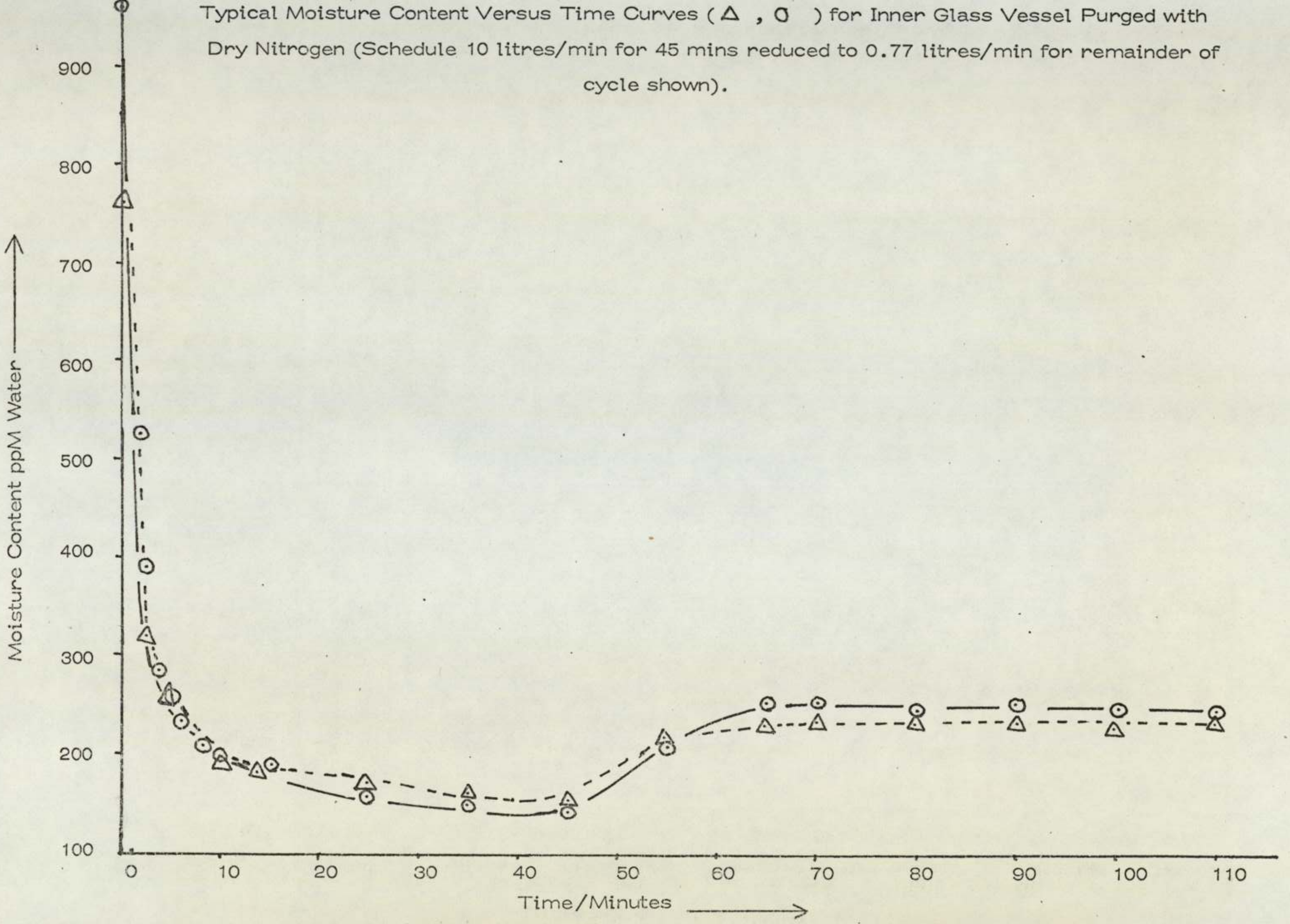


PLATE VI

Typical Moisture Content Versus Time Curves (Δ , ʘ) for Inner Glass Vessel Purged with Dry Nitrogen (Schedule 10 litres/min for 45 mins reduced to 0.77 litres/min for remainder of cycle shown).



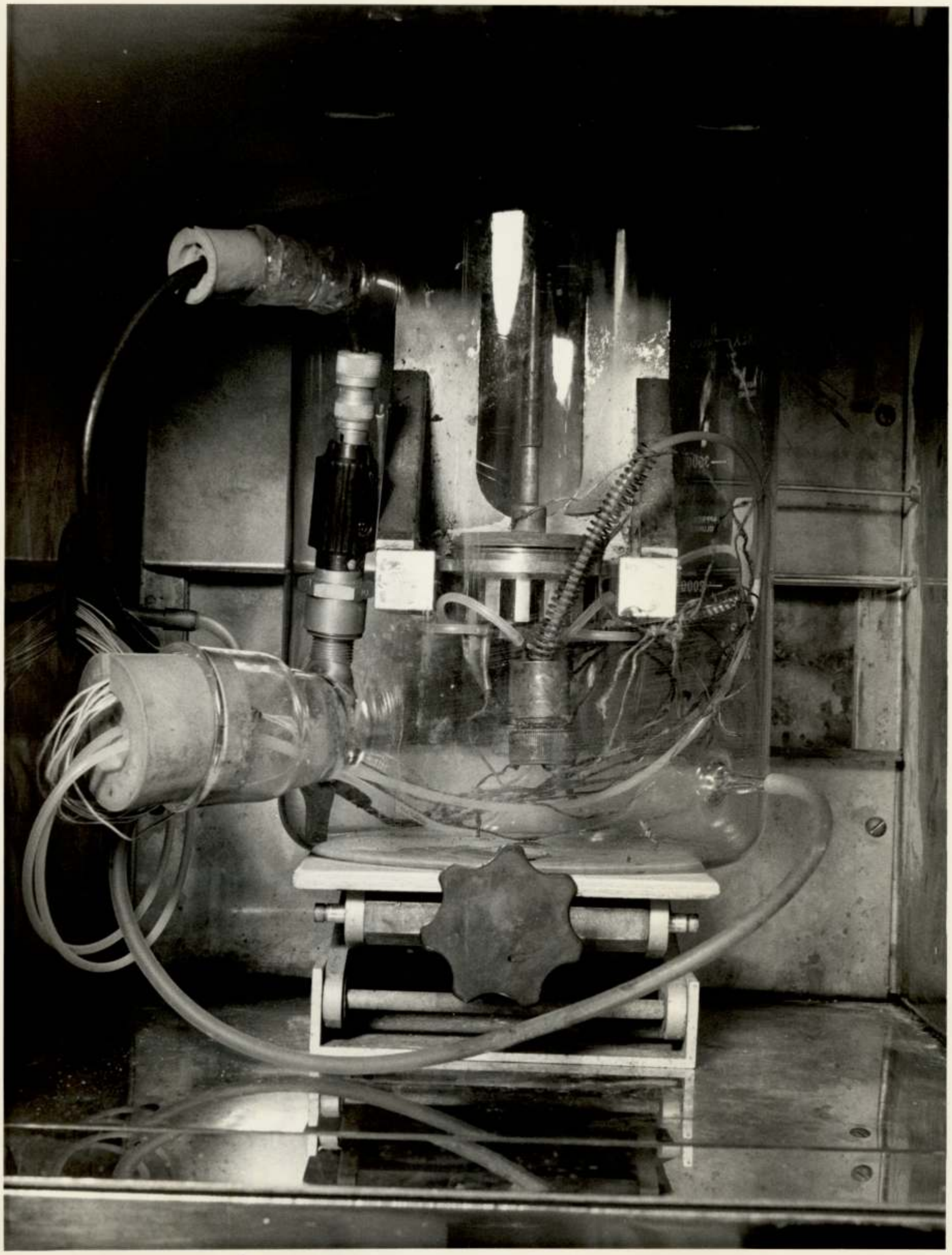


PLATE VII

design I except that assembly of the appropriate circulating jacket is no longer necessary in that the temperature required can now be set using the test chamber and assembly of the cone and plate measuring system entails positioning of the inner glass vessel in addition to the other necessary operations. It was also found convenient to position the stainless steel bracket which carried the cone and plate, using two laboratory jacks and a steel plate suitably positioned.

The apparatus in its final form as described above was found to operate satisfactorily for the purposes of this study and subsequent experimental work described in Chapter 5 was carried out using this apparatus.

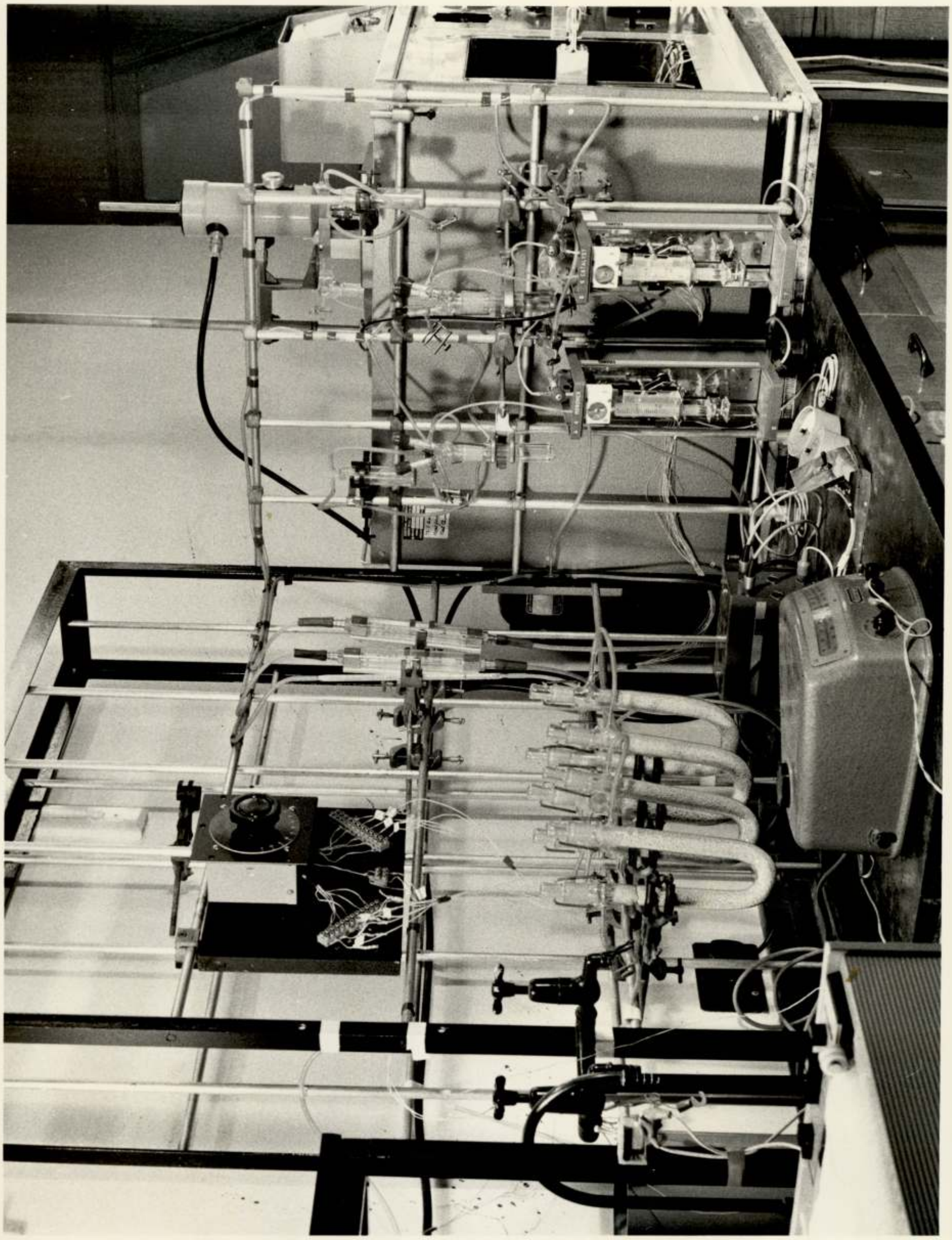


PLATE VIII

CHAPTER 4

Supplementary Experimental Techniques and Procedures

4.1 Supplementary Experimental Techniques

The Measurement of Gel Times of Cross Linking Systems

As a result of the literature survey presented in Chapter 2 and preliminary experimental work, coupled with the difficulties experienced during the development of the stopped flow rotational viscometer (Chapter 3), it was decided to carry out speculative studies involving the use of cationic initiators and cation sensitive monomers in the cross linking of a range of polyester resins. The reactivity of these latter systems was assessed on the basis of their respective gel times.

The apparatus developed for this work is shown in Plate IX, p. 108 a and consists of two manually operated syringes which enable resin, monomer and catalyst to be rapidly mixed via a glass 'T' piece, the resultant mix being received in a small beaker. An automatic recording gel timer (Model G.T.3. Tecam Ltd) with a fairly short cycle time (1/10 minute) monitored a probe which was cycled vertically in the mix contained in the beaker. As the mix approaches the point of gelation the considerable viscous drag on the probe causes a micro switch to be activated when the timer is automatically switched off, giving a read out of the appropriate gel time. All runs were carried out under nitrogen.

To assist in the adequate mixing of reagents in the beaker a magnetic stirrer and follower were used which enabled mixing to be carried out subsequent to the injection of reagents. For highly viscous mixes brief and rapid manual stirring with a spatula

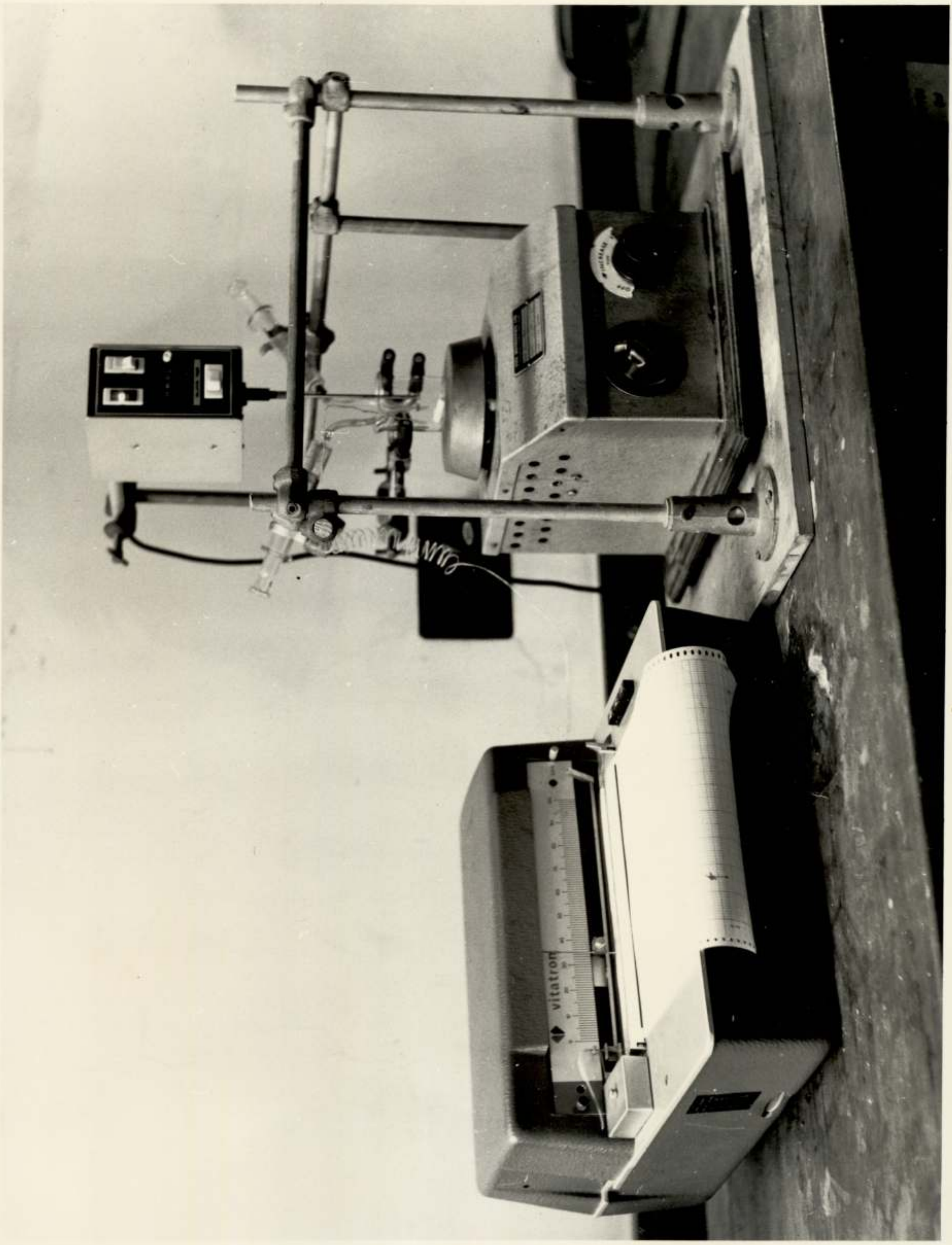


PLATE IX

was found to be necessary.

In later runs a thermocouple/potentiometric recorder was used to provide a time/temperature trace of the reaction exotherm.

Dry Box Technique

A schematic representation of the dry box layout in which various reagents were manipulated is shown in Figure 10, p. 110, and a general view of the apparatus is shown in Plate X, p. 109 a

Facilities for measuring both the moisture content of the air space in the dry box during its use together with that of the various solvents used in the box, were provided via the appropriate liquid and gas sensing elements coupled to the moisture meter, (Shaw Moisture Meters), described in Chapter 3, p. 79.

The levels of moisture in the dry box were maintained at around 10 p.p.M. Moisture was removed from the air space in the dry box by circulating the air through four ¼" I.D. glass coils immersed in acetone/solid carbon dioxide (Drikold) baths maintained at $-70^{o}C$. Fresh molecular sieve (Type 5A, regenerated by heating to $250^{o}C$ for 2 hours) was stored in the dry box at all times to assist in keeping moisture levels down particularly during periods when the dry box was not in use.

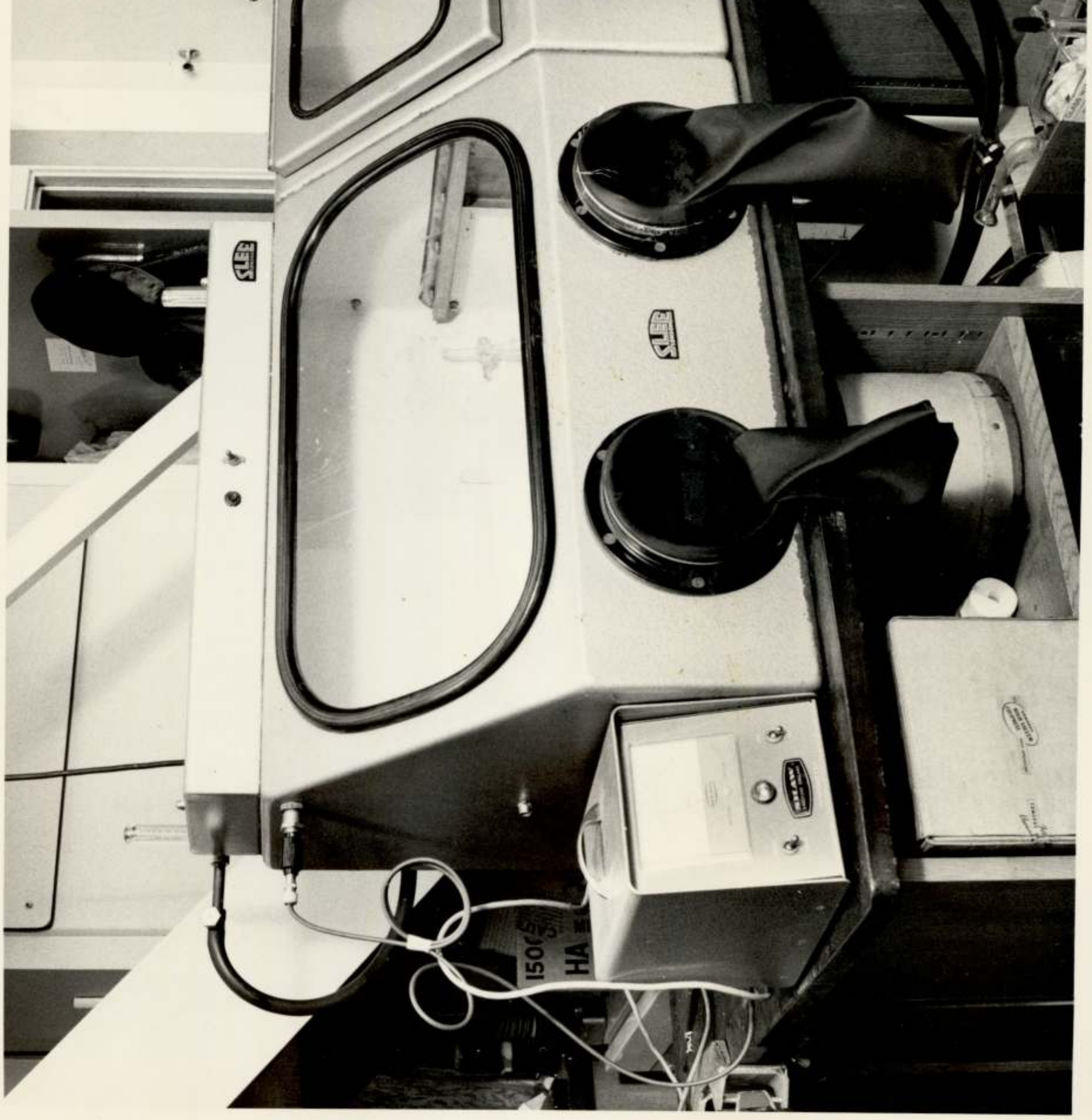


PLATE X

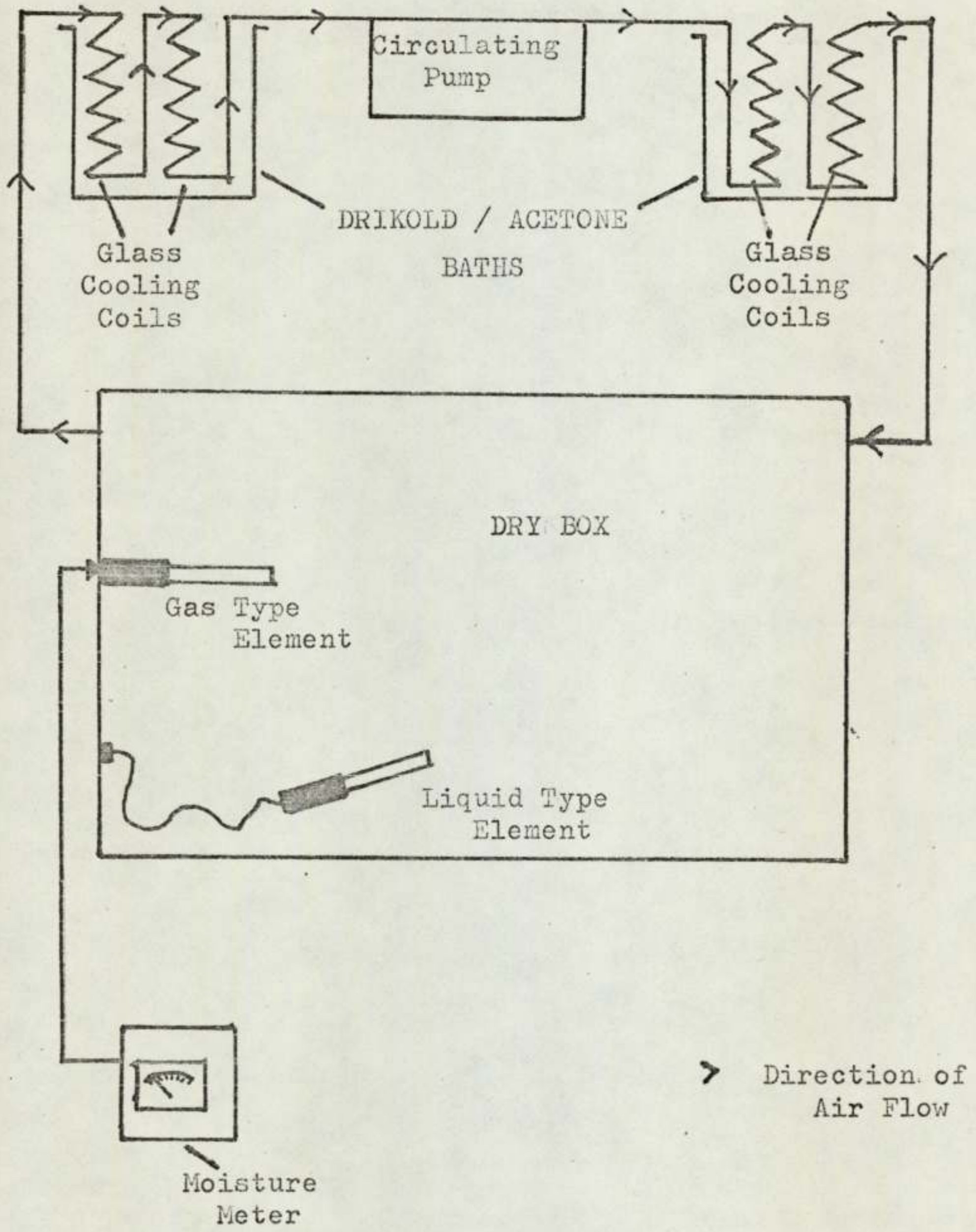

Circulating Pump
DRIKOLD / ACETONE BATHS
Glass Cooling Coils
Glass Cooling Coils
DRY BOX
Gas Type Element
Liquid Type Element
Moisture Meter
> Direction of Air Flow

FIGURE 10

4.2 Purification of Reagents

In this section details are given of the materials which were used in the work together with any purification procedures carried out.

Monomers

The following commercially available monomers were used:

Styrene (Hopkin and Williams)

α methyl styrene (Hopkin and Williams)

Butyl vinyl ether (Hopkin and Williams)

Cyclopentadiene (Koch Light)

Methyl cyclopentadiene (Koch Light)

1,3 Cyclohexadiene (Koch-Light)

1,4 Cyclohexadiene (Koch Light)

1,3 Cyclooctadiene (Koch Light)

cis,cis 1,5 Cyclooctadiene (Koch Light)

cis, cis 1,5 Cycloheptatriene (Koch Light).

The above monomers were purified by conventional pre-polymerisation and vacuum distillation techniques(127) and finally distilled onto molecular sieve (Type 5A, BDH Co Ltd). All monomers were stored at 0°C with the exception of cyclopentadiene (CPD) and methylcyclopentadiene (MCPD) which were both stored at -70°C., since both monomers dimerise rapidly at room temperature and 0°C. For this reason CPD and MCPD are available commercially only as the dimers, the respective monomers being readily obtained by destructively distilling the dimers at their boiling points at atmospheric pressure.

Dicyclopentadiene (b.pt 160°C) was redistilled under dry nitrogen at atmospheric pressure and the fraction boiling over the range 40-43°C collected over molecular sieve at -70°C and stored at the latter temperature in glass flasks sealed with serum type stoppers.

Dimethylcyclopentadiene (b.pt. 200°C) was redistilled in a similar fashion and the fraction boiling at 69 to 70°C was collected over molecular sieve at -70°C and stored at this temperature in glass flasks sealed with serum type stoppers.

Table 12, below summarises the G.L.C. analysis of the monomers prepared above.

Table 12

A Summary of the Composition Determined by Gas Chromatography of Cyclopentadiene (1) and Methyl Cyclopentadiene (2) prepared via the Destructive Distillation of the Corresponding Dimers. [Conditions of Analysis:- 5 foot Silicone Gum SE30 Column operated at a Temperature of 120°C using a Carrier Gas Flow Rate of 60 ml/min (Helium)].

	Component	Percentage Weight	Retention Time (Minutes)
1	Cyclopentadiene	97.0	1½
	Dicyclopentadiene	3.0	10
2	Methylcyclopentadiene	98.5	2
	Dimethylcyclopentadiene (4 isomers)	0.3,0.5,0.6,0.1	15,17,20,22½

Glycols

The glycols used were as follows;

Ethylene glycol (Hopkin and Williams)

Diethylene glycol (Hopkin and Williams)

Butene diol (Aldrich Chemical Company)

Hexylene diol (Aldrich Chemical Company).

The above reagents were used as received and stored over molecular sieve for at least 24 hours prior to use.

Anhydrides and Acids

The following materials were used as supplied by the manufacturers;

Maleic anhydride (Hopkin and Williams)

Phthalic anhydride (Hopkin and Williams)

Adipic acid (Hopkin and Williams)

Muconic acid (Aldrich Chemical Company).

Miscellaneous Reagents

The following materials were also used:

Methyl ethyl ketone, 60% solution in dimethyl phthalate (British Industrial Plastics),

Cobalt napthenate ('Accelerator B', British Industrial Plastics)

γ butyrolactone (Koch Light)

Terephthalic aldehyde (Koch Light)

Polyvinylpyrollidone (Mol. Wt. 24,500, Koch Light)

Ethyl bromide (Standard Laboratory Reagent, Fisons)

Magnesium metal (Grignard Reagent, Fisons).

The above reagents were used as received except in appropriate cases where materials were dried over molecular sieve.

Solvents

All solvents used were purified by conventional techniques(128) and stored over molecular sieve for at least 24 hrs prior to use, ether used in Grignard reactions being stored over sodium wire. The following solvents, obtained from Fisons Ltd, were used:

Toluene (Analar grade)

Chlorobenzene (Standard Laboratory Reagent)

Ether (Analar grade)

Dichloromethane (Standard Laboratory Reagent).

Drying Agents

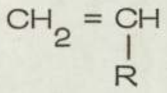
The drying agent used in the bulk of the work was molecular sieve (Type 5A BDH Chemicals Ltd).

CHAPTER 5

The Study of Rates of Homopolymerisation Reactions in Thin Film Using Stopped Flow Rotational Viscometry

Introduction

Initial experimental work using the stopped flow rotational viscometer was to be concerned with an assessment of the effect of alkyl, aryl and alkoxy groups substituted in the α position of mono α olefins of the general form XXI, on their rate of polymerisation using cationic initiators.



$$CH_2=\underset{R}{\underset{|}{CH}}$$

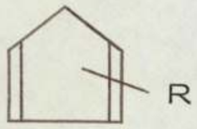
where R = alkyl, aryl or alkoxy

XXI

It has been stated previously (Chapter 1, p. 4) that the high rates of reaction observed for many cationic systems are due in the main to the high concentration of active species that are built up at the very early stages of reaction, as opposed to the rate of individual propagating steps which are, in general, slower than for corresponding reactions involving free radicals. It follows that the higher the concentration of active species the higher will be the rate of conversion to polymer for a given system. The concentration of active species (that is the concentration of cations present at any one time) can be increased by improving their stability which in turn can be achieved by substituting electron donating groups in structures of the above form (XXI). Theoretically however a point could be reached when cationic species derived from the latter become so stable that individual propagating reactions become virtually non existent. At this point monomer reactivity would be expected to decline.

It had been envisaged, therefore, that a fundamental study of the type outlined above could closely relate the reactivity of a monomer with its structure when cationically polymerised in thin film. Such a study would enable the selection of the most promising monomer type, in terms of reactivity, for further study in the context of this work or enable some prediction of monomer structures most likely to exhibit favourable reactivity levels.

The literature survey presented in Chapter 2 had revealed some particularly reactive monomers based on cyclic diene structures of the form XXII notably cyclopentadiene (CPD) and methylcyclopentadiene (MCPD).



where R = H or alkyl

XXII

Other monomer types which were found to have commanded a good deal of attention are those based on vinyl ethers. Although such materials are reported in the literature to have relatively high reactivity levels such levels are stated to be lower than those reported for the above cyclic dienes (CPD and MCPD). CPD and MCPD are reported by several workers to be the most reactive monomers which have been polymerised chemically(80,81,82), as opposed to those monomers polymerised using high energy radiation.

Preliminary work involving an assessment of the reactivity of CPD and MCPD proved so encouraging that the decision was made to modify the approach outlined above to the problem of the development of a rapid homopolymerisation system. Thus attention was directed away from a fundamental study of the reactivity of a series of mono α olefins and focused on a similar study involving an assessment of the reactivity of a series of commercially available cyclic dienes using the apparatus described in Chapter 3.

Experimental work described in the present Chapter is divided into three sections as follows:

a) The calibration of the apparatus.

b) The assessment of the suitability of the apparatus in measuring the rates and kinetic features of polymerisation reactions using a polymerisation reaction with well established kinetics.

c) The evaluation of the reactivity of styrene and a series of cyclic dienes in cationic polymerisation reactions using the above apparatus.

5.1 The Calibration of the Apparatus

i) The Determination of the Response Times of the Apparatus under Various Conditions

As stated in Chapter 3 the Rheomat operates at 15 different rotational speeds to cover the viscosity range 25 to 1,580 centipoise for the cone and plate measuring system used throughout this work. The overall time constant of the apparatus is governed, under certain conditions, by the minimum response time (full scale deflection) of the rheomat for a viscosity rise covered by a given rheomat speed. Values of response times determined for various rheomat speeds are shown in Table 13 together with the viscosity ranges covered by the rheomat speeds quoted.

Table 13

Minimum Response Times of the Stopped Flow Rotational Viscometer at Various Rheomat Speeds

Rotational Speed of the Cone in r.p.m.	Corresponding Viscosity Range in Centipoise	Time for Full Scale Deflection of Rheomat in seconds
352 (maximum speed)	0.252 - 25.2	0.75
77.98	1.14 - 114.0	1
17.40	5.10 - 510.0	3
5.595 (minimum speed)	15.8 -1,580	9.5

The results were obtained by instantaneously stopping the spindle of the rheomat manually thus simulating a near spontaneous polymerisation process taking place in the sample cavity. The signal produced by the Rheomat under these conditions was monitored on the recorder operated at its highest chart speed (1200 mm/min). The results show that the higher the initial viscosity of a system under study the higher will be the response time of the apparatus. Thus at the lowest rotational speed (5.595 r.p.m.) the apparatus is capable of studying rates of reactions with a half life of 9½ seconds or more while at the maximum rotational speed, rates of reactions with a half life in the region of 0.75 seconds or more can be studied. It should be emphasised, however, that for the measurement of rates of homopolymerisation (as opposed to the measurement of crosslinking rates) described in this work, systems were used which possessed an initial viscosity of around 0.2 centipoise. Initial rates of reaction were generally calculated for a viscosity rise of 0.2-20 centipoise, a range adequately covered by the viscometer at the maximum Rheomat speed which corresponds to a minimum response time of 0.75 seconds for the apparatus. (Table 13, p. 118).

The overall time constant of the apparatus is also governed under certain conditions by the time constant for sample mixing. The active volume of the sample cavity of the cone and plate measuring system used in this work is around 0.36 ccs which together with the volume of the entry ports leading from the mixing heads to the cavity constitutes a total sample volume of around

1.36 ccs. The flow rate of material entering the cavity was controlled at 3.3 ccs/second since 10 cc syringes were used for all runs described in this work (see Table 11, p. 84). This infers that the time constant for sample mixing and delivery is of the order of 0.4 seconds (i.e. the residence time of the mixed sample in the cavity during sample delivery is around 0.4 seconds). Under these conditions with the Rheomat operating at its maximum speed the minimum response time of the apparatus will correspond to that of the Rheomat i.e. 0.75 seconds (see Table 13). For flow rates of 1.8 cm^3/second or less the time constant for sample mixing and delivery increases to 0.75 seconds or more, when for the maximum Rheomat speed, the response time of the apparatus would be governed by the time constant for sample mixing and delivery.

ii) The Determination of Appropriate Temperature Levels and Temperature Equilibration Times

The temperature variation within the environmental test chamber described in Chapter 3, p. 103, was measured using chromel/alumel thermocouples incorporating a cold junction at $0^{\circ}C$. For the temperature range -30 to $+ 500^{\circ}$ temperature variation at any point in the cavity of the chamber was found to be $\pm\ 0.1^{\circ}C$.

The temperature variation at any point within the inner glass vessel shown in Plate VI, p.105a was also measured over the temperature range -30 to $+100^{\circ}C$ using a nitrogen purge of 0.77 litres/minute; this was found to be of the order of $\pm\ 0.5^{\circ}C$.

Temperature equilibration times, corresponding to the temperature range used in this work namely room temperature to +90°C, were measured for both the cone and plate measuring system and for material resident in the reservoirs A and B using thermocouples positioned as shown in Figure 5, p. 86. The equilibration time for the cone and plate was found to be of the order of 1½ hours and for materials in reservoirs A and B of the order of 8 minutes.

5.2 The Study of the Rates of the Free Radical Polymerisation of Styrene/Lauryl Peroxide Systems in Thin Film, using the Stopped Flow Rotational Viscometer

In order to ascertain to what extent results obtained using the stopped flow rotational viscometer could be validly applied to the assessment of the reactivity and reaction kinetics of a given polymerising system, an evaluation of the technique was carried out using a homogeneous free radical vinyl polymerisation system whose kinetic features are well known. The system used was based on styrene, lauryl peroxide being chosen as the initiator since this gave measurable rates of polymerisation under convenient conditions. The system was polymerised at 85°C using the levels of initiator indicated in Table 14, p. 123, which summarises the compositions of the systems studied.

Component A shown in Table 14 represents the composition of material (pure monomer) contained in one syringe and component B that contained in the second syringe (monomer plus initiator). Dispensing the system in this way enabled some appraisal of the efficiency of the mixing system to be carried out since in the event of valid results being obtained for the above system, the efficiency of operation of all component parts of the viscometer would be implied, including the mixing system.

Strictly speaking the method of sample delivery used in these experiments (see Table 14) prevents measurements in the sample cavity from being taken at t = 0, since initiator and monomer

Table 14

A Summary of the Composition of Styrene/Lauryl Peroxide Systems Studied using the Stopped Flow Rotational Viscometer

Component A Styrene (grams)	Component B		Concentration of Initiator in Mixed System in moles l^{-1}
	Styrene (grams)	Lauryl Peroxide (grams)	
25	24.475	0.525	0.0286
25	23.38	1.62	0.0885
25	22.79	2.21	0.1204
25	21.76	3.24	0.177

are premixed in one of the dispensing syringes prior to delivery. In practice, however, the residence times of the system, both at room temperature and in the reservoirs A and B (see Figure 5, p. 86) were kept to an absolute minimum (15 minutes and 2 minutes respectively). Since these particular reactions were fairly slow, however, the effect is seen to be relatively unimportant since temperature equilibration within the sample cavity involved a time period which is small compared to that involved with the polymerisation.

Typical viscosity versus time plots showing the full reaction profile are shown in Figures 11 and 12, p. 124 and 125. The form of these plots shows what appears at first sight to be a slow initial reaction rate or induction period followed by a fairly rapid polymerisation process. This latter phenomenon appeared to take place at a viscosity level of around 20 cps for all runs. Preliminary

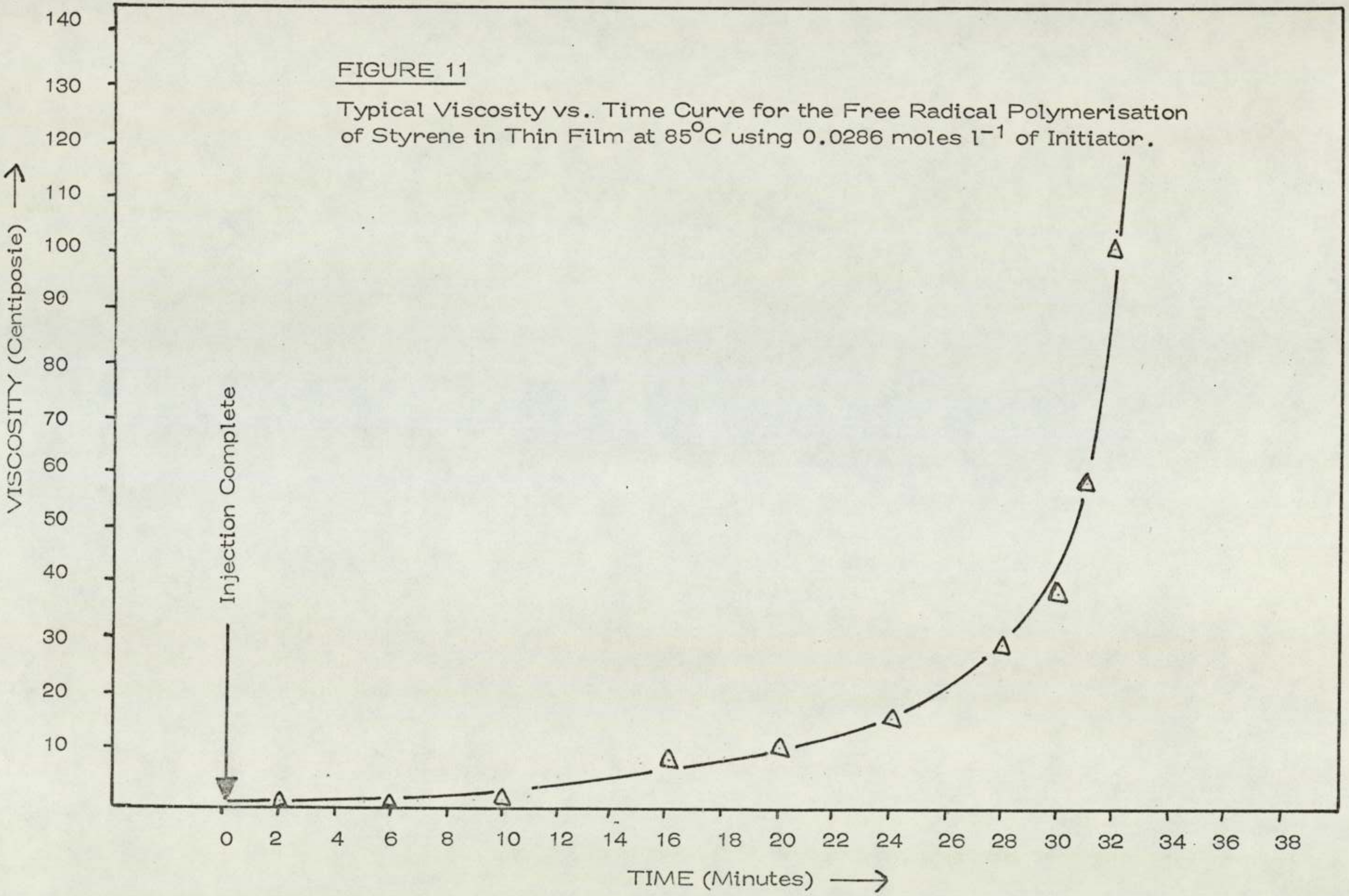


FIGURE 11

Typical Viscosity vs.. Time Curve for the Free Radical Polymerisation of Styrene in Thin Film at 85°C using 0.0286 moles l^{-1} of Initiator.

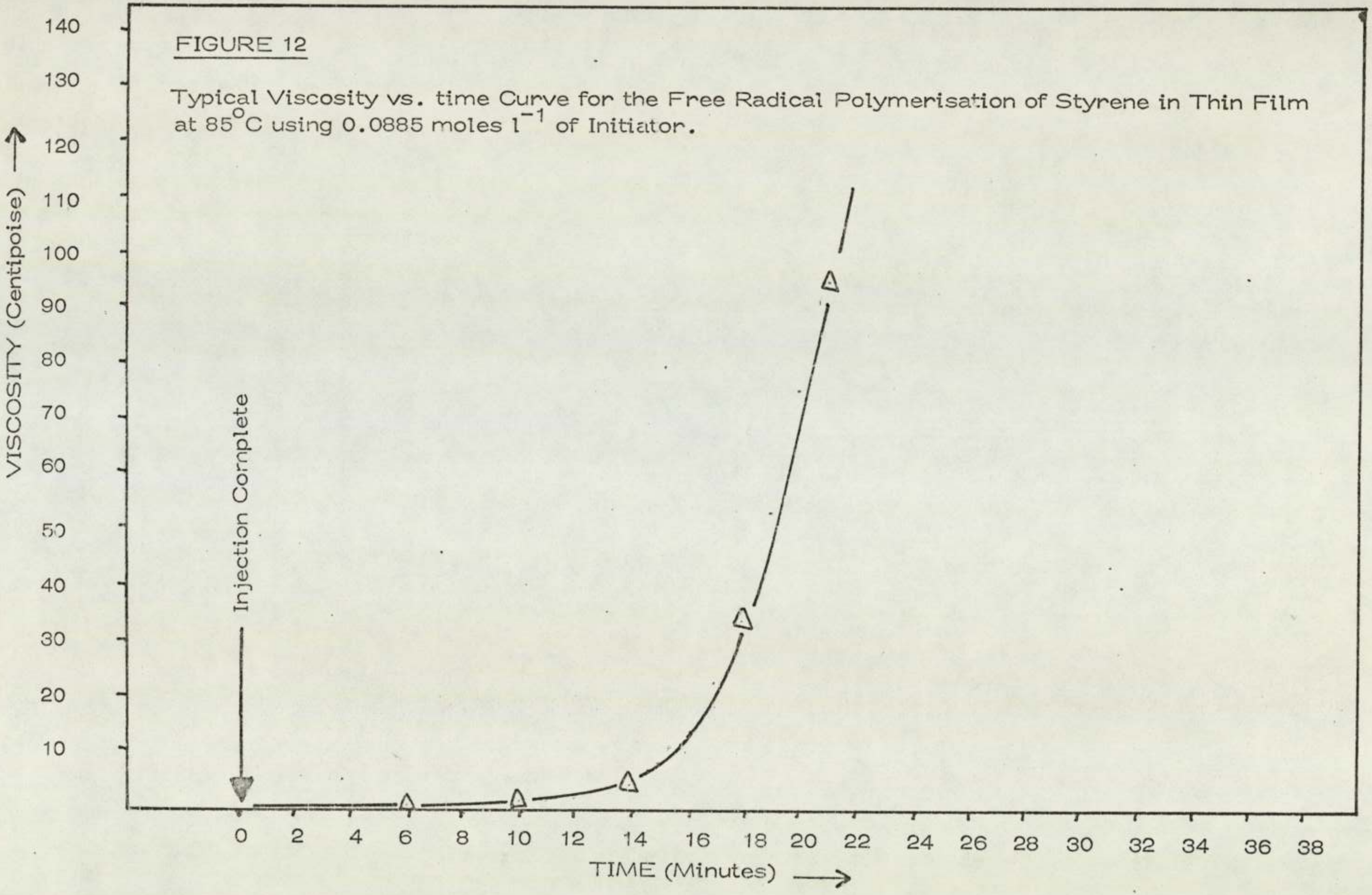


FIGURE 12

Typical Viscosity vs. time Curve for the Free Radical Polymerisation of Styrene in Thin Film at 85°C using 0.0885 moles l^{-1} of Initiator.

work on the determination of the viscosity of polystyrene (Mv 350,000)/styrene solutions showed that a 5% w/w solution of the latter gave a viscosity of 10.8 cps and a 10% w/w solution a viscosity of 39 cps. It appeared likely, therefore, that the marked increase in reaction rate observed for the above runs took place at between 5 and 10% conversion, a phenomenon which has also been observed for the free radical polymerisation of methyl methacrylate. An explanation for the latter has been presented by Trommsdorff et al(129-133), in which they point out that the formation of a relatively low proportion of chains results in a reduction of chain mobility which in turn reduces chain termination by transfer and combination reactions involving free radicals on chain ends. This results in a dramatic increase in reaction rate the phenomenon being termed the 'gel effect'.

Thus the apparent induction period is seen to be an initial rate (Figure 13, p. 127) and as such yields kinetic information relating to this part of the reaction. In addition rates were calculated at a point corresponding to ~ 8% conversion when deviation from the linear rate period was observed. The results of both analyses are summarised in Table 15, p. 128.

The repeatability of runs carried out in this section was of the order indicated in runs shown in Figure 6, p. 99.

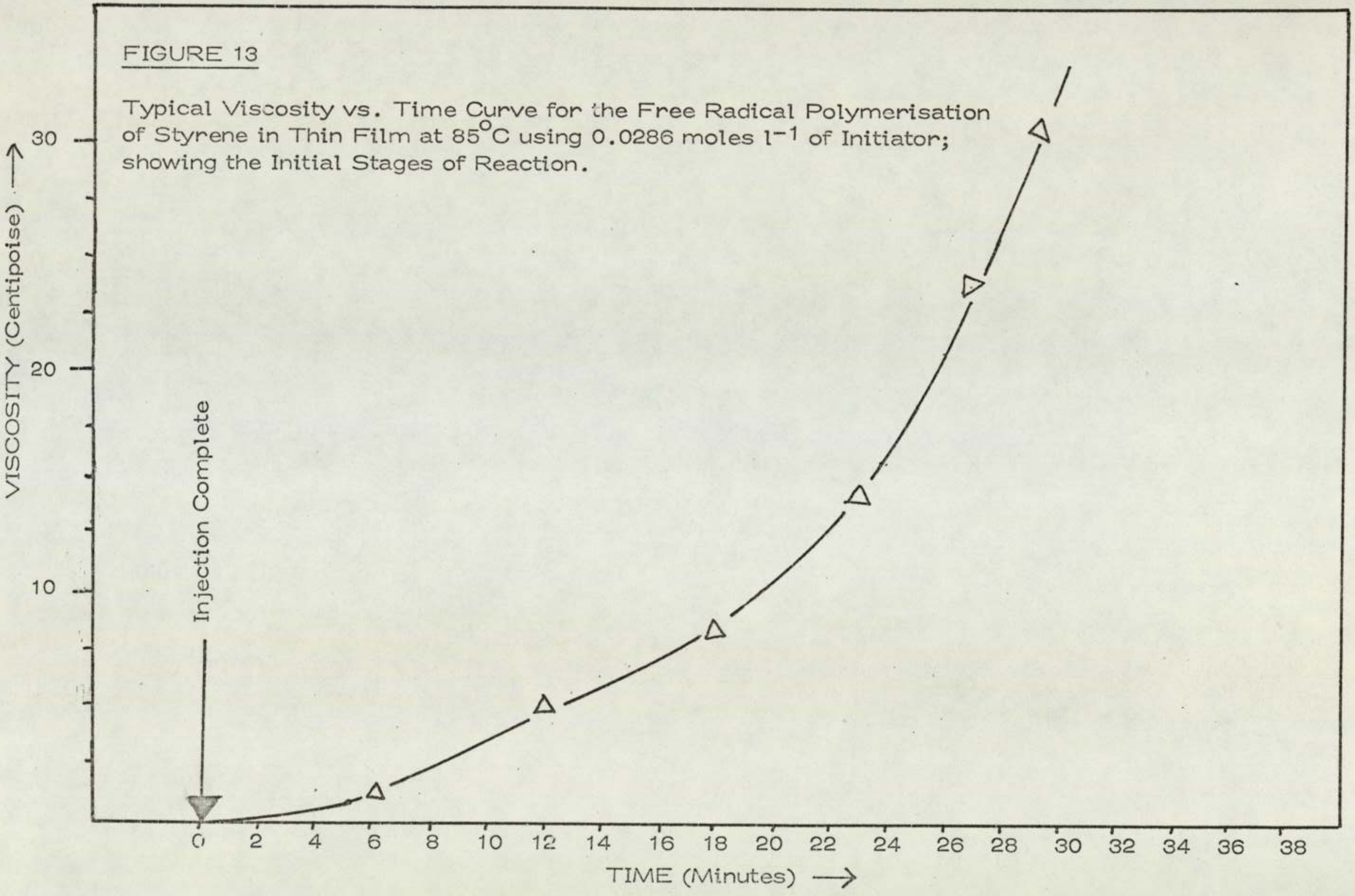


FIGURE 13

Typical Viscosity vs. Time Curve for the Free Radical Polymerisation of Styrene in Thin Film at 85°C using 0.0286 moles l^{-1} of Initiator; showing the Initial Stages of Reaction.

Table 15

A Summary of Initial Rates of Reaction for a Series of Styrene/ Lauryl Peroxide Systems Polymerised at 85°C

Initiator Concentration (moles l^{-1})	'Apparent Induction Period' (minutes)	Initial Rate calculated from 'apparent induction period' (moles $l^{-1}sec^{-1}$)	Initial Rate calculated from linear portion of viscosity/time curve (moles $l^{-1}sec^{-1}$)
0.0286	26.5	4.25×10^{-4}	1.59×10^{-3}
0.0885	15	7.50×10^{-4}	3.31×10^{-3}
0.1204	12	9.40×10^{-4}	3.71×10^{-3}
0.177	10.5	10.70×10^{-4}	5.12×10^{-3}

It has been well established(134) that the rate of propagation, R_p, for a free radical polymerisation process may be expressed as follows:

$$R_p = f\,k_d^{1/2}\,\frac{k_p}{k_t^{1/2}}\,[M]\,[I]^{1/2} \qquad \ldots\ 10)$$

where f is a factor which represents the fraction of primary radicals which initiate chains.

k_d is the rate constant for the decomposition of the initiator into two primary radicals.

k_p is the rate constant for chain propagation.

k_t is the rate constant for chain termination.

[M] represents the concentration of monomer present.

[I] represents the concentration of initiator present.

R_p may also be identified with the rate of polymerisation since the number of monomer molecules reacting with primary radicals to yield a chain radical can be assumed to be small compared with the number consumed in the propagation step. Therefore for a given concentration of monomer we can write:-

$$-\frac{dM}{dt} = K[I]^{\frac{1}{2}} \qquad \ldots 11)$$

where $K = f\,k_d^{\frac{1}{2}}\,\frac{k_p}{k_t^{\frac{1}{2}}}\,[M]$.

A plot of $\log_{10}$ (Initial Rate) versus $\log_{10}[I]$ should therefore yield a straight line graph of slope 0.5 for free radical polymerisation reactions obeying Equation 10). Values of $\log_{10}$ (Initial Rate) plotted against $\log_{10}[I]$ for the systems presented in Table 15 are shown in Figure 14, p. 130. Two plots are shown, one possessing a slope of 0.565 – for initial rates calculated using apparent induction periods, the other possessing a slope of 0.555 – for initial rates calculated using the linear portion of the viscosity/time curves. These results indicate that the stopped flow rotational viscometer is capable of yielding valid kinetic information for polymerisation reactions. In addition values of $\frac{k_p}{k_t^{\frac{1}{2}}}$ were calculated using Equation 10 for the above systems, these are summarised in Table 16, p. 131.

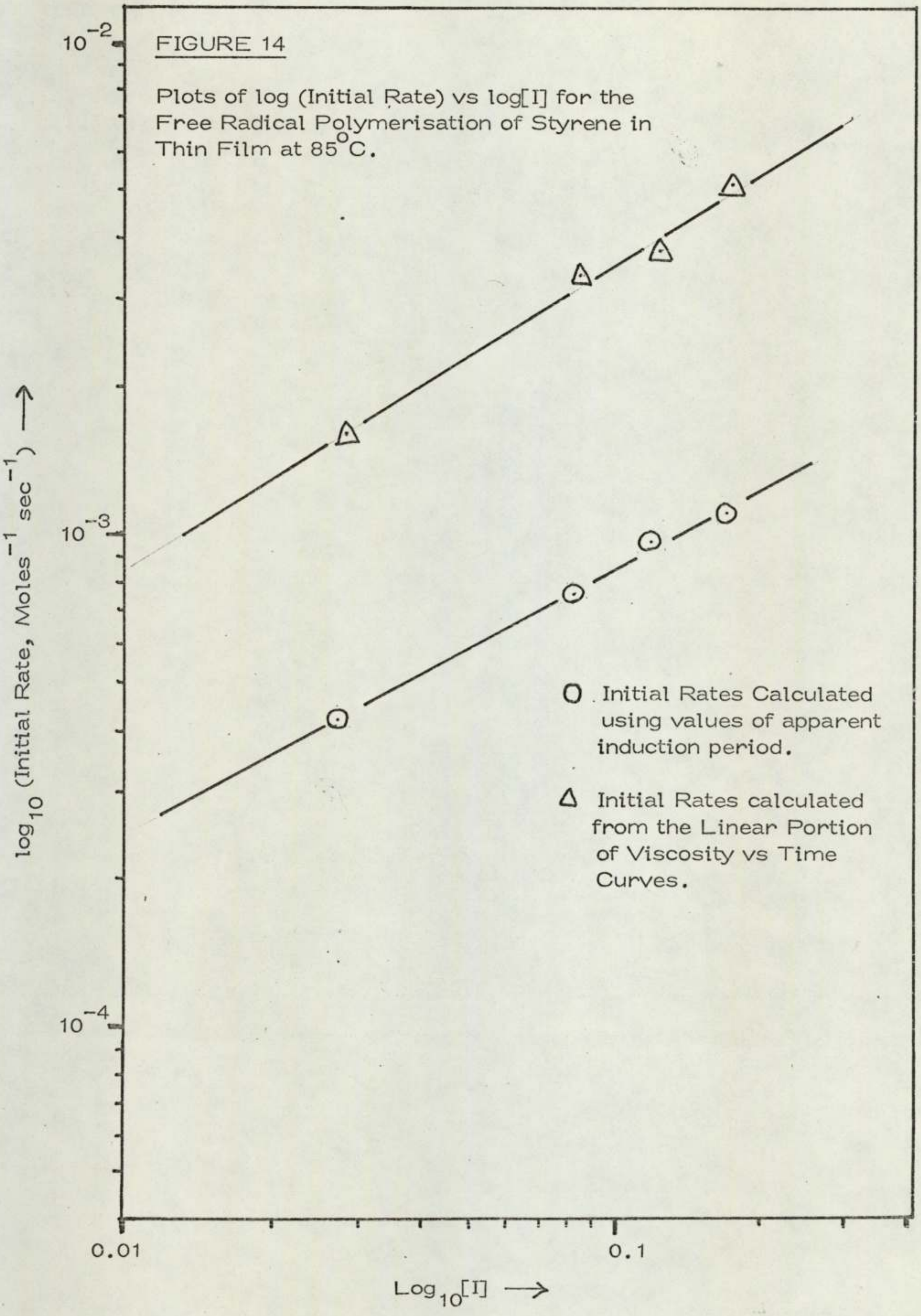


FIGURE 14

Plots of log (Initial Rate) vs log[I] for the Free Radical Polymerisation of Styrene in Thin Film at 85°C.

Table 16

A Summary of $\frac{k_p}{k_t^{1/2}}$ values for the Series of Styrene/Lauryl Peroxide Systems (Table 15) Polymerised at 85°C

Initiator Concentration (moles l^{-1})	$\frac{k_p}{k_t^{1/2}}$ l mole^{-1}sec^{-1} [Calculated using Initial Rates derived from 'Apparent induction period']	$\frac{k_p}{k_t^{1/2}}$ l mole^{-1}sec^{-1} [Calculated using Initial Rates derived from linear portion of viscosity/time curves].
0.0286	0.271	1.01
0.0885	0.086	0.381
0.1204	0.091	0.360
0.177	0.087	0.415

The values for $\frac{k_p}{k_t^{1/2}}$, shown in Table 16 are of the same order as those values quoted for styrene/benzoyl peroxide and styrene/azo-bis-isobutyronitrile systems(135), which again indicates that results obtained using the stopped flow rotational viscometer are valid for the systems studied.

The molecular weights of polymers formed from the styrene/lauryl peroxide systems were also determined using Gel Permeation Chromatography and values obtained are summarised in Table 17, p. 132.

