STUDIES ON THE CATIONIC POLYMERISATION OF SOME 1,3-DIOXACYCLOALKANES

by

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The work described in this thesis was carried out by the Author under the supervision of Dr. P.H. Plesch.

To my parents

ABSTRACT

This thesis concerns the polymerisation of 1,3-dioxacycloalkanes.

Chapter 2 is concerned with the preparation of monomers, initiators and other compounds and with the experimental techniques.

In Chapter 3 the effects of purity on the polymerisations of 1,3-dioxolan and 1,3-dioxepan by $HClO_4$ are re-examined. These reactions were also carried out in the presence of $n\text{-}Bu_4NClO_4$ and from the results estimates were made of the free ion and ion-pair rate-constants for dioxolan.

Chapter 4 is concerned with the polymerisation of 1,3-dioxolan with $MeSO_3F$, $TiCl_4$+ Acetyl Chloride, $TiCl_4$+"tert-Butyl" Chloride, Acetyl perchlorate, "tert-Butyl" perchlorate, NO_2SbF_6, $NOBF_4$, $NOSbF_6$ and $NOPF_6$. All these initiators gave side reactions and the active centres are not stable in these reactions.

Chapter 5 is concerned with the determination of secondary and tertiary oxonium ions. 1,3-Dioxolan, 1,3-dioxepan and 4-methyl-1,3-dioxolan were polymerised by anhydrous perchloric acid and the reactions were terminated by sodium ethoxide under high vacuum. Some of the reactions were carried out in the presence of known amounts of water. From these experiments it was shown that tertiary oxonium ions are mainly produced by water. Therefore Plesch and Westermann's original ring-expansion mechanism was found applicable. According to this mechanism, the

polymers formed were cyclic and the propagating species formed from protonic initiators must be secondary oxonium ions.

Chapter 6 concerns the polymerisation of 4-methyl-1,3-dioxolan by anhydrous perchloric acid. The equilibrium constant of polymerisation was determined analytically and from it and its temperature variation the thermodynamic characteristics of the polymerisation were calculated. It is also concerned with the polymerisation of 2-methyl-1,3-dioxolan.

Chapter 7 is concerned with some exploratory experiments:

a) 1,3-Dioxolan polymerisations by CF_3SO_3H.

b) The polymerisations of 4,5-disubstituted 1,3-dioxolan, i.e. cis- and trans-7,9-dioxabicyclo-[4.3.0]-nonane.

c) NMR investigations on the tertiary oxonium ions obtained from $MeSO_3F$.

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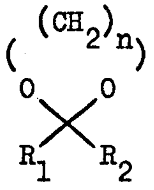
CHAPTER SEVEN: EXPLORATORY EXPERIMENTS

CHAPTER ONE

Introduction and Historical Background

The work to be described in this thesis is an extension of the work of Drs. P.H. Westermann[1] and F.R. Jones.[2] The aim of this work is to resolve a conflict of results in the literature concerning the polymerisation of 1,3-dioxacyclo-alkanes.

1,3-dioxacyclo-alkanes are represented by the general formula:



1.1

R_1 and R_2 can be hydrogen, alkyl, aryl etc. This thesis is concerned mainly with 1,3-dioxacyclo-alkanes in which $R_1 = R_2 = H$. These compounds are called cyclic formals and can be regarded as codimers of formaldehyde and cyclic ethers.[3] The most detailed work described in this thesis concerns the polymerisation of the five-membered cyclic formal (n = 2, 1,3-dioxolan). Other polymerisation experiments were carried out with the seven-membered cyclic formal (n = 4, 1,3-dioxepan) and a substituted 1,3-dioxolan (4-methyl-1,3-dioxolan) and some experiments were carried out on the polymerisation of a cyclic acetal (2-methyl-1,3-dioxolan).

In recent years the number of publications on the polymerisation of cyclic oxygen compounds has grown rapidly. Many papers and patents were published on the polymerisation of trioxan, tetrahydrofuran and 1,3-dioxolan. Recently, a number of bicyclic acetals derived from sugars have been shown to polymerise to high molecular weight, stereoregular, crystalline polymers.[4]

1,3-Dioxacyclo-alkanes are stable in basic media, but are cleaved easily in acidic solution. Acetal formation is therefore utilized frequently as temporary protection for hydroxyl groups in synthetic organic chemistry. 1,3-Dioxacyclo-alkane resins have found many uses because of their good physical and mechanical properties. However, their service life is limited in the presence of strong acids and oxidizing agents.[5]

Despite the real possibility of finding useful polymers with a variety of properties, this whole field has been very largely neglected and much remains to be done.

1,3-Dioxolan was first prepared in 1894 by Trillat.[6] In 1923 Hill[7] prepared a number of cyclic formals from acetylene and various diols (with mercuric salts and sulphuric acid).

Hill and Carothers[8] first investigated the cyclic formals. The seven-membered to twentyone-membered cyclic formals were polymerised in the presence of camphor sulphonic acid at temperatures of 100 to 150°. In that paper 1,3-dioxolan was not mentioned and 1,3-dioxan was not polymerised.

Gresham[9] polymerised 1,3-dioxolan with Lewis acids and mineral acids. He found that a 25% solution of 1,3-dioxolan in cyclohexane with 4% sulphuric acid at 100° gave only a small amount of low molecular weight oil. The bulk polymerisation with boron trifluoride etherate at 6° gave a crystalline, high molecular weight polymer.

High molecular weight poly-1,3-dioxolan was obtained by Muetterties[10] with phosphorus pentafluoride.

The equilibrium polymerisation of cyclic formals was first observed by Strepikheev and Volokhina.[11] They carried out polymerisations with camphor sulphonic acid, using benzene as a solvent at 100 to 150°. Although Dainton and Ivin's[12] papers on the theory of equilibrium polymerisation should have been known to them at that time, they were unable to explain their results.

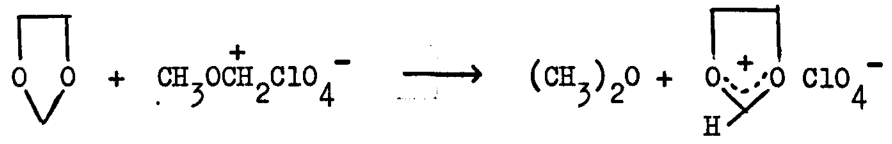
The first detailed kinetic study on polymerisation of 1,3-dioxolan has been done by Okada et al.[13] In this paper 1,3-dioxolan was polymerised with organo-aluminium compounds, acetyl chloride + metal halides, and acetic anhydride + perchloric acid. Polymerisations were carried out with bulk monomer, under nitrogen. No details of the purification of the initiators were given.

These authors proposed that an equilibrium between oxonium ions and carboxonium ions existed and that the active centre in the polymerisation was the carboxonium ion:

$$ROCH_2CH_2OCH_2^+ \longleftrightarrow ROCH_2CH_2O^+{=}CH_2 \qquad 1.2$$

This explanation is based on the cationic polymerisation of trioxan in which the active centre is a resonance stabilised carboxonium ion.[14] This paper[13] and another paper[15] by the same authors describe the cationic copolymerisation of 1,3-dioxolan with styrene in toluene, by boron trifluoride etherate as initiator. This reaction was interpreted by them as further evidence for the carboxonium ion mechanism. Kern et al.[16] have been able to copolymerise trioxan with styrene, whilst tetrahydrofuran, which is generally supposed to polymerise by an oxonium ion mechanism, will not copolymerise with styrene.

This argument is exceedingly weak, because an interesting experiment was carried out by Jaacks et al.[17] They tried to polymerise 1,3-dioxolan with methoxymethyl perchlorate. This compound is similar to the "active centre" proposed by Okada. However, the reaction in ethylene dichloride at 0° gave $2H^+$-1,3-dioxolanium perchlorate and dimethylether:



1.3

Therefore Okada's carboxonium theory is not applicable to 1,3-dioxolan polymerisation.

Kucera et al.[18] have studied the polymerisation of 1,3-dioxolan with octamethylcyclotetrasiloxane bisulphate. The experiments were carried out in open dilatometers at 40-70°. Most of the work was concerned with kinetic measurements and their interpretation. Unfortunately, the kinetic scheme was based on the assumption that the active centres are carboxonium ions which were supposed to be in equilibrium with unreactive tertiary oxonium ions. Although the scheme fitted the experimental results, there were no supporting experiments for this assumption. They found formaldehyde in the solution after polymerisation. This fact shows that their system contained a lot of water, because Ceder[19] showed that aqueous hydrolysis of 1,3-dioxolan gives formaldehyde. However, they found that water cocatalyses the polymerisation but an excess of water causes termination.

Gorin and Monnerie[20] made a kinetic study of the polymerisation of 1,3-dioxolan with mercuric chloride and boron trifluoride etherate.

Laurent et al.[21] carried out the polymerisation of 1,3-dioxolan with cadmium, mercuric and copper halides. Their kinetic measurements agreed with Kucera's scheme but no direct evidence for equilibrium between carboxonium ions and oxonium ions was presented.

Yamashita et al.[22] showed that a complex of 1,3-dioxolan and BF_3, isolated at low temperature, initiated polymerisation more rapidly than the boron trifluoride etherate. Their reaction scheme is not clear about propagation and they were unaware of the likely occurrence of hydride abstraction in the presence of BF_3Et_2O.

Miki et al.[23] published a series of papers on the polymerisation of cyclic formals with boron trifluoride etherate at 35°. By g.l.c. they found some cyclic oxygen compounds during the polymerisation. In fact, they observed these compounds when using the g.l.c. at high sensitivity and using large amounts of solution. However, under these conditions it is difficult to assess the meaning of these findings, without information about the initial purity of reagents and solvents.

Yamashita et al.[24] have published kinetic measurements on the polymerisation of 1,3-dioxolan and 1,3-dioxepan with triethyloxonium tetrafluoroborate. They calculated rate constants assuming the initiator to be 100% efficient. This was shown by Jones[2,25] to be erroneous because this initiator does not give 100% efficient initiation. Yamashita found an induction period and supposed that it was due to water, but high vacuum techniques did not reduce the induction period to zero.

Hayashi et al.[26] have reported the polymerisation of 1,3-dioxolan with maleic anhydride and benzoyl peroxide. The same experiments were carried out under vacuum by Jones,[2] but he did not get polymer.

Medvedev et al.[27] have published several papers on polymerisation of 1,3-dioxolan by triethyloxonium hexachloroantimonate. They postulated the active centre to be a carboxonium ion, because a solution of triethyloxonium hexachloroantimonate absorbs at 272 nm whereas in the presence of 1,3-dioxolan the solution absorbs at 228 nm. They consider the former absorption to be due to a tertiary oxonium ion and the latter to a linear carboxonium ion. However, later on Penczek et al.[28] showed that antimony pentachloride and antimony hexachloride salts absorb in methylene dichloride solution in the UV at 272 nm. Penczek concluded that no absorption in the UV for any aliphatic carbonium, carboxonium or oxonium ions can be expected above 200 nm and therefore the Russian authors' theory is not applicable to 1,3-dioxolan.

Enikolopyan et al.[29,30] published several papers on the polymerisation of 1,3-dioxolan. They carried out kinetic experiments with boron trifluoride etherate, triethyloxonium hexachloroantimonate, triethyloxonium hexachloroantimonate-methylal mixture, perchloric acid, antimony pentafluoride, tin tetrachloride, and trifluoromethane sulphonic acid. They also worked out the thermodynamics of polymerisation and their values are similar to those of Westermann.[1,35] Most of their work was carried out under argon or nitrogen. They tried to explain the S-shaped reaction curves without discussing hydride abstraction and basicity. They proposed an autocatalytic reaction and that the active centres are carboxonium ions.

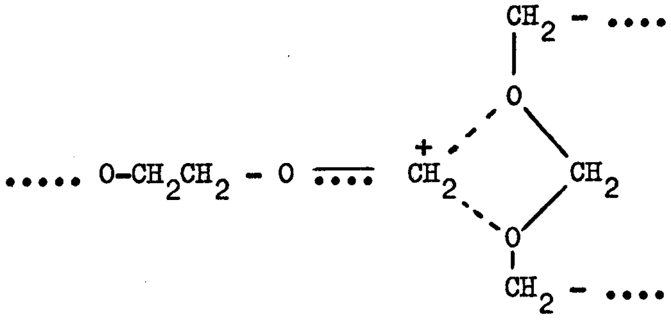
Busfield et al.[32] studied the equilibrium between gaseous monomer and amorphous polymer for 1,3-dioxolan and 1,3-dioxepan with boron trifluoride etherate or phosphorus pentafluoride as initiators and calculated ΔH^{o}_{gc}, ΔH^{o}_{lc}, ΔS^{o}_{gc} and ΔS^{o}_{lc}.

Jaacks et al.[17,32,33] showed that the active centres in the polymerisation of trioxan are alternating oxonium ion and carboxonium ions and then applied the same idea to the polymerisation of 1,3-dioxolan. They carried out polymerisations with perchloric acid in methylene dichloride under nitrogen. They killed the reactions with sodium ethoxide and determined polymer end-groups by g.l.c. They concluded that the reaction proceeds via tertiary oxonium ions and that ring-closure happens by back-biting. This mechanism was widely accepted for the polymerisation of 1,3-dioxolan.[35] This mechanism will be discussed in more detail in Chapter Five.

Westermann[1,35,36] has carried out the polymerisation of 1,3-dioxolan and 1,3-dioxepan with anhydrous perchloric acid in methylene dichloride, under high vacuum over a wide temperature range. He has done thermodynamic, kinetic and end-group determinations. He found that the number of end-groups was less than the number of moles of initiator. Therefore, he concluded that the active centre was a secondary oxonium ion and that propagation occurs by a ring-expansion mechanism.

Jones[2,25] carried out polymerisations with the above monomers and also some other cyclic oxygen compounds. He used anhydrous perchloric acid and some triethyloxonium salts for initiation. He showed that triethyloxonium salts did not give 100% initiation and that their reaction with the cyclic formals is not as simple as was postulated by Yamashita. When he used anhydrous perchloric acid he determined end-groups using Saegusa's[37] phenoxyl end-capping technique. He found that the number of end-groups was always less than the number of moles of initiator.

Recently Penczek[28,38] put forward another mechanism for the polymerisation of 1,3-dioxolan. He carried out polymerisations with triphenylmethyl salts in methylene dichloride under high vacuum. He studied hydride transfer reactions and polymerisations with these salts. He proposed a scheme as follows



1.4

Although his experimental results fitted his explanation, he showed that these salts did not give a simple, clean reaction; side reactions occurred at the same time. He observed that formate end-groups have never been seen at either Mainz or Keele. In one of his papers[38c] the propagation rate-constants were plotted against initiator concentration. This type of graph is shown in Chapter Three of this thesis (Fig. 3.3). The intercept of this graph showed impurity in the system. Their system contains 1.2×10^{-3} M impurity and as they sometimes used 10^{-4} M initiator concentration their results must be highly suspect. I presume that this impurity is more probably water and this caused the induction period. When they increased the initiator concentration, the induction period disappeared.

There has been very little work on the polymerisation of substituted cyclic formals. Especially after Dainton and Ivin[12] and Small's[39] papers, most research workers have believed that 2-methyl-1,3-dioxolan and 4-methyl-1,3-dioxolan cannot be polymerised for thermodynamic reasons. This is discussed in more detail in Chapter Six.

Okada[40] reported for the first time that 2-methyl and 4-methyl-1,3-dioxolan gave no polymerisation.

Okada et al.[13] made only two experiments on the bulk polymerisation of 4-methyl-1,3-dioxolan, with acetic anhydride-perchloric acid and acetyl chloride-zinc chloride mixtures. They gave only low yields and one low intrinsic viscosity result.

Yamashita et al.[41] have made bulk copolymerisations of 4-methyl-1,3-dioxolan and 3,3-bis(chloromethyl)oxacyclobutane with boron trifluoride etherate.

Duke[42] has described only one bulk polymerisation of 4-methyl-1,3-dioxolan with boron trifluoride. He claimed to get an orange coloured, fairly mobile oil.

Weissermel et al.[43] had prepared copolymers of trioxan and 1,3-dioxolan by mixing trioxan and 2-methyl-1,3-dioxolan. They have used tin tetrachloride as initiator and cyclohexane as solvent. They claimed that 2-methyl-1,3-dioxolan and trioxan eliminated acetaldehyde and formaldehyde groups to give copolymer.

There are a few patents[44,45] where it is claimed that copolymerisations of 2-methyl and 4-methyl-1,3-dioxolan with trioxane, dioxolan and ketene occur.

There is only one patent[46] which claimed that polymerisation of 2-methyl-1,3-dioxolan occurs in bulk or in carbon tetrachloride. Zinc halides were used as initiators.

Recently Krummenacher and Elias[47] have been able to polymerise 4-phenyl-1,3-dioxolan with anhydrous perchloric acid in methylene dichloride at -35°. They claimed that the polymer was cyclic.

More recent work was carried out by Okada et al.[48]. They polymerised 2-methyl-1,3-dioxepan in dichloroethane with triethyloxonium tetrafluoroborate and boron trifluoride etherate at temperatures of 20 to -20°. They determined the thermodynamic parameters. They also attempted polymerisation of 2,2-dimethyl-1,3-dioxepan with triethyloxonium tetrafluoroborate. They found a crystalline cyclic dimer only.

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CHAPTER TWO

Experimental Work

Part One: Materials

2.1.1 Solvents

2.1.1.1 Methylene dichloride. This solvent (Honeywill and Stein Ltd.) was purified as described by Weissberger[1] and Perrin,[2] then dried over calcium chloride and finally distilled over calcium hydride in a Normatron automatic laboratory distillation apparatus with a reflux ratio of 15:1. Head and tail fractions, each consisting of about 20% of the total volume were rejected and a middle fraction b.p. 39.5°/752 mm. (Lit.[1] 39.95°/760 mm.) was collected. No impurities were detected by g.l.c.

The middle fraction was collected in dark bottles and poured into the reservoir, (Fig. 2.1) which contained calcium hydride. The reservoir was then closed with a mercury seal, and the solvent was degassed and refluxed for several days, during which time it was mixed with a magnetic stirrer.

The methylene dichloride was then distilled on the vacuum line from the reservoir into a flask containing a fresh sodium mirror and sealed with a BiPl[3] or Plegli[4] metal valve. Normally the methylene dichloride was kept there overnight before use. The method is similar to that described by Cheradame.[5] Penczek[6] has shown that methylene dichloride distilled from sodium mirror contained about 10^{-6} M water.

2.1.1.2 Carbon tetrachloride. The commercial product (B.D.H.) was washed with conc. sulphuric acid, then with dilute sodium hydroxide, and refluxed over phosphorus pentoxide for 6 h. Finally, it was

Fig. 2.1

Methylene dichloride dosing apparatus.

B	Burette
M	BiPl taps
D	Distillation condenser
R	Reflux condenser
F	5 l Flask

The solvent is distilled into the burette by warming F gently.

Fig. 2.2

Purification and storage apparatus for ethanol.

T	Teflon taps
C_1 and C_2	Storage ampoules with break-seal.

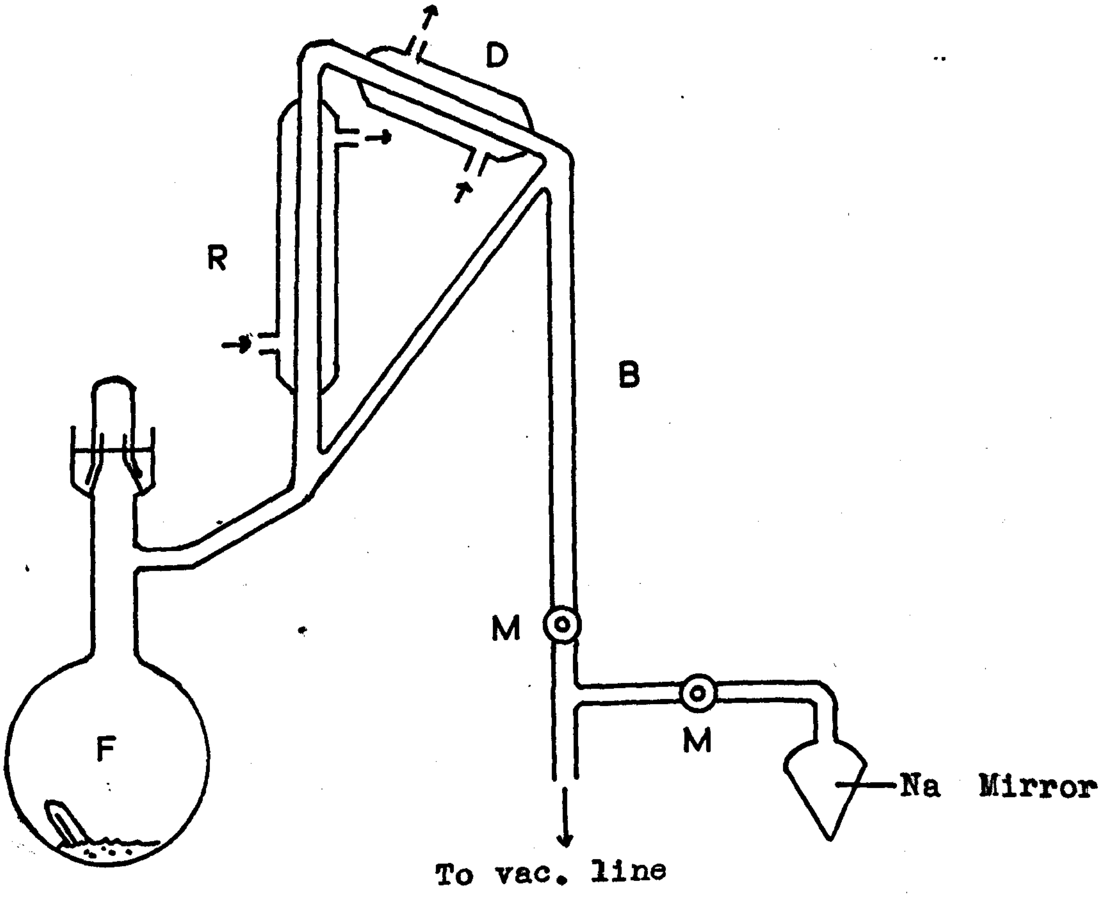


Fig. 2.1

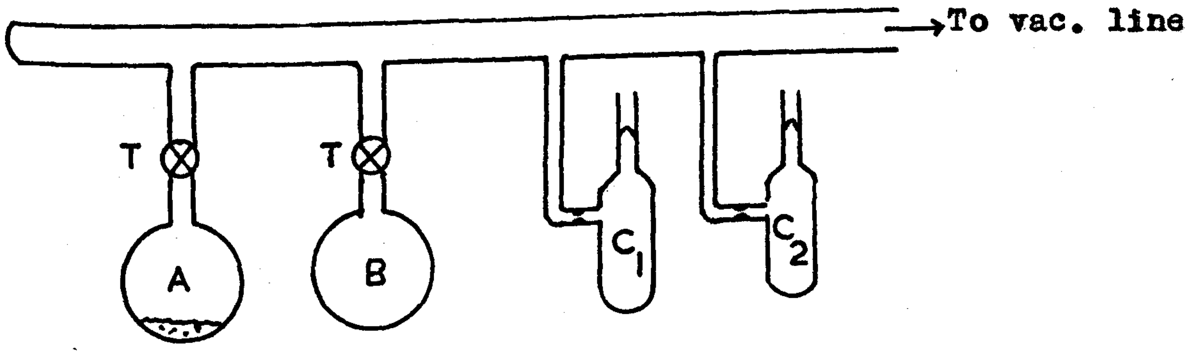


Fig. 2.2

distilled on a 1m column containing nickel-gauze, with a reflux ratio 10:1, b.p. 75°/750 mm, (Lit.[1] 76.75°/760 mm.) The middle fraction was collected in a dark bottle containing molecular sieves, type 4A. It was transferred to the vacuum line reservoir containing phosphorus pentaoxide and attached to the line via a Teflon tap.

A purity test by g.l.c. showed only a single peak.

2.1.1.3 Ethanol. The commercial product (B.D.H.) was purified according to the method of Perrin.[2] It was refluxed over magnesium turnings and then fractionally distilled onto calcium oxide, with a 1m column containing nickel-gauze, with a reflux ratio 10:1, b.p. 78°/755 mm, (Lit.[2] 78.3°/760 mm.) The flask A (Fig. 2.2) containing the ethanol was attached to the vacuum line and the ethanol was distilled into the reservoir B containing a sodium mirror. The ethanol was then collected in glass ampoules C_1 and C_2 fitted with break-seals.

A g.l.c. of the ethanol before it was distilled onto the calcium oxide showed only a single peak.

2.1.1.4 Di-ethyl ether. The commercial product (M. & B.) was purified according to the method of Perrin.[2] It was then fractionally distilled from sodium wire through a 1m nickel-gauze packed column, with a reflux ratio 7:1, b.p. 34°/750 mm, (Lit.[2] 34.5°/760 mm.) A g.l.c. showed a single peak only. This ether was attached to the vacuum line and distilled into a reservoir containing a sodium mirror. From there the ether was distilled into glass ampoules fitted with break-seals; the arrangement was similar to that shown in Fig. 2.2.

2.1.1.5 Nitromethane. The commercial product (B.D.H.) was washed with water several times, then dried with type 4A molecular sieves, and refluxed with sodium hydrogen sulphite for 4 h. to remove aldehydes. It was then fractionally distilled through a 50 cm. Vigreux column with a reflux ratio of 10:1; b.p. 101°/749 mm (Lit.[1] 114°/760 mm). No impurities could be detected by g.l.c. The middle fraction was transferred into a conical flask attached to the vacuum line, containing a magnetic stirrer and chromatographic silica gel which had been previously reactivated by heating it under vacuum at 300°.

2.1.2 Monomers

2.1.2.1 1,3-Dioxolan. This monomer (Koch-Light Ltd.) was purified by refluxing it over sodium hydroxide until no more sodium hydroxide was used up. It was then fractionally distilled, further refluxed for 24 h. over potassium metal, and finally fractionally distilled off potassium metal through a 75 cm column filled with Fenske-helices at a reflux ratio 6:1. A product having b.p. 75.5°/750 mm (Lit.[7] 75°/760mm) was obtained. The monomer was then distilled into a reservoir containing sodium-potassium (1:3) alloy, which was attached to the vacuum line. The monomer was completely degassed by repeated freeze-thawing and during that time it was stirred magnetically. The monomer was isolated from the dosing line by a BiPl valve; the dosing procedure has been described in the Fig. 2.3.

At the beginning of this work lithium aluminium hydride was used instead of sodium-potassium alloy. Although 1,3-dioxolan is reported[8] to be stable to lithium aluminium hydride, the reservoir always needed degassing before each distillation, because there was a slight evolution of gas. Jones[9] showed that degassing was still required even after three years' storage. I observed a similar gas evolution, and also that the volume did not decrease . I took a gas sample for mass-spectroscopic investigation, but it showed only 1,3-dioxolan. I left one batch of the 1,3-dioxolan over the lithium aluminium hydride for one year, after which time I found a crystalline compound and a gel in the reservoir. Similar results were obtained by Schlotterbeck[10] in Mainz.

Although my kinetic polymerisation results agreed well with those of Jones they showed that the monomer contained impurities in concentrations of ca. 10^{-3} M (See Chapter Three). Therefore I began to use sodium-potassium alloy for the final drying of the monomer.

A g.l.c. showed a single peak only.

2.1.2.2 1,3-Dioxepan. This monomer was prepared from butane 1,4-diol (B.D.H.) and paraformaldehyde (B.D.H.) as described by Laurent.[7] 296 ml of butane 1,4-diol was mixed with 102 g paraformaldehyde and 16.4 ml orthophosphoric acid. This mixture was made to react in, and distilled from, a flask fitted with a 50 cm fractionating column. A mixture of water and 1,3-dioxepan was distilled off, the fraction boiling at 90-120°/748 mm was collected; and the aqueous and non-aqueous layers were separated by salting out with calcium chloride. Sodium hydroxide was added to the non-aqueous layer, which was refluxed for 6 h and then distilled off. The product was refluxed over sodium for 24 h and then fractionally distilled through a 75 cm column containing Fenske-helices at a reflux ratio 6:1; b.p. 116°/748 mm. (Lit.[7] 117°/760 mm.)

A g.l.c. showed a small amount of tetrahydrofuran. This impurity cannot be removed by very careful distillation, even at a reflux ratio of 50:1.[11] This monomer was stored over lithium aluminium hydride.

2.1.2.3 4-Methyl-1,3-dioxolan. This monomer was prepared from 1,2-propylene glycol (Mersey Ltd.) and paraformaldehyde with orthophosphoric acid as catalyst.[12] The distillate showed two impurity peaks (~1:3 vol/vol) in the g.l.c. analysis. These impurities could not be removed by distillation. This monomer had b.p. 82°/760 mm (Lit.[13] 83.7-84.2°/756 mm.)

Because of the impurities in this first batch, a second batch of this monomer was prepared by Astle's method.[14] Commercial 1,2-propylene glycol (H. & W.) was distilled under reduced pressure b.p. 104°/32 mm. (Lit.[2] 104°/32 mm.) 1250 ml of distilled 1,2-propylene glycol was mixed with 450 g of paraformaldehyde (B.D.H.) and 120 g of Amberlite IR-120 (H) resin (H. & W.) and distilled. The organic and aqueous layers were separated and anhydrous sodium sulphate was added to the organic layer. It was then refluxed over sodium hydroxide for 2 days and distilled off. This distillate was refluxed over potassium for 24 h. and then distilled in a Normatron column with a reflux ratio 9:1 b.p. 85°/750 mm. This middle fraction showed only a single peak by g.l.c. It was then distilled into a reservoir, containing sodium-potassium alloy and attached to the vacuum line by a metal valve. The monomer was completely degassed by repeated freeze-thawing.

2.1.2.4 2-Methyl-1,3-dioxolan. This monomer was also prepared by Astle's method.[14] 150 ml of 1,2-ethylene glycol (B.D.H.) was mixed with 300 ml para-acetaldehyde and 40 g of Amberlite IR-120 (H) resin and distilled. The organic and aqueous layers were separated and anhydrous sodium sulphate was added to the organic layer. It was then refluxed over sodium hydroxide for 3 days and distilled off. This distillate was refluxed over potassium for 24 h. and then distilled through a 75 cm column filled with Fenske-helices with a reflux ratio of 7:1 b.p. 82.5°/746 mm (Lit.[14] 82-83°/760 mm). This monomer showed two small impurities by g.l.c.

2.1.2.5 cis and trans-7,9-Dioxabicyclo-[4.3.0]-nonane. We obtained as a gift from Robinson Bros. some cyclohexane-1,2-diol, both cis-trans mixture and a specimen of pure trans, and these were used for the preparation of these monomers. 60 g of cis-trans diol mixture was mixed with 150 ml of acetone, 150 ml of light petroleum ether and 0.1 g toluene sulphonic acid mono hydrate and refluxed.[15] The water was removed by a Dean and Stark trap and the solution was distilled under reduced pressure. The cis isomer gives a ketal easily, which distils out, and the trans diol is left in the flask. The residue in the flask was extracted with benzene and the solution then evaporated to obtain the crude trans diol, unreacted cis diol remaining in the flask.

The cis diol was mixed with paraformaldehyde and orthophosphoric acid. The resulting cis formal was distilled under reduced pressure. The product showed a carbonyl group in the IR spectrum. Therefore it was refluxed over sodium hydroxide and subsequently lithium aluminium hydride and distilled off. b.p. 60°/27 mm (Lit.[16] 69°/27 mm.)

The trans diol was mixed with paraformaldehyde and sodium methoxide and heated gently until the mixture melted. Orthophosphoric acid was added[17] and heated in the oil bath at 180° for 2 h. During that time water was collected in a Dean and Stark trap. Then the mixture was distilled under reduced pressure. b.p. 63°/19 mm. (Lit.[17] 66-67°/19 mm). This monomer was used without any purification.

2.1.3 Initiators

2.1.3.1 Anhydrous perchloric acid. This acid was prepared by dehydration of 72% perchloric acid (B.D.H.) with 20% oleum (B.D.H.). The method has been described in more detail by Mathias.[18,19] The purity of acid was checked with barium chloride and polarography,[20] and it was found to contain less than 10^{-6} M sulphuric acid.

2.1.3.2 Trifluoro methane sulphonic acid. A commercial product (3M Company) was put into a flask which was attached to the vacuum line via a Teflon tap and purified by bulb-to-bulb distillation.[18] The head fraction was rejected and the middle fraction was retained. The acid reacted with silicone grease, producing a white precipitate in the line, which was not distillable. Therefore, the second batch of acid was prepared by using only Teflon taps.

Mathias[18] assumed that the acid reacted with methylene dichloride thus:

$$CF_3SO_3H + CH_2Cl_2 \longrightarrow CF_3SO_3CH_2Cl + HCl$$

therefore it was decided to use carbon tetrachloride as a solvent. Unfortunately the acid is insoluble in carbon tetrachloride and gave two layers. The acid gave a suspension in the solvent layer and this layer was decanted, and used for polymerisation reactions. The concentration of acid was determined by acid-base titration.

2.1.3.3 Methyl fluorosulphonate. A simple preparation of alkyl fluorosulphonates was published recently.[21,22]

50 ml of fluorosulphonic acid (B.D.H.) and 99 ml of dimethyl sulphate (B.D.H.) were mixed and fractionally distilled at atm. pressure through a 30 cm Vigreux column; methyl fluorosulphonate passed over first, b.p. 94°/758 mm (Lit.[22] 92-94°/760 mm). After 15 min this colourless solution became pale brown and was redistilled using a 50 cm column containing Fenske-helices. The product was placed in the high vacuum line and transferred to the reservoir by bulb-to-bulb distillation. Methyl fluorosulphonate was distributed into phials by means of the tipping device.[23]

2.1.3.4 Acetyl perchlorate. Anhydrous silver perchlorate (B.D.H.) was put into the cross-shaped apparatus (See Fig. 2.4) in the dry-box. The apparatus was attached to the vacuum line via arm D and evacuated. During the evacuation it was flamed and then sealed from d. The anhydrous silver perchlorate was put into the apparatus in a dry-box and a B10 glass stopper fitted at A. The apparatus was attached to the vacuum line via arm B and the break-seal was broken by a "demon" in the same arm, for evacuation. Finally the apparatus was sealed off at b. The silver perchlorate was added to purified acetyl chloride by breaking break-seal c (Fig. 2.5). The reaction was carried out in methylene dichloride using excess of silver perchlorate. The solution was filtered through a sinter (porosity 3) and distributed into glass phials by means of the tipping device.

The concentration of acetyl perchlorate was determined by titration and also by adding triphenyl methyl chloride in the spectroscopic apparatus,[23,29] (Fig. 2.9) using $\lambda_{max} = 430$ nm, $\mathcal{E}_{max} = 3.8 \times 10^4$ mol^{-1} l cm^{-1}.

2.1.3.5 <u>"Tert-Butyl" perchlorate</u>. This substance was prepared by the same method as was used for acetyl perchlorate by mixing tert-butyl chloride and silver perchlorate. After ½ h. the solution had become pale yellow. The colour deepened with time, finally becoming dark brown. This substance was also prepared at 0°. In that experiment the colour developed again, but after a longer time. Finally it was prepared by adding anhydrous perchloric acid to isobutene in methylene dichloride at 0° under high vacuum conditions. The acid phial was broken in methylene dichloride and excess isobutene was added. The solution was kept in an ice-bath for ½ h., then pumped to remove excess isobutene. This solution was immediately put into the tipping device. The pale yellow colour developed but after a much longer time and this colour became constant after 2 weeks, if kept in the fridge.

2.1.3.6 <u>Nitronium hexafluoro-antimonate</u>. ($NO_2^+SbF_6^-$) The product (Schuchardt München ~ 90%) was put into the same device as described (Fig. 2.4) in the dry box. The salt was then transferred into the purified nitromethane by means of a device similar to that shown in Fig. 2.5, and then was distributed into the tipping device.

Fig. 2.3

A monomer dosing system.

Sodium and potassium put into A and pumped, then distilled into F via arm B.

M	BiPl tap
B	Burette

Fig. 2.4

An apparatus for handling hygroscopic salts.

Fig. 2.5

An apparatus for preparing acetyl and "tert-butyl" perchlorate.

A	Acetyl or tert-butyl chloride
B	Burette
F	Mixing flask
S	Sinter

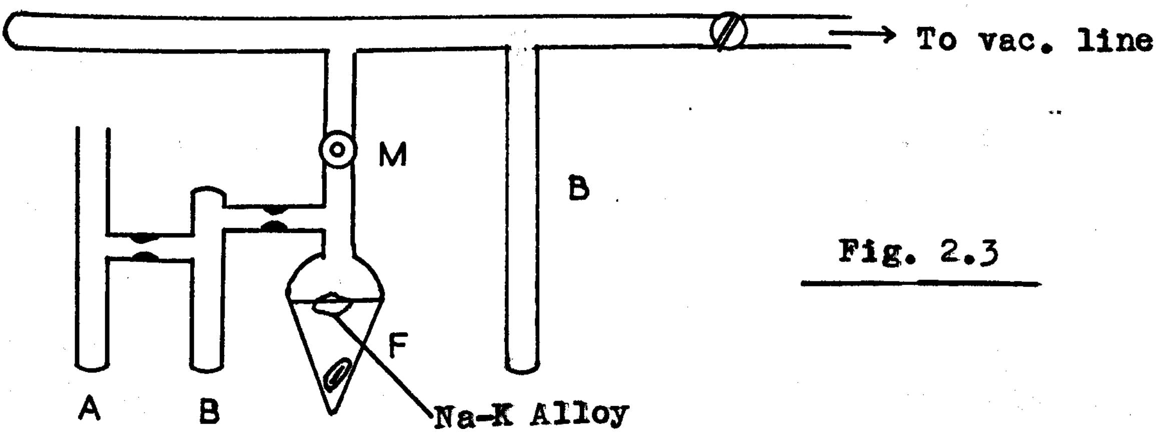


Fig. 2.3

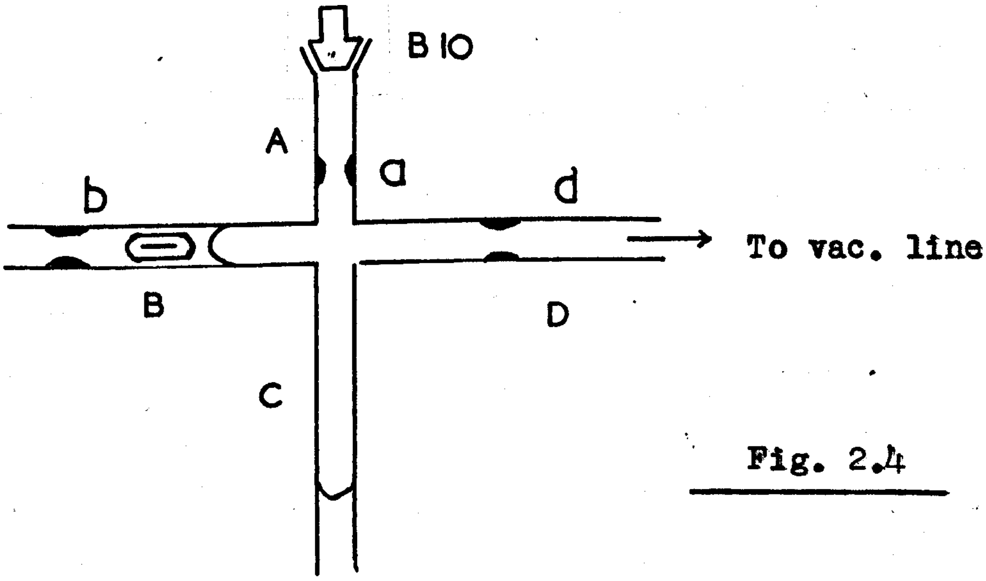


Fig. 2.4

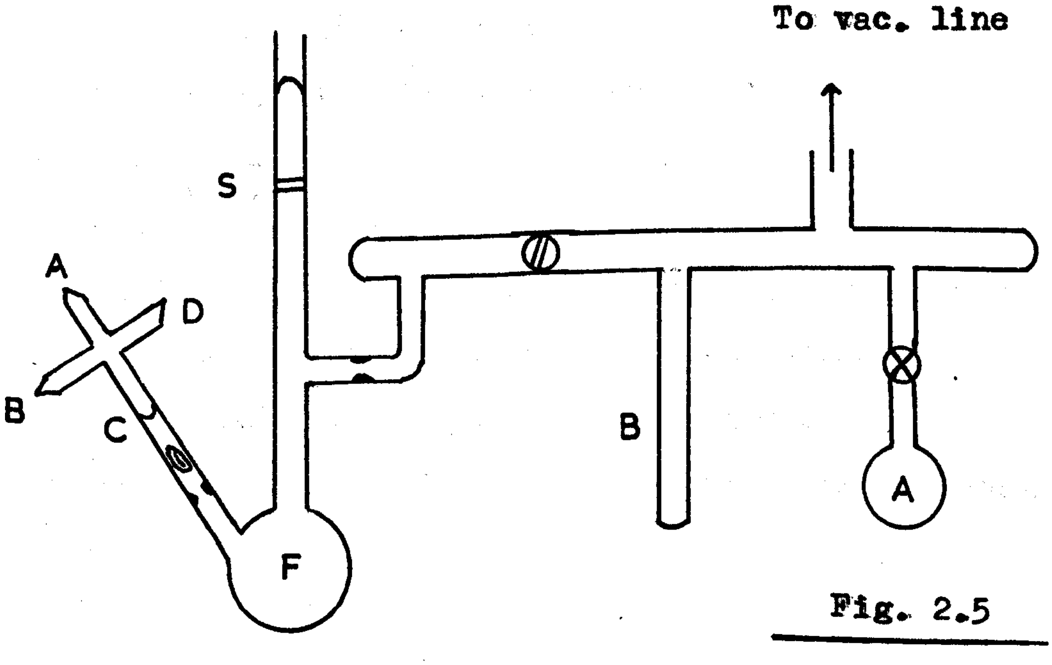
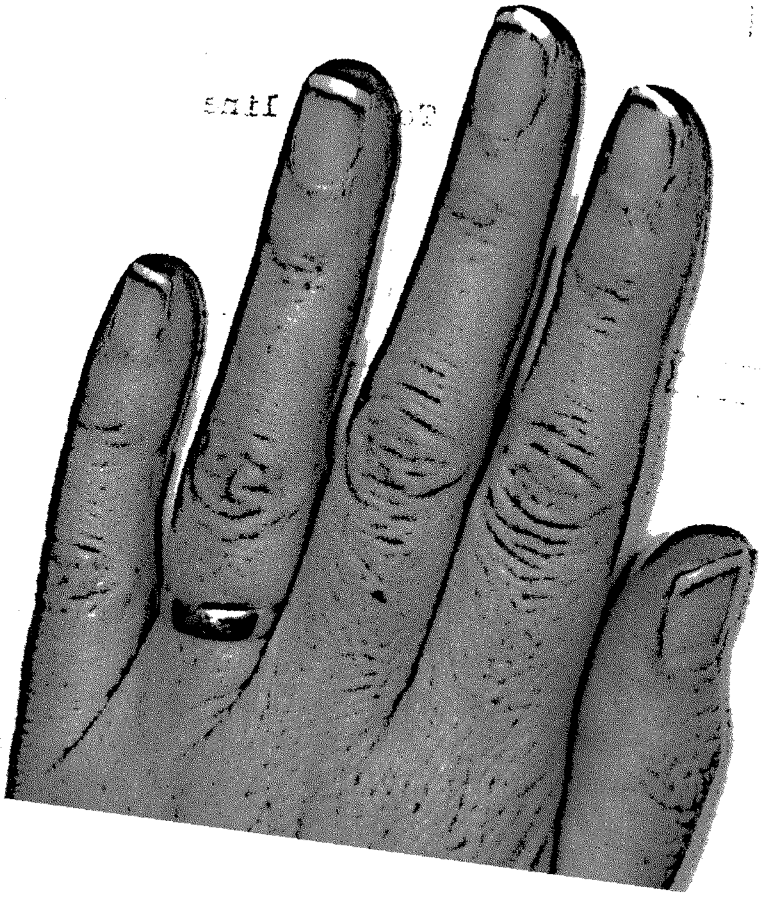


Fig. 2.5



The concentration of the salt was determined by titration. One of the salt phials was broken in an excess of 0.1 N sodium hydroxide solution and it was heated, then it was cooled down. This solution was back-titrated by 0.05 N hydrochloric acid.

