

Errata.

- p.12. Line 8. for "isobutylene" read "isobutyl".
- p.16. Line 8. "substituted tetrahydrofurans fail to polymerise".
- p.19. Line 8. for "as" read "is".
- p.27. Line 7. for "give" read "gives".
- p.28. Line 9. for "latter" read "later".
- p.32. Line 19. for "compund" read "compounds".
- p.36. Bottom delete "Degree of Polymerisation".
- p.39. Line 12. for "protanic acids" read "protonic acids".
- p.40. Line 3. for "Thomos" read "Thomas".
- p.40. last line but one. for "in" read "is".
- p.44. Line 7. for "alkyds" read "alkyls".
- p.64. Line 15. for "separzation" read "separation".
- p.66. Line 11. for "method" read "methods".
- p.68. Line 10. for "depheyl" read "diphenyl".
- p.84. Line 6. for "Ven" read "even".
- p.84. Line 13. omit "definitely".
- p.102. Line 16. read " $8-10^{\circ}\text{C.}$ ".
- p.105. Line 6. α -methyl.
- p.106. Line 9. for "carbonylic" read "carboxylic".
- p.109. 2nd line from bottom for "quanlitative" read "qualitative".
- p.119. Line 8. for "toulene" read "toluene".
- p.123. Line 4. for "11500 atm" read "11,300 atm".
- p.123. Line 8. for "0.5" read "8.3".
- p.169. Last line omit comma after "catalyst" and insert "these".
- p.172. Line 13. after "significant" insert "and".

THE POLYMERISATION OF CYCLIC ETHERS AT
HIGH PRESSURES.

A Thesis Submitted for the
DEGREE OF DOCTOR OF PHILOSOPHY
in Chemical Technology
in the Faculty of Science
of London University

by

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ABSTRACT.

The effect of pressure on the free radical and ionic polymerisation of seven cyclic ethers has been studied up to 12,500 atm. Benzoyl peroxide was most frequently used as the free radical initiator. Boron trifluoride diethyl etherate was used as the ionic initiator for the polymerisation of tetrahydrofuran, 3,3'-bis (chloromethyl)-oxacyclobutane and 1,3,5-trioxane; and a complex of ferric chloride with propylene oxide or styrene oxide for the ionic polymerisation of propylene oxide and styrene oxide, respectively.

The polymerisations of propylene oxide, tetrahydrofuran, cyclohexene oxide and 1,2-epoxy-4-vinyl-cyclohexane, were studied in most detail, and only brief investigations of the polymerisation of 3,3'-bis-(chloromethyl) oxacyclobutane, 1,3,5-trioxane and styrene oxide were made.

Tetrahydrofuran could not be polymerised at 1 atmosphere (60°C.) in the presence of boron trifluoride diethyl etherate, but at higher pressures this substance is an effective initiator and the polymerisation was studied up to 5400 atm. (60°C.).

In an effort to clarify the pressure-dependence of the rate of this polymerisation the effect of pressure

on the conductivity of $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ in di-iso-propyl ether was investigated. Wherever possible the overall reaction rate was determined as a function of pressure, and its dependence on the initiator concentration was examined.

Polymers ranging from syrups to tough, high molecular weight solids have been obtained in this work, depending on the structure of the monomer and the conditions employed, and molecular weights were determined where possible.

The results are considered in relation to possible reaction mechanisms, and are compared with existing data for vinyl addition polymerisations at high pressures.

ACKNOWLEDGEMENTS.

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This work is dedicated to my parents and
to my wife.

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SECTION I.

INTRODUCTION.

I. 1. The Objects of this Research.

Some classes of cyclic compounds form polymers by a process of ring opening and successive monomer additions. The cyclic ethers, such as ethylene oxide for example, may be polymerised by the addition of small amounts of substances capable of cleaving the ring with formation of a hydroxyl group. They are sometimes termed "step addition" compounds. However, ring opening polymerisations may be catalysed by reagents which typically polymerise vinyl monomers. Most of these are of the cationic and anionic type. Only a few free-radical polymerisations have been reported and they have not been well investigated. Moreover no information is available on the rate of polymerisation (ionic or free radical) at high pressure.