Table 17

A Summary of M_n, M_w and M_w/M_n Values of Polymer formed from the Styrene/Lauryl Peroxide System at Various Levels of Initiator Concentration ‡

Initiator Concentration (mole l^{-1})	M_n	$\frac{10^4}{M_n}$	M_w	M_w/M_n
0.0286	22,000	4.55	44,302	1.95
0.0885	14,150	7.1	24,428	1.73
0.1204	14,440	6.95	23,229	1.61
0.177	11,686	8.55	19,017	1.63

‡ Results obtained using Gel Permeation Chromatography; carried out by R.A.P.R.A. Polymer Supply and Characterisation Centre, Shawbury, Operating Conditions: Flow Rate: 1 cc/minute.

Solvent: Tetrahydrofuran plus 0.1% 2.6, di tert butyl p-Cresol as inhibitor.

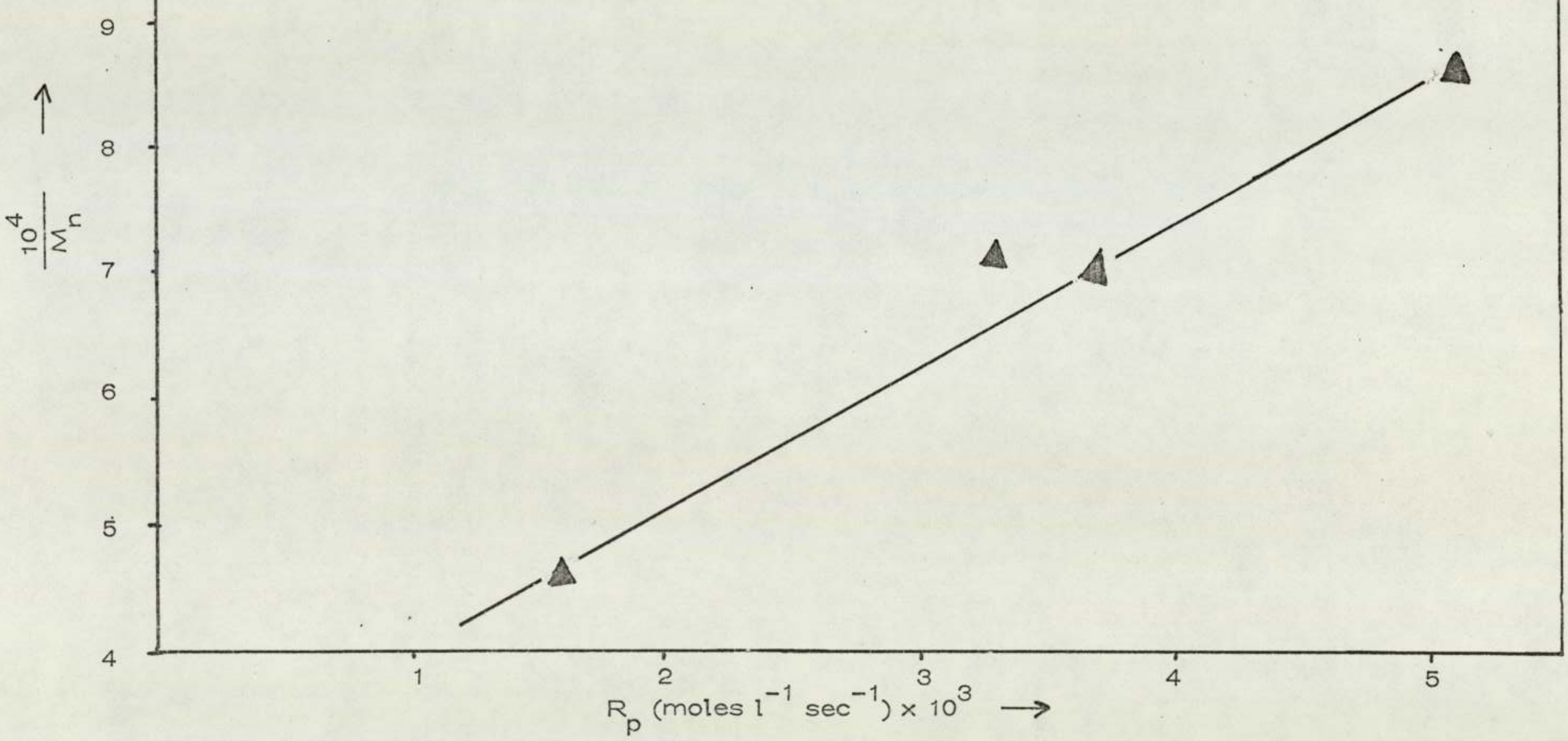
Temperature: Ambient.

A plot of $\frac{1}{M_n}$ versus initial rate of polymerisation R_p (calculated using the linear portion of viscosity/time curves obtained) is shown in Figure 15, p. 133, where a direct proportionality between $\frac{1}{M_n}$ and R_p is observed similar to that obtained for methyl methacrylate/benzoyl peroxide and methyl methacrylate/azo-bis-isobutyronitrile systems(136). A similar plot to that shown in Figure 15 is also observed for styrene systems

FIGURE 15

Plot of $\frac{1}{M_n}$ v. Initial Rate of Polymerisation, R_p for the Styrene/Lauryl Peroxide Systems Summarised in Table 17, p. 132.

[R_p values calculated from the linear portion of appropriate Viscosity/Time Curves; see Table 15, p. 128]



studied here when initial rates calculated from apparent induction times are used (Table 15, p. 128). These plots validate results obtained using the stopped flow rotational viscometer for the polymerisation of the styrene/lauryl peroxide system.

It should be noted that for the type of reaction studied above M_n remains virtually constant throughout the reaction so that calibration curves can be easily constructed by measuring viscosity levels for various polymer/solvent compositions using polymer of the appropriate molecular weight. Thus viscosity/conversion curves can be produced giving good accuracy.

The situation is more complicated, however, when

a) Viscosity/conversion relationships are not accurately known

and

b) M_n varies with time.

Within limits, however, the technique is sound for the quantitative determination of rates and in the two latter cases - if the results are interpreted with caution valuable information can be gained e.g. comparison of rates of conversion in systems having rapid rates of polymerisation.

5.3 The Study of the Rates of Cationic Polymerisation of Styrene and a Series of Cyclic Dienes Using Stopped Flow Rotational Viscometry

The cationic polymerisation of styrene and a series of cyclic dienes was studied using toluene as solvent and boron trifluoride etherate as initiator at 25°C in an atmosphere containing 250 ppM of moisture (see Figure 9, p. 106).

The systems studied are summarised in Table 18, p. 136.

Results

1) The Cationic Polymerisation of Styrene Systems

The polymerisation of systems A to D summarised in Table 18 was studied, viscosity/time characteristics for each system being measured using stopped flow rotational viscometry. Appropriate blends of monomer/solvent and initiator/solvent were dispensed separately as described in procedures summarised in Chapter 3.

Viscosity/time curves for the four systems in question are shown, for the first 20 seconds of reaction in Figure 16, p. 137. Table 19, p. 138 summarises the viscosity of each system as measured at longer periods of time. The plots shown in Figure 16 serve to give some indication of levels of conversion attained when compared with the viscosity levels mentioned on page 126 for polystyrene/styrene blends, assuming similar solution properties for the polymers involved. Table 19 also includes a summary of molecular weights of polymer obtained after 10 minutes of reaction.

Table 18

A Summary of Systems whose Rate of Cationic Polymerisation was Studied using Stopped Flow Rotational Viscometry, at 25^{o}C in an Atmosphere containing 200 ppM Moisture using Toluene as Solvent

System	Monomer	Monomer Concentration $[M]_o$ (mole l^{-1})	Initiator ($BF_3.OEt_2$) Concentration $[I]_o$ (mole l^{-1})	Solvent Concentration (mole l^{-1})	$[M]_o/[I]_o$
A	Styrene	1.74	0.8	6.58	2.17
B	Styrene	2.60	0.8	5.64	3.25
C	Styrene	3.48	0.8	4.70	4.35
D	Styrene	4.34	0.8	3.76	5.42
E	Cyclopentadiene	2.42	0.8	6.58	3.01
F	Cyclopentadiene	3.64	0.8	5.64	4.5
G	Cyclopentadiene	4.84	0.8	4.70	6.05
H	Methylcyclopentadiene	2.08	0.8	6.58	2.6
I	Methylcyclopentadiene	3.12	0.8	5.64	3.9
J	Methylcyclopentadiene	4.16	0.8	4.70	5.2
K	1,4 Cyclo hexadiene	2.08	0.8	6.58	2.6
L	1,3 Cyclo hexadiene	2.08	0.8	6.58	2.6

Cont:

Table 18 Continued

System	Monomer	Monomer Concentration $[M]_o$ (mole l^{-1})	Initiator ($BF_3.OEt_2$) Concentration $[I]_o$ (mole l^{-1})	Solvent Concentration (mole l^{-1})	$[M]_o/[I]_o$
M	Cycloheptatriene	3.12	0.8	5.46	3.9
N	1,3 Cyclooctadiene	3.12	0.8	5.64	3.9
O	1,5 Cyclo octadiene	3.12	0.8	4.70	3.9
P	Cyclopentadiene	3.12	0.016	6.58	195
Q	Methylcyclo pentadiene	3.12	0.016	6.58	195

FIGURE 16

Viscosity vs Time Curves for the Polymerisation in Thin Film at 25°C of Styrene/ BF_3OEt_2/Toluene Systems [ref Table 18, p. 136]. Systems A-D.

Key: Systems A, △ ; System B, ○ ; System C, □ ; System D, ● .

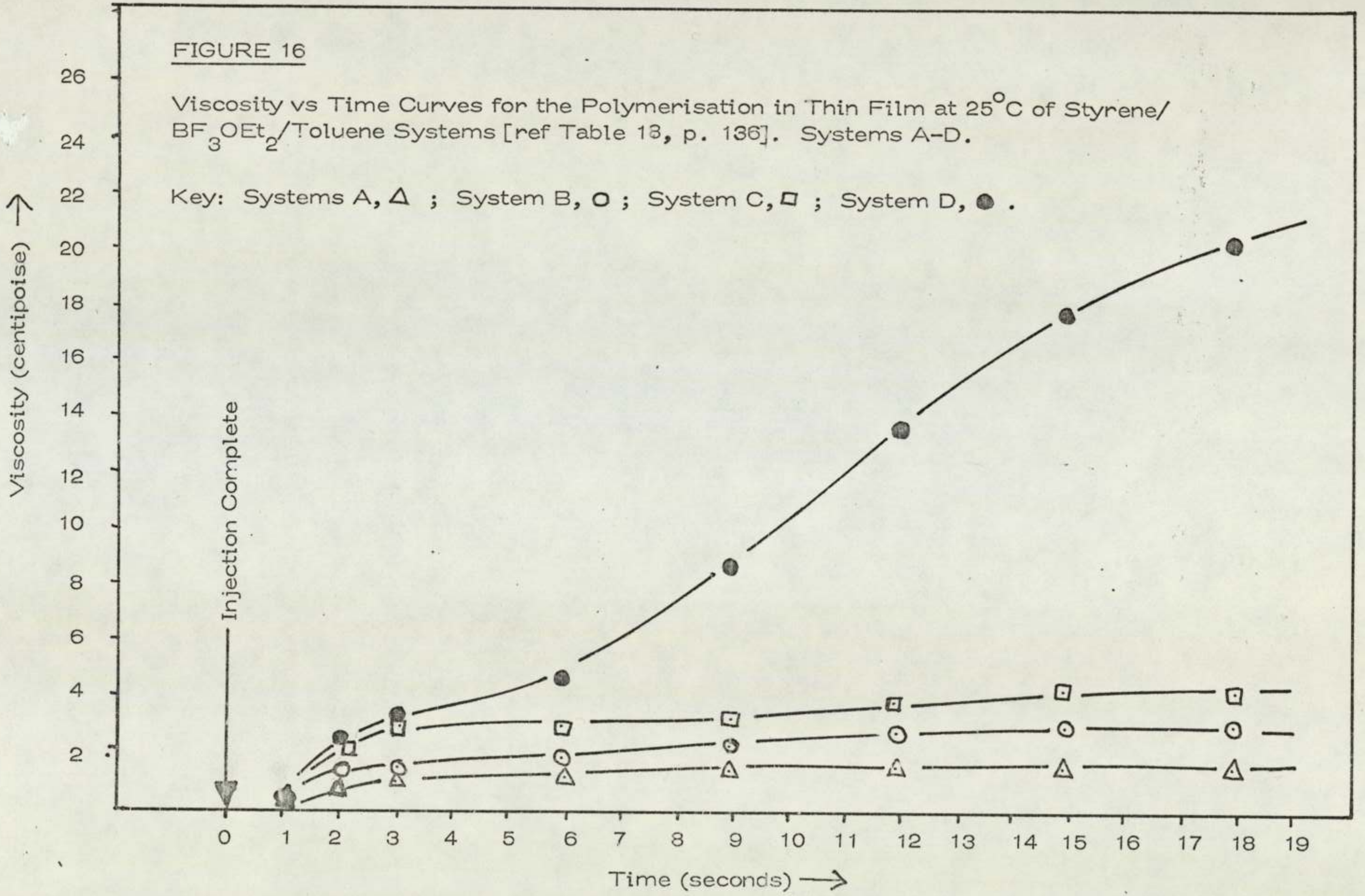


Table 19

A Summary of the Viscosity of Systems A to D (Table 18, p. 136) at given Periods of Time following Initial Mixing together with M_n, M_w and M_w/M_n Values Obtained for Polymers obtained after 10 Minutes Reaction using Gel Permeation Chromatography (RAPRA Polymer Supply and Characterisation Centre)

System	Time (minutes)	Viscosity (centipoise)	M_n	M_w	M_w/M_n
A	10	3	2,111	11,000	5.2
	4×10^4	5	–	–	
B	10	6	2,798	11,000	4.1
	4×10^4	20	–	–	
C	10	10	2,366	9,046	3.8
	4×10^4	30	–	–	
D	10	200	3,315	14,530	4.4
	4×10^4	1,400	–	–	

Operating Conditions: Flow Rate: 1ml/minute

Solvent: Tetrahydrofuran plus 0.1% 2.6 di tert butyl p-Cresol as Inhibitor

Temperature, Ambient

For the time scale of the experiments the level of reactivity shown by these systems appears to be low except for the system containing the highest monomer concentration (System D).

Again repeatability of the above runs was of the order indicated in plots shown in Figure 6, p. 99.

2) The Cationic Polymerisation of Cyclic Diene Systems (Table 18 Systems E-Q)

i) Preliminary Work

The first members of the above series, cyclopentadiene and methylcyclopentadiene, are known to dimerise rapidly at room temperature the monomers being stable for long periods of time only when stored at -70°C.

These dienes are therefore commercially available only as the dimers from which the monomers are readily obtainable by thermal dissociation. Thus distillation of dicyclopentadiene at 170°C readily yielded the monomer (b.pt. 42°C) and distillation of dimethylcyclopentadiene at its boiling point, 181°C readily yielded methylcyclopentadiene (b.pt. 70°C).

The fact that these monomers dimerise quite rapidly at room temperature posed problems not only from the point of view of the experimental work described in this section (which was carried out at room temperature) but also from the point of view of the possible commercial application of these materials should they possess promising levels of reactivity.

Accordingly it was decided that a detailed assessment of the rate of dimerisation of these monomers at various temperatures must be carried out prior to polymerisation rate studies. The temperatures chosen for this work were as follows:

a) $-70^{\circ}C$, the storage temperature recommended in the literature,

b) $0^{\circ}C$, a more acceptable storage temperature from the commercial point of view, providing dimerisation processes are relatively slow,

and c) $25^{\circ}C$, the temperature at which the experimental work described here was carried out.

Analysis of samples was carried out using Gas Liquid Chromatography employing a 5' SE30 silicone gum column operating at $120^{\circ}C$ with a helium flow rate of 60 ccs/minute.

Dicyclopentadiene was found to yield cyclopentadiene contaminated with a little dicyclopentadiene (on distillation) while dimethylcyclopentadiene was found to yield the 5 methyl, 2 methyl (predominating) and 1 methyl isomers contaminated with a small quantity of four isomeric dimers. Samples of the freshly distilled materials were immediately analysed and the results of this analysis are summarised in Table 20, p. 141.

Samples of each monomer were then allowed to stand at $25^{\circ}C$, $0^{\circ}C$ and $-70^{\circ}C$ and the composition of each sample determined after given times of standing.

Table 20

The Composition of Freshly Distilled Samples of Dicyclopentadiene and Dimethylcyclopentadiene using Gas Liquid Chromatography[+]

Sample	Component	Percentage Weight of Component	Retention Time (Minutes)
Distilled Dicyclopentadiene	Cyclopentadiene	97	1.5
	Dicyclopentadiene	3	10
Distilled Dimethyl cyclopentadiene	5 Methylcyclopentadiene	1.2	0.95
	2 Methylcyclopentadiene	95	1.20
	1 Methylcyclopentadiene	1.4	1.8
	Dimers[++]	2.4	15 17 20 22½

[+] Conditions of Analysis:

Column	Silicone Gum 5 foot SE30
Column Temperature	120°C
Gas Flow Rate	Helium 60 ccs/min.

[++] Total percentage weight of four isomeric dimers resolved.

The results obtained for the dimerisation of cyclopentadiene at -70, 0 and 25°C are presented in Figure 17, p. 143, and corresponding results for the dimerisation of dimethylcyclopentadiene are presented in Figure 18, p. 144.

The results for both monomers show that although long term storage at 25°C is totally unacceptable (2 days storage at 25°C results in 50% conversion to dimer) the monomers are sufficiently stable over the time scale of each experimental run (ca 1 hr) for results obtained to be unaffected by dimerisation processes.

Stability of monomers at 0°C is also shown to be relatively poor (after 100 hours around 25% conversion to dimer occurs), implying the impractibility of long term storage at this temperature.

Storage of the monomers at -70°C results in little or no dimerisation occurring. The monomers could therefore be satisfactorily stored at -70°C for the purposes of experimental work described here.

ii) Results of Cationic Polymerisation Experiments Relating to Cyclic Dienes

The polymerisation of systems E to Q summarised in Table 18, p. 136 was carried out in thin film, the viscosity/time characteristics for each system being measured under identical conditions to those used for the cationic polymerisation studies relating to styrene systems, p. 135.

The experimental work relating to the study of the polymerisation of the above systems was divided into two sections as

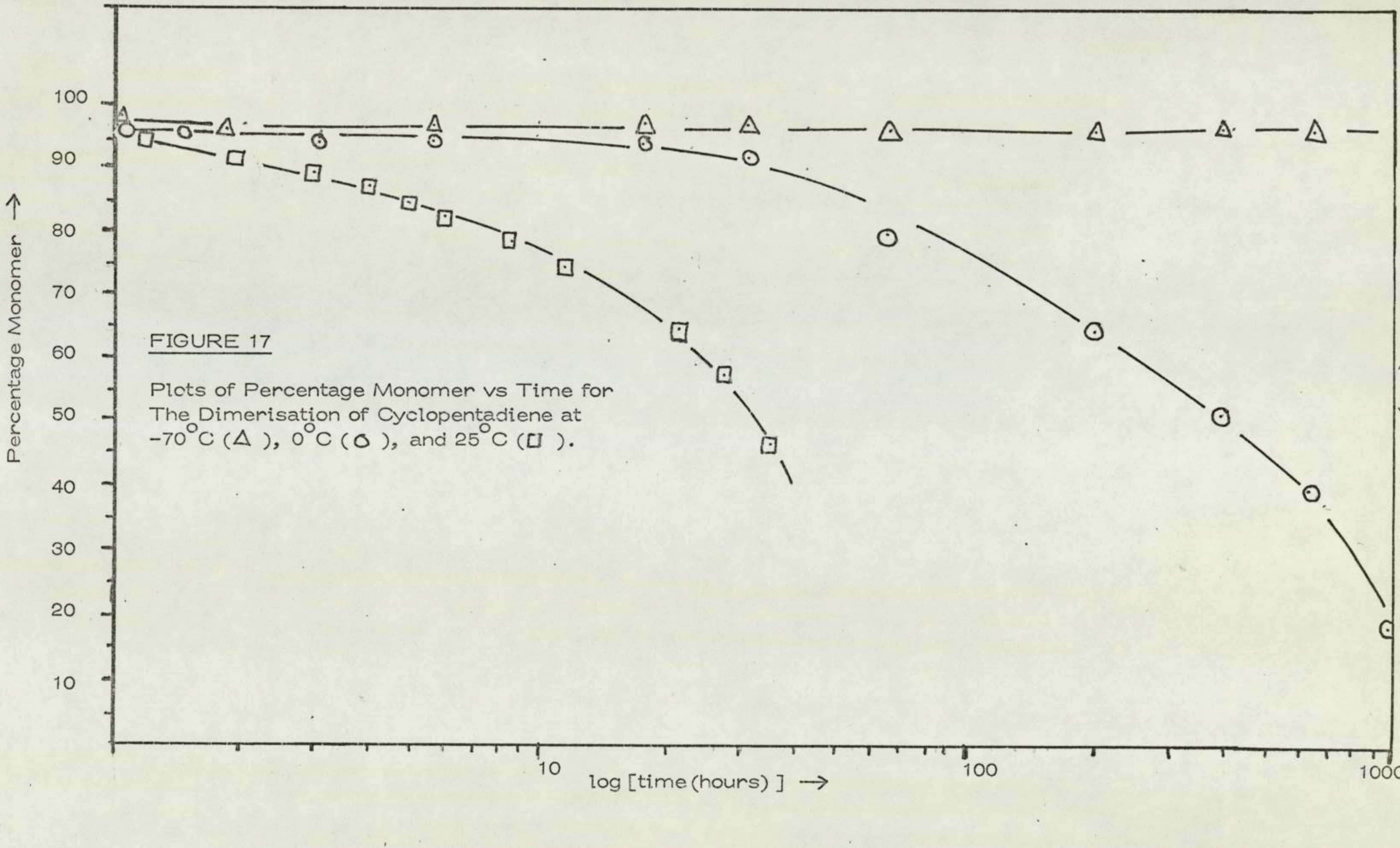


FIGURE 17

Plots of Percentage Monomer vs Time for The Dimerisation of Cyclopentadiene at -70°C (△), 0°C (⊙), and 25°C (⊡).

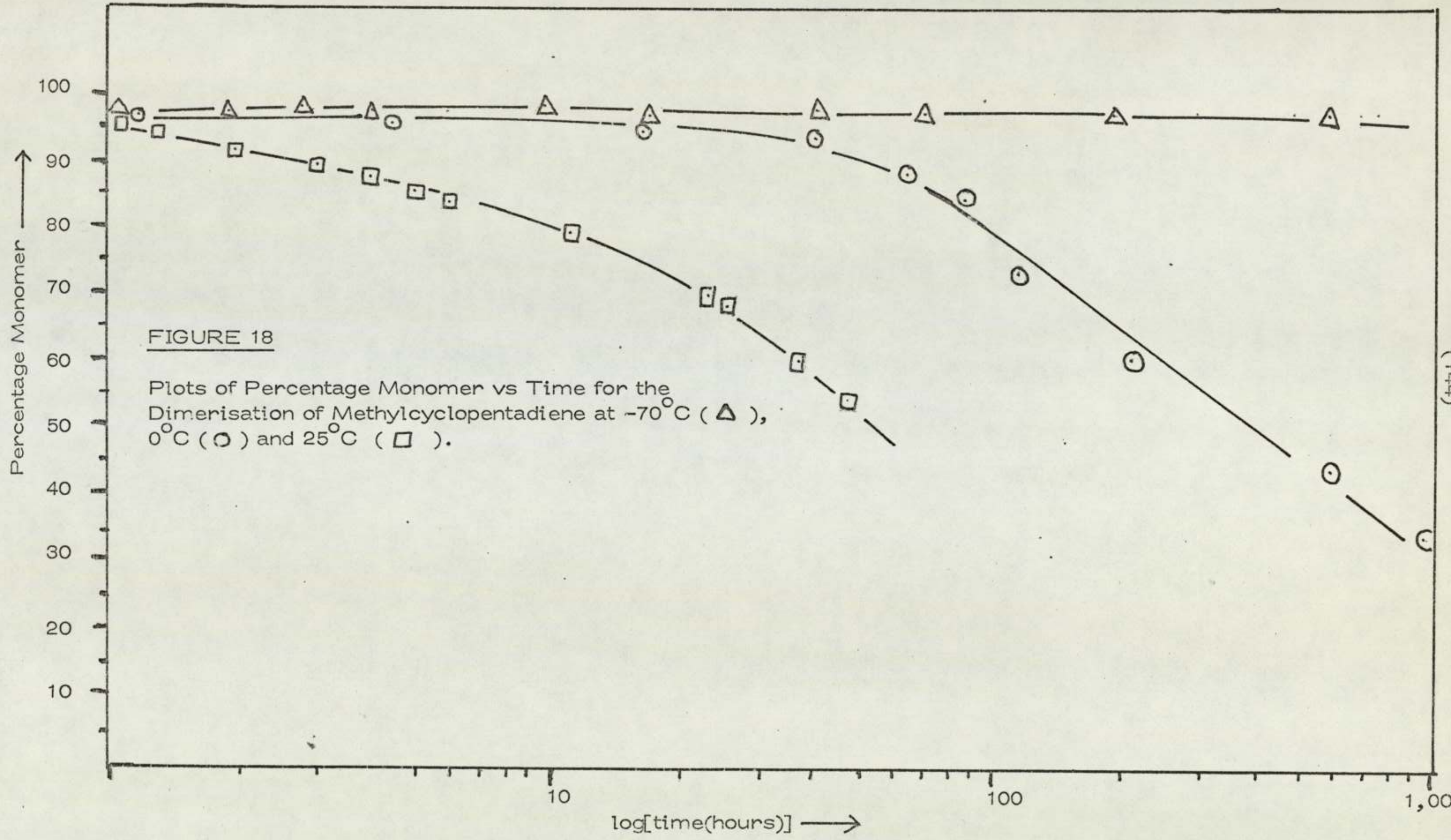


FIGURE 18

Plots of Percentage Monomer vs Time for the Dimerisation of Methylcyclopentadiene at -70°C (△), 0°C (○) and 25°C (□).

follows:

a) The determination of the viscosity vs time characteristics of systems containing relatively high levels of initiator concentration with ratios of monomer to initiator concentration ranging from 2.6 to 6.05. (Systems E to O Table 18, p. 136).

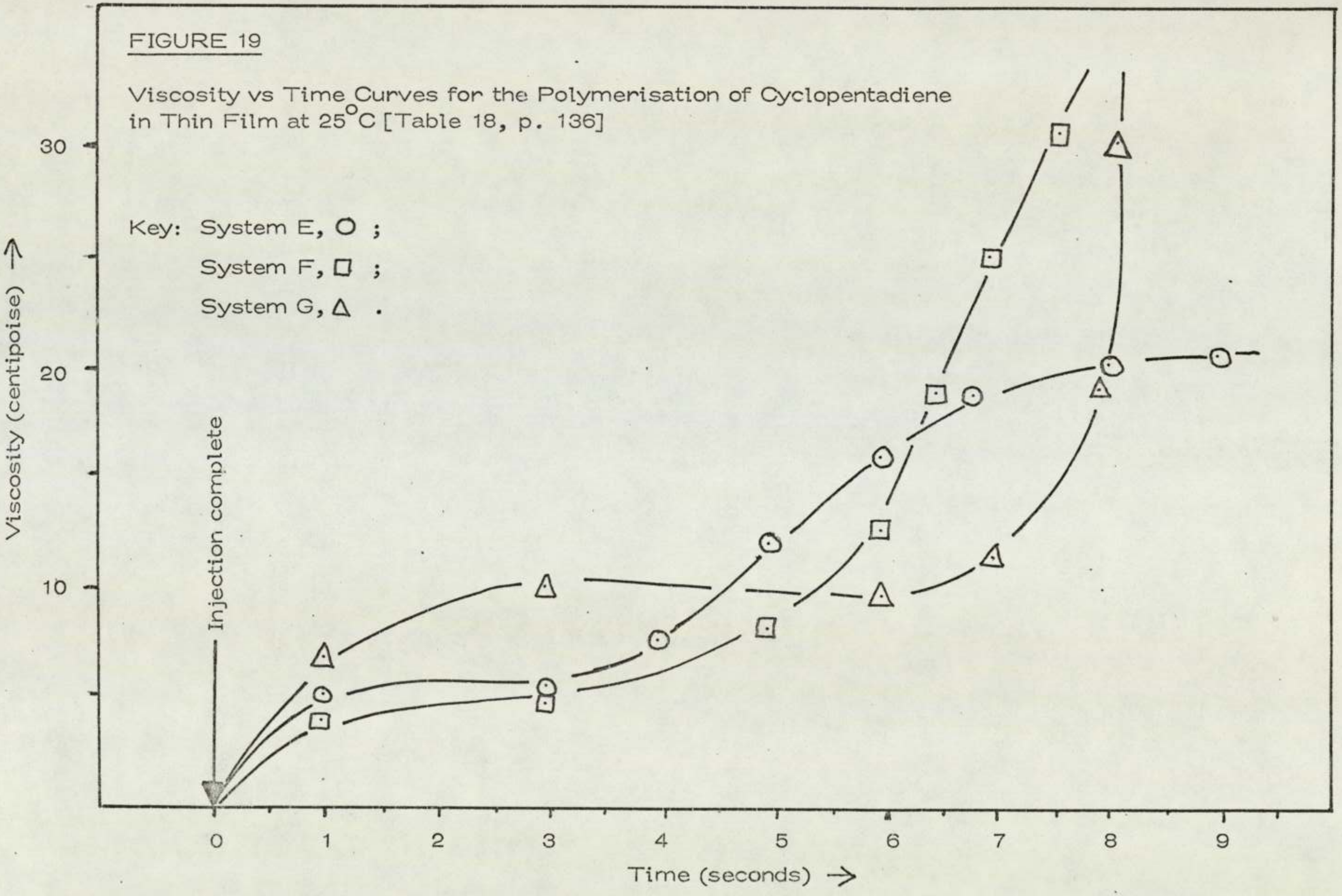
b) The selection of the most reactive systems from a) followed by the determination of the viscosity vs time characteristics of these systems using relatively low levels of initiator concentration, (Systems P and Q Table 18).

Results showing the viscosity vs time characteristics for the initial stages of reaction for the systems described above are presented in Figures 19-22, p. 146 to 149. Figure 19, p. 146 shows results obtained for the cationic polymerisation of cyclopentadiene systems, Figure 20, p. 147, corresponding results for methylcyclopentadiene systems, Figure 21, p. 148, those for 1:3 and 1:4 cyclohexadiene systems and Figure 22, p. 149, results obtained for the cationic polymerisation of cycloheptatriene, 1,3 cyclooctadiene and 1,5 cyclooctadiene.

The viscosity versus time curves shown for the cyclopentadiene and methyl cyclopentadiene systems (Figures 19 and 20) serve to illustrate results for polymerisation reaction rates which are approaching the limit of sensitivity of the apparatus. The results also highlight the high level of reactivity of the monomers in question despite inherent inaccuracies derived from factors such as monomer volatility, particularly in respect of cyclopentadiene.

FIGURE 19

Viscosity vs Time Curves for the Polymerisation of Cyclopentadiene in Thin Film at 25°C [Table 18, p. 136]



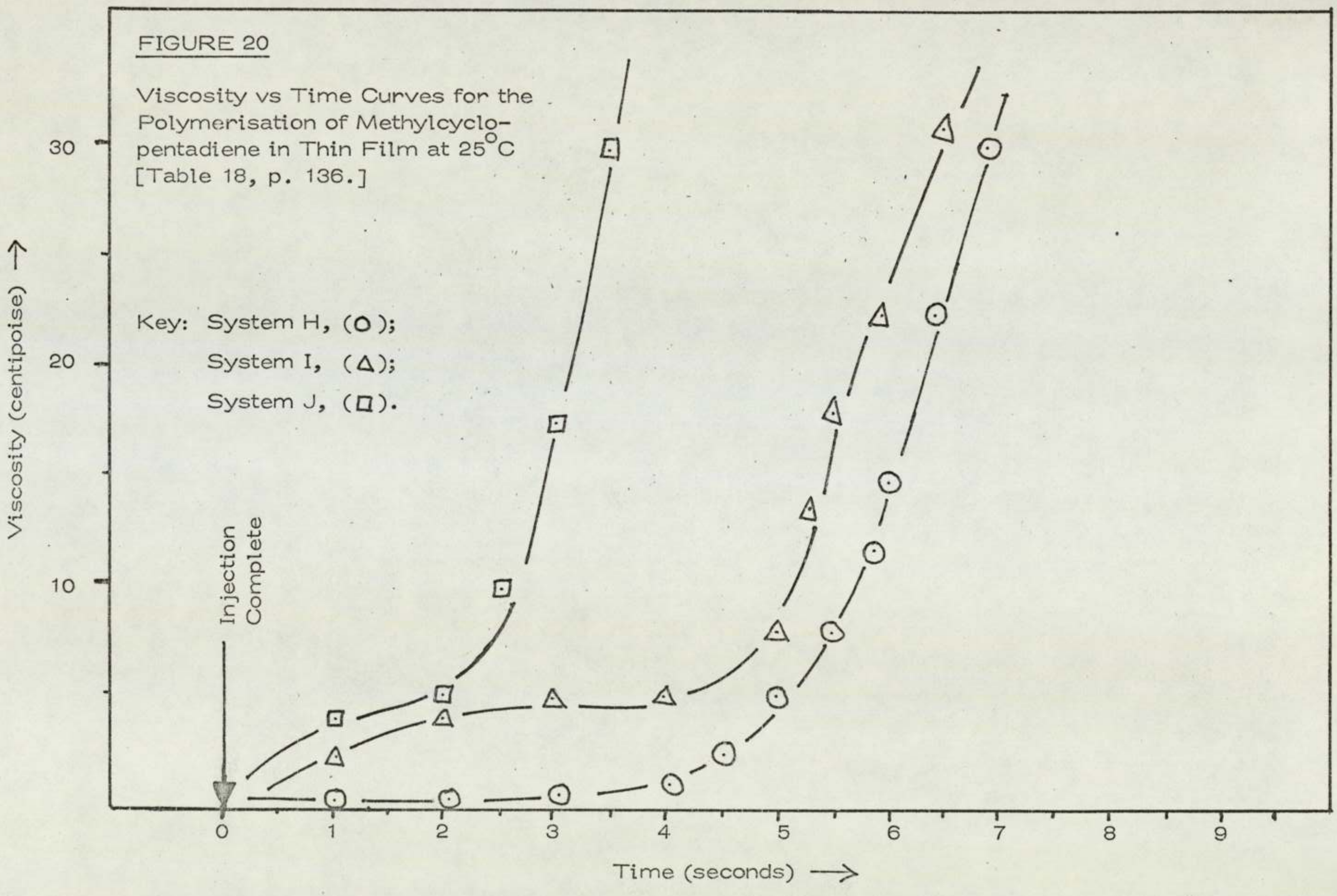


FIGURE 20

Viscosity vs Time Curves for the Polymerisation of Methylcyclopentadiene in Thin Film at 25°C [Table 18, p. 136.]

FIGURE 21

Viscosity vs Time Curves for the Polymerisation of 1,3 and 1,4 Cyclohexadienes in Thin Film at 25°C [Table 18, p. 136]

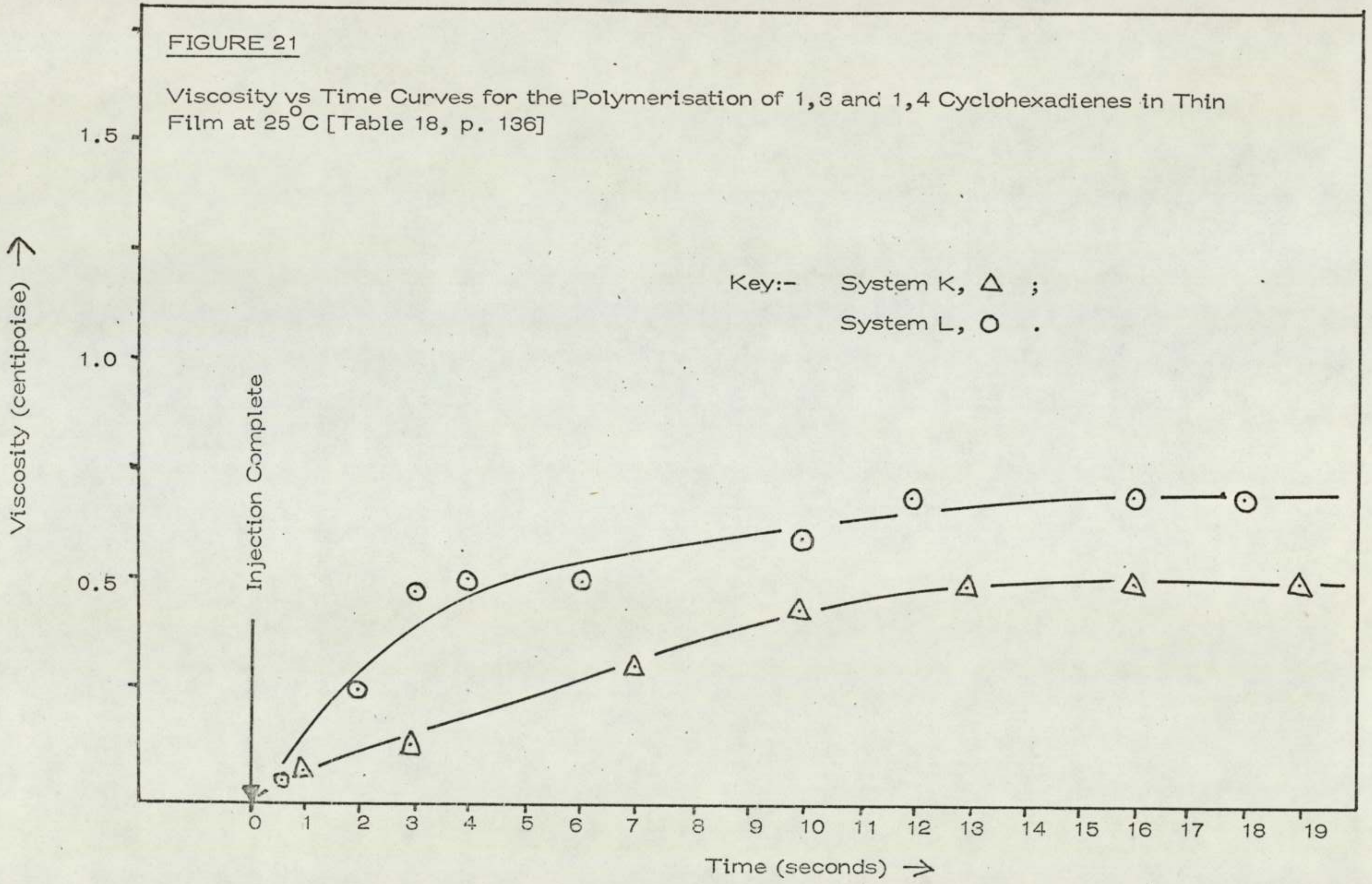
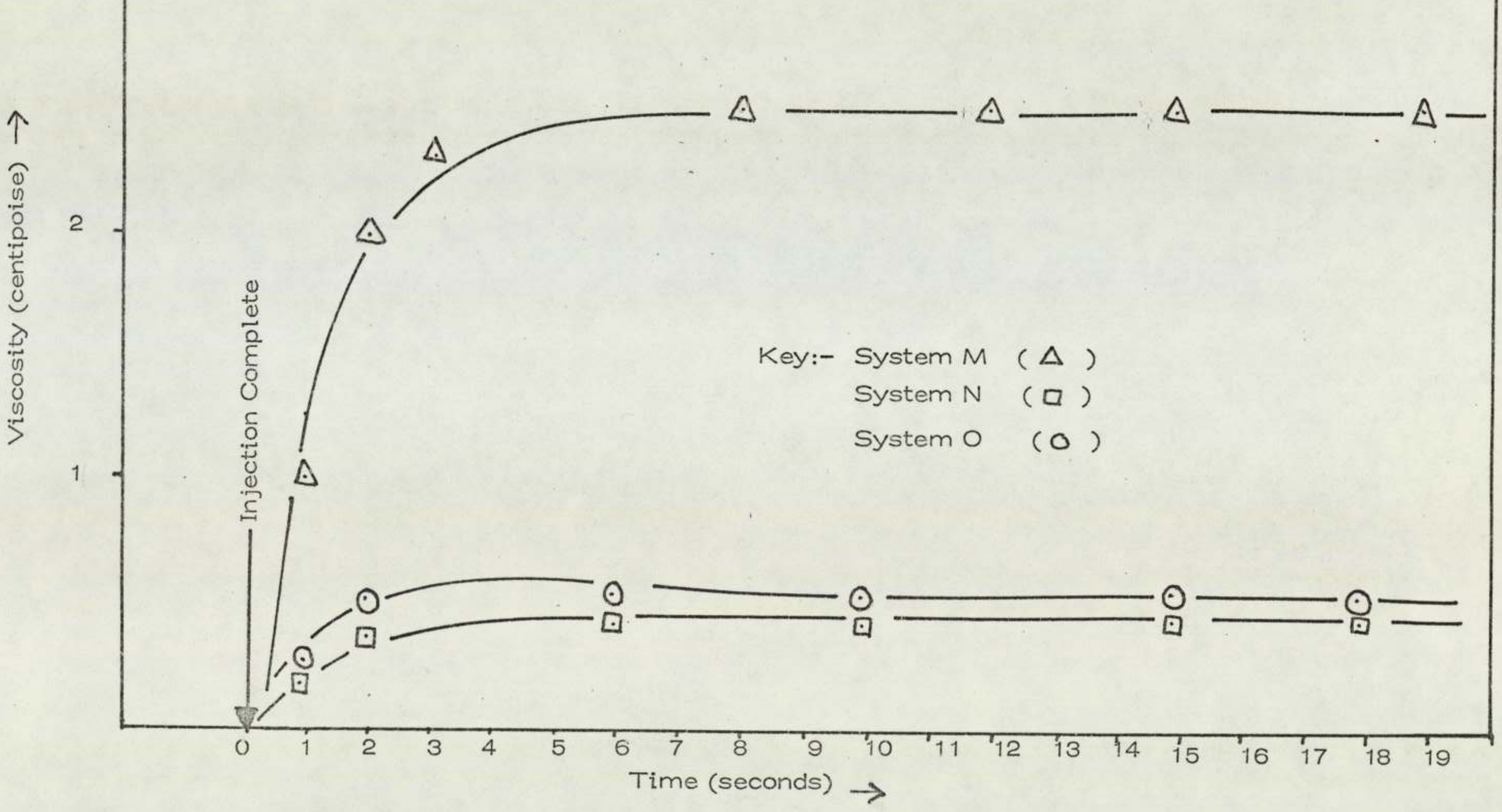


FIGURE 22

Viscosity vs Time Curves for the Polymerisation of Cycloheptatriene 1,3 Cyclooctadiene and 1,5 Cyclooctadiene in Thin Film at 25°C [Table 18, p. 136].



Repeatability of viscosity/time curves for a given system was of the order indicated in Figures 6, p. 99.

A complete evaluation of the comparative reactivities of monomers studied (Table 18, p. 136) would necessitate a comprehensive study of the effect on polymerisation rate of solvent type, the type and concentration of initiator, polymerisation temperature together with the type and concentration of cocatalyst used. Although the experimental results presented in this section relating to cationic polymerisation reactions cover this experimental arena in a somewhat limited fashion, they do provide strong evidence in favour of the high level of reactivity of cyclopentadiene and methylcyclopentadiene when the latter are polymerised in thin film using boron trifluoride etherate initiator.

In order to carry out a more critical assessment of the reactivity of these monomers, with particular reference to the ultimate aims of this work outlined elsewhere, the viscosity/time characteristics of systems based on cyclopentadiene and methyl cyclopentadiene were determined using low initiator concentrations (Systems P and Q, Table 18, p. 136). The results obtained are shown in Figure 23, p. 151 and indicate that methylcyclopentadiene is the more reactive monomer. Although accurate comparison of monomer reactivity is not possible using the above results due to problems, previously referred to, associated with the volatility of cyclopentadiene, the trend indicated in Figure 23 is supported by the work of Kohjiya (52) where methylcyclo-

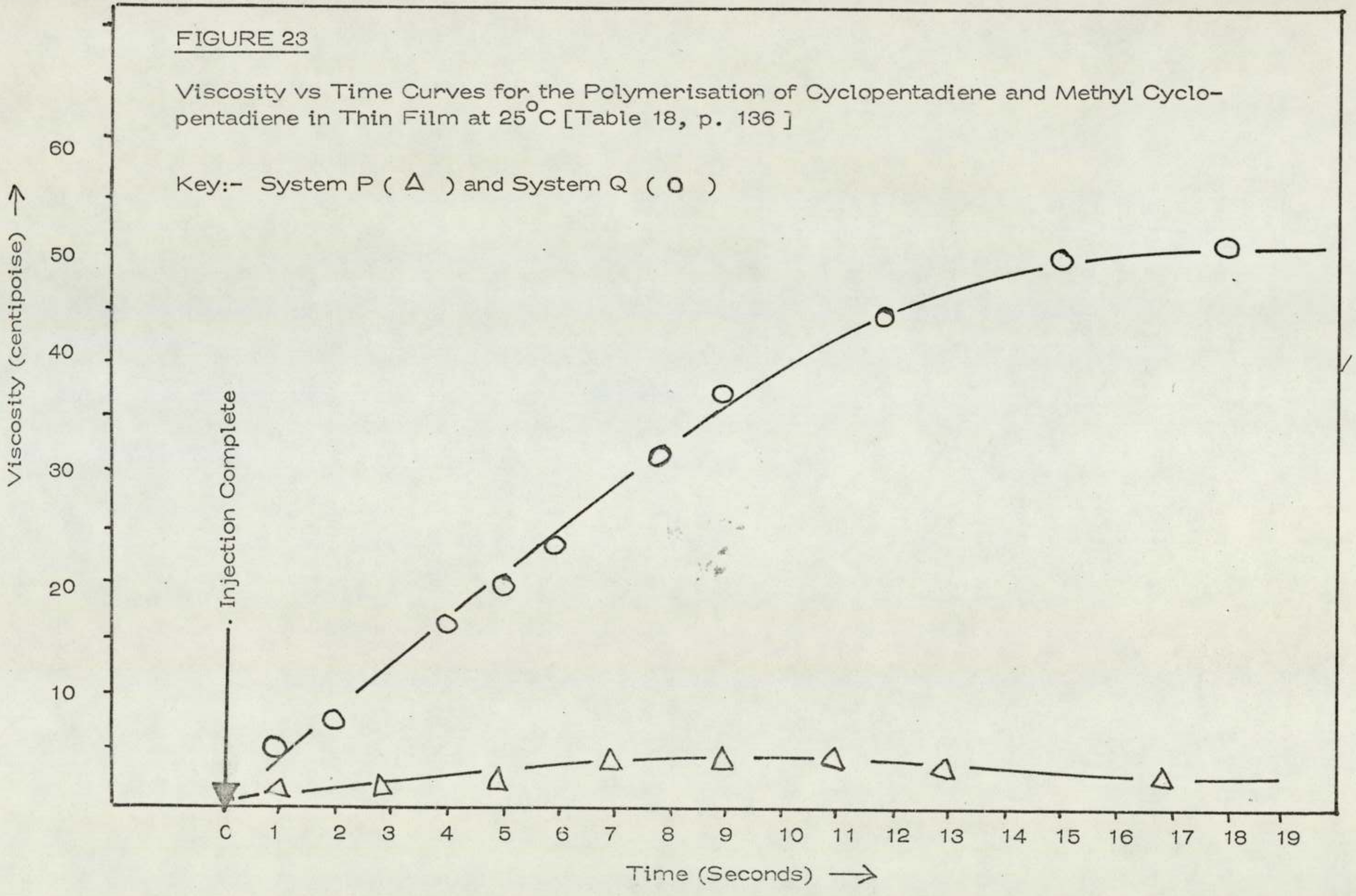


FIGURE 23

Viscosity vs Time Curves for the Polymerisation of Cyclopentadiene and Methyl Cyclopentadiene in Thin Film at 25°C [Table 18, p. 136] pentadiene is reported to be approximately ten times more reactive than cyclopentadiene.

A precise analysis of results obtained as a whole for the cationic systems studied (Table 18) is further complicated by the lack of knowledge available for viscosity/conversion relationships together with variation in M_n values with time likely to occur for such systems. Information on the latter could be obtained by the incorporation of a rapid sampling facility enabling the determination of M_n values for samples collected and quenched at very short intervals of time. As a simpler but less satisfactory and effective alternative to this somewhat impracticable proposition the molecular weight of polymer produced at the end of each run was determined where possible using gel permeation chromatography. The results obtained are summarised in Table 21, p. 153 and indicate that for systems where molecular weight measurement was possible high molecular weight polymer was formed.

Table 21

A Summary of M_n, M_w and M_w/M_n Values for Polymers formed from the Cationic Polymerisation of Cyclic Dienes (Systems E-Q$^+$, Table 18, p. 136). Results obtained using Gel Permeation Chromatography. $^{++}$(R.A.P.R.A. Polymer Supply and Characterisation Centre

System	Solvent Used in G.P.C. Determination	M_n	M_w	M_w/M_n
E	Orthodichlorobenzene	2.07×10^6	7.98×10^6	3.86
F	Orthodichlorobenzene	1.45×10^6	2.91×10^6	2.01
G	Orthodichlorobenzene	2.04×10^6	7.28×10^6	3.58
H	Orthodichlorobenzene	Multinodal Trace		
I	Tetrahydrofuran	6.20×10^3	1.5×10^4	41.3
J	Tetrahydrofuran	5.96×10^3	1.45×10^4	41.2

$^+$Systems K-Q, insufficient polymer formed after 10 minutes for accurate analysis to be carried out.

$^{++}$ Operating Conditions:

Flow Rate	1 cc/minute
Solvent	As specified
Temperature	Ambient (Tetrahydrofuran) 138°C (Orthodichlorobenzene).

5.4 Summary and Conclusions

The information gained from results presented in this chapter indicates that the stopped flow rotational viscometer can be validly applied to securing kinetic data for homopolymerisation reactions. Although precise analysis of results is difficult, particularly with respect to those results obtained for cationic systems studied where detailed knowledge of viscosity/conversion and M_n/time characteristics are not available, it can be seen that cautious interpretation of results obtained can yield valuable information on comparitive rates of conversion. Accordingly it has been shown that cyclopentadiene and methylcyclopentadiene are the most promising monomers in terms of their reactivity in cationic polymerisation reactions carried out in thin film. The high level of reactivity exhibited by these monomers thus provided a basis on which work could be initiated towards the development of rapid cross linking systems, described in Chapters 6 and 7.

CHAPTER 6

Cationic Cross Linking Studies:

A Preliminary Assessment

Introduction

On the basis of ideas derived from literature work (Chapter 2) together with the encouraging results obtained in monomer reactivity studies described in Chapter 5, certain relatively simple and speculative synthetic approaches to the problem of attaining reactive backbones were undertaken. A substantial part of the experimental work described in the present chapter together with that described in Chapter 7 was carried out by undergraduate and postgraduate students in the course of two projects(137)(138) under the direct supervision of the author.

A series of polyester resins was accordingly synthesised with reactive (i.e. residual unsaturation) sites which were significantly different in chemical structure. The aim of this was to provide resins which had a range of reactivities to cationic addition reactions in order to assess the effect of backbone structure on the rates of cross linking with various cross linking agents (vinyl monomers) and initiators.

The assessment of the latter was conveniently carried out using the apparatus described in Chapter 4, p. 108 and shown in Plate IX p.108a in which gel times are determined as a means of assessing relative reactivities of given systems. Boron trifluoride etherate was chosen as a suitable source of cationic initiating species because of its ready solubility and methyl ethyl ketone peroxide/cobalt naphthenate as a radical source for the same reason.

Hills(139) has shown that gelation times measured using the above apparatus are in good agreement with predicted Flory times. Flory(140) relates gelation time with the rate of copolymerisation. He states that the existence of a sharply defined gelation point at a given extent of reaction is a significant characteristic of a cross linking system, gelation occurring when a critical number of linkages have been formed.

In addition to the above an experiment is also described demonstrating the applicability of the stopped flow rotational viscometer to the measurement of cross linking rates in thin film.

6.1 The Synthesis of Polyester Backbones - based on Commercially Available Diols and Dicarboxylic Acids

This series of backbones were synthesised using resin formulations designated A-D (Table 22, p. 158). A standard technique$^{(127)}$ was used for resin preparation. A commercial resin, designated Resin E (Resin 4117, B.I.P. Chemicals) containing unsaturation based on maleic anhydride and styrene as the cross-linking agent, was also obtained for comparison with the above systems in later work involving cross-linking studies.

The use of gel permeation chromatography (carried out by R.A.P.R.A., Polymer Supply and Characterisation Centre) enabled molecular weights and molecular weight distributions to be determined fairly readily since the resins were all completely soluble in tetrahydrofuran. The chromatograms showed Resin E (the commercial material) to have a slightly higher (10-20%) molecular weight than resins prepared in the laboratory.

M_w and M_w/M_n values are summarised, for the resins prepared, in Table 23, p. 159. The only resin showing any unusual feature was Resin D derived from hexylene diol which contained appreciable quantities of low molecular weight material and was very discoloured. Since the resins A, B, C and E were fairly comparable with respect to molecular weight these were used for comparative cross-linking studies and Resin D was discarded.

Table 22

	A	B	C	D
Ethylene Glycol	2.75 moles	2.75 moles	1.0 moles	1.0 moles
Diethylene Glycol	2.75 moles	2.75 moles	1.0 moles	1.0 moles
Maleic Anhydride	3.5 moles	—	—	—
Phthalic Anhydride	0.75 moles	0.75 moles	2.5 moles	2.5 moles
Adipic Acid	0.75 moles	0.75 moles	2.5 moles	2.5 moles
Muconic Acid	—	3.5 moles	—	—
Butene 1,4 Diol			3.5 moles	—
Hexylene 2,5-Diol				3.5 moles

[The B.I.P. resin which contained maleic anhydride unsaturation is referred to as Resin E]

Table 23

A Summary of M_n, M_w and M_w/M_n Values for Resins A-E (Table 22, p. 158) - determined using Gel Permeation Chromatography[++]

	A	B	C	[+]D	E
M_n	2665	1656	2540	1081	2915
M_w	5144	2689	5838	1685	5676
M_w/M_n	1.93	1.62	2.30	1.50	1.94

[+] M_n, M_w, values obtained by adjustment of peak and as such do not reflect the true nature of the resin which gave a binodal G.P.C. trace, the low molecular weight peak being attributed to unreacted hexylene diol.

[++] Operating Conditions:-

Flow Rate	1 ml/minute
Solvent	Tetrahydrofuran, plus 0.1% 2,6 ditertbutyl p-Cresol as Inhibitor
Temperature	Ambient.

6.2 Cross Linking Studies of Unsaturated Polyester Resins Using Various Cross Linking Agents

These studies were carried out using the following cross linking agents, styrene, α methylstyrene, n-butylvinyl ether and methylcyclopentadiene in conjunction with the base resins A, B, C, and E summarised in Table 22. Results obtained for each resin system are presented for each cross linking agent in turn, styrene being used as a control.

6.2.1 Cross Linking Studies of Unsaturated Polyester Resins Using Styrene as the Cross Linking Agent

Styrene was chosen as the control monomer because of its near universal use in radical-initiated cross linking reactions and also because of its susceptibility to cationic polymerisation. The results obtained are summarised in Table 24, p. 161.

The type and concentration of both initiating species was arbitrarily chosen on the basis of normal practice for each type. Although this means that no direct correlation (i.e. at equivalent concentrations) can be achieved this would in any case be an unfruitful comparison because of the great difference in activity within cationic initiators as a class. The aim of these initial studies was to investigate the relative susceptibility of the various resins and cross linking agents used by keeping the concentrations of the two initiator types constant over the whole range of experiments. Having chosen the most effective combination of resin/cross linking agent it would then be a relatively straight forward matter

Table 24

A Summary of Gelation Times of Unsaturated Polyester Resins using Styrene as Cross Linking Agent and BF_3 Etherate and MEK Peroxide/cobalt naphthenate Initiators.

Base Resin	Cross-linking Agent	Gelation Time Radical Initiation	Gelation Time Cationic Initiation
A	Styrene	2 min	~ 2 min
B	"	580 min	> 24 hrs
C	"	660 min	~ 20 hrs
E	"	45 min	75 min

to investigate more active cationic species with a view to obtaining maximum rate.

In the light of these comments the results in Table 24 provide an interesting basis for the consideration of radical/ cationic reactivity.

General points which should be emphasised are the similarity in initial molecular weight and distribution of the four resins and the fact that A, B, and C were formulated to contain equivalent molar concentrations of backbone unsaturation. Resin E is the control material and contains less backbone unsaturation. It appears that with the particular initiator/cross-linking agent used, maleate unsaturation is much more active than that derived from either muconic acid or butylene diol. In the case of radical initiation the order of the decrease in conjugative stability of the radical adduct. It is interesting that butylene diol is more reactive than muconic acid to cationic initiation, probably a reflection of the balance between conjugative stabilisation and inductive destabilisation.

If these ideas were correct then by changing the cross linking agent from styrene to α-methyl styrene it should be possible to accentuate this effect. Thus the presence of the α-methyl group would tend to accelerate the rate of cationic cross-linking. (It is known to reduce the rate of the radical reaction.)

6.2.2 Cross Linking Studies of Unsaturated Polyester Resins using α methyl styrene as Cross Linking Agent and BF_3 Etherate as Initiator

The experiments were carried out under the same conditions as those involving styrene. The results are shown in Table 25.

Table 25

A Summary of Gelation Times of Unsaturated Polyester Resins using α methyl styrene as Cross Linking Agent and BF_3 Etherate as Initiator

Basic Resin	Cross-linking Agent	Gelation Time Cationic Initiation
A	α-methylstyrene	< 2 min
C	α-methylstyrene	253 min
E	α-methylstyrene	14 min

The results in Table 25 show a marked reduction in gelation time in each case when compared with corresponding results obtained for systems using styrene as cross linking agent (Table 24, p.161). For the case of the butylene diol resin in particular, the importance of regarding the cross linking reaction as a copolymerisation reaction is illustrated in which the reactivity ratios must be adjusted to the optimum level.

6.2.3 Cross Linking Studies of Unsaturated Polyester Resins using n-Butyl Vinyl Ether as Cross Linking Agent and BF_3 Etherate as Initiator

In order to examine an extreme case of the balance of reactivities referred to in 6.2.2. above a very cation sensitive monomer having a structure very different from that of the styrene family was chosen as cross linking agent. n-Butyl vinyl ether was chosen as a suitable cross linking agent to use in this context. The monomer has a strongly electron releasing substituent but little conjugative stability. Using the same conditions as in the previous experiments a very rapid cation initiated reaction was observed but without concurrent gelation. The n-butyl ether had undergone homopolymerisation rather than copolymerising with the backbone unsaturation. To examine this point further a cation-sensitive monomer having an all-hydrocarbon structure was examined and results obtained using such a monomer (methylcyclopentadiene) is described in section 6.2.4.