2.1.3.7 <u>Nitrosonium tetrafluoroborate</u>. ($NO^+BF_4^-$). The compound (Aldrich Chem. Comp.) was transferred into the phials as described in the previous Section (Fig. 2.4). Unfortunately this salt was only slightly soluble in nitromethane; therefore I prepared special large phials for this salt.

The concentration of salt was determined by titration as described.

2.1.3.8 <u>Nitrosonium hexafluorophosphate</u>. ($NO^+PF_6^-$) The product (ROC/RIC, 98%) was put into the device described in the previous Section (Fig. 2.4). The salt was dissolved in the nitromethane and transferred into phials by means of the tipping device.

The concentration of salt was determined by titration as described before.

2.1.3.9 <u>Nitrosonium hexafluoro-antimonate</u>. ($NO^+SbF_6^-$) The product (ROC/RIC, 97%) was put into the device as described in the previous Section (Fig. 2.4). The salt was dissolved in the nitromethane and transferred into phials by means of the tipping device.

The concentration of salt was determined by titration as described before.

2.1.3.10 <u>Titanium tetrachloride</u>. Titanium tetrachloride from an ampoule prepared by Dr. Beard was redistilled in the vacuum line and diluted with methylene dichloride. This solution was distributed into phials by means of the tipping device.

The concentration of the titanium tetrachloride was determined by Biddulph's[25] method.

2.1.4 Killing Reagents

2.1.4.1 Sodium ethoxide. Commercial sodium (B.D.H.) was purified by the cascade system. If sodium was purified by distillation, it gave a yellow-to-brown solution in ethanol.[26]

Sodium was purified in the apparatus shown in Fig. 2.6. Ca. 12 g of sodium with the skins on the pieces (mainly peroxide and hydroxide) were put into the tube A, which was then sealed at a_1 to the apparatus. This was then evacuated for 8 h. without heating the sodium and was then sealed at d_1. Tube A was heated gently and the melted sodium was transferred quickly into B. The peroxide and hydroxide stuck on the glass wall and tube A was separated by sealing it off at a_2. The process was repeated twice and clean, silver-shining sodium was collected in E.

Flask E was attached to the vacuum line via e as shown in Fig. 2.7. 300 ml of purified ethanol was distilled into the flask E. The reaction between sodium and ethanol was exceedingly slow in the high vacuum conditions. Sodium ethoxide was precipitated on the sodium and this caused the reaction to stop. Therefore, it was necessary to stir and heat the reaction mixture. Although mixing and heating increased the hydrogen evolution, it took three days for the reaction to go to completion. The hydrogen evolved was pumped off from time to time.

This solution was put into glass ampoules by a method essentially similar to those described and the excess of ethanol was evaporated off, leaving white crystalline sodium ethoxide in the ampoule (F). This was attached to the vacuum line and purified diethyl ether was distilled into it. The solution was filtered through two sinter-glass filters (Porosity 2and 3) on the apparatus shown in Fig. 2.8 and then it was transferred into the reservoir D of the tipping device. Sodium ethoxide dissolved in diethyl ether was distributed into the phials. The

Fig. 2.6

The cascade apparatus for purifying sodium.

Fig. 2.7

Apparatus for sodium ethoxide preparation.

Fig. 2.8

Apparatus for distribution to sodium ethoxide into the phials.

T	Teflon tap
SF_1 and SF_2	Sinter-glass filter
D	Tipping device

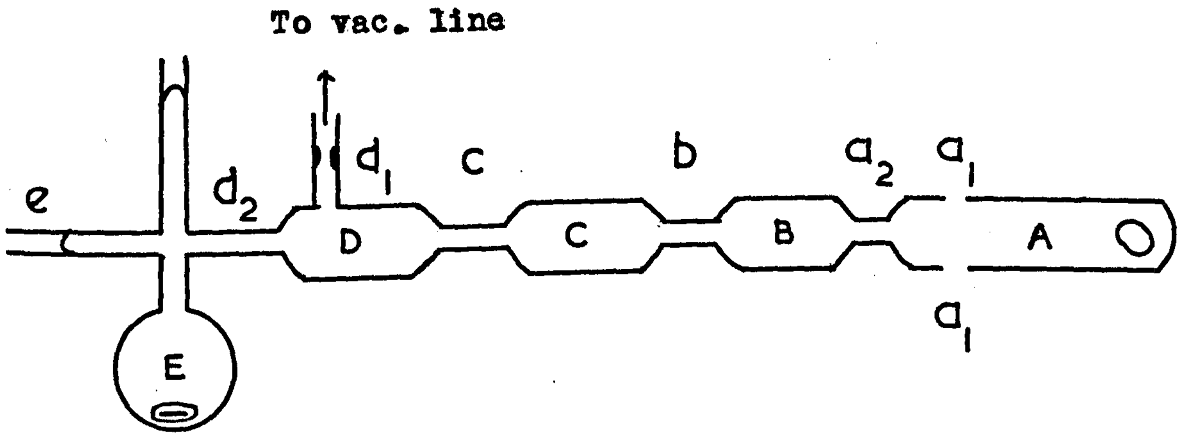


Fig. 2.6

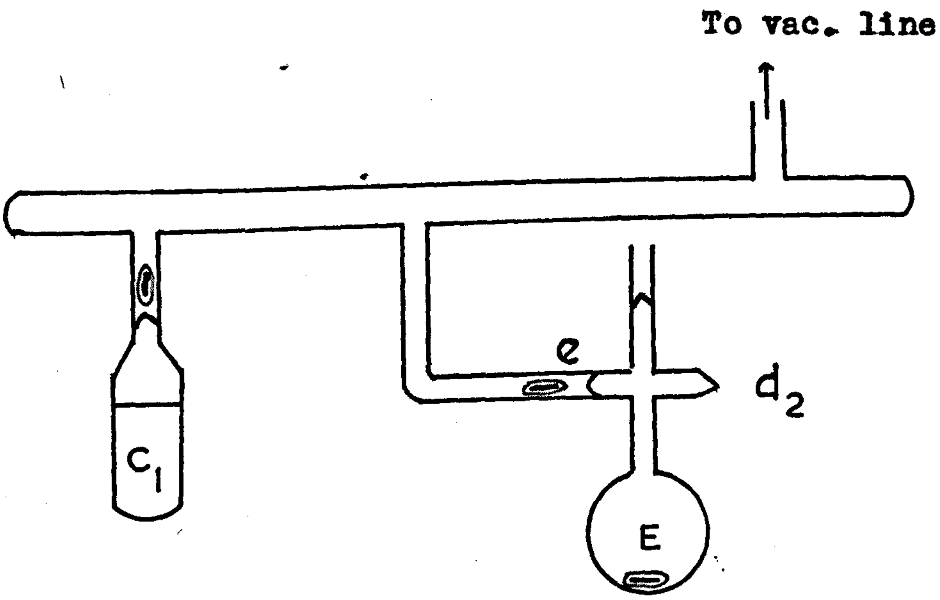


Fig. 2.7

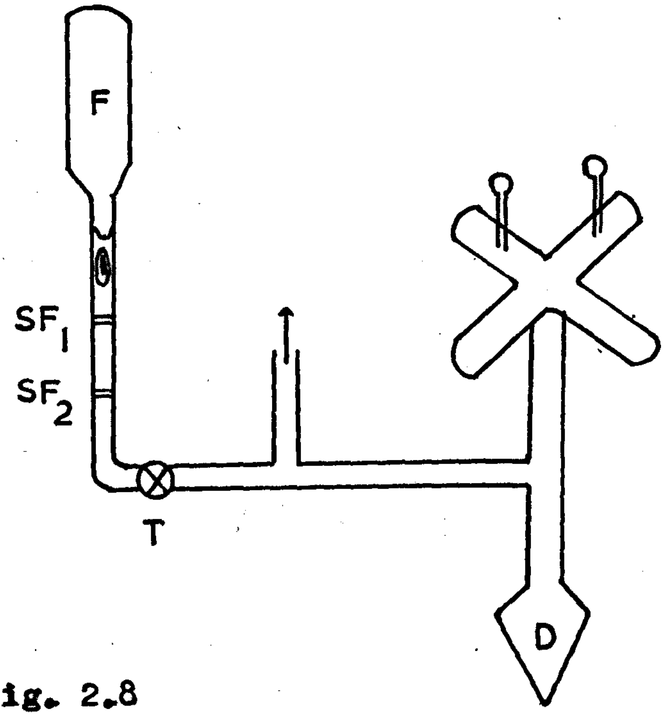


Fig. 2.8

concentration of sodium ethoxide in the phials was determined by titration.

2.1.4.2 Triethylamine. A commercial product (B.D.H.) was purified as described in Perrin.[2] It was first dried over potassium hydroxide, then distilled over calcium hydride; b.p. 89°/755 mm. (Lit.[2] 89.4°/760 mm.) A middle fraction was collected over molecular sieves (type 4A) and then distilled into the tipping device under high vacuum conditions.

2.1.5 Miscellaneous

2.1.5.1 Acetyl chloride. A commercial product (B.D.H.) was refluxed over phosphorus pentoxide and distilled. A middle fraction was redistilled from one-tenth its volume of dimethylaniline, b.p. 52°/748 mm. (Lit.[2] 52°/760 mm.) Middle fraction was redistilled bulb-to-bulb in the high vacuum line and kept in the flask with a Teflon tap.

2.1.5.2 tert-Butyl chloride. The puriss (Koch-Light) product was kept for two days on calcium chloride and then refluxed for 4 h and distilled, b.p. 50.5°/752 mm (Lit.[2] 50.4°/760 mm). The distillate was distilled bulb-to-bulb in the high vacuum line and kept in a flask with a Teflon tap.

2.1.5.3 Tetra-n-butylammonium perchlorate. 20 ml of tetra-n-butylammonium hydroxide was diluted with water to 400 ml and dilute perchloric acid was added slowly, the pH being measured with a pH-meter. The addition was stopped at pH=7.2. The precipitated salt was washed with the mother liquor, followed by distilled water, then recrystallised from an acetone-water mixture. The compound was dried in the vacuum oven at 20°/20 mm.

2.1.5.4 Tetra-n-butylammonium tetrafluoroborate. Technical (40%) fluoroboric acid was diluted with water using a polyethylene measuring cylinder. A dilute tetra-n-butylammonium hydroxide solution was added carefully. At pH=7.2 the addition was stopped. The salt was purified as described above.

Part Two: Apparatus and Techniques

2.2.1 Apparatus

2.2.1.1 The Adiabatic calorimeter. This apparatus was developed by Biddulph and Plesch[28] and fully described by Panton[29] and Mathias.[19] Fast reactions were followed by recording the time-temperature curve. The present version of the calorimeter also contains electrodes by means of which the conductivity of the polymerising mixture can be recorded. Reactions can be killed at any desired temperature without opening the calorimeter by crushing a phial of a killing agent.

2.2.1.2 Dilatometers. Slow reactions were followed in dilatometers, some of which were fitted with electrodes for conductance measurements.[30]

Some of the polymerisations were carried out in simple dilatometers without electrodes.

2.2.1.3 Spectroscopy apparatus. The apparatus was used for some of the concentration determinations under vacuum. This apparatus is shown in Fig. 2.9, and is fitted with 1 mm and 10 mm silica cells.

2.2.1.4 Electrodes in the adiabatic calorimeter. In the device described in Ref. 29 the electrodes were fitted in place with

Fig. 2.9

Spectroscopy apparatus.

PQ	Quartz-Pyrex graded seal.

Fig. 2.10

Electrodes fitted in the adiabatic calorimeter.

C-P	Copper-Pyrex seal
T	Tungsten
Pt	Platinum
S	Soda glass
B	Brass ring
P	Pyrex glass
C	Copper
L	Lead glass

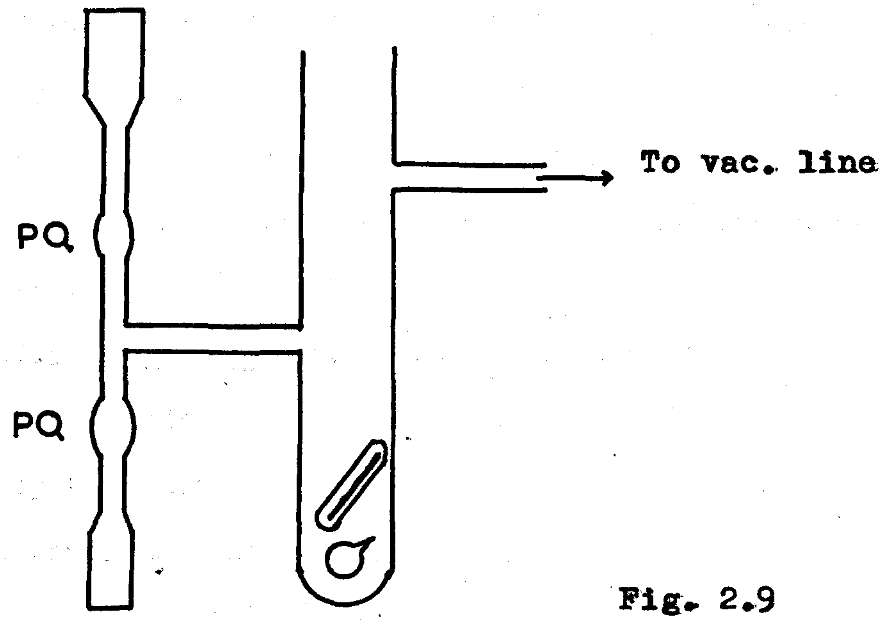


Fig. 2.9

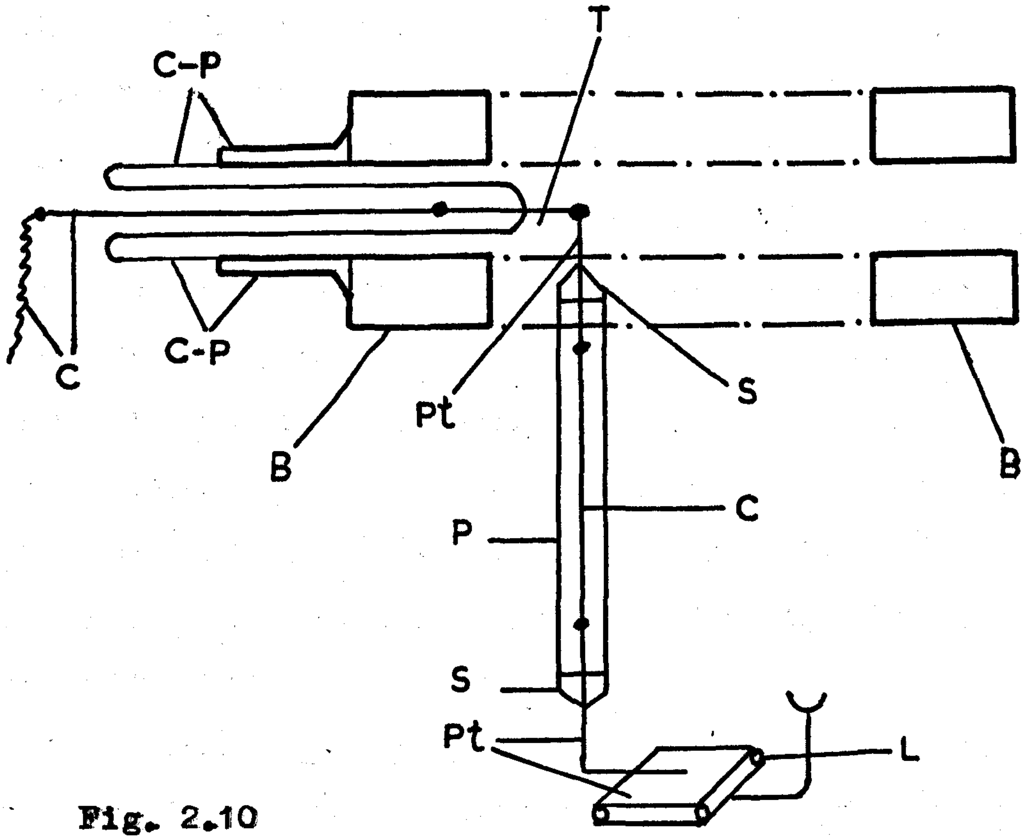


Fig. 2.10

Araldite. That system sometimes developed leaks as the Araldite was dissolved by methylene dichloride. The Araldite seal was replaced by a copper-glass seal, soldered into the brass ring, in the manner shown in Fig. 2.10. This system was completely air-tight and was used for more than two years without any trouble.

2.2.1.5 Cell constants. The cell constants of the adiabatic calorimeter electrodes and the dilatometer electrodes were obtained by the method of Lind, Zwolenik and Fuoss.[30]

Cell constants Calorimeter electrodes: 0.083 cm^{-1}
Dilatometer electrodes: 0.953 cm^{-1}

2.2.1.6 Distillations. Fractional distillations were performed with various sizes of columns, most of them containing Fenske-helices. Methylene dichloride and some monomers were distilled on a Normatron automatic distillation apparatus. This consists of a 1.5 m vacuum-jacketed, silvered column, filled with Fenske-helices and surmounted by a still-head in which the take-off was controlled by a magnetically operated valve. The column has a very high number of theoretical plates and can operate with a reflux ratio up to 99:1. The fractions collected were very accurately controlled by contact thermometers.

2.2.1.7 Thermostats. Dilatometry experiments were carried out in a water bath at 25° and a well stirred ice bath at 0°. The lower temperatures were obtained by the use of a "Minus Seventy Thermostat Bath" (Townson and Mercer Ltd.)

2.2.1.8 The Tipping Device. This device was used for the preparation of phials of initiations and also killing reagents under vacuum conditions. (Fig. 2.8) The phial contents were determined by the mid-point method.[31]

2.2.1.9 Water phials. A micro-syringe was used to fill small phials with the required quantity of distilled water. The phials were carefully dried, filled with the water and then sealed off.

2.2.1.10. Greaseless vacuum taps. Teflon (Rotaflo) and metal BiPl and Plegli taps were used. All monomers and some solvents were kept in vessels closed by one of these metal taps. The adiabatic calorimeter and the monomer and solvent dosing systems were sealed with metal taps.

2.2.1.11 Conductivity Bridges and Recorders. Conductivities for calibration purposes were measured with a Wayne-Kerr B221 Universal Bridge. The polymerisation experiments were followed with a Chandos Linear Conductivity Meter. For fast polymerisations the output of this meter was connected to one pen of a Rikadenki Kogyo fast-response two-pen recorder. The time-temperature curve from the adiabatic calorimeter was recorded by the second pen.

The g.l.c. experiments were carried out with a Servoscribe one-pen recorder.

2.2.1.12 Gas Liquid Chromatography (g.l.c.) The g.l.c. experiments were run with a Hewlett Packard 5700A, which is fitted with dual column analyzer, and FID and TC detectors. The injection and detector temperatures are controllable and the column oven has a temperature programming facility. All quantitative work was carried out with 2.5 m long, 3 mm diameter, stainless steel columns packed with 80-100 mesh Porapak Q columns.

Some experiments were carried out with 3 m long, 3 mm diameter, stainless steel columns, packed with 8% OV-10 1 Diatomite.

Helium was used as a carrier gas when the TC detectors were operated.

2.2.1.13 Molecular Weight Determinations. All molecular weights were determined with a Mechrolab Vapour Pressure Osmometer

Model 301A, with a non-aqueous probe at 37°. Chloroform was used as the solvent. The instrument was calibrated with benzil.

2.2.2 Spectroscopy

2.2.2.1 Ultraviolet and Visible Spectroscopy. The spectra reported in this work were obtained with a Unicam SP 800 recording spectrophotometer.

2.2.2.2 Infrared Spectroscopy. All infrared spectra were run on a Perkin Elmer 221 Grating Spectrophotometer. The instrument was calibrated by means of a polystyrene film.

All polymers were scanned in 1% carbon tetrachloride in the 1 mm cell. Spectra of liquid samples were taken with rock salt plates.

2.2.2.3 Nuclear Magnetic Resonance Spectroscopy. All n.m.r. spectra were run on a Perkin Elmer R10 N.M.R. or a Hitachi Perkin Elmer R-24 60 MHz spectrometer. These instruments were thermostatted at 32.5°. The position of the n.m.r. bands in carbon tetrachloride, deuterochloroform and methylene dichloride solution were determined by reference to T.M.S. at 10τ as an internal standard.

In a few experiments made under high vacuum the lead glass tube was sealed onto the vacuum line by means of a lead glass-to-pyrex seal. The tube was filled with a solution and frozen down and sealed off. It was then thawed and spectra were taken over a range of temperatures.

2.2.2.4 Mass Spectroscopy. All mass spectra were taken on a Hitachi RMU-6 mass spectrometer. The pressure was maintained at 10^{-6} mm Hg and the filament was made from tungsten. In these experiments the ion source had an energy of 80 eV.

2.2.3 Experimental Methods

2.2.3.1 Polymerisations and polymer isolation. All experiments were carried out under high vacuum conditions. Most of the glass apparatus was flamed during the pumping time.

Polymerisation experiments were carried out in the adiabatic calorimeter, in dilatometers and in vacuum-sealed tubes. Polymerisations were started by breaking a phial containing the initiator at the appropriate temperature.

The polymerisations were terminated in several ways. Most of them were terminated with ammonia vapour (from 0.88 ammonium hydroxide), some of them were terminated with 0.88 ammonium hydroxide. Some of the polymerisations were terminated by breaking phials of sodium ethoxide or triethylamine without opening the system to air.

Low molecular weight polymers of 1,3-dioxacycloalkanes are soluble in many solvents. Therefore, precipitation is an inefficient method of isolating the polymer. The polymers were isolated by evaporation of the neutralised reaction mixture in the Rotavapor-R for a few hours. Finally, the polymer was pumped to constant weight on the vacuum line.

More details of some experimental methods are given later in the appropriate sections.

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CHAPTER THREE

Effects of purity and of salts on some polymerisations

3.1 Introduction to Chapter Three

The work to be described in this Chapter is concerned with the effects of impurities and of salts on the cationic polymerisation of cyclic formals.

Westermann[1] was unable to devise a complete kinetic treatment for the polymerisation of 1,3-dioxolan. However, he found that the last part of the polymerisation, when the reaction had proceeded beyond the inflection point of the conversion curve, was a first-order reaction. The plots of first-order rate-constants against perchloric acid concentration were found to be linear, so that the last half of the polymerisation is also of first-order with respect to perchloric acid.

The rate-equation for the polymerisation is:

$$-dm/dt = k_1 m \qquad 3.1$$

with $$k_1 = k_2 \left[HClO_4\right] \qquad 3.2$$

m = monomer concentration

k_1 = First-order rate-constant

k_2 = Second-order rate-constant

Graphs of k_1 against perchloric acid concentration were straight lines, so that the values of k_2 at various temperatures could be calculated.

These graphs were used to find the impurity level in the system. The line should pass through the origin, but if the system contains one or more impurities which deactivate the acid, the line will not pass through the origin. Therefore, the impurity level can be checked kinetically. Most workers checked the purity of their monomers and solvents before the reaction by analytical methods. However, in the hands of Westermann[1] and Jones[2] the kinetic method showed that not all the perchloric acid reacts with the monomer. In Chapters Five and Six we will show in more detail that the level of impurity is very important in the polymerisation of 1,3-dioxacycloalkanes.

The salt effect is also of great importance when considering cationic polymerisations. It is well known that neutral salts can affect the rates of ionic reactions in solution. These results have been interpreted principally on the basis of the change in ionic strength and the mass-law effect.

Since the work of Szwarc,[3] it is generally accepted that in the anionic polymerisation of vinyl monomers at least two propagation reactions can be distinguished; these are propagation by free ions and propagation by ion-pairs.

Plesch[4] pointed out that the same results were obtained in cationic polymerisations and could also be interpreted by the existence of free ion and ion-pair propagations occurring at different rates. However, for cationic polymerisations it has only been possible to determine separate values of the two rate-constants for a few sulphur-containing monomers,[5] for styrene[6] and for tetrahydrofuran.[7] The main reason for this is that the dissociation constant of the reacting ionic species is not known. The reacting species in cationic polymerisations are extremely reactive, which makes it difficult to determine such dissociation constants. Furthermore, it is necessary to know the total concentration of growing chains and this too has proved to be difficult, especially for the cationic polymerisations of olefins. Therefore one aim of this work was to investigate the salt effect and then to try to calculate the free ion and ion-pair rate-constants.

Another reason for carrying out polymerisations in the presence of salts was to find the optimum reaction conditions, because parallel work was being carried out in the same lab, under similar conditions, on the polarography of polymerising solutions by Dr. F.G. Thomas. As such measurements could only be done in solutions in which the electrical conductivity was made sufficiently great by the addition of an electrolyte, it was essential to have some information on the effects of these salts on the polymerisations.

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3.2 Effect of impurity level on the cationic polymerisation of cyclic formals.

3.2.1 Polymerisation of 1,3-Dioxolan.

All the experiments with 1,3-dioxolan were run in the adiabatic calorimeter, fitted with all-metal BiPl or Plegli taps, under high vacuum conditions at 0°.

1,3-Dioxolan was distilled into the calorimeter from the reservoir via the burette. Methylene dichloride was used as solvent and a quantity measured from a burette was distilled into the calorimeter. The dosing systems are shown in Chapter Two. After distillation of the monomer and solvent the calorimeter was thermostatted and polymerisations were begun by crushing a phial of anhydrous perchloric acid in methylene dichloride and they were stopped by admitting to the reaction vessel the vapour from 0.88 ammonium hydroxide.

At the beginning of this work 1,3-dioxolan and 1,3-dioxepan were stored on lithium aluminium hydride. This reagent had been used successfully by Westermann[1] and Jones.[2]

Typical time-temperature (conversion) and time-conductivity curves are shown in Fig. 3.1. A first-order plot is shown in Fig. 3.2.

All results are shown in Table 3.1.

The first-order rate-constants are plotted against perchloric acid concentration in Fig. 3.3, line A. From the graph it was found that the system contained between 10^{-3} and 2×10^{-3} M impurity.

The second batch of monomer was dried with sodium-potassium alloy. The results obtained with this are shown in Table 3.1, Run No. 38B, 39B and 40B. The first-order rate-constants are plotted in Fig. 3.3, line B which shows that the system contained

Table 3.1

Data for Polymerisations of 2.0 M 1,3-Dioxolan at T = 0°

Run No.	43	41	32	38	40	38B*	39B*	40B*
$10^3[HClO_4]$ / M	2.75	3.40	3.49	3.62	3.87	2.90	3.69	4.66
Yield / %	25	39	35	37	38	45	38	36
k_1 / sec^{-1}	0.027	0.044	0.044	0.046	0.046	0.027	0.035	0.044
DP	8.9	8.5	14	10.5	9.3	11.7	8.5	8.4

* Na-K alloy used for drying

Fig. 3.1

Simultaneous plot of temperature and electrical conductivity against time for experiment 40B.

Fig. 3.2

First-order plot for experiment 40B. From the graph $k_1 = 0.044\ sec^{-1}$.

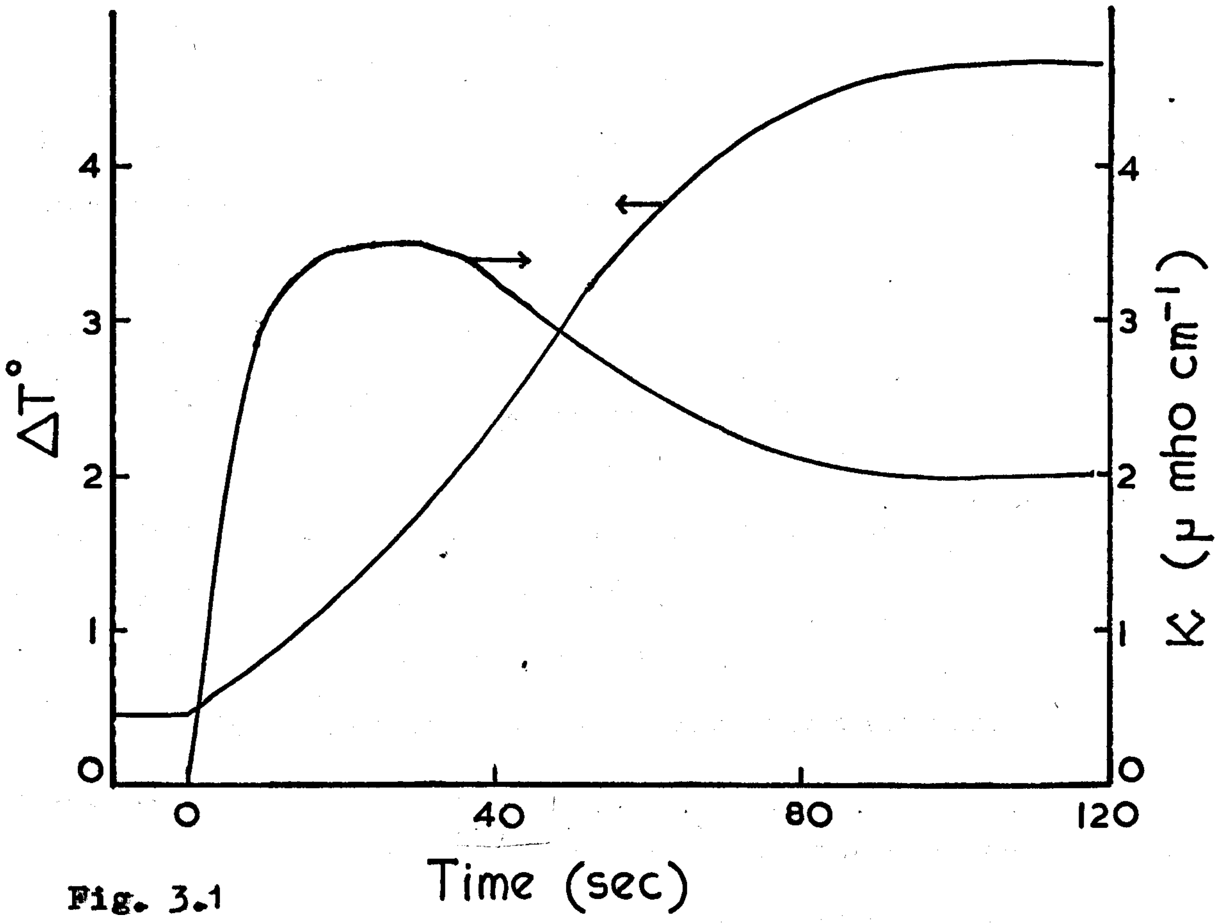

ΔT°
K (μ mho cm^{-1})
Time (sec)
0
1
2
3
4
0
40
80
120

Fig. 3.1

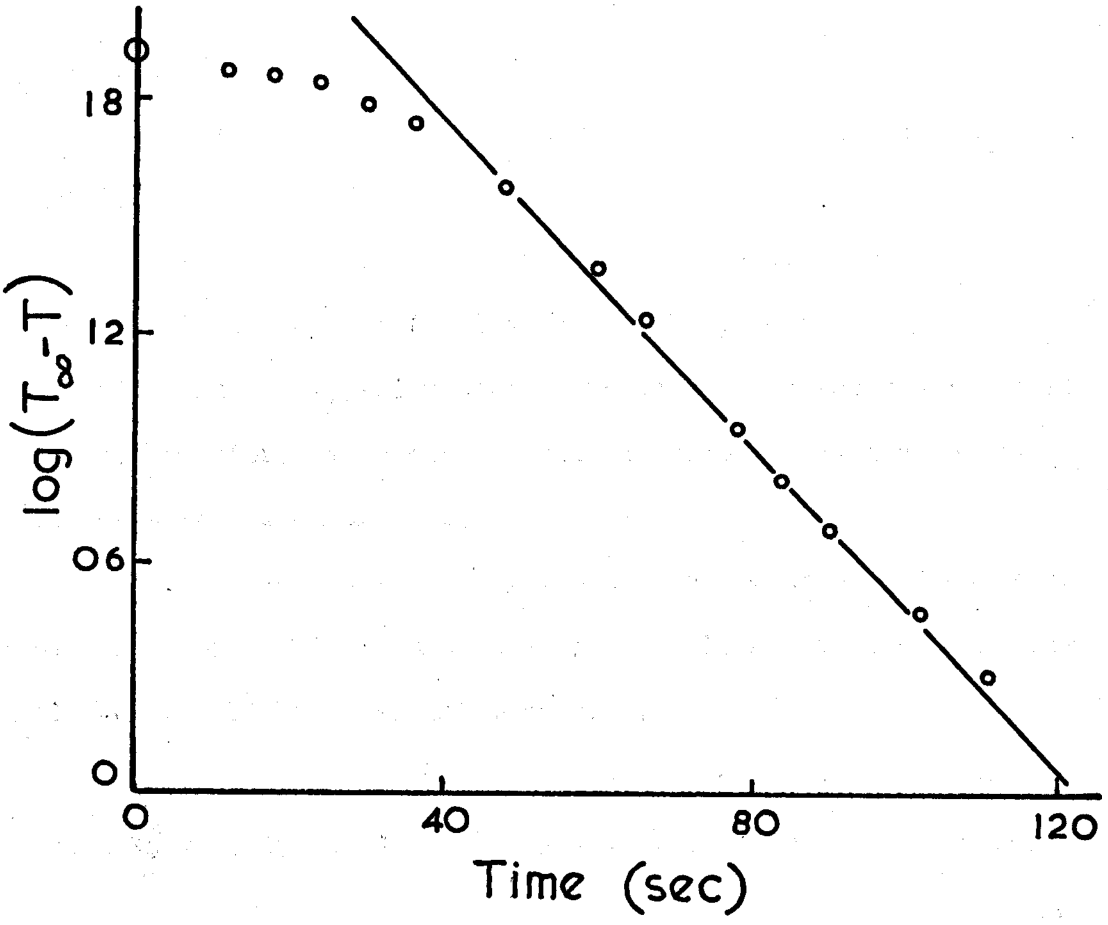

log(T$_\infty$-T)
18
12
06
0
40
80
120
Time (sec)

Fig. 3.2

about 10^{-4} M impurity. The second-order rate-constant was calculated from this line and the result agrees reasonably with Westermann's value.[1b]

This method of drying the monomer was used for all further experiments without any difficulty.

3.2.2 Polymerisation of 1,3-dioxepan.

Similar experiments were repeated with 1,3-dioxepan in the adiabatic calorimeter at -20°. First-order rate-constants were determined in the same way as for 1,3-dioxolan.

These results are shown in Table 3.2.

Typical conversion and conductivity curves are shown in Fig. 3.4.

The first-order rate-constants are not plotted against perchloric acid concentration because the scatter of the values of k_1 is too great.

3.3 Discussion.

3.3.1 Discussion and comparison with results of other workers.

Although Westermann and Jones used lithium aluminium hydride without any difficulty, Jones always observed gas evolution in the 1,3-dioxolan reservoir and the reservoir needed degassing before every experiment. He also observed a volume decrease for 1,3-dioxolan.

I have observed very little gas evolution and no decrease of volume of the 1,3-dioxolan even after it had been kept a long time on the lithium aluminium hydride.

A sample from this gas was taken for mass spectroscopy, but it gave only 1,3-dioxolan peaks. There was some uncondensable

Table 3.2

Data for Polymerisation of 0.79 M 1,3-Dioxepan at T = -20°

Run No.	19	17	20B
$10^4 [HClO_4]$ / M	2.3	3.1	3.37
Conversion / %	59	58	55
k_1 / sec^{-1}	0.174	0.166	0.193
DP	4.7	4.7	5

Fig. 3.3

Plot of the first-order rate-constant (k_1) against perchloric acid concentration for 1,3-dioxolan. From the graph B

$$k_2 = 9.4 \text{ l mole}^{-1} \text{ sec}^{-1}$$

$$k_2 = 10.3 \text{ l mole}^{-1} \text{ sec}^{-1} \text{ (Westermann)}$$

Fig. 3.4

Simultaneous plot of temperature and electrical conductivity against time for experiment 17.