The main purpose of this research was to study the effect of pressure on the rates of polymerisation of a number of types of cyclic ether and the nature of the polymers formed.

The effect of pressure on reactions is of considerable interest in the industrial field and has proved in some cases to be a reliable method of differentiating

between possible mechanisms and of elucidating the course of reaction at one atmosphere. Pressure appears to be as significant a variable as temperature in chemical reactions and with the development of new types of high pressure apparatus, it is now possible to investigate the effect of pressure on chemical reactions even up to 100,000 atm.

Generally such high pressures are not necessary, and studies at 1,000 atm. or even below, can yield much additional information about chemical reactions, although somewhat higher pressures are sometimes required, for example in polymerisation reactions. Over 30 years ago Conant et al. [1,2,3] and Starkweather [4] showed that some substances which failed to polymerise or gave only small amounts of polymer at ordinary pressure, gave substantial yields of polymer when subjected to pressures from 3,000 to 12,000 atm.

In the present work on cyclic ether polymerisation, pressures ranging from 1 atm. to 12,000 atm. have been used depending on the particular monomer and the catalyst employed.

I. 2. Historical Review.

Most of the previous work on the polymerisation of cyclic ethers has been carried out at atmospheric pressure and with few exceptions the polymerisation reactions were catalysed by ionic initiators.

(1) Polymerisation at High Pressure.

In 1932 Conant and Peterson [3] observed that certain aliphatic aldehydes can be polymerised at room temperature by the application of high pressures (3,000 - 18,000 atm.). They believed that peroxide catalysts were essential to the polymerisation and that the effect of pressure was to accelerate the reaction rate. They obtained hard solid polymers of aldehydes and of cyclohexene oxide, using 2-5% benzoyl peroxide as initiator, at 12,000 atm. Cyclohexene oxide polymer was found to be stable at room temperature.

In other work [5,6] under slight pressure (5-18 atm), with potassium hydroxide, sodium methoxide or sodium ethoxide as catalyst, at 100-200°C., propylene oxide has been polymerised and the molecular weight found to be 1000-1500.

Apart from the above sparse information, no work seems to have been done on the radical and non-radical polymerisation of cyclic ethers at high pressure.

Most of the existing high pressure studies refer to the radical polymerisation of vinyl and related compounds and very little information is available for ionic reactions.

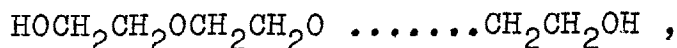
Recently Kilroe and Weale [7] found that the polymerisation of α -methyl styrene catalysed by trichloroacetic acid is accelerated by an increase in pressure to much the same extent as the free radical polymerisation of the monomer. The ionic polymerisations of isobutylene vinyl ether [8] and isopentyl vinyl ether [9] are also accelerated to a comparable degree.

(2) The Polymerisation of Some Cyclic Ethers at 1 atm.

(i) Propylene Oxide.

Ethylene oxide and mono-substituted ethylene oxides such as propylene oxide can be polymerised, and in recent years there has been much interest shown in this field.

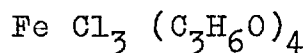
Ethylene oxide is the simplest member of the epoxide family and can be polymerised in the presence of small amounts of water to form poly-oxyethylene glycols :



which was also formed by heating the monomer with an alcohol or glycol. These reactions are slow but are accelerated in the presence of alkaline or acidic catalysts. Recently, detailed investigations have been carried out by Gee et al.

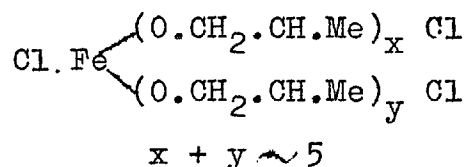
[10,11] with sodium hydroxide and sodium alkoxide catalysts. Polymerisation is usually slow and is considered to be an anionic chain reaction. The mechanism of the more rapid acid-catalysed reactions has been the subject of controversy[12]