6.2.4. Cross Linking Studies of Unsaturated Polyester Resins using Methylcyclopentadiene as Cross Linking Agent and BF_3 Etherate as Initiator.

Methylcyclopentadiene was selected as a result of the literature work presented in Chapter 2 and monomer reactivity studies described in Chapter 5. It has never, so far as published work indicates, been used as a cross-linking agent. Available evidence and the work described here suggests that its characteristics would make it a useful cross-linking agent in a situation where the reactivity ratio of the backbone unsaturation lies in a suitable range.

The material was obtained in the dimeric form which reverted to the monomer on distillation (as described in Chapter 5, p. 139). It was a relatively poor solvent for the polyester resin systems but solution was achieved with conventional mixing techniques and in all cases cationic initiation produced homogeneous gels. The results are summarised in Table 26, p. 165.

It is quite apparent that the use of methyl cyclopentadiene has a dramatic effect in reducing the gelation time of the resins used. Consider the series styrene, α-methyl styrene, methyl cyclopentadiene. The gelation times corresponding to these cross linking agents with cationic initiation and the butylene glycol resin (C) were, 24 hrs; 253 min; and 23 min. respectively. This illustrates dramatically the importance of monomer reactivity in determining gelation times. It must be realised, however, that

Table 26

A Summary of Gelation Times of Unsaturated Polyester Resins using Methylcyclopentadiene as Cross Linking Agent and BF_3 Etherate as Initiator.

Base Resin	Cross-linking Agent	Gelation Time (cationic Initiation)	Exotherm (max temp. °C)
A	Methylcyclopentadiene	Instantaneous	-
B	"	55 min	41
C	"	23 min	54
E	"	11.5 min	135

this is by no means the only factor. The results with n-butyl vinyl ether for example illustrates the importance of balancing the reactivity of the monomer with that of reactive sites within the backbone.

6.3 The Measurement of Viscosity versus Time Characteristics of a Free Radical Initiated Cross Linking System using Stopped Flow Rotational Viscometry

This experimental work was carried out to confirm the applicability of the Stopped Flow Rotational Viscometer to the study of cross linking reactions in addition to homopolymerisation reactions described in Chapter 5.

A commercial resin (Resin 4117, B.I.P. Chemicals) was used, which contained styrene as the cross linking agent; MEK peroxide/cobalt naphthenate was used as initiator. The system summarised in Table 27, p. 167, was polymerised in thin film at 85°C. Component A represents the composition of resin used in one syringe and component B represents the composition of resin mix used in the second syringe.

Figure 24, p. 168, shows duplicate runs for the polymerisation of the system presented in Table 27 at 85°C using the stopped flow rotational viscometer.

The viscosity/time curves obtained demonstrate that reasonable repeatability was achieved.

Table 27

A Summary of the Composition of Unsaturated Polyester Resin (Resin 4117, B.I.P. Chemicals) employed in Cross Linking Studies using Stopped Flow Rotational Viscometry

	Component A	Component B
Cobalt naphthenate	3g	–
Resin 4117	23.5g	23.5g
Toluene	23.5g	23.5g
M.E.K. Peroxide	–	5g

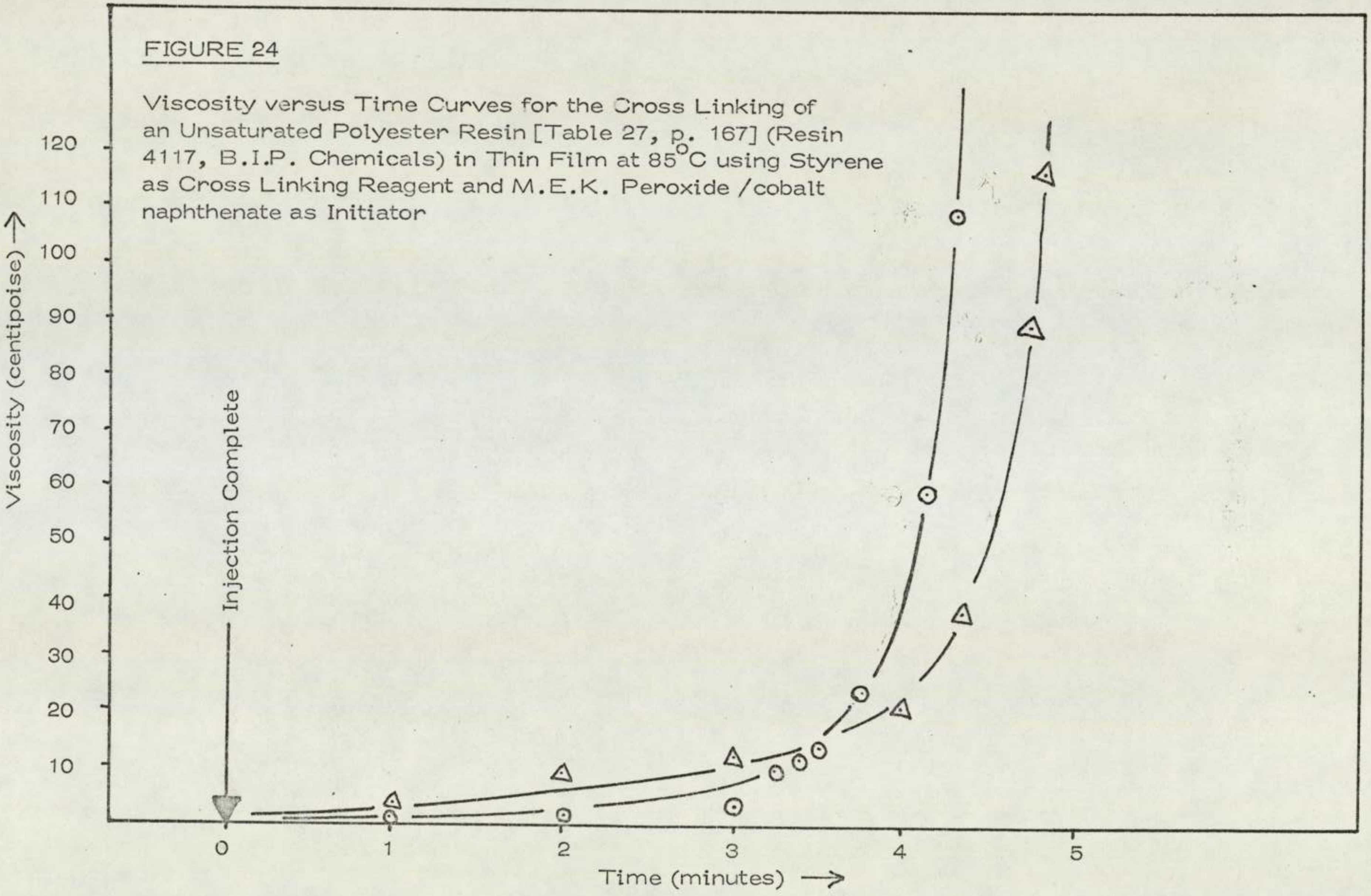


FIGURE 24

Viscosity versus Time Curves for the Cross Linking of an Unsaturated Polyester Resin [Table 27, p. 167] (Resin 4117, B.I.P. Chemicals) in Thin Film at 85°C using Styrene as Cross Linking Reagent and M.E.K. Peroxide /cobalt naphthenate as Initiator

6.4 Summary and Conclusions

In the series of resins considered above the activity to cationic addition reactions may be considered to be affected by two main factors.

(i) Activity will tend to be increased by conjugative stabilisation,

(ii) Activity will tend to be increased by electron releasing groups in the vicinity of the double bond and decreased by electron withdrawing groups in the same environment.

These factors, (i) and (ii), are not independent since the presence of a carbonyl group adjacent to a double bond will conjugatively stabilise cation addition but its electron withdrawing properties will have some tendency to deactivate the system.

The considerable activity of the maleic anhydride system suggests that the symmetrical arrangement of the carbonyl groups with respect to the double bond tend to counterbalance, to some extent, the deactivating effect of electron withdrawal. This is supported by the low activity of muconic acid. Thus the order of reactivity is as follows:

Resin A $>$ Resin C $>$ Resin B.

In order to obtain higher resin reactivity a more strongly electron releasing group must be incorporated into the structure (i.e. alkoxy), although it may well be preferable to use the reactivity of the existing maleic unsaturation and optimise the cross-linking agent/initiator system.

The reactivity of Resin A with methyl cyclopentadiene was marked by the fact that gelation occurred in some instances quite spontaneously on mixing the resin and cross-linking agent in the absence of initiator. This was no doubt due to the fact that the resins are carboxyl terminated and therefore undergo self generated protonic cross-linking with methylcyclopentadiene. The possibility of the commercial application of the phenomenon of spontaneous gelation of high acid value maleic resins with methylcyclopentadiene and related cross-linking agents may be worth considering further.

The results obtained and in particular those using n butyl vinyl ether as cross linking agent highlight the importance of matching the reactivity of cross linking agent used with that of reactive sites within the backbone. This fact combined with the generally encouraging nature of remaining results obtained indicated that further work should be carried out in which more determined efforts should be made to match more effectively the reactivity of cross linking agent with that of reactive sites within or pendant to the backbone. The results further indicate that the most promising monomer for use as a cross linking agent is methylcyclopentadiene.

The trial run using the stopped flow rotational viscometer was particularly promising, demonstrating that repeatable viscosity/time curves could be obtained for a cross linking system as well as for homopolymerisation systems described in Chapter 5.

CHAPTER 7

Synthetic Work Relating to the Preparation of Cationically Active Cross Linking Systems Based on Polyesters and Carbonylic Polymers

Introduction

The work described in this Chapter was carried out as an extension to the studies described in Chapter 6 in an attempt, via a more sophisticated approach to backbone synthesis, to effectively match reactivity of cross linking agent to that of reactive sites within or pendant to the backbone. Since methylcyclopentadiene has been presented in Chapter 5 as one of the most reactive monomers available and in the previous Chapter as an effective and reactive cross linking agent it seemed logical that any reactive site incorporated in a given backbone should be based on the methylcyclopentadiene structure. In this way it was hoped to obtain an almost perfect match between the reactivity of cross linking agent and that of the reactive site of the backbone which would thus lead to rapid cross linking reactions under appropriate conditions.

The synthetic work carried out, therefore, concentrated on acquiring backbone structures incorporating the methylcyclopentadiene structure, and can be conveniently summarised as follows:-

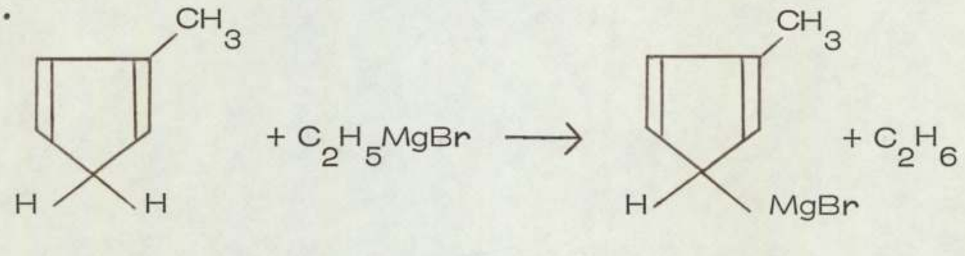
i) Synthetic work relating to the formation of polyester backbones containing pendant sites of unsaturation based on methylcyclopentadiene,

ii) Synthetic work relating to the formation of linear carbonylic polymers containing pendant sites of unsaturation based on methylcyclopentadiene.

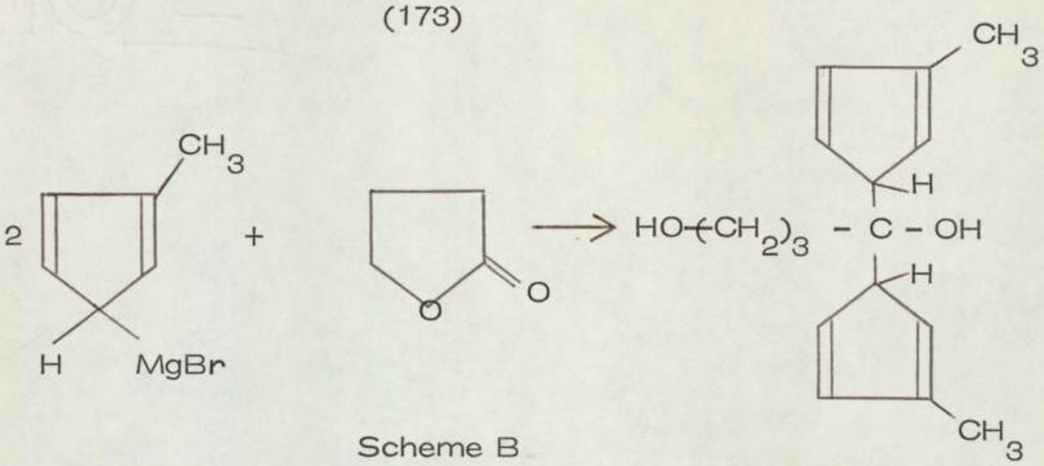
7.1 Synthetic Work Relating to the Formation of Polyester Backbones Containing Pendant Sites of Unsaturation Based on Methylcyclopentadiene

The synthetic route chosen for the preparation of backbones of the above type involved the preparation of appropriate Grignard reagents which could subsequently be reacted with γ butyrolactone or terephthalaldehyde to form diols containing cationically active sites of unsaturation. Once formed these diols could be reacted with suitable dicarboxylic acids to produce polyester backbones particularly active towards cross linking reactions initiated by cationic reagents.

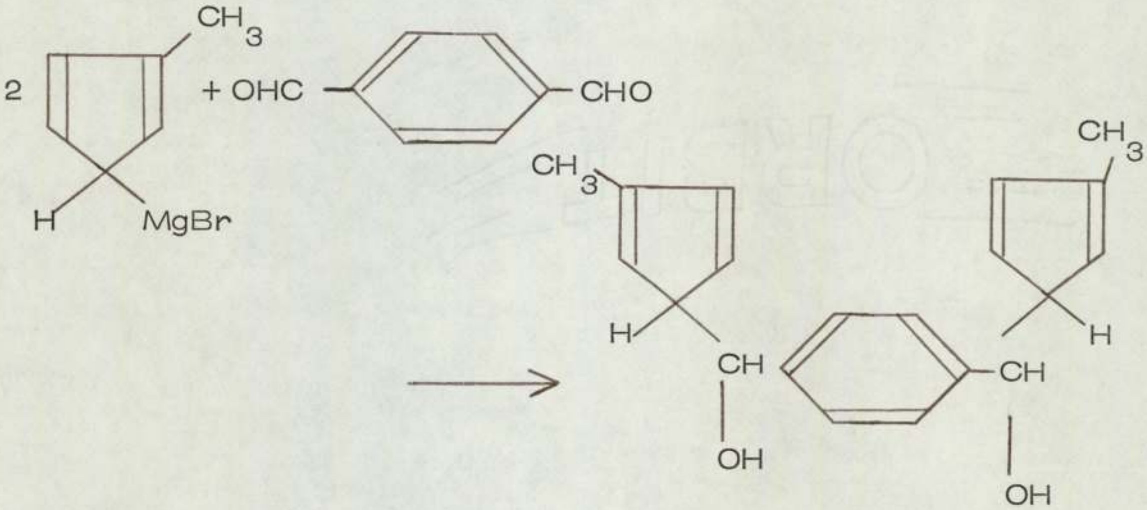
The first stage of synthetic work involved the preparation (Scheme A) of methylcyclopentadienyl magnesium bromide (MCPD Mg Br). This reagent was then reacted with γ butyrolactone (Scheme B) and terephthalaldehyde (Scheme C) in an attempt to form the corresponding diols containing methylcyclopentadienyl units.



Scheme A



Scheme B



Scheme C

The Preparation of Methylcyclopentadienyl Magnesium Bromide

Experimental Procedure

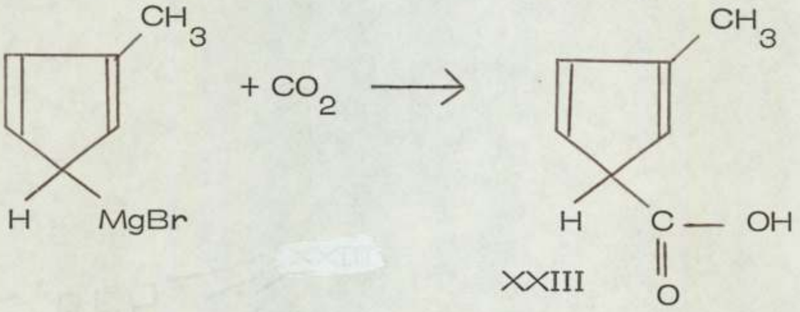
Cyclopentadienyl magnesium bromide was obtained by Courtot(141) in an exchange reaction between ethyl magnesium bromide and cyclopentadiene in ether or benzene/ether mixtures. The reaction took place in 12 hours using ether as solvent or in 3 to 6 hours when ether was partially replaced by benzene. This method was used for the preparation of MCPD MgBr.

MCPDMgBr was obtained in quantitative yield as follows. Ethylmagnesium bromide was prepared by reacting 6.5g (0.375

moles) of magnesium with 18.7 ccs (0.25 moles) of ethyl bromide in 150 ccs of ether. 21.7 ccs (0.25 moles) of methylcyclopentadiene in 150 ccs of toluene was then added slowly to the reaction mixture which was refluxed for 5 hours. 100 ccs of toluene were then added and 100 ccs of ether removed by distillation from the reaction mixture and refluxing continued for a further 2 hours. During this time the colour of the reaction mix changed from green to grey - the latter being the colour associated with cyclopentadienyl magnesium bromide by Courtot(140). The solution prepared in this way was used for reaction with γ butyrolactone, terephthalaldehyde and carbonyl polymers.

Analysis of MCPD MgBr

A sample of the final reaction mix from the preparation of MCPD MgBr was reacted with carbon dioxide to form the corresponding carboxylic acid of the form XXIII shown below:



XXIII

The solution obtained from the above reaction was evaporated which resulted in the formation of a white crystalline material (m.pt. 145°C). Analysis of the product using mass spectrometry showed the material to have a molecular weight of 124 corresponding to the carboxylic acid XXIII above. Other major peaks (m/e values) observed were as follows: 45 (COOH), 44 (CO_2), 18 (H_2O) and 17 (OH), together with peaks corresponding to the characteristic decomposition pattern of methylcyclopentadiene.

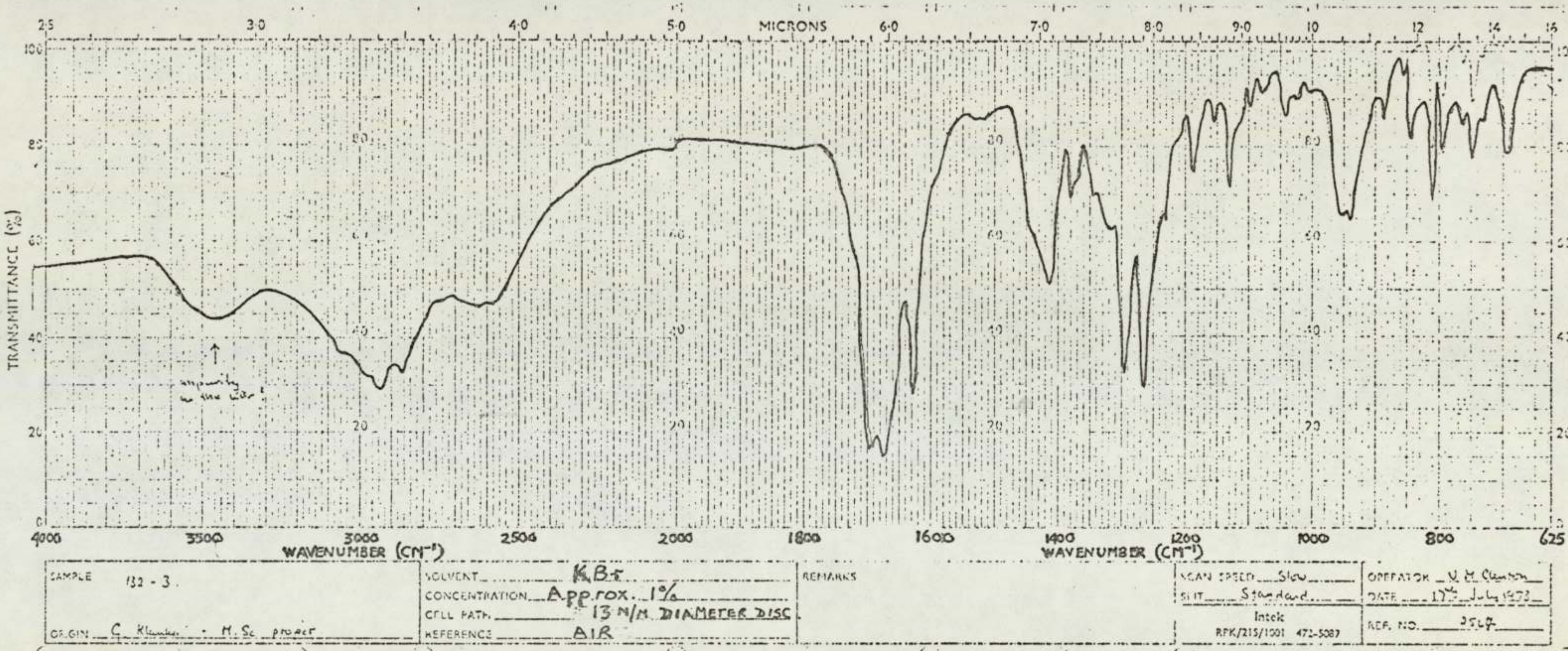
Figure 25, p. 176 shows the infra red spectrum of the compound obtained and indicates the presence of a carboxylic acid e.g. widening of absorption bands between 3,300 and 2,500 cm^{-1} together with absorption bands near 1700, 1412 and 1295 cm^{-1}, (cf The infra red spectrum for methylcyclopentadiene, Figure 25A, p. 177).

The Reaction of Methylcyclopentadienyl Magnesium Bromide with γ -Butyrolactone

Experimental Procedure

10 ccs (0.125 moles) of freshly distilled γ -butyrolactone in 100 ccs of ether were added dropwise to 0.25 moles of MCPD MgBr with stirring at 0°C. The reaction proceeded quickly a yellow precipitate being formed which quickly changed into a brown oil mass which eventually fouled the stirrer. The reaction product obtained was poured into water at 0°C and was decomposed by the careful addition of dilute hydrochloric acid. The water phase was then extracted several times with ether, the combined ether phases being neutralised with sodium hydrogen carbonate and dried with anhydrous sodium sulphate.

As ether was removed the extracts changed in colour from yellow to red, the removal of final traces of ether leaving a product which separated into two phases. One phase appeared to consist of toluene and polymethylcyclopentadiene. The second phase



SAMPLE 132 - 3.

ORIGIN C. Klemke · M.Sc project

SOLVENT KBr

CONCENTRATION Approx. 1%

CELL PATH 13 M/M. DIAMETER DISC

REFERENCE AIR

REMARKS

SCAN SPEED Slow

SLIT Standard

Intek
RFK/215/1001 472-5087

OPERATOR V. M. Clenton

DATE 17th July 1973

REF. NO. 2567

FIGURE 25

IR Spectrum of Methylcyclopentadienyl carboxylic acid

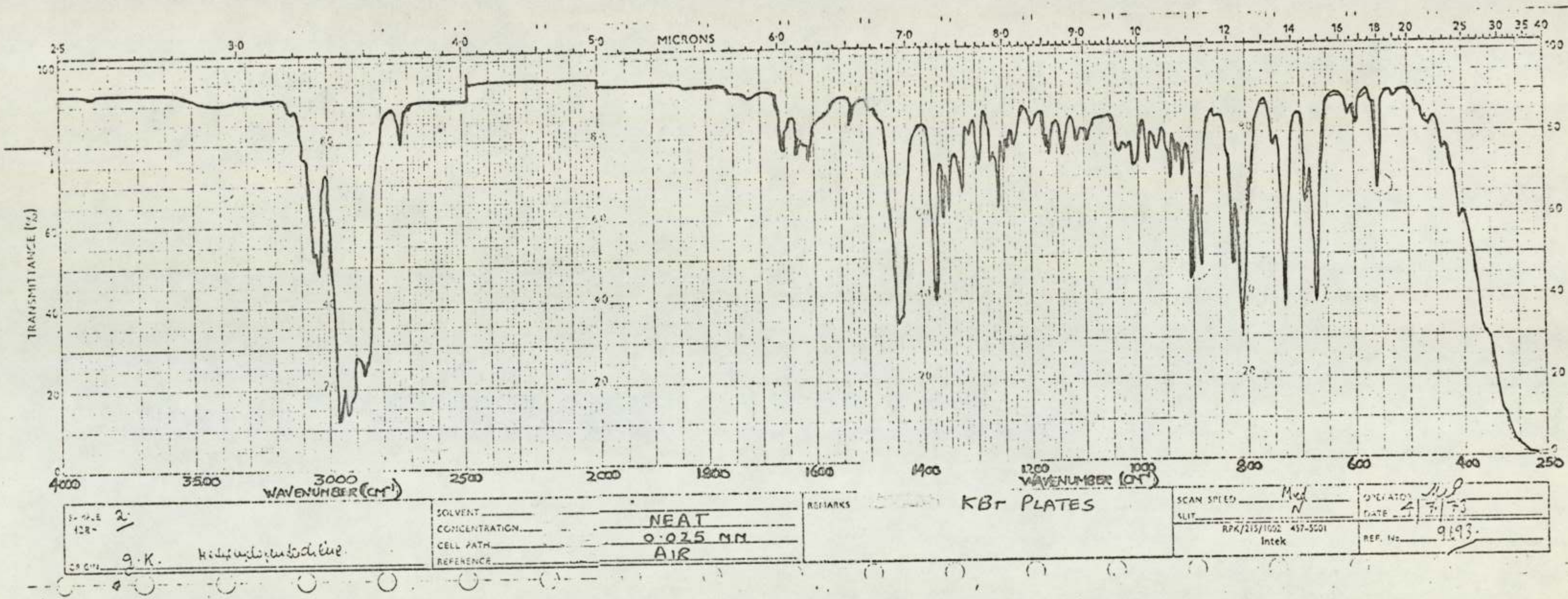
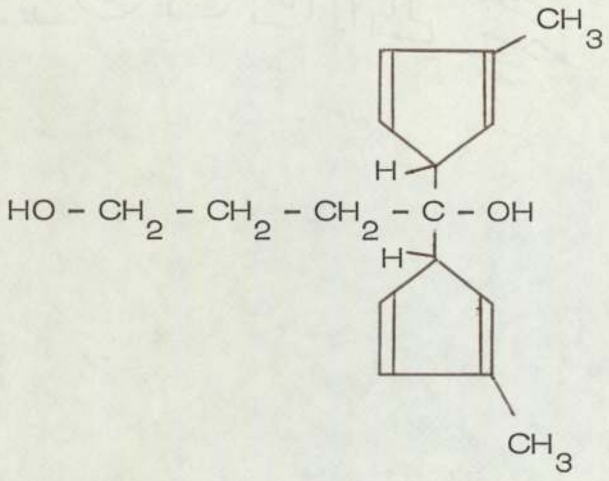


FIGURE 25A

IR Spectrum of Methylcyclopentadiene

consisted of a brown viscous oil which was dissolved in ethyl acetate and reprecipitated using petroleum ether. The expected product of the above reaction is shown below XXIV:



Molecular Weight 246

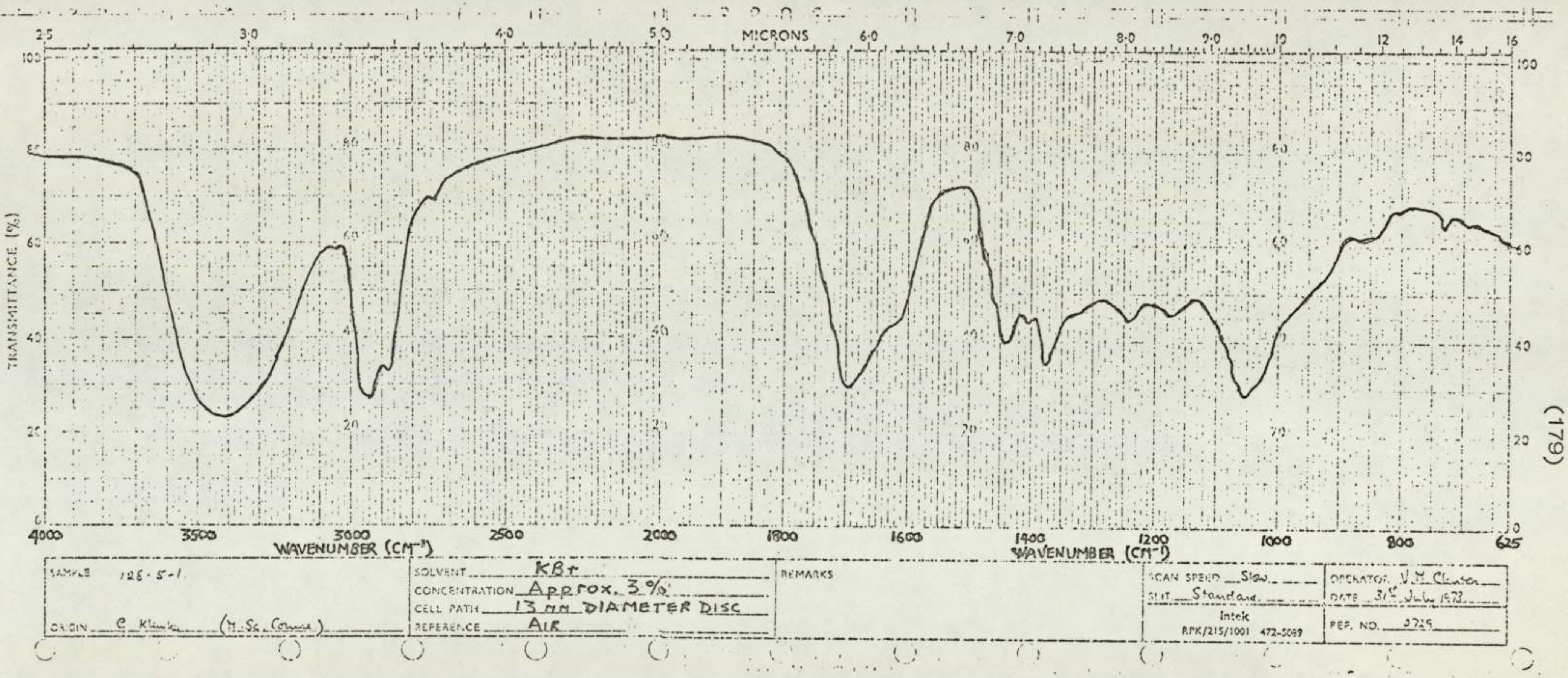
XXIV

The reaction was then repeated using the same procedure as above except that decomposition of the Grignard reagent was carried out using saturated ammonium chloride solution and subsequent handling of products was carried out under nitrogen.

Analysis of Products

Product analysis was carried out using infra red and mass spectrometry and indicated that products from both of the above reactions were identical.

Infra red spectra obtained for the two reaction products (Figures 26, p. 179 and Figure 27, p. 180) indicated the presence of a polymeric rather than a monomeric structure due to the poor resolution and broadness of absorption bands. Comparison of these spectra with that of γ butyrolactone (Figure 28, p. 181) indicates that the lactone had completely reacted – (disappearance of absorption



SAMPLE 128·5-1

ORIGIN C. Klinke (M.Sc. Course)

SOLVENT KBr

CONCENTRATION Approx. 3%

CELL PATH 13 mm DIAMETER DISC

REFERENCE AIR

REMARKS

SCAN SPEED Slow

SLIT Standard

OPERATOR V.M. Clinton

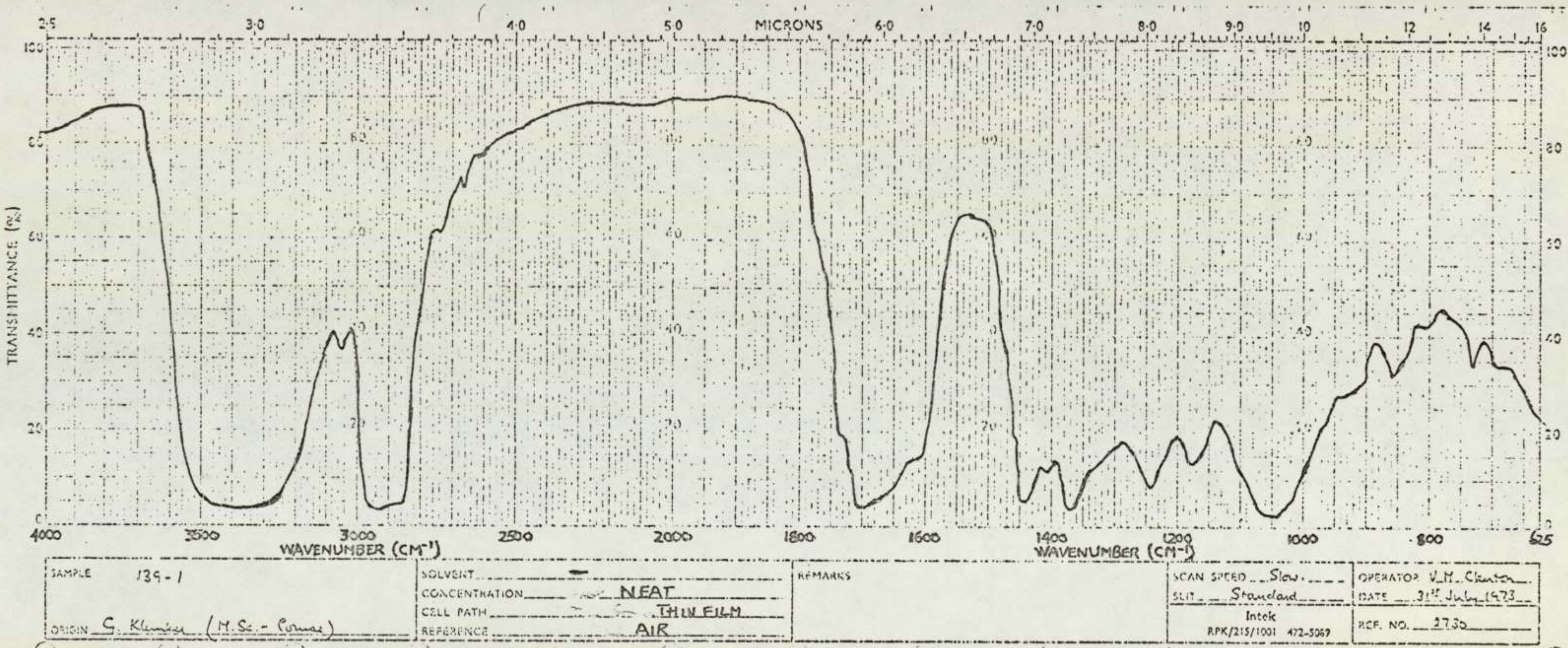
DATE 31st July 1973

REF. NO. 3725

Intek RPK/215/1001 472-5089

FIGURE 26

IR spectrum of the reaction product of MCPDylMgBr with γ-Butyrolactone



SAMPLE 139-1

ORIGIN C. Klemies (M.Sc. - Course)

SOLVENT —

CONCENTRATION NEAT

CELL PATH THIN FILM

REFERENCE AIR

REMARKS

SCAN SPEED Slow.

SLIT Standard

Intek

RPK/215/1001 472-5069

OPERATOR V.M. Clanton

DATE 31st July 1973

REF. NO. 2730

FIGURE 27

IR spectrum of the reaction product of MCPDylMgBr with γ-Butyrolactone

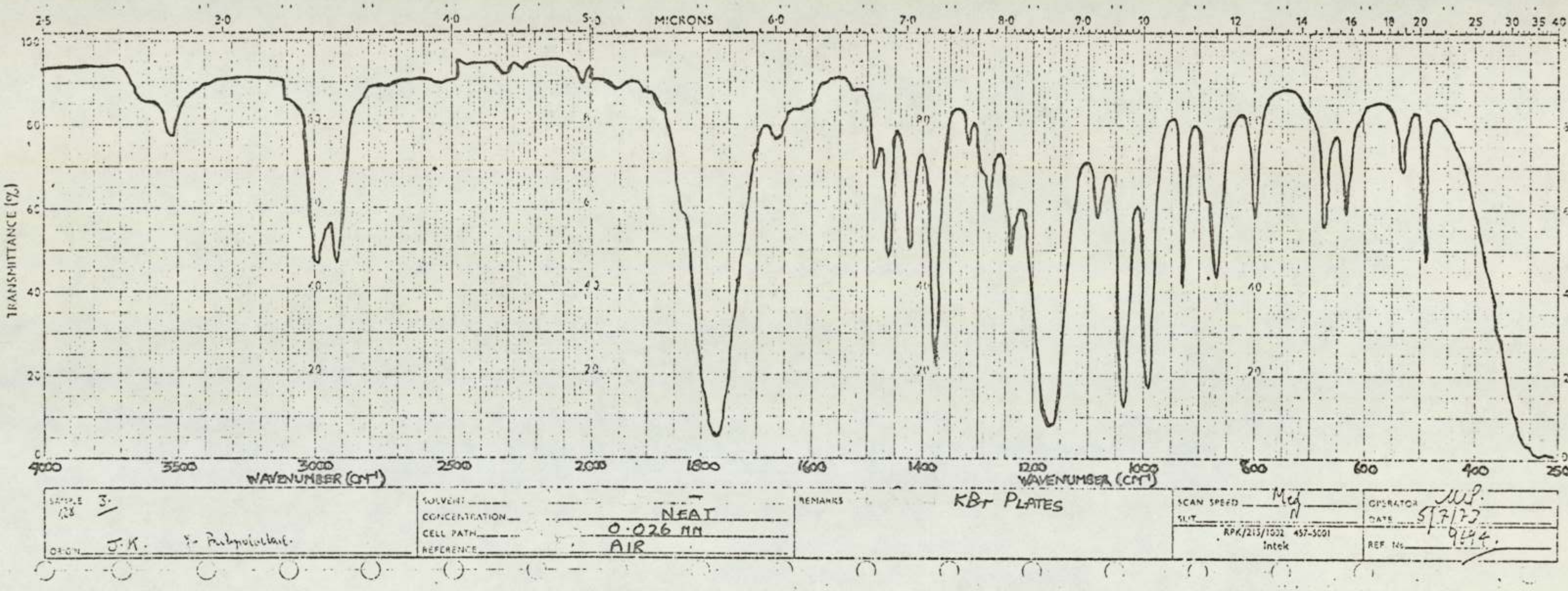
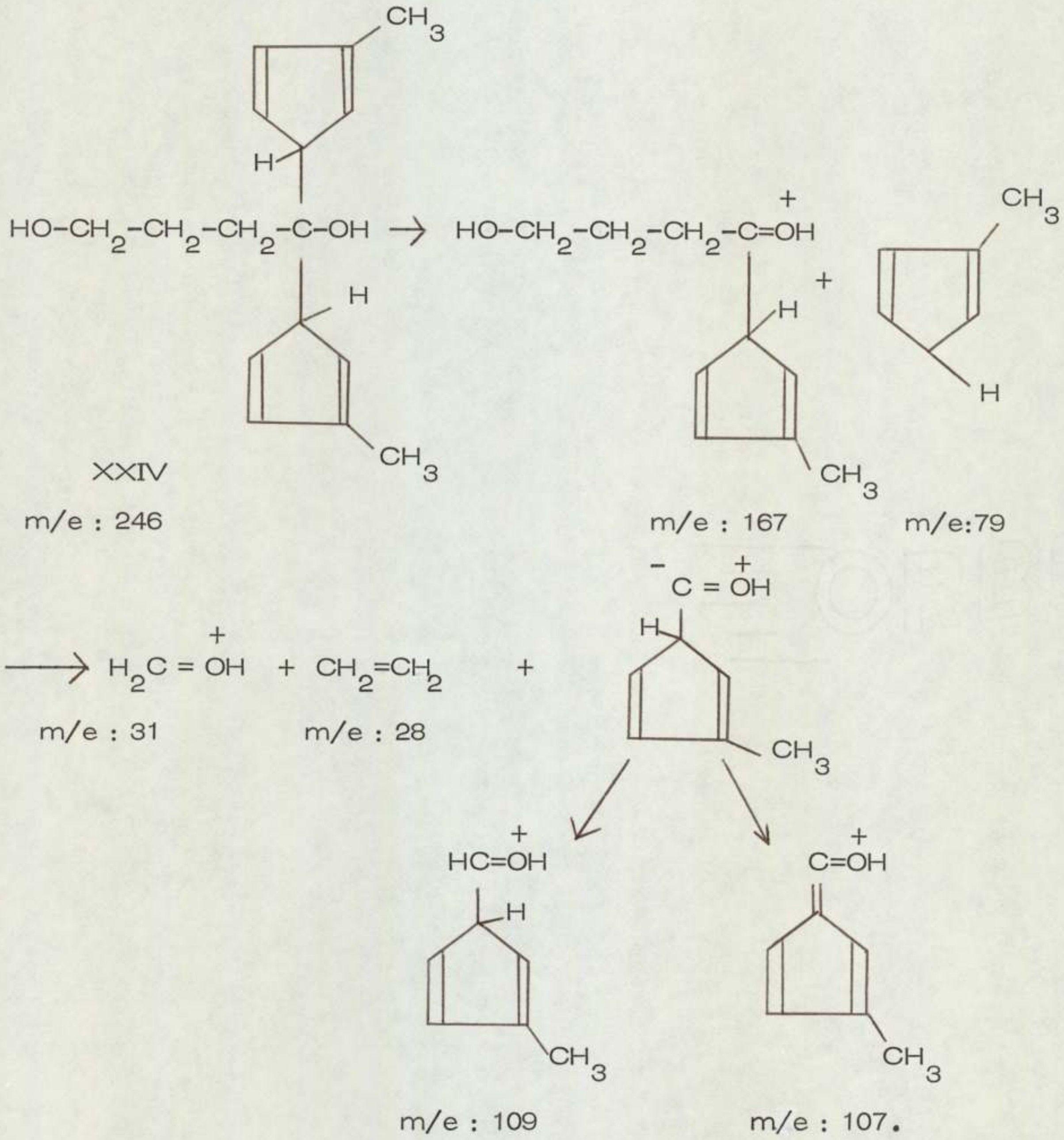


FIGURE 28

IR spectrum of γ-Butyrolactone

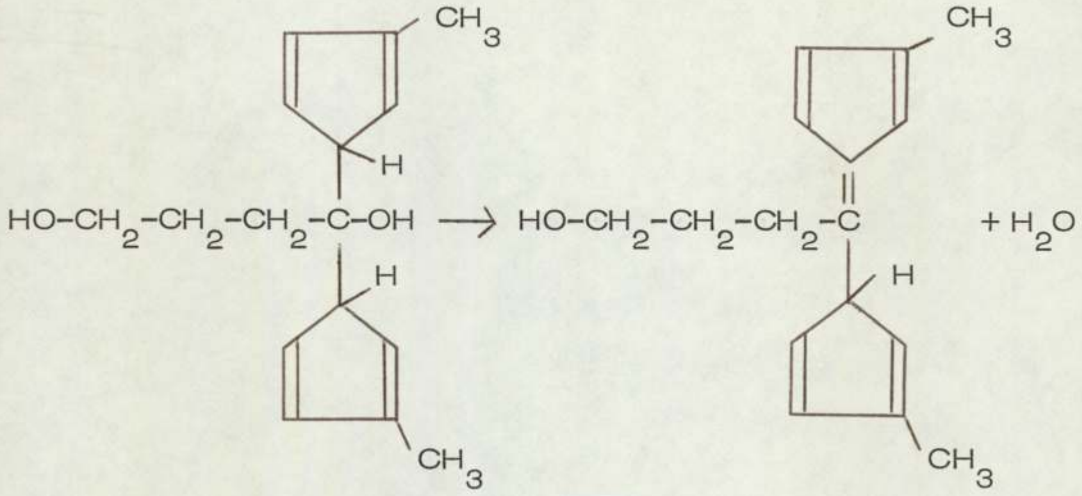
bands at 1800 cm^{-1} and 1165 cm^{-1}).

Mass spectra of both reaction products indicated however, that the expected product XXIV is absent since only very weak peaks were observed at m/e values of 244. Mass peaks of fragments corresponding to the expected decomposition pattern (Scheme D) of the structure XXIV were also not detected:



Scheme D

The expected reaction product (XXIV) could lose water to yield a product (XXV) as indicated below (Scheme E)

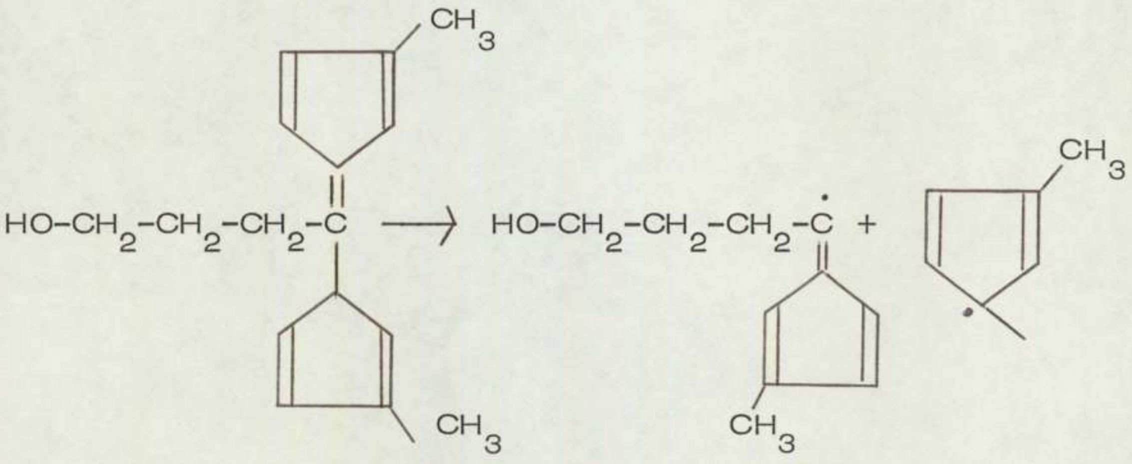


XXV

m/e: 228

Scheme E

A mass peak of medium intensity was observed at m/e of 228 together with strong mass peaks at m/e values of 149 and 79 which correspond to two of the expected decomposition products of (XXV) - indicated below (Scheme F).



XXV

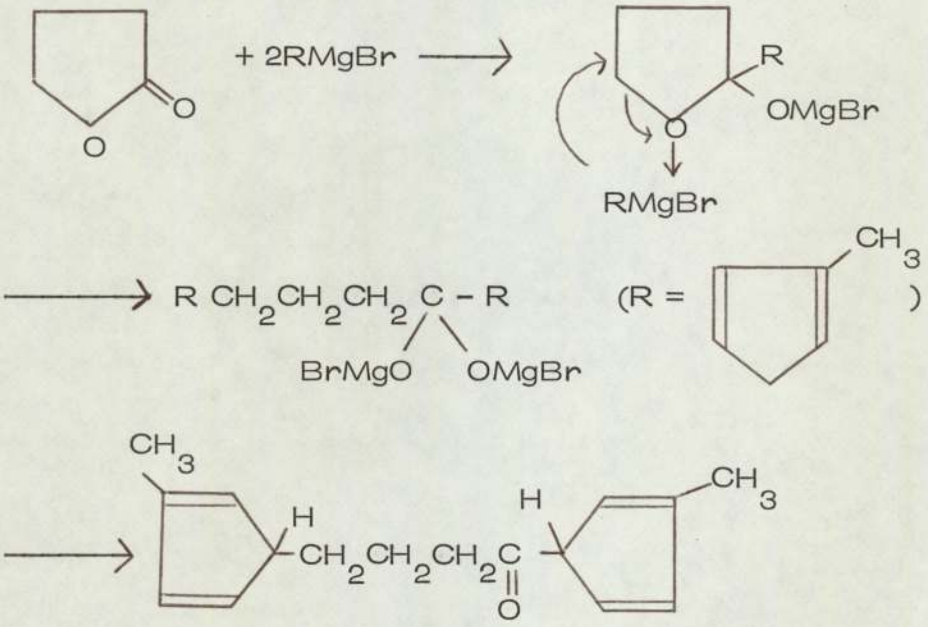
m/e : 149

m/e : 79

Scheme F

The compound (XXV) corresponds to the structure of a fulvene (a strongly coloured group of compounds) which could be responsible for the red colouration observed during the reaction between MCPD MgBr and γ butyrolactone.

A ketone of the form (XXVI) presented below could also be considered as a possible reaction product, formed from the following reaction (Scheme G).



(XXVI) m/e: 228

Scheme G

The mass spectra of the reaction product showed a medium intensity mass peak (m/e) at 228 thus indicating the presence of a product of the above form (XXVI).

Summary of Results; γ butyrolactone/methylcyclopentadienyl magnesium bromide reaction

The analytical results presented above for the products formed from the addition reaction between γ butyrolactone and methylcyclopentadienyl magnesium bromide show that the final structure formed is not that expected namely a diol incorporating methylcyclopentadiene residues (XXIV). It does seem likely however that the latter structure is formed as a primary reaction product which is unstable and subsequently loses water to form the fulvene structure (XXV).

The Reaction of Methylcyclopentadienyl Magnesium Bromide with Terephthalaldehyde

Following the unsuccessful attempt to form a stable diol containing methylcyclopentadiene residues from MCPD MgBr and γ-butyrolactone a further attempt was made to synthesis an appropriate structure using the reaction between terephthalaldehyde and MCPDMgBr summarised in Scheme C, p. 173.

Experimental Procedure

7.62 g (0.0625 moles) of terephthalaldehyde were suspended in powder form in 100 ccs of ether and added slowly to the solution of MCPD MgBr with stirring. A slight exotherm was observed and the reaction mix was maintained at room temperature for one hour during which time the solution changed colour from green to blue and finally to dark red.

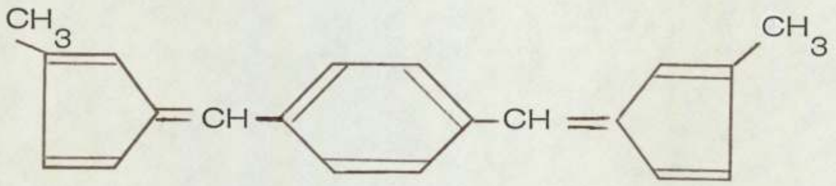
The reaction mixture was poured onto ice water and decomposed with dilute hydrochloric acid, the reaction product dissolving completely. The resulting solution was extracted with ether and on evaporation of the ether from the toluene solution, orange crystals were precipitated and separated by filtration.

Analysis of Reaction Product

On recrystallisation, using ethyl acetate as solvent, the product gave a melting point of 95°C, which corresponded to that for terephthalaldehyde.

The infra red spectra of this reaction product and terephthalaldehyde were identical indicating that little or no reaction had taken place.

The red colouration observed in the reaction mix could be attributed to the formation of a fulvene (XXVII) formed via an alternative reaction between MCPDMgBr and terephthalaldehyde(142) involving the splitting off of two molecules of water from the expected reaction product (Scheme C, p. 173) during the removal of ether from the reaction mix.



XXVII

Summary of Results: Terephalaldehyde/methylcyclopentadienyl magnesium bromide reaction

Since the carbonyl group, attached as it is to an aromatic nucleus, is somewhat deactivated it appears likely from results obtained that reaction with the MCPDMgBr compound does occur but under conditions used above only occurs to a limited extent. Any diol that is formed appears to be unstable, decomposing to yield a fulvene type of structure in a similar fashion to the diol formed using γ butyrolactone. (Scheme E, p. 183).

7.2 Synthetic Work Relating to the Formation of Carboxylic Polymers Containing Pendant Sites of Unsaturation based on Methylcyclopentadiene

An alternative approach to that described in 7.1 for the incorporation of methylcyclopentadiene into polymer backbones is to attempt a more direct incorporation of the monomer into a backbone structure via reactions between a suitable preformed polymer backbone (e.g. a structure containing carbonyl groups) and MCPDMgBr.

The polymer backbones chosen for this work were polyvinylpyrrolidone and a copolymer of styrene and maleic anhydride.

i) The Reaction of Methylcyclopentadienyl Magnesium Bromide with Polyvinylpyrrolidone

Experimental Procedure

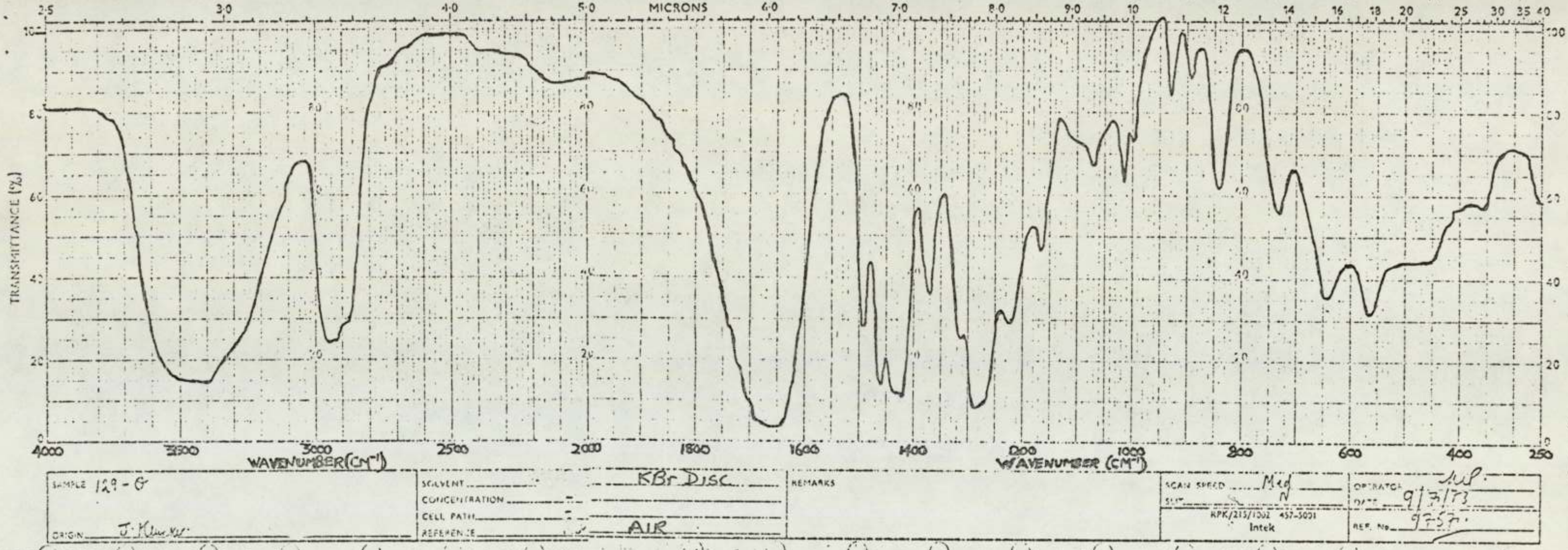
A 1 mole equivalent (28 g) of the repeat unit of polyvinylpyrrolidone suspended in ether was added to 0.25 moles of MCPD MgBr in ether and toluene. The reaction was exothermic, the reaction mixture changing in colour from green to yellow. The mixture was then poured into water at 0°C and the reaction mix acidified with dilute hydrochloric acid. The reaction product was recovered from the water phase as a green-brownish oil by precipitation with acetone and purified by redissolving it in water and repeating the treatment with acetone.

The oil obtained was dried over sodium sulphate overnight after which time the oil became dark brown and solidified after standing in air for three weeks. Previous experimental work described in Chapter 5 involving the polymerisation of methylcyclopentadiene had indicated that the polymer was susceptible to oxidation during which process the polymer became discoloured. A similar discolouration (yellowing) observed with the modified polyvinylpyrrolidone was attributed to the fact that methylcyclopentadiene had been successfully grafted onto the backbone of polyvinylpyrrolidone.

Analysis of Reaction Product

Infra red spectra of unmodified and 'modified' polyvinylpyrrolidone (Figures 29, p. 189, and 30, p. 190 respectively) suggest that the incorporation of methylcyclopentadiene onto the polyvinylpyrrolidone backbone had been successful.

Two principle reactions (Schemes H and I) involving the grafting of methylcyclopentadiene onto the polymer chain could occur as follows:



SAMPLE 129-G

ORIGIN J. [illegible]

SOLVENT KBr DISC

CONCENTRATION

CELL PATH

REFERENCE AIR

REMARKS

SCAN SPEED Med

SLIT N

KPK/213/1002 457-3001
Intek

OPERATOR M.P.

DATE 9/3/73

REF. No. 9757.