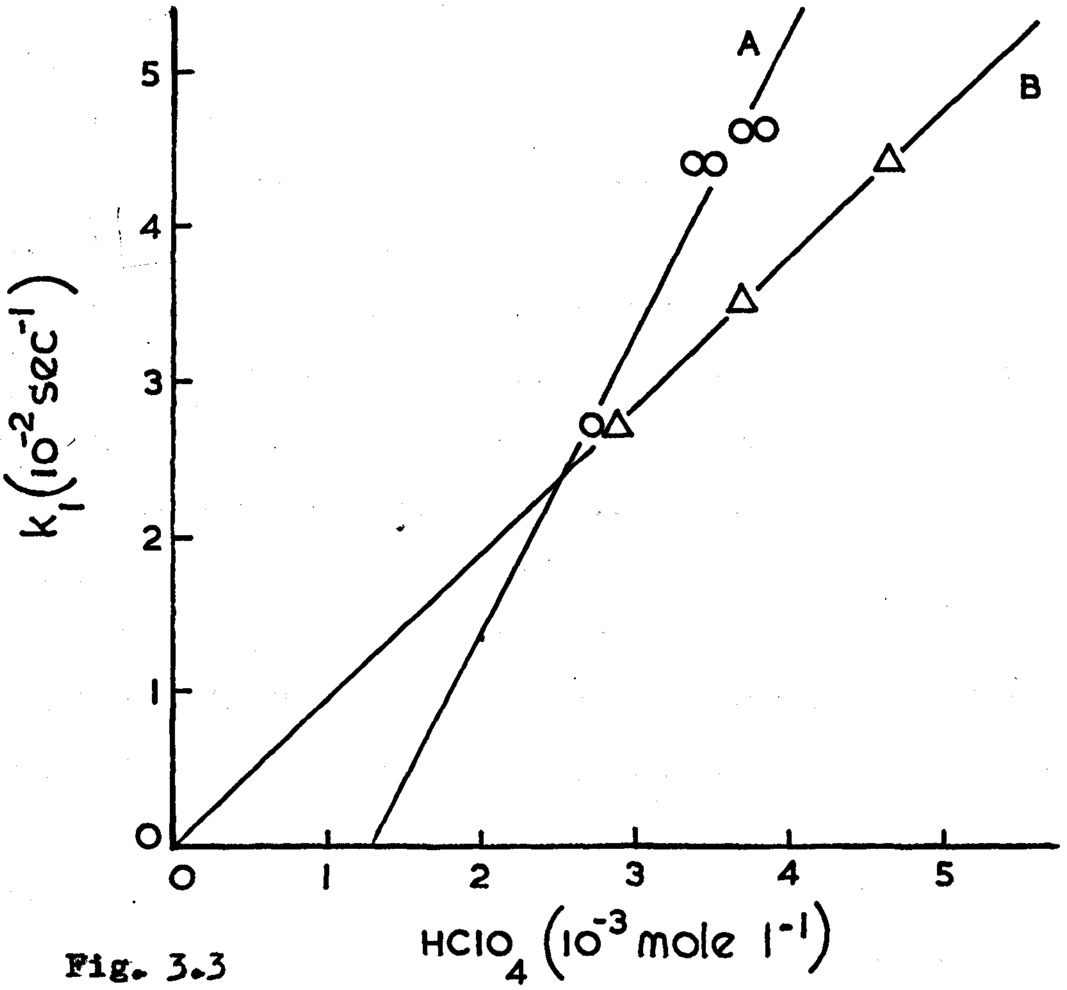

A
B
5
4
3
2
1
0
$k_1(10^{-2}\,sec^{-1})$
0
1
2
3
4
5
$HClO_4\,(10^{-3}\,mole\,l^{-1})$

Fig. 3.3

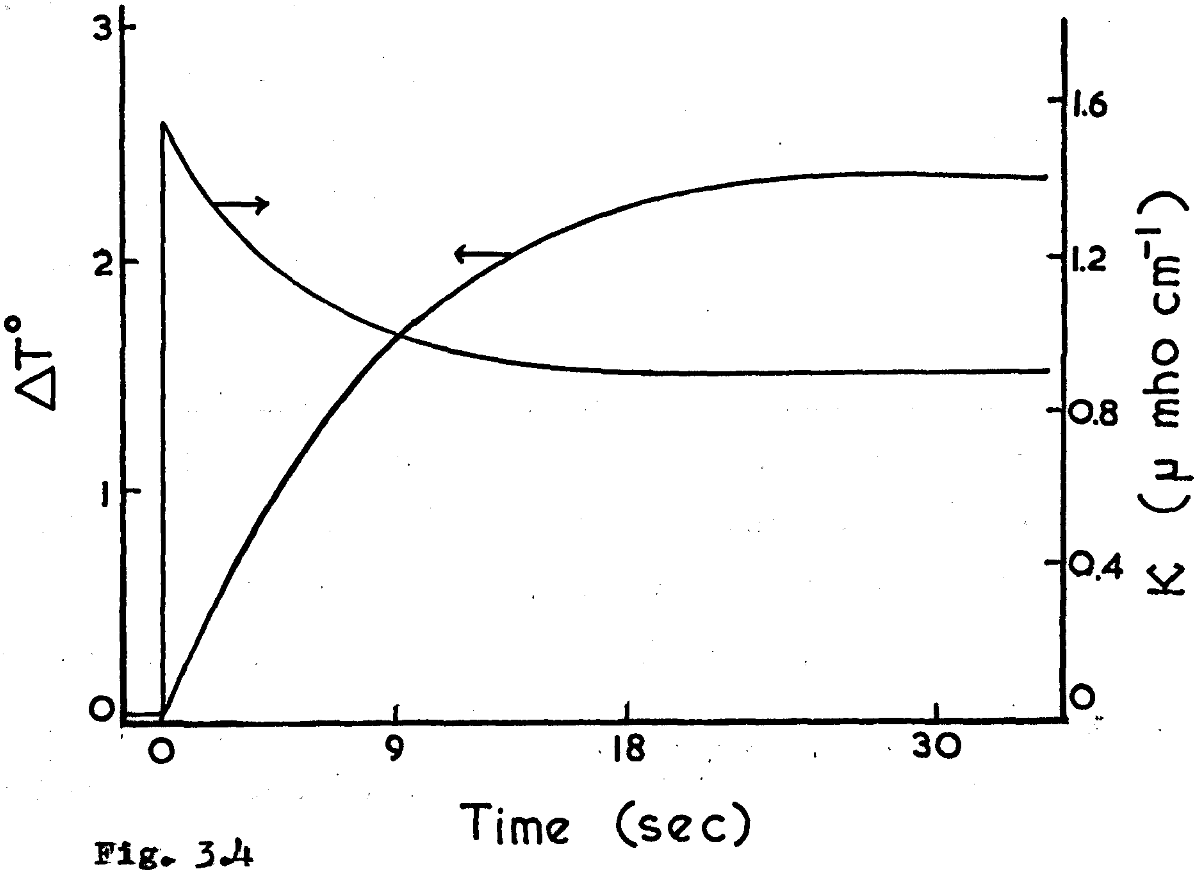

3
2
1
0
ΔT°
1.6
1.2
0.8
0.4
0
K (μ mho cm^{-1})
0
9
18
30
Time (sec)

Fig. 3.4

gas which was pumped off from the sample tube and it was most likely hydrogen.

When 1,3-dioxolan had been left over lithium aluminium hydride for more than a year there was found a gel and a white crystalline compound. This flask was opened to air and the monomer and lithium aluminium hydride suspended in it and the gel were decanted, leaving the white crystals adhering to the flask. These crystals were melted with Bunsen flame and a grey solid was left without charring.

We attempted to take a mass spectrum of this solid compound at 400°. The mass spectrum showed 1,3-dioxolan and dimer units. After the spectra had been taken the compound was found not to have melted. Therefore that spectrum cannot help very much to explain this mysterious compound.

This solid compound gives the lithium colour with a flame. Therefore, it might be an inorganic lithium compound which absorbs 1,3-dioxolan units on the surface.

3.3.2 Conclusion

These results showed clearly that sodium-potassium alloy is the best final drying agent for obtaining super-dry 1,3-dioxacycloalkanes.

3.4 Salt effects on the cationic polymerisation of cyclic formals.

All these experiments were carried out in the adiabatic calorimeter at 0°. Tetra-n-butylammonium perchlorate and tetrafluoroborate were kept in the desiccator and transferred rapidly from this into the adiabatic calorimeter. It was pumped out for 6 h, monomers and methylene dichloride were distilled into the calorimeter as described before. 1,3-Dioxolan and 1,3-dioxepan were used for

Table 3.3

Data for Polymerisations of 2.0 M 1,3-Dioxolan with n-Bu_4NClO_4 and n-Bu_4NBF_4 at T = 0^o

Run No.	37B	33D	33E	33B	33C	34B	34A	32B	35B	35A	36B	36A	44*	45B*	46*
$10^3[HClO_4]$/ M	1.82	3.06	4.85	3.32	2.83	3.17	3.55	3.35	3.41	3.74	3.63	3.93	2.81	2.34	2.94
$10^2[Salt]$/ M	1.9	3.05	3.08	3.41	3.42	6.1	6.24	7.34	9.1	11.3	12.7	15.3	3.2	3.38	2.86
Yield / %	38	39	36	37	36	36	38	38	35	36	36	36	15	3	2
k_1 / sec^{-1}	0.021	0.046	0.08	0.061	0.049	0.05	0.069	0.039	0.09	0.101	0.12	0.131	-	-	-

* These experiments were carried out with n-Bu_4NBF_4

these polymerisations. The reactions were stopped by admitting the vapour of ammonium hydroxide.

The conversion curves were obtained as for the experiments without salt. Although backing-off was used for measuring conductivity, the change in conductance during the polymerisation could not be followed very well because of the high concentration of ions.

3.4.1 Polymerisations of 1,3-dioxolan.

Table 3.3 shows the results obtained for 1,3-dioxolan with tetra-n-butylammonium perchlorate and tetrafluoroborate.

Fig. 3.5 shows the conversion curves for the runs 37B, 33C and 35B.

Fig. 3.6 shows the first-order plot for experiment 35B.

Fig. 3.7 shows the first-order rate-constants plotted against the perchloric acid concentration for experiments 33D, 33E, 33B and 33C. Other results are not shown in this figure because they have different salt concentrations and they must be shown by different lines.

Fig. 3.7 indicates that some of the initiator is deactivated by the impurity, so that the equation 3.2 cannot be used. Therefore, to find the actual initiator concentration, the intercept should be subtracted from the initial perchloric acid concentration.

$$k_2 = \frac{k_1}{\left[HClO_4\right]_0 - \text{Intercept}} \qquad 3.3$$

Fig. 3.8 shows the intercept plotted against salt concentrations. This line is drawn only for the intercept from Fig. 3.7 because no more intercepts were available. All the intercepts appropriate to other acid concentrations were calculated from this graph.

Fig. 3.5

Plot of $\triangle T$ against time for three polymerisations at different concentrations of salt and $HClO_4$. (See Table 3.3).

Fig. 3.6

First-order plot for experiment 35B. From the graph $k_1 = 0.09$ sec^{-1}.

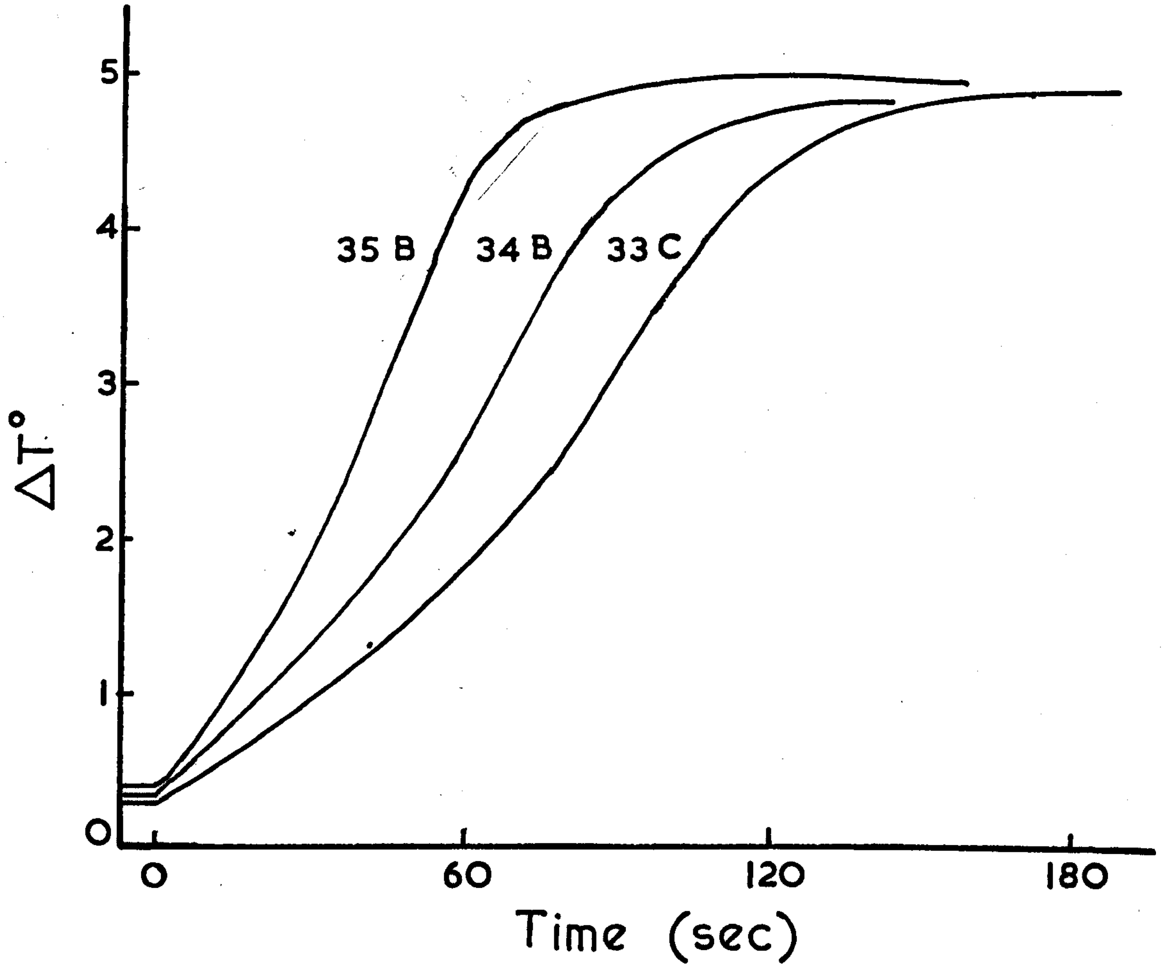

5
4
3
2
1
0
ΔT°
35 B
34 B
33 C
0
60
120
180
Time (sec)

Fig. 3.5

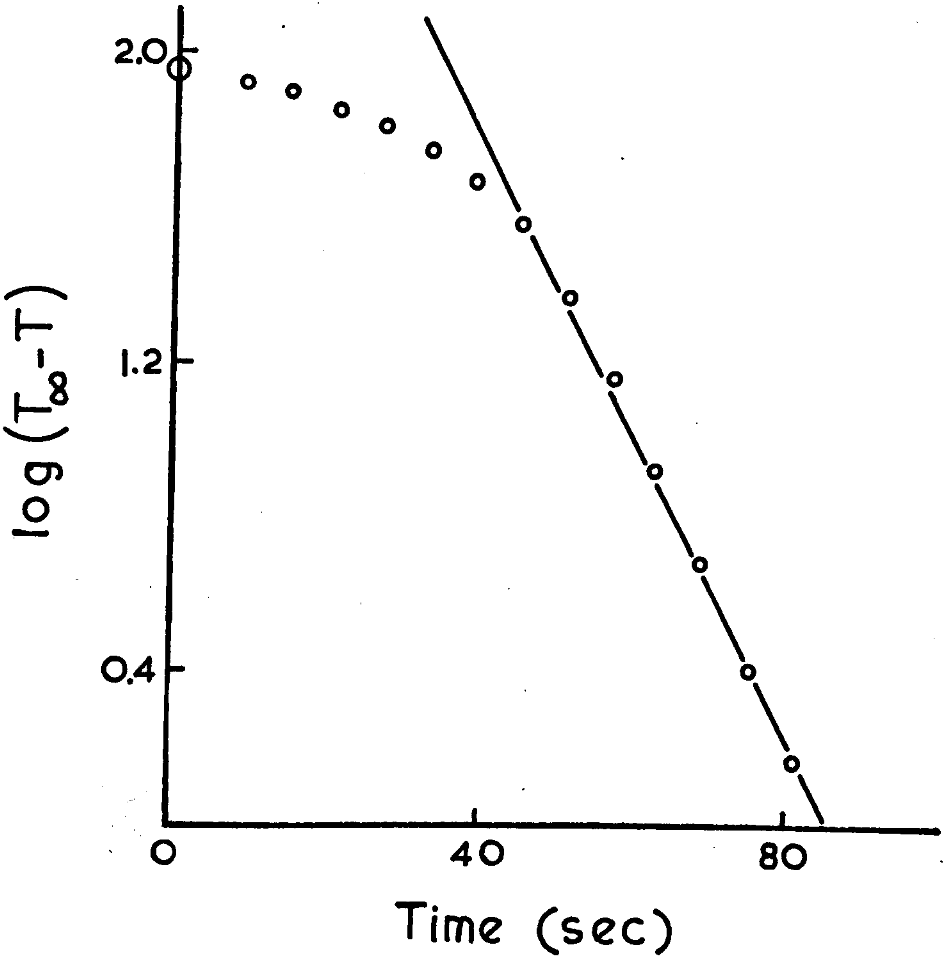

2.0
1.2
0.4
log(T∞-T)
0
40
80
Time (sec)

Fig. 3.6

Fig. 3.7

Plot of the first-order rate-constants against $HClO_4$ concentration for 1,3-dioxolan in the presence of salt. Run No. 33D, 33E, 33B and 33C.

Fig. 3.8

Plot of the intercept against salt concentration.

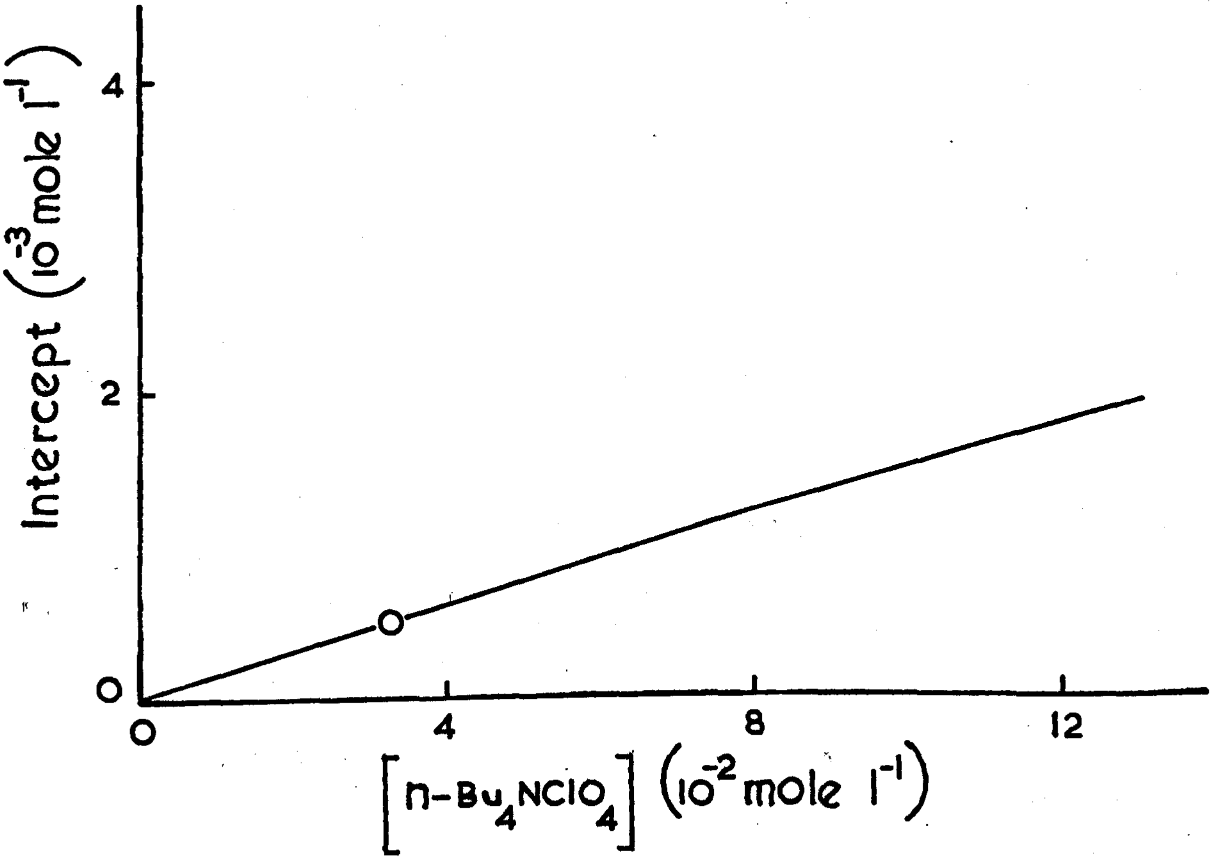


Fig. 3.8

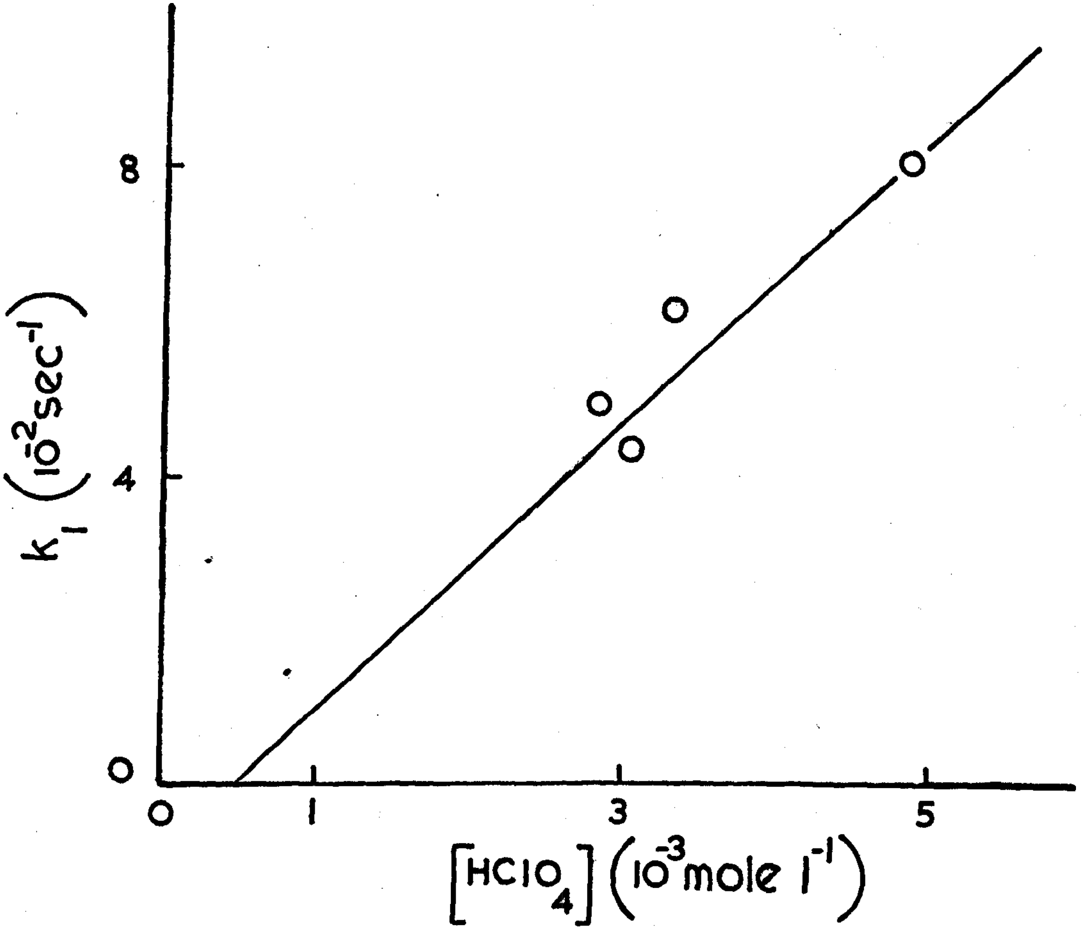
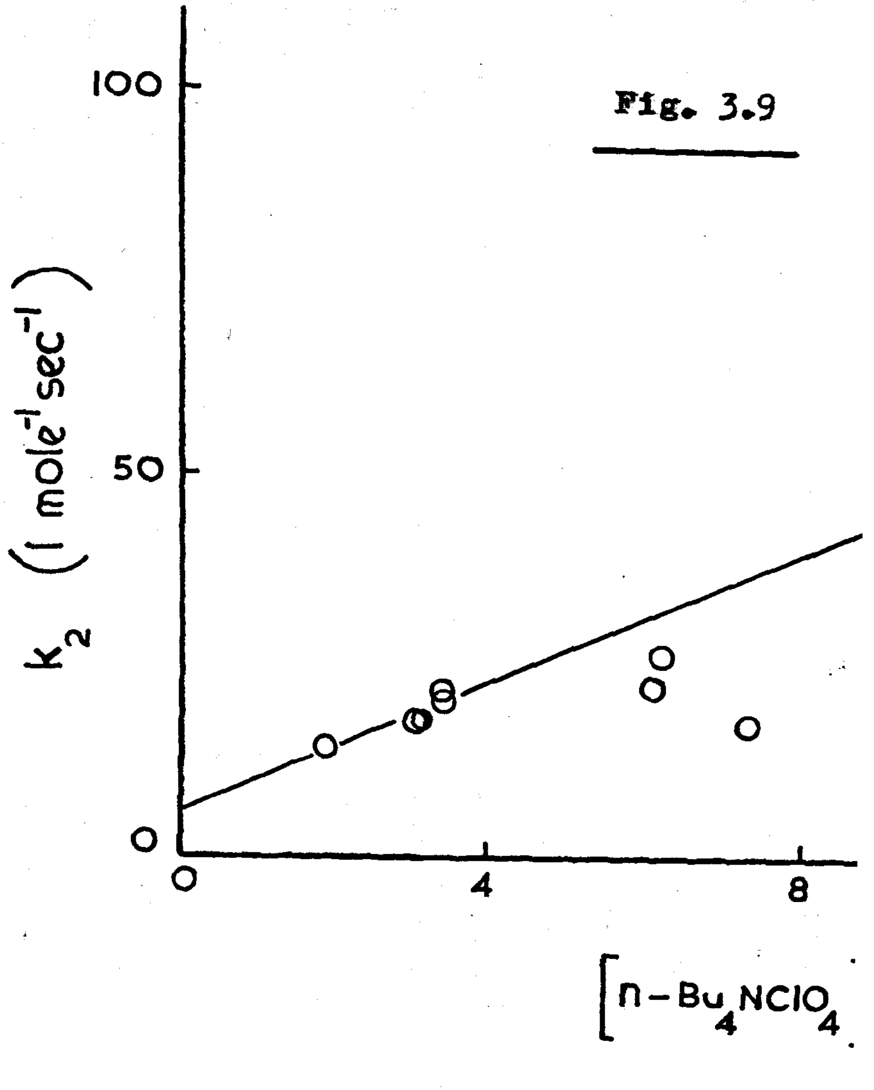


Fig. 3.7

Fig. 3.9

Plot of the second-order rate-constants against salt concentration for 1,3-dioxolan.

Fig. 3.9



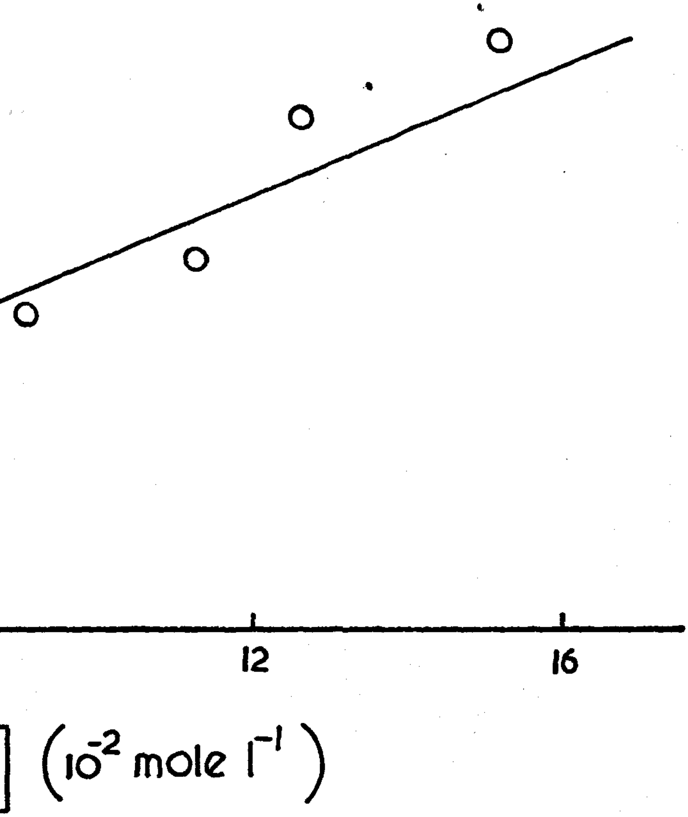

12
16
] (10^{-2} mole l^{-1})

Fig. 3.9 shows the k_2 values calculated from the equation 3.3, plotted against the salt concentration. This figure shows that k_2 increases with increasing salt concentration. This is shown qualitatively by the conversion curves in Fig. 3.5. This fact is shown in a different way in Fig. 3.14.

Some experiments (44, 45B and 46) have been carried out with tetra-n-butylammonium tetrafluoroborate. Unfortunately, this salt stopped the polymerisation. When the initiator phial was crushed, the conductivity increased slightly, but no heat evolution was observed. The calorimeter was thermostatted with an ice-water bath and left for one hour but even after this time only a very low yield of polymer was found.

3.4.2 Polymerisations of 1,3-dioxepan.

This part is concerned with experiments similar to the previous ones carried out with 1,3-dioxepan in the presence of tetra-n-butylammonium perchlorate. The results are shown in Table 3.4.

Fig. 3.10 shows the conversion and conductivity curves, and the corresponding first-order plot is shown in Fig. 3.11.

One experiment (Run No. 30) was carried out with some mercury in the reaction vessel. A few drops of mercury were put into the calorimeter with the salt and polymerisation was carried out in the usual way. The reason for this was that since the polarography cell contains mercury, therefore it was necessary to see whether mercury had any effect on the polymerisation.

All experiments were carried out at different salt concentrations. Therefore it does not make any sense if k_1 is plotted against the perchloric acid concentration. However, since perchloric acid concentration does not vary much the k_2 values were plotted

Table 3.4

Data for Polymerisations of 0.8 M 1,3-Dioxepan with salt at $T = 0^\circ$

Run No.	24	30*	26	28	29
$10^4[HClO_4]$/ M	2.37	2.39	1.99	2.29	2.97
$10^2[n\text{-}Bu_4NClO_4]$/ M	3.3	3.5	4.98	8.4	12.6
Conversion / %	37	37	28	30	39
k_1 / sec^{-1}	0.109	0.085	0.064	0.064	0.135

* salt and Hg together

Fig. 3.10

Simultaneous plot of temperature and electrical conductivity against time for experiment 28.

Fig. 3.11

First-order plot for experiment 28.

From the plot $k_1 = 0.064\ sec^{-1}$.

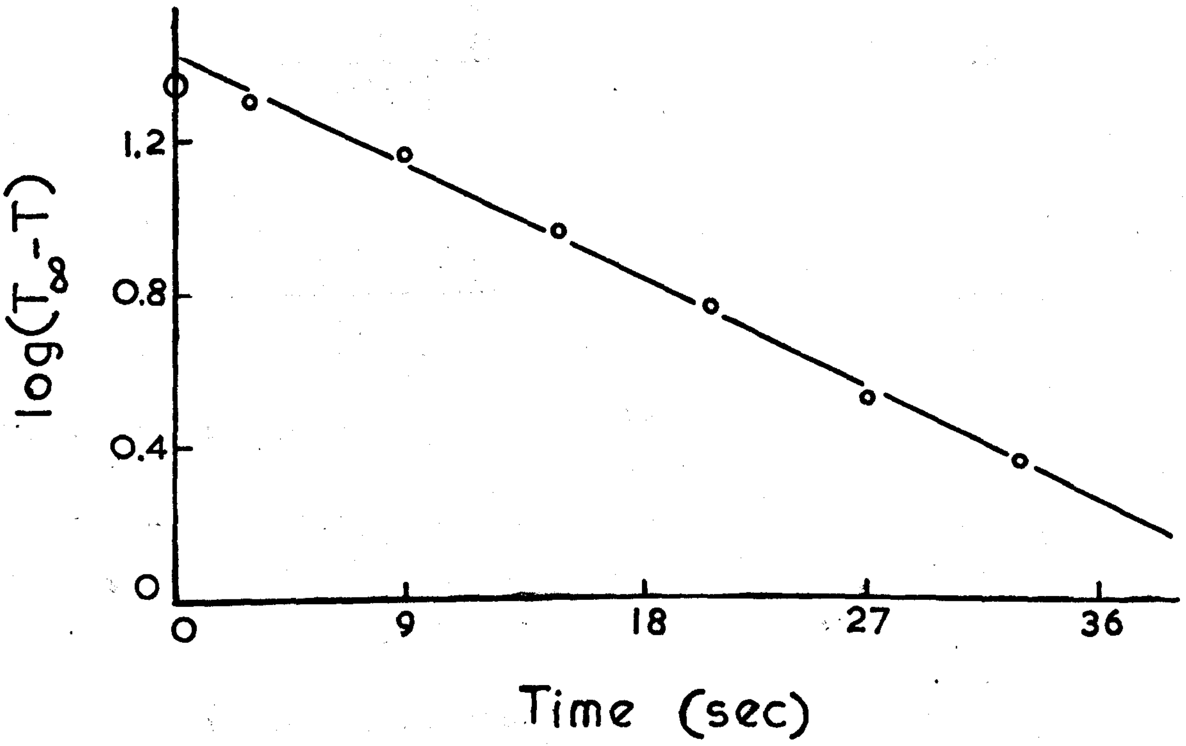


Fig. 3.11

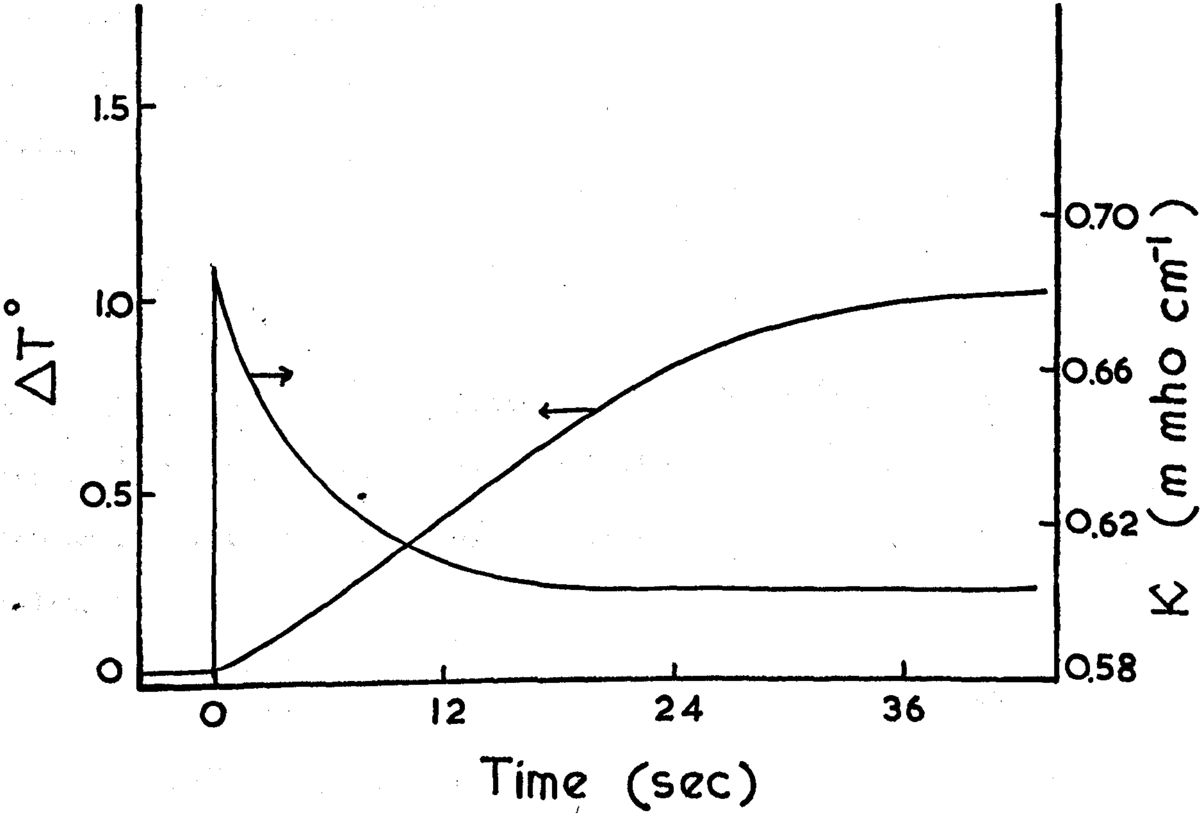


Fig. 3.10

against salt concentration in Fig. 3.12. Our results indicate that for this monomer the k_2 decrease with increasing salt concentration. This phenomenon is shown more clearly in Fig. 3.14.

3.5 Free ions and ion-pair rate constants.

I intended to calculate free ion and ion-pair rate constants using a method similar to that of Goethals[3] and Pepper.[4] In this method I tried to find effect of salt with common ion on concentration of propagating free ions and ion-pairs.

$$R^+A^- \rightleftharpoons R^+ + A^- \qquad 3.4$$

$$Q^+A^- \rightleftharpoons Q^+ + A^- \qquad 3.5$$

Equation 3.4 refers to the growing chains and equation 3.5 refers to the added salt.

$$K_1 = \frac{[R^+]\ [A^-]}{[R^+A^-]} \qquad 3.6$$

$$K_2 = \frac{[Q^+]\ [A^-]}{[Q^+A^-]} \qquad 3.7$$

The mass and charge balances are given by

$$c_1 = [R^+A^-] + [R^+] \qquad 3.8$$

$$c_2 = [Q^+A^-] + [Q^+] \qquad 3.9$$

c_1 = Total concentration of growing centres both kinds

c_2 = Total concentration of salt

$$[A^-] = [R^+] + [Q^+] \qquad 3.10$$

If $[Q^+]$, $[Q^+A^-]$, $[A^-]$ and $[R^+A^-]$ were eliminated from these equations

$$K_1(c_1 - [R^+]) = [R^+]^2 + \frac{c_2K_2[R^+]^2}{K_2[R^+] + K_1(c_1 - [R^+])} \qquad 3.11$$

Assuming $c_1 \gg [R^+]$ and $K_1 \approx K_2$

$$\therefore \quad K_1c_1 \gg K_2[R^+]$$

$$[R^+] = \left(\frac{K_1^2c_1^2}{K_1c_1 + K_2c_2}\right)^{\frac{1}{2}} \qquad 3.12a$$

$$[R^+A^-] = c_1\left(1 - \frac{K_1}{(K_1c_1 + K_2c_2)^{\frac{1}{2}}}\right) \qquad 3.13a$$

If $c_2 \gg c_1$

$$[R^+] = \frac{K_1c_1}{(K_2c_2)^{\frac{1}{2}}} \qquad 3.12b$$

$$[R^+A^-] = c_1\left(1 - \frac{K_1}{(K_2c_2)^{\frac{1}{2}}}\right) \qquad 3.13b$$

In the present system

$$k_1 = k_+[R^+] + k_\mp[R^+A^-] \quad * \qquad 3.14$$

$$k_1 = k_\mp c_1 + \frac{K_1c_1}{(K_2c_2)^{\frac{1}{2}}}(k_+ - k_\mp) \qquad 3.15$$

$$\frac{k_1}{c_1} = k_2 = k_+ + \frac{K_1}{(K_2c_2)^{\frac{1}{2}}}(k_+ - k_\mp) \qquad 3.16$$

* k_+ = Free ion rate constant

$k_\mp$ = Ion-pair rate constant

Fig. 3.12

Plot of the second-order rate-constants against salt concentration for 1,3-dioxepan.

Fig. 3.13

Plot of k_2 against $1/[\text{salt}]^{\frac{1}{2}}$ for 1,3-dioxolan. From the graph

$k_+ = 78 \text{ l mole}^{-1} \text{ sec}^{-1}$

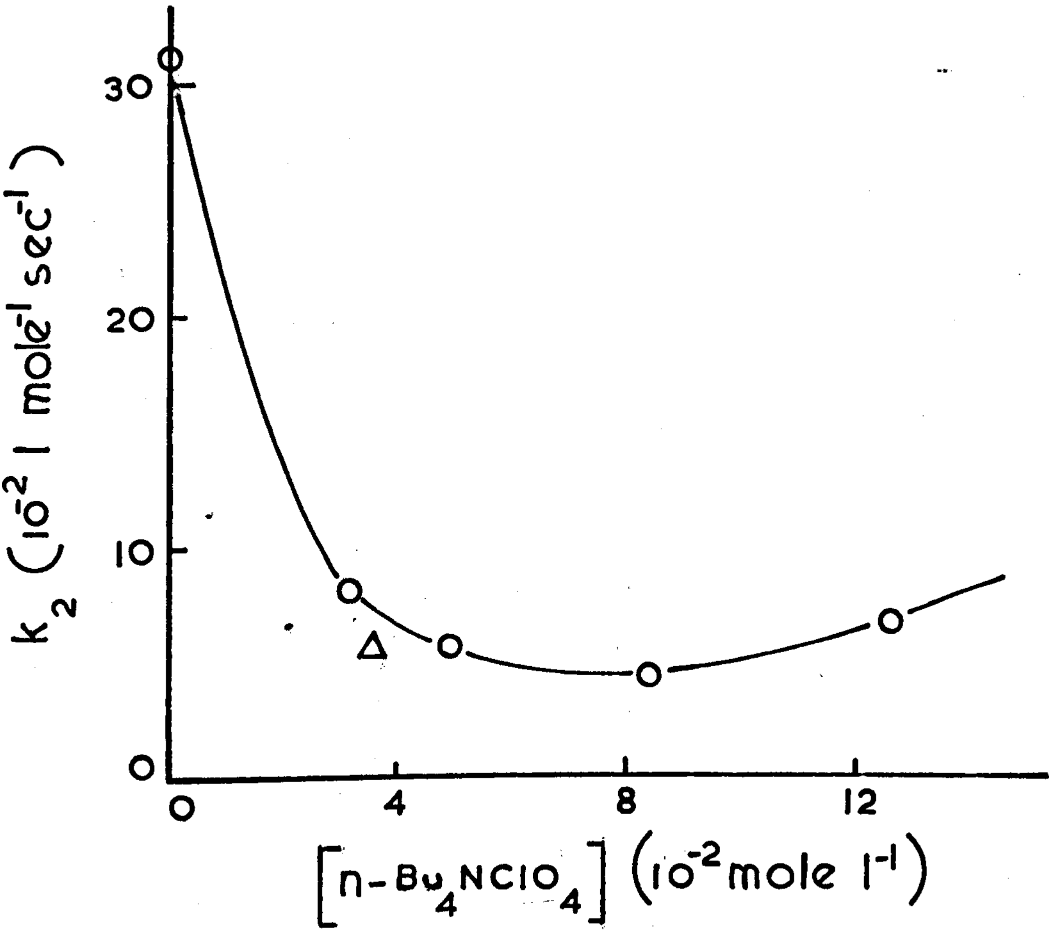


Fig. 3.12

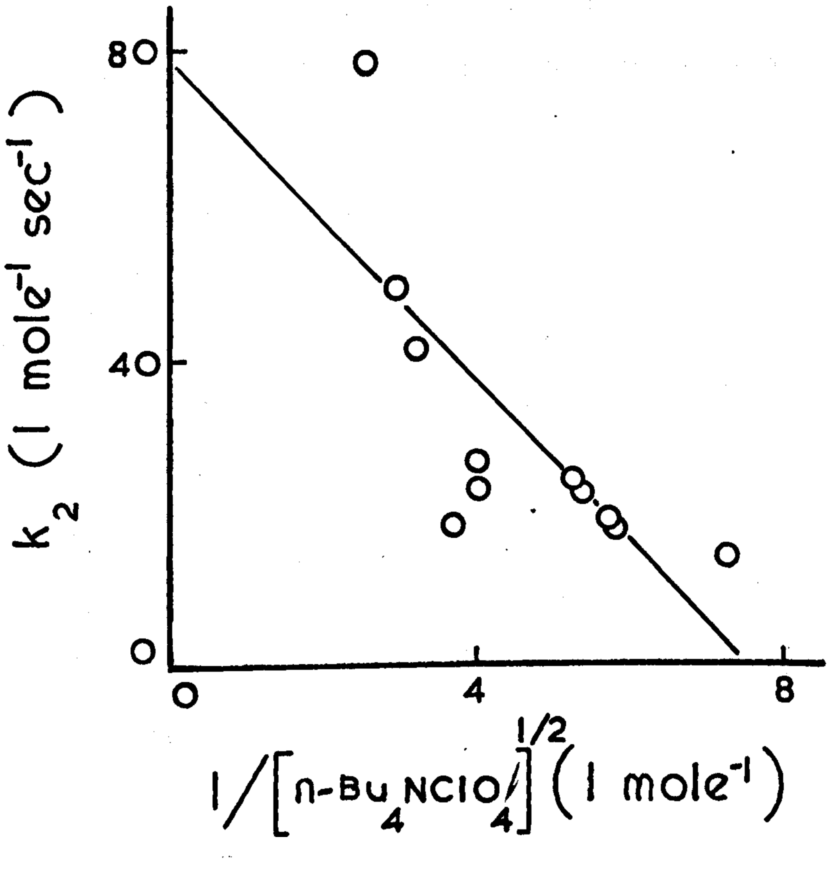


Fig. 3.13

Therefore, if one plots k_2 against the $1/c_2^{\frac{1}{2}}$ the intercept gives the free ion rate-constant k_+, and the slope gives $(k_+ - k_\mp)\lambda$. This is $\lambda(K_1/K_2^{1/2})$ shown in Fig. 3.13 and from this plot the rate-constant of free ions has been calculated. The free ion rate-constant was found to be 78 l $mole^{-1}$ sec^{-1} whereas the ion-pair rate-constant cannot be determined at present.