Propylene oxide can be polymerised to give crystalline polymer and in recent years very much interest has been shown in this field of work. Pruitt, Baggett and co-workers [13,14] disclosed that certain catalysts can polymerise racemic propylene oxide to give crystalline polymer. These catalysts are complex ferric salts such as ferric chloride hexahydrate, basic ferric chloride, and the condensation product of ferric chloride with propylene oxide. The latter complex is perhaps the most effective. Ferric chloride reacts rapidly with propylene oxide at room temperature giving a product which approximates to [15] :



Gee and co-workers [15] used this catalyst in a study of the kinetics of polymerisation of propylene oxide and ethylene oxide at 91.6°C. Price [16] observed that propylene oxide can be polymerised with ferric chloride to give a partially crystalline product and the reaction has two clearly defined stages. The first stage occurs at or below room temperature and the product of the reaction

appears to have the following structure [16,17] :



Apparently no further reaction takes place until mixture of this product and monomer are heated in the range 70 - 100°C[15].

In the mechanisms so far proposed for these polymerisation reactions, it is considered that the iron is probably bonded to oxygen, and that the incoming monomer enters the polymer by breaking and reforming this bond [16, 18,40]. Propylene oxide can also be polymerised at room temperature in the presence of solid KOH. Price and Osgan [16] observed that l-propylene oxide on polymerisation with KOH gives a low molecular weight optically-active crystalline polymer, while the polymer obtained from racemic monomer under similar conditions was liquid. They suggested a mechanism in which polymerisation of l-propylene oxide proceeds so as to retain the original configuration of the asymmetric centre.

(ii) Tetrahydrofuran.

In 1939 Meerwein and co-workers [19] prepared a series of tertiary oxonium salts and applied them to the polymerisation of tetrahydrofuran. Oxonium

salts, of the general formula $R_3O^+ \dots MX_n^-$, were prepared from the corresponding metal halide in a reaction with an epoxide (preferably epichlorohydrin) in ether solution. They proposed a reaction mechanism and suggested that in the series of halides only etherates of BF_3 , $SbCl_3$, $FeCl_3$ and $AlCl_3$ react in this way. The BF_3 and $SbCl_5$ derivatives were found [20] to be more effective than the ferric and aluminium compounds, but all produce polymer at moderate temperatures (-10 to $+48^\circ C$) and at low catalyst concentration (0.1 to 2 mole percent of the monomer). The proposed mechanism involves propagation through an oxonium ion and termination by reaction with the cation.

Subsequently, a wide variety of catalysts has been used for the polymerisation of tetrahydrofuran to a linear polyether. Meerwein et al. [19] have developed the use of BF_3 and $AlCl_3$ and other Lewis acids in combination with epoxides. Further, it has been suggested [21,22] that both $SbCl_5$ and PCl_5 alone can initiate polymerisation. Hachihama and Shono [23] used a mixture of perchloric acid and acetic anhydride, and more recently, Bawn et al. [24] used triphenylmethyl hexachloroantimonate ($Ph_3C^+SbCl_6^-$) and claimed it to be a more effective catalyst. The maximum molecular weight obtained by Meerwein was about 8,000 but

in more recent work [22,23] values of about 329,000 and 25,000 are reported. In only one investigation [23] were studies of the effect of catalyst concentration on the rate of conversion and the polymer molecular weight undertaken.

Although both tetrahydrofuran and the five-membered ring dioxolane [25] polymerise cationically to high molecular weight polymers at room temperature or below, according to German workers [20], the substituted tetrahydrofuran fails to polymerise.

Boron trifluoride is reported not to catalyse the polymerisation of tetrahydrofuran [26]. However, boron trifluoride does catalyse the copolymerisation of tetrahydrofuran and ethylene oxide in 1,2 dichloroethane at 0°C., with ethylene glycol as co-catalyst.

(iii) 3,3-bis-(Chloromethyl)-Oxacyclobutane.

No work seems to have been done on the radical polymerisation of oxacyclobutane and 3,3,-bis-(chloromethyl)-oxacyclobutane. However, 3,3-bis-(chloromethyl)-oxacyclobutane was cationically polymerised by Farthing and Reynold [27] in the presence of BF_3 or its complexes.