FIGURE 29

IR spectrum of Polyvinyl pyrrolidone

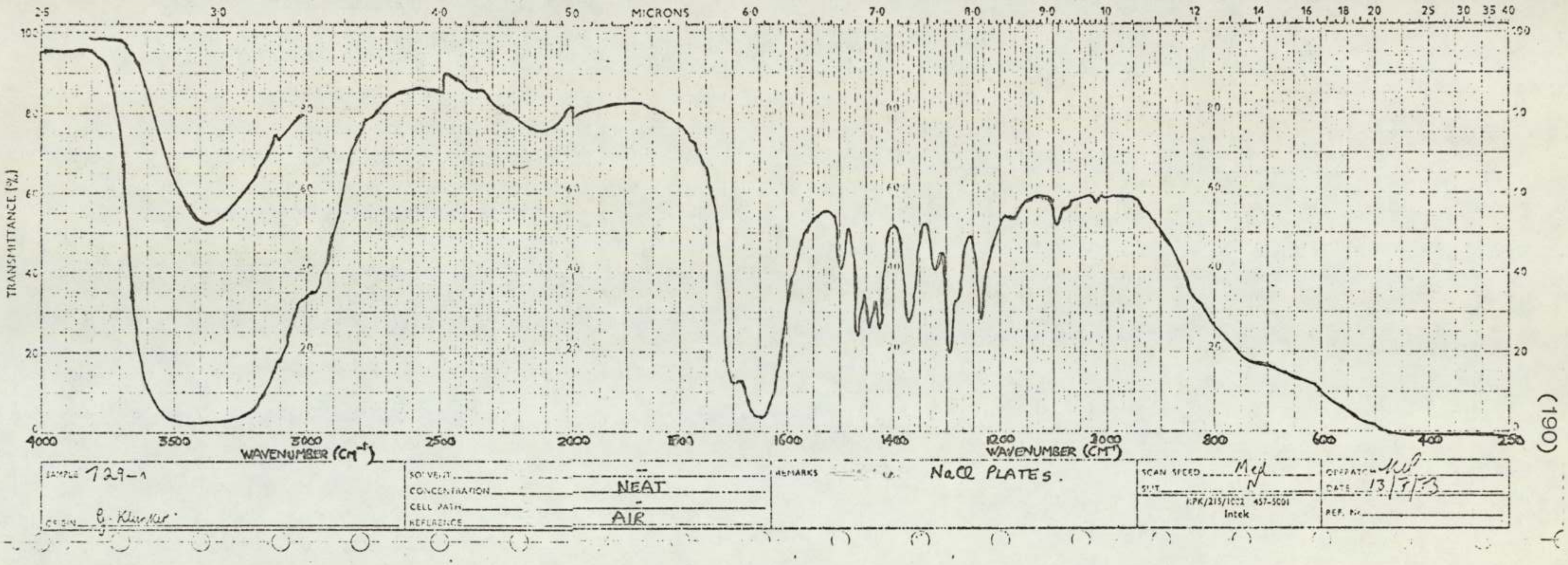
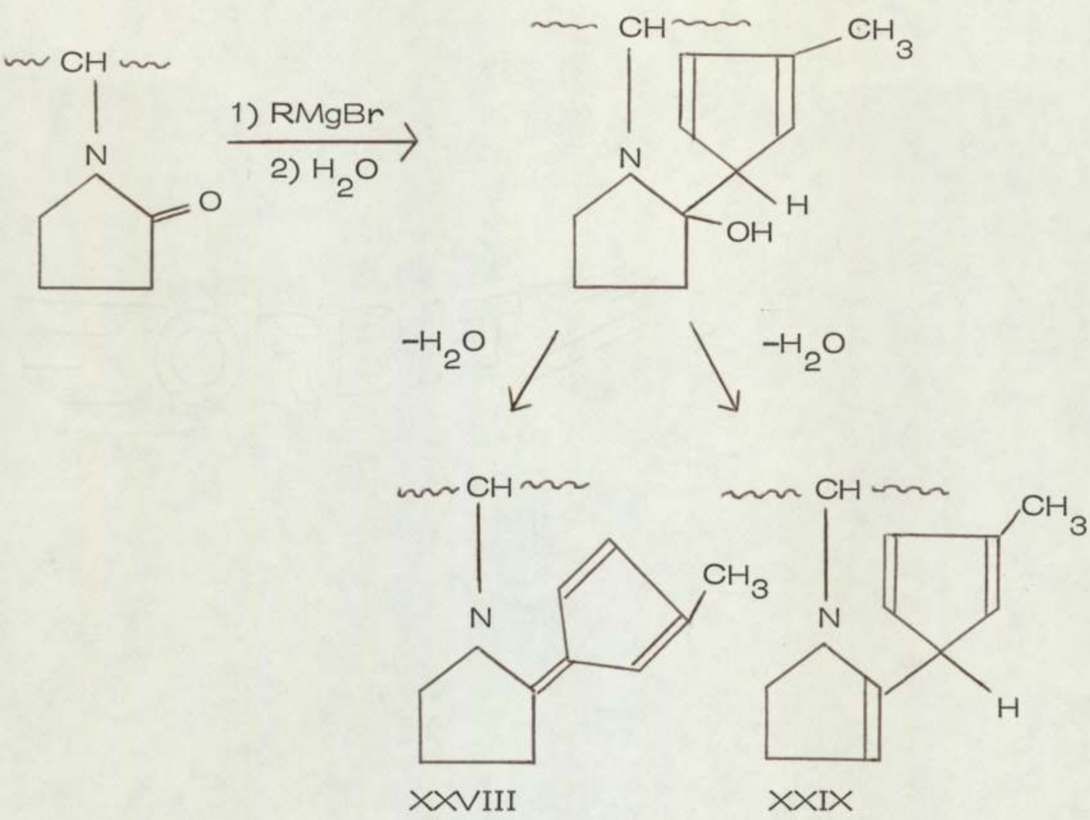
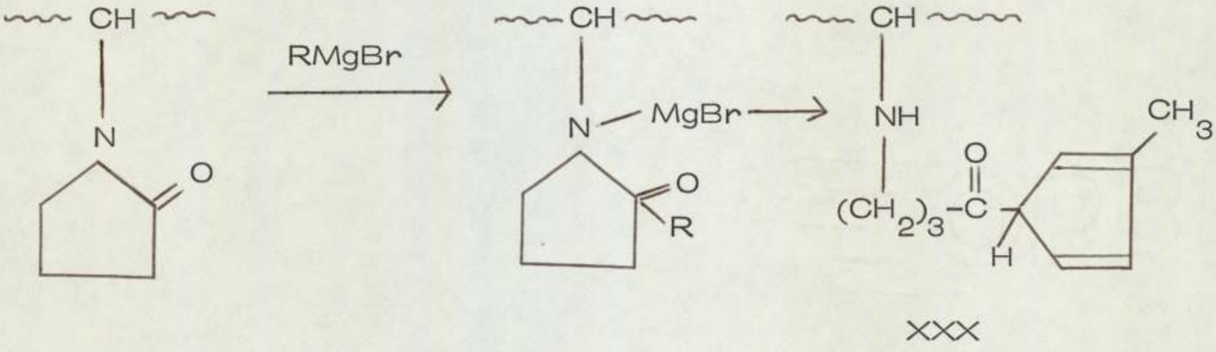


FIGURE 30

IR spectrum of the reaction product of MCPDylMgBr with Polyvinyl pyrrolidone



Scheme H



Scheme I

<u>Summary of Results. Polyvinylpyrrolidone/methylcyclopentadienyl magnesium bromide reaction</u>

The results obtained for the products obtained from the reaction between MCPDMgBr and polyvinylpyrrolidone indicate the successful incorporation of methylcyclopentadiene into the backbone although evidence as to which of the products (XXVIII) to (XXX) presented in Schemes H and I, predominate was not obtained. Closer examination of these structures reveals that structure XXIX is likely to be the more interesting product from the point of view of this work due to the more favourable, electron donating ability of groups adjacent to the cationically reactive site.

ii) The Reaction of Methylcyclopentadienyl bromide with Maleic Anhydride - Styrene Copolymer

Experimental Procedure

Grafting of methyl cyclopentadiene onto the copolymer of maleic anhydride and styrene was achieved by carrying out the following experimental procedures, a) and b) described below.

a) A suspension of maleic anhydride-styrene copolymer containing the equivalent of 0.039 moles (7.59g) of the repeat unit in ether was added to 0.125 moles of MCPDMgBr in ether and toluene. A slightly exothermic reaction occurred and the colour of the solution changed from green to yellow green.

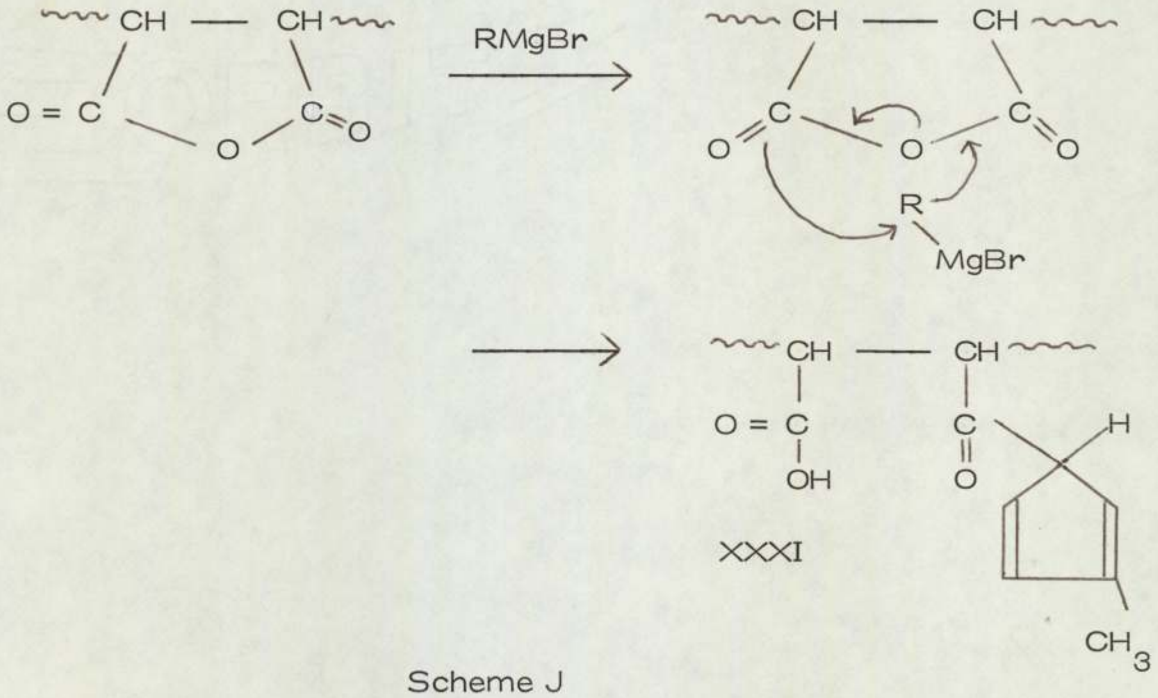
The reaction mix was poured onto ice and hydrolysed with dilute hydrochloric acid. The insoluble product was recovered by filtration and subsequently washed with ether. The solid was subsequently dissolved in acetone yielding a yellow orange viscous solution from which a white fibrous polymer was obtained by addition of tetrachloroethane followed by filtration.

The polymer was redissolved in acetone giving a solution which yielded a clear yellow transparent film upon the removal of the solvent by evaporation.

Analysis of Reaction Product

The infra red spectra of the original and modified copolymer are shown in Figures 31, p. 194 and 32, p. 195 respectively. Comparison of the spectra reveals a decrease in absorption intensity at the C=O stretching frequency (for cyclic anhydrides) at 1783 and 1800 cm^{-1} for the polymer after reaction with MCPD MgBr together with an increase in absorption intensities at 1710–1730, 1270 and 1020 cm^{-1} corresponding to the carboxylic group formed from the opening of the anhydride ring (see XXXI below).

The product obtained could be of the form indicated below XXXI (Scheme J).



Scheme J

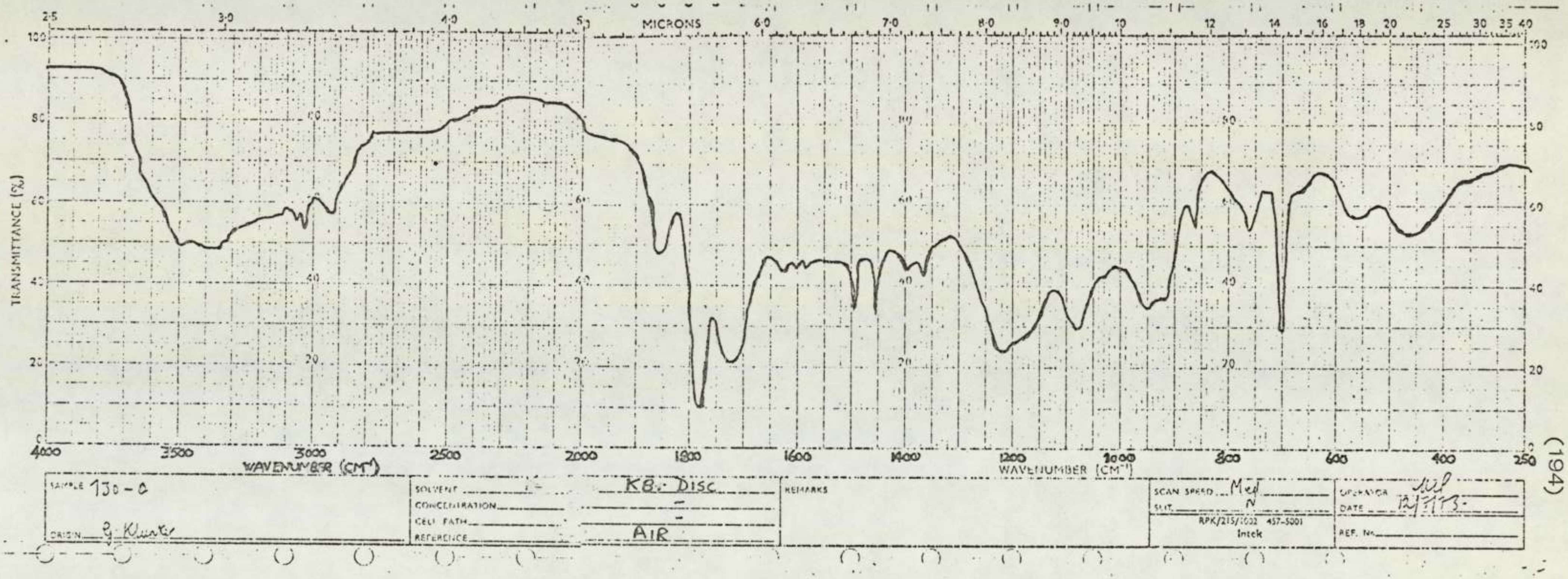


FIGURE 31

IR spectrum of Maleic anhydride - Styrene - Copolymer

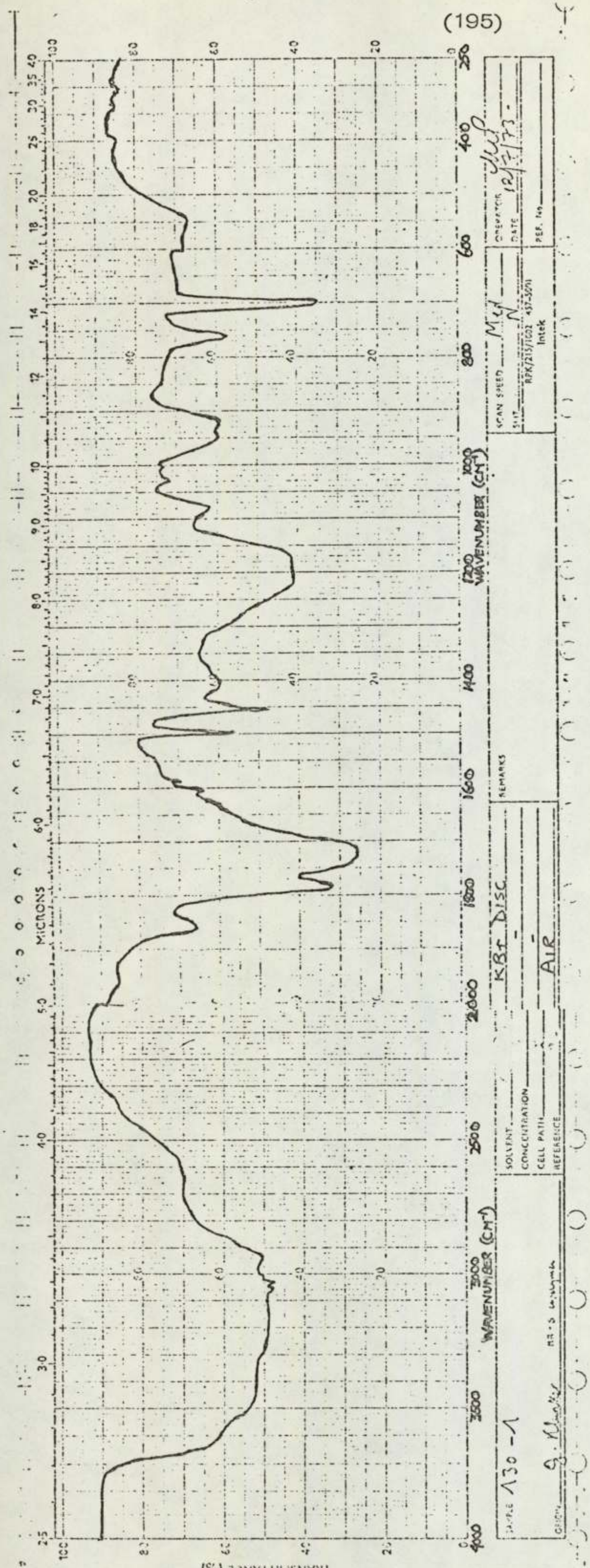


FIGURE 32

IR spectrum of the reaction product of MCPDylMgBr with Maleic anhydride - Styrene - Copolymer

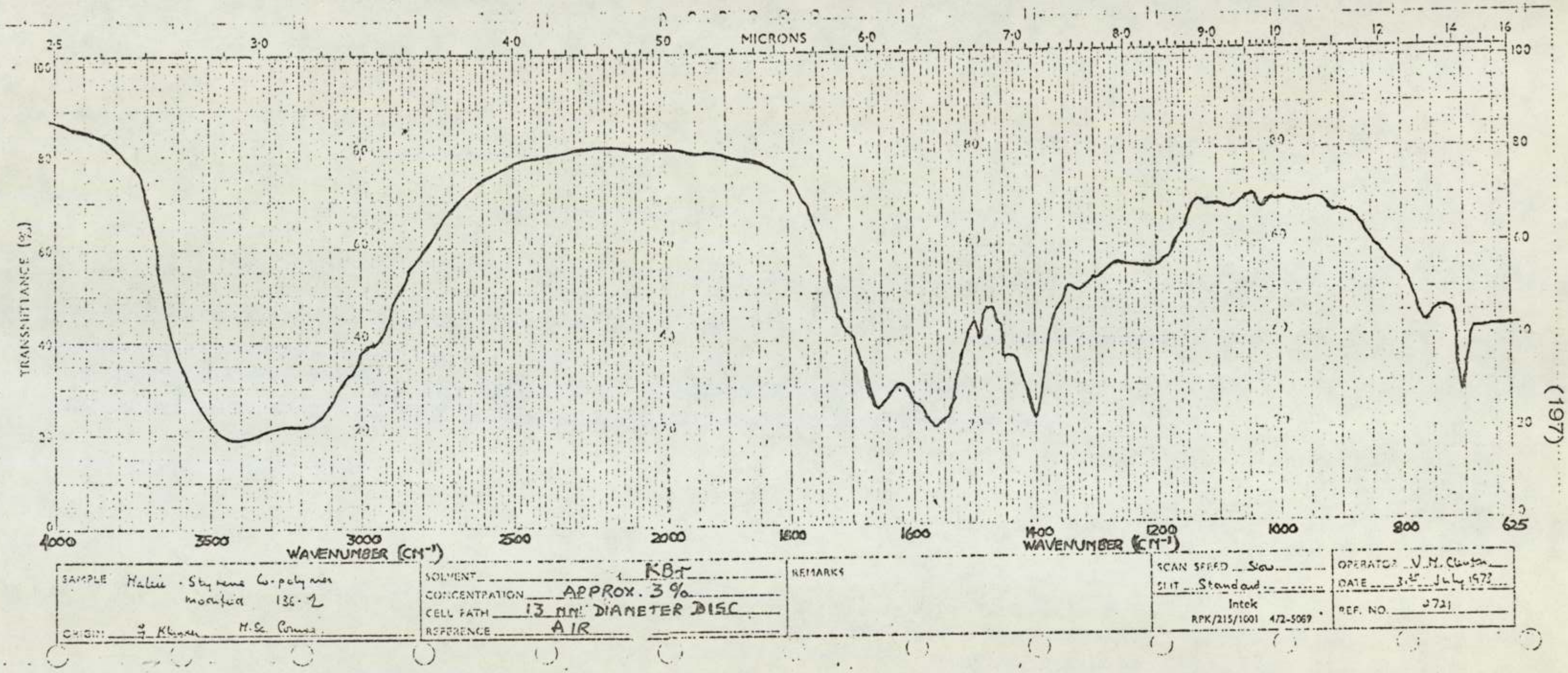
b) The second synthetic procedure was carried out as follows. 0.06 mole equivalent (12.8 g) of the repeat unit of the styrene/maleic anhydride copolymer was suspended in ether and 0.125 moles of MCPDMgBr solution in ether and toluene were added. The resultant mixture was refluxed with stirring for one hour and the reaction mix poured onto ice and decomposed with saturated NH_4Cl solution. The product was filtered off, washed with water followed by methanol refiltered, and dried.

A light orange to brown powder was obtained which was found to be infusible and smelled strongly of methyl cyclopentadiene.

Analysis of Reaction Product

The infra red spectra of the unmodified and modified copolymer are shown in Figures 31, p. 194 and 33, p. 197, respectively. The latter spectrum Figure 33 showed no absorption bands corresponding to carbonylic or carboxylic groups.

The mass spectrum of the modified copolymer showed the same decomposition pattern as methylcyclopentadiene dicarboxylic acid: a top mass peak (m/e) value of 124. The presence of methylcyclopentadiene was also indicated mass peak of medium intensity of m/e value of 79 and 77 together with carbon monoxide, strong peak at an m/e value of 28 and water a strong peak at an m/e value of 18. The reaction product obtained from the second synthetic procedure could be of the form shown in XXXII, p. 198.



SAMPLE Maleic - Styrene Co-polymer modified 136·2

ORIGIN J Khan M.Sc Course

SOLVENT KBr

CONCENTRATION APPROX. 3%

CELL PATH 13 MM DIAMETER DISC

REFERENCE AIR

REMARKS

SCAN SPEED Slow

SLIT Standard

Intek
RPK/215/1001 472-5069

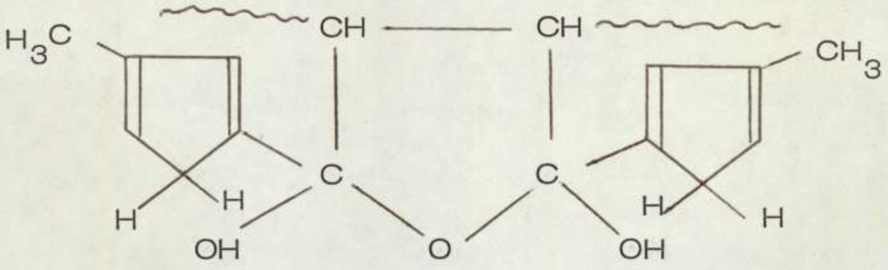
OPERATOR V.M. Clinton

DATE 3rd July 1972

REF. NO. 2721

FIGURE 33

IR spectrum of the reaction product of MCPDylMgBr with Maleic anhydride - Styrene - Copolymer



XXXII

The variation in the mode of preparation of the Grignard reagent together with the variation in the method used for the decomposition of the reagents (water - hydrochloric acid or saturated ammonium chloride solution) could account for the formation of the different reaction products.

Summary of Results: Styrene-Maleic Anhydride Copolymer/ Methyl Cyclopentadienyl Magnesium Bromide Reaction

The reactions carried out to incorporate methylcyclopentadiene into styrene, maleic anhydride copolymer appear to be successful although reaction products obtained probably differ depending on the reaction procedure adopted (cf. structures XXXI and XXXII, p.193 and 198 respectively).

7.3 Summary and Conclusions

Although attempts to synthesise polyester backbones using novel cationically active diols containing methylcyclopentadiene residues and prepared via Grignard reagents appeared unsuccessful; the work involved in introducing methylcyclopentadiene more directly onto formed backbones again using Grignard reagents was particularly encouraging. Successful incorporation of methylcyclopentadiene onto polyvinylpyrrolidone and a copolymer of styrene and maleic anhydride was achieved and the products obtained certainly merit further investigation in terms of rates of cross linking using methylcyclopentadiene as cross linking agent.

CHAPTER 8

Summary, Conclusions and Suggestions for Further Work

8.1 Summary and Conclusions

This section of project work was concerned with a study of the feasibility of producing a rapid cation-initiated cross linking system for metals coating applications. The approach to this problem involved in the first instance the development of a rapid homopolymerisation reaction which could subsequently be harnessed to a cross linking reaction.

The experimental work presented in the earlier part of this section of the thesis confirms the high level of reactivity reported in the literature for monomers of the cyclic diene type, methylcyclopentadiene and cyclopentadiene when these are polymerised using cationic initiators, although higher members of the series were found to be somewhat less reactive. Assessment of monomer reactivity was carried out using a novel technique, stopped flow rotational viscometry developed as part of this study in which a given system is polymerised in thin film under carefully controlled conditions and rates of reaction calculated from the viscosity/time plots obtained. Kinetic data previously obtained from similar plots for a free radical system were found to be in good agreement with the documented data recorded for the system thus establishing the validity of the technique for use in the assessment and evaluation of kinetic parameters for homopolymerisation reactions.

Synthetic work is described in which polymer backbones were prepared containing reactive sites from which it was hoped rapid cross linking could take place using a reactive monomer such as methylcyclopentadiene as the cross linking agent.

A speculative approach to the problem involved the comparatively simple task of preparing polyester backbones from condensation reactions between commercially available diols and dicarboxylic acids containing sites of unsaturation potentially active to cationic species. The backbones formed in this way were cross linked using a series of monomers, styrene (as control), α methylstyrene, methylcyclopentadiene and n-butyl vinyl ether. The assessment of cross linking rates was carried out using gel times of the various systems measured with a commercially available instrument. Results obtained highlighted the importance of matching the reactivity of cross linking agent and reactive site within or pendant to the backbone so that cross linking reactions predominate over homopolymerisation reactions involving the cross linking agent.

An attempt was therefore made to synthesise polymer backbones containing reactive sites identical in structure to that of the cross linking agent so that ideally reactivities of cross linking agent and reactive site within the backbone are identical. Since methylcyclopentadiene was known to be the most promising monomer in terms of reactivity this monomer was chosen as the basis on which to carry out this section of work. One approach to this problem analogous to that used for the speculative work summarised above, involved the synthesis via Grignard reactions of diols containing reactive sites based on methylcyclopentadiene.

These structures once prepared could then be easily incorporated into polyester backbones using conventional condensation reactions with dicarboxylic acids. Since synthetic difficulties were encountered in which diols derived from γ butyrolactone and terephthalaldehyde appeared to spontaneously lose water to form fulvene structures, an alternative approach to the problem was decided upon in which a more direct incorporation of methylcyclopentadiene onto polymer backbones was carried out using the reaction between carbonyl groups in polyvinylpyrrolidone or a styrene maleic anhydride copolymer, and methylcyclopentadienyl magnesium bromide. These reactions involving the insertion of methylcyclopentadiene units pendant to the polymer backbone appeared to take place satisfactorily for the two polymers used, - and as such these results constitute one of the most encouraging aspects of the work carried out. Cross linking rates for these backbones, using methylcyclopentadiene as the cross linking agent, could not be determined due to limitations in the time available.

The stopped flow rotational viscometer referred to above and used in the assessment of monomer reactivity performed satisfactorily in its final form for the purposes of this work. Later work (described in Chapter 6) demonstrated that the technique, which had been designed to cope with the measurement of both homopolymerisation rates and rates of cross linking, could be applied equally satisfactorily to the measurement of the latter. The application of the technique it is suggested could also be extended to the determination of kinetic parameters for other polymerisation reactions particularly in cases where the stringent control of the environment in which the reaction is carried out, is essential (e.g. moisture sensitive polymerisation reactions such as the ring opening polymerisation of anhydro-sulphites and carboxylates).

8.2 Suggestions for Further Work

Suggestions for further work can conveniently be summarised as follows:

i) An extension of the study of the reactivity of the more promising monomer types (cyclic dienes, vinyl ethers) in terms of the effect of temperature and of the type and concentration of solvent, initiator and co catalyst on polymerisation rates using cationic initiation.

ii) A study of the reactivity of substituted cyclopentadienes (other than methylcyclopentadiene) in cationic polymerisation reactions.

iii) A study of the cross linking rates of backbone structures containing methylcyclopentadiene units ('substituted' polyvinylpyrrolidone and styrene - maleic anhydride copolymer).

iv) A study of the oxidative stability of both homopolymers and cross linked materials incorporating methylcyclopentadiene.

These areas of proposed study are discussed in more detail in turn below.

i) As stated earlier solvent effects can do much to increase the reactivity of a given propagating species via its effect on the charge separation involved. The use of solvents where this charge separation might be involved (e.g. the use of chlorobenzene in place of toluene) could lead to substantial improvements in polymerisation rates.

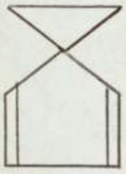
The cationic initiator chosen for the bulk of this work was boron trifluoride etherate because of its ready solubility and convenience of handling. The determination of the effect of other more reactive initiator systems, e.g. titanium tetrachloride, stannic chloride/trichloroacetic acid, on polymerisation rates attained with boron trifluoride etherate would be useful. In conjunction with this aspect of the work an evaluation of the effect on polymerisation rate of less toxic protonic acid initiators particularly phosphoric acid would be of considerable interest from the point of view of the ultimate aims of this study.

The effect on polymerisation rate of various concentrations of water as the cocatalyst would be of interest although studies using co catalysts other than water might prove less attractive at this stage of work since the latter is readily available, can relatively easily be controlled and is effective as a co catalyst.

Although vinyl ethers are considered to be somewhat less reactive than the cyclic dienes studied in this work (methylcyclopentadiene and cyclopentadiene) they do appear to be the next most reactive group of monomers available and as such it is thought desirable to include the more reactive members of this group of monomers in the experimental programme outlined above.

ii) A significant restriction to the commercial application of methylcyclopentadiene and cyclopentadiene for use as cationic cross linking agents would appear to be their susceptibility to dimerisation processes which occur rapidly at room temperature.

Since the dimers formed are relatively unreactive towards cationic polymerisation these processes need to be inhibited by storing the materials at $-70^{\circ}C$. Apart from the possibility of retarding dimerisation by chemical inhibitors, recent work by O'Hara et al(143) describes an alternative means by which the dimerisation process can be stopped altogether. He found that Spiro [2,4] hepta 4,6-diene (XXXIII) gave cationic polymerisation rates comparable to those obtained for cyclopentadiene and found that the monomer unlike cyclopentadiene was not susceptible to dimerisation processes.



XXXIII

The monomer (XXXIII) can be readily prepared from cyclopentadiene and ethylene dichloride.

A study of cationic polymerisation rates obtained for this monomer, under various conditions summarised in i), using the stopped flow rotational viscometer, would be of great value to this work.

iii) It has been demonstrated (Chapter 6) that the stopped flow rotational viscometer can be used successfully to measure cross linking rates. An obvious extension of experimental work carried out to date would be to use the instrument in this context to evaluate the cross linking rates obtained for reactive backbone structures synthesised in Chapter 7 under various conditions.

iv) Since homopolymers of cyclopentadiene and methylcyclopentadiene appear to be susceptible to oxidative attack, a study of the extent and nature of such instability (together with its effect on properties) on cross linked material incorporating these structures would be desirable.

SECTION II

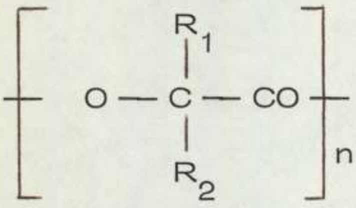
The Development of Apparatus for Use in the Detailed Study of the Thermal Degradation of Polymers and its Application to The Study of The Thermal Degradation of Poly-α-esters

CHAPTER 1

Introduction and Summary of Literature

1.1 Introduction

During the course of an M.Sc. project undertaken by the author(144), thermal degradation apparatus was developed in prototype form for use in the study of the thermal degradation of poly-α-esters (XXXIV).



$$\left[-O-\overset{R_1}{\underset{R_2}{C}}-CO- \right]_n$$

XXXIV

In the course of initial stages of the work described in Section I of this thesis the prototype equipment referred to above was rebuilt and set up in a more permanent state, since it was ultimately hoped to apply the apparatus in its fully derived form to the study of the thermal degradation of novel cross linked systems which were to be developed as the objective of work described in Section I.

There was, therefore, some connecting philosophy at the outset between Sections I and II although as the research progressed it became apparent that it would not be possible to bring systems discussed in Section I to the stage where this equipment could be usefully used in their evaluation.

The work described in this section was concerned with the construction and use of combined thermal degradation analysis techniques. This involved the construction of equipment, based on the prototype apparatus, capable of obtaining complementary information about degradation pathways of poly-α-esters. The equipment was constructed in its final form with the help of work shop facilities early on in the project and used by the author to study the thermal degradation of poly (isopropylidene carboxylate) and β chlorinated poly α esters. This work was followed by a study of the effect of main chain substituents on the thermal stability of poly α esters carried out as MSc projects two of these(145, 146), being carried out under the direction of the author over the period 1971–1973. Published papers(168, 173–176) covering work carried out to-date on this topic are presented in the rear of this section.

1.2 Literature Survey

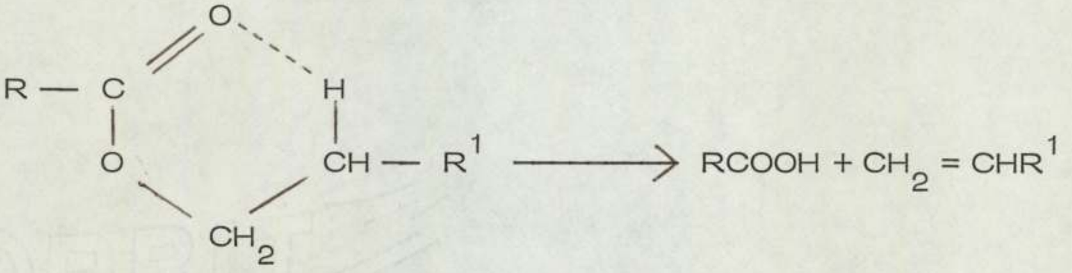
Little work has been reported concerning poly-α-ester degradation but the examination of reported work on other linear polyesters indicated the spectrum of analytical and kinetic information that would be required to characterise the degradation of poly-α-esters of various structures. Thus the basis was established for the design and assembly of the apparatus described in Chapter 2, p. 216.

Poly-α-esters (XXXIV, p. 208) represent the class of polyesters having the simplest repeat unit but little is known of their degradative characteristics and in particular the ways in which these are affected by substituents R^1 and R^2. This may be partially due to the absence of a general condensation route applicable to all members of series, the polymers being synthesised via ring opening reactions discussed in detail elsewhere(147–152).

The degradation of polyesters as a general class has been widely but unsystematically studied. A survey of earlier literature up to 1928 has been compiled by Hurd(153). Much of the subsequent work reported on the degradation of polyesters serves as a source of valuable guidance as to the type and sophistication of equipment required for a detailed study of the thermal degradation of poly-α-ester polymers.

Carothers(154) prepared a series of glycol esters of carbonic acid showing that diethylene carbonate and trimethylene carbonate undergo reversible transformation between cyclic monomeric and polymeric forms. He found that a stable dimer of tetramethylene carbonate could be obtained by thermal decomposition of the polymer. He also showed(155) that many aliphatic polyesters undergo simple intramolecular ester interchange reactions producing dimeric and monomeric cyclic esters on thermal degradation. Polyglycollic acid (XXXIV, R^1, R^2 = H) and polylactic acid (XXXIV, R^1 = H, R^2 = Me) were for example found to degrade to form glycollide and lactide respectively.

Pohl(156) demonstrated that the degradation of many polyesters has its origin in the abstraction of hydrogen from the β carbon of the glycol segment a mechanism which is well known for example in the pyrolysis of model compounds, leading to the formation of olefinic and carboxyl terminated fragments (Scheme XXV below).



XXXV

Trischler and Hollander(157) demonstrated that aliphatic carboxylic acids provide ready degradation sites because of radical abstraction reactions involving hydrogen atoms on the α carbon of the carboxylic acid segment (Scheme XXXVI).

$$\begin{aligned} R^1CH_2CH_2COOC_6H_5 &\longrightarrow R^1CH_2\dot{C}HCOOC_6H_5 \\ &\longrightarrow R^1\cdot + CH_2{=}CHCO_2{-}C_6H_5\cdot \end{aligned}$$

XXXVI

These workers remarked that should degradation sites leading to reactions (XXXV) and (XXXVI) above, be absent and the polyester does not readily undergo intramolecular ester interchange very stable polyesters may be obtained(157). Zhuravleva and Rode(158) point to the occurrence in such cases of two distinct ester group scission mechanisms with resultant competitive formation of carbon monoxide and carbon dioxide (Scheme XXXVII), the former predominating at higher temperatures:-

$$ROCOR^1 \begin{array}{l} \nearrow R\cdot + \cdot OCOR^1 \longrightarrow R\cdot + R\cdot^1 + CO_2 \\ \searrow RO\cdot + \cdot COR^1 \longrightarrow RO\cdot + R^1\cdot + CO \end{array}$$

XXXVII

Perhaps the most complete and more systematic studies have been carried out on poly(ethyleneterephthalate) and related model compounds notably by Ritchie(159), Goodings(160), Wall(161) and Marshall and Todd(162) with a concise review of the work by Buxbaum(163). A chain scission reaction was found similar to that presented in Scheme XXXVII above due to β hydrogen availability the main degradation products being carbon dioxide terephthalic acid and acetaldehyde. Degradation carried out in the presence of oxygen was found to lead to predominantly radical reactions giving rise to a large number of degradation products. Ross(164) and Berr(165) have demonstrated that intramolecular elimination reactions also take place by isolating macrocyclic degradation products. Megna and Koroscil(166) also isolated rings of similar size from aliphatic polyesters.

The work on poly(ethylene terephthalate) as reviewed by Buxbaum(163) was found to be particularly valuable in that kinetic results obtained by different workers using a variety of techniques based on several different reaction parameters provided complementary information relating to the various contributory degradation mechanisms. This highlighted the importance of carrying out degradation studies over as wide a range of conditions as possible, particularly in terms of temperature and environment in order to gain a detailed, complete, and accurate picture of degradation processes for a given polymer. The work described in this survey also provided valuable information as to the essential techniques required to carry out valid degradation studies.

The kinetic methods chosen for studies of poly-α-ester degradation described here, include both thermogravimetry and evolved gas analysis the latter being more sensitive to small gaseous fragments such as carbon monoxide and dioxide. This technique carried out as it is using enclosed probes, is particularly valuable in providing evidence as to the fate of and possible catalysis by primary degradation products when kinetic results are compared with those obtained by thermogravimetry where primary degradation products are continuously swept away. Golomb and Ritchie(167) have shown for example that substituted glycollides, whose formation must be expected in poly-α-ester degradation, undergo ring scission reactions leading to ketone and carbon monoxide. Should glycollides be formed as primary degradation products in the thermal decomposition of poly-α-esters the latter reactions would be classed as secondary degradation processes and would be detected as such by evolved gas analysis. Thermogravimetric analytical techniques, where degradation products are continuously swept away, would however only be sensitive to the formation of primary degradation products.

Since the measurement of rheological properties during degradation processes had been shown by Marshall and Todd(162), to be of value, this technique was also incorporated in equipment used in these studies whereby chain-scission reactions or the occurrence of cross linking during degradation could be diagnosed.

Finally, degradation studies carried out by previous workers have emphasised the importance of being able to separate and identify products of degradation. Since both volatile (e.g. carbon monoxide and dioxide) and relatively involatile (e.g. cyclic products) are likely to be formed a dual-column gas liquid chromatography (G.L.C.) technique was chosen which incorporated facilities for the isolation and collection of degradation products to enable less readily identifiable species to be separately analysed using appropriate techniques e.g. infra red analysis and mass spectrometry). The G.L.C. technique chosen also incorporated precolumn pyrolysis facilities to enable preliminary studies of the effect of degradation temperature on degradation products to be carried out.

CHAPTER 2

The Design and Calibration of the Degradation Apparatus

Introduction

The work presented in this chapter describes the design and calibration of equipment(168) combining thermogravimetric and evolved gas analyses together with gas liquid chromatography (G.L.C.) for use in poly α ester degradation studies. In line filament and curie point pyrolysis techniques coupled to the G.L.C. equipment are also described. In addition a rheogoniometer was also incorporated utilising temperature control facilities used in conjunction with the apparatus outlined above.

The factors taken into consideration when choosing the type of general equipment most applicable to these studies outlined above have been presented in the previous chapter, p. 213.

2.1 Description of the Apparatus

A schematic representation of the apparatus is shown in Figure 34, p. 218. The apparatus consists essentially of two furnace cavities the first of which, shown in detail in Figure 35, p. 219, carries the thermogravimetric and gas evolution analyses probes within a glass reaction vessel. A photograph of this vessel with the furnace and evolved gas analysis probes in position is shown in Plate XI, p.218a. This vessel also carries a facility whereby volatile degradation products can be continuously monitored as they are evolved from the thermogravimetric analysis sample via a sampling valve coupled to the G.L.C. unit. A sample collection device is also incorporated in the latter enabling analysis of degradation products to be carried out using infra red and mass spectrometric analyses particularly when filament or Curie point pyrolysis units are in use.

The second furnace cavity (Figure 34) houses the rheogoniometer probe which enables the melt viscosity of polymer at various temperatures to be monitored with time.

The G.L.C. unit (Figure 34) consists of twin columns linked by a variable stream splitter. Column 1 (Figure 34) is typically a 3 ft. x 1/8 in O.D. packed column maintained at some temperature between 150 and 250°C coupled to a flame ionisation detector. To avoid problems associated with condensation of the degradation products on the 'cold spots' in the system, the latter column, sampling valve and as much effluent pipework as possible

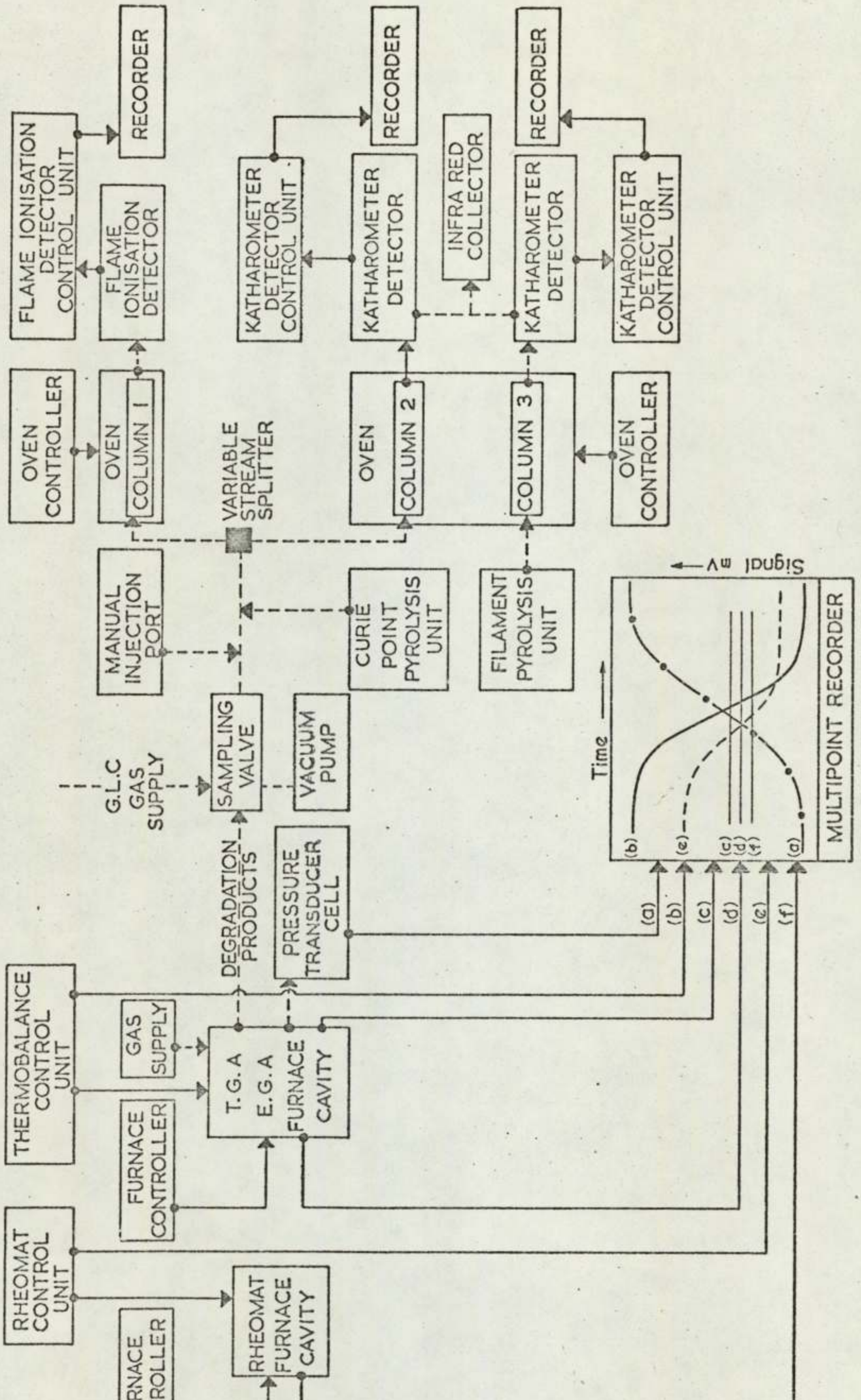


FIGURE 34

Schematic representation of degradation apparatus

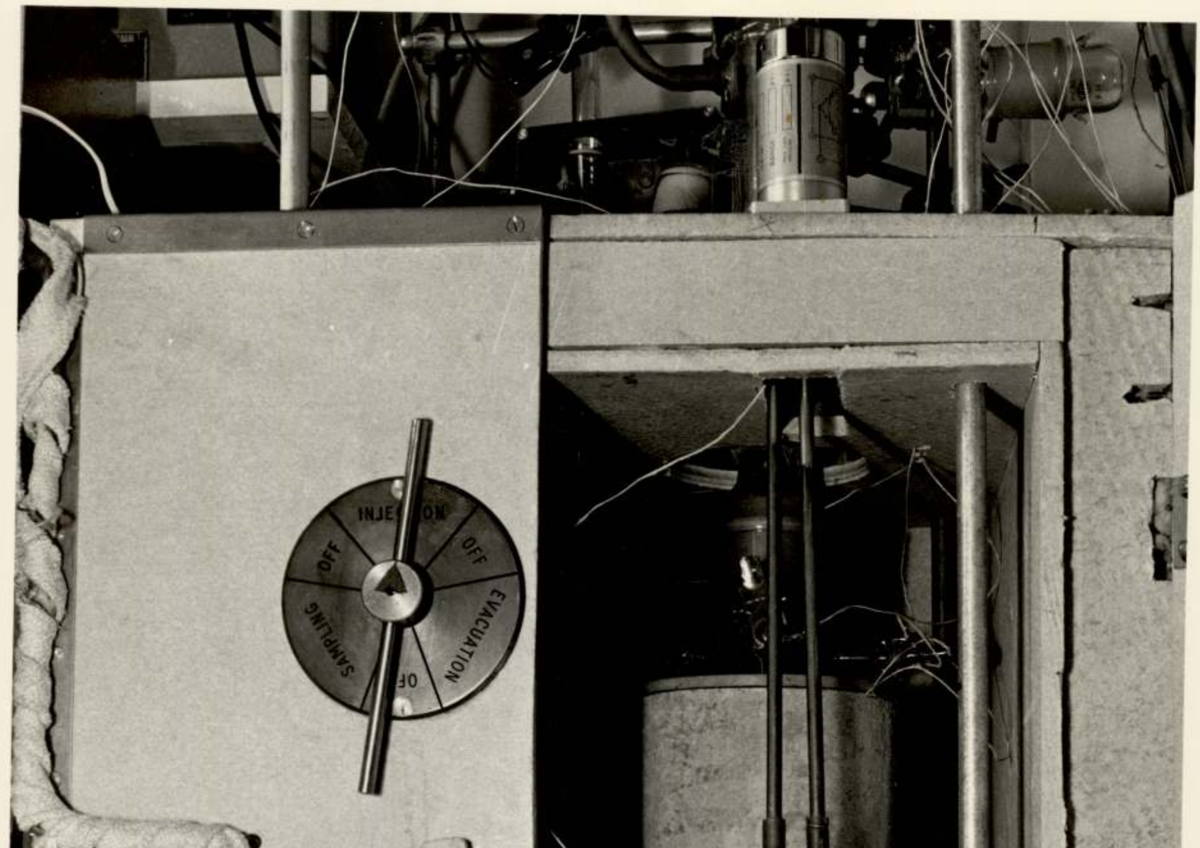


PLATE XI

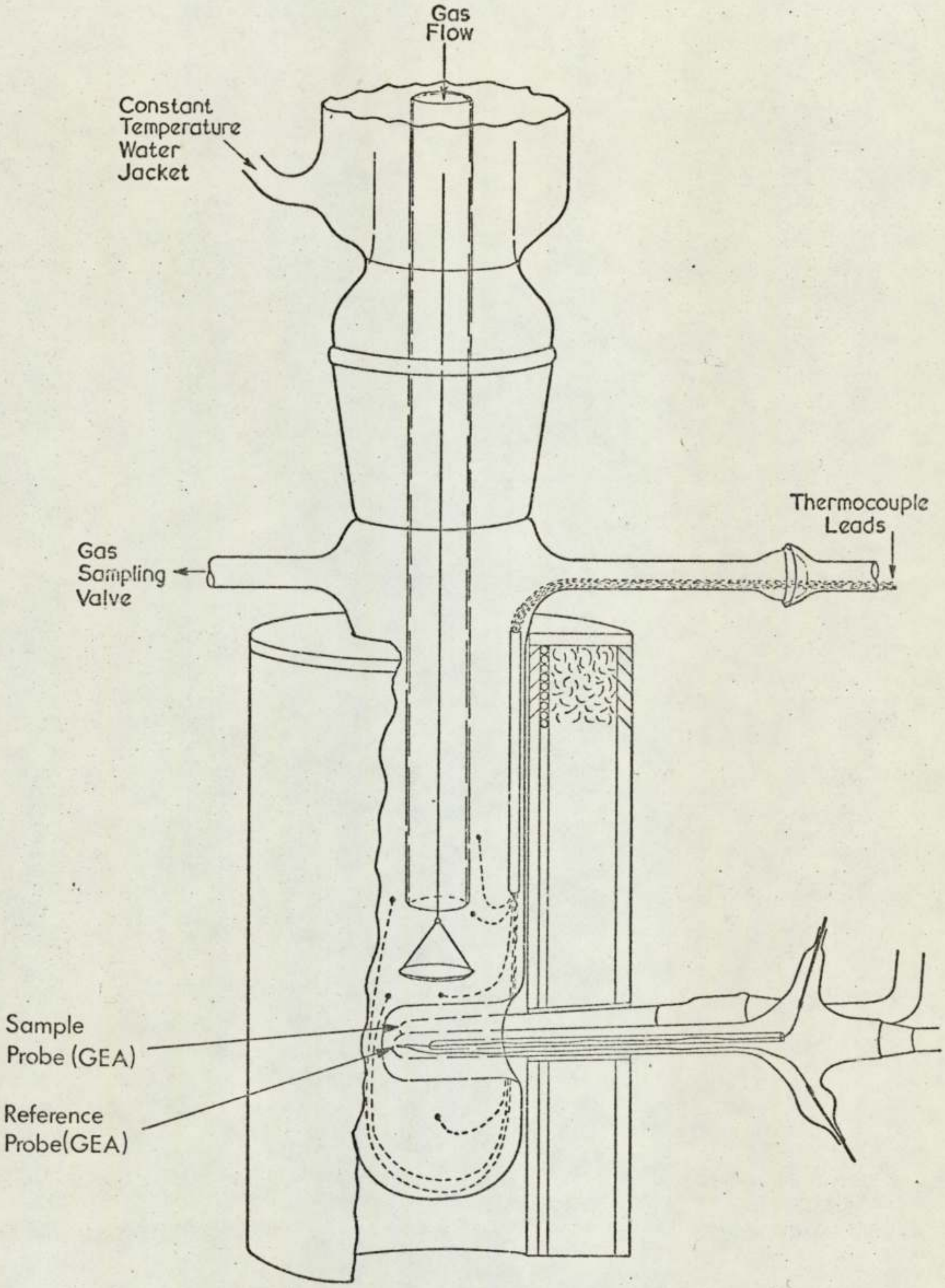


FIGURE 35

Detailed diagram of the main reaction vessel is housed in an insulated thermostatically controlled oven which also contains the furnace cavity shown in Figure 35.

The second column (Column 2, Figure 34) a 10 ft × ¼ in O.D. packed column is contained in a separate oven operated between 25 and 200°C and linked to a thermistor katharometer detector. This column is linked to the sample collection device described above.

The third column (Column 3, Figure 34) of similar characteristics to Column 2 is coupled to a filament pyrolysis unit of the type described by Barlow et al(169). This enables appreciable quantities of minor degradation products to be collected and analysed using the collector technique from the pyrolysis of relatively large quantities ($>$ 10 mg) of polymer. A second pyrolysis unit of the Curie point type can also be included in the system before the stream splitter enabling the preliminary examination of degradation products over a wide temperature range to be carried out using columns 1 and 2.

Column 1 (flame ionisation) and Column 2 (katharometer) systems further enable the detection and separation of the less volatile and more volatile degradation products. Thus Column 1 being fairly short and maintained at high temperatures is most useful for less volatile products while Column 2 maintained at low temperatures is most appropriate for volatile degradation products, in particular those species carbon monoxide and carbon dioxide which are not detected using the flame ionisation technique.

The overall rate of formation of volatile degradation products was monitored using a gas evolution analysis technique. The sample probe of the latter is situated immediately below the thermogravimetric analysis sample pan (Figure 35, p. 219). The probe together with a blank of identical volume, is connected to either side of a differential pressure transducer (Ether Controls Ltd). The rate of increase in vapour pressure due to the formation of volatile degradation products is thus monitored, the blank essentially cancelling out effects due to purely thermal expansion in the sample probe. Problems associated with this technique were in the main traced to condensation of degradation products particularly the less volatile fragments. These were successfully eliminated by housing the pressure transducer lines in the thermostatically controlled oven which encloses the gas sampling valve, the reaction vessel itself and the first G.L.C. column.

The rheological properties of the polymer during the course of degradation were also monitored using the Rheomat (Contraves Industrial Products Ltd), described in Section I, p. 74 of this thesis. The probe of this instrument is situated in a second furnace cavity (Figure 34, p. 218) which is separately controlled but maintained at the same temperature as the cavity housing the thermogravimetric and evolved gas analysis probes. Because of the possible influence of shear rate on degradation and the importance of cone and plate geometry on sensitivity and reproducibility extensive work was carried out in parallel with the

Farol-Weissenberg rheogoniometer(170, 171).

A photograph of the complete assembly is shown in Plate XII, p. 222a.

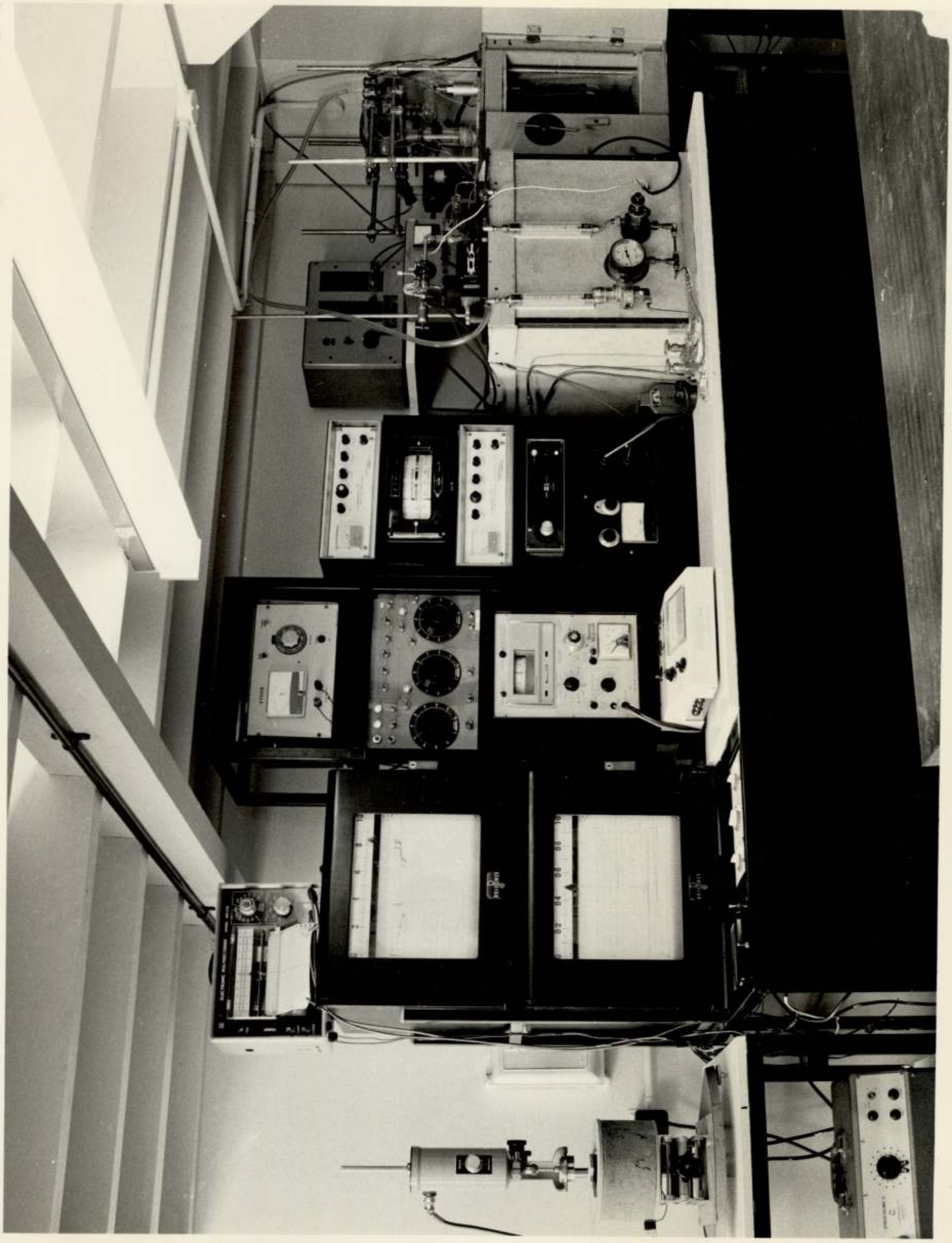


PLATE XII

2.2 Calibration of the Apparatus

The more general requirements borne in mind with respect to the design of the degradation apparatus described above (Chapter 2.1, p. 217) with particular reference to the acquirement of acceptably repeatable results can be summarised as follows:

i) Horizontal and vertical temperature gradients within reaction vessels and various ovens used must be minimal.

ii) Temperature levels within the reaction vessels and ovens must be stable.

iii) A polymer sample on test must reach the temperature of study in the shortest possible time and this period of time must be repeatable for a given set of conditions.

iv) As a consequence of iii) sample introduction must be rapid and easily carried out.

v) Turbulence in the region of the thermogravimetric analysis sample must be minimal.

vi) Spattering of thermogravimetric analysis samples must be eliminated.

viii) Condensation of degradation products must be avoided where gas liquid chromatography and gas evolution analysis are carried out.

Calibration carried out for the equipment as a whole bearing the above requirements in mind will be described for each component part of the apparatus in turn.

2.2.1 Calibration relating to the Thermogravimetric Analysis Technique

The instrument used for thermogravimetric work was a Mark 2, Model B Microforce Balance (C.I. Electronics, Andover, England). The weighing head of the instrument is mounted remotely in a pyrex glass vacuum bottle allowing the change in sample weight to be monitored in atmospheres of nitrogen, oxygen or other gas as appropriate. The weighing head produces an electrical output (proportional to the applied weight) which is fed via a control unit to one channel of a multi-channel recorder. The instrument possesses working ranges of 0-25μg to 0-100 mg with a sensitivity of 0.5% (full scale) and a reproducibility of ± 0.5μg. To prevent condensation of volatile materials on the weighing head thus giving rise to possible weighing inaccuracies, the gas, in which a particular run is carried out, is passed over the weighing head prior to its passage through the reaction vessel so that any volatile material produced is swept out of the apparatus as it is formed.