3.6 Discussion.

In practice, it has been confirmed that a common ion depresses the dissociation of an ion-pair and decreases the propagation rate in anionic polymerisation. In cationic polymerisations such a generalisation has not been found yet.

Goethals[3] found that for 3,3-dimethyl thietan both rate-constants are equal in nitrobenzene but the rate-constant for free ions is 40 times higher than that for ion-pairs in methylene dichloride.

Worsfold et al.[5] carried out tetrahydrofuran polymerisation with triethyloxonium tetrafluoroborate in methylene dichloride. They found that the free ion rate-constant is 7 times higher than the ion-pairs rate-constant.

Pepper[4] carried out polymerisations of styrene with perchloric acid in methylene dichloride. He found the ion-pair rate-constant to be 28 times higher than the free ion rate-constant at -80°.

In our system it is not easy to see rate increase or decrease from simple plots. Therefore, I have made a three dimensional model of my system. Fig. 3.14 is a drawing from a tracing of the photograph of the three dimensional model. The five lines containing dots show the results obtained with 1,3-dioxepan and the others are for 1,3-dioxolan. From this Fig. it is very clearly seen that the rate increases with increasing salt concentration at a constant $HClO_4$ concentration (line c). The direct conclusion is that the rate increase can be explained by a primary salt effect and possibly also by the assumption that ion-pairs propagate faster than free ions. From the Fig. 3.13 ion-pair and free ion rate-constants were calculated and it was found that the ion-pair rate-constant is a little higher than the free ion rate-constant. This subject needs more experiments to find more precise values, because there is an uncertainty of the approx. ∓ 20 in the intercept and a corresponding uncertainty in the slope.

1,3-Dioxepan shows a behaviour different from that of 1,3-dioxolan. The addition of a salt decreases the rate and after a minimum it increases.

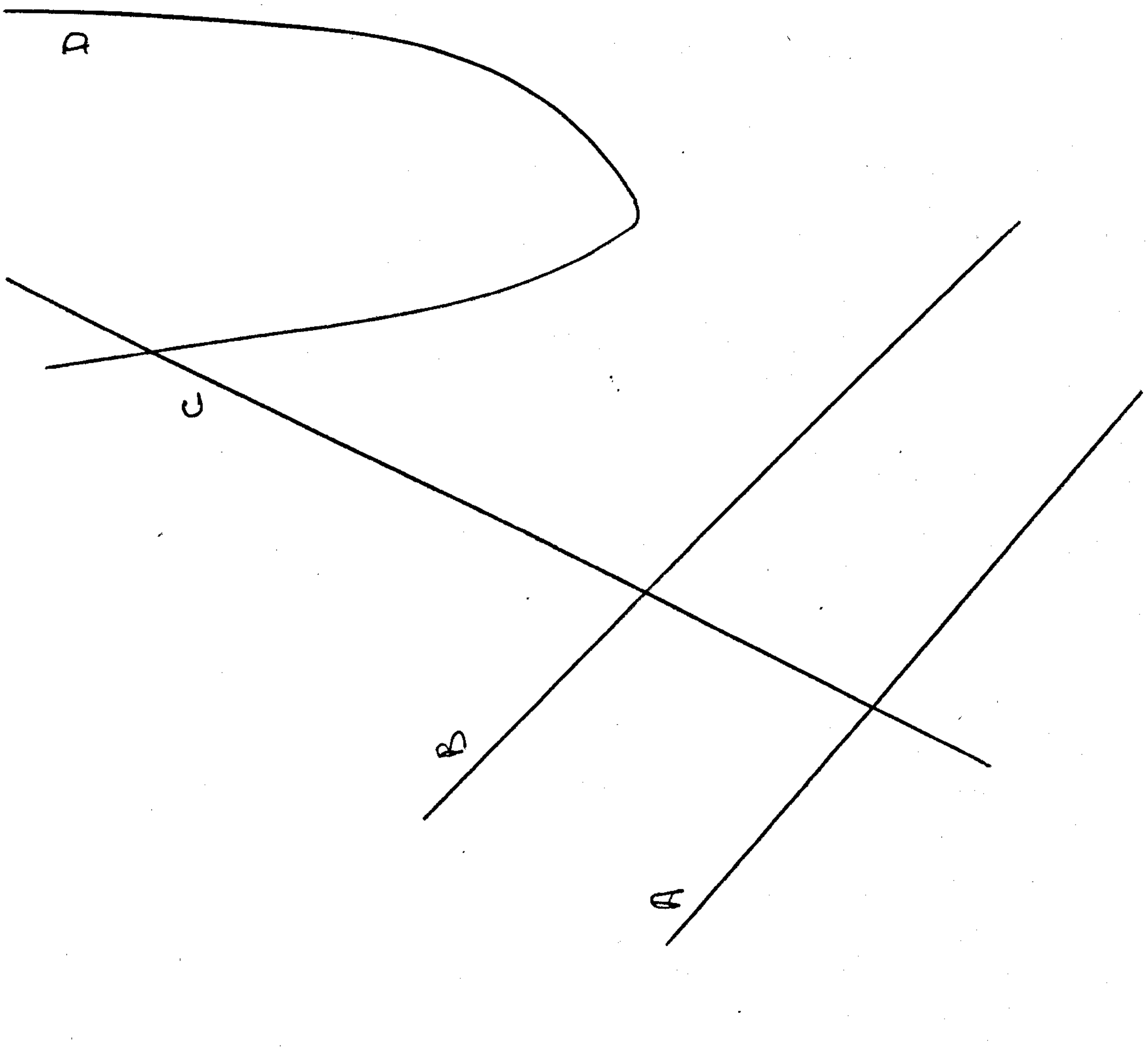
The only difference between the two monomers is the dipole moment: 1,3-dioxolan being much less polar than 1,3-dioxepan. Therefore, competition between solvation and pair formation probably leads to two different processes.

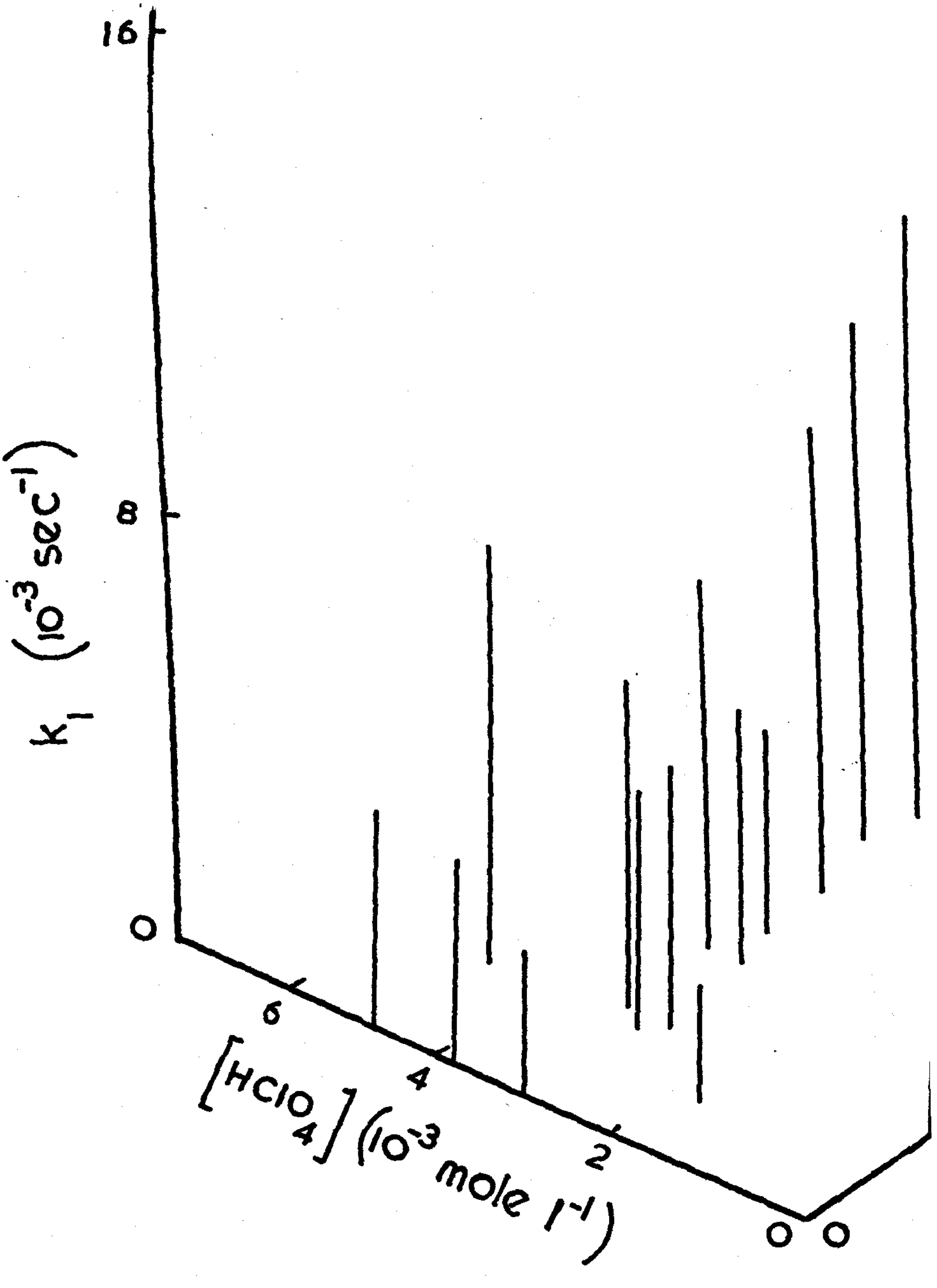
For both monomers $n\text{-}Bu_4NClO_4$ does not affect the yield. Unfortunately the polymers have solubility similar to that of this salt. Therefore, I could not separate completely the salt from the polymer for the molecular weight determinations.

$n\text{-}Bu_4NBF_4$ possibly contains impurities which deactivate perchloric acid. This impurity cannot be removed by recrystallisation.

Fig. 3.14

Tracing of the three dimensional model's photograph for 1,3-dioxolan and 1,3-dioxepan.


A
C
B
A


16
8
0
k_1 (10^{-3} sec^{-1})
6
4
2
$[HClO_4]$ (10^{-3} mole l^{-1})
0
0

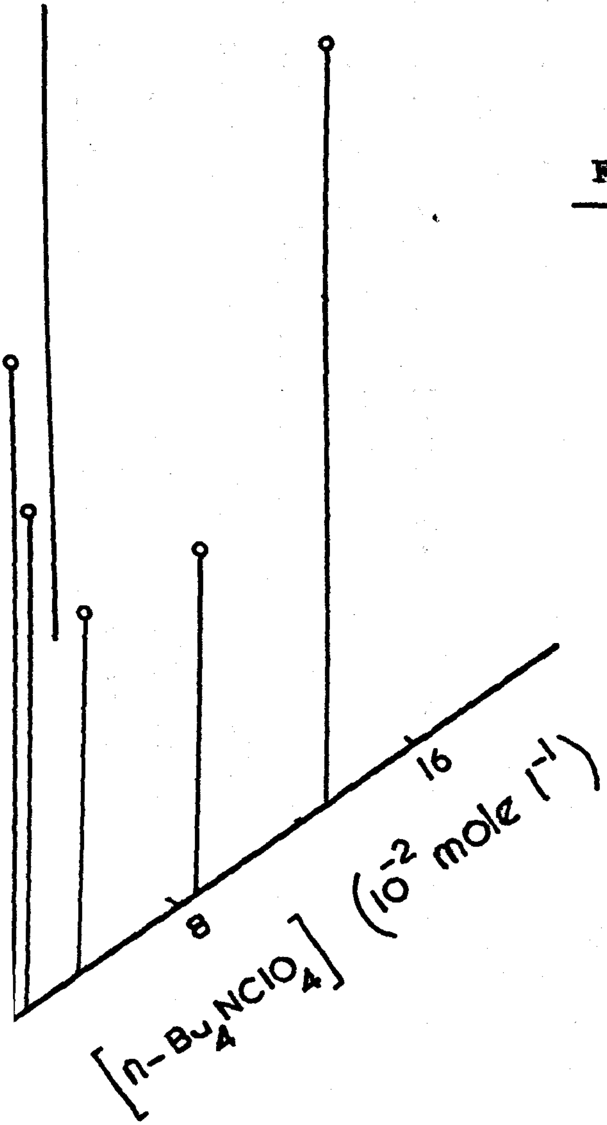


Fig. 3.14

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1b. P.H. Westermann, Ph.D. Thesis, Keele, 1967.

2. F.R. Jones, Ph.D. Thesis, Keele, 1970.

3a. W. Drijvers and E.J. Goethals, Symp. on Macromolecules, Boston, 1971, Rep. 663.

3b. E.J. Goethals, W. Drijvers, D.V. Ooteghem and A.M. Buyle, J. Macromol. Sci., 1973, 7, 1375.

3c. E.J. Goethals, Makromol. Chem., 1974, 175, 1309.

4. D.C. Pepper, Makromol. Chem., 1974, 175, 1077.

5. J.M. Sangster and D.J. Worsfold, Am. Chem. Soc. Div. Polymer Chem. Polymer Preprints, 1972, 13, 72.

CHAPTER FOUR

Polymerisation of 1,3-dioxolan with tertiary oxonium ions

4.1 Introduction to Chapter Four

When the present work was started there were three different theories about the polymerisation mechanism of 1,3-dioxacycloalkanes.

The first reaction mechanism was proposed by Okada et al.[1] They suggested that the active centres are carboxonium ions.

Westermann[2] carried out polymerisation experiments with 1,3-dioxolan and perchloric acid under high vacuum. In order to explain the lack of end-groups (which had previously been noted by Gresham[3]) in the resulting polymers, Plesch and Westermann proposed a ring-expansion mechanism in which the active centres are secondary oxonium ions. They concluded that the rings are never opened and the polymers are cyclic.

Jaacks et al.[4] carried out polymerisation experiments with 1,3-dioxolan and perchloric acid under nitrogen. On the basis of their analytical results they proposed that the active centres are tertiary oxonium ions and that ring closure occurred by back-biting.

Jones[5] showed that the ring-expansion mechanism was applicable for initiation with triethyloxonium salts.

Recently Penczek[6] proposed a new mechanism for 1,3-dioxolan polymerisation with trityl salts. He proposed a four-centre propagating species, i.e. a carboxonium ion stabilised by co-ordination of two O-atoms forming part of a polymer. In this situation it became important to find an experimental method of discriminating between the mechanisms.

One possible method could be based on the different reactions of different types of oxonium ions. Thus, with a protonic acid, the Keele mechanism would give secondary oxonium ions as the propagating species, whereas according to the Jaacks mechanism any initiator gives tertiary oxonium ions as the propagating species. However, the properties of Penczek's species are so ill-defined that we could see no method by which we could test the validity of his mechanism. It seems possible to discriminate between the secondary and tertiary oxonium ions on the basis of kinetic measurements.

Rose[7,8] had shown that tertiary oxonium ions are much more reactive than secondary oxonium ions and are thus kinetically distinguishable from them. It is highly probable that propagation involving secondary oxonium ions would have a different rate from that of tertiary oxonium ions. The activation energy of the polymerisation of 1,3-dioxolan by perchloric acid was determined by Westermann.[2b] Therefore if it is possible to find an initiator which gives stable, countable tertiary oxonium ions the activation energy could be determined directly from the kinetic runs. This should be different from that of the polymerisation by perchloric acid.

One might think that triethyloxonium salts could fulfil this requirement because they are very strong alkylating reagents. However, Jones showed that triethyloxonium salts are not 100% efficient initiators for the polymerisation of 1,3-dioxolan. Therefore we searched for other initiators.

References to Introduction to Chapter Four

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2a. P.H. Westermann, M.Sc. Thesis, Keele University, 1965.

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2c. P.H. Plesch and P.H. Westermann, J. Polymer Sci. C, 1968, 16, 3837.

2d. P.H. Plesch and P.H. Westermann, Polymer, 1969, 10, 105.

3. W.F. Gresham, U.S.P., 2394910, 1946.

4a. V. Jaacks, K. Boehlke and E. Eberius, Makromol. Chem., 1968, 118, 354.

4b. K. Boehlke, H. Frank and V. Jaacks, Symp. on Makromolecules, Prag 1965, Preprint 506.

5. F.R. Jones, Ph.D. Thesis, Keele University, 1970.

6. S. Penczek, Makromol. Chem., 1974, 175, 1217.

7. J.B. Rose, J. Chem. Soc., 1955, 3648.

8. P.H. Plesch, The Chemistry of Cationic Polymerization, (Pergamon, 1963).

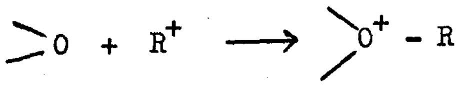
Table 4.1

Data for polymerisations of 1,3-Dioxolan with $MeSO_3F$.

Run No.	52	54	55	57	53
[1,3-Dioxolan]/M	2	2	2	4	4
$10^{-1}[MeSO_3F]/M$	1.19	1.01	1.13	0.16	0.68
T/°C	0	25	-65	25	25
Time/h	1	3	0.25	3	25
Yield/%	12	1.4	0.2	0.97	50
DP	4.7				5.9

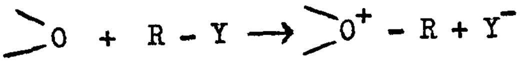
4.2 Polymerisation with methyl fluorosulphonate.

The formation of tertiary oxonium ions by the alkylation of an ethereal or carbonyl oxygen atom can be represented schematically in terms of free alkyl cations:



4.1

However, the added alkyl cations arise from alkylating agents R - Y. In the simplest case the anion Y^- remaining after the transfer of the alkyl group can form a salt with the oxonium ion produced:



4.2

If $MeSO_3F$ does initiate, the initiation follows the scheme shown by 4.2. Methyl fluorosulphonate has been used for alkylation of cyclic and acyclic ether compounds.[1,2]

4.2.1 Polymerisation experiments and results.

All experiments were carried out under high vacuum. The adiabatic calorimeter, dilatometry and vacuum sealed reaction tubes were used. 1,3-Dioxolan and methylene dichloride were distilled into the reaction vessels. The reactions were begun by crushing methyl fluorosulphonate phials and stopped by adding either 0.88 ammonium hydroxide or its vapour. The results are shown in Table 4.1. Runs 52 and 55 were carried out in the adiabatic calorimeter. When the initiator phial was crushed, the conductivity of the solution immediately increased but the temperature did not change.

As can be seen from the table the highest yield and molecular weight were achieved at 25° and with a longer reaction time than would have been necessary with triethyloxonium salts.

4.2.2 IR and NMR measurements.

IR measurements on the oligomers showed that their structures are similar to those of polymers obtained with perchloric acid. The OH peak is observed at 3500 cm^{-1}, but this is due to the use of an aqueous killing reagent. The NMR spectrum is similar to that of polymers formed with perchloric acid.

4.2.3 Discussion.

Although alkyl fluorosulphonates are similar to triethyloxonium salts as powerful alkylating agents, we did not find the methyl ester to be a useful polymerisation initiator.

The reaction takes longer than with the same concentration of triethyloxonium salts.[3] The reaction products are of low molecular weight and the yield is lower than that obtained with triethyloxonium salts.

HCl gives no polymerisation with 1,3-dioxolan but it gives $HOCH_2CH_2OCH_2Cl$.[4] Therefore in these polymerisations the initiator must have a weakly nucleophilic anion. Apparently SO_3F^- is not a weak enough nucleophile.

Conductivity measurements showed the formation of very short-lived tertiary oxonium ions: these ions probably decay to methane and the $2H^+$-1,3-dioxolanium salt.

After killing the reaction mixture a high yield of salt (presumably NH_4SO_3F) was obtained. Therefore the polymers were extracted with chloroform to separate them from the salt.

Unfortunately this compound did not give the expected result. Only Run 53 gave the expected yield, but of low molecular weight polymer.

Table 4.2

Reaction chart for the polymerisation of 1,3-dioxolan by acetyl perchlorate. Run No. 58.

κ_n: Conductivity of the solution.

		T/°C	κ_n/ mho cm^{-1}
1.	Depolym.	40	1.23
2.	Polym.	0	
3.	Depolym.	40	1.22
4.	Polym.	-25	
5.	Depolym.	40	1.25
6.	Polym.	-42	
7.	Depolym.	40	1.25
8.	Polym.	0	
9.	Depolym.	40	1.28
10.	Polym.	-25	
11.	Depolym.	40	1.28
12.	Polym.	-42	
13.	Depolym.	40	1.31
14.	Polym.	0	
15.	Depolym.	40	1.28
16.	Polym.	-25	
17.	Depolym.	40	1.28
18.	Polym.	-42	
19.	Depolym.	40	1.28

4.3 Polymerisation with organic perchlorates.

Jaacks and Kern[5] found acetyl perchlorate an effective initiator for trioxan polymerisation. I intended to use acetyl perchlorate and t-butyl perchlorate as initiators for 1,3-dioxolan polymerisations in methylene dichloride.

All these polymerisations were carried out under vacuum in the dilatometer fitted with platinum electrodes. They differed from that used previously in that polymerisation, depolymerisation and repolymerisation experiments were done successively without opening the dilatometer. This cycle was repeated at different temperatures.

4.3.1 Polymerisations with acetyl perchlorate.

A typical reaction sequence is shown in Table 4.2. The phial of initiator in methylene dichloride was broken above the ceiling temperature of 1,3-dioxolan and the conductivity was measured. The dilatometer was then put into the ice-water bath and the first polymerisation was observed at 0°. When equilibrium was reached, the dilatometer was taken from the ice-bath and put into the 40° thermostat for the depolymerisation, and the conductivity was recorded. Then the dilatometer was put into the -25° bath and the second polymerisation was observed, followed by a second depolymerisation. The process was repeated three times and the reaction stopped by addition of 0.88 ammonium hydroxide. The results are shown in Table 4.3.

Typical conversion and conductivity curves are shown in Fig. 4.1 and the corresponding first-order plots are shown in Fig. 4.2.

Some of the polymerisations appeared not to be of first-order. For unknown reasons the shapes of the reaction curves are

Table 4.3

Data for polymerisation of 1.2 M 1,3-Dioxolan with CH_3COClO_4.

Run No.	58	59	61	62
$10^3 [CH_3COClO_4]$ / M	3.46	2.97	2.3	2.15
T/°C		-40	0	0
Yield/%		12	4	4

Fig. 4.1

Plots of conversion and conductivity against time for Run 58 at 0°.

Fig. 4.2

First-order plot for experiment 58.

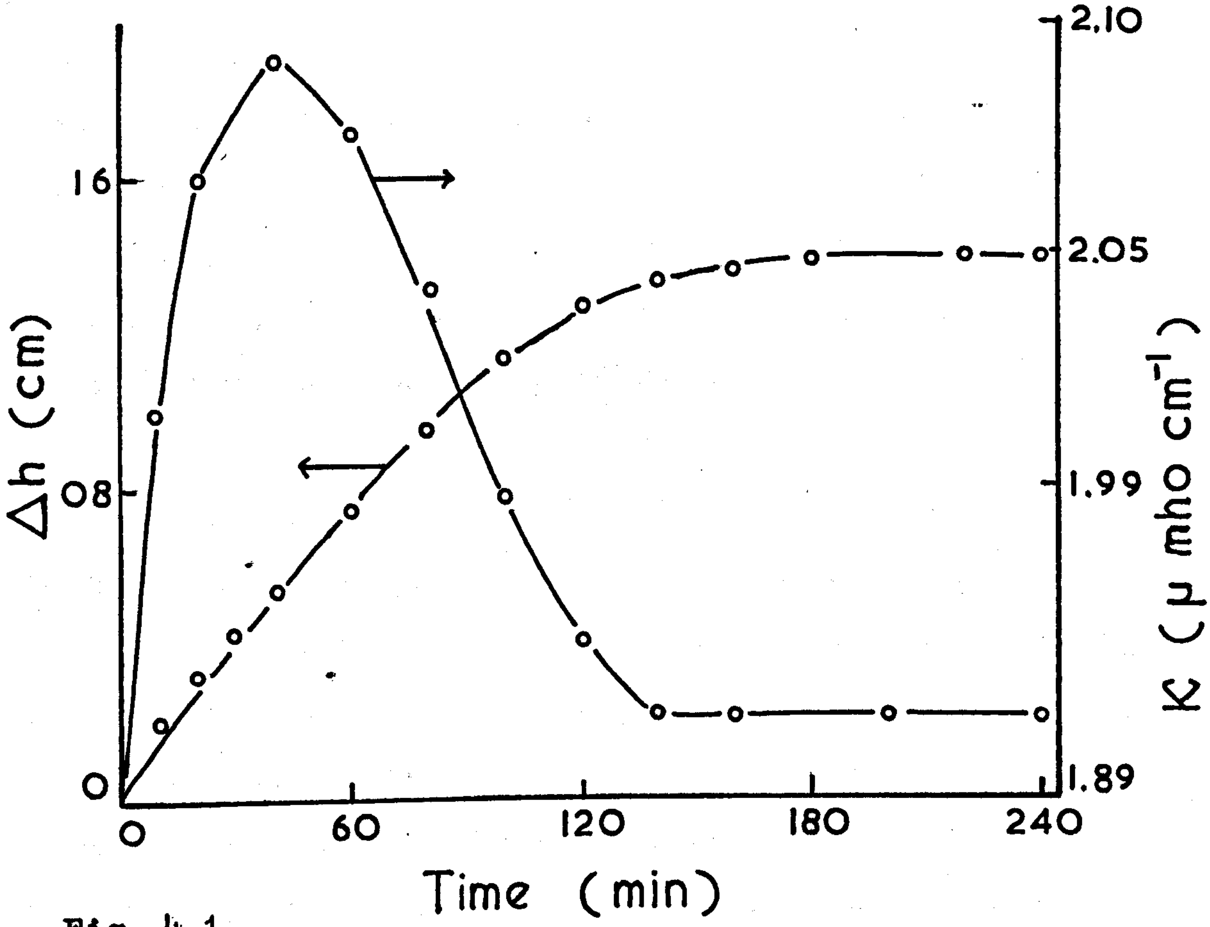

16
08
0
Δh (cm)
2.10
2.05
1.99
1.89
K (μ mho cm^{-1})
0
60
120
180
240
Time (min)

Fig. 4.1

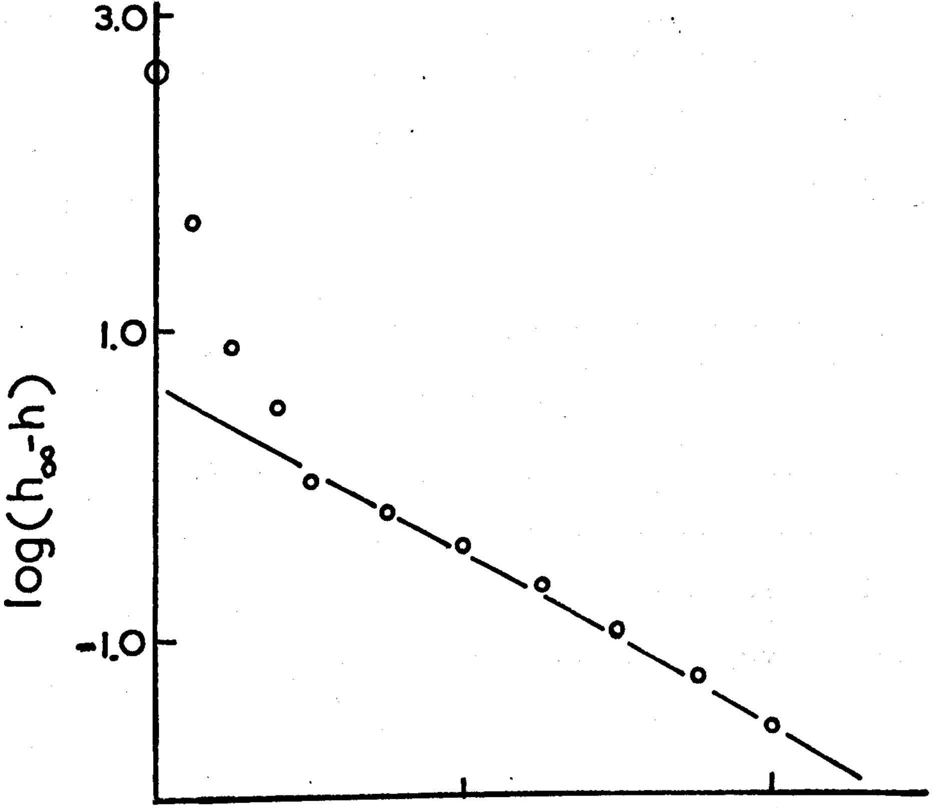

3.0
1.0
-1.0
log(h$_\infty$-h)
0
80
160
Time (min)

Fig. 4.2

irreproducible and irregular. It is possible that side reactions are occurring in this system. In that case one might expect a different conductivity each time. Therefore, all the conductivity results are plotted in Fig. 4.3. From this it can be seen that the conductivity did not change very much after the depolymerisation, but that the final conductivities of some runs at the same temperatures were different.

The acetyl perchlorate used for experiments 58 and 59 contained some chloride. This was found by the analytical method. This chloride was removed from the second batch by adding silver perchlorate to the solution and filtering it under vacuum. The acetyl perchlorate used in runs 61 and 62 contained no chloride.

Conductivity measurements during the reactions showed that the conductivity variations were similar to those in reactions initiated by perchloric acid or triethyloxonium salts. In some of the reactions the conductivity continued to change although equilibrium had been reached.

After these cycles the yield of polymer was always very low. Experiment 92 was carried out without any cycling. 3M of 1,3-dioxolan was polymerised by 2.5×10^{-3} M CH_3COClO_4 at 25°. This reaction gave 33% conversion and the polymer had DP = 16.3.

The yield and DP were lower than those of polymers obtained by triethyl oxonium salts.

4.3.2 Polymerisations with "tert-butyl" perchlorate.

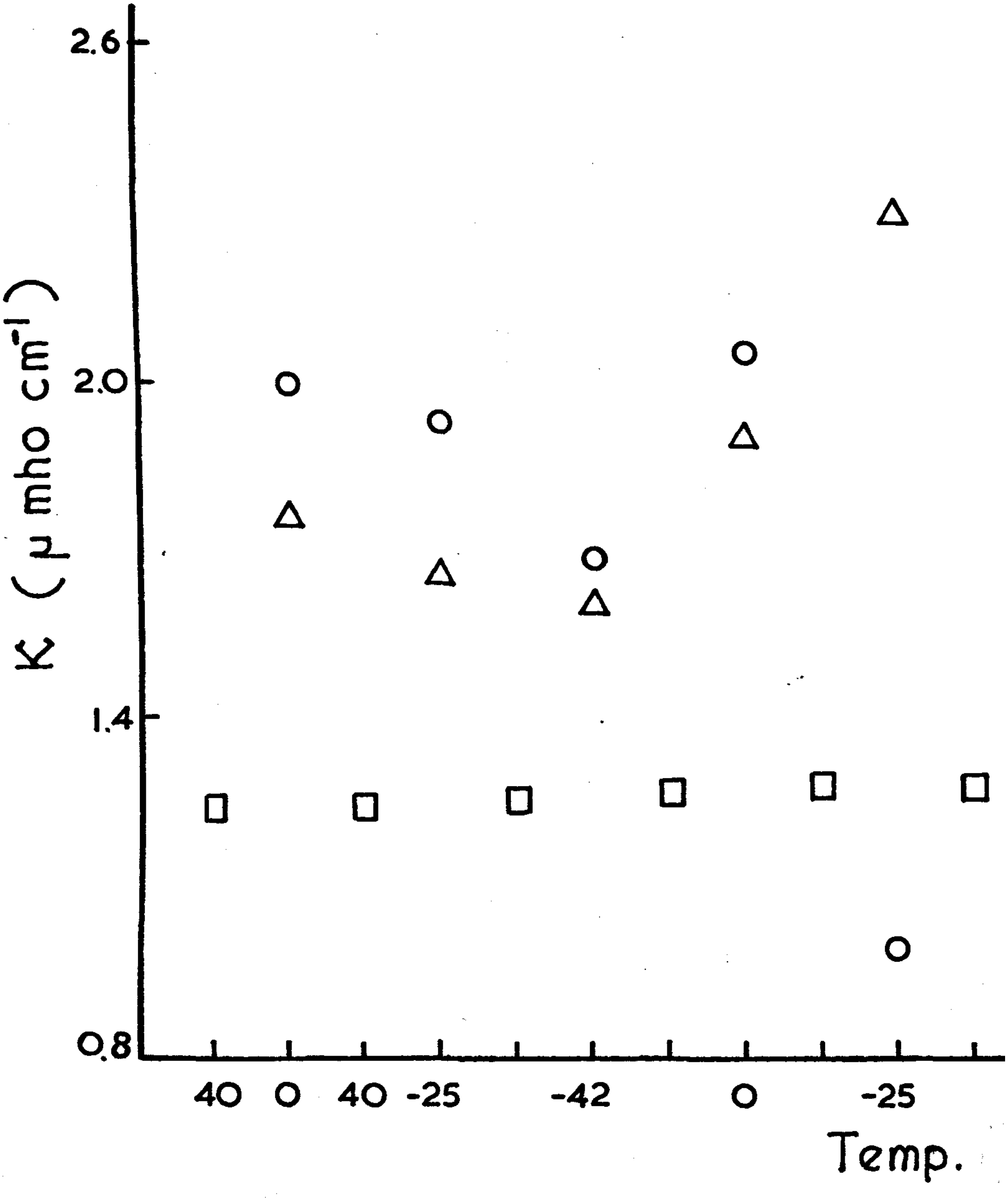
The same dilatometry experiments were carried out with "tert-butyl" perchlorate. This compound was prepared in two ways as described in Chapter Two. The two batches gave the same results.

All the results are shown in Table 4.4.

Fig. 4.3

Data for initial and final conductivities at different temperatures for Run 58, in sequence going from left to right (see Table 4.2).

△	initial
○	final
□	conductivity of depolymerised mixture


2.6
2.0
1.4
0.8
K (μ mho cm^{-1})
40
0
40
-25
-42
0
-25
Temp.

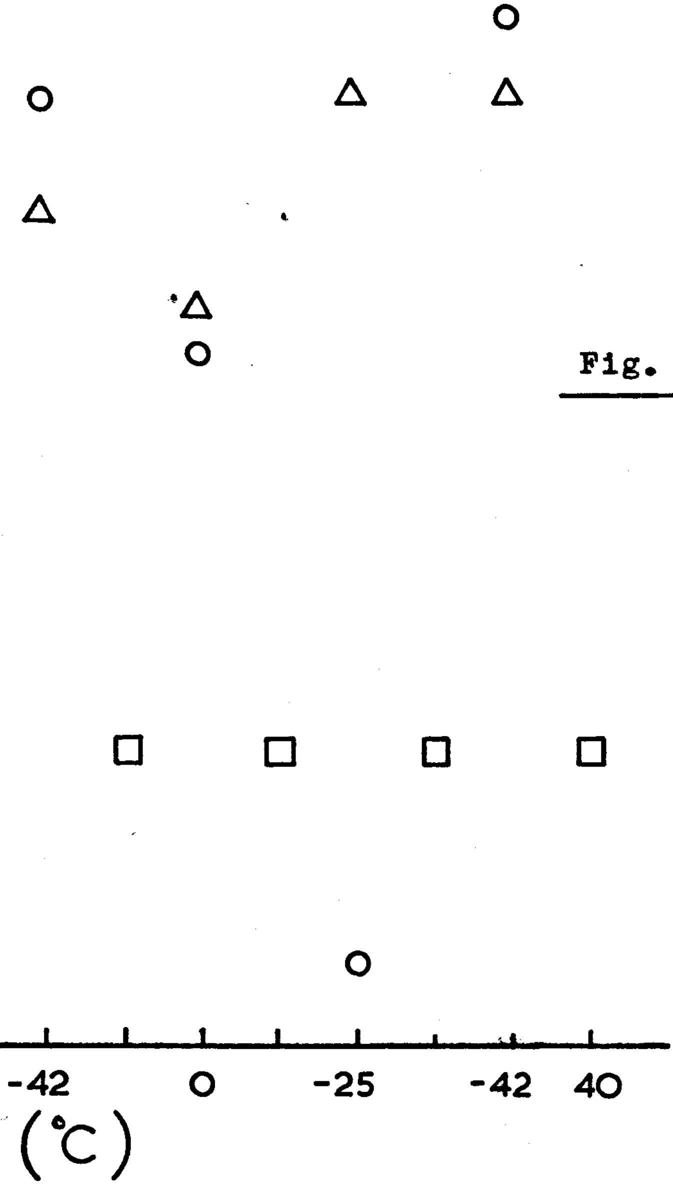


Fig. 4.3

Table 4.4

Data for polymerisation of 1.2M 1,3-Dioxolan with t-$BuClO_4$.

Run No.	60	63	64
$10^3\left[(CH_3)_3CClO_4\right]$/ M	2.77	2.08	1.6
T/°C	0	0	-20
Yield/%	5	27	12

Fig. 4.4

Simultaneous plot of dilatometer reading and conductivity against time for Run 60 at 0°.

Fig. 4.5

First-order plot for Run 60.