In 1955 Farthing reported [28] that oxacyclobutane can readily be polymerised cationically to a linear polymer

of high molecular weight, and Rose [29] carried out an investigation of the effect of temperature on the polymerisation. There are now many references to the polymerisation of this monomer but little attention has been given to reaction mechanism. In one investigation kinetics, together with heats of polymerisation, have been reported [29]. In this work BF_3 or its etherate were used as catalysts, and the reaction is highly exothermic, and sometimes proceeds with violence. The heat of polymerisation of oxacyclobutane and 3,3,-dimethyloxacyclobutane have been determined [29] as 19.3 kcal/mole and 16.1 kcal./mole, respectively, in a mixture of ethyl and methyl chlorides at -9°C .

More recently Penczek and Penczek [71] carried out a detailed study of the kinetics and mechanism of the heterogeneous polymerisation of 3,3-bis-(chloromethyl)-oxacyclobutane catalysed with gaseous boron trifluoride in methylenedichloride (-60° to $+20^\circ\text{C}$.). They observed that the molecular weights are independent of conversion, that the kinetics are first order with respect to monomer, catalyst and co-catalyst for $\text{H}_2\text{O}/\text{BF}_3$ ratios < 0.5 ., and that the degree of polymerisation is directly proportional to monomer concentration, inversely proportional to water concentration and does not depend on catalyst concentration.

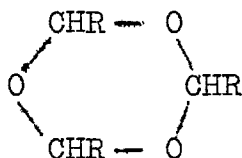
According to Farthing [28], water is an essential co-catalyst. BF_3 failed to polymerise 3,3-bis-(chloromethyl)-oxacyclobutane in a carefully dried system, but the polymerisation started on addition of water. The solvents used were methylene dichloride, benzene and diethyl ether, and the molecular weights of polymers obtained under similar conditions were found to be approximately the same. However, no attempt was made to correlate rates of reaction with the nature of the solvent.

The bulk polymerisation [30] of 3,3-bis-(chloromethyl)-oxacyclobutane has been carried out at 200°C . in the presence of AlEt_3 catalyst. Polymers of very high molecular weight were obtained, but low molecular weight polymer was formed at lower temperatures ($90\text{--}125^\circ\text{C}$.) with the same catalyst [31]. Most of the work on oxacyclobutanes has been concentrated on the polymerisation of this monomer [28,32].

The polymers obtained are insoluble in all the usual organic solvents and in more powerful solvents such as dimethylformamide, formic acid and m-cresol. They have high melting points (180°C .) and are tough, and can be formed into fibres and films.

(iv) Trioxane.

Polymers of formaldehyde were described by Staudinger [33] in one of the earliest systematic accounts of high polymers. Many aldehydes form cyclic trimers of the following general formula :



where $R = \text{H}, \text{CH}_3$ or CHCl_2

and trioxane as the trimer of formaldehyde.

Trioxane can be polymerised to a linear high molecular weight polymer in the presence of ionic catalysts. These include inorganic fluorides such as AlF_3 , SbF_5 , TiF_4 , in the absence of water [34], and boron trifluoride-di-butyl etherate [35], in dioxane as solvent.

The liquid phase polymerisation of trioxane proceeds very rapidly in the presence of cationic catalysts such as boron fluoride. A kinetic investigation [36] of this polymerisation has been carried out and no co-catalyst is required.

Recently the kinetics of cationic polymerisation of trioxane in the solid state, with the monomer crystals suspended in n-hexane containing boron trifluoride diethyl ether, have been studied [37].

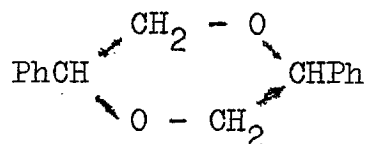
The unsubstituted 6-membered ring cyclic ethers, such as tetrahydropyran and dioxane, appear never to have been polymerised. No attempt appears to have been made to polymerise cyclic ethers containing one oxygen atom and more than six atoms in the ring.

(v) Styrene Oxide.