Runs carried out at 350°C showed that turbulence only affected thermograms to any extent on very sensitive ranges of the microbalance (0-10 mg) and even these results obtained could be interpreted giving rate constants comparable to values obtained using less sensitive ranges of the instrument as shown in Figure 36, p. 225. Turbulence effects were reduced to a minimum by supporting the balance pan by a multilinkage arm which reduced

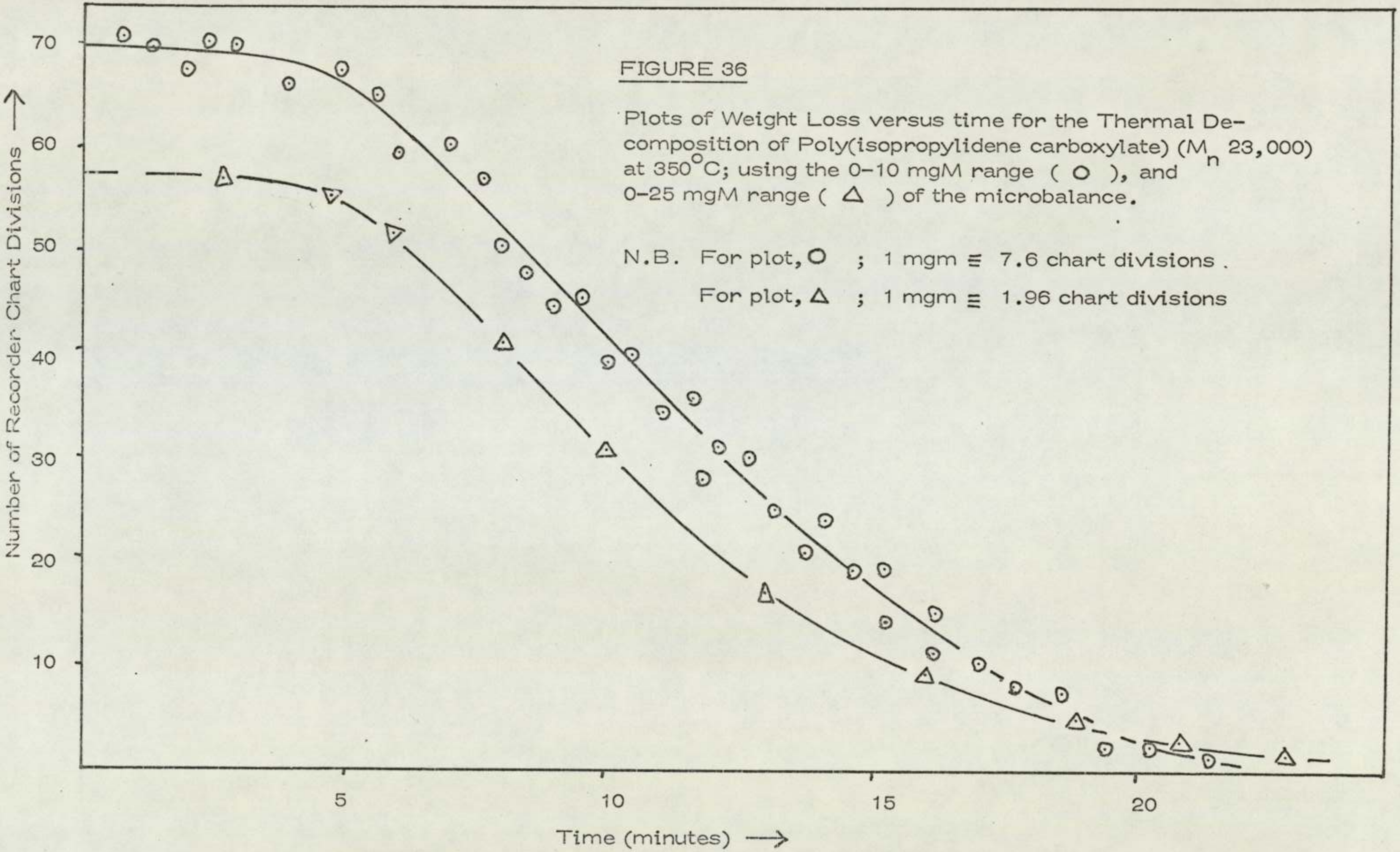


FIGURE 36

Plots of Weight Loss versus time for the Thermal Decomposition of Poly(isopropylidene carboxylate) (M_n 23,000) at 350°C; using the 0–10 mgM range (O), and 0–25 mgM range (△) of the microbalance.

N.B. For plot, O ; 1 mgm ≡ 7.6 chart divisions .
For plot, △ ; 1 mgm ≡ 1.96 chart divisions

oscillatory motion of the latter caused by turbulence effects.

The microbalance was calibrated under operating conditions using standard weights over the weight ranges used as shown in Figure 37, p. 227. This calibration was checked weekly.

A common source of weighing error, that caused by decrepitation and spattering of sample(172) was minimised by weighing the sample into an aluminium foil bucket which was subsequently 'folded in' leaving a small but adequate vents to allow the escape of volatile material.

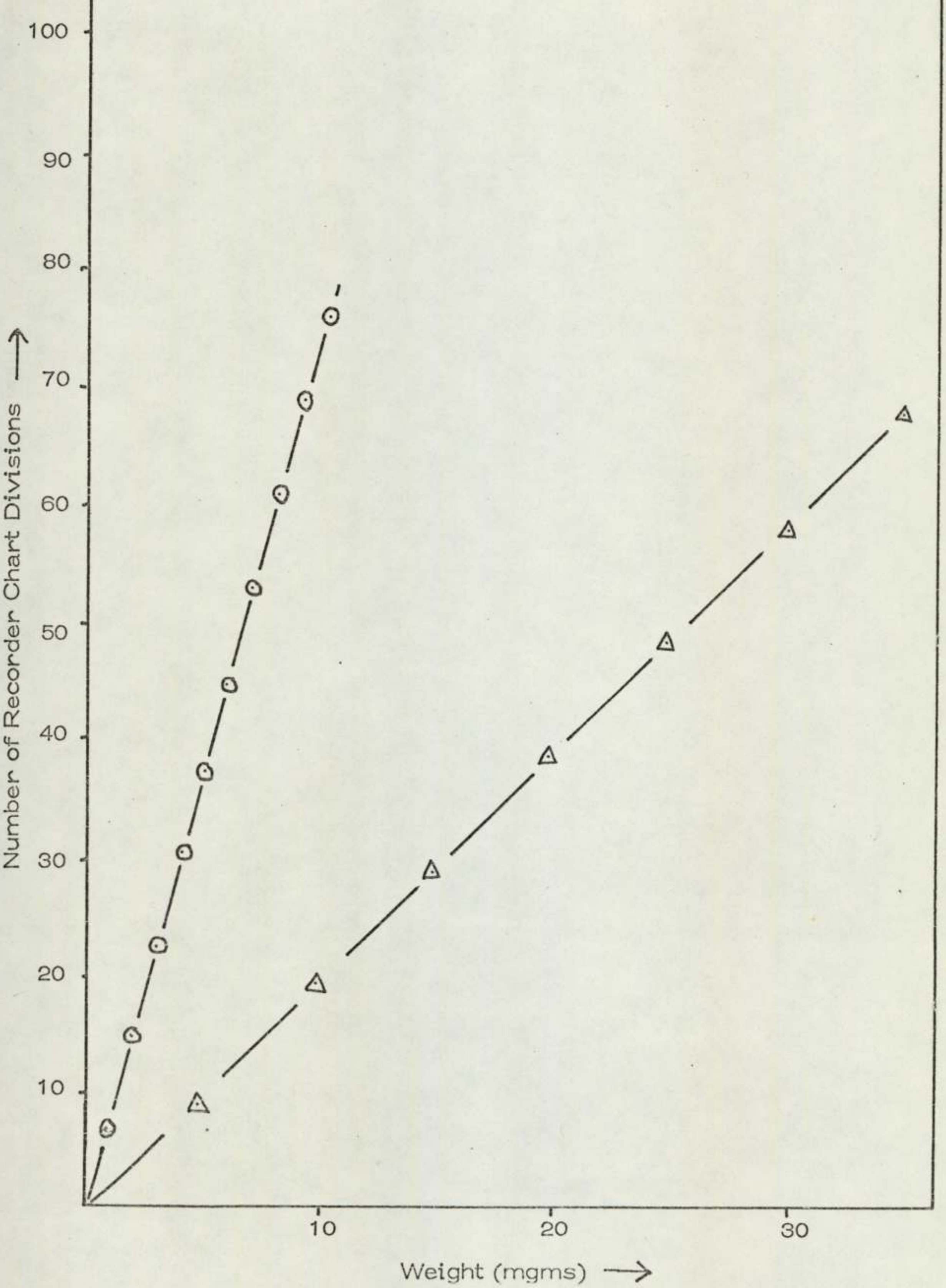
The framework carrying the microbalance was set up on an antivibration rubber pad to protect the instrument from mechanical shock.

2.2.2 Calibration Relating to the Gas Evolution Analysis Technique

The instrument used for this analysis was a differential pressure transducer (Type UP4, Ether Ltd., Stevenage). As indicated in Figure 35, p. 219, the transducer is connected to sample and reference (or blank) arms, the former of which is easily detachable for ease of sample introduction. The arms are connected to either side of a pressure sensitive diaphragm, within the transducer, which is displaced as pressure is developed within the sample arm. For convenience the thermocouple used for measuring sample temperature is situated in the reference arm as indicated in Figure 35, p. 219. Blank runs at 250 and 400°C showed that the temperature within each arm was identical to within ± 3°C. The displacement of the diaphragm (proportional

FIGURE 37

The Calibration Curve for the Microbalance used in Thermogravimetric Runs Showing the Number of Recorder Chart Divisions plotted against Actual Weight;
○ , 0–10 mgm range, △ , 0–25 mgm range.



to applied pressure) is transformed into an electrical signal, proportional to the latter which can then be fed into a suitable recorder. The transducer produces 3.877 mV output/volt input via a Wheatstone bridge arrangement and is capable of measuring ± 50 cms of mercury pressure. Since a 12 volt input was used 46.52 mV output from the transducer represents a pressure of 50 cms of mercury.

The volumes of the sample and reference arms was adjusted so that no output was obtained when these were placed without sample at various temperatures. This enabled subsequent pressure/time plots for sample runs to be drawn directly in which pressure increase observed was due solely to the vapour pressure of degradation products obtained.

As indicated previously condensation of degradation products was minimised by locating the pipework relating to the transducer in a thermostatically controlled oven shown in Plate XI, p.218a. A typical gas evolution curve (compared with a corresponding thermogravimetric curve) showing condensation of degradation products is shown in Figure 38, p. 229. Also shown is the form of the curve when secondary degradation of primary degradation products occurs.

2.2.3. Calibration Relating to Gas Liquid Chromatographic Analysis

The equipment used for gas liquid chromatographic analysis has been summarised above and is shown schematically as part

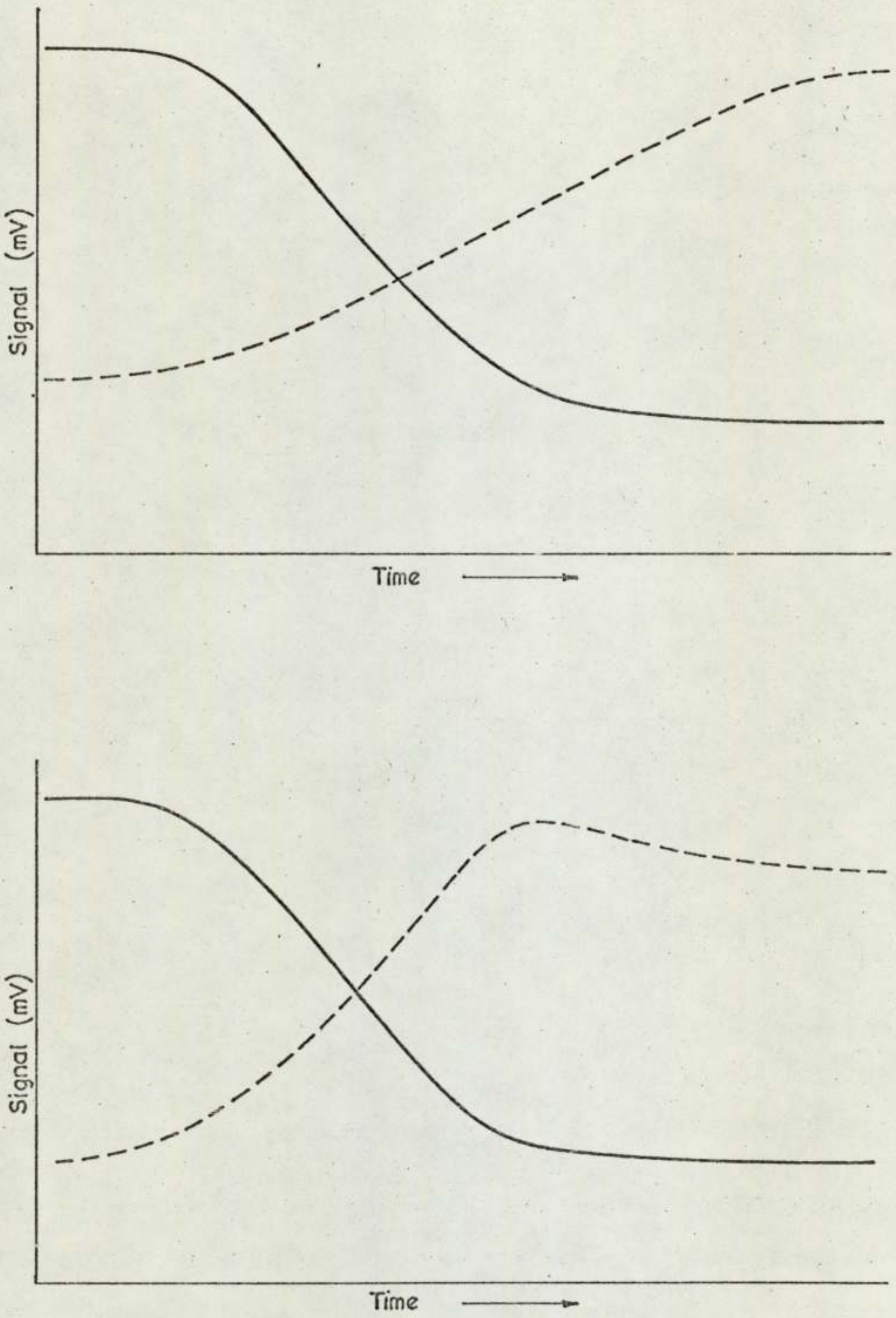


FIGURE 38

Typical (———) thermogravimetric and (- - - - - -) gas evolution Curves: (upper) secondary degradation of primary degradation products; (lower) condensation of degradation products within the gas evolution system.

of Figure 34, p. 218. The temperatures within ovens used was controlled by means of platinum resistance thermometers coupled to a temperature control unit. Temperature fluctuations at any one point of ± $2^{\circ}C$ were obtained for the temperature range 25°-$200^{\circ}C$, temperature variations within the ovens being less than ± $1^{\circ}C$ (measured at any point).

The identification of unknown degradation products formed during a particular run, was best carried out as required by comparison of retention times of the latter with corresponding times exhibited by known materials in calibration runs carried out under identical conditions.

2.2.4 Calibration Relating to the Rheomat

The instrument used is described in detail elsewhere (Section I, p. 74). The rheomat was used in its unmodified form using measuring systems of the cone and plate type.

The instrument produced absolute values of viscosity (for Newtonian fluids) via the use of calibration tables supplied by the manufacturer.

To ensure accurate alignment of the measuring gap or sample cavity which can be of a particularly thin section depending on the measuring system used, a special high precision support was employed. To ensure accurate measurement the assembly needed to be levelled using the spirit level fitted to the support bracket.

2.2.5 Calibration Relating to Temperature Measurement

Chromel/Alumel thermocouples (Saxonia Products Ltd) were used for temperature measurement throughout this work. In order that standard conversion tables (e.m.f. versus temperature) could be used cold junctions (at 0°C) were incorporated in each thermocouple circuit. Thermocouples used were each checked against two standard chromel/alumel thermocouples (E.I. DuPont Nemours, Wilmington) which were guaranteed to read within ± 1°C up to 400°C.

i) Measurement of Sample Temperature

Errors will inevitably occur in the temperature measurement of a sample unless the thermocouple is inserted into the sample itself. Such a measure was found to be impracticable, however, and an accurate assessment of temperature levels in the region of the thermogravimetric analysis sample for example was carried out by determining temperature gradients one centimetre above and one centimetre below the balance pan of the microbalance. The temperature gradient observed over this region using the array of thermocouples shown in Figure 35, p. 219 was found to be linear and values obtained were as follows: 3°C/cm at 200°C and 5°C/cm at 400°C using a nitrogen carrier gas flow rate of 50 ccs/minute. The horizontal temperature gradient was also found to be linear and of the order of 2°C/cm at 200°C and 3°C/cm at 400°C using a similar carrier gas flow rate. Thus the temperature of the thermogravimetric analysis sample could be accurately assessed particularly since samples of small cross section were employed thus minimising temperature gradients within the sample itself.

Temperature measurement relating to the evolved gas analysis sample has been referred to previously, p. 226 .

The measurement of the temperature of the sample during rheological studies was identical to that carried out for samples used for homopolymerisation systems, i.e. via thermocouples housed in the base plate of the measuring system. Since samples used were of small cross section (around 0.009") temperature equilibration would be expected to take place very quickly when the measuring system (of high thermal capacity) is preheated to the required level prior to the introduction of the sample. The equilibration temperature of the sample would be expected to be very close to that of the base plate of the system.

Temperature control for the furnaces was effected using an Ether Transitrol Temperature Controller. The instrument produced temperature fluctuations of $\pm$ 3°C at 400°C in the furnace cavity which were reflected as fluctuations of $\pm$ 2°C in the reaction vessel (thermogravimetric and evolved gas analysis samples) and $< \pm$ 1°C for the base plate of the rheomat.

The temperature control of various G.L.C. ovens has been described elsewhere.

CHAPTER 3

The Study of Poly-α-ester Degradation

Introduction

The work presented in this chapter described results obtained for the degradation of poly(α esters) of the form [(XXXIV) p. 208] summarised in Table 28 over the temperature range 200–800°C in nitrogen using the kinetic and analytical techniques described in the previous chapter(173–176). The thermal degradation of poly(isopropylidene carboxylate) will be discussed in most detail followed by a less detailed summary and discussion of the thermal degradation of the remaining polymers presented in Table 28 below, with particular reference to the effect of main chain substituents on the thermal stability of the polymers.

Table 28

A Summary of Poly-α-esters used for the Thermal Degradation Studies described in the present chapter.

		R_1*	R_2*
1	Polyglycollide	H	H
2	Polyisopropylidene Carboxylate	CH_3	CH_3
3	Poly (2-ethyl-2-hydroxy Butyric Acid)	C_2H_5	C_2H_5
4	Poly (3 chloro-2-hydroxy 2 methyl propionic acid)	CH_2Cl	CH_3
5	Randomly Chlorinated Polymer	CH_2Cl , $CHCl_2$, plus residual CH_3 groups	

* Structure XXXIV, p. 208.

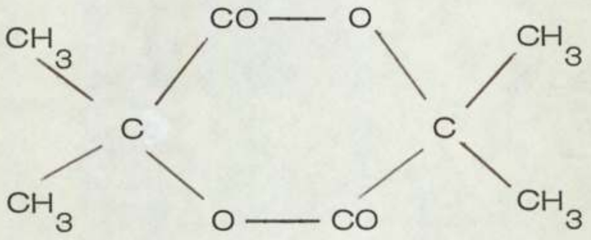
3.1 The Thermal Degradation of Poly(Isopropylidene Carboxylate)

Results obtained are summarised in two parts, product analysis and kinetic analysis results.

3.1.1 Product Analysis Results

The products of degradation were identified using the filament pyrolysis(177) and G.L.C. facilities of the equipment described in the previous chapter coupled with conventional gas liquid chromatography, infra red and mass spectrometry.

Three major products of degradation were identified namely carbon monoxide, acetone and tetramethylglycollide (XXXVIII),



(XXXVIII)

In some circumstances, bulk degradation was carried out in Caris tubes, when methacrylic acid was also detected as a product of degradation.

Carbon monoxide and acetone predominated at higher temperatures as tetramethylglycollide gradually disappeared. Figure 39, p. 235 shows the plot of [carbon monoxide + acetone]/ [Tetramethylglycollide] versus temperature. The ratio [Carbon Monoxide]/[Acetone] was also plotted versus temperature (Figure 40, p. 236).

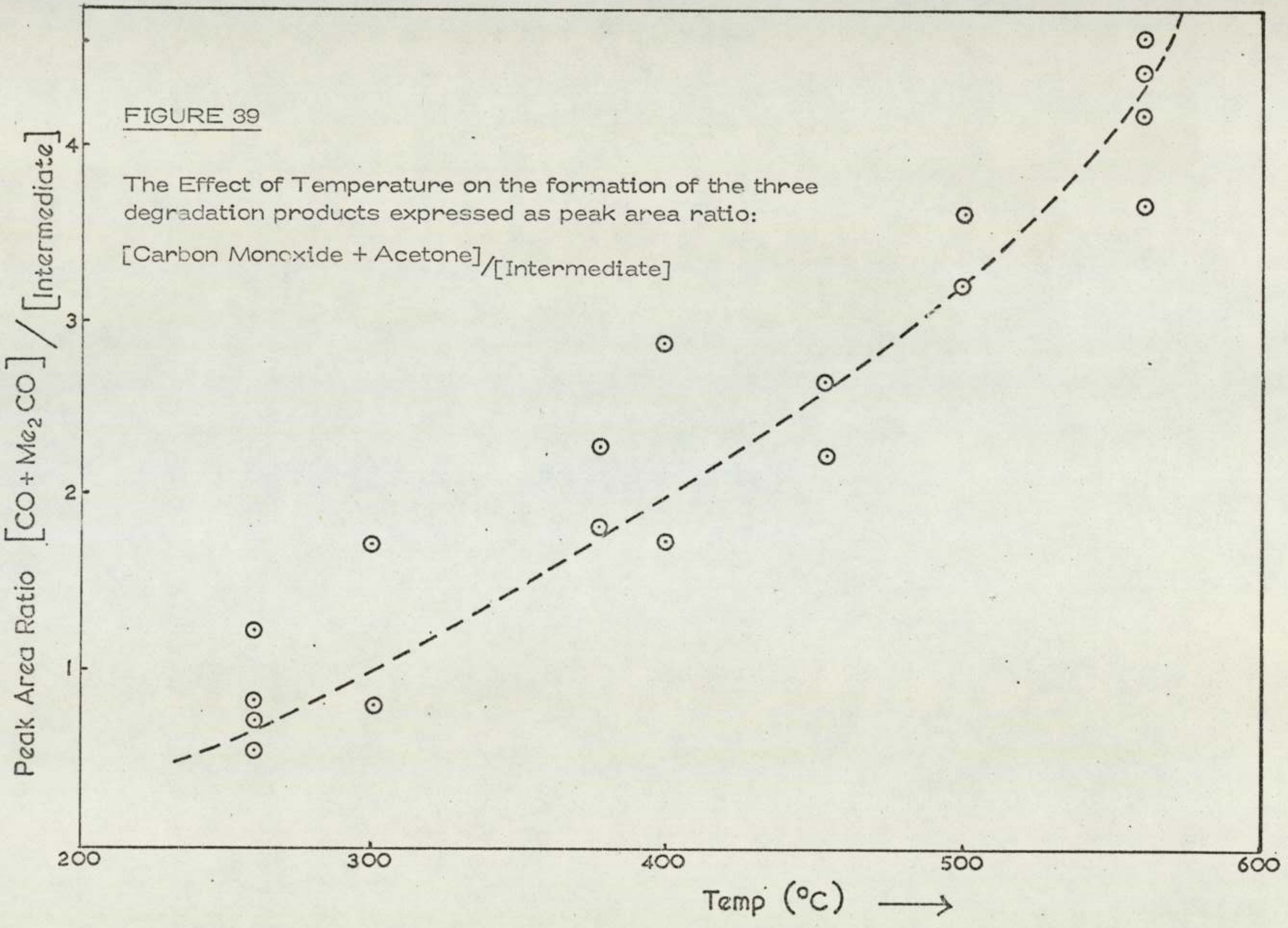


FIGURE 39

The Effect of Temperature on the formation of the three degradation products expressed as peak area ratio:

[Carbon Monoxide + Acetone]/[Intermediate]

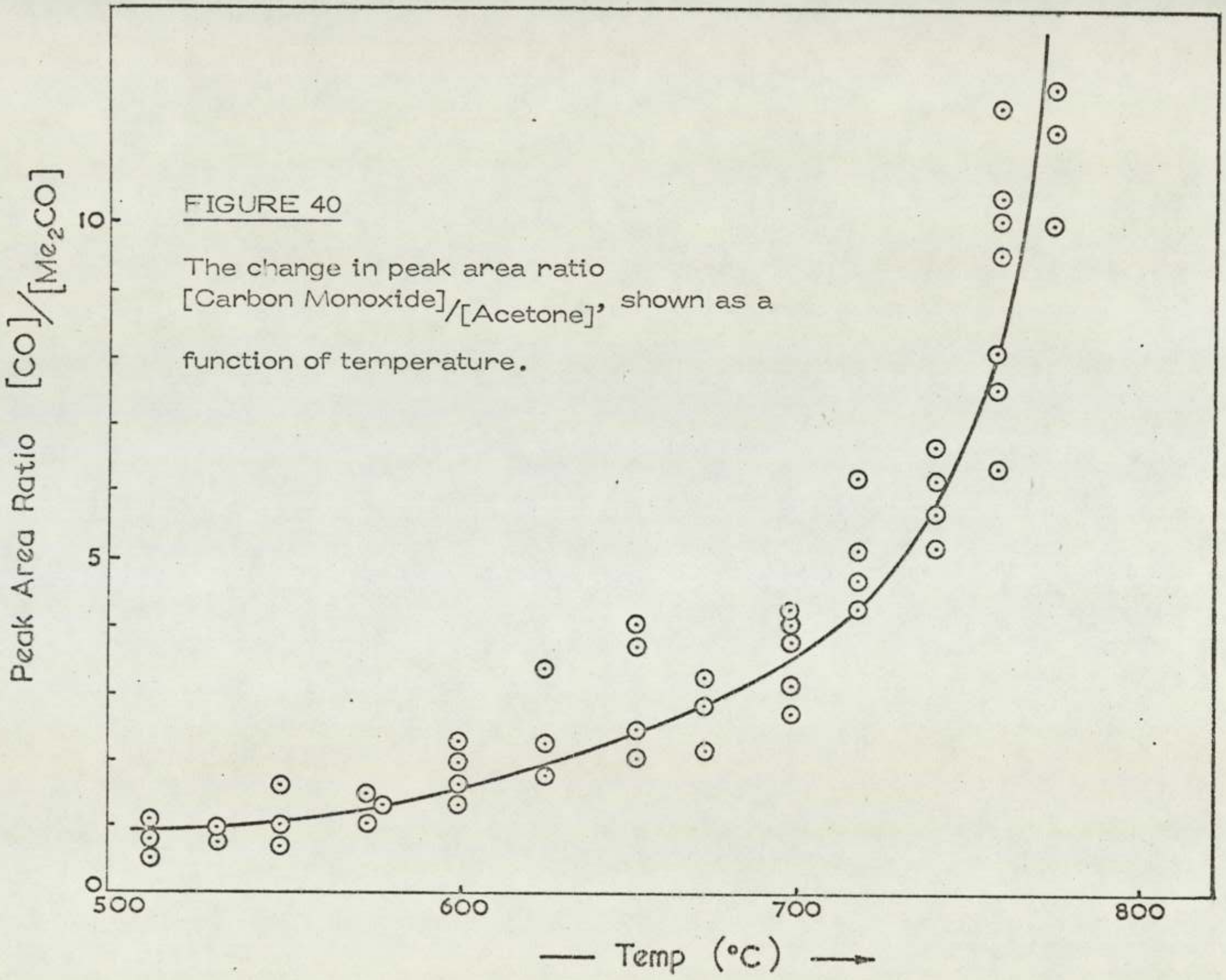


FIGURE 40

The change in peak area ratio $[\text{Carbon Monoxide}]/[\text{Acetone}]$, shown as a function of temperature.

The former of these plots (Figure 39) indicates that pyrolysis of tetramethylglycollide was occurring producing carbon monoxide and acetone; while the latter plot (Figure 40) indicates the increased tendency towards carbon monoxide formation at higher temperatures. Increased residues of carbonaceous char was also noted as temperature increased.

3.1.2 Kinetic Analysis Results

Kinetic analysis of the degradation process was carried out using thermogravimetric and evolved gas analysis(173). Typical first order plots using these techniques are shown in Figure 41 and 42, p.238 and 239 respectively. Since plots obtained were without exception linear into the second decade it can be deduced that the predominant rate determining reaction corresponding to the degradation process carried out under these conditions, is first order with respect to residual polymer.

Kinetic parameters derived from first order rate constants calculated using both thermogravimetric and evolved gas analysis techniques are summarised in Table 29, p. 240.

The rates of degradation of a series of polymers of different number average molecular weights were also determined using isothermal thermogravimetry. Although progressive deviation from first order behaviour was observed for samples having an $M_n < 10{,}000$, it was possible to obtain first order rate constants for around 60% of the reaction for comparative purposes. The results obtained are summarised in Table 30, p. 241.

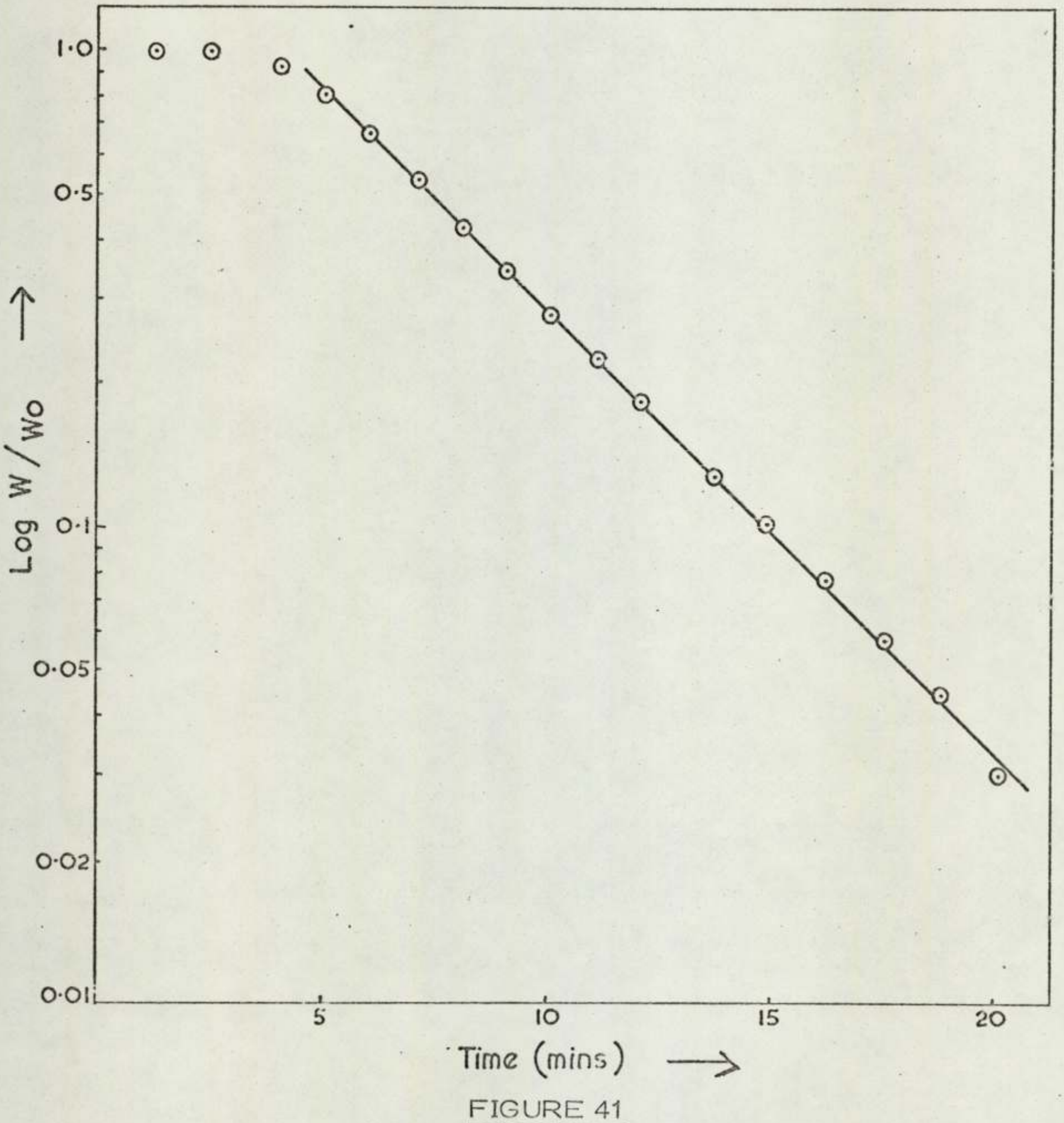


FIGURE 41

First order representation (log W/W_o vs. time) of a typical isothermal thermogram for the degradation of poly(isopropylidene carboxylate)

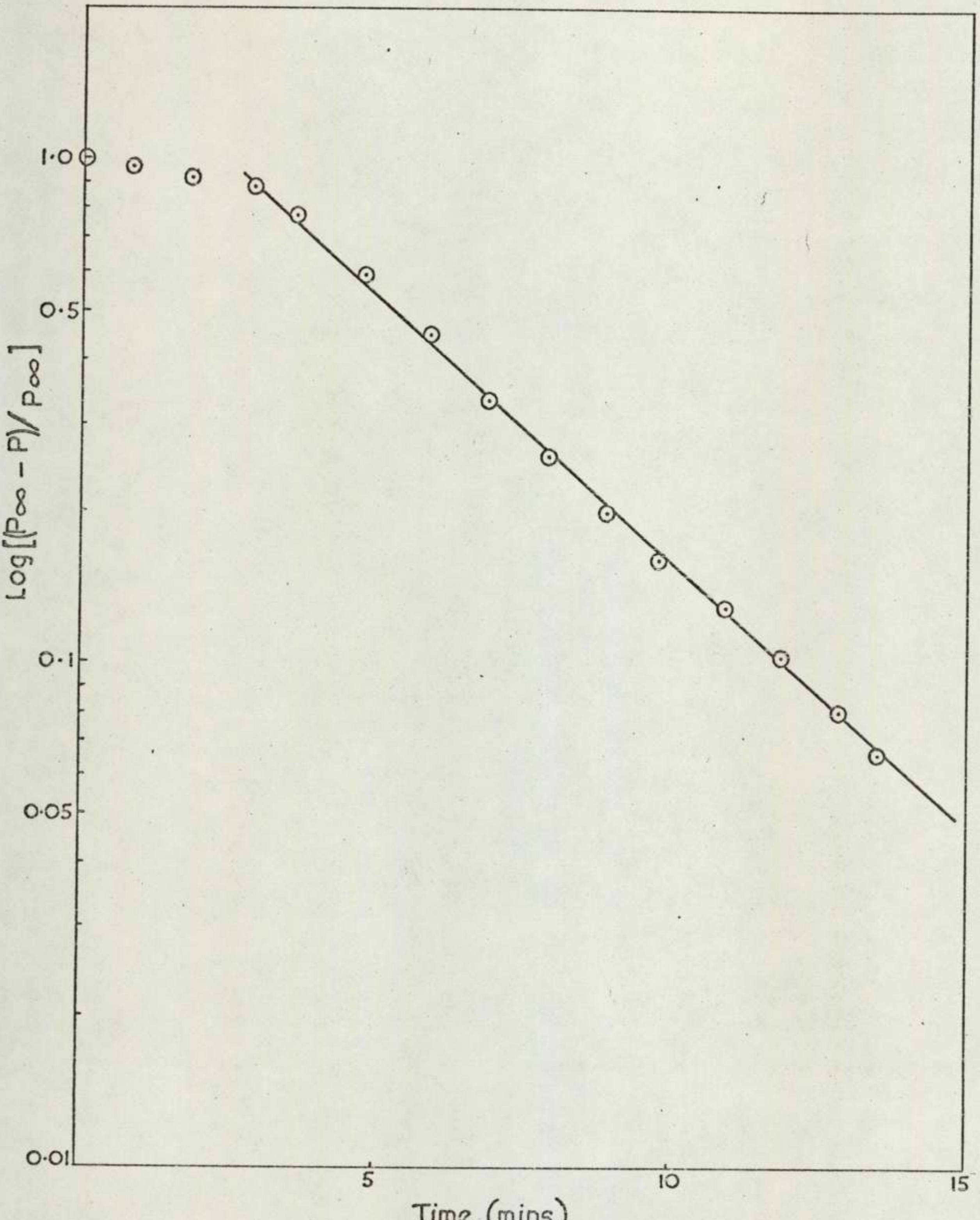


FIGURE 42

Typical first-order representation ($\log[(p_{\infty} - p)/p_{\infty}]$ v.s. time) of gas evolution data for the degradation of poly(isopropylidene carboxylate)

Table 29

A Summary of Kinetic Parameters Calculated using Thermogravimetric and Evolved Gas Analysis Techniques for the Degradation of Poly(isopropylidene Carboxylate) over the Temperature Range 250–400°C in Nitrogen.

Technique used	E (kcals/mole)	Δ H (kcals/mole)	A sec^{-1}	Δ S $\neq$ (cals/deg mole)
Thermogravimetric Analysis	27.2	28.4	4.1×10^7	-29
Evolved Gas Analysis	28.3	25.0	2.6×10^8	-24

Table 30

The Effect of M_n on First-Order Rate Constants k, for the Thermal Decomposition of Poly(isopropylidene carboxylate) in Nitrogen at $353^\circ C$

Temperature $^\circ C$	M_n	k, sec^{-1}
353	2,720	1.73×10^{-2}
353	5,000	5.74×10^{-3}
353	12,000	3.74×10^{-3}
353	19,000	3.10×10^{-3}
353	19,500	2.90×10^{-3}
353	23,000	2.72×10^{-3}
353	30,000	2.66×10^{-3}

All preceeding experiments were carried out in the complete absence of oxygen, and in order to assess the effect of the latter on the kinetics of the decomposition of poly(isopropylidene carboxylate), thermogravimetric analysis was carried out using oxygen. The results obtained are typified by those at $265^\circ C$ which were as follows:

$$k = 4.5 \pm 0.3 \times 10^{-4} \text{ sec}^{-1} \text{ (nitrogen)}$$

and $k = 12.5 \pm 0.3 \times 10^{-4} \text{ sec}^{-1}$ (oxygen).

3.1.3 Discussion of Results Relating to the Thermal Degradation of Poly(isopropylidene Carboxylate)

The possible modes of degradation of a polymer chain of the poly-α-ester type can be summarised as follows:-

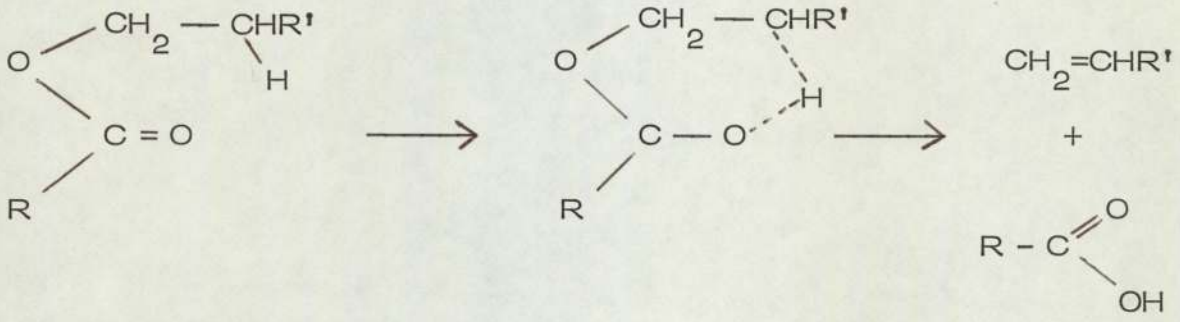
i) Random homolytic or heterolytic chain scission (possibly followed by chain depolymerisation from the scission site).

ii) Inter or intra molecular ester interchange.

iii) Chain depolymerisation or unzipping from chain ends.

iv) Molecular decarboxylation or decarbonylation possibly accompanied by chain recoupling.

The observed activation energies for simple ester pyrolysis are found to be around 40 kcals/mole as opposed to the theoretically calculated value of 60 kcals/mole for scission of the ester linking. The lower value obtained in practice is generally taken to indicate the existence of a cyclic transition state(178) (XXXIX):



(XXXIX)

Hine(178) puts forward evidence for the multicentre type of mechanism (via a transition state of the above type (XXXIX)) which includes first order kinetics and negative entropy of activation. These conditions are satisfied for the degradation of poly(isopropylidene carboxylate).

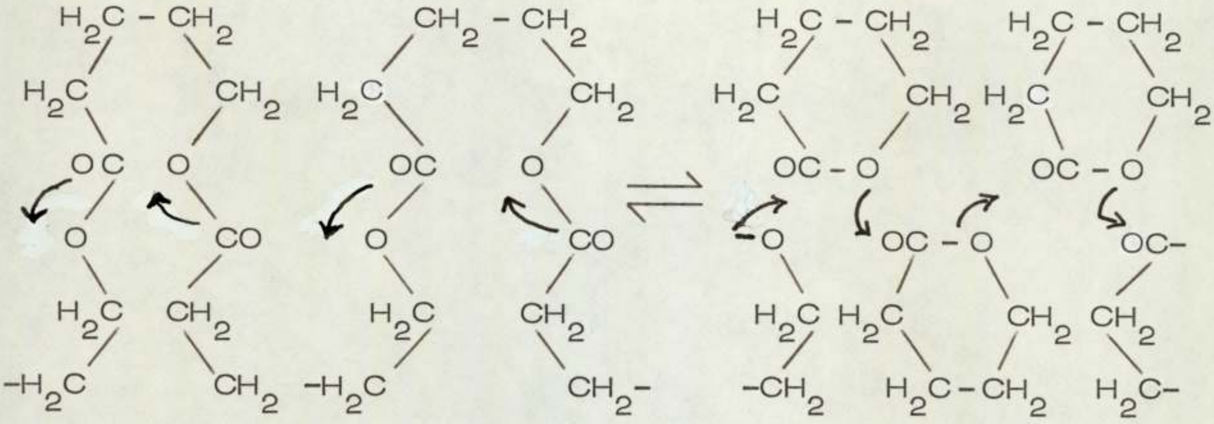
The fact that activation energies (Table 29, p. 240) even lower than those obtained for simple ester pyrolysis were found for the degradation of poly(isopropylidene carboxylate) could be taken as evidence that the poly-α-ester chain contains points of weakness which could have been introduced during synthesis. Alternatively the lower activation energy could indicate the existence of an energetically preferred degradation process which is structurally possible in poly(isopropylidene carboxylate) decomposition but not in simple ester pyrolysis.

Of the possible degradation routes summarised above, p. 242 decarboxylation or decarboxylation (at ~400°C) can be discounted since such a route does not account for the predominance of tetramethylglycollide. On the basis of results summarised in Table 30, p. 241 chain depolymerisation reactions must be discounted as a major route except where chain end concentration is high (as in the case of low molecular weight polymer).

Radical processes resulting from homolytic scission are of little importance below 400°C although at higher temperatures (~600°C) they become quite feasible. Ionic processes resulting from heterolytic scission are energetically improbable under the conditions used.

A specific process in which tetramethylglycollide is eliminated in the rate determining step is required to account for the degradation characteristics of high molecular weight polymer.

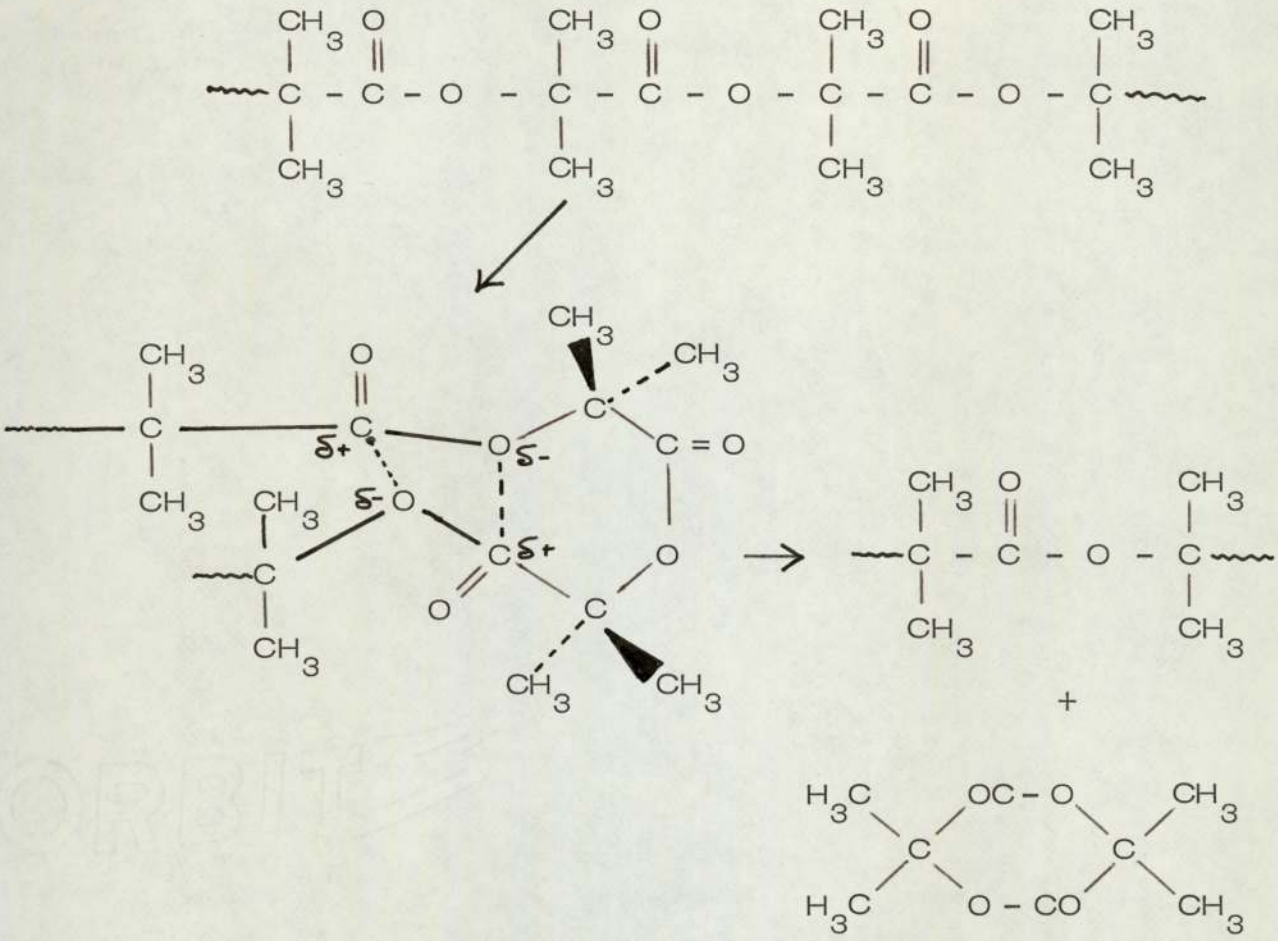
The intramolecular ester interchange reaction presented above as a possible degradation route appears to offer the most accurate description of the decomposition since this gives the required first order kinetic behaviour coupled with tetramethyl glycollide formation. A similar type of mechanism has been suggested by Stannett and Szwarc(179) (Scheme XL below).



Scheme XL

Extending these ideas to poly(isopropylidene carboxylate) the mechanism presented in Scheme XLI correlates well with observed kinetic behaviour and explains the formation of tetramethyl glycollide by the type of dipolar process likely to be favoured over the temperature range studied.

The frequency factor A is normally factorised into a collision number Z and steric factor p. The magnitude of Z in solution has been found to be around 10^{12}, substantially the same as the value calculated from the kinetic theory of gases. Changes in pZ over several powers of 10 are normally attributed to changes in p. The lower values of A obtained for the thermal decomposition of poly(isopropylidene carboxylate) [Table 29, p. 240], indicate therefore, a fairly high degree of steric order which supports the mechanism proposed. The substantially negative entropy of activation calculated for the decomposition adds further evidence in favour of this mechanism.



Scheme XLI

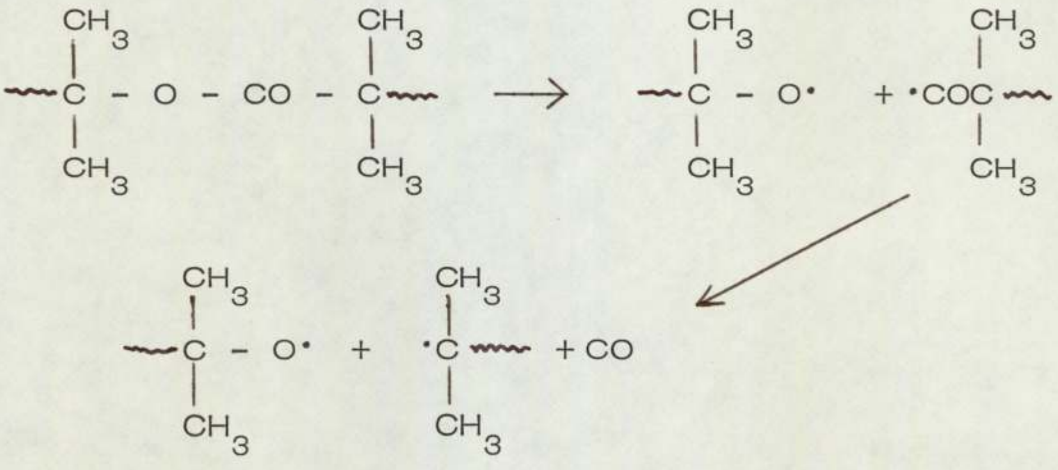
The above mechanism also implies a relatively slow lowering of molecular weight with time which accords well with the persistence of first order behaviour throughout much of the reaction (Figure 41 p. 238). Further confirmation is presented via results of rheological studies of the polymer melt during the course of thermal decomposition using the Farol-Weissenberg rheogoniometer(175). The decomposition was found to be first order with respect to the molecular weight of residual polymer and a relatively slow lowering of molecular weight with time was also observed. Derived kinetic parameters were found to be in good agreement with those previously obtained by other techniques.

Radical processes seem to play a more important part at higher temperatures as evidenced by Zhuravleva and Rode(180) for the decomposition of certain polyaryl esters (Scheme XLII) at temperatures above 400°C:

$$\mathrm{ROCOR'} \longrightarrow \mathrm{RO\cdot} + \mathrm{\cdot COR'} \longrightarrow \mathrm{RO\cdot} + \mathrm{R'} + \mathrm{CO}$$

Scheme XLII

It has been stated previously that above 400°C tetramethyl glycollide assumes the role of an unstable intermediate decomposing to form carbon monoxide and acetone. The increased tendency towards carbon monoxide formation (Figure 40, p. 236) at higher temperatures (ca 600°C) together with the appearance of carbonaceous char is probably, partially due to the fragmentation of acetone to carbon monoxide, but more extensively due to processes of the type shown below, (Scheme XLIII) identical to processes outlined by Zhuravleva and Rode(181)



Scheme XLIII

The experimental results obtained for the decomposition of poly (isopropylidene carboxylate) are summarised in Table 34, p. 265 .

3.2 The Thermal Degradation of β Chlorinated Poly-α-esters

Two versions of β chlorinated poly(isopropylidene carboxylate were studied(174): poly (3 chloro-2-methyl-2 hydroxy propionic acid) and the randomly β chlorinated analogue of poly(isopropylidene carboxylate) containing monochloromethyl and dichloromethyl substituents in addition to residual parent methyl substituents present in approximately equal abundance as shown by NMR analysis(181),

3.2.1 The Thermal Degradation of Poly (3 chloro-2-methyl-2 hydroxy Propionic acid)

Samples of polymer having number-average molecular weights of 20,000 were used and experiments were carried out isothermally in nitrogen unless otherwise stated using combined thermogravimetric and gas evolution techniques described previously.

Both techniques showed that the predominant rate determining degradation reaction was first order over the temperature range studied. Table 31, p.249 summarises the kinetic parameters calculated from first order rate constants obtained.

Experiments carried out in oxygen using the Farol-Weissenberg rheogoniometer(175) indicated substantial deviation from first order behaviour as the degradation progresses. Although the initial slope was indistinguishable from that obtained in nitrogen, as the reaction proceeded a progressive acceleration rather than a deceleration (as in nitrogen) was obtained.

Table 31

A Summary of Kinetic Parameters Calculated using Thermogravimetric and Evolved Gas Analysis Techniques for the Degradation of Poly (3 chloro-2-methyl-2-hydroxy Propionic Acid) over the Temperature Range 250-400°C in Nitrogen

Technique	E (kcals/mole)	ΔH (kcals/mole)	A sec^{-1}	$\Delta S^{\neq}$ (cals/deg mole)
Thermo-gravimetric Analysis	24.6	25.3	3.0×10^{6}	-34
Evolved Gas Analysis	24.3	22.0	3.1×10^{6}	-36

Product analysis over the temperature range studied showed that hydrogen chloride, a carbonaceous residue and a compound having a glycollidic structure were the primary products of degradation. The carbonaceous residue which formed 20-25% by weight of the total products was shown to consist in the main of carbon, oxygen and hydrogen.

3.2.2 The Thermal Degradation of Randomly Chlorinated Poly (isopropylidene carboxylate)

The thermal degradation of this polymer was studied by using techniques and conditions similar to those employed for the study of poly (3 chloro-2-methyl-2-hydroxypropionic acid) decomposition. Samples of the polymer having number-average molecular weights of 12,000 were used, experiments being carried out isothermally in nitrogen unless otherwise stated.

Thermogravimetric results indicated that the decomposition was no longer first order although gas evolution analysis showed fairly good first order dependence. Kinetic parameters calculated using first order rate constants obtained from gas evolution analysis were as follows: E, 21.5: kcal/mole, A:1.3×10^{6} sec^{-1}, $\Delta S^{\neq}$: -30 cal/deg mole.

Product analysis results were qualitatively similar to those obtained for poly(3-chloro-2-methyl-2 hydroxypropionic acid) but much more complex.

3.2.3 Discussion of Results Relating to the Thermal Degradation of Poly(3-chloro-2-methyl-2-hydroxy propionic acid) and Randomly Chlorinated Poly(isopropylidene Carboxylate)

Comparison of the various kinetic parameters and product analysis results obtained for poly (3 chloro-2-methyl-2-hydroxy propionic acid) with those obtained for poly(isopropylidene carboxylate) indicated that the two polymers degrade via processes involving similar mechanisms namely intramolecular ester interchange. Additional complications are evident with respect to the chlorine containing polymer however. This is evidenced by the greater stability of the polymer, its tendency to form hydrogen chloride yielding an involatile residue and greater disparity between thermogravimetric and gas evolution results.

Analysis of the carbonaceous char indicated the presence of cross linked material of considerable stability containing ester linkages. The elimination of hydrogen chloride leading to such residues undoubtedly involves free radical processes superimposed upon the predominant first order elimination process leading to glycollide fragments. Kinetic techniques used here are more sensitive to the latter process, however although the hydrogen chloride trapped as it is in a sealed system might produce some acid catalysed degradation which would explain the higher rate constant observed with gas evolution analysis.

The increased stability however is thought to be due to the inhibition of the intramolecular ester interchange reaction by mutual repulsion of chloromethyl groups. This effect is thought to swamp the opposing effect whereby the carbonyl group of the polyester is rendered more susceptible to nucleophilic attack by the chloromethyl substituent.

The overall effect is not a large one however as indicated by the temperature based thermogram shown in Figure 43, p. 252.

The deviation from first order behaviour exhibited by the randomly chlorinated polymer for isothermal thermogravimetric analysis is thought to be due to the irregularity of the polymer backbone which is not conducive to the intramolecular ester interchange reaction described for the decomposition of the other polymers in the series described to-date. In addition the polymer samples used possessed a broad molecular weight distribution showing a long low molecular weight tail which leads to a more

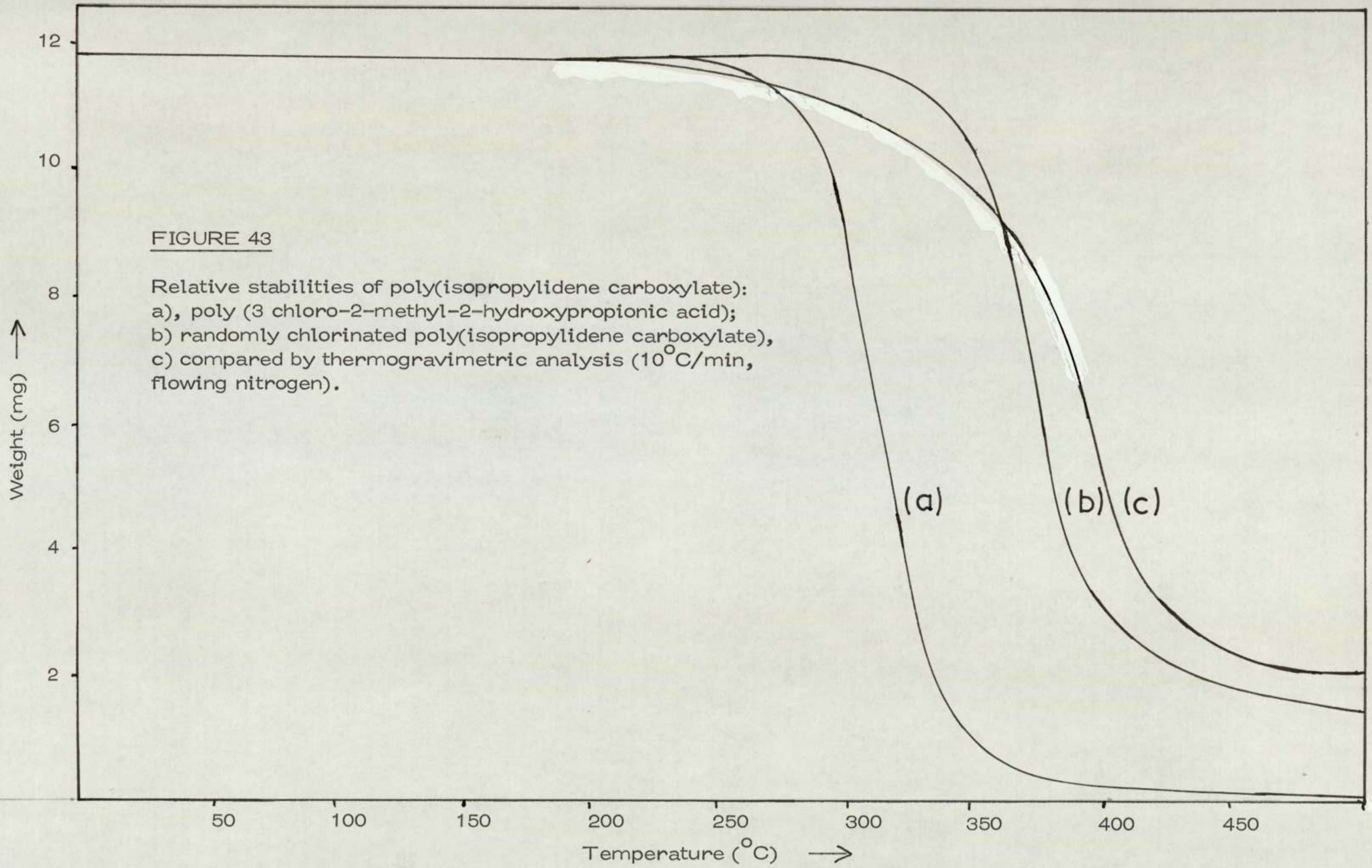


FIGURE 43

Relative stabilities of poly(isopropylidene carboxylate):
a), poly (3 chloro-2-methyl-2-hydroxypropionic acid);
b) randomly chlorinated poly(isopropylidene carboxylate),
c) compared by thermogravimetric analysis (10°C/min, flowing nitrogen).

marked tendency to decomposition at low temperatures ($\sim 300^{o}C$)[175].