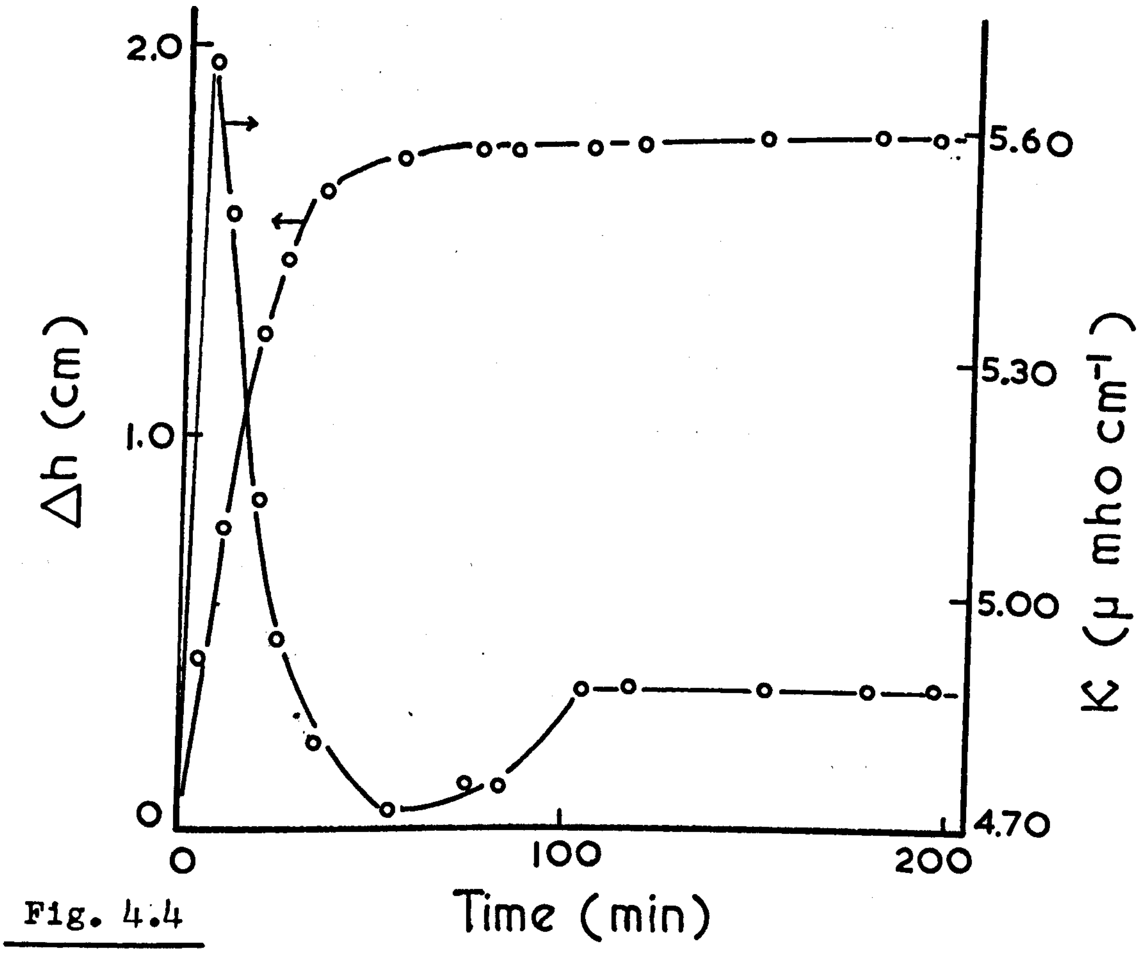

2.0
1.0
0
Δh (cm)
0
100
200
Time (min)
5.60
5.30
5.00
4.70
K (μ mho cm⁻¹)

Fig. 4.4

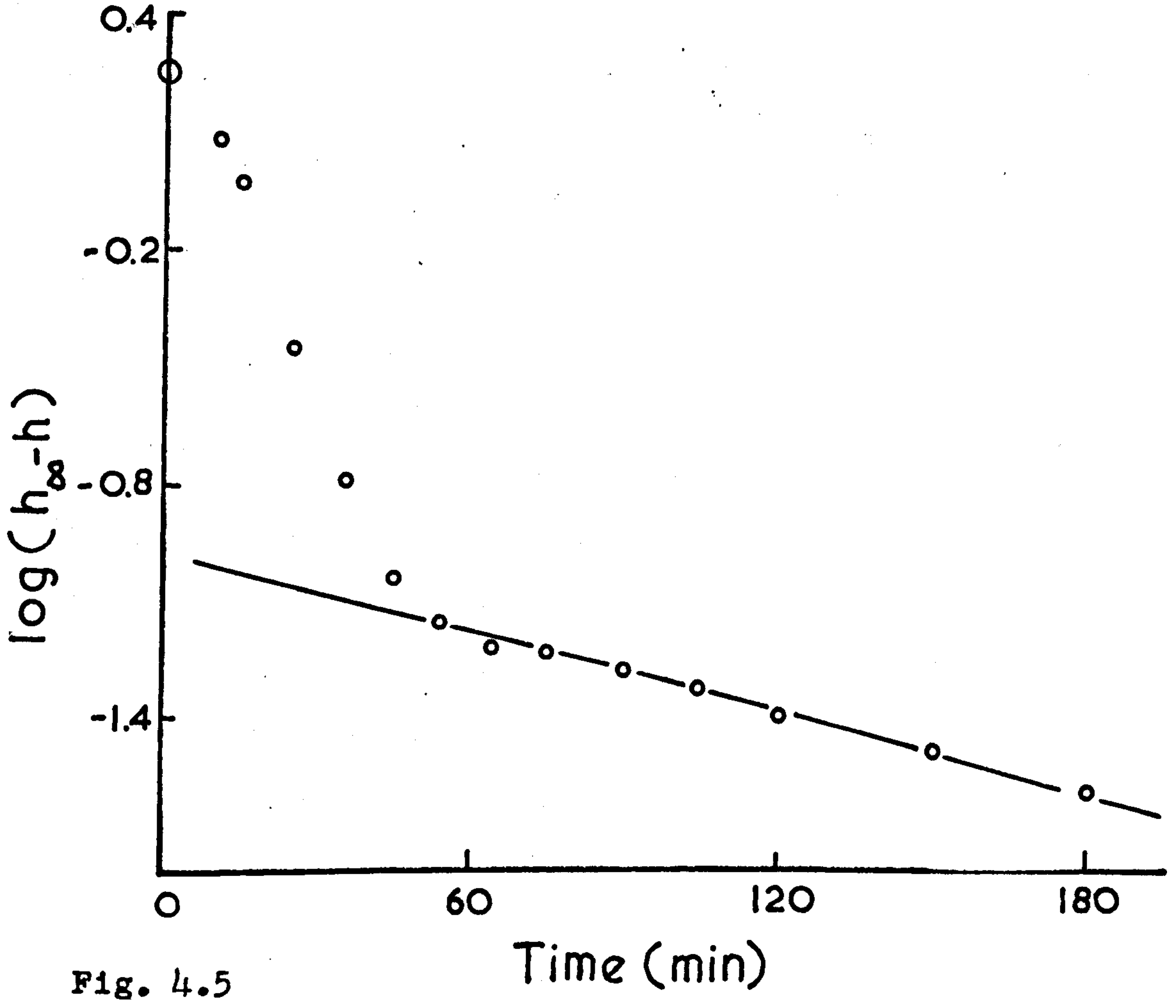

0.4
-0.2
-0.8
-1.4
log(h∞-h)
0
60
120
180
Time (min)

Fig. 4.5

Experiment 60 was carried out with "tert-butyl" perchlorate prepared from silver perchlorate.

When the initiator phial was broken the solution turned violet and kept this colour during the polymerisation.

Conductivity measurements during the polymerisations showed a different pattern from that observed with other initiators. During the polymerisation runs the conductivity of the solutions always decreased and finally reached a constant value. This is shown in Fig. 4.4 and the corresponding first-order plot is shown in Fig. 4.5.

These polymerisation experiments also gave low yields of polymer.

Experiment 79B was carried out in the vacuum spectroscopy device described in Chapter Two. 3M 1,3-Dioxolan was polymerised by 2.7 x 10^{-3} M "tert-butyl" perchlorate. The solution changed colour from pink to green during the polymerisation. The spectra at various times are shown in Fig. 4.6. The spectra show changing absorbance during the polymerisation but this does not identify the active centres. This topic will be developed further in the Discussion section.

4.3.3 IR and NMR measurements.

Polymers obtained from polymerisations using acetyl and "tert-butyl" perchlorate showed a small OH peak in the IR spectrum at 3500 cm^{-1}. Other peaks are similar to those of the polymers obtained with perchloric acid.

The NMR spectra of the polymers are similar to those of polymers obtained with perchloric acid. Therefore, these polymers are probably also cyclic polymers.

Fig. 4.6

Polymerisation of 1,3-Dioxolan carried out with "tert-butyl" perchlorate in the vacuum spectroscopy device. Run No. 79B.

I	Immediately	
II	10 min	after start of reaction
III	20 min	
IV	5 h	

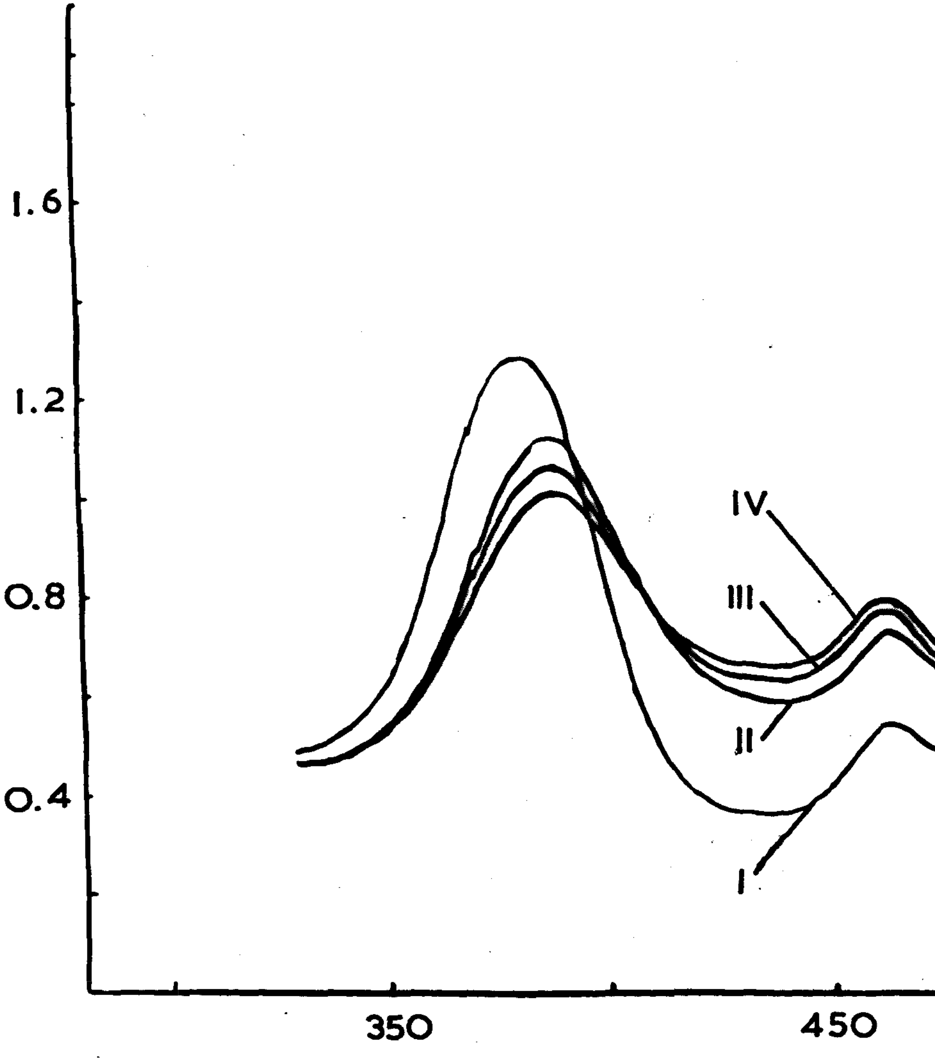
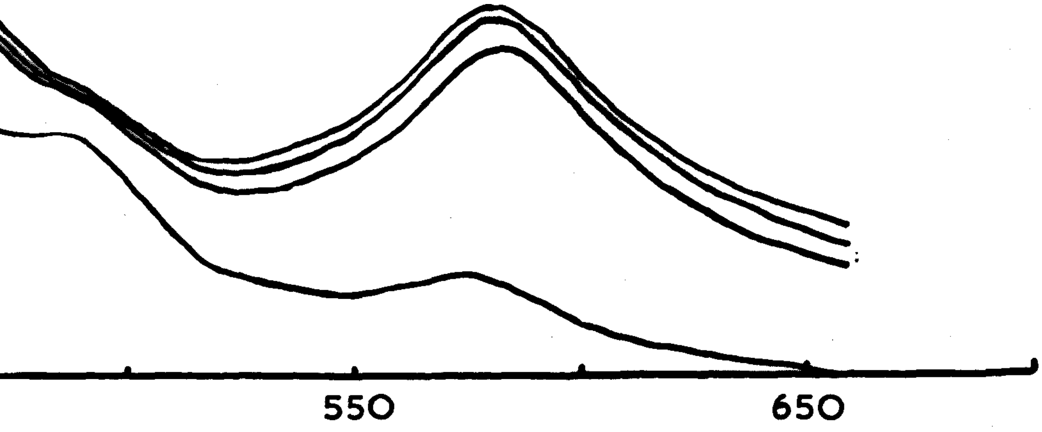

1.6
1.2
0.8
0.4
350
450
IV
III
II
I

Fig. 4.6



4.3.4 Discussion.

These polymerisations were carried out with the object of determining the activation energy of the polymerisation reactions from the Arrhenius plots.

Both initiators give very complicated reactions. It appears that side reactions, the most likely being hydride abstraction, proceed at the same time as the propagation reaction. Experiments showed that acetyl perchlorate sometimes gives a different order of reaction. "Tert-butyl" perchlorate is very difficult to handle, due to its high reactivity. It reacts with itself and solutions turn dark brown after 1 week. This reaction yields many rearrangement products.[6,7] Deno[5a] showed that $(CH_3)_3C^+$ is best prepared by extracting $(CH_3)_3CF$ or other precursors dissolved in fluorinated hydrocarbons with liquid SbF_5 at reduced temperature. Our initiator was not a pure compound, therefore which compound caused the reaction is open to speculation.

Unfortunately, these initiators did not give the hoped-for results, but they showed that the active centres are not stable; it appears that the polymers are cyclic under these conditions.

4.4 Polymerisations with binary initiators.

Okada et al.[8] reported that polymerisation of 1,3-dioxolan by metal halides gives poor yields and low molecular weights, but solid polymers are easily obtained by binary initiators, e.g. acetyl chloride + metal halide. Therefore, polymerisation of 1,3-dioxolan was carried out with $TiCl_4 + CH_3COCl$ and $TiCl_4 + (CH_3)_3CCl$ mixtures under vacuum conditions.

Table 4.5

Data for the polymerisation of 1,3-Dioxolan with binary initiators.

Run No.	93B	94A	94B	95	96B*
[1,3-Dioxolan]/M	2.5	4	4	3	3
$10^3[TiCl_4]$/M	3.49	18	18.1	7.2	
$10^3[CH_3COCl]$/M	3.49	18	-	-	8.34
$10^3[(CH_3)_3CCl]$/M	-	-	18.1	7.2	-
T/°C	0	25	25	0	0
Yield/%	1	3	4	1	1
Polym. time/h	17	4	24	5	8

* $AlBr_3$ + CH_3COCl mixture was used,

$[AlBr_3] = 8.34 \times 10^{-3}$ M

4.4.1 Polymerisations with titanium tetrachloride + acetyl chloride or tert-butyl chloride mixtures.

Polymerisations were carried out in the adiabatic calorimeter and in dilatometers. After the monomer and methylene dichloride were distilled into the reaction vessels, first the acetyl or tert-butyl chloride phial was broken and then a phial of $TiCl_4$ in methylene dichloride was crushed to start the polymerisation. When the $TiCl_4$ phial was broken a bright yellow colour appeared and immediately disappeared. The reactions were stopped by 0.88 ammonium hydroxide or its vapours.

All the results are shown in Table 4.5.

All the yields were very poor and the polymers were oily.

Experiment 93B was carried out in the adiabatic calorimeter. When the $TiCl_4$ phial was broken no conductivity or temperature change was observed. The calorimeter was thermostatted with a water-ice bath, left for 17 h and the reaction stopped by admitting 0.88 ammonium hydroxide vapour.

The other polymerisation experiments were carried out in the dilatometer with platinum electrodes.

The experiment 96B was carried out with aluminium bromide (supplied by Dr. D.W. Grattan) and acetyl chloride, because the Japanese authors carried out experiments with this mixture. This initiator gave the same result as the titanium tetrachloride mixtures.

4.4.2 IR and NMR measurements.

When the polymerisation mixture was killed with ammonium hydroxide it gave a white precipitate. This precipitate was filtered off and washed with methylene dichloride and the methylene dichloride solution was then evaporated.

The oily polymers showed the same NMR spectrum as had been observed before, but their IR spectra were different, containing a broad OH peak at 3500 cm^{-1} and strong C=O absorption at 1740 cm^{-1}.

4.4.3 Discussion.

Although the Japanese authors had carried out similar experiments with bulk monomer, no detailed experimental conditions were given.

In the solution one might expect $CH_3CO^+TiCl_5^-$ ions to appear and these ions to initiate the polymerisations. However, the experimental results showed that these binary initiators produced no conductivity and were completely inefficient. Germain et al.[9] stated that systems containing acetylium ion are not as simple as expected. Thus, the system also contains species such as $Ac_2CHCO^+MX_{n+1}^-$ and the acetylium ion itself can undergo polymerisation. Possibly such a reaction occurred in our system, because when the titanium tetrachloride phial was broken a bright yellow colour appeared and then disappeared.

4.5 Polymerisations with nitronium and nitrosonium salts.

The fundamental studies of Ingold and Hughes[10] established that the reactive nitrating agent in electrophilic nitration is the nitronium ion, NO_2^+. Olah and Kuhn[11] introduced stable nitronium salts as the most efficient nitrating reagents in aprotic, organic solvents. One patent[12] and a paper by Olah[13] showed that these salts can be used to initiate polymerisations. In the patent the use of nitronium and nitrosonium salts for polymerisation and copolymerisation of cyclic ethers and 1,3-dioxacycloalkanes is described.

Table 4.6

Data for the polymerisation of 1,3-Dioxolan with NO_2SbF_6 in vacuum sealed test tubes.

Run No.	69	71	70	72	73B	76B
[1,3-Dioxolan]/M	1.5	2	3	4	4.7	12
10^3 [NO_2SbF_6]/M	2.8	2.9	3.66	1.6	8.6	16.3
T/°C	0	2	0	20	0	0
Yield/%	39	50	71	58	56	89.2
Polym. time/h	2	2	2	16	0.25	0.25
DP	16.1	21	67	9.2	9.8	23.7

Table 4.7

Data for the polymerisation of 1,3-Dioxolan with NO_2SbF_6 in the vacuum dilatometer.

Run No.	74	76A	77
[1,3-Dioxolan]/M	1.2	1.2	1.2
10^3 [NO_2SbF_6]/M	2.1	0.38	0.3
T/°C	0	0	0
Yield/%	29	3	3
DP	5.5		4

If these salts nitrate 1,3-dioxolan, obviously a tertiary oxonium ion would be formed and this would initiate the polymerisation.

4.5.1 Polymerisations with nitronium hexafluoroantimonate.

These polymerisations were carried out in the adiabatic calorimeter, vacuum dilatometer and vacuum sealed test tubes.

Exploratory experiments were carried out in vacuum sealed test tubes. The reactions occurred with violent gas evolution, and a high yield of high molecular weight polymers was isolated. These results are shown in Table 4.6.

A few experiments were carried out in the dilatometer. These results are shown in Table 4.7. Experiments 74 and 76 were carried out in the same way as the acetyl perchlorate initiations. The polymerisation, depolymerisation and repolymerisation experiments showed that the active centres are not stable. The polymer yields and molecular weights were low.

Gas samples were taken from the experiments 76B and 74 for mass spectroscopy. Figs. 4.7 and 4.8 show bar-graphs of these mass spectra. The polymerisation solutions contained nitromethane, methylene dichloride and unreacted monomer. Therefore, the gas samples also contained these compounds, especially methylene dichloride. The mass spectra of methylene dichloride, 1,3-dioxolan and nitromethane were taken separately.

Relative abundances were calculated with methylene dichloride as base for experiment 74.

The spectrum of 76Bwas drawn in such a way that the peak of highest intensity was taken as 100. The peak at mass 30 appears in all spectra and corresponds to NO. Also the gas mixture

Fig. 4.7

Mass spectrum of gas sample taken from Run 74.

Fig. 4.8

Mass spectrum of gas sample taken from Run 76B.

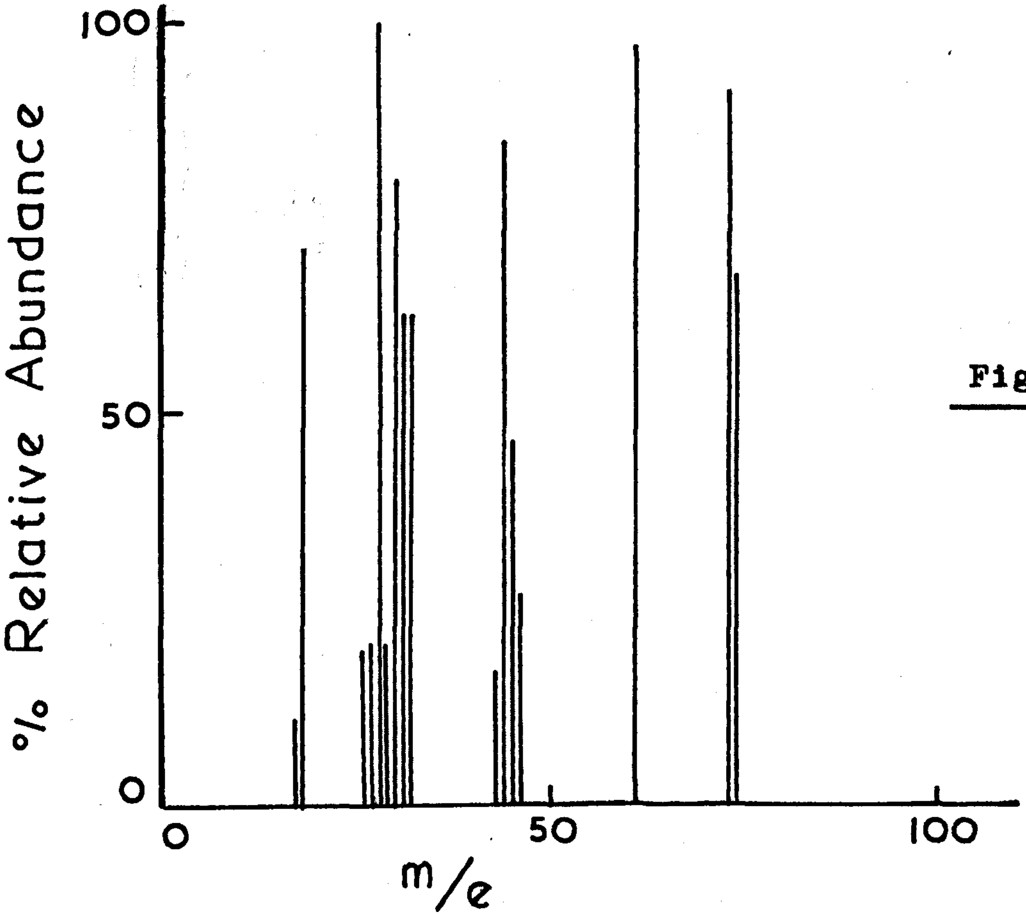


Fig. 4.8

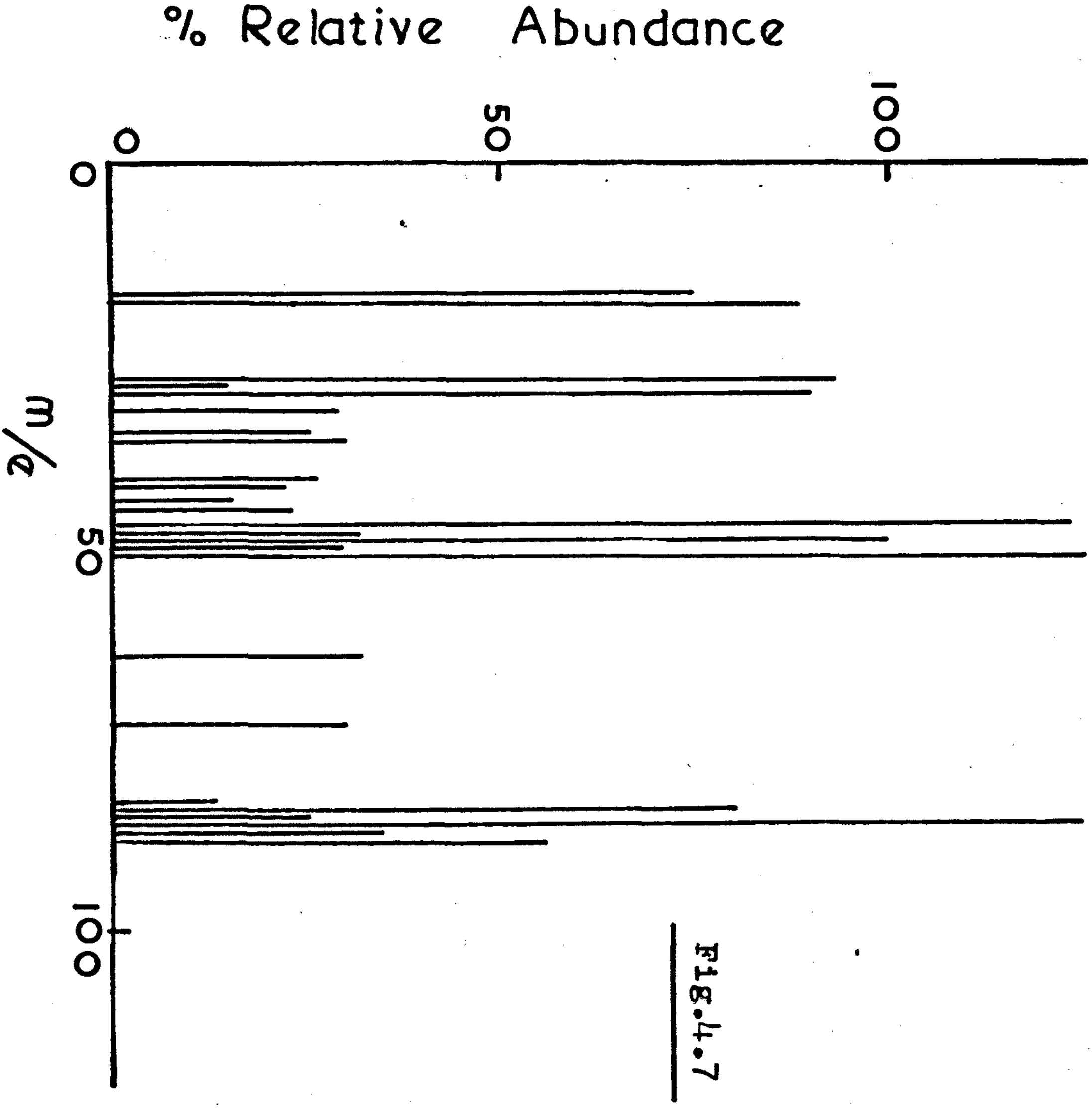


Fig.4.7

Fig. 4.9

Plots of conversion and conductivity against time for polymerisation of 1,3-dioxolan with NO_2SbF_6 (Run No. 75B)

Fig. 4.10

First-order plot for experiment 75B.

From the graph $k_1 = 0.29$ sec^{-1}.

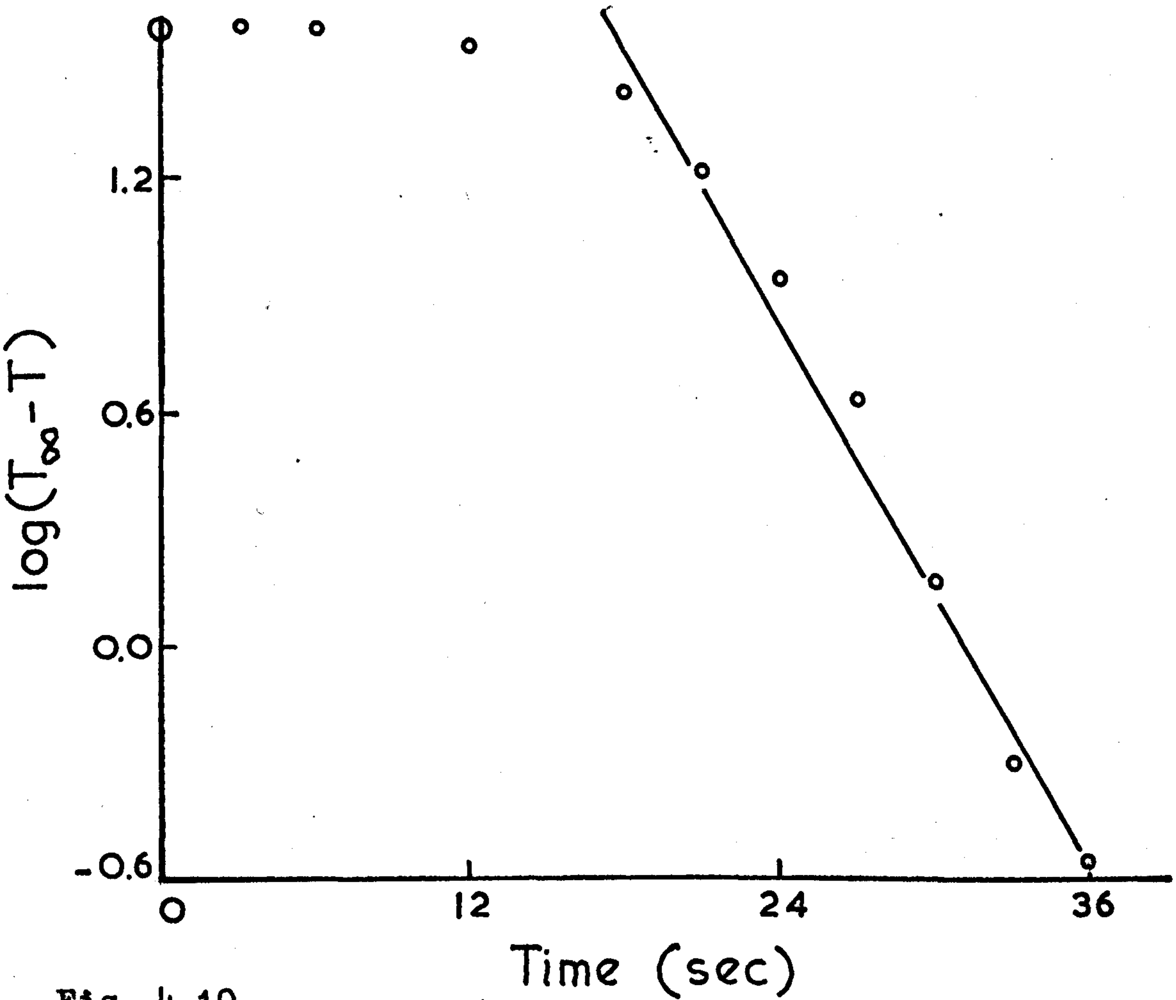


Fig. 4.10

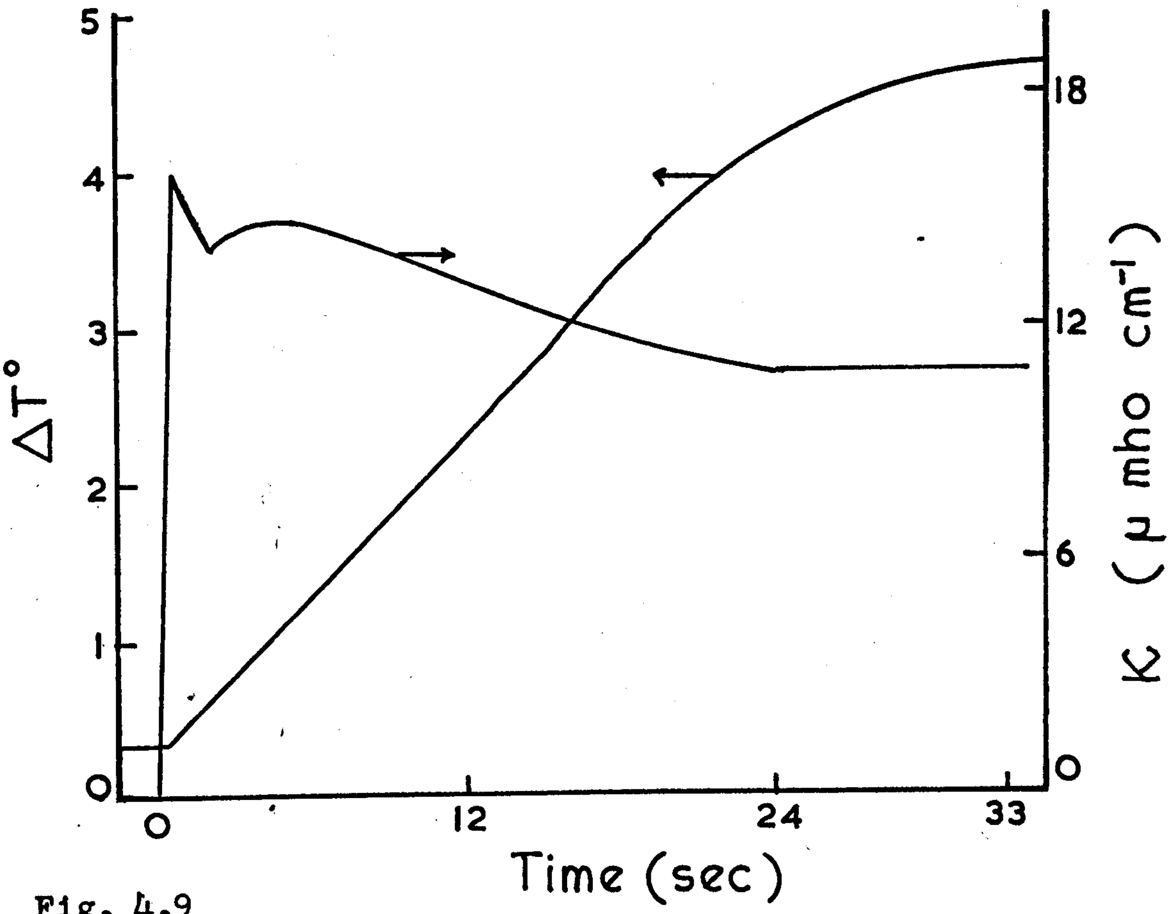


Fig. 4.9

Table 4.8

Data for polymerisations of 1,3-Dioxolan with NO_2SbF_6 in the calorimeter.

Run No.	84	75B	78	80	81	73A	82	85	83
[1,3-Dioxolan]/M	1.59	1.8	1.8	1.8	1.8	2	1.8	1.8	1.8
$10^3[NO_2SbF_6]$/M	2.0	1.83	1.43	1.5	2.6	1.79	1.8	2.86	2.37
Temp./°C	0	0	0	0	0	0	-20	-20	-40
Yield/%	32	30	9		30	39	62	76	82
DP	12	11	9	9	9	18	19	14	18
k_1/sec^{-1}	0.175	0.29		0.115	0.318		0.226	0.150	0.041

became brown when air was admitted to the flask.

Some of the polymerisations were carried out in the adiabatic calorimeter. 1,3-Dioxolan and methylene dichloride were distilled into the calorimeter and the reactions were begun by crushing a phial of NO_2SbF_6 in nitromethane, and they were stopped by admitting to the reaction vessel the vapour from 0.88 ammonium hydroxide.

All results are shown in Table 4.8.

Fig. 4.9 shows typical conversion and conductivity curves and Fig. 4.10 the corresponding first-order plot for experiment 76B.

Conductivity measurements during the polymerisations had a different shape from that obtained with other initiators. When the initiator phial was crushed the conductivity of the solution increased immediately (this is similar to the behaviour of 1,3-dioxepan with $HClO_4$), then dropped; rose again to a maximum, and then fell slowly to a constant value.

A few rate-constants were calculated but the values were not reproducible. Therefore these experiments were discontinued.

4.5.2 Polymerisations with nitrosonium tetrafluoroborate.

Because of the low solubility of this salt in nitromethane only a few polymerisations were done. This salt is also less soluble in methylene dichloride than the others which we tried and therefore these polymerisations were not homogeneous reactions.

No polymers were isolated from these experiments. (Runs No. 86, 87 and 88).

The homogeneous polymerisations were carried out with specially large initiator phials.

All results are shown in Table 4.9.

Table 4.9

Data for the polymerisation of 1,3-Dioxolan by $NOBF_4$.

Run No.	86	87	88	89	90	91
[1,3-Dioxolan]/M	2	4	4	2.5	2.4	4
$10^3[NOBF_4]$/M	1.1	1.1	1.1	0.46	2.13	2.37
T/°C	0	0	20	0	0	0
Polym. time/h	7	7	20	7	4	24
Yield/%	-	-	1	4	-	30
DP				10.6		24

Experiments 89 and 90 were carried out in the calorimeter. When the initiator phial was crushed, no conductivity or temperature change was observed. The calorimeter was thermostatted with an ice-water bath and the reaction was stopped by admitting 0.88 ammonium hydroxide vapour.

Slow evolution of gas was observed in all these reactions.

4.5.3 Polymerisations with nitrosonium hexafluorophosphate.

This salt is readily soluble in nitromethane. Polymerisations were carried out in the calorimeter and in the dilatometer with platinum electrodes.

Experiments 104, 117 and 118 were carried out in the adiabatic calorimeter. Typical conversion and conductivity curves are shown in Fig. 4.11 and a corresponding first-order plot is shown in Fig. 4.12. The conductivity curves are similar to those obtained with nitronium hexafluoroantimonate. All results are given in Table 4.10.

When the initiator phial was crushed a rapid reaction and gas evolution were observed. After the gas evolution stopped, a white colloidal precipitate was obtained. The brown gas, NO_2, was observed when the reaction vessels were opened to air. Apparently this salt also gives some side reactions.

Although it has been reported that nitronium and nitrosonium salts are stable in solution, one might expect an equilibrium such as

$$NOPF_6 \rightleftarrows NOF + PF_5 \qquad 4.3$$

Therefore, experiment 121 was run in the H-shaped reaction vessel.

Table 4.10

Data for the polymerisation of 1,3-Dioxolan by $NOPF_6$.

Run No.	98	99	104	117	118	120
$[1,3\text{-Dioxolan}]/M$	2	4	2	2	1.4	3.5
$10^3[NOPF_6]/M$	8.3	6.1	2.99	0.21	3.26	0.41
T/°C	0	25	0	0	0	0
Yield/%	65	60	35	1	29	29
DP	16.6	11.6				
k_1/sec^{-1}					0.123	

Fig. 4.11

Conversion and conductivity curves for polymerisation with $NOPF_6$ (Run No. 118).

Fig. 4.12

First-order plot for experiment 118.

From the plot $k_1 = 0.123$.

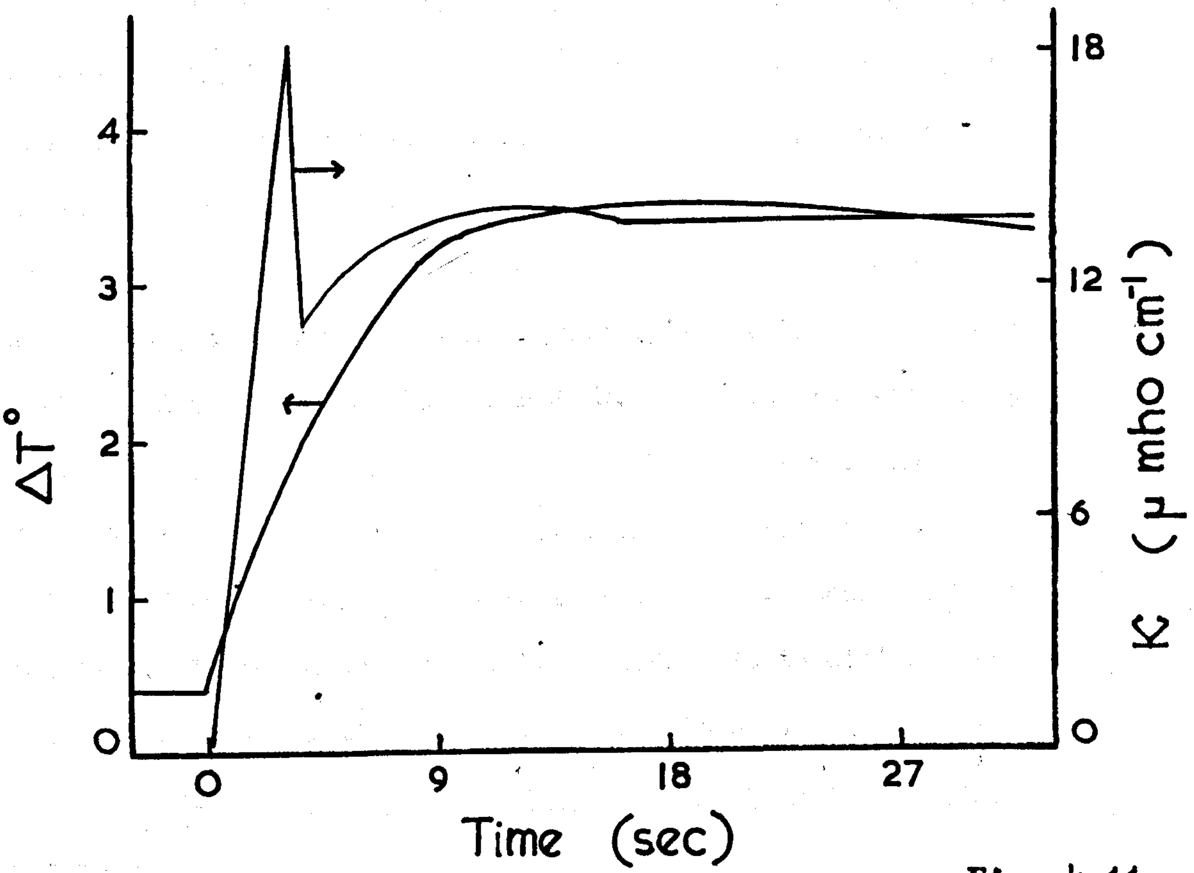


Fig. 4.11

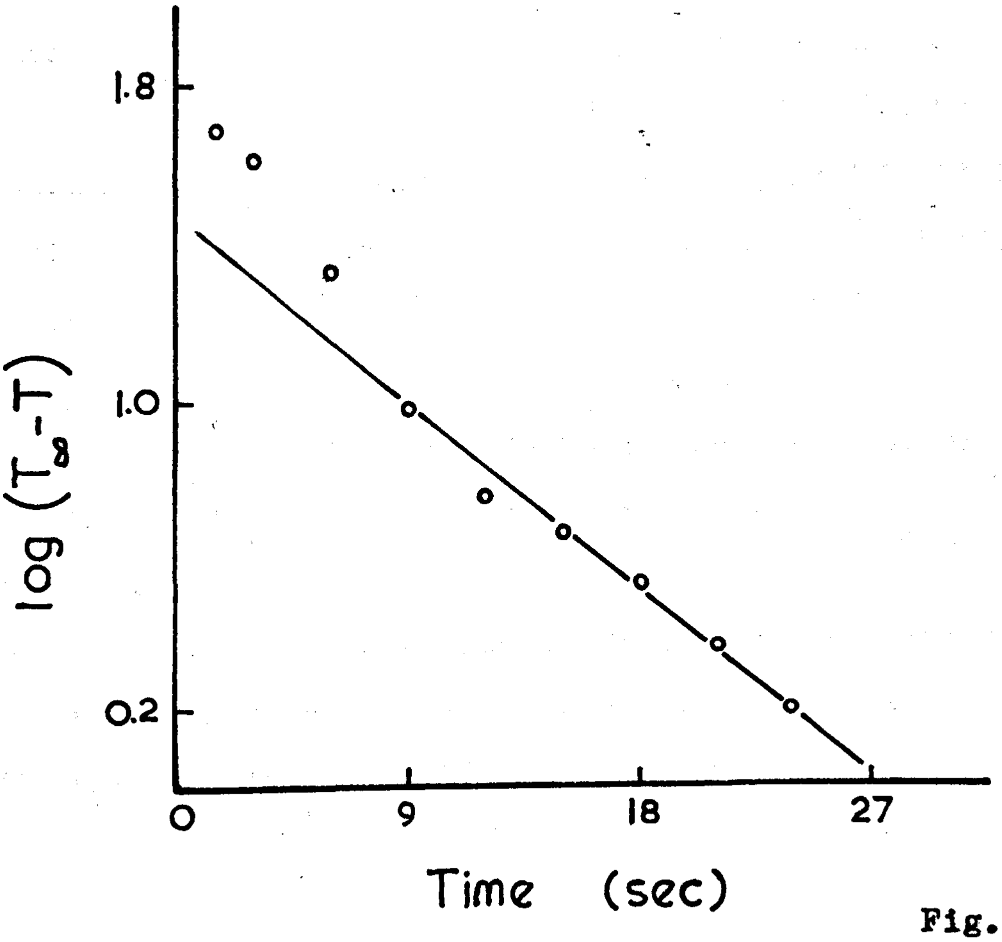


Fig. 4.12

Methylene dichloride was distilled into arm A, which contained a phial of $NOPF_6$ in nitromethane and the phial was broken. All the volatile compounds were distilled into arm B, that was attached to an ampoule via a break-seal which contained 1,3-dioxolan. The arms A and B were separated from each other and arm B was put into the ice-bath. The 1,3-dioxolan ampoule was broken and the solution left for 22 h. The reaction was stopped by adding 0.88 ammonium hydroxide and 11% of polymer was obtained. It follows that an initiator species had distilled out of arm A into arm B and therefore presumably reaction 4.3 occurred in the solution. In the mass spectra it is difficult to distinguish between NOF and CH_2Cl^{35+} under these conditions.