Most of the available information on the polymerisation of styrene oxide appears in recent patent literature. Styrene oxide can be polymerised [38] in solution (pentane) at -29°C , by BF_3 to give a viscous oil and some semi-solid polymer having molecular weights of 400-700. Another patent [39] reports that styrene oxide has been polymerised at 80°C . to a crystalline resinous homopolymer with a molecular weight of about 3000. The ferric chloride-styrene oxide complex was used as catalyst.

Gee and Colclough [40] studied catalysis by inorganic halides, and polymer was produced by AlCl_3 , SbCl_3 , BeCl_2 , SnCl_4 , TiCl_4 and ZnCl_2 .

The product included a very low yield of crystalline material ($>10\%$), melting sharply at 152°C , which is believed to be the dimer, and to have the structure:



After removal of dimer the polymer was highly viscous at room temperature, and of low molecular weight.

Dainton et al. [41] polymerised styrene oxide with BF_3 -diethyl ether as catalyst. No work seems to have been done on the kinetics of polymerisation.

(vi) 1,2 - Epoxy-4-Vinylcyclohexane.

Very little information is available on the polymerisation of 1,2-epoxy-4-vinylcyclohexane or related compounds. Vinyl-cyclohexane-3,4 epoxide has been polymerised [43] by breaking the epoxy linkage with HClO_4 and also by free radical attack on the vinyl group. Copolymers with vinyl acetate have been obtained [44] and another patent [45] reports the preparation of linear and cross-linked polymers.

In 1960, Baily and France reported [42] the relative rates of copolymerisation of ethylene oxide and of styrene oxide with 4-vinylcyclohexane monoxide and with propylene oxide. Zinc carbonate, calcium glyoxide, calcium amide and dibutyl zinc were used as catalysts. They observed that the primary effect in the co-polymerisation was not a wide range in the monomer selectivity, but rather a strong dependence of overall rate of reaction on the monomer structure. This trend in reactivity is summarised below:

I.3 (1) Theories of the Effect of Pressure on Liquid-Phase Reactions.

Various theories have been put forward to explain the effects of pressure on chemical reaction rates in the liquid phase. At first it was generally assumed that the effect of pressure on reaction rates was due to changes in concentration and ionisation caused by the compression of the liquid. But later it was seen that the above factors were not a sufficient explanation for the extent of the pressure effects.

However, the effect of pressure on reaction rates does in a few cases correspond to changes in viscosity [46]. The increase in viscosity under pressure is of particular interest in polymerisation, for reactions between very large molecules can become diffusion-controlled.

The suggestion has been made [47] that high pressures may alter the structure of the molecules and change the chemical activity. This seems unlikely to occur below 10^6 atm. except in the case of some metallic elements [48]. There is reason to believe that these very high pressures will cause the spontaneous breaking of covalent bonds [49] and in this way bring about extremely fast reactions, but the pressures required to do this have not yet been reached

under static conditions.

In the range at present attainable, the influence of pressure is greatest when one or more reactants is a gas, since compression then produces large changes in the concentration of this component. On the other hand, liquids, which are less compressible, require pressures of the order of 10^3 atm. to give easily measurable effects.

According to le Chatelier's principle, an increase in pressure will favour any process which tends to reduce the volume of the system and suppress any change which would increase the volume. This principle can be applied to rates of reactions if we consider not the overall volume change (which causes pressure to change the equilibrium), but the volume change on the formation of the transition-state.

The Transition-State Theory of Pressure Effects.

On the basis of the transition-state theory Evans and Polanyi [50] derived an equation in which the effect of pressure on the rate constant, k , is related to the difference in molar volume, ΔV^* , between the reactants and the transition state :

$$\left(\frac{\partial \ln k}{\partial P} \right)_T = - \frac{\Delta V^*}{RT} \quad (1)$$

For example, in the emulsion polymerisation of styrene [51a], the rate constant for chain growth, k_p , is increased tenfold at 5,000 atmospheres. The derived value for $\Delta V^* = -11.5$ cc/mole compared with the overall ΔV for styrene polymerisation of -17.3 cc/mole at 40°C . Equation (1) has become the basis for the description of the effect of pressure on reaction rates.