The gas evolution results are thought by the author to be valid reflecting genuine first order behaviour. This reasoning stems from the fact that this technique is specific to processes producing more highly volatile fragments - i.e. those derived from the unchlorinated and monochlorinated segments as opposed to the highly chlorinated segments which would produce less volatile fragments. This conclusion is supported by the kinetic parameters obtained and their close similarity to corresponding results obtained for the dimethyl and monochlorinated polymers thus reflecting a dipolar process involving a fairly high degree of steric order. This implies that even for the randomly chlorinated polymer the intramolecular ester interchange reaction is still a major process.

Table 34, p. 265 summarises the experimental results obtained for the degradation of the β chlorinated polymers, together with results obtained for other members of the series studied.

3.3 The Thermal Degradation of Polyglycollide

The thermal degradation of polyglycollide(145,176) [poly (methylene carboxylate] of $M_n > 20,000$ was studied over the temperature range 250–400°C by using the combined kinetic and analytical technique described in the previous chapter.

The kinetic aspects of the degradation were studied using the combined thermogravimetric and gas evolution techniques previously described.

The effect of temperature on the decomposition in nitrogen and oxygen using thermogravimetric analysis was carried out and the results obtained are summarised in Table 32, p. 255. The decomposition was found to be substantially first order demonstrated by the linearity over more than one decade of conventional first order plots.

First order plots for gas evolution results consistently deviated from linearity in the latter portion of the reaction although first order rate constants could be calculated for initial portions of the reaction. The degradation proved to be autocatalytic once an average of 75% of the decomposition had occurred. Results obtained are summarised in Table 33, p.256 .

Molecular weight change during degradation was estimated using solution viscometry and was shown to fall much more quickly during gas evolution analysis than in thermogravimetric analysis.

Table 32

First Order Rate Constants k, Activation Energies E, Frequency Factors A and Entropies of Activation, $\Delta S^{\ddagger}$ for the Thermal Degradation of Polyglycollide by Thermogravimetric Analysis

Temperature	$k \times 10^{5}$, sec^{-1}	
°C	Nitrogen Atmosphere	Oxygen Atmosphere
270	1.28	
289		3.02
315		15.0
320	21.5	
333	29.3	
340		24.3
342	56.4	
343	58.3	
364	197	157
390	525	
E, kcal/mole	32.6	36.8
A, sec^{-1}	2.09×10^{8}	5.89×10^{9}
$\Delta S^{\ddagger}$ cal/deg-mole	-23.8	-17.8

Table 33

First Order Rate Constants k, Activation Energies E, Frequency Factors A, and Entropies of Activation $\Delta S \neq$ for the Thermal Degradation of Polyglycollide by Gas Evolution Analysis

Temperature ^{o}C	k, $\times 10^{3}$, sec^{-1}
303	1.57
306	1.90
308	1.78, 1.83
327	4.52
330	4.02
354	9.03
357	10.7
380	11.3
388	19.2
E, kcal/mole	20.9
A sec^{-1}	1.35×10^{5}
$\Delta S \neq$ cal/deg-mole	-30.4

3.3.1 Discussion of Results Relating to the Thermal Degradation of Polyglycollide

A comparison of the results obtained for polyglycollide decomposition with those obtained for other polymers indicated that the intramolecular ester interchange mechanism described for poly(isopropylidene carboxylate) represented the predominant degradation route.

The comparable rates of degradation found in nitrogen and oxygen atmospheres for thermogravimetric results showed that random homolytic scission does not make an important contribution to the decomposition.

Results obtained by gas evolution gave higher rate constants and deviation from first order behaviour when compared with corresponding results obtained by thermogravimetric analysis, however. These deviations were attributed to a hydrolysis mechanism by acidic fragments such as glycollic acid which would remain in the vicinity of the degrading sample in the case of gas evolution analysis but not in the case of thermogravimetric analysis. In this latter situation, therefore, the intramolecular ester interchange reaction appears to predominate throughout the course of the decomposition rather than for the initial portion of the decomposition only as observed in gas evolution results.

Table 34, p.265 summarises the experimental results obtained for polyglycollide decomposition together with corresponding results for the remaining polymers studied.

3.4 The Thermal Degradation of Poly(2 ethyl 2 hydroxy Butyric Acid) PEHB

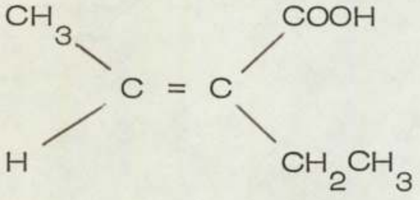
The thermal degradation of PEHB was studied over the temperature range 250–400°C in nitrogen(146) by using the combined kinetic and analytical technique previously described in Chapter 2 (Section II, p. 217), the kinetic aspects of the degradation being studied using the combined thermogravimetric (TGA) and gas evolution (GEA) techniques.

Random rate kinetics (i.e. the form classically associated with the thermal decomposition of polystyrene) were observed for the decomposition reaction using both T.G.A. and G.E.A. techniques, individual rate constants being substantially greater than corresponding values obtained for the other members of the poly-α-ester series studied.

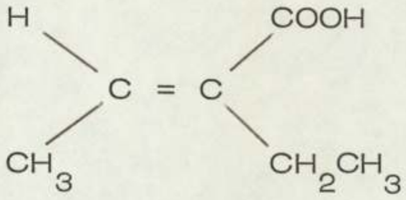
The activation energy for the process was found to be 48 kcals/mole, much larger than the value obtained for the decomposition of the other members (e.g. E_a for the decomposition of poly(isopropylidene carboxylate) was found to be 27 kcals/mole, see Table 34, p. 265).

The entropy of activation ($\Delta S^{\neq}$) and frequency factor (A) for the decomposition reaction were found to be + 10 cal/deg-mole and 10^{15} sec^{-1} respectively indicating that in contrast to the decomposition of other members of the series studied the rate determining step proceeds via a transition state which involves little degree of steric order.

The predominant products of the decomposition are cis (XLIV) and trans (XLV) ethyl crotonic acids in yields of 53.5 and 44.5% respectively together with diethyl ketone (2% yield).



(XLIV)



(XLV)

The yield of these products was found to be virtually quantitative over the temperature range quoted by carrying out several decomposition reactions in sealed Carius tubes. The products were identified and their percentage composition was determined using gas liquid chromatography, nuclear magnetic resonance, infra red and mass spectrometry.

The lowering of molecular weight with time was also determined for the decomposition reaction and was found to be more rapid than for other members of the series studied. The process is so marked that continuous melt viscosity versus time measurements using rheogoniometry(175,182) could not be obtained over a reasonable time period.

3.4.1 Discussion of Results Relating to the Thermal Degradation of Poly(2 Ethyl 2 Hydroxy Butyric Acid) PEHB

Any mechanism presented for the thermal decomposition of PEHB must be able to satisfactorily account for the following observations (i – v) together with the fact that they differ so markedly from the relevant data for previous members of the series.

i) The random rate kinetics observed.

ii) The values obtained for the activation energy (48 kcals/mole), entropy of activation (+ 10 cal/deg-mole) and frequency factor ($\sim 10^{15}$).

iii) The dramatically higher rates of degradation observed for PEHB as compared to corresponding rates for other members of the series studied (see Table 34, p. 265).

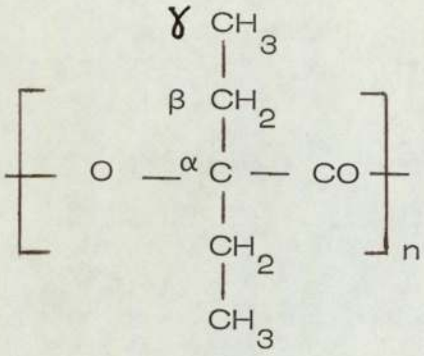
iv) The near quantitative production of cis and trans ethyl crotonic acids as the major products of degradation.

v) The form of the molecular weight versus time curve, which indicates the occurrence of a random scission process since an initial rapid decrease in molecular weight is observed.

The above experimental observations do not satisfy the requirements of the intramolecular ester interchange reaction postulated as the major degradation route for the thermal decomposition of other members of the poly-α-ester series so far studied.

Structural features which are present in PEHB but which are absent in poly(isopropylidene carboxylate) must therefore be sought for. These features must be capable of accommodating random scission processes seen necessary to accord with random rate kinetics together with the molecular weight versus time profiles observed.

One of the structural features which distinguishes PEHB from other members of the poly-α-ester series studied is the presence of γ hydrogen atoms (XLVI).

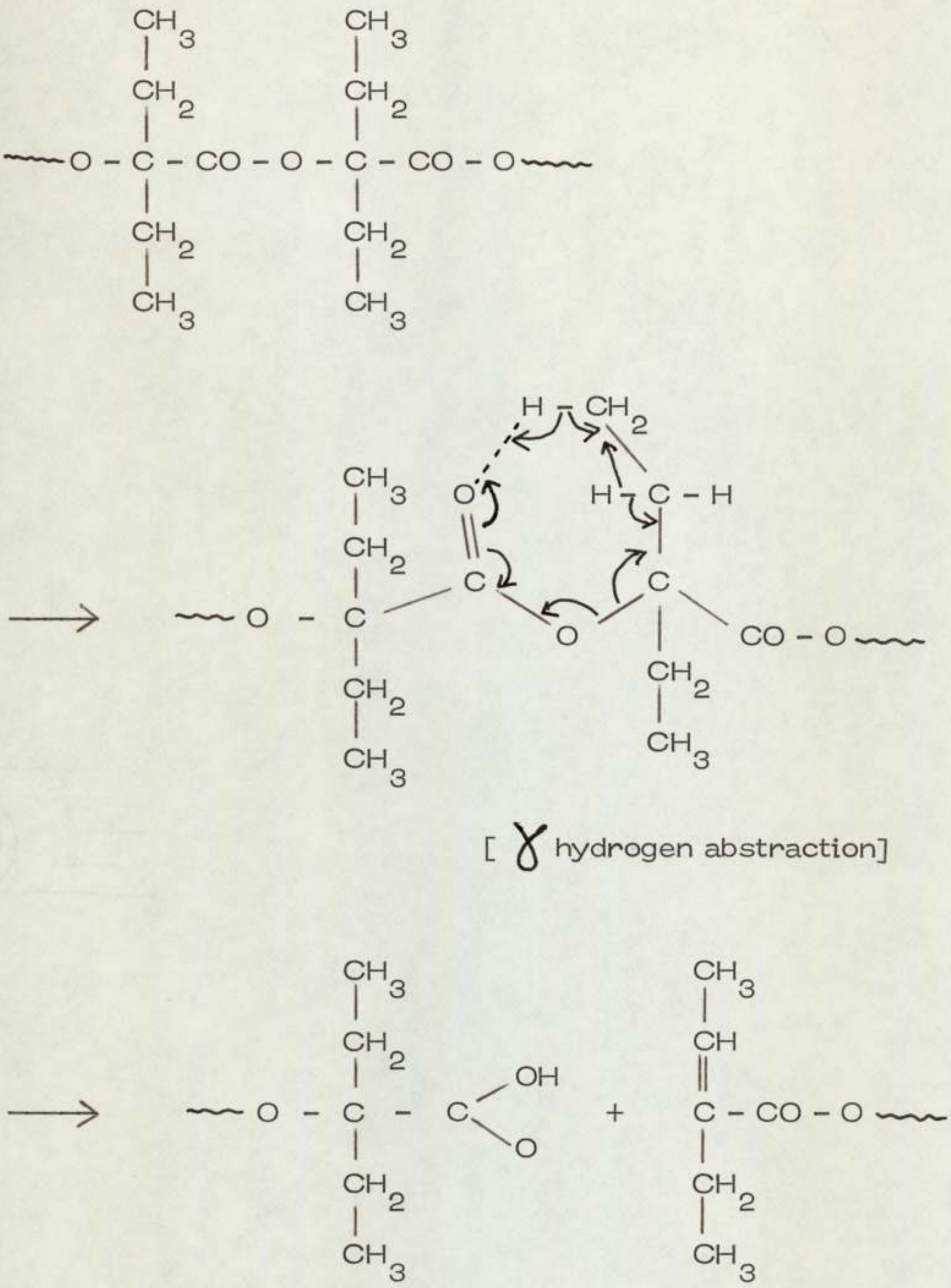


XLVI

On the basis of kinetic and analytical results it is thought that these γ hydrogens are involved in an abstraction process which ultimately leads to the formation of cis and trans ethyl crotonic acids via random chain scission.

The γ hydrogen abstraction process (Scheme XLVII) analogous to the well known β hydrogen elimination process presented by Pohl(156) (XXXV, p. 211) is seen as the non rate determining step of the decomposition as sensed by thermogravimetric and gas evolution analysis.

The process described in Scheme XLVII, p. 262 is seen to result in random scission of the PEHB chain. As the reaction progresses fragments possessing critical chain lengths for volatilisation will be formed. The concentration of such fragments reaches a maximum after a finite time which correlates with the maximum rate phenomena associated with random rate kinetics.



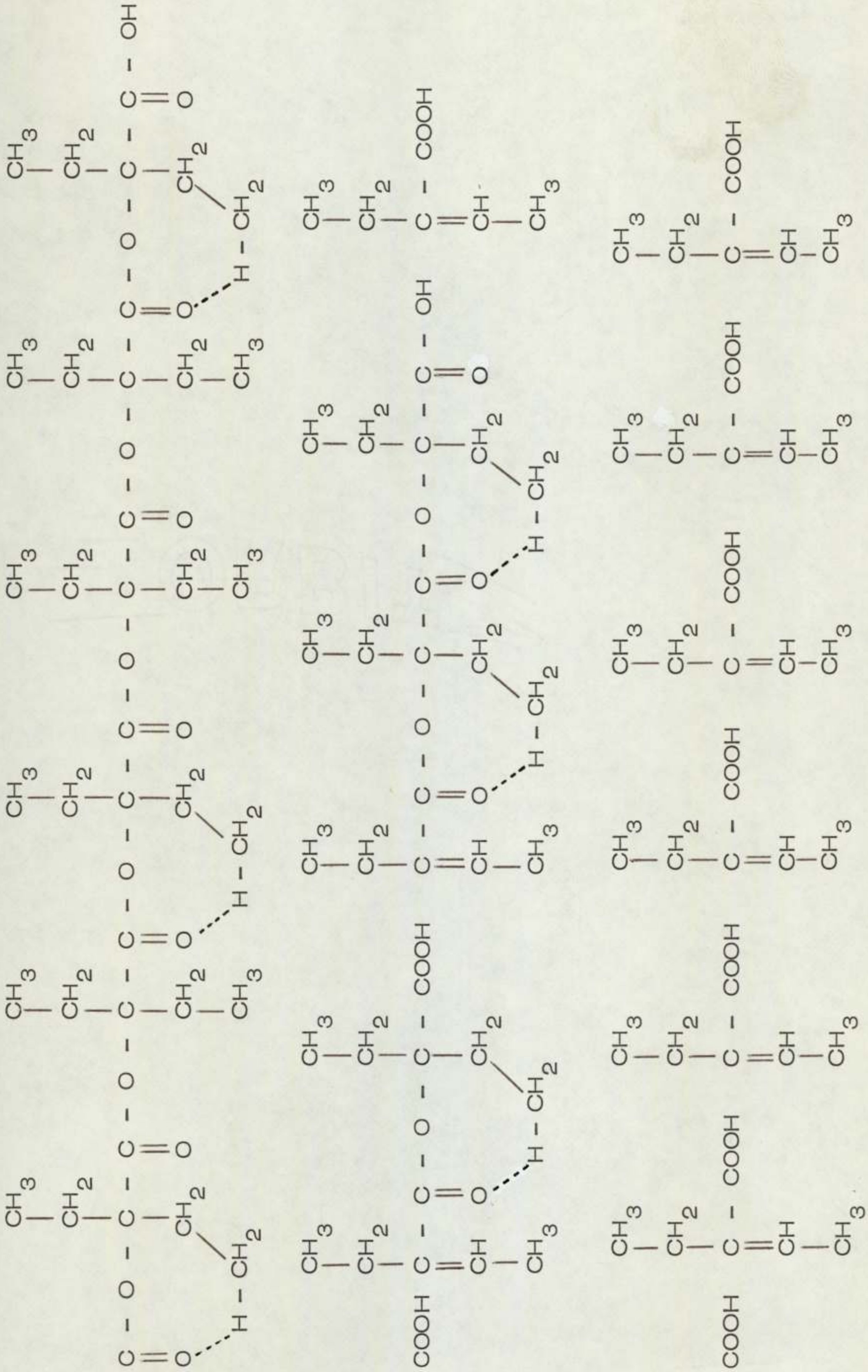
Scheme XLVII

In contrast to previous cases because of the existence of a critical chain length for volatilisation the rate determining step is not associated with the initial chain scission under the conditions used the critical fragments formed are cis and trans ethyl crotonic acids (Scheme XLVIII, p. 264).

The overall mechanism presented above for the degradation of PEHB namely that of random scission involving a γ hydrogen elimination process correlates well with the kinetic profile (observed for the decomposition (see Table 34, p. 265). The mechanism also explains the rapid lowering of molecular weight with time which would be expected for random chain scission.

It is unlikely that free radical reactions play any appreciable part in the decomposition of the polymer over the temperature range studied. In addition unzipping from chain ends is thought to be relatively unimportant since such reactions would lead to only relatively low rate of molecular weight decrease.

A summary of kinetic and analytical results obtained for PEHB decomposition is included in Table 34, p. 265. This table presents, for ease of comparison, corresponding results obtained for other members of the poly-α-ester series studied.



Scheme XLVIII

Table 34

A Summary of the Relative Rates of Degradation, Kinetic Profiles, Degradation Products and Major Degradation Mechanisms for the Thermal Decomposition of the Series of Poly-α-esters Studied

Main Chain Substituents (XXXIV, p. 208)		Relative Rates of Degradation at 253°C in Nitrogen (T.G.A. Results)	Kinetic Profile (T.G.A. Results)				Kinetic Profile (G.E.A. Results)				Major Primary Degradation Products (250°C)	Minor Degradation Products (250°C)	Major Degradation Mechanism
R_1	R_2		Order of Reaction	E_a kcals/ mole	S cal/ deg-mole	A sec^{-1}	Order of Reaction	E_a kcal / mole	S cal/ deg-mole	A sec^{-1}			
H	H	1	First Order	32.6	-23.8	2.0×10^8	Some Deviation from first Order	20.9	-30.9	1.35×10^5	Glycollide Monomer	Glycollic Acid (Tracial)	Intramolecular Ester Interchange and hydrolysis (G.E.A.)
CH_3	CH_3	25	First Order	27.2	-29	4.1×10^7	First Order	28.3	-24	2.6×10^8	1,1-4,4, Tetramethyl Glycollide	Methacrylic acid, Carbon monoxide, Acetone and Some Carbonaceous Char	Intramolecular Ester Interchange
CH_3	CH_2Cl	3	First Order	24.6	-34	3.0×10^6	First Order	24.3	-36	3.1×10^6	Glycollidic Fragments, HCL gas	Substantial Quantities of Carbonaceous Char	Intramolecular Ester Interchange and cross linking reactions
Random chlorination		7.5	Deviation from First Order	–	–	–	First Order	21.5	-30	1.3×10^6	Complex Glycollidic Fragments, HCL gas	Substantial Quantities of Carbonaceous Char	Intramolecular Ester Interchange and cross linking reactions
C_2H_5	C_2H_5	2,500	Random Rate Kinetics	47	+ 10	10^{15}	Random Rate Kinetics	43	+ 10	10^{15}	Cis and Trans Ethyl Crotonic Acids	Diethyl Ketone	Random Chain Scission via γ hydrogen abstraction process

CHAPTER 4

Summary, Discussion and Suggestions for Further Work

4.1 Summary and Discussion

The work described in this section has presented the development of equipment for the detailed study of polymer degradation processes. The degradation of a series of poly-α-esters has highlighted the effect of main chain substituents on the degradation route likely to be favoured.

The simplest polymer of the series, polyglycollide degrades predominantly via an intra molecular ester interchange reaction although under suitable conditions the polymer is susceptible to hydrolytic degradation by acidic fragments produced during degradation.

The dimethyl substituted polymer on the other hand is less susceptible to these hydrolysis reactions due to the presence of the methyl groups sterically hindering such processes. The intra molecular ester interchange reaction predominates for this polymer over the temperature range 200-400°C while at higher temperatures (~ 600°C) radical fragmentation of the polymer chain becomes more important.

The introduction of β chlorine atoms is seen to reduce the rate of thermal decomposition of poly-α-esters. In the case of poly (3 chloro-2-methyl-2-hydroxy propionic acid) the intermolecular ester interchange reaction is shown to be still an important process which is retarded by the presence of the chloromethyl groups mutually repelling each other during the course of the formation of the glycollidic structure thus inhibiting the decomposition process. Superimposed on the latter however is an intermolecular reaction involving the elimination of hydrogen chloride and the subsequent formation of cross links leading to the formation of a carbonaceous char.

In the case of the randomly chlorinated version of poly (isopropylidene carboxylate) the situation is complex. Although the intramolecular ester interchange reaction is significantly interfered with by the irregularity of the polymer chain as evidenced by departure from first order kinetics, in thermogravimetric runs this process is shown by gas evolution analysis to still be an important process.

Initial studies of the thermal degradation of the diethyl substituted polymer have shown that the predominant degradation process involves γ hydrogen abstraction leading to random chain scission. The presence of γ hydrogen atoms substantially reduces the stability of the polymer (see Table 34, p. 265). The production of small quantities of diethyl ketone indicates the minor occurrence of intramolecular ester interchange reaction.

4.2 Suggestions for Further Work

An obvious extension to studies carried out to-date on the thermal decomposition of poly-α-esters would be to study the effect of other substituents on polymer stability and mode of degradation. A series of poly-α-esters of potential interest in this respect is presented in Table 35, p. 269.

Of the structures presented in Table 35 the cyclopentyl, cyclohexyl and pentafluorophenyl substituted polymers would provide particularly new and interesting avenues of experimental investigation.

Synthetic techniques for poly-α-esters have now been developed for the synthesis of polymers up to R_1, R_2 = octyl. These poly-α-esters provide particularly valuable model systems for the study of degradation reactions occurring in oil modified alkyd (polyester) resins and other structurally related polymers used in surface coatings.

Table 35

A Summary of Poly-α-ester Structures Suggested as Possible Candidates for Future Thermal Degradation Studies

Polymer	R_1^*	R_2^*
Poly(2 hydroxy 2 propyl pentanoic acid)	n propyl	n propyl
Poly(1 hydroxy cyclopentane carboxylic acid)	cyclopentyl	
Poly(1 hydroxy cyclohexane carboxylic acid)	cyclohexyl	
Poly(1 hydroxy cycloheptane carboxylic acid)	cycloheptyl	
Poly (2 hydroxy 2(pentafluorophenyl pentanoic acid)	Pentafluorophenyl	Methyl

[*] See Structure (XXXIV), p. 208 .

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Poly-α-Ester Degradation Studies. I. Introduction: Design and Construction of Equipment

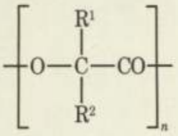
G. J. SUTTON and B. J. TIGHE, *Department of Chemistry, The University of Aston, Birmingham B4 7ET, England*

Synopsis

The various types of polyester degradation known to occur at elevated temperature are briefly summarized with particular reference to features of potential diagnostic value. Although little is known of poly-α-ester degradation in particular, examination of work on other linear polyesters indicates the spectrum of analytical and kinetic information that will be needed to characterize the degradation of poly-α-esters of various structures. On the basis of this review, an apparatus has been designed which enables kinetic information to be simultaneously obtained by thermogravimetry, gas evolution analysis, and rheological studies of the residual polymer melt. In addition a gas sampling procedure enables twin-column gas–liquid chromatographic analysis to be carried out on the degradation products. Samples of the chromatographically separated degradation products are collected in a microcollector cell for infrared and mass spectrometric analysis. Other refinements include in-line filament and Curie-point pyrolysis techniques.

Introduction

Despite the fact that poly-α-esters (I) represent the class of polyesters having the simplest repeat unit, little is known of their degradative characteristics and the ways in which this is affected by substituent R^1 and R^2.



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

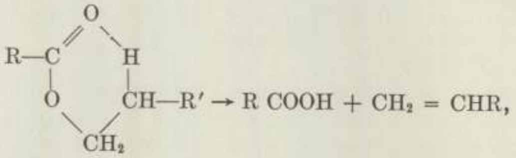
I

This situation is, in turn, partially due to the lack of a general condensation route applicable to all members of the series, a problem which, together with the use of ring-opening reactions to form these polymers, has been discussed in detail elsewhere.[1–6] The degradation of polyesters as a general class has been widely but unsystematically studied. A good survey of the earlier literature (up to 1928) has been compiled by Hurd.[7]

Carothers,[8] in 1930, prepared a series of glycol esters of carbonic acid and showed that diethylene carbonate and trimethylene carbonate undergo reversible transformation between cyclic monomeric and polymeric forms.

He also found that a stable dimer of tetramethylene carbonate could be obtained by thermal decomposition of the polymer. In a subsequent series of papers[9] Carothers showed that many aliphatic polyesters undergo fairly simple intramolecular ester-interchange reactions producing dimeric and monomeric cyclic esters on thermal degradation. Thus polyglycollic acid (I, $R^1 = R^2 = H$) and polylactic acid (I, $R^1 = H$; $R^2 = Me$) were shown to degrade to form glycollide and lactide, respectively.

Pohl[10] demonstrated that degradation of many polyesters has its origin in the abstraction of hydrogen from the β-carbon of the glycol segment of the polymer. This mechanism, which is well-known, for example, in the pyrolysis of model compounds [eq. (1)], leads to the formation of olefinic



(1)

and carboxyl-terminated fragments.

The significance of the mechanism has been neatly demonstrated by Trischler and Hollander[11] by means of fluorine substitution techniques. These workers also demonstrated that aliphatic carboxylic acids provide ready degradation sites because of radical abstraction reactions involving hydrogen atoms on the α-carbon of the carboxylic acid segment [eq. (2)].

$$R'CH_2CH_2COOC_6H_5 \rightarrow R'CH_2\dot{C}HCOOC_6H_5 \rightarrow R'\cdot + CH_2{=}CHCO_2{-}C_6H_5 \quad (2)$$

Aromatic acids are intrinsically more stable since they have no labile α-hydrogen.

If degradation sites leading to reactions of types (1) and (2) are absent and the polymer does not readily undergo intramolecular ester interchange, remarkably stable polyesters may be obtained.[11] In such cases, studies such as those of Zhuravleva and Rode[12] point to the occurrence of two distinct ester-group scission mechanisms with resultant competitive formation of carbon monoxide and carbon dioxide, the former predominating at higher temperatures.

The most complete and systematic studies of polyester degradation have been carried out on poly(ethylene terphthalate) and related model compounds. Notable contributions have been made by Ritchie,[13] Goodings,[14] Wall,[15] and Marshall and Todd.[16] The situation is concisely reviewed by Buxbaum.[17] Because of β-hydrogen availability, a chain scission reaction resembling (1) takes place, and the main degradation products are carbon dioxide, terepthalic acid, and acetaldehyde. Decomposition in the presence of oxygen leads to the predominance of radical reactions and a greater number of degradation products.

The fact that intramolecular elimination reactions also play a part in the decomposition of aromatic polyesters is illustrated by the isolation of macrocyclic degradation products.[18,19] Rings of similar size have been isolated from aliphatic polyesters.[20]

One instructive feature emerging from work on poly(ethylene terephthalate) is the fact that kinetic results obtained by different workers using a variety of techniques[17] based on several different reaction parameters give valuable complementary information relating to the various contributory degradation mechanisms.

Although previous work enables no precise estimate to be made of the effect of substituents R^1 and R^2 on the degradation of polyesters of type I, it does provide some indication of the likely spectrum of degradation products. In designing an apparatus to study the kinetics and mechanisms of poly-α-ester degradation, therefore, several factors must be taken into consideration. Separation and identification of the degradation products is obviously important. Since the formation of cyclic products seems to be a general feature of polyester degradation, some monitoring technique capable of handling fairly nonvolatile organics is required.

On the other hand, there is obviously a need to distinguish quantitatively between, for example, carbon monoxide and carbon dioxide formation. This suggests the use of a dual-column gas–liquid chromatography (GLC) technique, preferably with facilities for isolation and collection of degradation products to enable less readily identifiable species to be subjected to appropriate analytical techniques. Precolumn pyrolysis would offer obvious advantages in preliminary studies of the effect of degradation temperature on reaction products.

In choosing kinetic methods to monitor the degradation processes, thermogravimetry, although valuable, cannot be considered as a single technique. A supplementary technique which is more sensitive to small gaseous fragments such as carbon monoxide and dioxide would be valuable, particularly if this enabled some information to be obtained relating to the fate of primary degradation products. (Substituted glycollides, whose formation must be expected in poly-α-ester degradation, have been shown to undergo ring-scission reactions leading to ketone and carbon monoxide.[21]) It would be particularly desirable to monitor the rheological properties of the residual polymer during the degradation process either by simple melt-viscosity measurements such as those used by Marshall and Todd[16] in their studies of poly(ethylene terephthalate) degradation, or by determination of a more complex shear–shear strain dependence. Chain-scission reactions of different types and the occurrence of crosslinking could thereby be diagnosed. On the basis of these considerations, equipment has been designed to study poly-α-ester degradation *in vacuo* and in various gaseous atmospheres.

Poly-α-ester Degradation: Design and Calibration of Equipment

A schematic representation of the equipment is shown in Figure 1, details of the main reaction vessel in Figure 2, and a photograph of the complete assembly in Figure 3. Samples of the material under examination are introduced into the two matched furnace cavities (Fig. 1). The function of the first is to provide thermogravimetric and gas evolution anal-

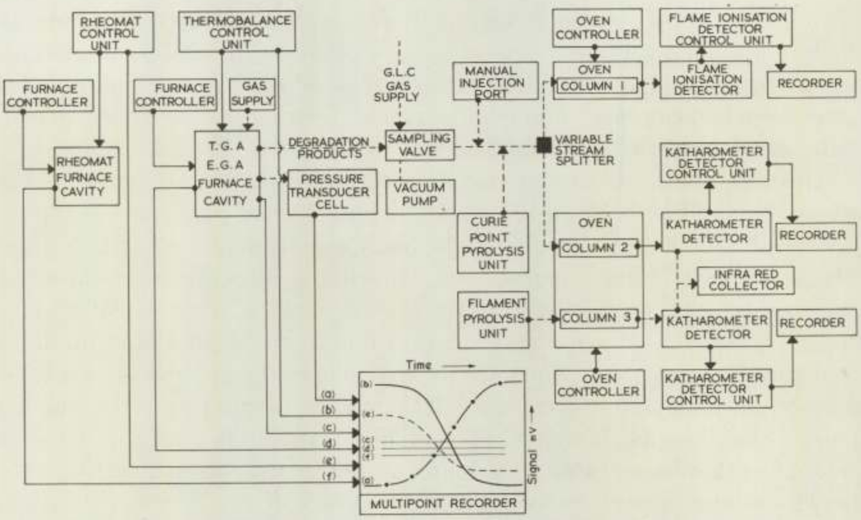


Fig. 1. Schematic representation of degradation equipment.

ysis data. The thermogravimetric information is fed via a remote weighing head to one channel of the multipoint recorder. All degradation products which have an appreciable vapor pressure at the degradation temperature are swept from the cavity for analysis. At appropriate intervals, predetermined quantities of this effluent are introduced by means of a gas sampling valve into the analysis system. This consists of a twin-column GLC unit linked by a variable stream splitter. Column 1 (Fig. 1) is typically a 3 ft × $^1/_8$ in. OD packed column maintained at some temperature between 150 and 250°C and coupled to a flame ionization detector. For convenience, this column, together with the gas sampling valve and as much of the effluent pipework as possible, is enclosed in an insulated, thermostatically controlled oven which also contains the furnace cavity. In this way problems associated with condensation of the degradation products on the "cold spots" in the system are avoided. Column 2, which is typically a 10 ft × $^1/_4$ in. OD packed column, is contained in a separate oven operated between 25 and 200°C and linked to a thermistor katharometer detector. This column is fitted with a micro infrared collector facility (Beckman-RIIC extrocell unit) which enables samples of individual degradation products to be collected directly into silver chloride infrared cells without the need for an intermediate transference operation. A facility also exists for these cells to be coupled directly to an A.E.I. M.S9 mass spectrometer.

A parallel $^1/_4$ in. OD column (column 3) of similar characteristics is coupled to a filament pyrolysis unit of the type described by Barlow et al.[22] This is used for preliminary analytical work and pyrolysis of (>10 mg) samples of polymer in order that appreciable quantities of minor degradation products can be collected and analyzed by using the collector technique. Facility for incorporation of a second pyrolysis unit of the Curie-

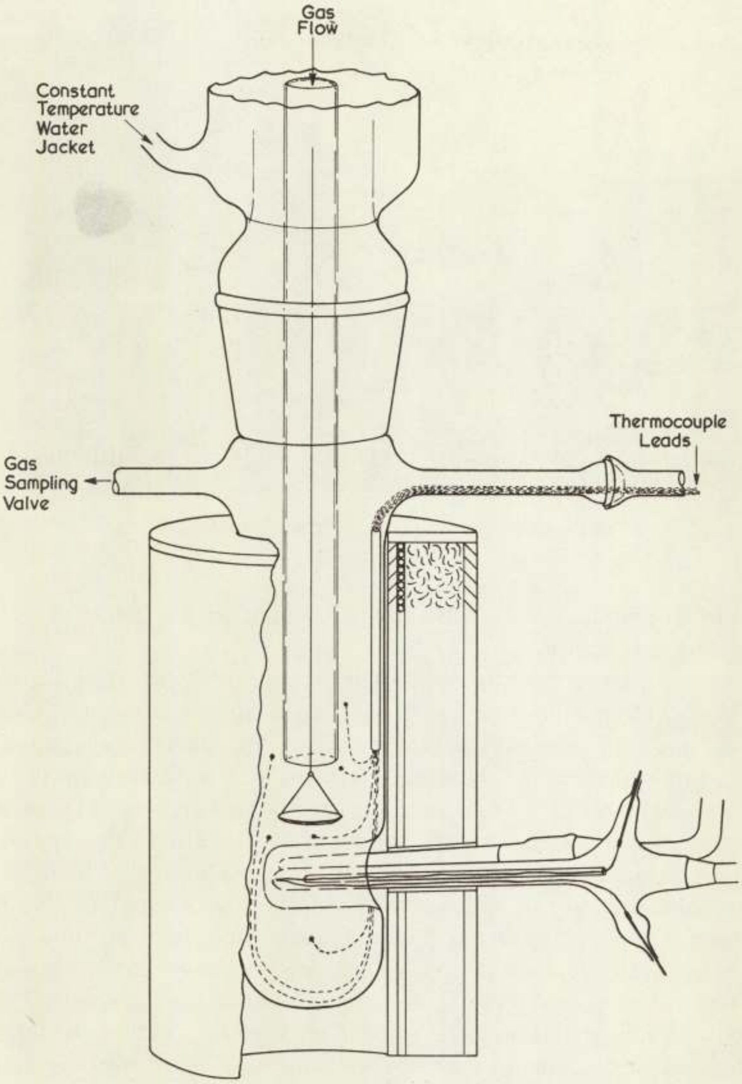


Fig. 2. Detailed diagram of main reaction vessel.

point type is included in the system before the stream-splitter. Preliminary examination of degradation products over a wide temperature range on both columns 1 and 2 is thereby possible.

The separate advantages of the two types of pyrolysis unit have been described by Lehrle.[23] Column 1, being fairly short and maintained at a relatively high temperature, is most useful for separation and detection (flame ionization) of the less volatile degradation products. The column 2/katharometer detection system, maintained at a lower temperature, is most appropriate for the volatile degradation products, including species

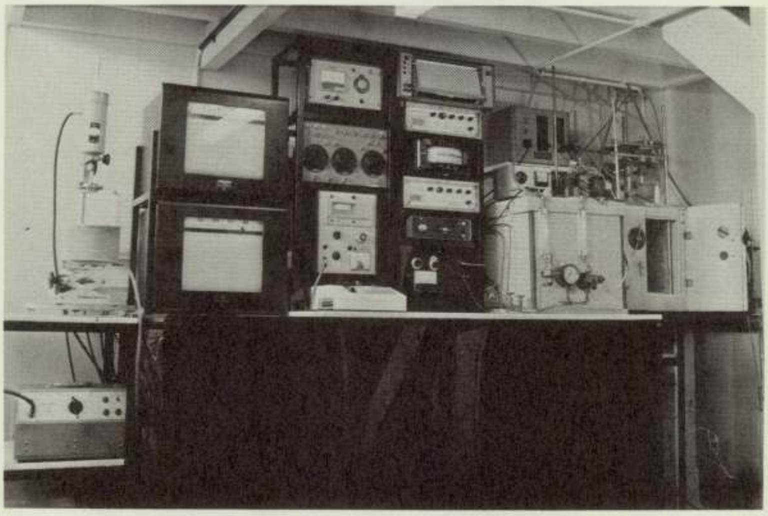


Fig. 3. Photograph of degradation equipment.

such as carbon monoxide and carbon dioxide which are not detected by the flame ionization technique.

In addition to the separation and identification of the volatile degradation products, their overall rate of formation is also monitored. This is carried out in the furnace cavity used for thermogravimetry by means of a separate sample probe placed immediately below the thermogravimetric analysis sample pan (Fig. 2). This probe, together with a blank of identical dimensions which is placed beside it, are connected to either side of a differential pressure transducer (Ether Controls Ltd.). The rate of increase in vapor pressure due to the formation of volatile degradation products is thereby monitored. The pressure transducer sample lines are housed in the thermostatically controlled oven which encloses the gas sampling valve, main reaction vessel and first GLC column. Problems associated with condensation of degradation products on cold spots are thereby largely eliminated. The signal from the pressure transducer is fed into the multipoint recorder.

The rheological properties of the polymer throughout the degradation process are, where appropriate, monitored by a Rheomat (Contraves Industrial Products) probe. Earlier attempts to house the probe in the same furnace cavity as the thermogravimetric and gas evolution systems proved impractical where precise temperature control and minimum temperature gradients are required. A twin furnace cavity, separately controlled but maintained at the same temperature, is therefore used, the signal being fed into the multipoint recorder.

In addition to the rheomat, thermogravimetry, and gas evolution signals, temperatures corresponding to each sample and monitored by thermocouples appropriately placed are also fed into the (6-channel) multipoint

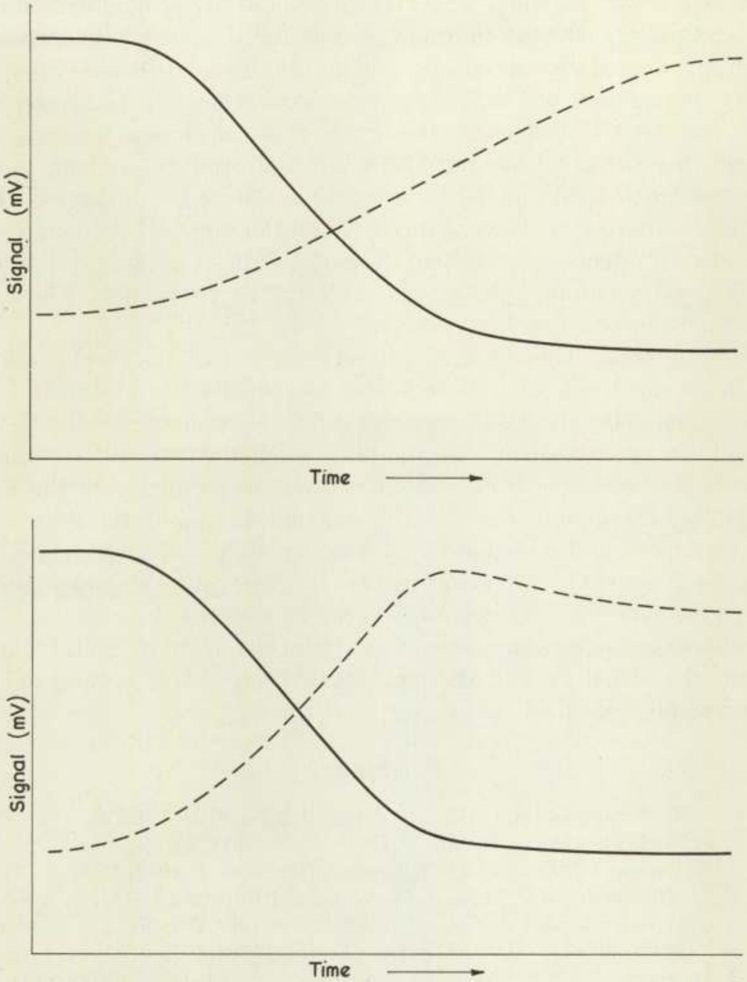


Fig. 4. Typical (——) thermogravimetric and (---) gas evolution Curves: (upper) secondary degradation of primary degradation products; (lower) condensation of degradation products within the gas evolution system.

recorder. Each reaction vessel and other parts of the system are intermittently monitored by a series of thermocouples and a thermocouple switch. The temperature profiles in the reaction vessel are particularly important. Figure 2 illustrates the arrangement of thermocouples in the main cavity. For most purposes, chromel–alumel couples were found to be adequate, provided that appropriate precautions were taken with respect to insulation, cold junctions and compensating cable. A considerable amount of attention was given in an initial series of calibration experiments to the procedural factors known to affect reproducibility in thermal analysis.[24] The final cell design minimized variation due to, for example, turbulence, temperature gradients, and sample sputter, duplicate runs being reproducible within ± 1%.

The advantage of using gas evolution analysis in conjunction with thermogravimetry is that information relating secondary decomposition of primary degradation products can be obtained. In cases where the primary degradation products are themselves stable under the condition of the experiment, thermogravimetry and gas evolution analysis yield identical rate data. If the initial degradation products undergo further decomposition at a rate similar to or less than the rate of primary degradation, the techniques give complementary information. If condensation of degradation products occurs within the gas evolutions analysis system (e g., at cold spots) a characteristic reversion of the curve occurs. These phenomena are illustrated in Figure 4.

A series of preliminary experiments established that the rheological data were most effectively and reproducibly obtained with a cone-and-plate probe system. Because of the possible influence of shear rate on degradation and the importance of cone and plate geometry on sensitivity and reproducibility, extensive work was carried out in parallel with the Farol-Weissenberg rheogonimeter.[25,26] This instrument enables the degradation to be monitored under oscillatory or rotatory shear conditions. By comparing the effect of the two modes at various shear rates the contribution of shear to the overall rate of degradation can be assessed.

In subsequent papers the use of this equipment to study the relationship between the structure and thermal degradation characteristics of poly-α-esters will be described.

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Poly-α-Ester Degradation Studies. II. Thermal Degradation of Poly(Isopropylidene Carboxylate)

G. J. SUTTON, B. J. TIGHE, and M. ROBERTS, *Department of Chemistry, The University of Aston, Birmingham B4 7ET, England*

Synopsis

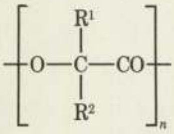
The thermal degradation of poly(isopropylidene carboxylate) has been studied over the temperature range 200–800°C by using the kinetic and analytical techniques described in Part I of this series. Over a wide range of temperature, tetramethyl glycollide, acetone, carbon monoxide, and, to a lesser extent, methacrylic acid are observed when the products are rapidly swept away from the reaction zone. As decomposition temperature is increased, tetramethyl glycollide takes on the role of an intermediate, the more stable products carbon monoxide and acetone being formed from it. At the highest temperature examined, carbon monoxide begins to predominate, and its formation is accompanied by formation of small amounts of a carbonaceous residue. When the reaction products are allowed to remain in the reaction zone, which is possible at the lower end of the temperature range, methacrylic acid becomes the major product. This is interpreted as a dual decomposition route, involving the tetramethyl glycollide intermediate. Kinetic studies have shown that the decomposition is a first-order process and that the first-order rate constant k is related to temperature (T) by the expression:

$$k = 4.1 \times 10^{7} e^{-27,200/RT} \text{ sec}^{-1}$$

The results are interpreted in terms of an intramolecular ester interchange process involving tetramethyl glycollide as the primary decomposition product.

INTRODUCTION

In the preceding paper[1] we have briefly summarized the known effects of polyester structure on degradation behavior and referred to the existing state of knowledge concerning factors affecting poly-α-ester (I) decomposition.



$$\left[\text{—O—}\overset{\displaystyle R^1}{\underset{\displaystyle R^2}{\overset{|}{\underset{|}{C}}}}\text{—CO—} \right]_n$$

I

Carothers,[2] in his classic studies on the reversible polymerization of cyclic esters, demonstrated that glycollide and lactide could be converted to polyglycollic acid (I; $R^1 = R^2 = H$) and polylactic acid (I; $R^1 = H$, $R^2 = Me$), respectively. Since polymers reverted to the cyclic monomer at elevated temperature, Carothers envisaged the reactions as being essentially similar, and described them both as ester exchange processes. Attempts to polymerize 1,1,4,4-tetramethyl glycollide were, however, unsuccessful, an observation confirmed by Hall[3] and his co-workers. This raises the point, based on Carothers' inference, that if it were possible to produce the polymer by some other route, the degradation pattern might be quite different from that of poly(glycollic acid) and poly(lactic acid). Circumstantial support for this view is found in the work of Sarel,[4] who observed that in the reversible polymerization of 2,2-disubstituted 1,3-propanediol carbonates, branching at C–2 of the diol moiety has an effect on depolymerization behavior.

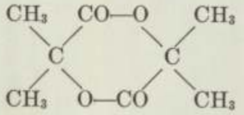
The polyglycollide in question, poly(α-hydroxyisobutyric acid) or more correctly, poly(isopropylidene carboxylate), (I; $R^1 = R^2 =$ Me), may be conveniently synthesized from the anhydrosulfite of α-hydroxy-isobutyric acid.[5,6] We have previously studied the kinetics of polymerization and the structure of the polymer[5] and now present the results of thermal degradation studies.

RESULTS

Preliminary Pyrolysis Studies

Samples of poly(isopropylidene carboxylate) having number-average molecular weights between 10,000 and 30,000 were examined by using filament and Curie-point pyrolysis–GLC techniques in flowing nitrogen at temperatures between 300 and 750°C. The chromatograms were characterized by three major peaks whose relative areas varied over the temperature range studied. The two most readily eluted peaks, which were identified as carbon monoxide and acetone, predominated at higher temperatures, whereas the third, which had a considerably larger retention volume, gradually disappeared.

Samples of this third component were obtained by use of the GLC micro collector-cell technique,[1] subjected to infrared and mass spectrometric analysis, and its identity, which was confirmed by peak enrichment studies, established as 1,1,4,4-tetramethyl glycollide (II).



II

Table I and Figure 1 summarize the relevant data. As subsequent discussion will show, methacrylic acid must be considered as a possible degradation product. Use of the pure compound as a marker[1] in GLC work established that methacrylic acid was formed only in very minor quantities which became larger with low molecular weight polymers ($\bar{M}_n$ <5000). An additional point established by pyrolysis studies was the fact that at higher temperatures, pyrolysis of tetramethyl glycollide itself produced predominantly carbon monoxide and acetone.

TABLE I
Analytical Data Relating to Poly(isopropylidine Carboxylate) Degradation Products

Product 1 (tetramethylglycollide)	Product 2 (acetone)	Methacrylic acid
	Infrared absorption frequencies, cm^{-1}	
2920–3000 (w)	2900–3000 (w)	3000–3500 (broad)
1800 (sh)	1720 (s)	2900–3000 (w)
1760 (s)	1420 (w)	1700 (s)
1450)	1370) (m)	1640)
1385) (w)	1220)	1450) (m)
1350)		1430)
1260 (m)	1095) (w)	1375 (w)
1200 (sh)	900)	1300 (m)
1140)		1225) (m)
1100)		1205)
1045) (m)		1010 (w)
1055)		950 (m)
	Mass spectra, major peaks (*m/e*)	
172, 155, 127, 114, 87, 86, 70, 69, 45.	58, 44, 32, 28, 15, 14.	86, 69, 68, 60, 58, 56, 41.

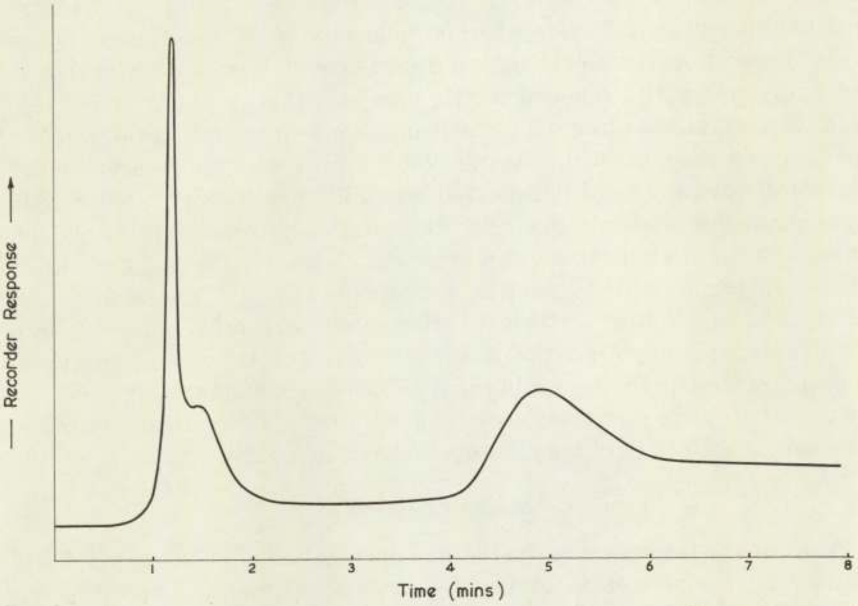


Fig. 1. GLC trace showing (in order of appearance) carbon monoxide, acetone, and tetramethyl glycollide.

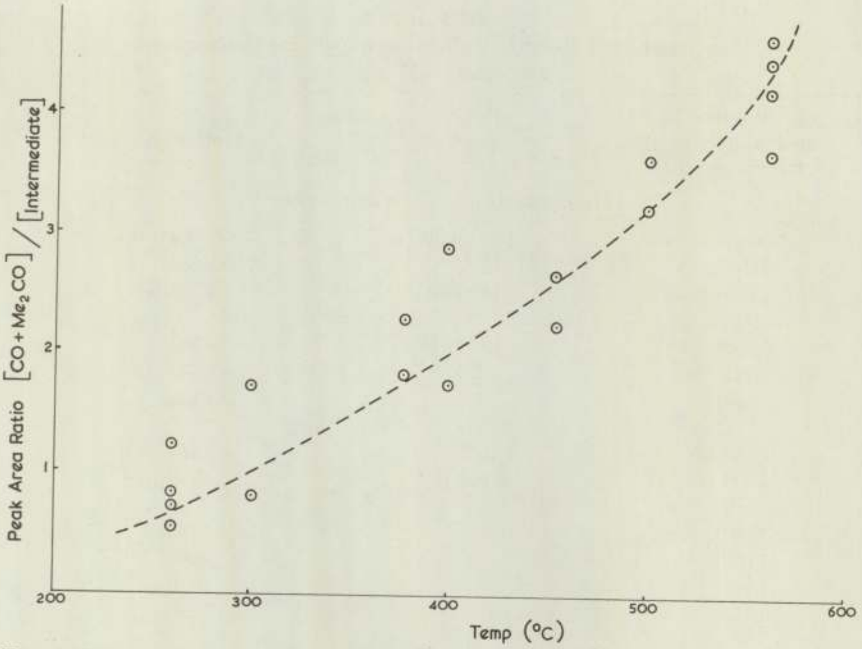


Fig. 2. Effect of temperature on the formation of the three degradation products expressed as peak area ratio: [carbon monoxide + acetone]/[intermediate].

The effect of temperature on the formation of the three degradation products was investigated by measurement of peak area ratios as a function of filament current. Figure 2 shows the peak area ratio: 1,1,4,4-tetramethyl glycollide/(acetone + carbon monoxide). Although there is considerable scatter, the points show a definite trend, representing as they do over fifty runs with a range of sample sizes. Within this range (0.5–5 mg), sample size was not observed to have any significant effect on the values of peak area ratio obtained. At the lower end of the temperature range, substantial quantities of tetramethyl glycollide were formed, and the relative quantities of carbon monoxide and acetone remained reasonably constant. As the temperature was increased, however, the yield of carbon monoxide began to predominate at the expense of that of acetone; in addition, the formation of a residual carbonaceous char was noted (at lower temperatures depolymerization was quantitative). At temperatures where this effect began to be significant, yields of tetramethyl glycollide diminished to zero. The variation of peak area ratio, carbon monoxide/acetone, as a function of temperature is shown in Figure 3.

Kinetic Studies

Various kinetic aspects of the thermal degradation of poly(isopropylidene carboxylate) were studied by using the combined thermogravimetric and gas evolution techniques described in the preceding paper.[1] Unless otherwise stated, samples used were of $\bar{M}_n \simeq 30{,}000$, and experiments were carried out isothermally. The shape of thermograms obtained under these conditions indicated that the decomposition was predominantly first-order. This was confirmed by applying the Wilhelmy equation [eq. (1)] to the results, which were

$$C_t = C_0\, e^{-kt} \tag{1}$$

represented graphically in the form log W_t/W_0 versus time, where W_0 and W_t are the weights of polymer initially and at time, t, respectively. A typical example is shown in Figure 4. In addition, results were examined in the form (Fig. 5) of plots[7] showing instantaneous rate of volatilization (%/min) versus sample volatilized (%).

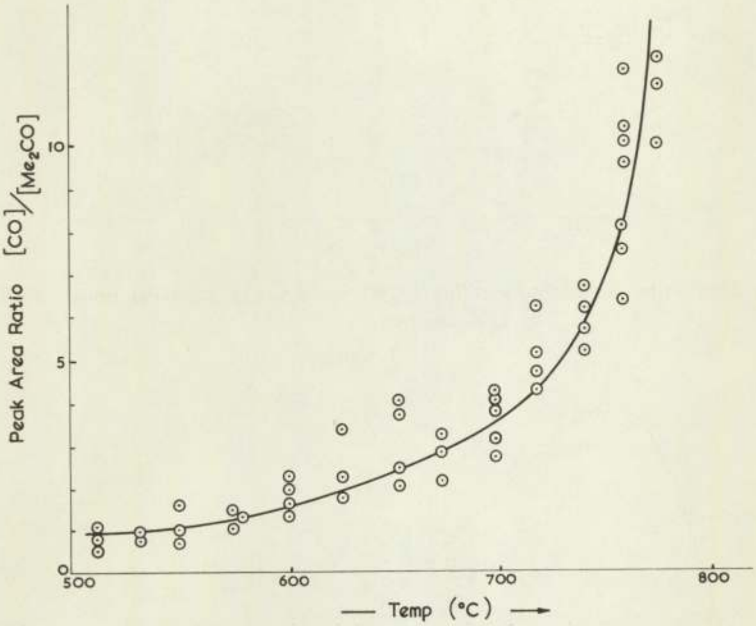


Fig. 3. Change in peak area ratio [carbon monoxide]/[acetone] shown as a function of temperature.

Figures 4 and 5 demonstrate that the reaction is substantially first-order and that an initial zero-order process is not involved (since if this were the case the portion A-B of Fig. 5 would become horizontal[8]). The predominantly first-order nature of the degradation is reflected in the linearity of the portion B-C of Figure 5 and compares well with established first-order processes, for example, the degradation of poly-α-methylstyrene.[9] The absence of a random decomposition mechanism such as that shown by polystyrene[9] is indicated by the absence of curvature, particularly in the early portion of Figure 5. Here, the initial rapid rise (A-B) to a maximum, representing as it does a period of under 2 min, obviously corresponds to thermal equilibration.

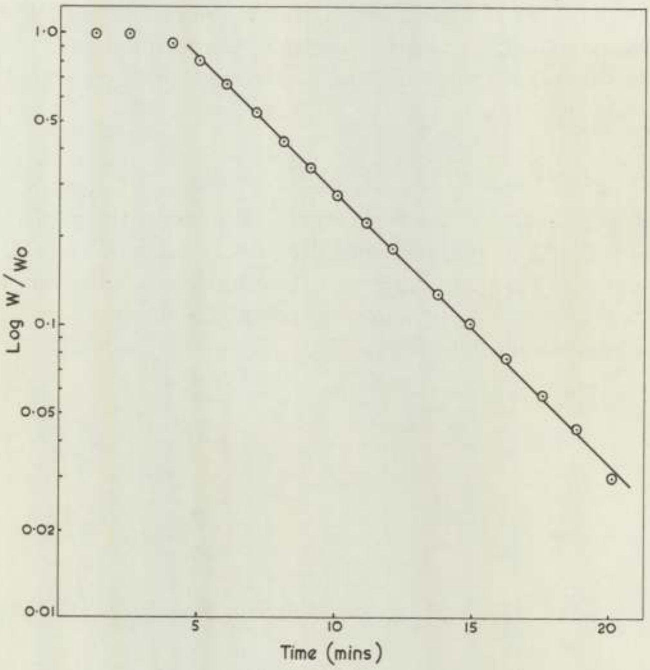


Fig. 4. First-order representation (log W/W_0 vs. time) of a typical isothermal thermogram.

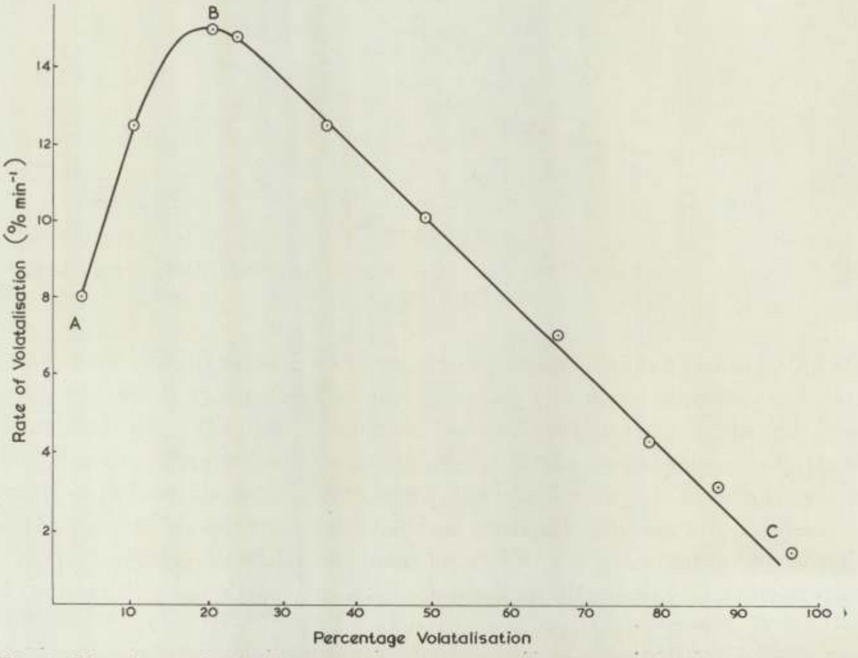


Fig. 5. Plot of rate of volatilization vs. percentage of sample volatilized for the degradation of poly(isopropylidene carboxylate) at 353°C in nitrogen.