4.5.4 Polymerisations with nitrosonium hexafluoroantimonate.

Only two experiments were attempted with this salt, because we understood that these salts gave side reactions.

These experiments were carried out in the adiabatic calorimeter. The reaction was begun by crushing a phial of $NOSbF_6$ in nitromethane and stopped by admitting 0.88 ammonium hydroxide vapour.

The results are shown in Table 4.12.

The conversion and conductivity curves are shown in Fig. 4.13 and the corresponding first-order plot is shown in Fig. 4.14.

The reaction was again very fast and the conductivity of the solution showed a similar pattern to that found with other nitronium and nitrosonium salts.

Table 4.11

Data for the polymerisation of 1,3-Dioxolan by $NOSbF_6$.

Run No.	119	122
$[1,3\text{-Dioxolan}]/M$	1.4	1.4
$10^3 [NOSbF_6]/M$	3.09	4.76
$T/^{\circ}C$	0	0
Yield/%	27	22
k_1/sec^{-1}	0.161	

Fig. 4.13

Conversion and conductivity curves for polymerisation of 1,3-Dioxolan with $NOSbF_6$ (Run No. 119).

Fig. 4.14

First-order rate plot for experiment 119.
From the plot $k_1 = 0.161\ sec^{-1}$.

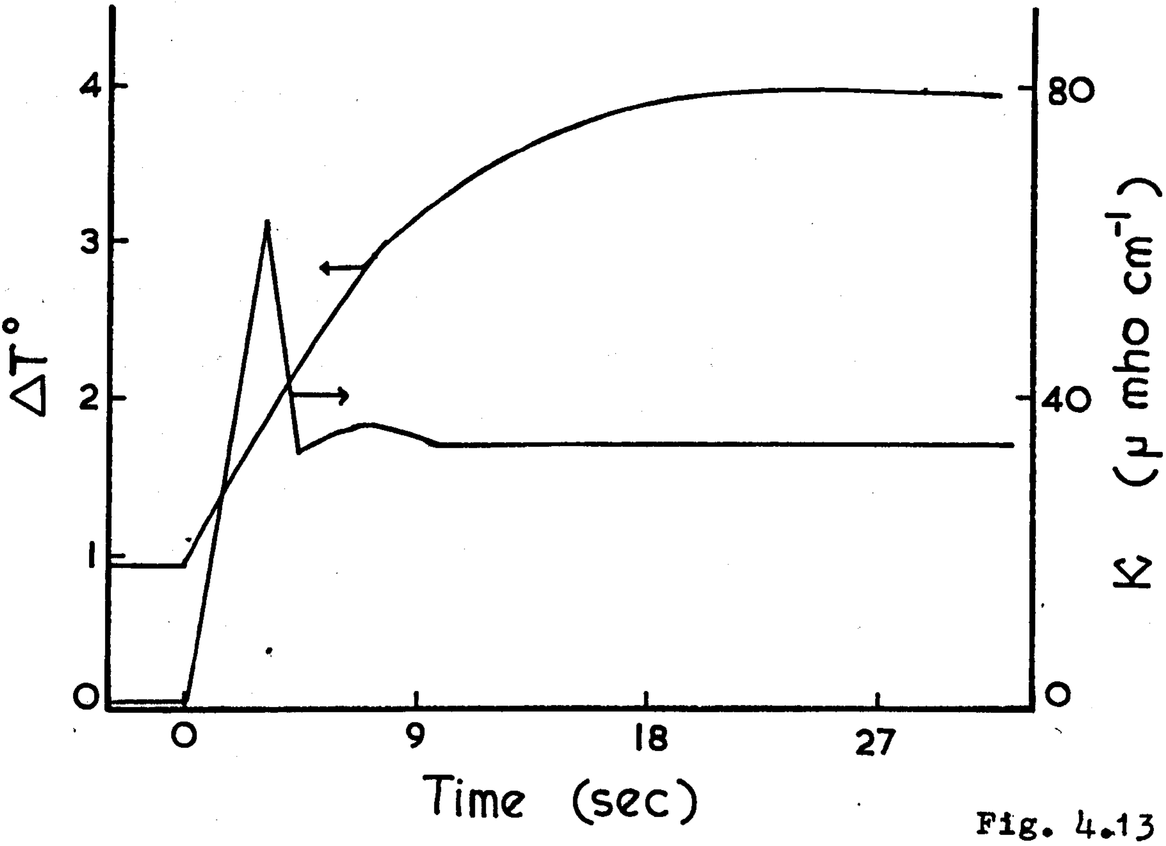


Fig. 4.13

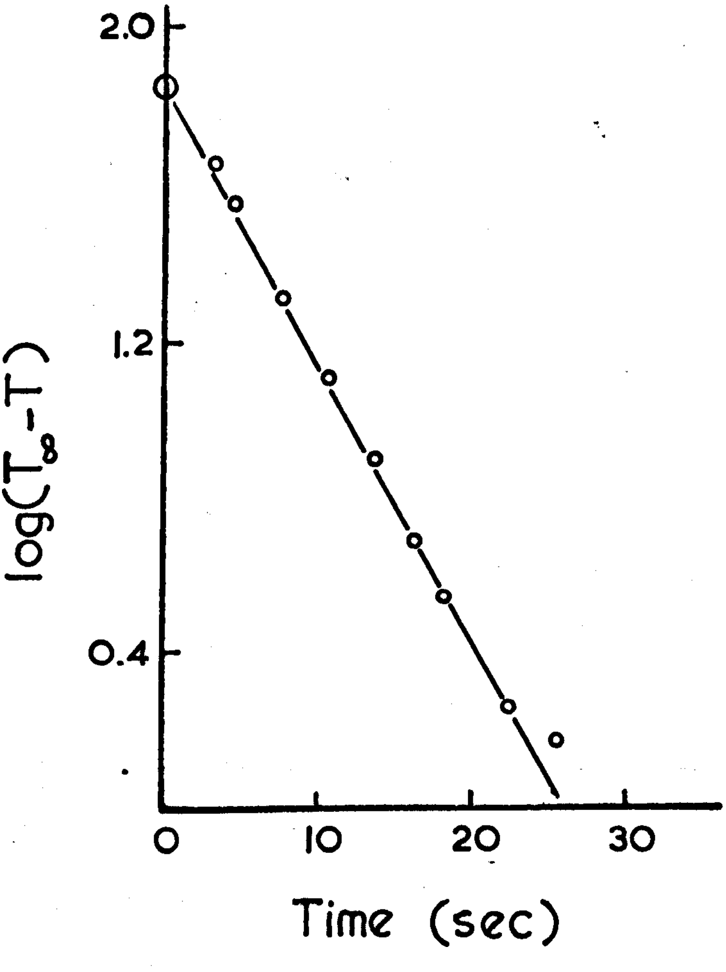


Fig. 4.14

4.5.5 IR and NMR measurements.

The NMR spectra of the polymers were similar to those obtained with other initiators.

The IR spectra of the polymers showed a different pattern. Some of the polymers showed C=O absorption at 1740 cm^{-1}. Also, the IR spectra and nitrogen analysis showed that some of the polymers contained nitrogen. NO group vibrations are found at 1650 cm^{-1} in the IR spectrum. It was found that C=O and N-O bonds are mutually exclusive in the polymers.

All IR spectra contain small OH peaks at 3500 cm^{-1}.

The following end-groups could be shown to be absent.

Vinyl ether	3105 - 3050 cm^{-1}
Carbon-Chlorine	700 - 750 cm^{-1}
Primary or secondary amine	3500 - 3300 cm^{-1}
Quaternary Ammonium ion	3130 - 3030 cm^{-1}

(The values are taken from Cross[14]).

4.5.6 Discussion.

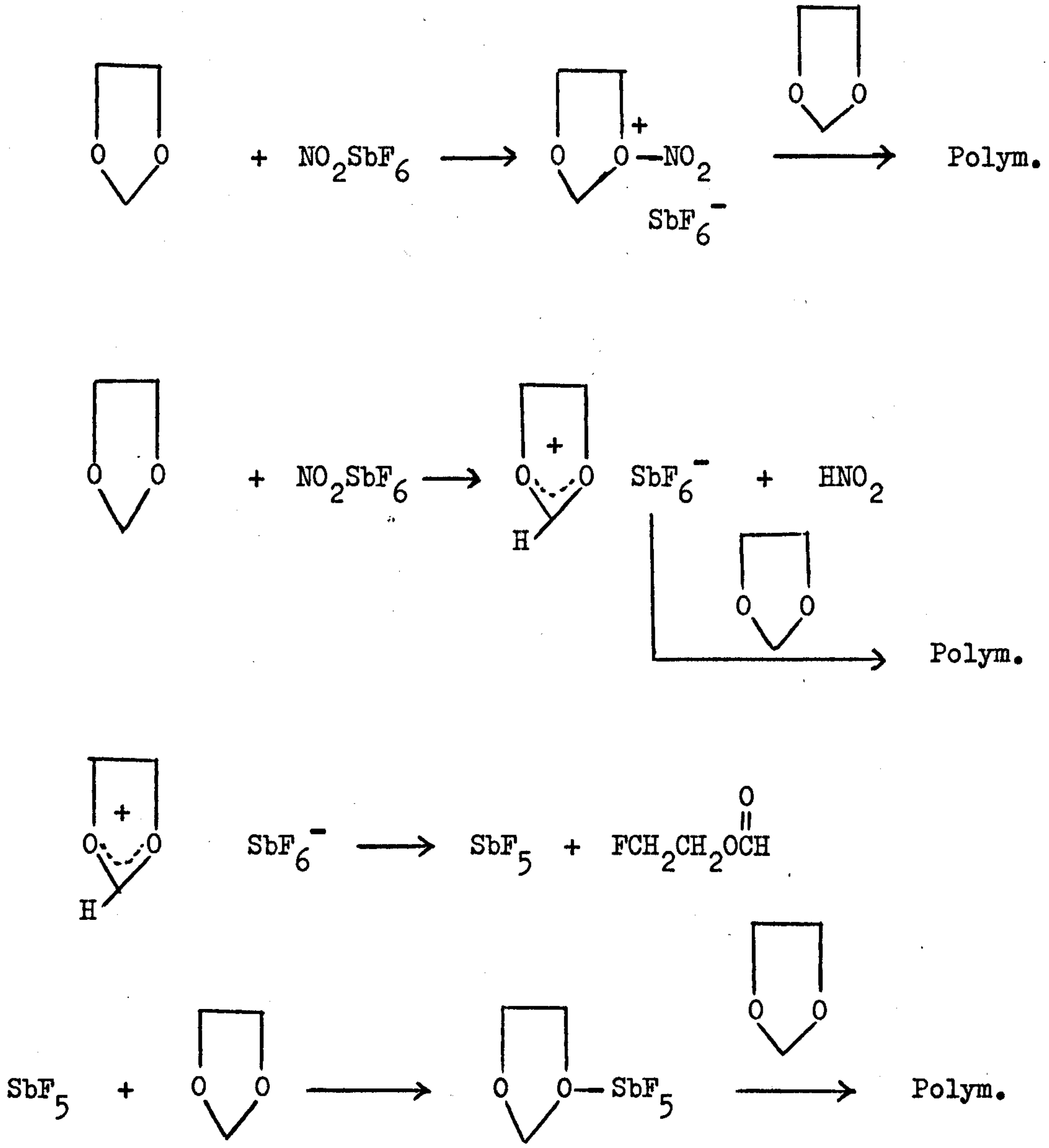
There is no detailed study of the polymerisations initiated with nitronium and nitrosonium salts in the literature, so that this is the first investigation of polymerisations initiated by these salts.

All the salts gave a fast reaction with 1,3-dioxolan with evolution of gas. All the salts also gave high yields of polymers. These yields are almost equal to the expected yields.

Our suggested reaction mechanism is summarised in Fig. 4.15. The mass-spectrum and analytical experiments showed that the gas evolved from the reaction mixture contained NO. This can be explained only by hydride abstraction. It is well known that these salts easily undergo hydride abstraction. The nitronium salts give

Fig. 4.15

Scheme for the polymerisation of 1,3-Dioxolan initiated by NO_2SbF_6.



HNO_2 and nitrosonium salts give $(HNO)_2$ in solution.[15]

This scheme can also be applied to nitrosonium salts. According to the scheme polymerisations were begun either by hydride abstraction or by the formation of tertiary oxonium ions. Hydride abstraction leads to side-reactions, one of which produces powerful initiators, e.g. SbF_5, PF_5 which would contribute to the yield of polymer. SbF_5 and PF_5 can appear according to the equation 4.3. Therefore since many side-reactions seem to have been going on together, it is difficult to say which initiator dominates the polymerisation.

If one compares the polymerisation initiated by $HClO_4$ with those initiated by the nitronium and nitrosonium salts, when the initiator concentrations are the same, it may be supposed that the concentration of the propagating species are the same. The k_1 values for the nitronium and nitrosonium salts are bigger than those obtained with $HClO_4$, therefore one can conclude that the k_2 of these particular tertiary oxonium ions may be greater than that of the secondary oxonium ions.

I could not find out whether the presence or absence of C=O and NO in the polymers depended on temperature or time of reaction.

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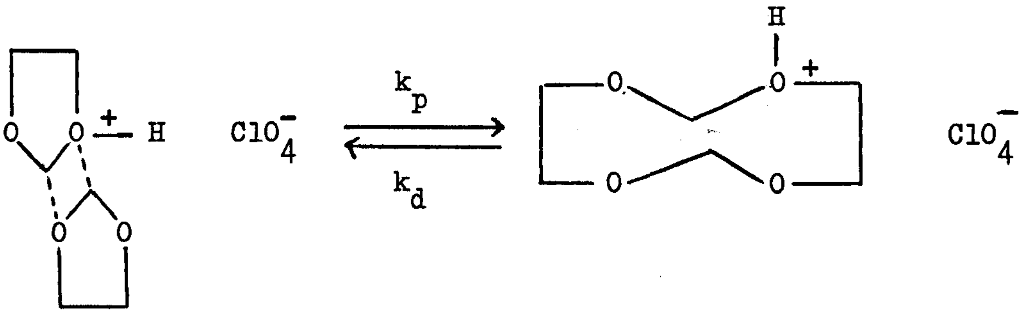
CHAPTER FIVE

Determination of tertiary and secondary oxonium ions on polymers of 1,3-dioxolan, 1,3-dioxepan and 4-methyl-1,3-dioxolan

5.1 Introduction to Chapter Five.

Plesch and Westermann proposed that the equilibrium polymerisation of 1,3-dioxolan[1] and 1,3-dioxepan[2] by anhydrous perchloric acid occurred through a four-centred transition state to produce cyclic polymer.



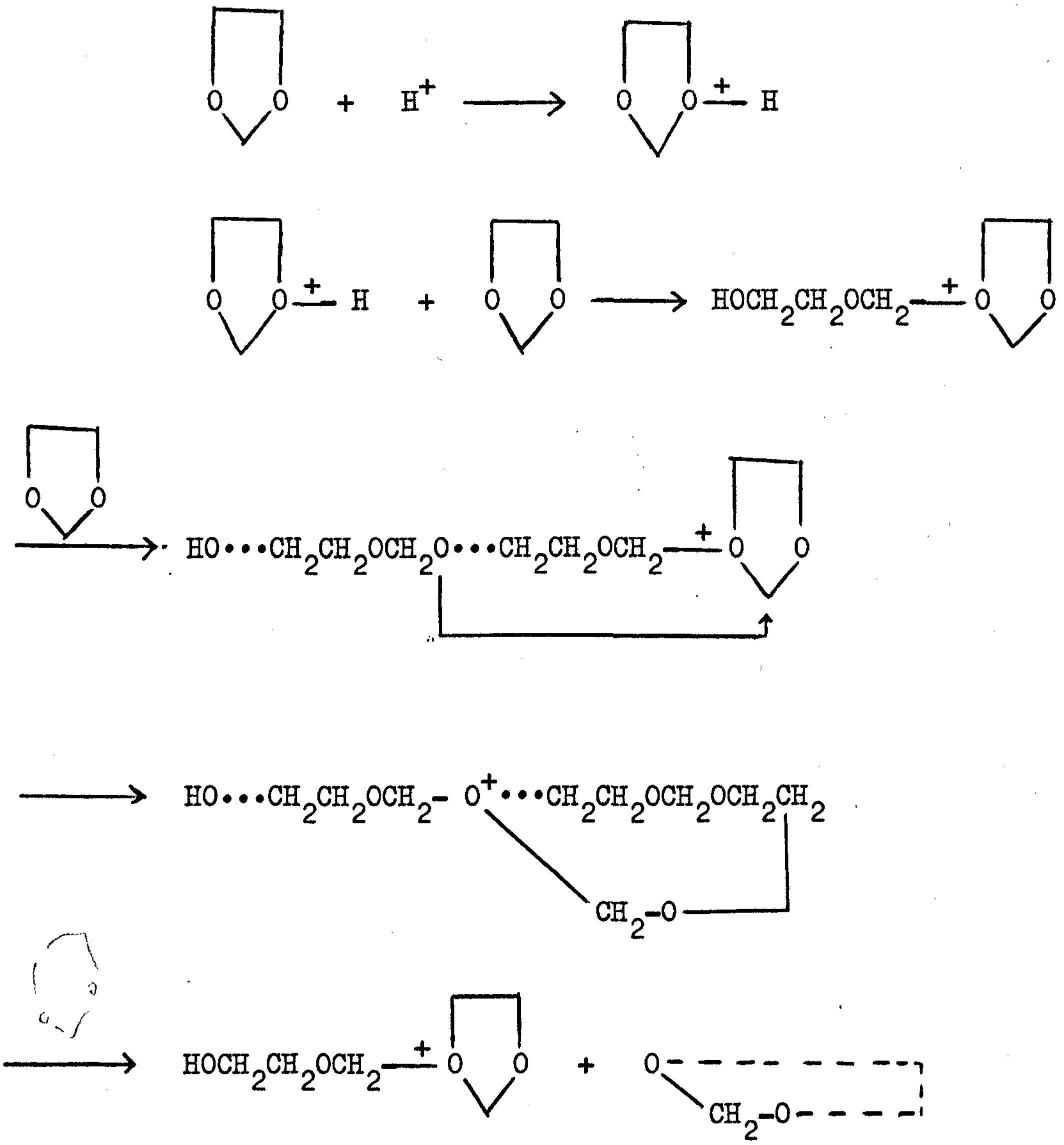
5.1

The mechanism proposed was a ring-expansion in which the ring never opened. This mechanism accounts simply for the cleanness of the monomer-polymer equilibrium and for the high yields of cyclic dimers which are obtainable from 1,3-dioxepan,[2,3] 1,3-dioxan,[2,4] 2,2-dimethyl-1,3-dioxepan,[5] 7,9-dioxabicyclo-[4,3.0]-nonane.[6] According to the ring-expansion mechanism, the active centres are secondary oxonium ions as shown in equation 5.1 if the initiator is a protonic acid.

Although Jaacks[7] agreed that the polymers are cyclic he has questioned the ring-expansion mechanism and proposed his own mechanism for the production of the macrocyclic rings. He considered that the reaction proceeds via tertiary oxonium ions and that ring-closure is

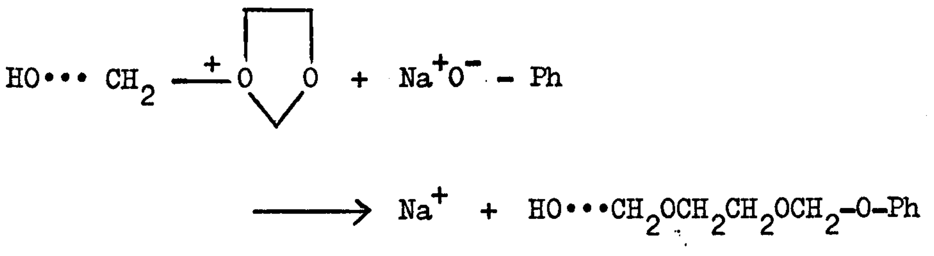
Fig. 5.1

The mechanism of the polymerisation of 1,3-dioxolan of Jaacks.



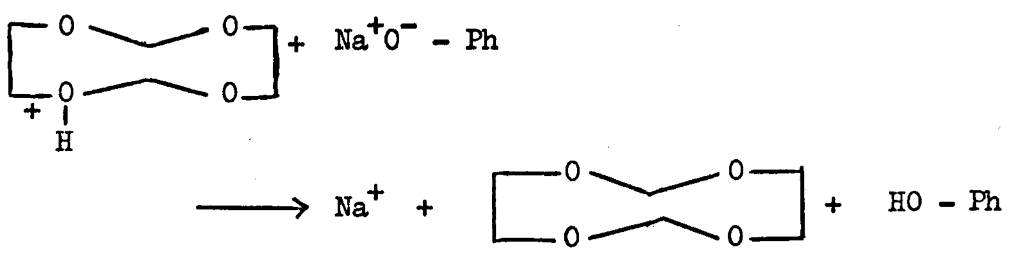
achieved by back-biting. This mechanism, illustrated in Fig. 5.1, is based on the evidence from trioxan and 1,3-dioxolan polymerisations that were killed with sodium ethoxide, as shown in Fig. 5.2. If killed by this method, the polymer contains an -OEt end-group which is converted into ethanol by hydrolysis with aqueous hydrochloric acid. The amount of ethanol was determined by g.l.c. Their results showed the slow formation of tertiary oxonium ions at the expense of secondary oxonium ions throughout the polymerisation.

Jones[4] used Saegusa's[8] phenoxyl end-capping method for determining secondary and tertiary oxonium ions. The polymerisations of 1,3-dioxolan and 1,3-dioxepan by anhydrous perchloric acid were terminated by sodium phenoxide. The tertiary oxonium ions give the phenoxy end-groups (e.g. 5.2).



5.2

The secondary oxonium ions always react by splitting off H^+ [8] (e.g. 5.3).



5.3

The tertiary and secondary oxonium ions were determined by UV spectroscopy.

Fig. 5.2

Jaacks' method of estimating end-groups.

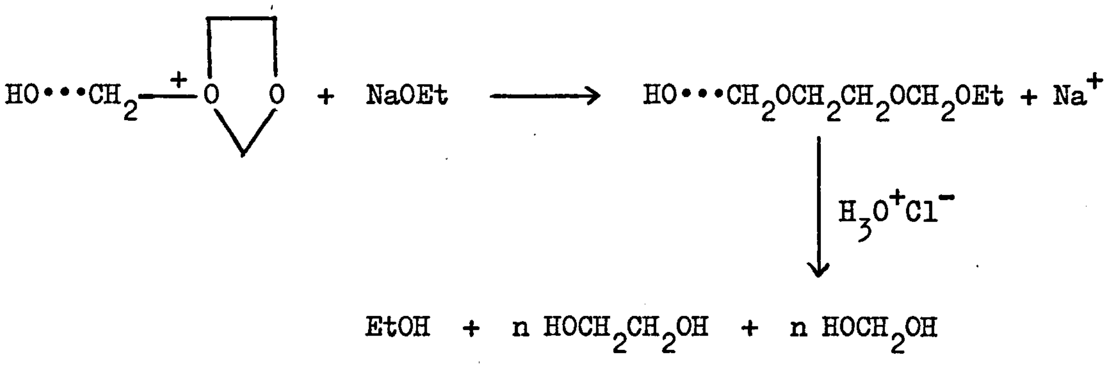
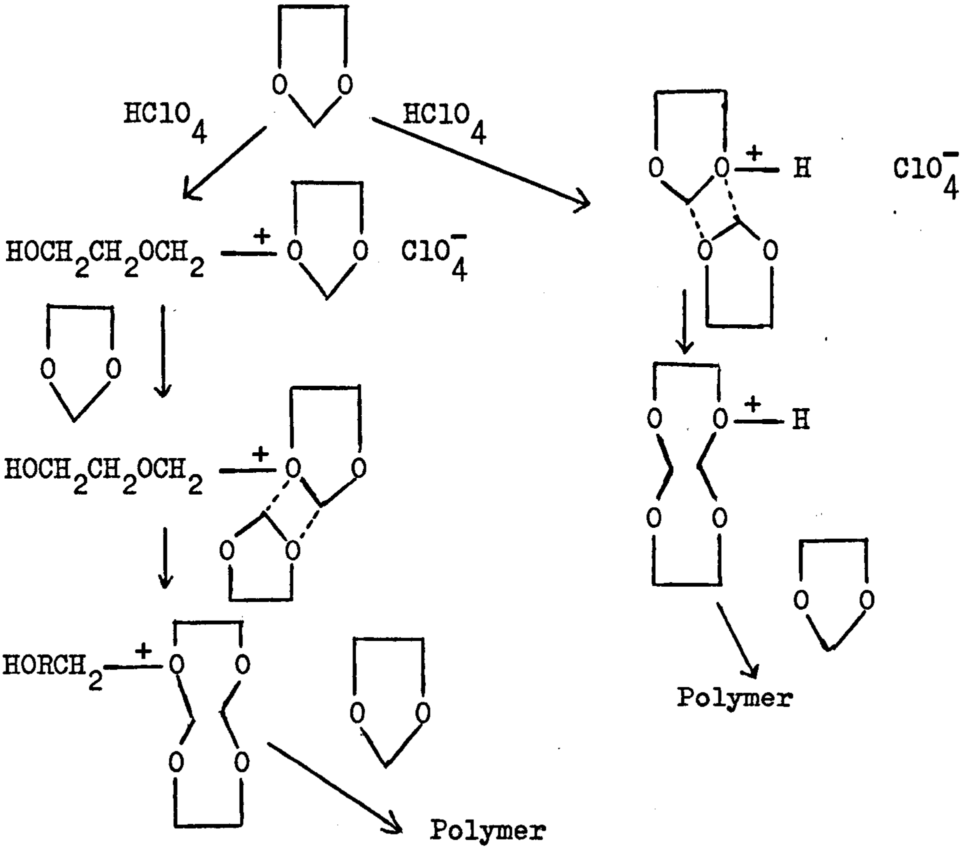


Fig. 5.3

The mechanism of the polymerisation of 1,3-dioxolan proposed by Jones.



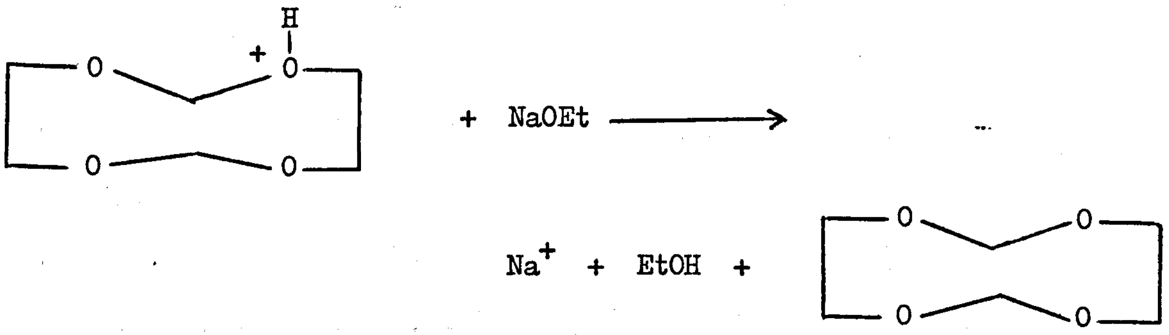
This method had been used successfully for cyclic ethers[9] and Jones for the first time applied it to cyclic formals, and using high vacuum techniques. He found that the concentration of tertiary oxonium ions is always less than the acid concentration (provided that the monomer concentration is not too high, since the concentration of the tertiary oxonium ions appeared to depend on the monomer concentration). He also found that these tertiary oxonium ions are formed at the beginning of the reaction (Fig. 5.3) and that their number does not increase during the polymerisation.

In Chapter Four we showed that the kinetic method failed to solve the problem of the reaction mechanism of cyclic formals. Therefore we searched for other methods.

Westermann and Jones had shown that the IR spectra of the polymers did not help, because of the lack of accuracy in the quantitative estimation. They showed that qualitatively the intensity of the -OH band in the polymer spectra depends on the killing reagent; anhydrous killing reagents gave a very small -OH peak at 3500 cm^{-1}.

The NMR spectra of the polymers are even less helpful than the IR spectra. It is impossible to see -OH protons in the NMR spectrum. Hydroxyl protons also could not be observed in the 100 MHz spectrum of poly 1,3-dioxolan. (This spectrum was taken by Dr. T. Demir at Birkbeck College).

Therefore we intended to use Jaacks' method of end-group determination on polymers prepared under high vacuum. If the Mainz theory is correct, the number of end-groups must equal the number of moles of initiator. If the Keele theory is correct, then according to the equation 5.4



5.4

the polymer does not contain ethoxyl end-groups, but instead this termination reaction produces ethanol which can be determined by g.l.c. on the unhydrolysed polymer.

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5.2 Method.

The termination by sodium ethoxide has been used successfully in Mainz on polymers prepared under nitrogen.[1,2,3] The concentration of ethanol was measured by g.l.c. with acetone as internal standard. Therefore, it is necessary to make a calibration curve.[4] An aqueous solution containing 10^{-2} M ethanol and 7.8×10^{-3} M acetone was prepared. This solution was successively diluted and $3\,\mu l$ of each of these solutions was injected into the g.l.c. In these experiments the dual Porapak Q columns were used; the properties of these columns are explained in Chapter Two. The g.l.c. working conditions were: column temperature 150°, injection temperature 200°, and detector temperature 250°. The peak areas were calculated by the half-peak height method, i.e. from the height of the peak multiplied by half of the peak width. The calibration curve is shown in Fig. 5.4.

The polymerisation reactions were killed with a phial of sodium ethoxide in diethyl ether without opening the reaction vessel to air. The solutions containing the polymers were evaporated in the Rotavapor-R apparatus. It is obvious that if any sodium ethoxide were carried through to the hydrolysis stage it would also give ethanol. Therefore, water was added from time to time to the solution and evaporated. This is the important part of the experiment because if the excess of sodium ethoxide were not removed before the hydrolysis of the polymer it would give erroneous results. The polymer was finally dried under a high vacuum.

The preliminary experiments showed that water in the polymerisation system will cause the formation of tertiary oxonium ions. Therefore, to remove water from the solvent and monomer, we evolved the drying techniques described in Chapter Two. Thus, methylene dichloride was distilled from the reservoir into a flask containing a sodium-film and attached to the vacuum line with a Plegli valve. This measured amount of solvent was left over sodium overnight and any volatile gas pumped out with freezing and thawing and then the solvent was distilled into the reaction vessel.

When we understood that the tertiary oxonium ions were produced from water, the reactions were carried out in vacuum sealed tubes instead of in the calorimeter, so as to reduce the residual water concentrations. These reaction tubes are fitted with side-arms, in which phials can be stored so that more than one phial can be used. The experiments involving the addition of water to the reaction mixture were also carried out in these reactors. The phial of water is broken at room temperature in the solution which is then cooled to 0^{o}. After the solution was thermostatted, the phial of anhydrous perchloric acid in methylene dichloride was broken to start the polymerisation.

Further experiments were carried out in the H-shaped reaction tubes for the determination of the ethanol produced by proton abstraction from the secondary oxonium ions (e.g. 5.4). The reactions were carried out in arm A. All the volatile products were distilled into arm B after the killing, and the reaction tubes were then separated from each other without opening them to air. The polymer left in tube A was used for determination of the tertiary oxonium ions, and the volatiles in tube B were used in the determination of the secondary oxonium ions. This procedure is as follows. 0.1 g of a dried polymer was put into the special tube fitted with a ground-glass-joint stopper fixed with two springs. 1 ml of 0.1 N HCl and 10 μl of standard acetone solution in water were added, and the tube was heated in a water bath for 1 h. The

Table 5.1

The quantitative estimation of end-groups for the polymerisation of 1,3-Dioxolan.

Run No.	97	65[a]	66B	108	110[b]	113[b]	116[b]	105B	67	106[b]	115	111B	114	101	102	103
[1,3-Dioxolan]/M	1.86	1.89	1.9	1.9	1.9	1.9	1.9	2	2.86	1.9	1.9	1.9	1.9	1	1	1.4
10^3 [$HClO_4$]/M	2.27	1.64	3.52	4.64	4.66	6.14	6.27	3.77	8.51	4.38	5.12	4.69	4.86	3.16	2.92	3.5
T/°C	0	0	0	0	0	0	0	0	0	0	0	0	0	-30	-30	-60
10^3 H_2O /M[c]	-	-	-	-	-	-	-	-	-	2.4	1.28	2.4	4.86	-	-	-
10^3 [Secon.Ox.i.]/M	0.31			0.7											0.1	
10^3 [Tert.Ox.i.]/M	0.1	0.1	0.1	0.1				0.1	0		7.8	8.5	9	0.1	0.1	0.1

a Killed before equilibrium was reached.

b Polymer decomposed during the evacuation.

c Added water.

solution was left to cool and was then neutralised with solid $NaHCO_3$. A 3 μl sample from this solution was injected into the g.l.c. Ethanol and acetone peak areas were calculated and the concentration of ethanol was found from the calibration curve. The g.l.c. of the hydrolysis products are shown in Fig. 5.5.

The ethanol in the volatile compounds collected in arm B was difficult to determine quantitatively. I could not find a suitable internal standard for these experiments because of the awkward retention times. The retention time of the internal standard must be less than that of ethanol because a broad methylene dichloride peak follows the ethanol peak. Although methanol fulfilled this requirement I could not obtain a good calibration curve with this compound. Therefore I used the method of making a known addition of methanol to the mixture after distillation. A blank experiment showed that this method can be applied under these conditions.

5.3 Results.

All the results for 1,3-dioxolan are shown in Table 5.1. Some of the polymers were decomposed during the evacuation time so that no result could be obtained. From the table it is seen clearly that the concentration of tertiary oxonium ions in the absence of added water is ca. 10^{-4} M and that it did not vary significantly with an approx. 6-fold variation in $HClO_4$ concentration. At most the concentration of the tertiary oxonium ions was 10% of that of the initiator. Some of the experiments were carried out with a known amount of added water. These experiments (111B, 114 and 115) show clearly that the tertiary oxonium ions were produced mostly by water. Only one experiment (Run No. 67) showed no tertiary oxonium

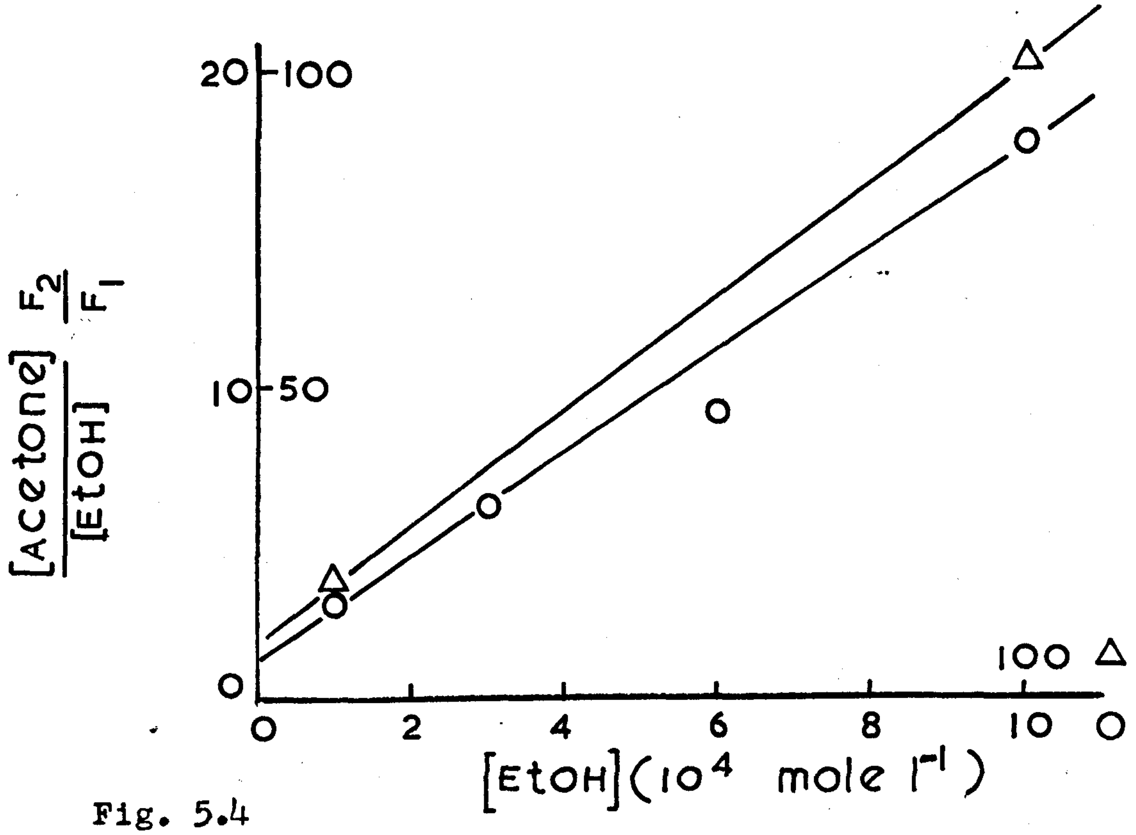
Fig. 5.4

Calibration curve for the quantitative estimation of ethoxyl end-groups.

Fig. 5.5

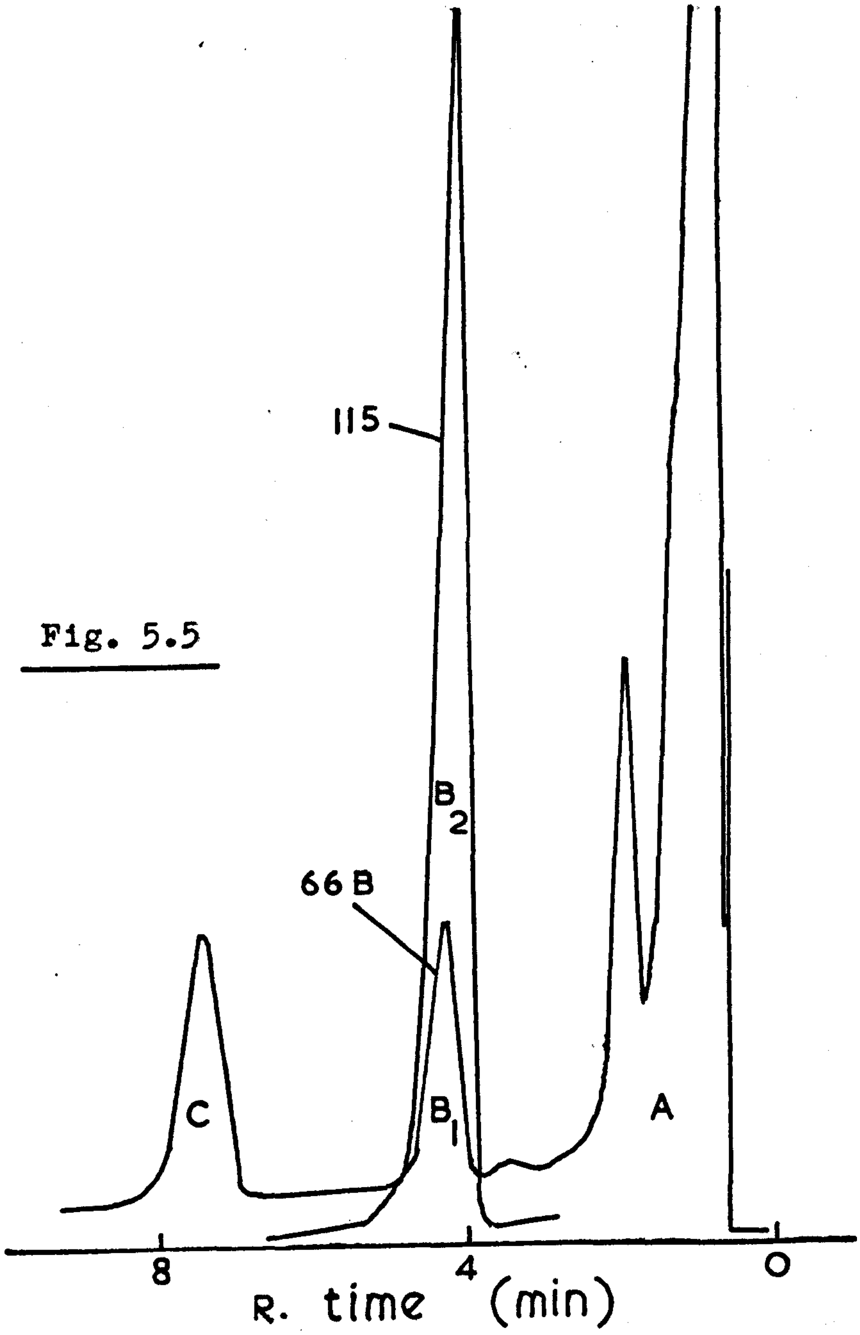
The g.l.c. of the hydrolysis products of 1,3-Dioxolan.