Evans and Polanyi [50] divided the activation volume, ΔV^* , into ΔV^*_1 and ΔV^*_2 . ΔV^*_1 represents the change in volume due to the reacting molecules themselves, when they form the transition-state, and ΔV^*_2 , is the corresponding volume change of the surrounding solvent, due to different interaction with the reactants and with the transition state. The second term is likely to be large only when there is a very marked change in the intermolecular forces, arising for instance from the development or disappearance of electrical charges in the transition state.

In a simple unimolecular dissociation :

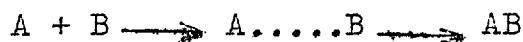


Some stretching of the breaking bond occurs in order to form the transition state. This will cause ΔV^*_1 to be positive and if no opposing electrorestriction effects occur, as will be the case in a free radical dissociation, the reaction

rate will be decreased by pressure.

Stearn and Eyring [52] pointed out that if the reaction mechanism, including the approximate geometry of the activated complex is known, ΔV^*_1 can be calculated.

In the case of a bimolecular addition reaction



ΔV^*_1 will be negative and if ΔV^*_2 is unimportant, as it will usually be for a non-polar reaction, the reaction rate will increase with pressure.

The magnitude of ΔV^*_2 can be calculated by regarding the solvent as a continuous dielectric medium to which the theory of electrorestriction can be applied. It is calculated [49] that the decrease in volume accompanying the development of a single ionic charge on a small spherical molecule is between 10 and 30 cm³ mole⁻¹ for most solvents. In a reaction which involves changes in ionic charges this effect (ΔV^*_2) may clearly be greater than ΔV^*_1 , the volume change due to bond formation and dissociation.

I.3 (2) The Effect of Pressure on Polymerisation Reactions.

A marked effect of pressure on the rate of liquid phase polymerisations was first observed by Conant and Bridgman [53] and has since been studied by a number of groups of workers, notably in the U.K., U.S.A. and U.S.S.R. A recent review by Weale [57] on addition polymerisation at high pressure give an account of the development of this field of study in this period.

Conant and Bridgman [53] observed that styrene, vinyl acetate, isoprene and 2,3,dimethyl butadiene can be polymerised at room temperature and 9,000-12,000 atms., under conditions in which negligible reaction occurs at atmospheric pressure. Starkweather [54] and Tamman and Fape [55] also reported an increase in the reaction rate with pressure. The latter concluded that a pressure of 1,500 atm. (140°C.) accelerated the rate of polymerisation of styrene by the very large factor of 2.24×10^6 . Subsequently these figures were proved to be wrong by Gilham [56] who showed that the factor is considerably less than 10, and that experimental shortcomings, particularly failure to carry out the reaction isothermally, had led to the error. By taking the necessary precautions to avoid

impurities and temperature fluctuations he found a tenfold increase in the rate of polymerisation of styrene at 3,000 atm. ($100^{\circ}\text{C}.$) with an increase in the polymer molecular weight of about 1.55-fold.

Merrett and Norrish [58] carried out a very detailed study on the polymerisation of styrene initiated by benzoyl peroxide at $60^{\circ}\text{C}.$ and pressures up to 5,000 atm. They obtained reproducible kinetic results which have been confirmed by latter workers. They discussed their results in some detail and their main findings are :

1. The logarithm of the overall rate is nearly a linear function of pressure. The polymerisation rate rises continuously with pressure, increasing by 10 to 12-fold at 5,000 atm.

2. The polymer molecular weight is approximately tripled between 1 and 3,000 atm. but increases only slightly at higher pressure.

3. The rate of polymerisation is proportional to the square root of the initiator concentration at 1 atm., but this order decreases a little with increase in pressure (0.4 at 3,000 atm.).

They explained the changes in rate and molecular weight in terms of the effect of pressure on the separate steps of the reaction, i.e. initiation, propagation, chain transfer and termination.