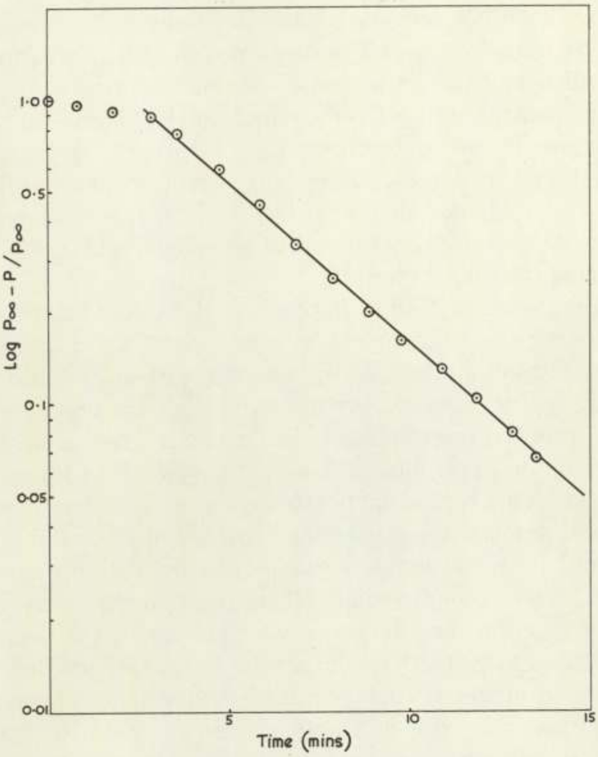


Fig. 6. Typical first-order representation as log $[(P_\infty - P)/P_\infty]$ vs. time, of gas evolution data for the degradation of poly(isopropylidene carboxylate).

Perhaps the most convincing demonstration of the predominance of first-order behavior is provided by the linearity (constant half-life) over two decades of Figure 4. Thermal equilibration is again apparent in the initial portion of the graph.

Gas evolution analysis results were similarly found to indicate the existence of a first-order process in that plots of log $[(P_\infty\text{-}P)/P_\infty]$ versus time were linear (Fig. 6). Here P is the pressure developed at any time by the formation of volatile degradation products, and P_∞ is the pressure corresponding to complete degradation of the polymer. The observed identity of the gas evolution results with those obtained by thermogravimetry has several implications. Some of these have been referred to in the preceding paper, the most significant of these in the present context being the absence of a rate-determining step involving secondary fragmentation of the primary decomposition products. In addition, since the gas evolution results are obtained in a closed system it indicates the absence of catalysis or inhibition of the primary decomposition process by degradation products.

Preliminary pyrolysis studies have shown that the predominant products of degradation in the range 250–750°C are tetramethyl glycollide, carbon monoxide, acetone, and in some circumstances methacrylic acid. The gas sampling GLC facilities previously described[1] enabled analysis of effluent from the thermogravimetry cell to be carried out at intervals during each run. No evidence of carbon monoxide or acetone was found at the lower end of the temperature range (250°C) used for the kinetic studies. As the temperature was increased however, their formation in progressively increasing quantity was noted. On cooling the gas evolution probe, a waxy condensate was isolated which was shown by infrared and mass spectroscopy to consist of acetone, tetramethyl glycollide, and methacrylic acid, the latter being the major product.

The results of product analysis in pyrolysis–GLC and kinetic experiments may conveniently be summarized at this point. Over a wide range of temperature, tetramethyl glycollide, acetone, carbon monoxide, and, to a lesser extent, methacrylic acid, are observed when the products are rapidly swept away from the reaction zone. As decomposition temperature is increased, tetramethyl glycollide takes on the role of an intermediate, the more stable products carbon monoxide and acetone being formed from it. At the highest temperatures examined, carbon monoxide begins to predominate, and its evolution is accompanied by the formation of small amounts of a carbonaceous residue. If the reaction products are allowed to remain in the reaction zone, however, which is possible at the lower end of the temperature range, methacrylic acid is the major product. One possible explanation of this is that tetramethyl glycollide can break down in two ways, carbon monoxide and acetone being formed by pyrolytic fragmentation and methacrylic acid by an acid-catalyzed elimination mechanism. The former process will be favored at higher temperatures and in pyrolysis–GLC experiments, whereas the latter will be favored as residence time of the decomposition products in the reaction zone increases. Thus gas evolution analysis experiments indicate that, whereas reaction products do not catalyze the primary polymer decomposition process, they provide conditions which favor the rapid (nonrate-determining) secondary decomposition of tetramethyl glycollide to methacrylic acid.

Rates of degradation of a series of polymers of different number average molecular weights were examined by isothermal thermogravimetry. Progressive deviation from first-order behavior was observed with samples having $\bar{M}_n < 10{,}000$. In such cases, however, it was possible, for comparison purposes, to obtain first-order rate constants from ~60% of the reaction. Polymers having $\bar{M}_n > 10{,}000$ showed relatively little sensitivity to molecular weight variation. The results are presented in Table II.

The effect of temperature on the rate of decomposition processes was examined. No significant deviation from first-order behavior was observed. The first-order rate constants and derived kinetic parameters obtained by thermogravimetry are shown in Table III and those calculated from gas evolution data in Table IV.

Although all preceding experiments were carried out in the complete absence of oxygen, studies of poly(isopropylidene carboxylate) decomposition in an atmosphere of oxygen were carried out to assess its effect. The

TABLE II

Effect of $\bar{M}_n$ on First-Order Rate Constants k for the Thermal Decomposition of Poly(isopropylidene Carboxylate) in Nitrogen

Temperature, °C	$\bar{M}_n$	k, sec^{-1}
353	2,720	1.73×10^{-2}
353	5,000	5.74×10^{-3}
353	12,000	3.74×10^{-3}
353	19,000	3.10×10^{-3}
353	19,500	2.90×10^{-3}
353	23,000	2.72×10^{-3}
353	30,000	2.66×10^{-3}

TABLE III

First-Order Rate Constants k, Energies of Activation E, Frequency Factors A, and Entropies of Activation S Obtained from Thermogravimetric Studies of Poly(isopropylidene Carboxylate) Decomposition in Nitrogen

Temperature, °C	k, sec^{-1}
260	4.2×10^{-4}
266	4.9×10^{-4}
280	1.0×10^{-3}
309	3.8×10^{-3}
324	7.4×10^{-3}
345	1.5×10^{-2}
E, kcal/mole	27.2
A, sec^{-1}	4.1×10^{7}
ΔS, cal/deg mole	−29

TABLE IV

First-Order Rate Constants k, Energies of Activation E, Frequency Factors A, and Entropies of Activation S Obtained from Gas Evolution Analysis of Poly(isopropylidene Carboxylate) Decomposition

Temperature, °C	k, sec^{-1}
253	8.4×10^{-4}
300	4.3×10^{-3}
324	1.4×10^{-2}
339	2.2×10^{-2}
346	3.8×10^{-2}
374	5.3×10^{-2}
E kcal/mole	28.3
A, sec^{-1}	2.6×10^{8}
ΔS, cal/deg-mole	−24

results are typified by those at 265°C. At this temperature in triplicate runs the values obtained were:

$$k = 4.5 \pm 0.3 \times 10^{-4}\ \text{sec}^{-1}\ \text{(nitrogen)}$$

and

$$k = 12.5 \pm 0.3 \times 10^{-4}\ \text{sec}^{-1}\ \text{(oxygen)}$$

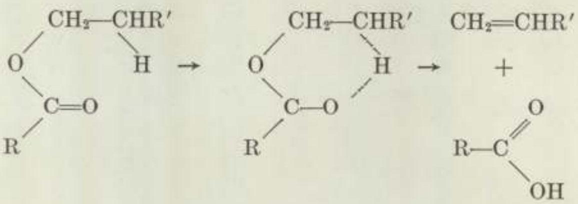
DISCUSSION

The requirements of the kinetic and analytical results exert a considerable restriction on the characteristics of the mechanism which can be proposed for the thermal decomposition of poly(isopropylidene carboxylate). We may consider the following types of reactions to represent all possibilities: (a) random homolytic or heterolytic chain scission, possibly followed by chain depolymerization from the scission site; (b) inter- or intramolecular ester interchange; (c) chain depolymerization or "unzipping" from the chain ends; (d) molecular decarboxylation or decarbonylation, possibly accompanied by chain recoupling.

Of these, molecular decarboxylation or decarbonylation cannot be of major importance in the lower (<400°C) temperature range, because it cannot account for the predominance of tetramethyl glycollide formation. Similarly, on the basis of the results summarized in Table II, chain depolymerization must be discounted as the major route except in the case of lower molecular weight polymer, where the chain-end concentration is high. The general weight of evidence suggests that radical reactions resulting from homolytic scission are of little importance below 400°C, although they become quite feasible in the higher temperature range (>600°C). An ionic heterolytic scission process is energetically improbable under the conditions used although a molecular dipolar process might be acceptable. A very specific process in which tetramethyl glycollide is eliminated in the rate-determining step is required, however, to account for the degradation characteristics of high molecular weight polymer. Of the ester interchange processes, only the intramolecular exchange would give the required first-order kinetic behavior coupled with tetramethyl glycollide formation, and it is this, or a dipolar scission step which seems to offer the most accurate description of the decomposition.

In addition to the general molecular requirements of the experimental observations, it is relevant to take into consideration the energetics of ester decomposition based on model compound studies. Investigation of the kinetics of simple ester decomposition reactions have shown[10,11] that they are homogeneous, show first-order behavior in both liquid and vapor phase, and are unaffected by radical scavengers. Observed activation energies for ester pyrolysis were around 40 kcal/mole, whereas theoretical values for direct thermal scission of the ester linkage are in the region of 60 kcal/mole.

The lower experimental values are generally taken to indicate the existence of a cyclic transition state (III).[12]

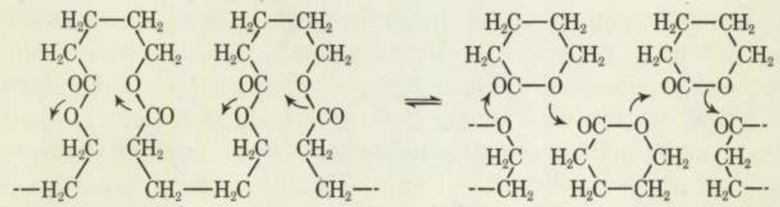


(2)

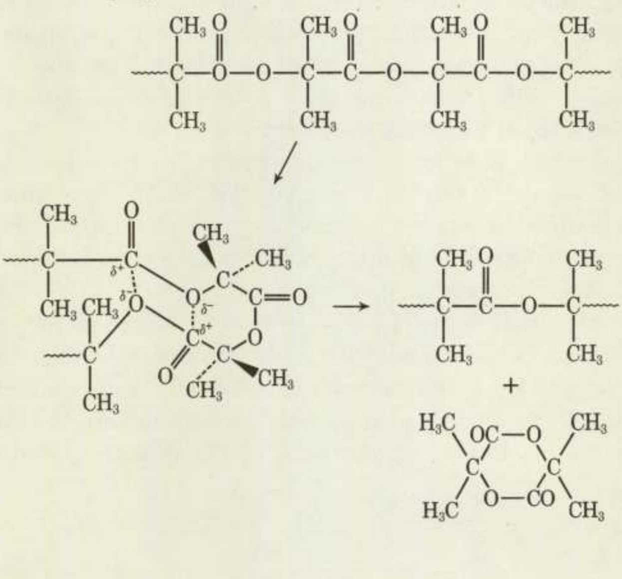
III

Activation energies of 27.2 and 28.3 kcal/mole for the degradation of poly(isopropylidene carboxylate) indicate a similar situation leading to the formation of tetramethyl glycollide. The fact that these values are even lower than those obtained for simple ester pyrolysis could be taken as evidence that the poly-α-ester chain contains linkages more susceptible to degradative attack (such as points of weakness introduced during polymer synthesis). Alternatively, and more probably, the lower activation energy could indicate the existence of an energetically preferred degradation process which is structurally possible in poly(isopropylidene carboxylate) decomposition but not in simple ester pyrolysis.

Hine[12] puts forward evidence for the multicenter type of mechanism (via transition state of type III), which includes first-order kinetics and negative entropy of activation. These conditions are satisfied for the degradation of poly(isopropylidene carboxylate) and are further reinforced by the fact that tetramethyl glycollide is a major product of the degradation. Bearing these facts in mind we believe that an intramolecular ester interchange provides the most accurate description of the process which predominates when chain end concentration is low. This type of mechanism has been suggested by Stannett and Szwarc[13] in connection with the reversible polymerization of six-membered lactone rings. He suggested that spatial configurations of liquid monomer units and polymer chains are very similar and that the process may take place with little or no movement of the carbon centers [eq. (3)].


(3)

Extending these ideas to poly(isopropylidene carboxylate), the mechanism presented in eq. (4) correlates well with observed kinetic behavior and


(4)

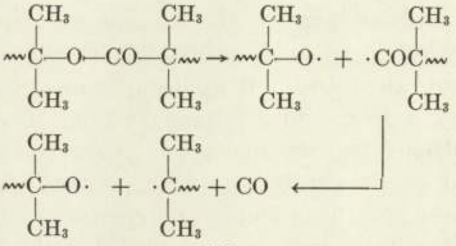
explains the formation of tetramethyl glycollide by the type of dipolar process which is likely to be favored over the temperature range studied. The mechanism also implies a relatively slow lowering of molecular weight with time which accords well with the persistence of first-order behavior throughout much of the reaction (Fig. 4). The formation of ring structures in polymer degradation has been reported by several authors, the most important of which have been previously summarized.[1]

The frequency factor A, is normally factorized into a collision number Z and steric factor p. The magnitude of Z in solution has been shown to be substantially that calculated from the kinetic theory of gases, i.e., $\sim 10^{12}$. Changes in pZ over several powers of 10 are normally attributed to changes in p. Thus the lower values of A (Tables III and IV) indicate a fairly high degree of steric order, which is in good accord with the mechanism proposed. Viewed in terms of the requirements of the substantial negative entropy of activation (Tables III and IV) such a mechanism possessing as it does an ordered, highly polar, transition state, is quite consistent with the values obtained.

This mechanism offers the advantages of satisfying the experimentally determined kinetic and analytical requirements and conforms to previously accepted ideas on the general form of this type of decomposition. It is interesting to note that an essentially similar four-center mechanism has been recently proposed[14] to account for the formation of cyclic tetramer from polydimethylsiloxane.

Although it is unlikely that a free-radical process plays any appreciable part in the decomposition of poly(isopropylidene carboxylate) over the temperature range used for kinetic studies, such reactions undoubtedly become more important at higher temperatures. The observation that carbon monoxide and acetone become the major decomposition products at the expense of tetramethyl glycollide as the temperature is raised accords well with the work of Ritchie.[15] In studying the pyrolysis of various glycollides at 500°C, he reported a near-quantitative fragmentation of tetramethyl glycollide by a concerted molecular mechanism. Additional studies in the presence of a free-radical scavenger demonstrated that a competing radical process was also involved, but to a relatively minor extent. It is also relevant to note that at this temperature relatively little evidence of the expected scission to methacrylic acid was found.

These observations provide sound evidence for the view that at temperatures above 400°C tetramethyl glycollide begins to assume the role of an unstable intermediate giving rise to acetone and carbon monoxide formation. In addition, and taken together with the results of pyrolysis–GLC work (Fig. 3) at the highest temperatures studied (650–750°C), they support the view that radical fragmentation becomes more important under these conditions. The increased tendency towards carbon monoxide formation together with the appearance of carbonaceous char is no doubt partially due to the well-known fragmentation of acetone to carbon monoxide, but probably more extensively to processes of the type described by eq. (5).



$$\sim C(CH_3)_2{-}O{-}CO{-}C(CH_3)_2\sim \;\rightarrow\; \sim C(CH_3)_2{-}O\cdot + \cdot COC(CH_3)_2\sim \;\rightarrow\; \sim C(CH_3)_2{-}O\cdot + \cdot C(CH_3)_2\sim + CO \qquad (5)$$

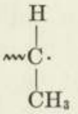
IV

This is effectively identical to the mechanism suggested by Zhuravleva and Rode[16] [eq. (6)] to account for the increased yield of carbon monoxide from

$$ROCOR' \rightarrow RO + \cdot COR' \rightarrow RO\cdot + R' + CO \qquad (6)$$

certain polyaryl esters at temperatures above 400°C.

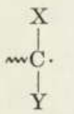
The circumstantial support provided by Ritchie's work for this type of process is quite strong and can best be viewed in terms of steric stabilization of the radical of structure IV. He found that, whereas 1,1,4,4-tetramethyl glycollide showed some sensitivity to radical scavengers, 1,4-dimethyl glycollide (lactide) was completely unaffected, presumably due to the lower stability of the radical of structure V, which is therefore not formed.



$$\sim C(H)(CH_3)\cdot$$

V

A parallel case of radical stabilization is observed in the decomposition of substituted olefinic polymers, where the extent of depolymerization to monomer is related to the stability of the radical VI produced on chain scission.



$$\sim C(X)(Y)\cdot$$

VI

Thus in the case of poly(methyl methacrylate) (X = Me; Y = COOMe), combined steric and electronic factors lead to high radical stability and virtually quantitative depolymerization to monomer. On the other hand, the terminal radical produced from polypropylene (X = Me; Y = H) is of very low stability, and consequently little monomer is produced on degradation. Introduction of a second methyl substituent as in the case of polyisobutylene (X = Y = Me) leads to enhanced radical stability, however, and to a substantial (approximately tenfold) increase in the yield of monomer produced on degradation.

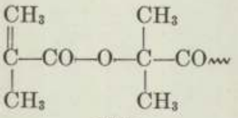
Oxygen was found to increase the rate of poly(isopropylidene carboxylate) degradation to some extent at 266°C, consistent with the enhancement of a radical process. It appears, however, that since the increase in first-order rate constant is only twofold on changing from an atmosphere of nitrogen to one of oxygen, the contribution of radical processes initiated or accelerated by traces of adventitious oxygen is negligible. This confirms the potential existence of radical processes in the degradation of this polymer and demonstrates that they are relatively unimportant under the conditions described here for kinetic studies.

In addition to the postulated intramolecular ester interchange process, the elimination of tetramethyl glycollide could also occur via alcoholysis or acidolysis taking place specifically from chain ends. In this way, intramolecular ester interchange reactions will have a reaction involving unzipping from chain ends superimposed upon it. These acidolysis and alcoholysis reactions will be bimolecular processes but kinetically first-order with respect to residual polymer. The net effect is shown in eq. (7), where f is a factor to account for the relative efficiency of carboxyl and

$$-dW/dt = k_1W + k_2W(f/\bar{M}_n) \tag{7}$$

hydroxyl ends.

Table II shows the variation in overall rate constant with molecular weight for the decomposition of poly(isopropylidene carboxylate). The results show that only at high chain end concentration (i.e., low molecular weight) is the overall rate constant markedly affected, presumably due to increased contribution from k_2. At higher values of $\bar{M}_n$, the overall rate constant approaches k_1. Substantially, the same arguments apply to dehydration of hydroxyl-terminated chain ends to form VII, followed by elimination of methacrylic acid fragments.



$$\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\overset{\|}{\mathrm{C}}}}\text{—CO—O—}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\text{—CO}\sim$$

VII

Although this process, involving as it does the well-known β-hydrogen-elimination ester-decomposition mechanism,[11,12] is undoubtedly feasible, the results indicate that the contribution is small in decomposition of high molecular weight polymer.

EXPERIMENTAL

Poly(isopropylidene carboxylate) samples were synthesized and characterized by techniques previously described.[6]

Pyrolysis–GLC experiments were carried out by using apparatus described in the previous paper.[1] A 10-ft column packed with poly(ethylene glycoladipate) on 80–100 mesh firebrick support was used. Data presented in Figure 2 were obtained with a column temperature of 200°C and those in

Figure 3 with a temperature of 120°C. In both cases a nominal flow rate of 100 ml/min was used.

Kinetic experiments were carried out by using the thermogravimetric and gas evolution analysis techniques described in the previous paper[1] under the various conditions specified in the text.

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Poly-α-ester Degradation Studies. III. Effect of β-Chlorination on Polymer Degradation

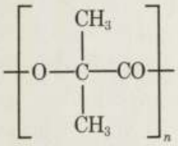
A. PATTERSON, G. J. SUTTON and B. J. TIGHE, *Department of Chemistry, The University of Aston in Birmingham, Gosta Green, Birmingham, B4 7ET, England*

Synopsis

The thermal degradation of two β-chlorinated versions of poly(isopropylidene carboxylate) has been studied by the combined thermogravimetric and gas evolution techniques described previously. Poly(3-chloro-2-methyl-2-hydroxypropionic acid) was found to decompose by a predominantly first-order process which was characterized by kinetic parameters similar to those obtained for poly(isopropylidene carboxylate). These are interpreted in terms of an intramolecular ester-exchange process. As the reaction proceeds intermolecular elimination of hydrogen chloride leads to crosslinking and ultimately to the formation of a carbonaceous char. This process is much more marked in the randomly β-chlorinated analog of poly(isopropylidene carboxylate). With this polymer, drastic deviation from first-order behavior is observed in thermogravimetric results, even in the early stages of reaction. Gas evolution analysis, being more influenced by degradation fragments having an appreciable vapor pressure, yields reasonable first-order data and indicates that the intramolecular interchange mechanism is still an important process. In general, the introduction of β-chlorine atoms is seen to reduce the rate of thermal decomposition of poly-α-esters.

INTRODUCTION

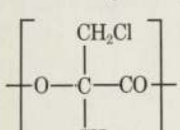
In a preceding paper[1] we have described in detail the thermal degradation of poly(isopropylidene carboxylate) (I):



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

I

We now present results of thermal degradation studies on polymers of the above type which have chlorine substituents in the β position. The polymers examined during the course of this work were: (a) the monochlorinated polymer, poly(3-chloro-2-methyl-2-hydroxypropionic acid) (II),



$$\left[-O-\overset{\displaystyle CH_2Cl}{\underset{\displaystyle CH_3}{C}}-CO- \right]_n$$

II

and (b) a randomly chlorinated polymer derived from poly(isopropylidene carboxylate) and containing monochloromethyl and dichloromethyl in addition to residual parent methyl substituents.

Replacement of methyl substituents by chloromethyl has been shown to have a profound effect on other short repeat unit heterochain polymers, particularly in terms of melting point, glass transition temperature, and to some extent thermal stability. Particular interest in the polymers studied here stems from the synthetic difficulties encountered in direct synthesis of the chlorinated polymers from the appropriate chlorinated anhydrosulfite[2,3] compared with the relative ease of direct chlorination of the readily obtainable poly(isopropylidene carboxylate).[4]

EXPERIMENTAL

Preparation of Polymers

Poly(3-chloro-2-methyl-2-hydroxypropionic acid) (II) was synthesized from the anhydrosulfite of α-hydroxy-β-chloroisobutyric acid.[2] The randomly chlorinated polymer was prepared by the direct chlorination of poly(isopropylidene carboxylate).[5,6]

Analysis of Polymers

NMR analysis of the randomly chlorinated polymer showed that methyl, chloromethyl, and dichloromethyl groups were present in approximately equal abundance.[6] The monochlorinated polymer was similarly shown to have the structure represented as II.

The x-ray diffraction studies showed that the polymers were amorphous as prepared. The melting process was poorly characterized but was in the case of both polymers complete by 250°C. Because of their noncrystalline nature, these poly-α-esters were readily soluble in a range of organic solvents, thus enabling molecular weight distributions to be characterized by gel-permeation chromatography in tetrahydrofuran. Whereas poly(3-chloro-2-methyl-2-hydroxypropionic acid) possessed the $\bar{M}_w/\bar{M}_n$ ratio typically associated with polymers prepared from anhydrosulfites (ca. 1.5) the randomly chlorinated polymer had a somewhat broader distribution ($\bar{M}_w/\bar{M}_n \sim 2.5$) with an appreciable low molecular weight tail.

RESULTS

Thermal Degradation of Poly(3-chloro-2-methyl-2-hydroxypropionic Acid)

Various kinetic aspects of the thermal degradation of poly(3-chloro-2-methyl-2-hydroxypropionic acid) (PCMHP) were studied by using combined thermogravimetric and gas evolution techniques described in Part I of this series.[7] Samples of polymer having number-average molecular weights of 20,000 were used, and experiments were carried out isothermally in nitrogen unless otherwise stated.

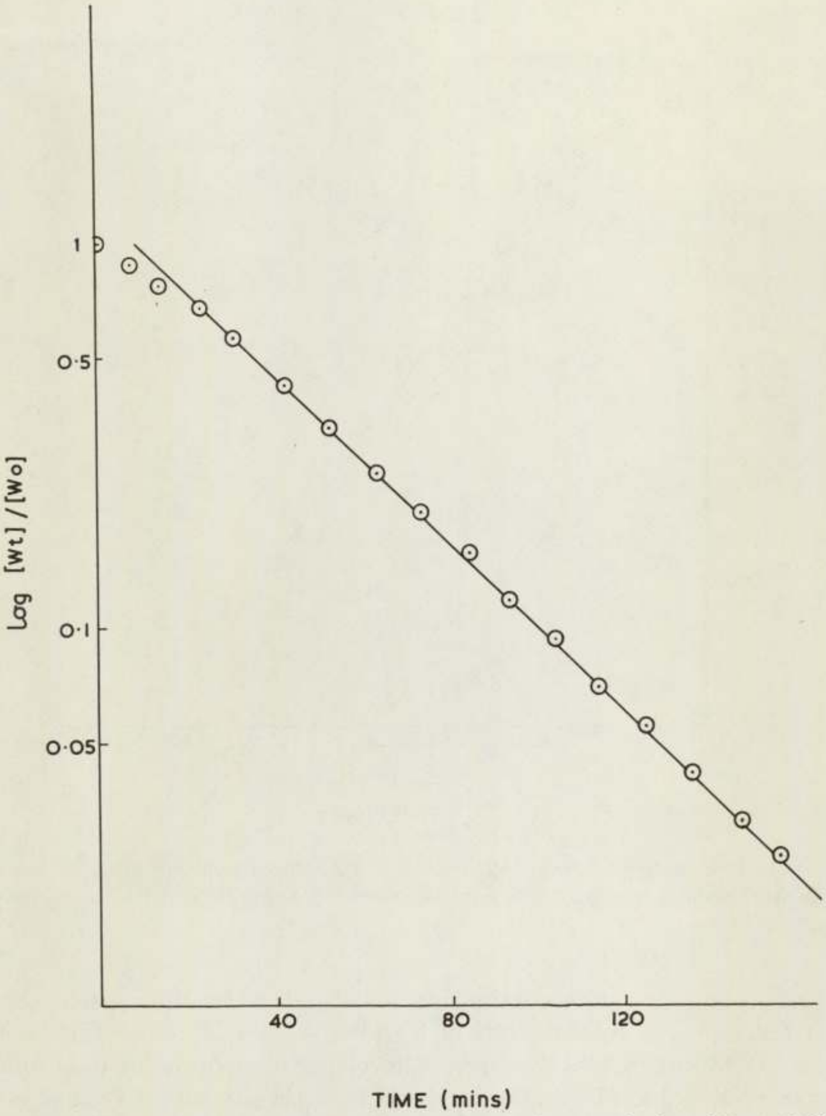


Fig. 1. Degradation of poly(3-chloro-2-methyl-2-hydroxypropionic acid) at 292°C in an atmosphere of nitrogen. First-order representation (log $[W_t]/[W_0]$ vs. time) of thermogravimetric results.

The application of the Wilhelmy equation to thermogravimetric results in a manner identical to that described in Part II of this series[1] confirmed that the decomposition of the polymer under the above conditions was predominantly first-order. The results were represented graphically in the form log $[W_t]/[W_0]$ versus time where $[W_0]$ and $[W_t]$ are the weights of polymer present initially and at time t, respectively. A typical example shown in Figure 1 demonstrates that the reaction is substantially first-order by the linearity (constant half-life) into the second decade.

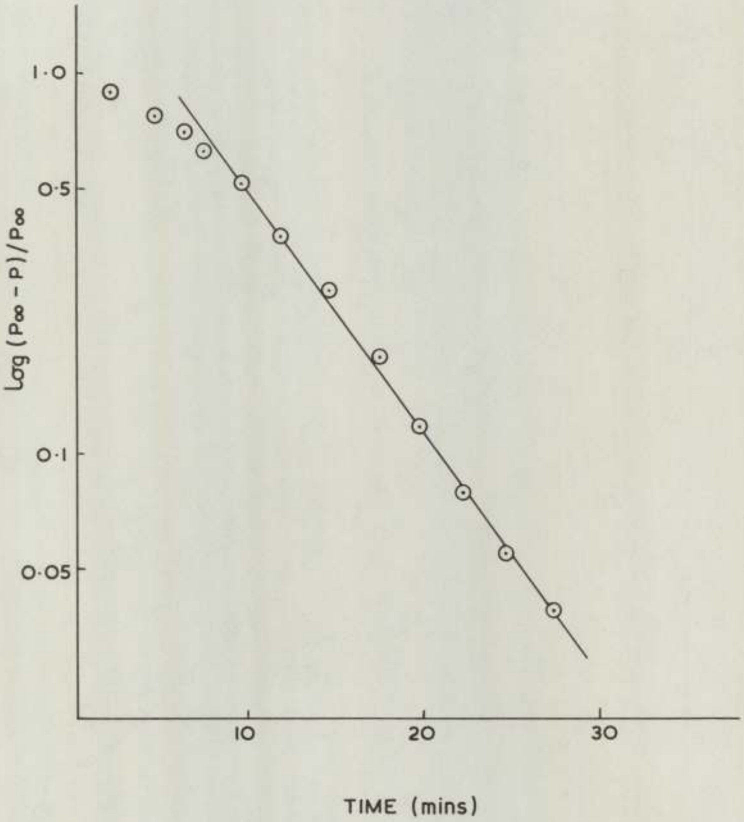


Fig. 2. Degradation of poly(3-chloro-2-methyl-2-hydroxypropionic acid) at 315°C in an atmosphere of nitrogen. First-order representation (log $[(P_\infty - P)/P_\infty]$ vs. time) of gas evolution results.

Gas evolution results were similarly found to indicate the existence of a first order process in that plots of $\log[(P_\infty - P)/P_\infty]$ versus time were linear (Fig. 2) where P is the pressure developed at any time by the formation of volatile degradation products and P_∞ is the pressure developed corresponding to complete degradation of the polymer.

The effect of temperature on the rate of the decomposition process was examined by using the above techniques. No significant deviation from first-order behavior was observed over the temperature range studied. First-order rate constants and derived kinetic parameters obtained by thermogravimetry and those calculated from gas evolution data are shown in Tables I and II, respectively. The results of both techniques are compared in the form of a single Arrhenius plot in Figure 3.

No experiments carried out in oxygen have been described, since these had indicated some deviation from first-order behavior. This aspect of the decomposition of β chlorinated poly-α-esters is described in Part IV of this series.[8]

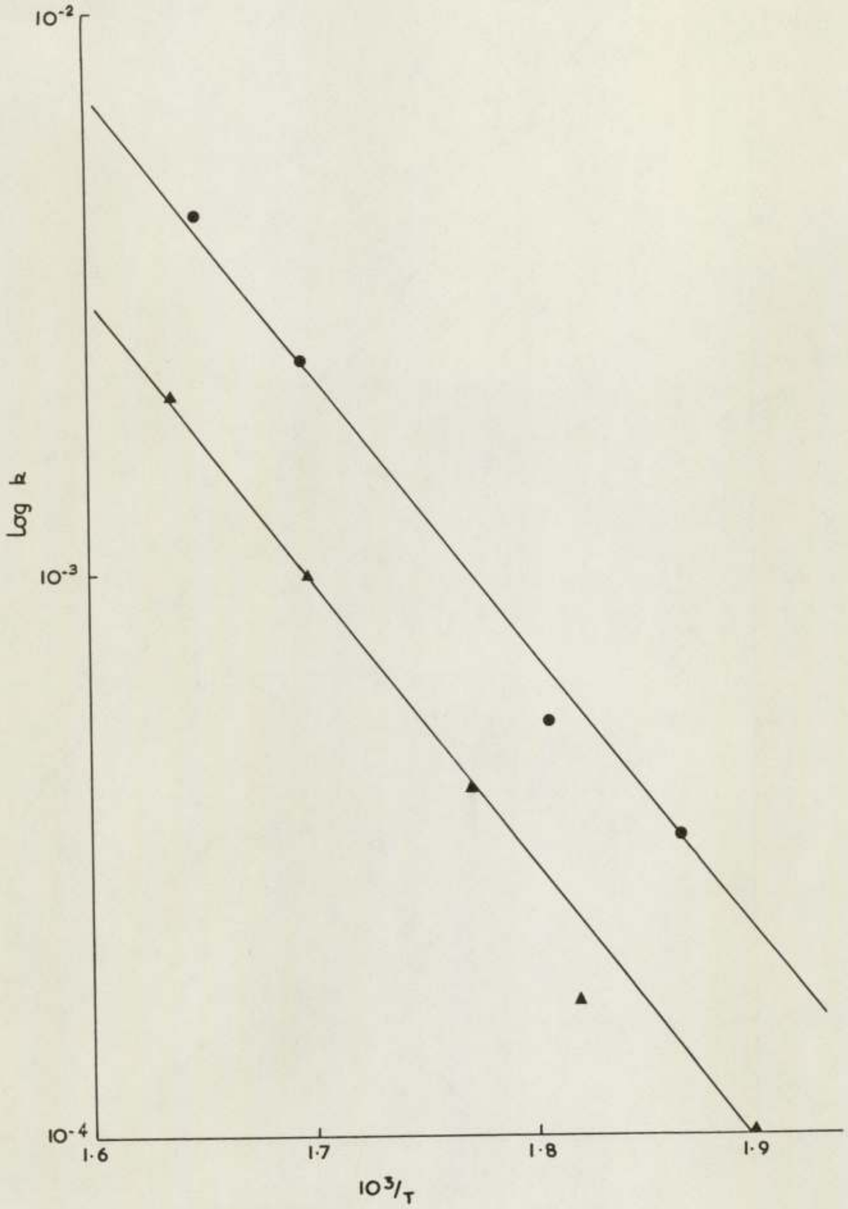


Fig. 3. Arrhenius plot showing (▲) thermogravimetric and (●) gas evolution results for a sample of poly(3-chloro-2-methyl-2-hydroxypropionic acid) of $\bar{M}_n \sim 20{,}000$.

The rate of degradation of poly(3-chloro-2-methyl-2-hydroxypropionic acid) was found to be more sensitive to molecular weight variation than poly(isopropylidene carboxylate). Figure 4 summarizes results obtained by gas evolution analysis for polymer having an $\bar{M}_n$ value of ~10,000. Thermogravimetry on the same polymer showed a similar trend.

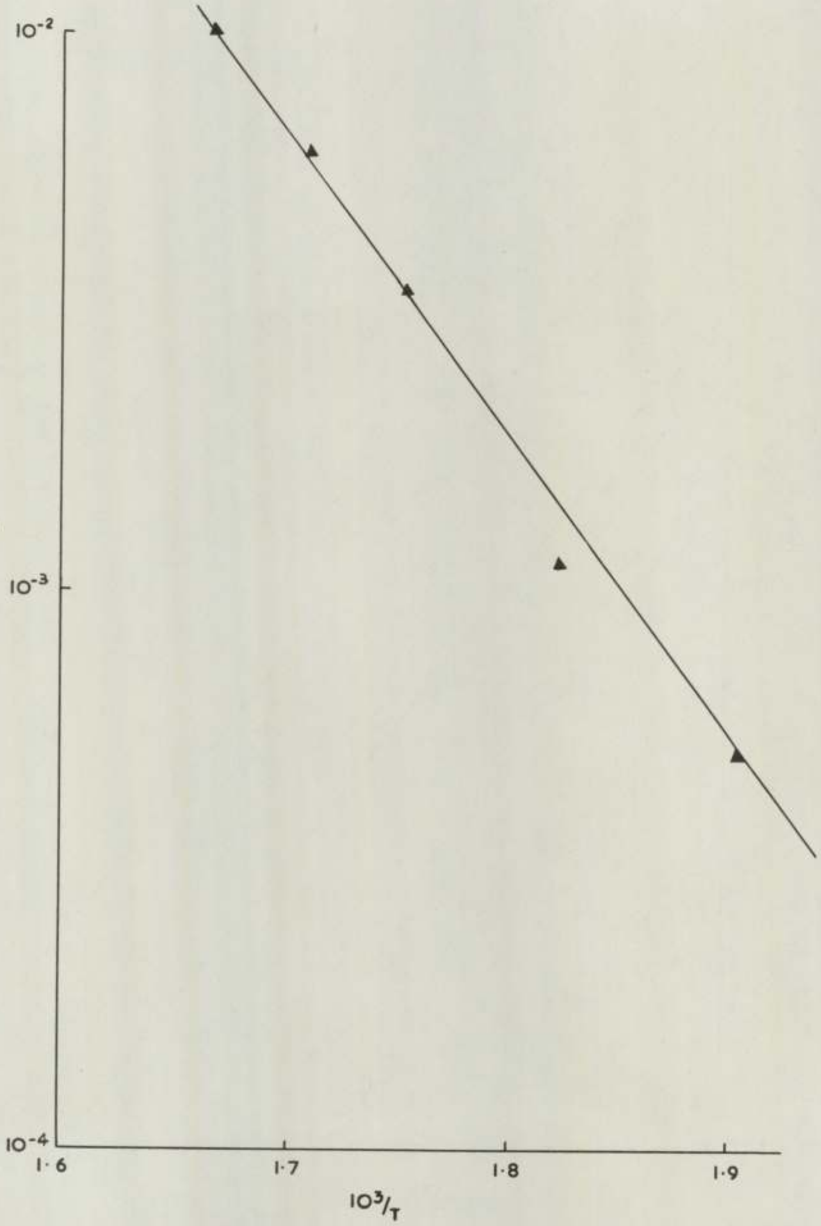


Fig. 4. Arrhenius plot showing gas evolution results for a sample of poly(3-chloro-2-methyl-2-hydroxypropionic acid) of $\bar{M}_n \sim 12{,}000$.

Product analysis over the temperature range studied showed that hydrogen chloride, a carbonaceous residue, and a compound having a glycollidic structure were the primary products of degradation. The carbonaceous residue which formed 20–25% by weight of the total products was shown to consist in the main of carbon, oxygen, and hydrogen. Table III

TABLE I

First-Order Rate Constants k, Energy of Activation E, Frequency Factor A, and Entropy of Activation $\Delta S\ddagger$ Obtained from Thermogravimetric Studies of the Decomposition of Poly(3-chloro-2-methyl-2-hydroxypropionic Acid) in Nitrogen

Temperature, °C	k, sec^{-1}
253	1.00×10^{-4}
276	1.86×10^{-4}
292	4.31×10^{-4}
315	1.00×10^{-3}
337	2.16×10^{-3}
E, kcal/mole	24.6
A, sec^{-1}	3.0×10^{6}
$\Delta S\ddagger$, cal/deg-mole	−34

TABLE II

First-Order Rate Constants k, Energy of Activation E, Frequency Factor A, and Entropy of Activation $\Delta S\ddagger$ Obtained from Gas Evolution Analysis of the Decomposition of Poly(3-chloro-2-methyl-2-hydroxypropionic Acid) in Nitrogen

Temperature, °C	k, sec^{-1}
263	3.54×10^{-4}
281	5.65×10^{-4}
315	2.47×10^{-3}
334	4.38×10^{-3}
384	2.38×10^{-2}
E, kcal/mole	24.3
A, sec^{-1}	3.1×10^{6}
$\Delta S\ddagger$, cal/deg-mole	−36

TABLE III

Percentage Weight and the Composition of Carbonaceous Residue Formed during the Thermal Decomposition of Poly(3-chloro-2-methyl-2-hydroxypropionic Acid) at Various Temperatures in Nitrogen

Temperature, °C	Residue formed, wt-%	Carbon in residue, wt-%	Hydrogen in residue, wt-%
326	25.7	—	—
353	19.4	51.7	4.2
395	20.5	—	—

summarizes the analysis carried out on the residue. Attempts were made to remove samples during the course of the reaction and follow the progress of crosslinking by isolation of the insoluble gel formed in chloroform. The results indicated that gel formation was negligible below 60% decomposition but that it increased rapidly thereafter. This information was too imprecise to be of great value, although it does correlate with the general form of the rheological studies presented in Part IV of this series.[8]

For the major part of the reaction, then, the glycollidic compounds and the secondary decomposition products formed from them[1] predominated.

Thermal Degradation of Randomly Chlorinated Poly(isopropylidene carboxylate)

The thermal degradation of this polymer was studied by using techniques and conditions similar to those employed for the study of poly(3-chloro-2-methyl-2-hydroxypropionic acid) decomposition.

Samples of the polymer having number-average molecular weights of 12,000 were used, and experiments were carried out isothermally in nitrogen unless otherwise stated.

Analysis of thermogravimetric results indicated that decomposition processes were no longer first-order. A typical plot is shown in Figure 5.

Results of gas evolution analysis, however, showed fairly good first-order dependence, in that plots of log $[(P_\infty - P)/P_\infty]$ versus time were substantially linear (Fig. 6). Table IV summarizes first-order rate constants and derived kinetic parameters obtained by gas evolution data.

Results obtained by product analysis were qualitatively similar to those obtained for poly(3-chloro-2-methyl-2-hydroxypropionic acid) but considerably more complex.

TABLE IV

First-Order Rate Constants k, Energy of Activation E, Frequency Factor A, and Entropy of Activation $\Delta S\ddagger$ Obtained from Gas Evolution Analysis of Randomly Chlorinated Poly(isopropylidene Carboxylate) Decomposition in Nitrogen

Temperature, °C	k, sec^{-1}
273	1.03×10^{-3}
279	1.34×10^{-3}
291	3.72×10^{-3}
293	4.10×10^{-3}
304	6.13×10^{-3}
304	5.43×10^{-3}
315	6.33×10^{-3}
328	1.12×10^{-2}
339	1.67×10^{-2}
351	2.20×10^{-2}
351	2.76×10^{-2}
363	4.17×10^{-2}
E, kcal/mole	21.5
A, sec^{-1}	1.3×10^{6}
$\Delta S\ddagger$, cal/deg mole	-30

DISCUSSION

The thermal decomposition of poly(isopropylidene carboxylate) has been shown to occur by a first-order process involving predominantly a dipolar intramolecular ester interchange process leading to tetramethyl glycollide as one of the major primary products of degradation.[1] Comparison of the various kinetic parameters calculated for poly(isopropylidene carboxylate) and poly(3-chloro-2-methyl-2-hydroxypropionic acid) coupled with product analysis indicates that the degradation of the two polymers involves similar mechanisms. Despite the basic similarity. however, it is clear that additional complications are encountered in the decomposition of the chlorine containing polymer. The greater stability of this polymer, its tendency to eliminate hydrogen chloride yielding an involatile residue, and the greater

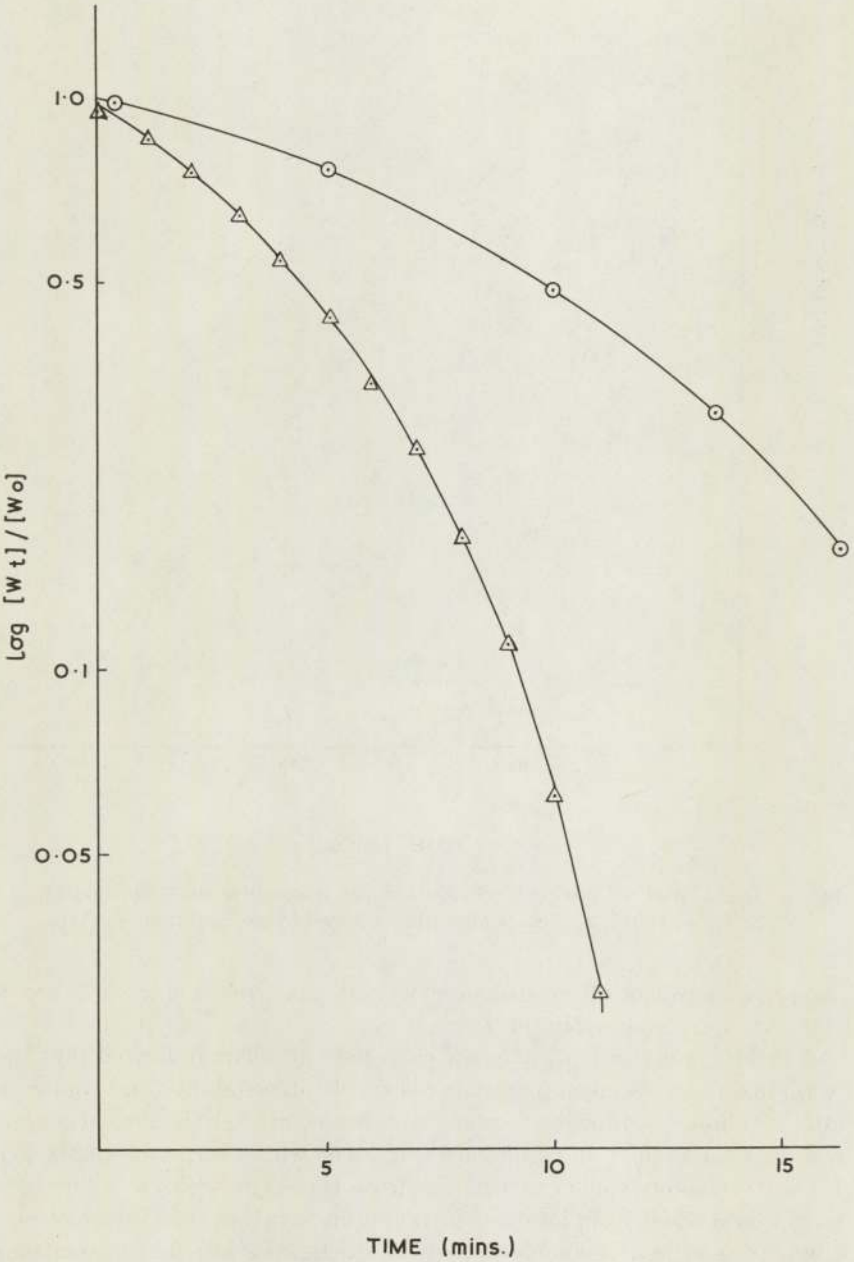


Fig. 5. Degradation of randomly chlorinated poly(isopropylidene carboxylate): (⊙) 298°C; (△) 306°C. Reaction profiles obtained by thermogravimetry.

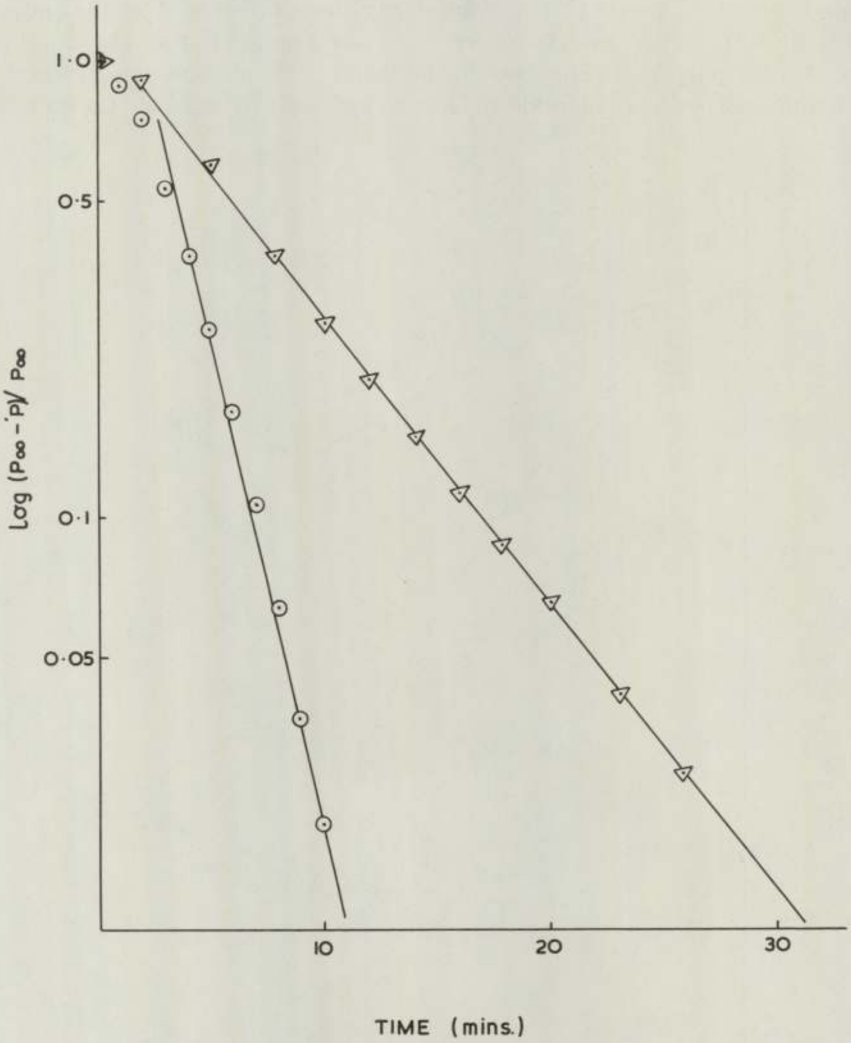
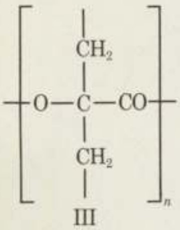


Fig. 6. Degradation of randomly chlorinated poly(isopropylidene carboxylate): (Δ) 273°C; (⊙) 291°C. Reaction profiles obtained by gas evolution analysis.

disparity between thermogravimetric and gas evolution results are all factors to be considered in this respect.

A careful analytical study of the carbonaceous chars indicated that they were, in fact, crosslinked materials of considerable stability and containing ester residues. Although the material is not completely homogeneous with respect to structure, all results are consistent with a structure of the type III, with possibly some contribution from the spiro form IV. The latter form would result from localized intramolecular rather than intermolecular elimination of hydrogen chloride but its existence is at present a matter of speculation.



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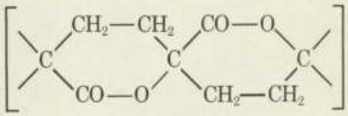


IV

The elimination of hydrogen chloride with formation of crosslinked residual material undoubtedly involves processes of a free-radical nature. These are superimposed upon the predominant first-order elimination process leading to glycollidic fragments as the primary decomposition product. The kinetic techniques employed here are more sensitive to the latter process, although trapped hydrogen chloride may produce some acid-catalyzed degradation in a sealed system and thereby may cause the slight increase in rate constant observed with gas evolution analysis.

There is nonetheless a noticeable increase in stability upon the introduction of a single chlorine atom per repeat unit of poly(isopropylidene carboxylate). It is undoubtedly the intramolecular elimination which is affected, and that significantly, right from the outset of the reaction. The increase in stability is, therefore, not dependent upon the progressive crosslinking which does not become effective until the later stages of the reaction.[8]

It can be argued that the chloromethyl substituent will render the carbonyl carbon of the repeat unit more susceptible to nucleophilic attack. This is certainly true, and if it were the only effect would increase rather than decrease the rate of thermal decomposition of the chlorinated polymer.

It is apparent that the electronic effect of the chloromethyl substituents on the carbonyl groups is swamped by the mutual repulsion of these groups and the restriction that this imposes on the formation of the cylic intermediate. The overall effect is not a large one, as evidenced by the relative stabilities of all three polymers compared in a temperature-based thermogram (Fig. 7).

Although the degradation rates fall into a well-defined order at higher temperatures, the thermogram profile of the randomly chlorinated polymer shows some peculiarities in the low temperature region. Thus, although this polymer appears to be the most stable at higher temperatures, it also shows a more marked tendency to decomposition in the region of 300°C.

In addition, this is the only polymer which gives isothermal thermogravimetric reaction profiles which show appreciable deviation from first-order behavior.

This is not surprising, since one requirement for first-order behavior in the mechanism under consideration[1] is a regular backbone structure, and this is the only one of the three polymers not possessing that requirement. The other major difference between the randomly chlorinated polymer and the others lies in molecular weight distribution. The direct chlorination tech-

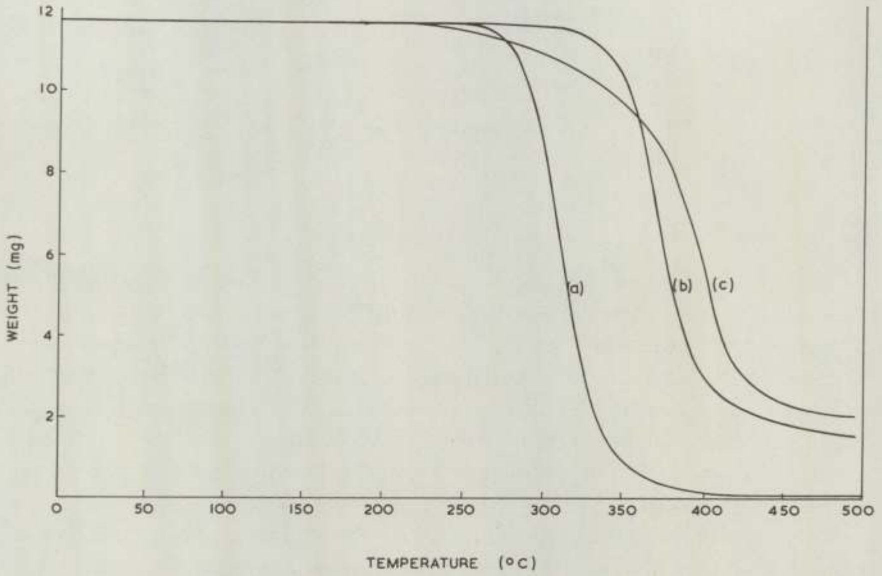
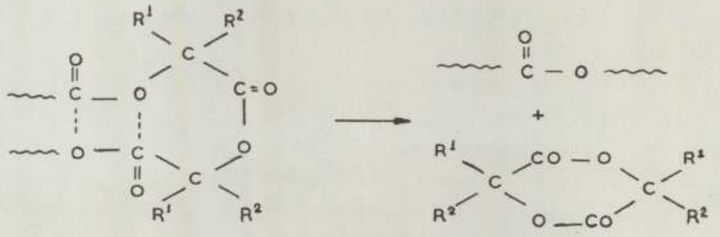


Fig. 7. Relative stabilities of poly(isopropylidene carboxylate); (*a*), poly(3-chloro-2-methyl-2-hydroxypropionic acid); (*b*) randomly chlorinated poly(isopropylidene carboxylate); (*c*) compared by TGA (10° C/min, flowing nitrogen.)

nique results in some chain scission with consequent broadening of distribution. The predominant feature of this is a longer low molecular weight tail which, given the molecular weight dependence observed with this type of mechanism,[1] leads to a more marked tendency to decomposition at low temperatures (i.e., ~300°C).

Despite the abnormality of the thermogravimetric results we believe that the gas evolution results are quite valid and reflect genuine first-order behavior. The reason for the difference is seen in the fact that the latter technique, unlike the former, is specific to processes which liberate fragments having an appreciable vapor pressure, sensitivity being proportional to volatility. Since the more highly chlorinated segments will produce less volatile fragments gas evolution analysis will be more specific for the unchlorinated and monochlorinated segments. Support for this view is seen in the activation parameters (Table IV) which are comparable to those obtained with the dimethyl[1] and the monochlorinated polymers (Tables I and II) and reflect a dipolar process involving a fairly high degree of steric order. The implication is that even in the randomly chlorinated

Eq. 1



polymer the intramolecular ester-interchange reaction represented by eq. (1) is still a major process. Information about the interrelation of molecular weight, melt viscosity, and chain end effects together with a more accurate assessment of the development of crosslinked structures can be obtained from rheological studies of the residual polymer melt. This aspect of the work is discussed in Part IV of the series.[8]

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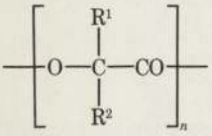
Poly α-Ester Degradation Studies.
IV. Rheological Studies of Polymer Degradation

A. J. LOVETT, W. G. O'DONNELL, G. J. SUTTON, and
B. J. TIGHE, *Department of Chemistry, The University of Aston,*
Gosta Green, Birmingham, B4 7ET, England

Synopsis

The Farol-Weissenberg rheogoniometer has been used to follow molecular weight changes during the degradation of certain poly-α-esters in the melt state. By observing the change in melt viscosity at low shear rates it had been shown that the decomposition of the poly(isopropylidene carboxylate) is substantially first-order with respect to the molecular weight of the residual polymer. The derived kinetic parameters are in good agreement with those previously obtained by other techniques. This provides a substantial piece of supporting evidence for the view that degradation takes place predominantly by intramolecular ester interchange involving the formation of 1,1,4,4,-tetramethylglycollide. The introduction of β-chlorine atoms into the polymer structure leads to a more complex degradation pattern. Thus the presence of a single β chlorine atom per repeat unit, as in poly(3-chloro-2-methyl-2-hydroxypropionic acid) leads to a substantially similar dependence on molecular weight with the added complication of progressive crosslinking which becomes more apparent in later stages of the reaction. This crosslinking reaction plays an increasingly important part as the extent of chlorination of the polymer is increased. In addition, the presence of chlorine leads to an increased sensitivity of the degradation reaction to the presence of oxygen.

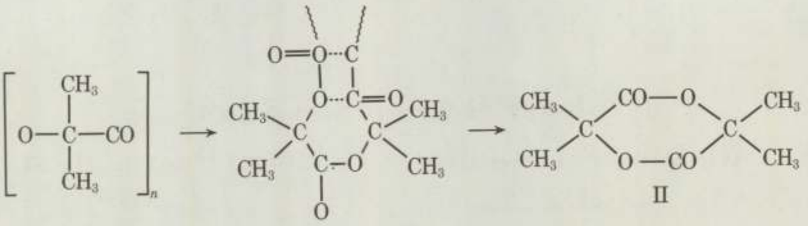
In previous papers in this series we have described equipment which enables thermogravimetric and gas evolution kinetic analysis to be used in conjunction with analytical techniques for monitoring the degradation products.[1] The application of these combined techniques to the study of poly(isopropylidene carboxylate) (I; $R^1 = R^2 = \mathrm{Me}$) degradation[2] and that of its chlorinated analogs has also been reported.



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

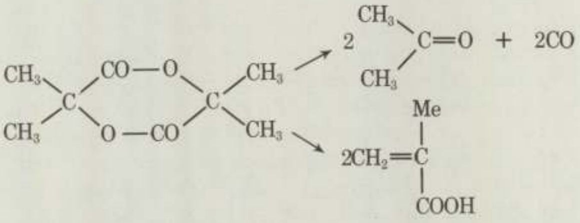
I

The kinetic and analytical results obtained from a study of the thermal degradation of I suggested a predominantly intramolecular ester exchange process which leads [eq. (1)] to the elimination of 1,1,4,4-tetramethylglycollide (II) and concurrent re-formation of the chain.