A	CH_2O peaks
B	EtOH peaks for polymers 66B and 115
C	Acetone peak



20
100
10
50
$\frac{[\text{Acetone}]}{[\text{EtOH}]}\frac{F_2}{F_1}$
100 △
0
2
4
6
8
10
○
[EtOH](10^4 mole l^{-1})

Fig. 5.4



115
B_2
66 B
C
B_1
A
8
4
0
R. time (min)

Fig. 5.5

Table 5.2

The quantitative estimation of ethoxyl end-groups for the polymerisation of 1,3-dioxepan (A) and 4-methyl-1,3-dioxolan (B).

	A			B	
Run No.	107	109	112	Y31B	Y32B
[Monomer]/M	0.8	0.7	0.74	3	3
$10^4[HClO_4]$/M	2.32	5.8	3.07	2.89	2.88
T/°C	0	-30	-60	-56	-50
10^3[Tert. OX. ion]/M	0.1	0.1	0.1	0.1	0.1

ions at all in the polymer.

Some similar experiments were carried out with 1,3-dioxepan. Poly-1,3-dioxepan is surprisingly difficult to hydrolyse by aqueous HCl. The polymers showed hydrophobic character and the aqueous acid did not react with them. Therefore, the polymers were hydrolysed in aqueous dioxan. These results are shown in Table 5.2 and they also show that the tertiary oxonium ion concentration was ca. 10^{-4} M.

Only two experiments were carried out with 4-methyl-1,3-dioxolan (Table 5.2). These polymers were even more hydrophobic than the poly-1,3-dioxepans, and so they were also hydrolysed in aqueous dioxan. For these too the concentration of tertiary oxonium ions was ca. 10^{-4} M.

5.4 Discussion.

Jaacks' group showed by means of the ethanol determinations that the production of the tertiary oxonium ions from protonated 1,3-dioxolan and protonated poly-1,3-dioxolan is a slow process.[1,2] If his mechanism (shown in Fig. 5.1) is correct, each perchloric acid molecule must produce a linear polymer with an -OH end-group. According to his explanation, the basicity of chain oxygen is higher than that of monomer oxygens; therefore, it is possible to have attack of the growing ion on the polymer instead of the monomer in the random coil polymer.

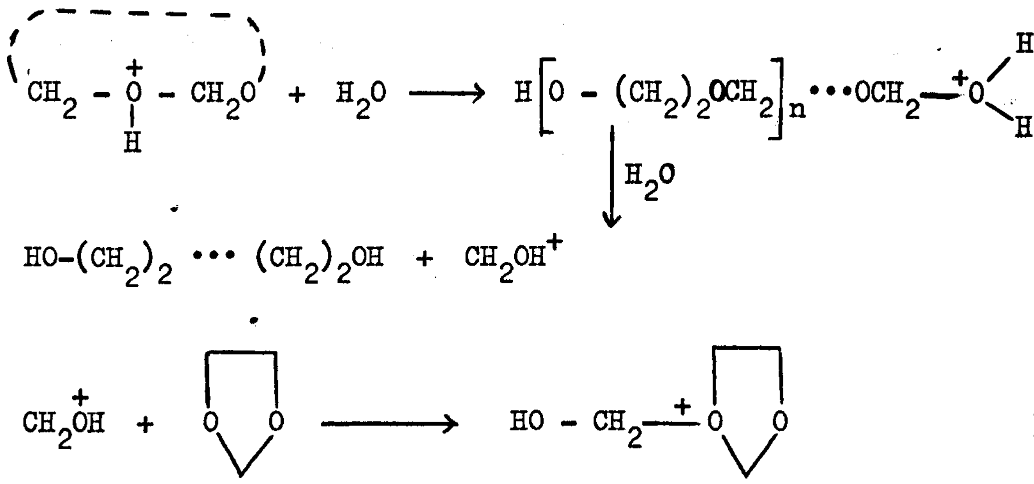
Schlotterbeck[3] found that in reaction mixtures initiated by $HClO_4$ the concentration of ethoxyl end-groups was higher than the initiator concentration. These results can now be explained in the light of our findings by the presence of residual water in the system.

Westermann's[5] results are not in agreement with the slow transformation of the secondary oxonium ions to tertiary oxonium ions which was reported by the Mainz group. He found that over a ten-fold variation of initiator concentration there was a linear relation between the first-order rate-constant and the perchloric acid concentration and the final conductivity of the polymer solution was dependent on the initial acid concentration. The repolymerisation followed the same way as the first polymerisation and the conductivity reached the same value as before. Also with perchloric acid initiation the low DP's observed for these polymers were considered to be due to excessive transfer in which the H^+ was mobile over all the oxygen atoms in the system.

Jones[6] found some tertiary oxonium ions in the reaction by the phenoxyl method. He also found that by far the greater part of the active species are secondary oxonium ions. The concentration of tertiary oxonium ions showed linear dependence on monomer concentrations. I think his monomer contained more impurity (especially water) than my monomer. I can say the same thing also for the solvent because a sodium film was used for final drying in our experiments.

I took 1,3-dioxolan for investigation because it is the smallest compound in this group and a highly purified product can easily be obtained. Therefore more experiments for determination of ion-type have been done with 1,3-dioxolan. The results show that it is highly probable that the very low concentration of tertiary oxonium ions merely reflects the impurity level of the system. This impurity mainly comes from the monomer. In Chapter

Three we showed that 1,3-dioxolan contains 10^{-4} M of an impurity which is probably water. Since the water addition experiments showed that tertiary oxonium ions were produced from water, it seems reasonable to suppose that without added water the tertiary ions are formed from the residual water. The effect of water could be explained by the following sequence of reactions:



5.5

5.6

5.7

According to the equation 5.6 every water molecule gives a linear fragment containing two -OH groups, one at each end. This reaction (5.6) produces a protonated formaldehyde which gives tertiary oxonium ions with 1,3-dioxolan and at least one more OH group. These equations explain why the polymers contain -OH groups if the reaction is killed with a wet killing reagent.

The determinations of ethanol in the volatile products showed that the concentration of secondary oxonium ions was less than expected. The most likely explanation is that ethanol was trapped in the polymer, so that the volatile products did not contain all the ethanol produced by proton abstraction.

Analagous experiments were carried out with 1,3-dioxepan and 4-methyl-1,3-dioxolan in order to generalize the mechanism of polymerisation to other 1,3-dioxacycloalkanes. These experiments also showed that the concentration of tertiary oxonium ions was very much less than the initiator concentration.

Therefore, in the light of these experimental results I concluded that the polymerisation of cyclic formals proceeds via a ring-expansion mechanism and that when $HClO_4$ is the initiator, the active centres are secondary oxonium ions. This means that the original theory of Plesch and Westermann is completely supported by the present findings.

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CHAPTER SIX

Polymerisation of substituted 1,3-dioxacycloalkanes

6.1 Introduction to Chapter Six.

There has been very little work on the polymerisation of substituted 1,3-dioxacycloalkanes. Especially after Dainton and Ivin[1] and Small's[2] papers most research workers have believed that 2-methyl and 4-methyl-1,3-dioxolan cannot be polymerised for thermodynamic reasons.

Dainton and Ivin have been able to calculate semi-empirically the standard free energy of polymerisation (ΔG^{o}_{1c}, liquid monomer-solid polymer) for several cyclo-alkanes and plotted this against the number of atoms in the ring. Three different curves were obtained for unsubstituted, methyl and 1,1-dimethyl substituted cyclo-alkanes at 25°. Small showed that these curves can be applied to oxygen- and nitrogen-containing heterocyclic compounds. According to these plots methyl and 1,1-dimethyl substituted five-membered rings give positive ΔG^{o}_{1c} at 25°C. Therefore these monomers cannot be polymerised to high polymers at 25° under standard conditions.

Okada,[3] in his first paper on the polymerisation of cyclic formals, stated that 2-methyl and 4-methyl-1,3-dioxolan gave no polymerisation.

Okada et al.[4] in a later paper reported only two experiments on the bulk polymerisation of 4-methyl-1,3-dioxolan with acetic anhydride-perchloric acid and acetyl chloride-zinc chloride mixtures at 0° and -15°. They reported only low yields and one low intrinsic viscosity result without any detail.

Yamashita et al.[5] carried out the bulk copolymerisation of 4-methyl-1,3-dioxolan and 3,3-bis(chloro methyl)oxacyclobutane with boron trifluoride etherate at 0°.

Duke[6] has described only one bulk polymerisation of 4-methyl-1,3-dioxolan with boron trifluoride. This experiment gave an orange coloured fairly mobile oil.

Weissermel et al.[7] carried out copolymerisation of 2-methyl-1,3-dioxolan and trioxan in cyclohexane with tin tetrachloride. They claimed that 2-methyl-1,3-dioxolan and trioxan eliminate acetaldehyde and formaldehyde groups to give 1,3-dioxolan-trioxan copolymers.

There is only one Patent[8] which claims the polymerisation of 2-methyl-1,3-dioxolan. According to this Patent polymerisations could be done in carbon tetrachloride or bulk with zinc halides.

Krummenacher and Elias[9] have been able to polymerise 4-phenyl-1,3-dioxolan with anhydrous perchloric acid in methylene dichloride under high vacuum. They estimated the bulk monomer ceiling temperature ca. $T_c = 20^{\circ}$ and claimed that the polymer was cyclic.

Okada et al.[10] carried out the polymerisation of 2-methyl-1,3-dioxepan in dichloroethane with triethyloxonium tetrafluoroborate and boron trifluoride etherate. They determined ΔH_{ss} and ΔS^{o}_{ss} and the standard ceiling temperature. They also attempted the polymerisation of 2,2-dimethyl-1,3-dioxepan but it produced only a crystalline cyclic dimer.

There are some works on the polymerisation of 6,8-dioxabicyclo-[3.2.1]octane, which can be regarded as a 2,4-disubstituted-1,3-dioxolan. These polymerisations were carried out by Kops,[11] Sumitomo et al.[12] and Steuck et al.[13] in methylene dichloride with PF_5 under high vacuum.

In the synthetic field of polymerisation of 1,6-anhydropyranoses, which have the same skeleton as 6,8-dioxabicyclo(3.2.1)-octane, there has been the pioneering work of Korshak et al.[14] which was followed by a series of extensive investigations by Schuerch et al.[15] and the recent study of Wollwage.[16]

The cis- and trans-7,9-dioxabicyclo[4.3.0]-nonane polymerisations will be explained in Chapter Seven.

This short review shows how unexplored the area of the polymerisation of substituted 1,3-dioxacycloalkanes is. There has been no intensive work in this area, especially on substituted cyclic formals, presumably because of the discouraging effect of Dainton and Ivin's papers, as mentioned earlier.

In Chapter Five we showed that the ring-expansion mechanism applied to 1,3-dioxolan and 1,3-dioxepan. In order to generalise our investigations of this topic we have chosen substituted 1,3-dioxolans, rather than larger rings, as they provided chemically new types of monomers.

The reviews on the thermodynamics of polymerisations are lacking in thermodynamic data for the equilibrium polymerisation of substituted 1,3-dioxacycloalkanes. Therefore another aim was to provide some data in this area.

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6.2 Thermodynamics of polymerisation of 4-methyl-1,3-dioxolan.

The exploratory bench experiments gave no polymer with acetic anhydride 70% perchloric acid mixture at 0° in bulk or in methylene dichloride.

The first batch of monomer was prepared by Clarke's[1] method. G.l.c. showed that an impurity was present in this monomer and this was not removed by fractional distillation. This monomer did not polymerise even under high vacuum conditions with anhydrous perchloric acid.

The second batch of monomer was prepared by Astle's[2] method and this batch was used for all the experiments without difficulty.

Most of the experiments were carried out in the vacuum-sealed test tubes. However, it is difficult to kill high molecular weight polymers since the killing reagents cannot diffuse through the solution because of the high viscosity of the polymers. Therefore, some of the polymerisations were carried out in the large-surface vacuum-sealed reaction vessels, shown in Fig. 6.1. A few experiments were carried out in the dilatometer fitted with platinum electrodes.

The polymerisations were begun by crushing a phial of anhydrous perchloric acid in methylene dichloride and stopped by adding 0.88 ammonium hydroxide. Some of the polymerisations were stopped by crushing a phial of anhydrous triethylamine or sodium ethoxide in ether. Methylene dichloride was used as solvent.

A series of polymerisation runs was made with various concentrations of monomer. Polymerisations were carried out with high monomer concentrations because of the low ceiling temperature of this monomer.

The depolymerisation of the polymers gave the monomer only. Twice the monomer was polymerised and then after the

<u>Table 6.1</u>

Data for the polymerisation of 3M 4-methyl-1,3-dioxolan.

Run No. Y	14	26B	16	17	15	32B	31B
$10^2[HClO_4]$/M	1.66	0.24	1.35	1.25	1.76	0.288	0.289
T/°C	-40	-50	-55	-64	-75	-50	-56
Yield/%	4	20	39	60	70	32	37
$[M]_e$/M	2.85	2.39	1.79	1.19	0.88	-	-
K/M^{-1}	0.253	0.362	0.510	0.792	1.084	-	-
ΔG^{ϕ}_{ss}/kJ mole^{-1}	2.65	1.86	1.21	0.4	0.12	-	-
DP	3.6	7.4	11.5	17.3	21.6		
k_1/sec^{-1}		43					35.5

Table 6.2

Data for the polymerisation of 5M and 7M 4-methyl-1,3-dioxolan.

Run No. Y	13	10	9	8	11	19	22	20	23B	30B	27	4	7B	25
$[\text{Monomer}]/M$	5	5	5	5	5	5	5	7	7	7	7	7	7	7
$10^2[HClO_4]/M$	1.58	1.24	1.60	1.88	1.65	1.75	0.418	1.12	1.73	1.32	2.49	2.05	2.16	1.79
T/°C	-20	-30	-40	-60	-60	-75	-75	-20	-30	-36	-40	-42	-60	-53
Yield/%	2	18	27	49	49	26	66	37	49	67	66	26.6	10	23.4
$[M]_e/M$	4.88	4.26	3.6	2.5	2.5	-	1.7	4.39	3.46	2.24	2.37	-	-	-
K/M^{-1}	0.152	0.203	0.253	0.375	0.375	-	0.564	0.211	0.27	0.426	0.404	-	-	-
ΔG^{ϕ}_{ss}/kJ mole^{-1}	3.94	3.2	2.65	1.73	1.73	-	0.94	3.26	2.63	1.67	1.75			
DP	3.9	7.3	11.3	16	16	29.1	24.3	14.2	15.5	22	22.9	21	7	8.2

Fig. 6.1

Reaction vessel of large surface area for the polymerisation of 4-methyl-1,3-dioxolan.

A Killing Reagent

B $HClO_4$ phial

Fig. 6.3

Plot of T_c against monomer concentrations.

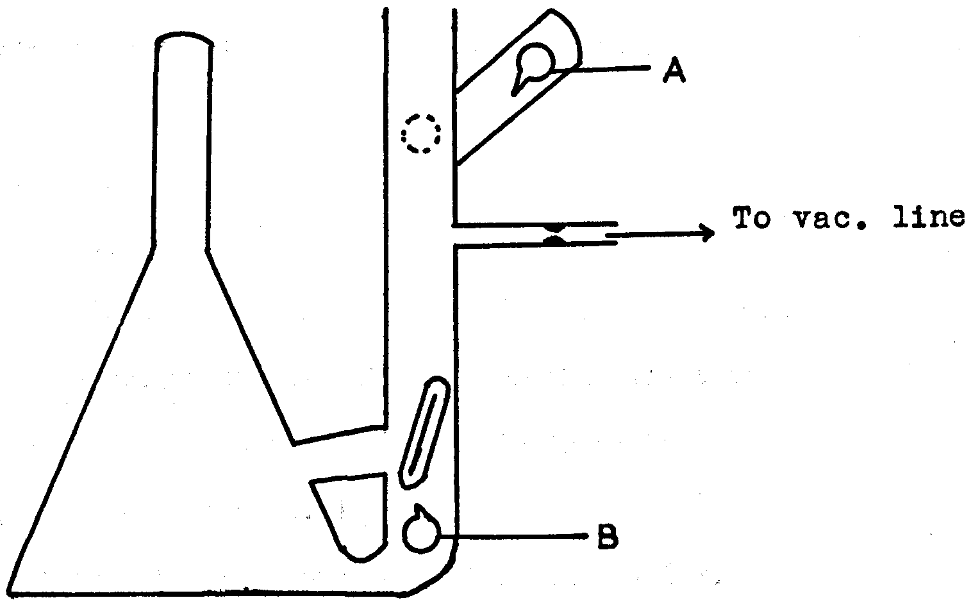


Fig. 6.1

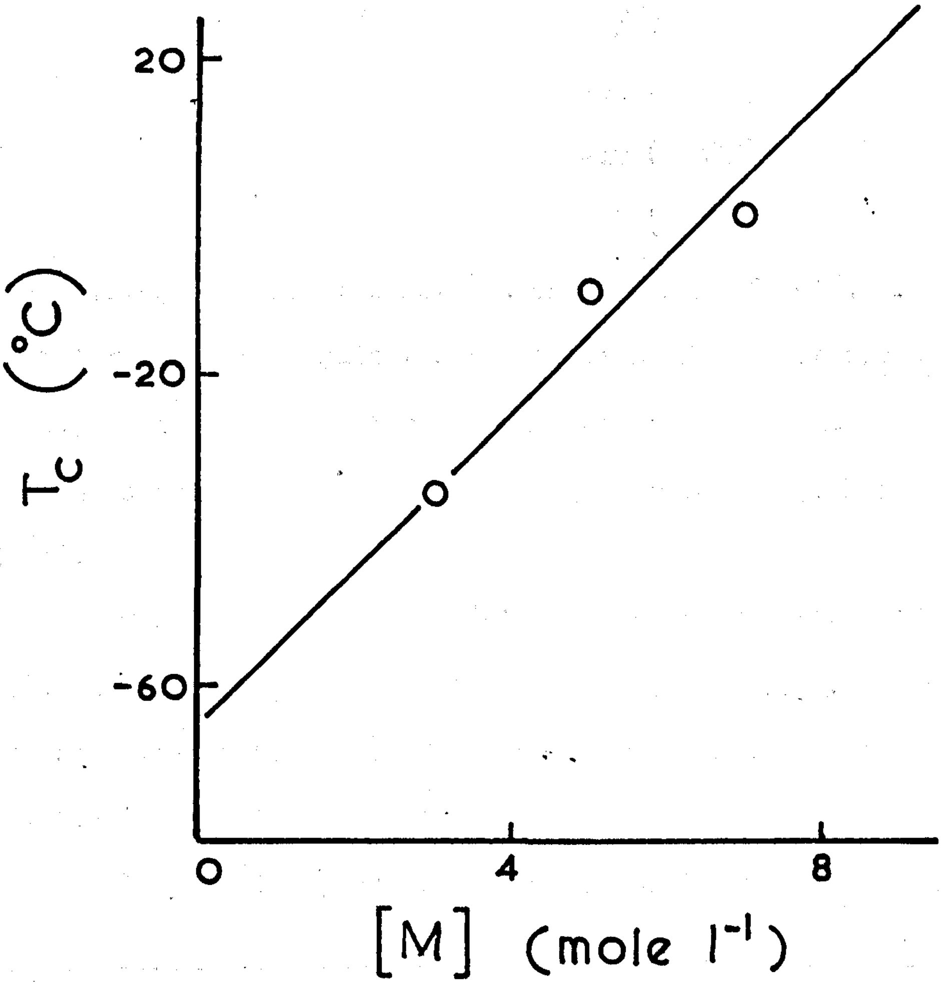


Fig. 6.3

temperature rose above the ceiling temperature, triethylamine and/or 0.88 ammonium hydroxide was added. This solution was injected into the g.l.c. which showed that only monomer and solvent were present.

The equilibrium monomer concentration was determined by subtracting the weight of the polymer from the weight of monomer.[3] The equilibrium constants were calculated by Tobolsky's[4] equation (equation 6.2).

All the results are shown in Tables 6.1 and 6.2.

Fig. 6.2 shows the DP plotted against temperature for the three different monomer concentrations. At DP = 1, the temperature corresponds to the ceiling temperatures. The ceiling temperatures were found to be:

$[\text{Monomer}]$/M	$T_c/^{\circ}C$
3	-35 (238°K)
5	-10 (263°K)
7	0 (273°K)

These ceiling temperatures have an uncertainty of 2-4°. The ceiling temperatures plotted against concentration of monomer are shown in Fig. 6.3. It is assumed for the sake of argument that the highest probable value of the standard ceiling temperature (1 M monomer) is -55° (218°K).

The equilibrium constants were plotted against 1/T (Fig. 6.10). As this graph is a van't Hoff plot, the slopes of the lines give the enthalpy (ΔH^{ϕ}_{ss}) of the polymerisation.* This will be discussed in the discussion section.

It was also possible to calculate the apparent standard free energy

---

* The superscript ϕ denotes that the quantity concerned has been calculated from the stoichiometric equilibrium constants K and not from thermodynamic equilibrium constants; they will be called "apparent standard".

Fig. 6.2

Plot of DP against T for three different monomer concentrations. DP = 1 gave Tc.

○	3M
△	5M
□	7M

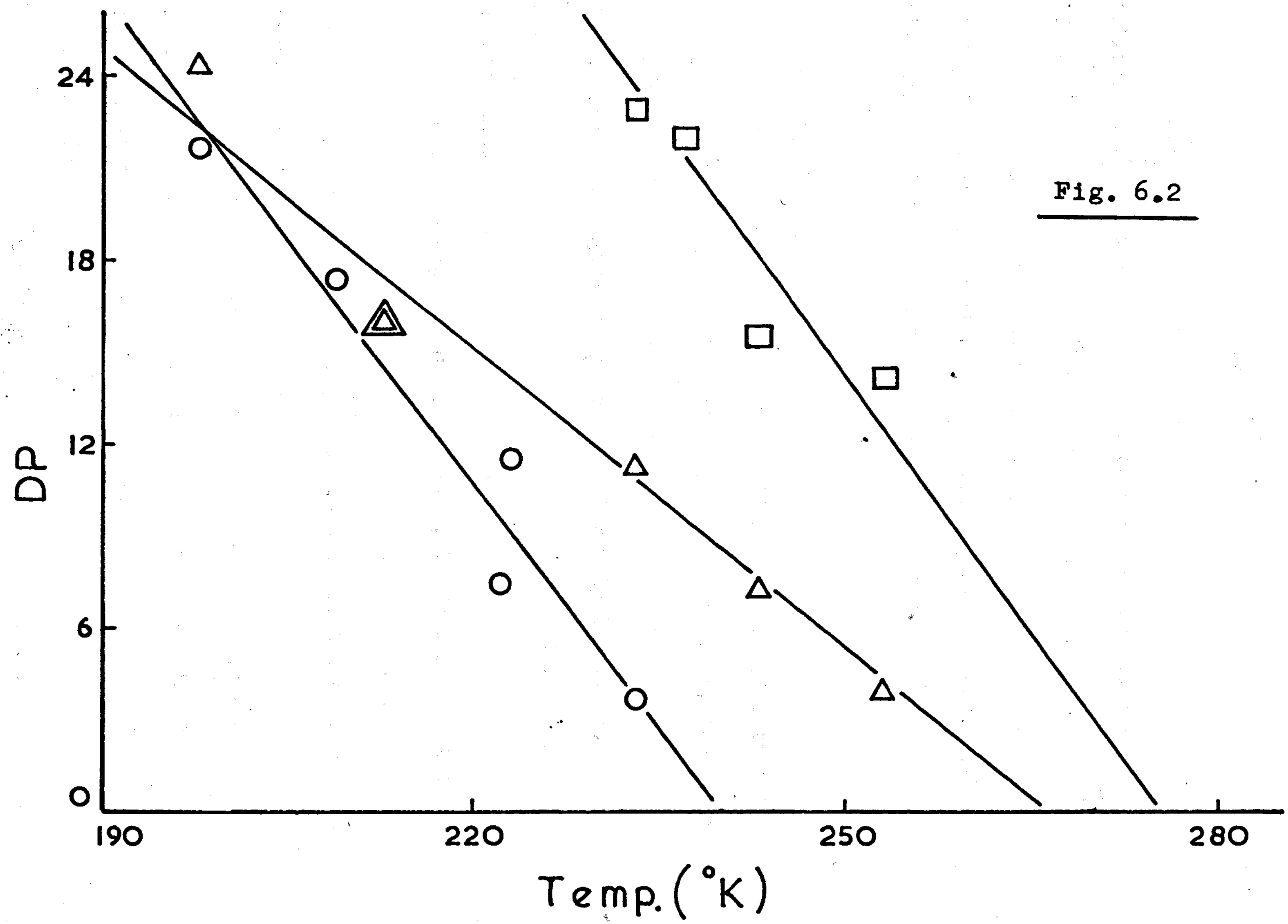


Fig. 6.2

changes of this reaction at various temperatures from the relation:

$$\Delta G^{\phi}_{ss} = -RT \ln K \qquad 6.1$$

This equation will be discussed in more detail in the discussion section. ΔG^{ϕ}_{ss} plotted against the temperature is shown in Fig. 6.11. From the slope ΔS^{ϕ}_{ss} can be determined.

The temperature at which $\Delta G^{o}_{ss} = 0$ gives the standard ceiling temperature but it cannot be determined from Fig. 6.11. This will be discussed in the discussion section.

6.3 Kinetics of polymerisation.

The reaction mixture of Run 10 was separated into two parts. The first part was killed after polymerisation, the second part was killed after successive polymerisations and depolymerisations. Both parts gave the same molecular weight polymer. Therefore, the active centres had not disappeared during the polymerisations and depolymerisations.

Only two experiments (Runs Y26B, Y32B) were carried out in the dilatometer for kinetic measurements. In Fig. 6.4 and 6.6 are shown conversion curves and in Fig. 6.5 and 6.7 the corresponding first-order plots.

The conductivity curves show fast protonation and the conversion curves show that the reaction proceeds without acceleration. Obviously these experiments would be seen much better in the adiabatic calorimeter.

One experiment was carried out in an n.m.r. tube. If the monomer-polymer peaks are well separated the thermodynamic constants can be determined and also the reaction may be followed

Fig. 6.4

Conversion and conductivity plots for polymerisations of 4-MeDIOX at -51°. Run Y26B.

Fig. 6.5

First-order plot of Run Y26B.

From the plot $k_1 = 43\ \mathrm{sec}^{-1}$.

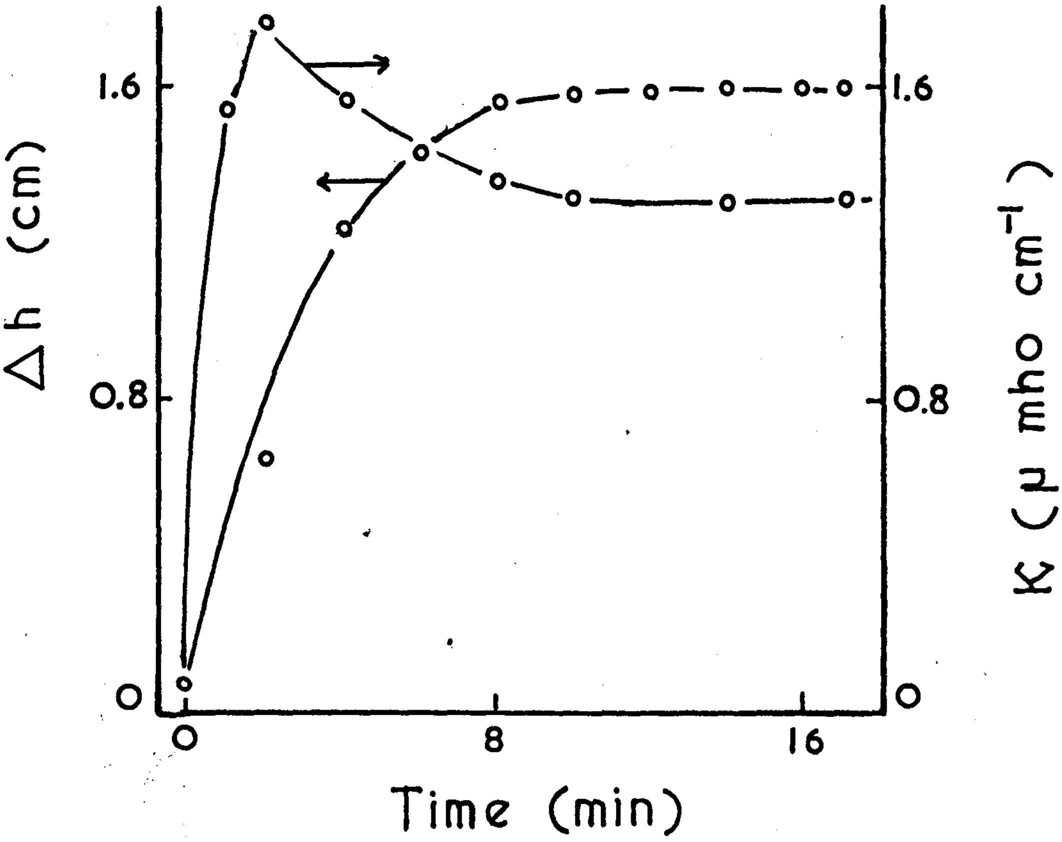

1.6
0.8
0
Δh (cm)
1.6
0.8
0
κ (μ mho cm^{-1})
0
8
16
Time (min)

Fig. 6.4

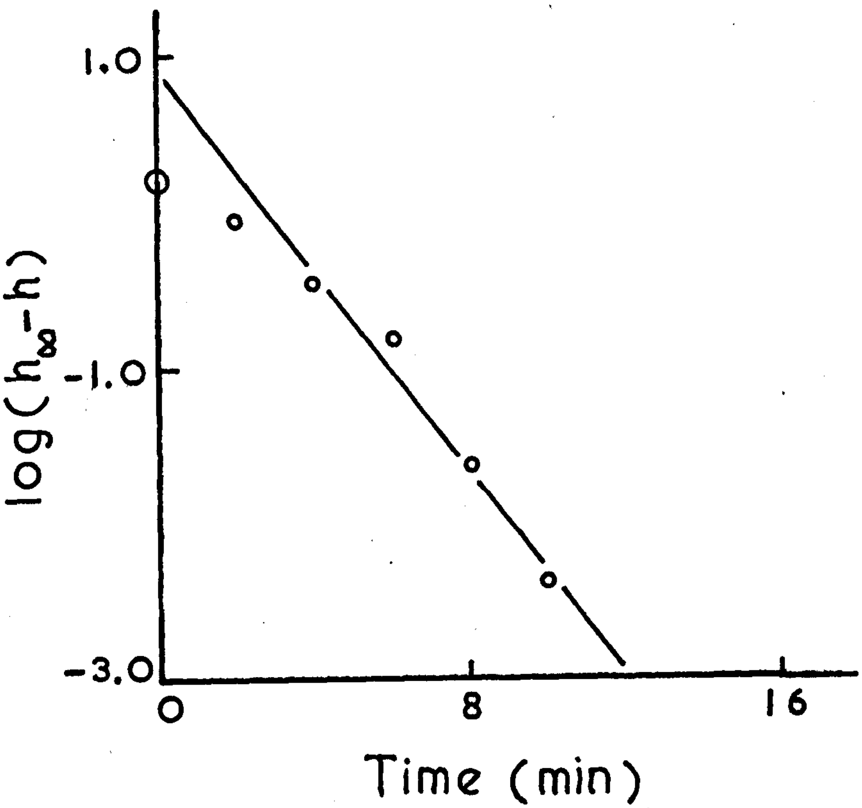

1.0
-1.0
-3.0
log(h_∞-h)
0
8
16
Time (min)

Fig. 6.5

Fig. 6.6

Conversion and conductivity plots for polymerisations of 4-MeDIOX at -56°. Run Y31B.

Fig. 6.7

First-order plot of Run Y31B.

From the plot $k_1 = 35.5\ \text{sec}^{-1}$.

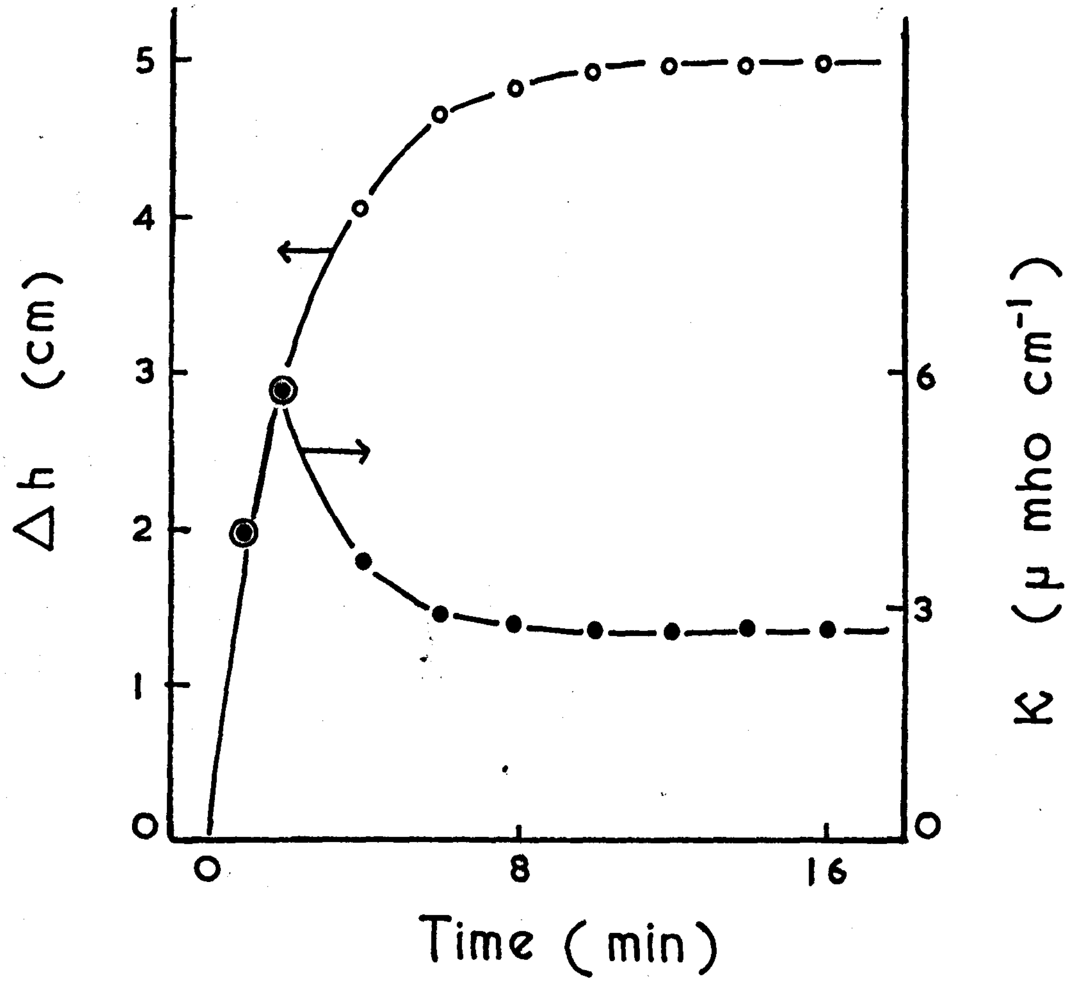

5
4
3
2
1
0
0
8
16
Time (min)
Δh (cm)
6
3
0
K (μ mho cm^{-1})

Fig. 6.6

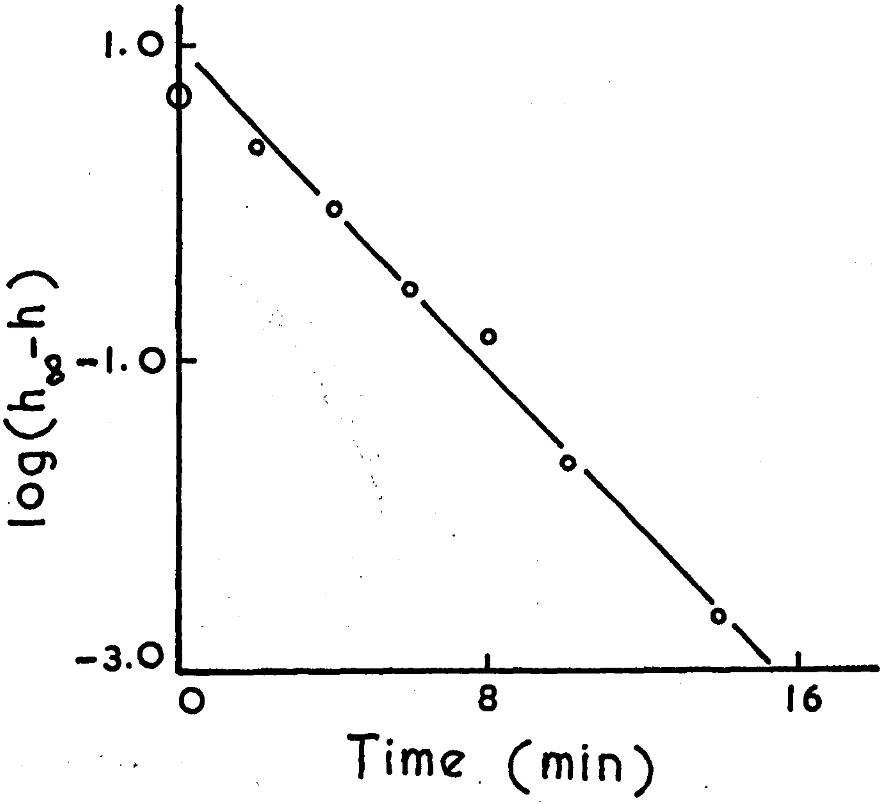

1.0
-1.0
-3.0
0
8
16
Time (min)
log(h$_∞$-h)

Fig. 6.7

by nmr. This experiment was carried out in an nmr probe at different temperatures and methylene dichloride was used as internal standard. Only a very small upfield shift was observed. Therefore, monomer and polymer peaks were not well separated. This experiment would be performed more efficiently with a 220 MHz nmr spectrometer.

6.4 Characteristics of the polymers obtained from 4-methyl-1,3-dioxolan.

The low molecular weight polymers are oily but high molecular weight polymers are rubbery solids. These polymers are soluble in acetone, dioxane, benzene, ethanol, etc. but are insoluble in water and only slightly soluble in hexane.

The low (DP = 7) and high (DP = 22) molecular weight polymers showed similar IR spectra. The spectra contain a very small OH peak at 3500 cm^{-1}. The following groups were shown to be absent:

Table 6.3

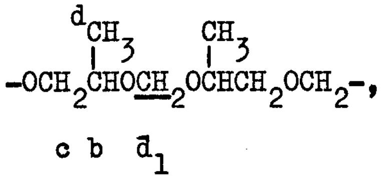
Vinyl ether	3105 - 3050 cm^{-1}
Carbonyl groups	1740 - 1720 cm^{-1}
Carbon-chlorine	750 - 700 cm^{-1}
Primary or secondary amine	3500 - 3300 cm^{-1}
Quarternary ammonium ion	3130 - 3030 cm^{-1}

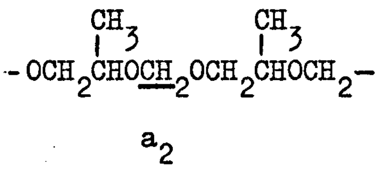
The nmr spectra of the polymers showed 4 peaks (Fig. 6.8). A triplet at 5.19 τ (a), a multiplet at 6.1 τ (b), a doublet at 6.5 τ (c) and a doublet at 8.7 τ (d). The integral ratio of the peaks was 2:1:2:3. Therefore, the structure of the polymer is as shown:

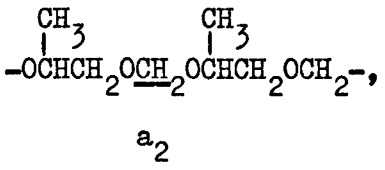
Table 6.4

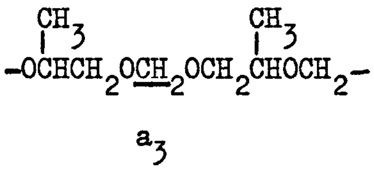
Data for the polymerisation of 2-methyl-1,3-dioxolan.