(1)

1,1,4,4-Tetramethylglycollide which represents the primary decomposition product can then undergo further decomposition by two routes. The first of these [eq. (2a)] is the thermal cleavage to carbon monoxide and acetone, and the second the well known β-abstraction ester scission process [eq. (2b)] leading to methacrylic acid.



(2a)

(2b)

The kinetic results associated with chlorinated poly-α-ester decomposition[3] indicate that reactions of the type represented by eq. (1) form the basis of the predominant degradation route. In addition, free-radical crosslinking reactions leading to residual char formation make some contribution.

The ability to follow the rheological properties of the residual polymer is valuable in the characterization of processes of these types. This was recognized in providing such a facility in the initial assemblage of techniques.[1] Studies of this nature involve control work to demonstrate that shear-dependent degradation does not occur. Initial studies have therefore been carried out with the Farol-Weissenberg rheogoniometer at various shear rates and by using oscillatory as well as rotatory shear. On using this information, conditions have been chosen to study the shear-independent degradation of poly(isopropylidene carboxylate) and its chlorinated analogs. In this way the molecular weight dependence of the degradation processes have been examined, and the associated kinetic parameters derived.

EXPERIMENTAL

Rheogoniometry

Details of the Farol-Weissenberg rheogoniometer and its mode of operation are adequately dealt with in the literature.[4–6] The instrument is essentially a highly instrumented and sensitive cone-and-plate viscometer with facility for measuring normal and tangential forces generated within the fluid. The input disturbance may be continuous rotation, oscillation, or oscillation superimposed on continuous rotation.

Plates and cones of diameter ranging from 2.5 to 10 cm were used with cone angles varying from 0.5° to 4° from the horizontal. A torsion bar determines the rigidity of the top platen and the use of interchangeable torsion bars of different diameters enables a wide range of fluid viscosities to be studied. Platens of 7.5 cm diameter having a cone angle of 1°34′ were used in conjunction with a torsion bar of 0.25 in. diameter for the work described here.

Initial studies were carried out on the effect of oscillatory and rotatory shear in order to establish conditions under which both viscosity and the degradation reaction were shear independent. As a result, continuous rotation at a speed of 0.375 rpm was chosen for degradation studies. The instrument is equipped with a heating chamber which enclosed the platens. A continuous gas flow was maintained over the platens and the temperature continuously monitored. Polymer was introduced on to the platens in the form of film or powder.

Polymers

Synthesis of the polymers[2,3] involved ring-opening techniques previously described.[7–9] Preparation of the randomly chlorinated polymer involved initial formation of poly(isopropylidene carboxylate) in this way, followed by direct chlorination with molecular chlorine in the presence of ultraviolet light.[10]

RESULTS AND DISCUSSION

Reaction Profile: Poly(isopropylidene Carboxylate)

The use of the rheogoniometer to follow the rate of polymer decomposition with respect to the molecular weight of residual polymer depend upon the ability to relate the polymer melt viscosity η to its molecular weight. Several such relationships have been proposed, notably by Flory,[11] by Cross,[12] and by Bueche.[13] Of these, the last was found to be most convenient in the present work because of the ease with which it could be manipulated to produce an expression relating the molecular weight at time t ($\bar{M}_t$) with the initial value ($\bar{M}_0$) in the form $\log(\bar{M}_t)/(\bar{M}_0)$.

Bueche's relationship may be expressed in the form

$$\log \eta = x \log Z_w + C \tag{3}$$

where Z_w is the weight-average chain length and C is a constant whose value depends upon the polymer system in question. The value of x depends upon the molecular weight of the polymer and for the range of molecular weights encountered in poly-α-esters will lie between 1 and 2. For most of this work, polymers having molecular weights <20,000 were chosen, since these lie in the domain where $x = 1$. Thus from eq. (3) we obtain:

$$\log (\eta_t/\eta_0) = \log (Z_{wt}/Z_{w0}) = \log (\bar{M}_t/\bar{M}_0) \qquad (4)$$

and

$$\log (\bar{M}_t/\bar{M}_0) = \log (\eta_t/\eta_0) \qquad (5)$$

where $\bar{M}$ is a weight-average molecular weight.

Values of η_t were calculated from torsion bar deflection values (Δ_T) taken directly from the rheogoniometer output chart by using the expression (6):

$$\eta = 2\pi\alpha\Delta_T k_T/94.25\beta d^3 \qquad (6)$$

where α is cone angle (in degrees), Δ_T is the movement of the torsion head transducer (in 10^{-3} in.), k_T is the torsion bar constant (in dynes-cm/10^{-3} in. movement of the transducer), β is the angular rotation of the platens (in radians/sec), and d is the diameter of the platens (in cm).

Table I shows the application of this relationship to the determination of the decrease in melt viscosity with time for the thermal decomposition of poly(isopropylidene carboxylate) under nitrogen at 245°C. The initial point at issue is the extent to which the first-order behavior observed by other techniques[2,3] is followed when molecular weight is taken as the reaction variable. Combining eq. (5) and the first-order expression which would be obeyed in such circumstances:

$$\bar{M}_t = \bar{M}_0 \, e^{-kt} \qquad (7)$$

we obtain

$$2.303 \log (\eta_t/\eta_0) = -kt \qquad (8)$$

Figure 1, which represents the application of this expression to the results, shows that remarkably good first order dependence is observed into the second decade.

TABLE I
Degradation of Poly(isopropylidene Carboxylate) at 245°C: Results of Rheogoniometer Studies at 0.375 rpm in a Nitrogen Atmosphere

Time t, min	Torsion head reading Δ_T	Viscosity η, Poise	η_t/η_0
0	0.200	42.96	1.00
4	0.160	34.36	0.80
7	0.110	23.63	0.55
12	0.100	21.48	0.50
17	0.080	17.18	0.40
24	0.050	10.74	0.25
32	0.035	7.51	0.17
42	0.020	4.29	0.10
52	0.010	2.15	0.05

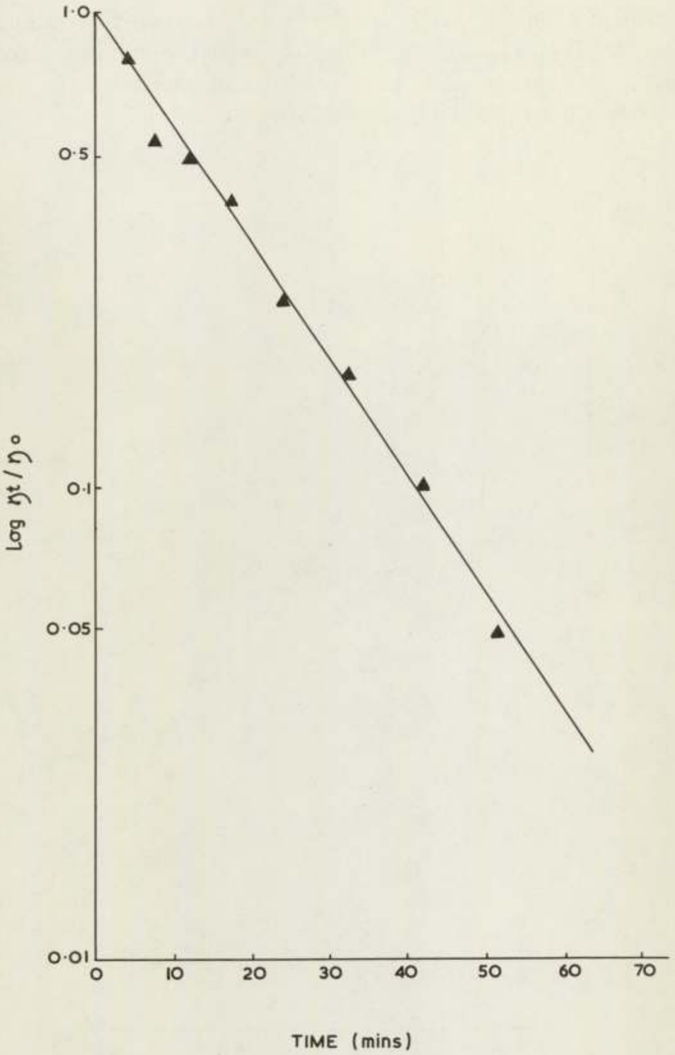


Fig. 1. Variation of log η_t/η_0 with time for the degradation of poly(isopropylidene carboxylate) at 245°C in nitrogen.

Temperature Dependence and Effect of Oxygen

Results of experiments carried out at 210, 230, and 245°C were processed as shown in Figure 1, and first-order rate constants were calculated. Figure 2 shows the values previously quoted and derived from thermogravimetry for polymer of similar molecular weight. In addition results of isothermal studies with the Dupont thermal analyzer and the values obtained from the rheogoniometer experiments described here are included.

The kinetic parameters derived from the rheogoniometric studies were energy of activation Ea (22.8 kcal/mole), frequency factor A (4×10^6 sec^{-1}), and entropy of activation $\Delta S^\ddagger$ (-29 cal/deg-mole).

The effect of a flowing atmosphere of air or oxygen through the platen oven was investigated. Little difference from the runs in nitrogen was discernable. The effect was undoubtedly minimized by the very small surface of the polymer (at the platen edge) which is exposed to the gas stream.

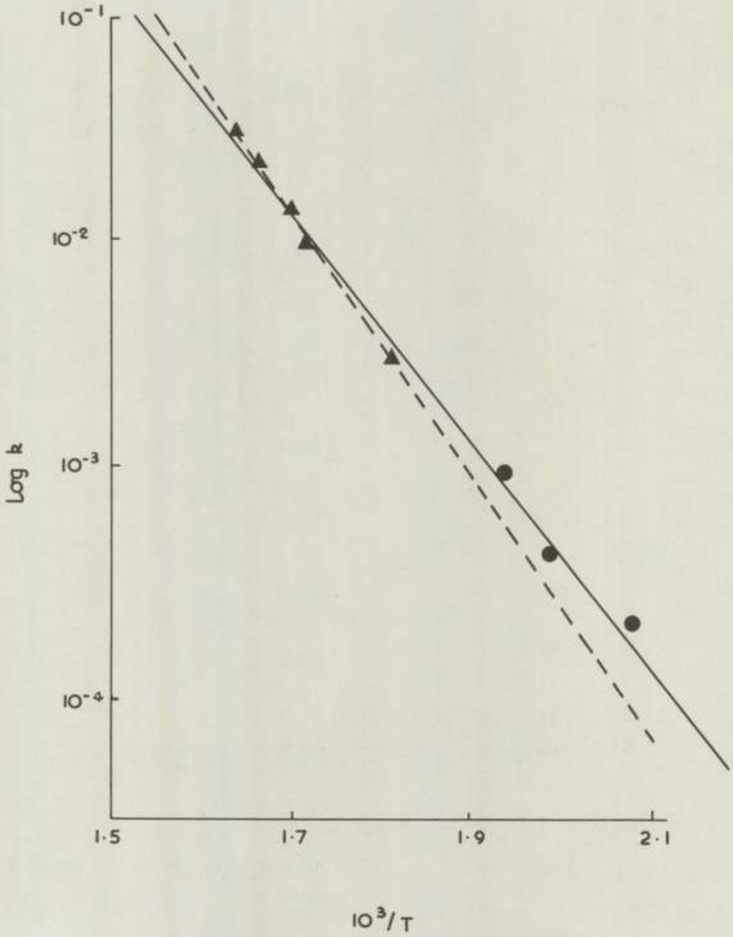


Fig. 2. Arrhenius plot showing (●) rheogoniometric and (▲) thermogravimetric results for poly(isopropylidene carboxylate) ($\bar{M}_n \sim 12{,}000$), degradation in a nitrogen atmosphere; (— —) extrapolated time based on activation energy, previously calculated from thermogravimetric data.

The residual polymer was removed from the platens at the end of all experiments. Figure 3 shows infrared spectra (2000–4000 cm^{-1}) of polymer before and after a period of degradation (30 min at 210°C). The most interesting feature of the spectra is the fact that the hydroxyl groups have apparently diminished in concentration but not disappeared. No evidence of carbon–carbon unsaturation was found in other regions of the spectrum.

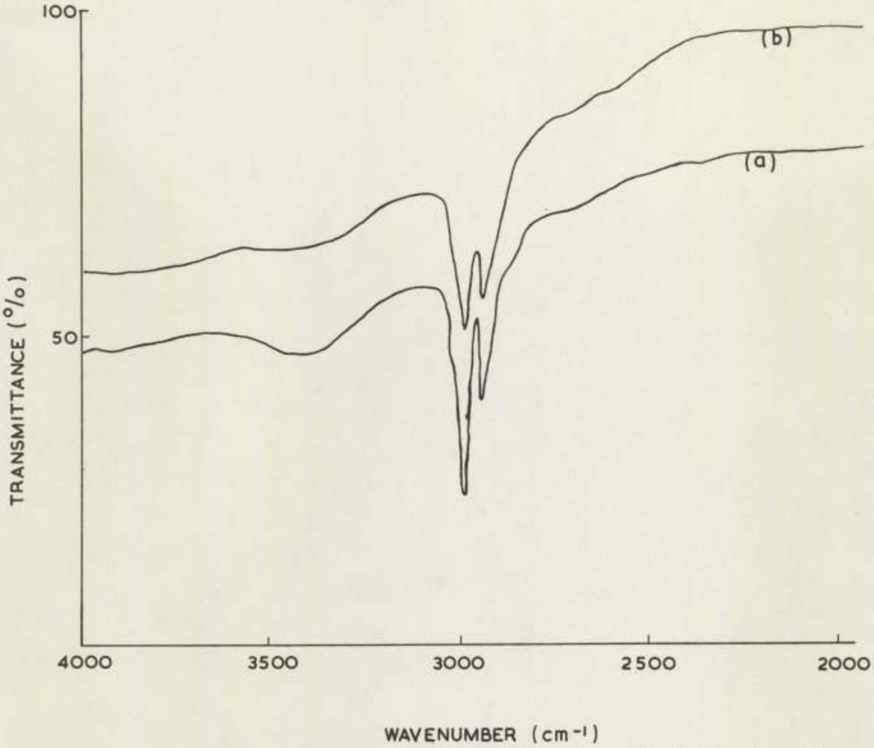


Fig. 3. Infrared spectra of poly(isopropylidene carboxylate) (*a*) before degradation and (*b*) after rheogoniometric study at 210°C for 30 min.

β-Chlorinated Polymers

The degradation of poly(3-chloro-2-methyl-2-hydroxypropionic acid) (I; $R^1 = CH_3$, $R^2 = CH_2Cl$) was studied by using the same procedure and precautions as previously described for poly(isopropylidene carboxylate). The degradation profile of the two polymers as monitored by change in melt viscosity showed several differences, however. These are best represented in the form of graphs of $\log(\eta/\eta_0)$ versus time. Figure 4 shows the degradation at 210°C in an atmosphere of flowing nitrogen of a sample of poly-(3-chloro-2-methyl-2-hydroxy propionic acid) having a molecular weight of 4000. The figure shows distinct deviation from first-order behavior as the degradation progresses. In order to determine the extent to which molecular weight change might affect the instantaneous rate of degradation, polymers of different molecular weight were studied. It was observed that molecular weight had a more marked effect than was the case with poly-(isopropylidene carboxylate), lower molecular weights tending to give faster rates and higher initial values of k_1 (Table II).

The effect of molecular weight on k_1 became vanishingly small at values of around 10,000 and above although the curved first-order plot of log (η/η_0) versus time was characteristic of all samples studied. The initial

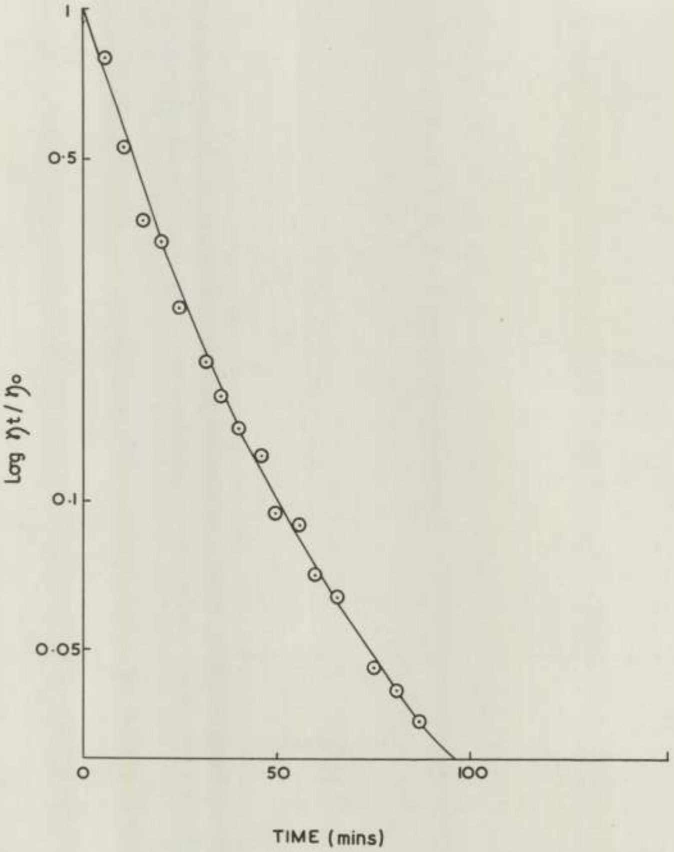


Fig. 4. Degradation of poly(3-chloro-2-methyl-2-hydroxypropionic acid) at 210°C in nitrogen, expressed as log η_t/η_0 vs. time.

TABLE II
First-Order rate Constants k Relating to Initial Rates of Decomposition Obtained from Rheogoniometer Traces Illustrating the Effect of Molecular Weight on Poly(3-chloro-2-methyl-2-hydroxypropionic Acid) Decomposition and Comparing Gas Evolution Analysis and Rheogoniometric Results from Both Chlorinated Polymers

Temperature, °C	$\bar{M}_n$	Rate constant, sec^{-1}
	Poly(3-chloro-2-methyl-2-hydroxypropionic Acid)	
210	1,500	4×10^{-2}
210	4,000	1×10^{-2}
210	6,000	2×10^{-3}
210	8,000	4.5×10^{-4}
210	10,000	2.7×10^{-4}
210	15,000	1.5×10^{-4}
210	15,000[a]	0.9×10^{-4}
	Randomly Chlorinated Poly(isopropylidene Carboxylate)	
256	12,000	1.5×10^{-4}
256	12,000[a]	2.4×10^{-4}

[a] Gas evolution analysis results extrapolated from data in ref. 4.

slope of such a plot for a sample having a molecular weight of 15,000 gave a value of 1.5×10^{-4} sec^{-1} for the first-order rate constant k_1. The deviation from linearity obtained as the decomposition progresses (Fig. 4) occurs in the opposite sense to that predicted on the basis of molecular weight change and clearly has a quite different molecular origin.

The effect of oxygen on the degradation reaction was examined and again the pattern of results differed from those obtained with poly(isopropylidene carboxylate). The initial slope was indistinguishable from that obtained in nitrogen but as the reaction proceeded a progressive acceleration rather than deceleration (as in nitrogen) was obtained. The acceleration was more marked than could be explained on the grounds of molecular weight change alone and obviously represented a chemically significant process since, as has been pointed out, a relatively small area of polymer melt is exposed to the gas stream. Figure 5 shows the variation in log (η/η_0) with time for the degradation of a sample of poly(3-chloro-2-methyl-2-hydroxypropionic acid) at 210°C in flowing oxygen.

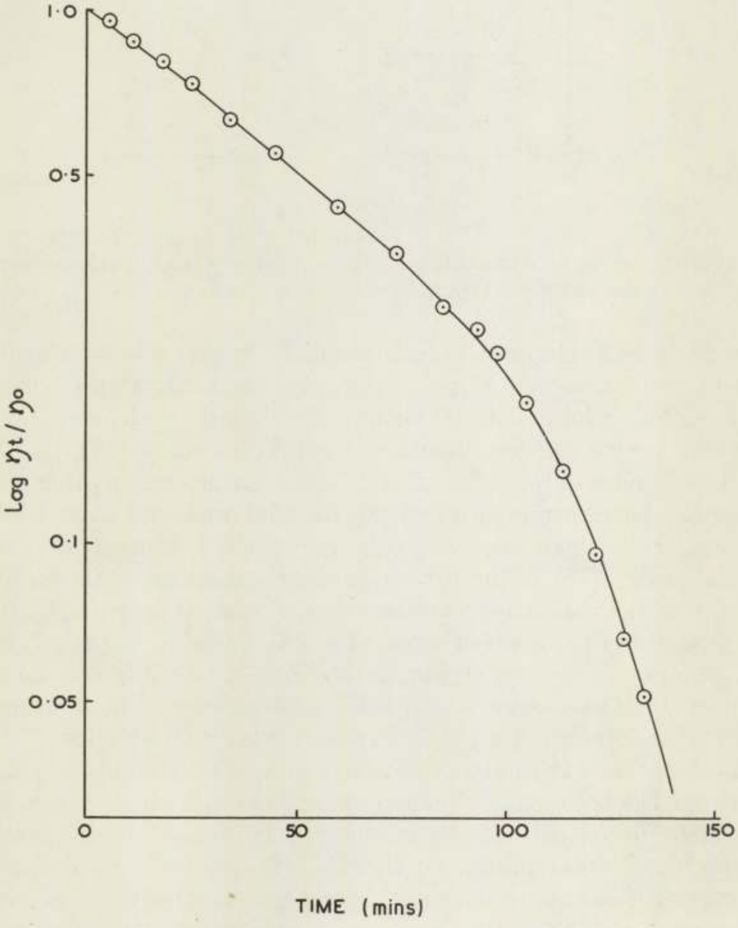


Fig. 5. Variation of log η_t/η_0 for the degradation of a sample of poly(3-chloro-2-methyl-2-hydroxy propionic acid) ($\bar{M}_n \sim 12{,}000$) at 210°C in flowing oxygen.

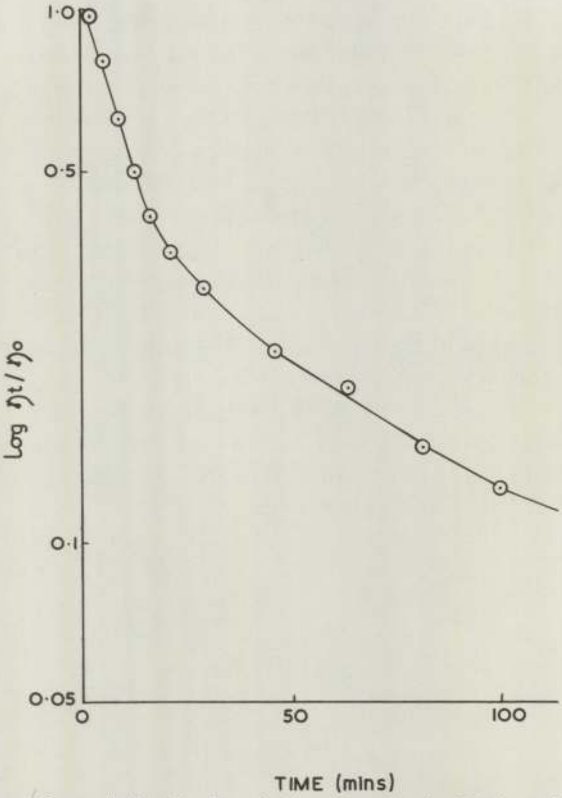


Fig. 6. Variation of log η_t/η_0 for the degradation of randomly chlorinated poly(isopropylidene carboxylate) in an atmosphere of nitrogen at 256°C.

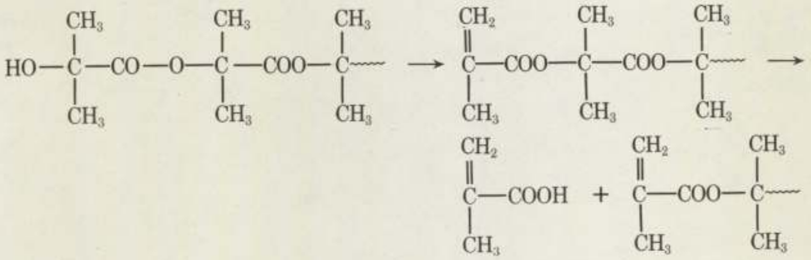
The effect of β-chlorination on the reaction profile was further investigated by using a sample of poly(isopropylidene carboxylate) which had been randomly chlorinated with molecular chlorine.[10] Elemental analysis and NMR spectroscopy indicated that the polymer contained CH_3, CH_2Cl, and $CHCl_2$ groups in the ratio 1:1:1. The structure was in other respects unaltered. The general features of the reaction profile for the degradation were similar to those observed with poly(3-chloro-2-methyl-2-hydroxypropionic acid). The major distinction was the more dramatic retardation in the rate of decrease in melt viscosity as the reaction progressed. This is illustrated in Figure 6, which shows the decomposition of the polymer at 256°C in an atmosphere of flowing nitrogen. These conditions have been chosen to facilitate comparison with Figure 4, since the initial decomposition rates (linear portion) in these two cases are virtually identical.

Because of the more complex reaction profiles of the chlorinated polymers no attempt has been made to characterize them by a single rate constant and thereby derive activation parameters. It is worth noting, however, that the initial linear portion of the log (η/η_0) versus time graphs yield first-order rate constants which are in good agreement with those obtained by other methods[3] (Table II).

As a result of previous kinetic studies using thermogravimetry and gas evolution analysis in conjunction with product analysis, a mechanism corresponding to eq. (1) has been proposed to represent the thermal degradation of poly(isopropylidene carboxylate). Such a mechanism correlates well with the observed kinetic behavior (first-order decomposition having an activation energy of 28 kcal/mole and an entropy of activation of −25 cal/deg-mole) and the formation of 1,1,4,4-tetramethylglycollide as the primary degradation product. It is a consequence of such a mechanism that fall in molecular weight should bear a direct relationship to the rate of glycollide elimination. Thus the type of expression which applies to weight loss should apply equally well to the reduction in chain length and the relationship shown in eq. (7) should be obeyed. It is to an examination of this equation that the work described here is directed.

A necessary approximation originates in the fact that whereas one ought to consider a number average molecular weight relationship, melt viscosity techniques and the available relationships necessitated the use of weight average parameters throughout. The discrepancy is minimized by the fairly narrow initial molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.2$) of reprecipitated polymer.[7]

Despite this necessary approximation the general results described provide remarkably good support for the intramolecular elimination mechanism. Thus the first-order behavior shown in Figure 1 can be explained only by a mechanism which involves a reduction in chain length by one unit for every step in the degradation process, and contrasts markedly with the drastic molecular weight reduction which results from, for example, random chain scission mechanisms. The relatively small contribution of the mechanism involving elimination of methacrylic acid from the chain ends [eq. (9)] is emphasized by the persistence of hydroxyl end-groups in the residual polymer (Fig. 3).

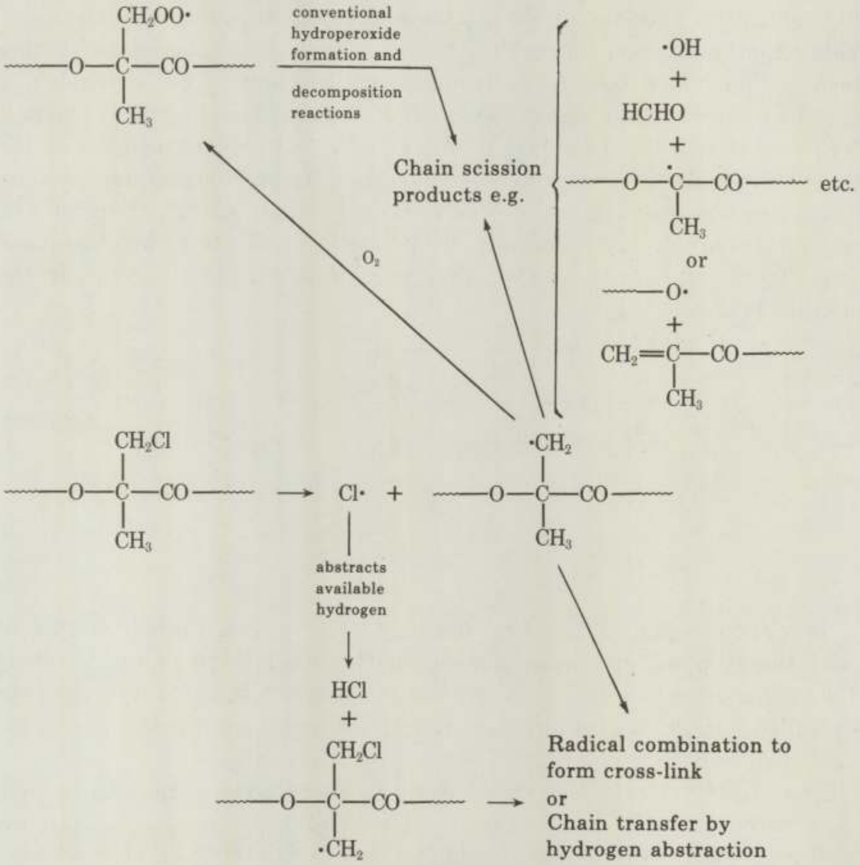


$$\mathrm{HO{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CO{-}O{-}\underset{CH_3}{\overset{CH_3}{C}}{-}COO{-}\underset{CH_3}{\overset{CH_3}{C}}{\sim}} \rightarrow \mathrm{\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}}{-}COO{-}\underset{CH_3}{\overset{CH_3}{C}}{-}COO{-}\underset{CH_3}{\overset{CH_3}{C}}{\sim}} \rightarrow \mathrm{\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}}{-}COOH} + \mathrm{\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}}{-}COO{-}\underset{CH_3}{\overset{CH_3}{C}}{\sim}} \qquad (9)$$

It is encouraging to note that not only is the reaction profile consistent with the proposed intramolecular elimination mechanism but additionally the rate constants and derived activation parameters agree well with the extended Arrhenius plot obtained from thermogravimetric and gas evolution analysis results.

The effect of chlorination on the degradation behavior of poly(isopropylidene carboxylate) is quite marked. The results presented here correlate well with those previously obtained by other techniques.[3] The results are best explained in terms of two major effects which are superimposed upon the intramolecular elimination mechanism. The first of these is a crosslinking process which originates with the labile C—Cl bond. The extent and rate of crosslinking are dependent upon the extent of chlorination in the polymer.

The second is a competitive chain-scission reaction which, from its sensitivity to oxygen, is undoubtedly radical-initiated. The importance of this reaction as a competitive degradation route in the β-chlorinated polymers is illustrated by comparing their behavior with that of poly(isopropylidene carboxylate). Radical scission reactions of this type are known[2] to make a small but definite contribution to the degradation of poly(isopropylidene carboxylate). In the system used here, however, oxygen access is restricted to the very small surface of polymer exposed at the edge of the platens and runs in oxygen are identical to those in nitrogen. Such is the sensitivity to oxygen of the chlorinated polymers, on the other hand, that a quite dramatic change is observed in these circumstances (Figs. 4 and 5). This suggests that a radical reaction is initiated at the exposed surface and propagates through the bulk of the polymer.



Despite these competitive reactions the general form of the results provides a substantial piece of corroborative evidence for the existence of the proposed intramolecular ester interchange reaction as the major reaction pathway in the degradation of poly-α-esters of this type. By comparison, crosslinking and oxygen-promoted chain scission occur to a relatively small extent, and in the absence of a more detailed study any mechanistic proposals related to these reactions must be completely speculative.

In our view the scheme which most completely accounts for the relative magnitudes and chemical specificity (ie, as between one polymer and another) of these reactions involves the initial homolytic scission of the carbon–chlorine bond. The possible sequence of reactions resulting from this step is shown in the scheme (10). The consequent balance favors crosslink formation in the absence of oxygen and chain scission in its presence. This is presented as a result of the interaction of oxygen with radical intermediates whose primary appearance is independent of the presence of oxygen (ie, the presence of oxygen affects their fate rather than their formation). Although it seems probable that the production and subsequent decomposition of hydroperoxidic structures formed in this way (i.e., as a result of the interaction of oxygen and radical intermediates) leads to chain scission, it is impractical at this stage to speculate on the precise course of such reactions.

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Poly α-Ester Degradation Studies. V. Thermal Degradation of Polyglycollide

D. R. COOPER, G. J. SUTTON, and B. J. TIGHE,
Department of Chemistry, The University of Aston,
Gosta Green, Birmingham, B4 7ET, England

Synopsis

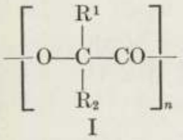
The thermal degradation of polyglycollide [poly(methylene carboxylate)] has been studied over the temperature range 250–400°C by using the combined kinetic and analytical technique previously described. The results obtained from thermogravimetry and product analysis were in many ways similar to those from previous work involving higher poly-α-esters. Thus the reaction was predominantly first-order and the major degradation product was glycollide monomer. This confirms the observations of Carothers and is best interpreted in terms of an intramolecular ester interchange process. Kinetic studies have shown that the first-order rate constant k is related to temperature T by the expression:

$$k = 2.1 \times 10^{8}\, e^{-32{,}600/RT}\ \mathrm{sec}^{-1}$$

The results from gas evolution analysis showed consistent and marked deviation from first-order behavior. This is interpreted in terms of the greater sensitivity of this technique to traces of acidic degradation products. Solution viscometry was used to demonstrate the effect of degradation conditions on molecular weight change in both thermogravimetric and gas evolution techniques.

INTRODUCTION

Previous papers in this series[1-4] have described the use of apparatus which combines several techniques suitable for degradation studies of poly-α-esters (I) and its application to the degradation of this class of polymer. The work has shown that in the cases so far studied, the principal primary degradation products are substituted glycollides, although the nature of the substituents has been demonstrated to exert a marked effect on the subsequent degradation, both in terms of steric hindrance and elimination reactions involving β-hydrogen atoms. We now describe the results obtained with a polymer



$$\left[\!-\mathrm{O}-\overset{\mathrm{R}^1}{\underset{\mathrm{R}_2}{\mathrm{C}}}-\mathrm{CO}-\!\right]_n$$

I

in which such β hydrogen atoms are absent.

Poly(methylene carboxylate), better known as polyglycollide, the poly-α-ester having the simplest structure (I; $R^1 = R^2 = H$) and its major degradation product glycollide, have been known for several years. In fact, in 1932 Carothers[5] pointed out that the reaction involving this polymer and glycollide is quantitatively reversible. Commercially the polymer has been successfully exploited as a surgical suture under the trade name Dexon. This is made possible because of its excellent fiber-forming properties and ideal rate of hydrolysis in the human body. Surprisingly, however, only a limited amount of work has been reported on the kinetics of the decomposition reaction.

Chujo[6] has examined the degradation of polyglycollide and some of its copolymers by thermogravimetric analysis, differential thermal analysis, and viscometric techniques. He reports that random chain scission may be the main decomposition reaction of the polymer at high temperatures, at least in the initial stages of decomposition. This conclusion does not appear to be consistent with either the classical work of Carothers or the previous work on similar polymers carried out in this department. Although this work was carried out on poly(isopropylidene carboxylate) (I; $R^1 - R^2 = Me$) and its chloro derivatives, there are many aspects of the degradation of these polymers, in which the main products are based on glycollide homologs, which suggest that random chain scission cannot adequately explain the degradation of polyglycollide.

Several reasons can be proposed to explain these discrepancies; for instance, different polymerization techniques may confer differing mechanisms of decomposition on the resultant polymer. Furthermore, the unexpected and dramatic change in degradation mechanism which could be involved in going from poly(isopropylidene carboxylate) to its homologous polyglycollide might be due to the influence of the pendant methyl groups. It is also possible that the over-riding random scission degradation process was postulated by Chujo for polyglycollide because of insufficient information.

Therefore it was concluded that these mechanistic problems, together with a minimum of published information on this commercially and structurally important polymer, polyglycollide, warranted a further and more detailed investigation into its mechanism of thermal degradation.

EXPERIMENTAL

Polyglycollide was produced by the well known ring-opening reaction of glycollide.[7] The commercial material Dexon, being a pure polymer of high molecular weight (>20,000), was also used in this work.

The various kinetic aspects of thermal degradation of polyglycollide were studied using the combined thermogravimetric and gas evolution techniques previously described.[1] A relatively minor but significant improvement upon the apparatus previously described lies in the reduction of the induction period due to thermal equilibration in thermogravimetric analysis experiments. This has been achieved by increasing the rate at which the furnace and lower portion of the glass reaction vessel are raised and lowered, resulting in virtual elimination of initial plateau (Fig. 1) and corresponding initial positive slope (Fig. 2). The thermal equilibration period for gas evolution analysis runs is unchanged and remains at approximately 2 min. Modifications at present in hand will reduce this time considerably.

RESULTS

Polyglycollide Decomposition: Thermogravimetry

The shape of the thermogram obtained by using thermogravimetry under nitrogen indicated that the decomposition was predominantly first-order. This was confirmed by applying the Wilhelmy equation, eq. (1), to the results which were represented graphically in the form log W_t/W_0 versus time (where W_0 and W_t are the weights of polymer

$$C_t = C_0e^{-kt} \tag{1}$$

initially and at time t, respectively). A typical example is shown in Figure 1. In addition, results were examined in the form of plots[8] (Fig. 2) showing instantaneous rates of volatilization (% min) versus amount of sample volatilized (%).

Figures 1 and 2 demonstrate that the reaction is substantially first-order and that an initial zero-order process is not involved (since a horizontal curve is not shown in the early stages in Fig. 2).[9] The predominantly first-order nature of the degradation is reflected in the linearity of the curve of Figure 2 which can be compared with established first-order degradation processes such as that found with poly-α-methylstyrene.[10] Furthermore the absence of a marked curvature, particularly in the early stages in Figure 2, indicates that random decomposition as exhibited by polystyrene is not taking place.

Perhaps the most convincing demonstration of first-order behavior is provided by the linearity (constant half-life) over more than one decade in Figure 1.

The effect of temperature on the decomposition in nitrogen was studied over the temperature range 200–400°C. No deviation from first-order behavior was evident over the temperature range examined. Table I summarizes the variation of first-order rates with temperature and the derived kinetic parameters.

The effect of oxygen on the degradation reaction was then studied by using otherwise similar conditions. The general form of the reaction was identical, with no change in the amount of residual char. The first-order rate constants, together with the kinetic parameters, are included in Table I.

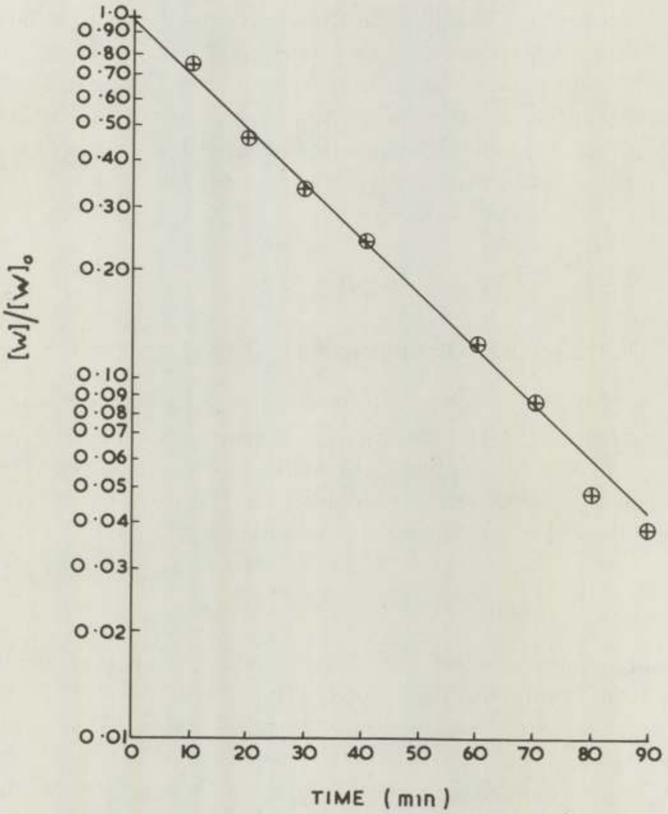


Fig. 1. Degradation of polyglycollide at 342°C in an atmosphere of nitrogen. First-order representation (log W_t/W_0 vs. time) of thermogravimetric results.

Polyglycollide Decomposition: Gas Evolution Analysis

Gas evolution analysis (GEA) results were treated in a similar manner by plotting log $[(P_\infty - P)/P_\infty]$ versus time. Here P is the pressure developed at any time by the formation of volatile degradation products and P_∞ is the pressure corresponding to complete degradation of the polymer. However, after allowing for thermal equilibration the gas evolution analysis plots consistently deviated from linearity in the latter portion of the reaction (Fig. 3). The degradation proved to be autocatalytic, an effect which becomes more marked once an average of 75% of the decomposition had occurred. The effect of temperature on the first-order rate constants derived from the early linear portion of the gas evolution analysis plots is illustrated in Table II. A convenient comparison of the first-order rate constants is supplied by the Arrhenius plots in Figure 4 and by viscometry in Figure 5 and Table III.

Molecular weight change during degradation was estimated by using solution viscometry. Samples of polyglycollide were degraded for different times at 200°C under both thermogravimetric and gas evolution analysis

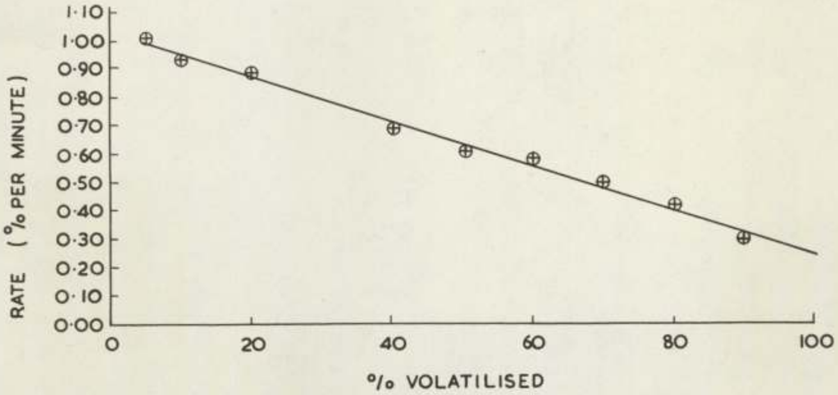


Fig. 2. Plot of rate of volatilization (%/min) vs. % volatilized for thermogravimetric degradation of polyglycollide at 333°C in an atmosphere of nitrogen.

conditions. At this temperature a weight loss of less than 5% was recorded during thermogravimetric analysis. The degraded samples were dissolved at known concentrations in benzyl alcohol for 10 minutes at 190°C. Viscosities were carried out at 40°C by using an Ubbelohde viscometer. Intrinsic viscosities $[\eta]$ were calculated by the conventional double extrapolation techniques and by the Solomon and Cuita method[11] [eq. (2)]. In the latter equation, c represents the concentration of polymer

$$[\eta] = [(2)^{1/2}/c](\eta_{sp} - \ln \eta_r)^{1/2} \tag{2}$$

100 g of solution, η_{sp} and η_r are the specific and relative viscosities respectively. The results are given in Table III and Figure 5.

TABLE I

First-Order Rate Constants k, Activation Energies E, Frequency Factors A, and Entropies of Activation, $\Delta S\ddagger$ for the Thermal Degradation of Polyglycollide by TGA

Temperature, °C	$k \times 10^5$, sec^{-1}	
	Nitrogen atmosphere	Oxygen atmosphere
270	1.28	
289		3.02
315		15.0
320	21.5	
333	29.3	
340		24.3
342	56.4	
343	58.3	
364	197	157
390	525	
E, kcal/mole	32.6	36.8
A, sec^{-1}	2.09×10^8	5.89×10^9
$\Delta S\ddagger$, cal/deg-mole	−23.8	−17.8

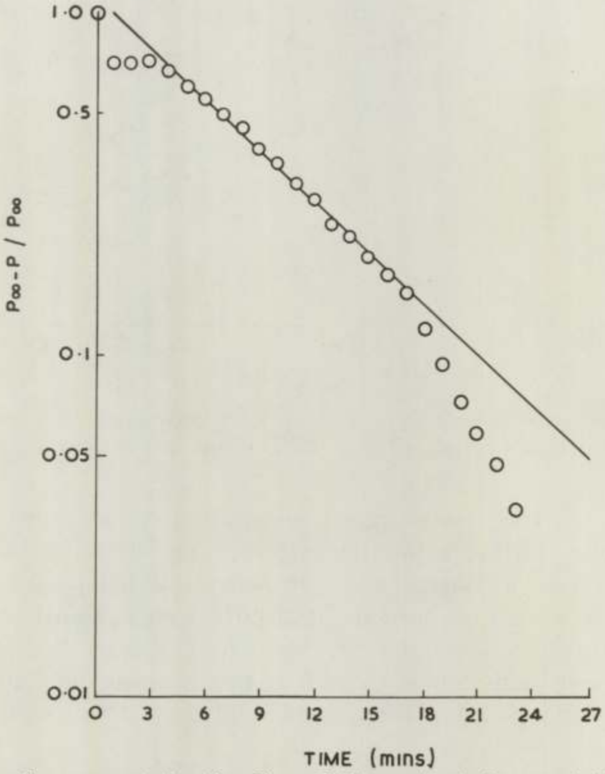


Fig. 3. First-order representation (log $P_\infty - P/P_\infty$ vs. time) of gas evolution results for degradation of polyglycollide at 305°C in an atmosphere of nitrogen.

TABLE II

First-Order Rate Constants k, Activation Energies E, Frequency Factors A, and Entropies of Activation $\Delta S\ddagger$ for the Thermal Degradation of Polyglycollide by GEA

Temperature, °C	k, $\times 10^3$, sec^{-1}
303	1.57
306	1.90
308	1.78 and 1.83
327	4.52
330	4.02
354	9.03
357	10.7
380	11.3
388	19.2
E, kcal/mole	20.9
A, sec^{-1}	1.35×10^5
$\Delta S\ddagger$, cal/deg-mol	−30.4

The viscosity results confirm that the molecular weight falls much more quickly during gas evolution analysis than in thermogravimetric analysis. This must be a consequence of the differing conditions of the two techniques. In gas evolution analysis the polymer sample is surrounded by a

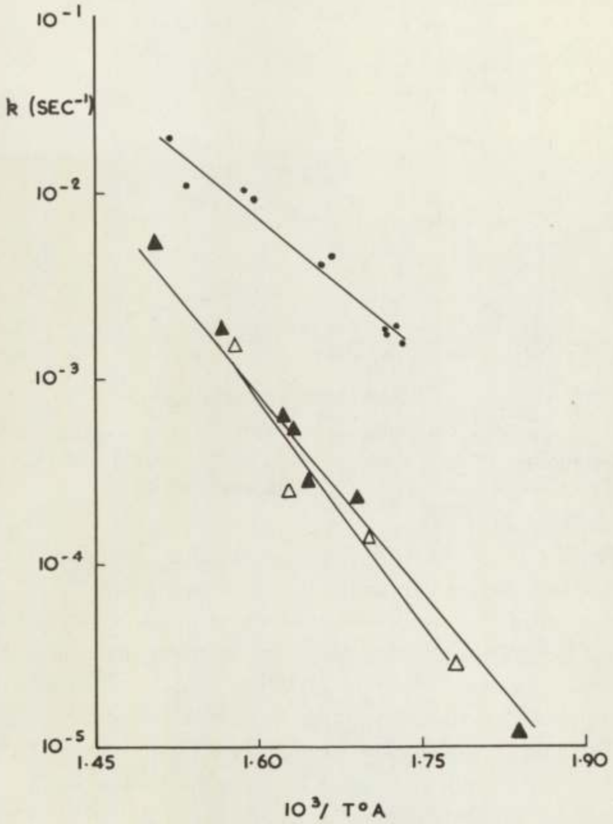


Fig. 4. Arrhenius plots showing (●) gas evolution results and (thermogravimetric results in an atmosphere of oxygen (△) and in (▲) nitrogen) for polyglycollide.

stagnant atmosphere enriched with its own volatile degradation products. In thermogravimetric analysis the sample was exposed to a constantly replenished supply of nitrogen, which must be effective in removing volatile degradation products away from the polymer.

In an attempt to simulate gas evolution analysis conditions using thermogravimetric analysis, the polymer was degraded in the presence of benzoic acid in a stagnant atmosphere. The results, as displayed in Figure 6, demonstrate that the degradation rate is dramatically increased by the presence of acid.

DISCUSSION

We have previously illustrated how the mechanism of degradation of poly(isopropylidene carboxylate) can be characterized by the kinetic and analytical results. The following types of reaction are taken to represent all possibilities: (a) random homolytic or heterolytic chain scission, possibly followed by chain depolymerization from the scission site; (b) inter- or intramolecular ester interchange; (c) chain depolymerization or

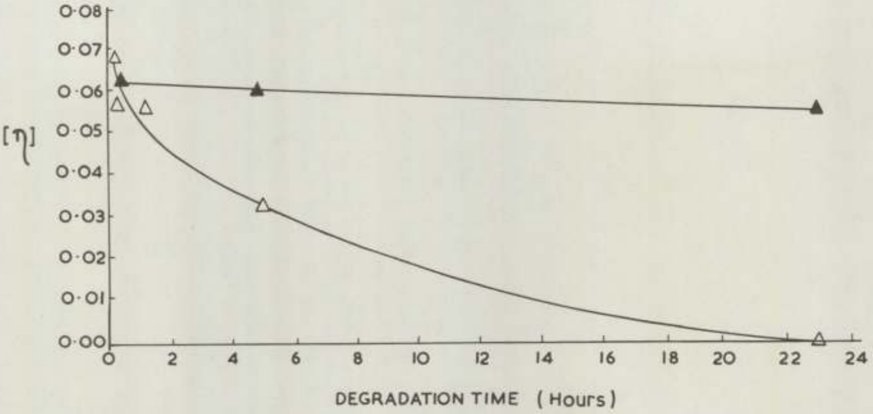


Fig. 5. Degradation of polyglycollide at 200°C by (△) gas evolution and (▲) thermogravimetric techniques. Plot of intrinsic viscosity [η] calculated by the Solomon and Cuita method vs. time for solutions of polymer in benzyl alcohol.

unzipping from the chain ends; (d) molecular decarboxylation or decarbonylation, possibly accompanied by chain recoupling.

By comparison of the results with those of other workers using similar polymers and by examination of the kinetic requirements of the mechanisms involved, it was concluded that an intramolecular ester-interchange mechanism represented the predominant degradation route.

A similar method can be used to elucidate the mode of degradation of polyglycollide. Mechanism (d) can be ruled out, since it cannot account for the first-order kinetics displayed in thermogravimetric analysis. For the same reason, any major part played by intermolecular ester interchange can be discounted. Furthermore, these two mechanisms together with random homolytic chain scission do not explain how glycollide can be formed as the main decomposition product.

The comparable rates of degradation found in nitrogen and oxygen atmospheres during thermogravimetry give reinforcement to the belief that random homolytic chain scission does not make any important contribution. This conclusion is consistent with the work of Ritchie,[12] who,

TABLE III
Intrinsic Viscosities [η], Calculated by Conventional Double Extrapolation Techniques for Samples of Solutions of Polyglycollide Thermally Degraded at 200°C under TGA and GEA Conditions

Degradation time, hr	[η], dl/g	
	TGA (nitrogen)	GEA
0.167	0.063	0.043
0.5	0.065	0.043
1.0	0.040	0.031
5.0	0.063	0.020
23.0	0.063	0

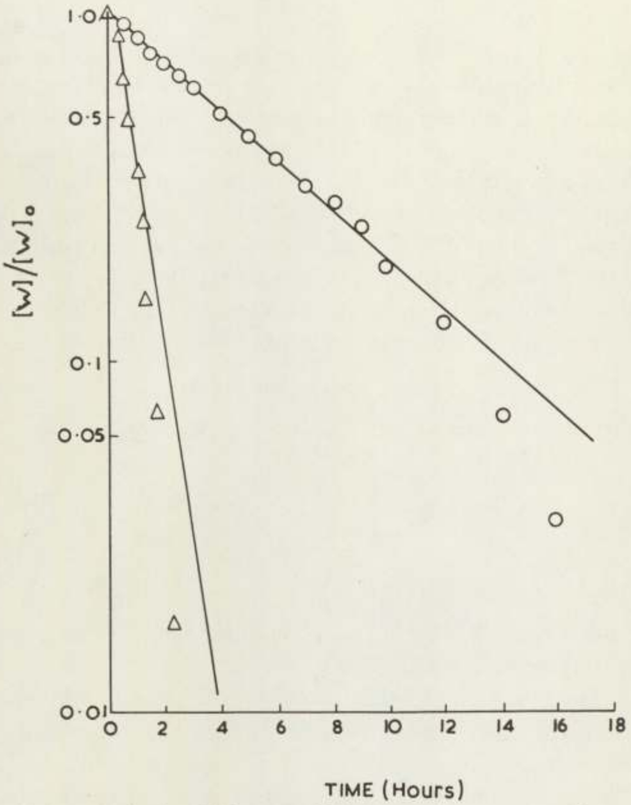
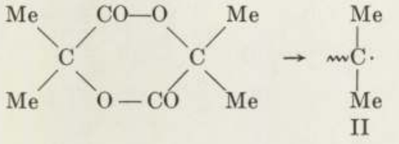


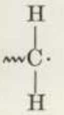
Fig. 6. Degradation of polyglycollide at 291°C (○) in a nitrogen atmosphere and (△) in a stagnant local atmosphere containing 15.3% benzoic acid based on the polymer weight.

when pyrolyzing various glycollides at 500°C, observed that degradation by a free radical mechanism plays a small but significant part in the case of tetramethyl glycollide, presumably because of the stability of the derivative radical (II).



(3)

No such contribution was detected with lactide. It is not unreasonable to assume that the stability of the intermediate radical influences the degradation pathway, and that the proportion of product obtained via this radical is related to its stability. Therefore, extending these assumptions to glycollide itself and polyglycollide, we expect the radical III to play little or



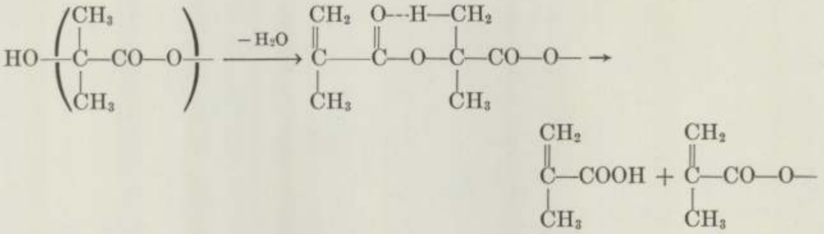
$$\sim\!\!\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\cdot$$

III

no part in the degradation process, since it would be expected to have high radical stability if the production of glycollide (the major degradation product) was to be justified by any type of free radical scission mechanism.

The low values of A observed indicate that a fairly high degree of steric order is involved in the transition state of the rate controlling step. Similarly, the large and negative value of the entropy of activation is also indicative of high steric order. Consequently these parameters show that any overriding random homolytic chain scission can be disregarded, and they provide further evidence that mechanism (d) can be excluded.

Any possibility of unzipping from chain ends by the well known β-hydrogen abstraction process[13,14] given in eq. (4) can be ignored because of the

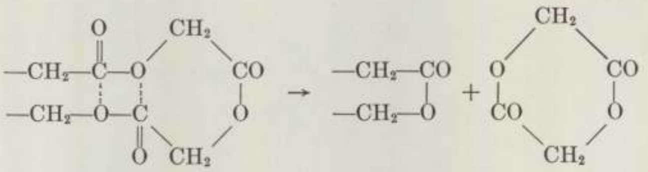


(4)

absence of β-hydrogen atoms in polyglycollide; this mechanism would also not explain the formation of glycollide.

Although alcoholysis and acidolysis from chain ends may contribute to a small extent, the kinetic requirements of this type of mechanism are completely inconsistent with the experimental results presented here. It has been concluded[2] that, although these processes are feasible in a molecular sense for poly(isopropylidene carboxylate) decomposition, their contribution can only be small in high molecular weight polymer decomposition.

The possibilities of random heterolytic chain scission and intramolecular ester interchange remain. While the latter can be reasonably envisaged, [eq. (5)] the former cannot explain the observed first-order kinetic behaviour.



(5)

Degradation in nitrogen studied by thermogravimetry gives results which are fully compatible with the occurrence of an intramolecular ester interchange reaction. First-order kinetics are obeyed over the first decade of the decomposition; a large and negative entropy of activation is found, together with a low value for the frequency factor. The activation energy is close to that of 27.2 kcal mole found with poly(isopropylidene carboxylate) and is indicative of an energetically preferred degradation process, structurally possible in poly(isopropylidene carboxylate) but not in simple ester pyrolysis.

The presence of glycollide as a major degradation product both confirms the work of Carothers and provides further evidence that eq. (5) represents the major decomposition route. A relatively slow reduction in molecular weight with time is implied by the mechanism, which accords well with the first order behavior and the results obtained by viscometry.

Degradation results by gas evolution analysis revealed several major differences when compared to thermogravimetry. First, the first-order rates were markedly higher; then a consistent deviation from first-order linearity was exhibited over an average of the last 25% of reaction. Neither of these differences was found to any significant extent with poly(isopropylidene carboxylate). Also, viscometric studies revealed that the fall in polymer molecular weight is much more severe under gas evolution analysis conditions.

The most striking structural difference between polyglycollide and poly(isopropylidene carboxylate) is the presence of pendant methyl groups in the latter polymer which are effective in hindering hydrolysis of the main chain. The apparatus has been constructed in such a way that any hydrolyzing agent present as a product of polymer degradation would be held in the surrounding atmosphere during gas evolution analysis but would be swept away in a current of nitrogen in thermogravimetric analysis. Hence, a secondary heterolytic scission degradation process is probably responsible for the increased rate of decomposition found during gas evolution analysis. A hydrolysis mechanism which involves acidic fragments such as glycollic acid, produced by the hydrolysis of glycollide, the primary degradation product, is feasible. Although the quantities of glycollic acid produced are initially minimal, the reaction is effectively autocatalytic. Therefore, as the reaction proceeds, progressively more pronounced deviation from first-order behavior is observed. In thermogravimetric analysis where the volatile degradation products are swept away immediately, however, heterolytic scission should play a very minor role, so that the first-order intramolecular ester-interchange process would predominate.

In poly(isopropylidene carboxylate) the presence of the two methyl groups decreases interchain forces, causing departure from the regular planar extended zigzag. This is also reflected in the fact that the rate of isothermal crystallization of polyglycollide is much more rapid than that of poly(isopropylidene carboxylate). In addition the presence of the methyl groups restrict the rotational freedom of the chains tending to constrain them in such a way that the formation of the six-membered intermediate [as in eq. (5)] occurs more readily.

The artificial creation in the thermogravimetry cell of the conditions existing in the gas evolution analysis probe (Fig. 6) provides very good confirmation of the susceptibility of the main chain to scission by acidic degradation products and of the related points made in the preceding discussion. Thus, the degradation of polyglycollide in the absence of additives and under conditions which allow primary degradation products to diffuse away takes place predominantly by an intramolecular ester-interchange process and is thereby seen to behave in a manner consistent with the mechanism proposed in cases previously studied.[2–4]

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