Run No. Y	34	38B	36	33	39	37	35
$[\text{2-MeDIOX}]$/M	5	7	7	7	7	7	7
$10^2[\text{HClO}_4]$/M	5	2.08	5.57	2.77	3.02	3.46	5.78
T/°C	-75	-50	-59	-75	-75	-75	-75
Time/h	24	26	30	39	24	0.75	26
Yield/%	0	4	9	1	4	2	44
DP	-	5	5.2	3.3	5.1	-	10.6


$-\mathrm{OCH_2}\overset{{}^{d}\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}\mathrm{O}\underline{\mathrm{CH_2}}\mathrm{O}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}\mathrm{CH_2OCH_2}-,$


$-\mathrm{OCH_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}\mathrm{O}\underline{\mathrm{CH_2}}\mathrm{OCH_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}\mathrm{OCH_2}-$


$-\mathrm{O}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}\mathrm{CH_2O}\underline{\mathrm{CH_2}}\mathrm{O}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}\mathrm{CH_2OCH_2}-,$


$-\mathrm{O}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}\mathrm{CH_2O}\underline{\mathrm{CH_2}}\mathrm{OCH_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}\mathrm{OCH_2}-$

(a) is split due to the different environments.

6.5 Polymerisation of 2-Methyl-1,3-Dioxolan.

Some of the polymerisations of 2-methyl-1,3-dioxolan were carried out in the vacuum-sealed tubes. The reactions were started by crushing a phial of anhydrous perchloric acid in methylene dichloride and were stopped by adding 0.88 ammonium hydroxide or by breaking a phial of anhydrous triethylamine.

All the results are shown in Table 6.4.

The polymerisations reached equilibrium after a long time. One hour later an initiator phial had been broken an unidentified white compound began to precipitate from the solution. Therefore Run Y37 was stopped just before the precipitate appeared but a very poor yield of polymer was isolated. The molecular weight of the polymer could not be determined because there was too little of it.

The reaction mixture of Run Y34 turned yellow-green one hour after an initiator phial had been broken and no polymer was isolated.

Fig. 6.8

NMR spectra of the poly-4-methyl-1,3-dioxolan.

A: DP = 7

B: DP = 21

Fig. 6.9

NMR spectrum of the poly-2-methyl-1,3-dioxolan.

Fig. 6.8

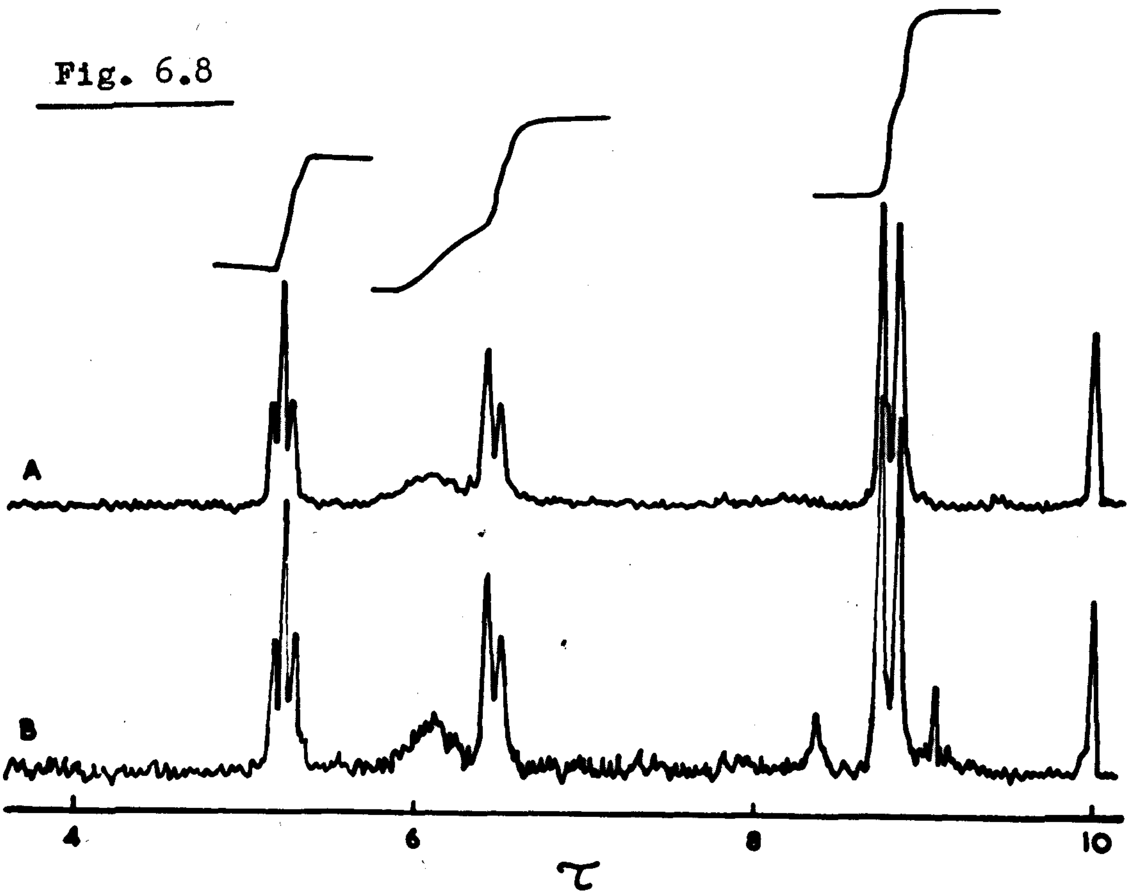
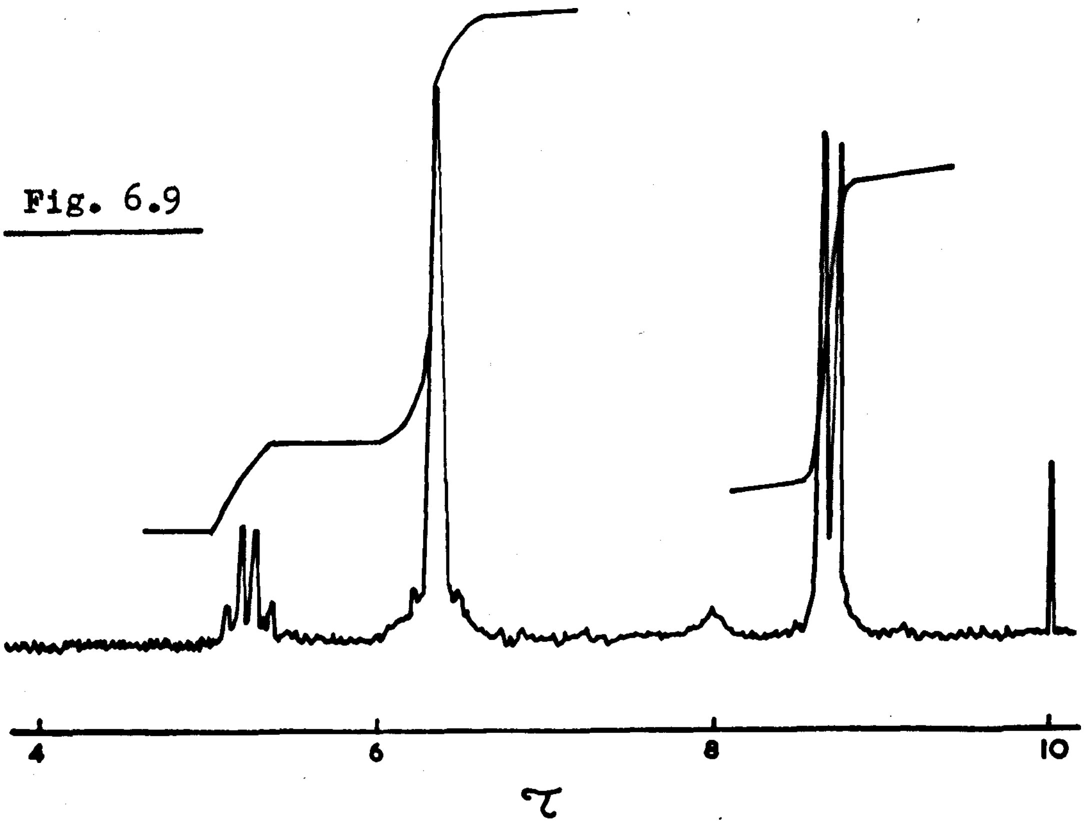


Fig. 6.9



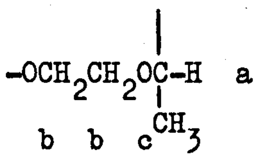
A high yield and relatively high molecular weight were obtained only in Run Y35, but this yield and molecular weight are still less than would have been expected for this monomer by analogy with 4-methyl-1,3-dioxolan. In my observation a high yield of polymers was obtained but these polymers were decomposed during the evacuation.

6.6 Characterisation of polymers obtained from 2-methyl-1,3-dioxolan.

Only viscous polymers were obtained of DP between 4 and 10.5.

The IR spectra of these polymers showed a very small OH peak at 3500 cm^{-1}. The end-groups which are listed in Table 6.3 were shown to be absent.

The nmr spectra of the polymers are very simple (Fig. 6.9). The spectra contain a quartet at 5.2τ (a), a singlet at 6.3τ (b) and a doublet at 8.6τ (c). The integrals ratios are 1:4:3. Therefore, these peaks correspond to H, CH_2 and CH_3 protons as shown:



$$\underset{b}{-OCH_2}\underset{b}{CH_2}O\underset{c\;CH_3}{\overset{|}{\underset{|}{C}}}-H \quad a$$

6.7 Discussion.

It has been believed for a long time that substituted 1,3-dioxolan and tetrahydrofuran cannot polymerise.[6,7] However, low-temperature polymerisations of 3-methyl tetrahydrofuran,[8] 4-phenyl-1,3-dioxolan[9] and 2-methyl tetrahydrofuran[10] have been reported recently. All the results were qualitative, the present study is the first giving detailed quantitative information on substituted 1,3-dioxacycloalkanes.

No polymerisation occurred in the open experiments or when the monomer contained impurity. If the monomer (4-methyl-1,3-dioxolan) was thoroughly purified, it gave a polymer with anhydrous perchloric acid.

The DP-temperature curves showed that the molecular weight of the polymers increased with decreasing temperature and increasing monomer concentration.

The equilibrium constants were calculated from the Tobolsky equation:

$$K = \frac{DP-1}{DP[M]_e} \qquad 6.2$$

In this equation the $[M]_e$ could be the equilibrium activity of the monomer, in which case the K would be the thermodynamic K. However, in our work we measured the equilibrium concentration of monomer, and so the K is the stoichiometric and not the thermodynamic equilibrium constant. It follows that the ΔG values calculated from our K values are <u>not</u> ΔG^{o}_{ss}, but "apparent" ΔG^{o}_{ss} which we will call ΔG^{ϕ}_{ss}; similarly, the ΔS and ΔH values derived from ΔG^{ϕ}_{ss} are ΔS^{ϕ}_{ss} and ΔH^{ϕ}_{ss}, i.e. "apparent" quantities, and not ΔH^{o}_{ss} and ΔS^{o}_{ss}.

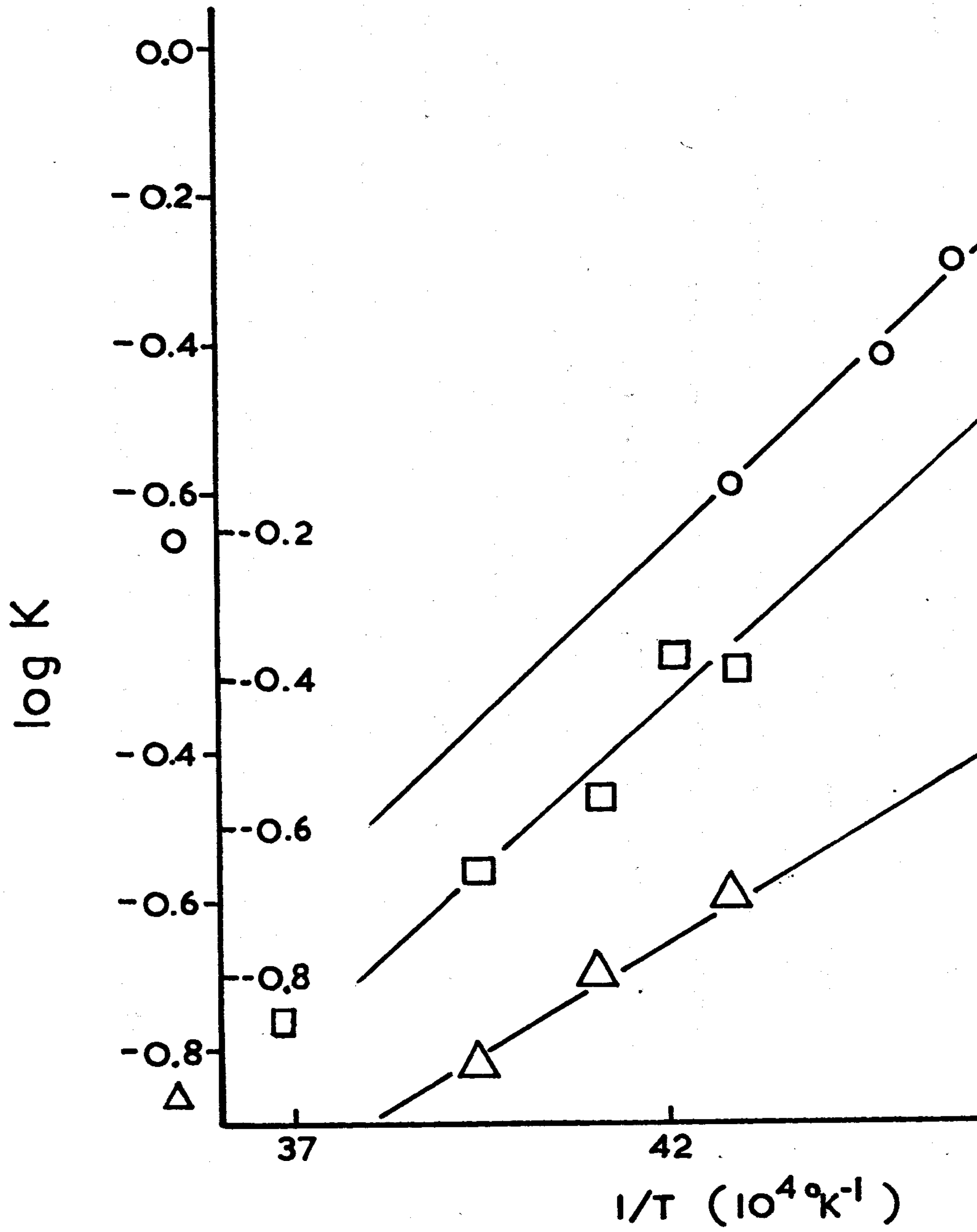
Log K plotted against 1/T is shown in Fig. 6.10. On the evidence we have got, the correct correlation is that these are curves. If we draw the best straight line the slope gives an average ΔH^{ϕ}_{ss}.

ΔG^{ϕ}_{ss} against temperature is shown in Fig. 6.11. From the slope ΔS^{ϕ}_{ss} is determined:

Fig. 6.10

Plot of log K against 1/T for three different monomer concentrations.

○	3M
△	5M
□	7M


0.0
-0.2
-0.4
-0.6
-0.2
-0.4
-0.4
-0.6
-0.6
-0.8
-0.8
log K
37
42
1/T (10⁴ °K⁻¹)

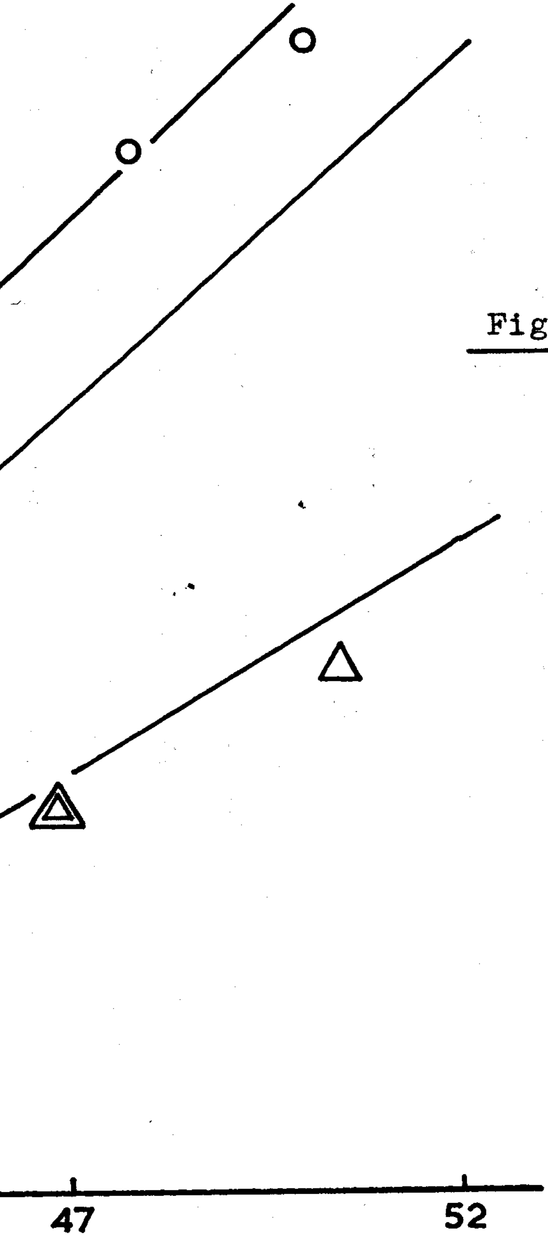


Fig. 6.10

$[\text{Monomer}]/\text{M}$	$-\Delta H^{\phi}_{ss}/\text{kJ mole}^{-1}$	$-\Delta S^{\phi}_{ss}/\text{J}^{o}\text{K}^{-1}\text{mole}^{-1}$
3	18.4	53.5
5	17.6	78.6
7	18.4	76.9

ΔH^{o}_{ss} and ΔS^{o}_{ss} can be calculated from the Dainton and Ivin formula: (Fig. 6.12).

$$\ln[M]_e = \frac{\Delta H}{RT} - \frac{\Delta S^o}{R} \qquad 6.3$$

However, this formula is valid only if the mixture of monomer and polymer behaves ideally over the range of compositions covered by the experiments and if the DP is so great that ΔH and ΔS do not depend upon it. In fact, we used very high monomer concentrations and these solutions were not ideal. Therefore, three different monomer concentrations gave three different lines for the ΔG^{ϕ}_{ss}. These lines cannot be due to experimental scattering, because some of the repeat runs gave similar results to those obtained before.

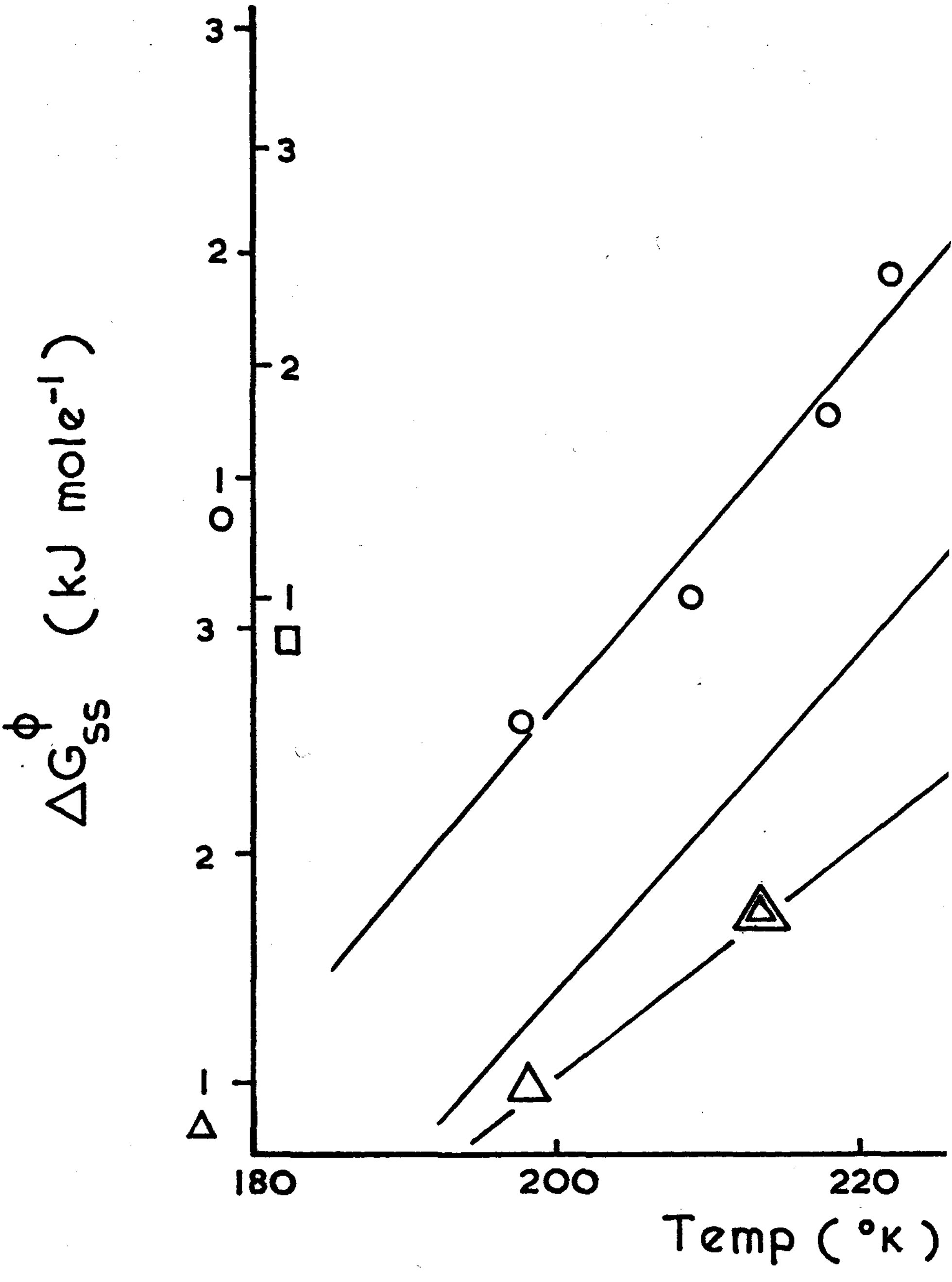
In the literature there is only one paper which concerns polymerisation in concentrated solutions.[11] But there is a formula given by Bywater[12] for the calculations of free energy. His formula contains the molar free energy of mixing of polymer and monomer with solvent, interaction parameters and volume fractions. It is obvious that we need these parameters and these parameters have been determined for very few polymers.

It is interesting to notice that although the ΔH^{ϕ}_{ss} for three different monomer concentrations are equal within the experimental error, the $-\Delta S^{\phi}_{ss}$ at high monomer concentration is greater than at low monomer concentration. This might be explained by the supposition that at high concentration the polymer has less freedom of

Fig. 6.11

Plot of ΔG^{ϕ}_{ss} against T for three different monomer concentrations.

○	3M
△	5M
□	7M



3
3
2
2
1
○
1
3
□
2
1
Δ
ΔG_ss^φ (kJ mole^-1)
180
200
220
Temp (°K)

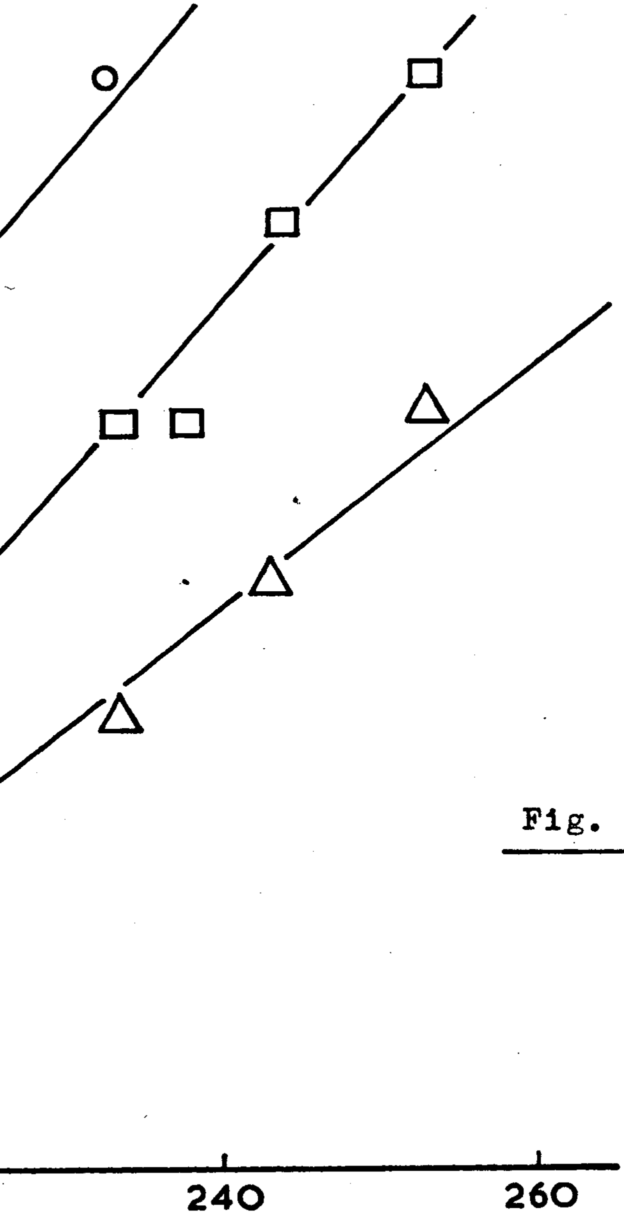


Fig. 6.11

Fig. 6.12

Plot of $\ln[M]_e$ against 1/T for three different monomer concentrations.

○	3M
△	5M
□	7M

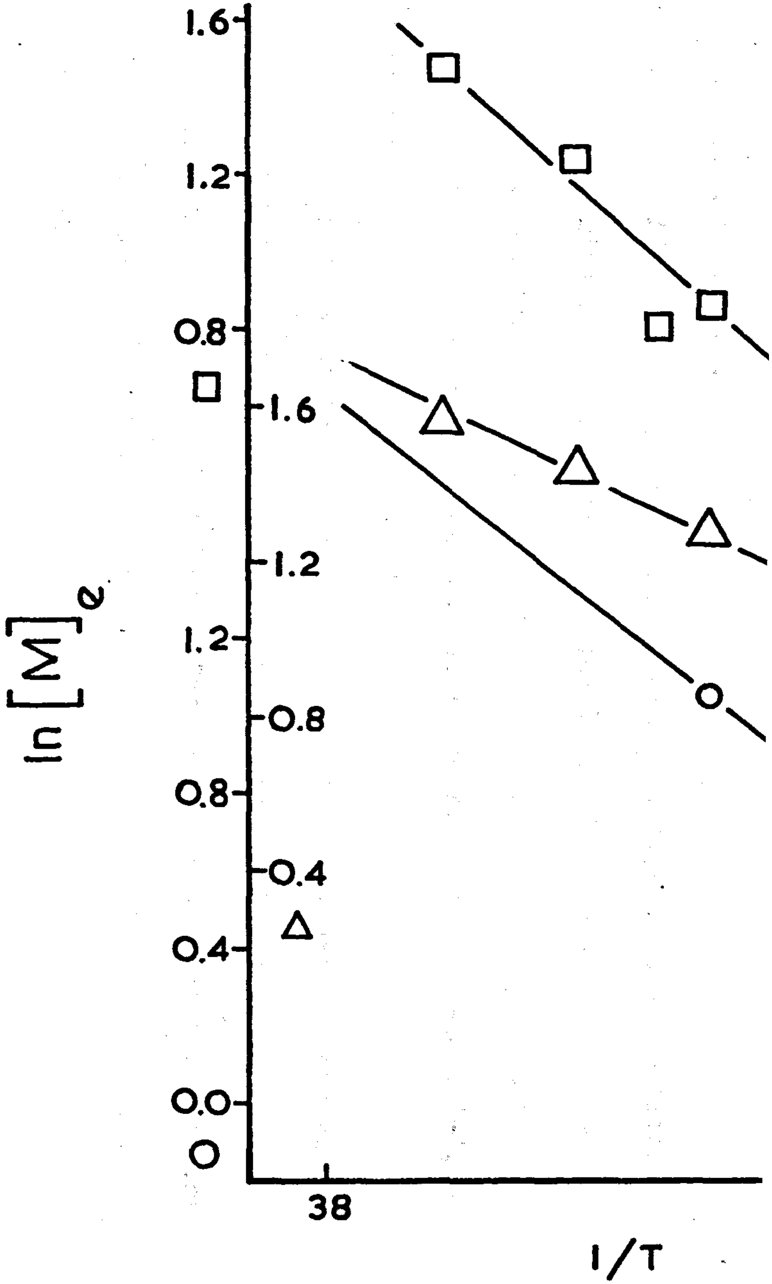
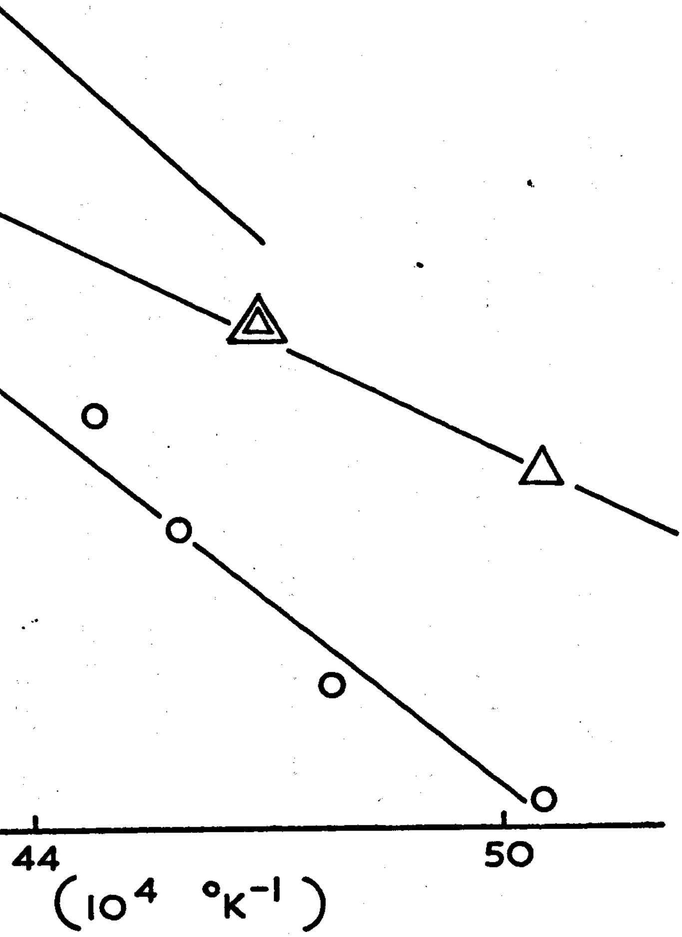

1.6
1.2
0.8
1.6
1.2
1.2
0.8
0.8
0.4
0.4
0.0
38
ln[M]e
1/T

Fig. 6.12



movement than at low monomer concentrations.

The two kinetic experiments showed that fast protonation occurred. k_2 was calculated for 4-methyl-1,3-dioxolan and compared with k_2 of 1,3-dioxolan and 1,3-dioxepan obtained by Westermann.[13]

	-51^o, k_2/l $mole^{-1}sec^{-1}$	-56^o, k_2/ $mole^{-1}sec^{-1}$
1,3-Dioxolan	4.9×10^3	3.9×10^3
1,3-Dioxepan	40.5×10^3	34.6×10^3
4-Methyl-1,3-dioxolan	17.6×10^3	12.3×10^3

Although we have only two results for 4-methyl-1,3-dioxolan, these indicate that this monomer gives a faster reaction than 1,3-dioxolan and slower than 1,3-dioxepan. A similar phenomenon was recently observed by Saegusa et al.[13] They showed that the introduction of methyl groups into the oxetane ring increased the rate.

Two tertiary oxonium ion determinations were given in Chapter Five. From these and IR and NMR spectra we concluded that 4-methyl-1,3-dioxolan gives cyclic polymers according to the ring-expansion mechanism.

After the polymerisation of 4-methyl-1,3-dioxolan we tried the polymerisation of 2-methyl-1,3-dioxolan. We have seen that 4-methyl-1,3-dioxolan can be polymerised, therefore there appears to be no thermodynamic reason against the polymerisation of 2-methyl-1,3-dioxolan.

Unfortunately, I was able to do only a few experiments with 2-methyl-1,3-dioxolan. This monomer polymerised after a long time and an unknown white precipitate was formed but this disappeared during the evacuation. Although a very high monomer concentration was used the highest polymer obtained had DP = 10.6.

Obviously this monomer needs more detailed work.

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CHAPTER SEVEN

Exploratory Experiments

This chapter contains an account of a few exploratory experiments related to the polymerisation of 1,3-dioxacycloalkanes.

7.1 The polymerisation of 1,3-Dioxolan by Trifluoromethane sulphonic acid.

All the results showed that anhydrous perchloric acid gave a 100% efficient reaction with 1,3-dioxolan.[1,2] This is a unique initiator and previously no initiator had been found that gave 100% efficiency for 1,3-dioxolan polymerisations. Therefore, we searched for other protonic initiators.

Trifluoromethane sulphonic acid is the strongest acid known and we tried to use this acid, especially as the $CF_3SO_3^-$ anion is a weaker nucleophile than the ClO_4^- anion.

This acid was first mentioned as an initiator for 1,3-dioxolan polymerisation by Enikolopyan,[3] but no details or even reaction curves were given.

Penczek et al.[4] carried out the copolymerisation of trioxan and 1,3-dioxolan with trifluoromethane sulphonic acid anhydride ($(CF_3SO_2)_2O$) in cyclohexane. In this paper, the polymerisation of 1,3-dioxolan was mentioned.

Mathias[5] suggested that this acid reacts with methylene dichloride as shown

$$CF_3SO_3H + CH_2Cl_2 \longrightarrow CF_3SO_3CH_2Cl + HCl$$

Table 7.1

Data for the polymerisation of 1,3-dioxolan by CF_3SO_3H.

Run No.	48	50	49	51
[Monomer]/M	1.4	1.8	2	2
10^3 [CF_3SO_3H]/M	6.9	5.5	3.12	4.96
T/°C	0	0	0	0
Time/h	1	0.5	0.5	24
Yield/%	28	22	5	7
Expected yield/%	35	46	48	48
DP	6.5	6.7	4.3	5.2

For this reason we attempted to use carbon tetrachloride as the solvent, but unfortunately the acid is only slightly soluble in carbon tetrachloride and gave a suspension. The two phases were separated by decanting and the carbon tetrachloride phase was used for the polymerisations.

The polymerisations were begun by crushing a phial of trifluoromethane sulphonic acid in carbon tetrachloride and stopped by adding 0.88 ammonium hydroxide. Methylene dichloride was used as a solvent.

All the results are shown in Table 7.1.

This initiator gave a low yield and the polymers formed were of low molecular weight.

The concentration of acid is possibly in error because of the suspension.

The nmr spectra of the polymers are similar to those obtained with perchloric acid. The IR spectra of these polymers showed a very big and broad OH peak at 3500 cm^{-1} and a small C=O peak at 1740 cm^{-1}.

These experiments should be carried out in another solvent.

7.2 Polymerisations of cis- and trans-7,9-Dioxabicyclo-[4.3.0]-nonane.

The cis- and trans- monomer preparations were explained in Chapter Two. These monomers are 4,5-disubstituted 1,3-dioxolans. They are potentially new monomers for generalising the ring-expansion mechanism.

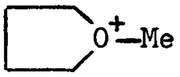
It is only recently that attention has been paid to the fact that the cis and trans forms of the monomer may behave quite differently. This was observed for cis- and trans-8-oxabicyclo-[4.3.0]-nonane by Kops et al.[6] We tried to apply the same idea to our monomers.

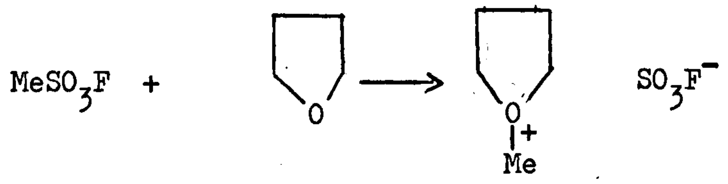
These monomers were distilled only with small columns, due to the small amounts available. Therefore, both monomers contained unidentified impurities.

The polymerisations were carried out in bulk and in solution by boron trifluoride etherate and 72% perchloric acid + acetic anhydride mixture at 0° and 25°. The monomers were kept in a reaction flask sealed with a rubber septum. The reactions were begun by adding the initiators with a syringe through the rubber septum, and were stopped by adding 0.88 ammonium hydroxide. The reaction mixtures were left for between 3 days and a week. Unfortunately most of the reactions gave no polymer and a few of them gave dimers only for both monomers.

These monomers are difficult to obtain, difficult to purify and difficult to handle under high vacuum, due to their high b.p. Therefore, these experiments were discontinued.

7.3 NMR studies of tertiary oxonium ions.

Methyl fluorosulphonate is an excellent alkylating agent; this was explained in Chapter Four. We tried to use this ester as a solvent like Olah's "Magic Acid",[7] because in view of the high "methyl pressure" it could be expected to methylate cyclic formals or ethers. For example,  has been prepared only as a salt. If it is prepared in the MeSO$_3$F by reaction 7.1



7.1

it might remain in solution, so that its spectroscopic and polarographic characteristics might be determined.

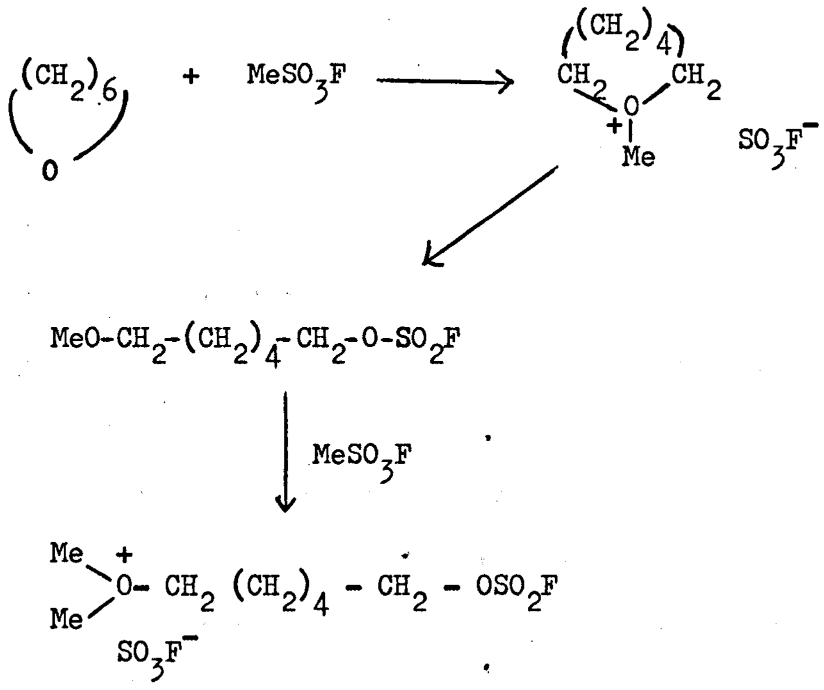
All the reactions were carried out in an nmr tube at 35°. 50% (vol/vol) solutions of the compounds in carbon tetrachloride were prepared and these were added drop by drop to the ester, while the ester was vigorously stirred with a magnetic stirrer. After the addition was finished nmr spectra were taken at regular time intervals. In all the experiments, TMS was used as internal standard. All the compounds (except 1,3-dioxolan, tetrahydrofuran and 1,3-dioxepan) were taken from the "Puriss" labelled bottles.

Diphenyl ether and hexamethyl 1,3-dioxolan gave no reaction.

Ethyl, n-butyl, iso-butyl and 2-chloroethyl vinyl ethers gave the typical colour changes of vinyl ethers in a strongly acidic medium but the nmr spectra were not fully interpreted.

Tetrahydrofuran, tetrahydropyran and 1,4-dioxan gave crystalline compounds. These compounds were not soluble in CCl_4 and the tetrahydrofuran spectrum was taken in $CDCl_3$. I did not find the multiplet at 5.28 τ but the other peaks were the same as given by Whiting et al.

Oxepan gave a triplet at 5.4 τ, a singlet at 5.8 τ, a triplet at 6.4 τ, a singlet at 6.7 τ and a broad doublet at 8.4 τ. The peaks at 6.4 τ and 8.4 τ are due to oxepan; possibly the following reaction has occurred:



Di-ethyl ether gave a methyl-ethyl exchange as given by Whiting et al.

1,3-Dioxolan gave five singlets after 75 min. The two singlets at 5.2 τ and 6.2 τ for 1,3-dioxolan and at 5.3 τ , 5.8 τ and 6.3 τ were due to polymerised 1,3-dioxolan.

Although most of the reactions with MeSO$_3$F gave colour changes, the reactions were not followed by nmr. One might expect that due to the influence of the positive charge on the oxygen, the α-CH$_2$ peaks would be shifted down-field. Our experiments showed that very little down-field shift occurred, and some compounds even gave an upfield shift.

The detailed interpretation of the spectra will require much further work.

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Further Suggestions

Although this Thesis cleared up some problems it opened the window to some new problems.

The salt effect on the 1,3-dioxepan polymerisation needs more detailed work.

t-BuClO$_4$ could be made in the reaction mixture by making isobutene and perchloric acid react in methylene dichloride and then adding monomer quickly.

Nitronium and nitrosonium salts gave tertiary oxonium ions which are different from those produced by alkylating tertiary oxonium ions. It needs more detailed study to understand their nature.

The kinetics of the polymerisation of 4-methyl-1,3-dioxolan have not been studied.

The thermodynamics of 4-phenyl, 4-chloromethyl and 2-methyl-1,3-dioxolan can be investigated.

A further aspect for study is the polymerisation of larger ring 1,3-dioxacycloalkanes. The information from these would help in the drawing of "new Dainton and Ivin" curves.