The rate of decomposition of free-radical initiations (a unimolecular dissociation) has been found to be retarded by pressure. The decomposition of benzoyl peroxide involves the stretching and breaking of the O-O bond, so that the volume of activation ΔV^* (equation (1)) is likely to be positive for this reaction. The rate of decomposition will therefore be decreased by pressure. The propagation (chain growth) reactions are bimolecular addition processes involving bond formation so that ΔV^* will be negative and acceleration by pressure may be expected and has been confirmed. Merrett and Norrish considered that termination reactions between two large radicals would be diffusion-controlled and so retarded at high pressure because of the increase in viscosity of the medium. This was confirmed in the case of styrene polymerisation by Nicholson and Norrish [59].

Besides these quantitative studies of polymerisations under pressure, there has been extensive work, notably by Jacobson, Carothers [60], Starkweather [54], Newitt et al. [61], and by Holmes-Walker and Weale [62], with a view to establishing how the pressure effect varies with monomer structure.

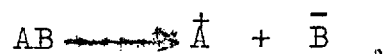
A general conclusion can be drawn from the results that the molecular weight of the polymer increases with

pressure [61,62,63] and that pressure can bring about the polymerisation of some monomers which normally resist polymerisation for steric reasons.

1.3 (3) The Effect of Pressure on Electrolytic Dissociation.

The effect of pressure on ionic equilibrium is considered here because of its potential importance in ionic polymerisation. The first indication that pressure might enhance the ionisation of weak electrolytes was found in Ostwald's [64] measurements of the volume changes which accompany the neutralization of acids by bases in water. The ionisation of acetic acid involves a contraction [48] of $-10.5 \text{ cm}^3 \text{ mole}^{-1}$, and it should therefore be favoured by an increase in pressure.

A considerable amount of work on the measurement of dissociation equilibria (in aqueous solutions) has been done [48]. For example in reactions of the type :



The equilibrium constant relationship is given by Van't Hoff's equation :

$$\frac{\partial \ln k_m}{\partial P} = - \frac{\Delta \bar{V}^0}{RT} \quad (2)$$

where k_m is the equilibrium constant and $\Delta \bar{V}^0$ is the

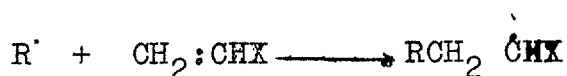
difference between the partial molar volumes in the ionised and unionised form.

The main reason why pressure increases the ionisation of weak electrolytes is that it enhances the solvation of the ions and in this way lowers their free energy with respect to that of the unionised molecules. Moreover separate ions will be more tightly solvated than an ion-pair dipole and there will be a contraction in volume on dissociation, and hence an increase in k_m .

I.4. Radical Polymerisation.

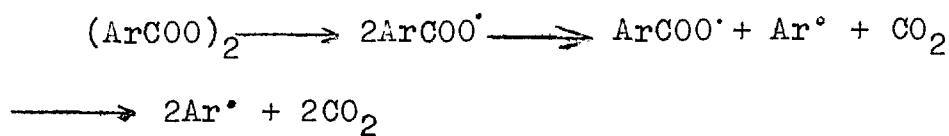
In the free radical reaction, for example a vinyl polymerisation initiated by an organic peroxide, a free radical $R^{\cdot}$, is formed by decomposition of the initiator. This reacts with a monomer molecule to form a new radical which is progressively re-generated terminally by the further addition of monomer molecules. The radical, $R^{\cdot}$, thus becomes a part of the polymer chain.

The best evidence for the free radical nature of a polymerisation is obtained by the introduction of free radicals into a monomeric system. Thus, triphenyl methyl readily initiates polymerisation of styrene in solution. Further, large numbers of organic and inorganic substances which are known to form free radicals upon decomposition act as initiators for vinyl polymerisations. These compounds include the acyl and aryl peroxides and hydroperoxides, diazonium compounds and persulphates. The odd electron in the radical formed by the decomposition of any of these compound pairs with one of the π electrons (of opposite spin) from the double bond of a monomer molecule, at the same time repelling the other electron (with the same spin) to the far end of the monomer molecule, thus reforming a free radical :



It is not necessarily true, however, that the introduction of free radicals into a monomer system will automatically initiate polymerisation and that the process is free of activation energy.

The most commonly employed initiators are organic peroxides, such as benzoyl peroxide, which decompose slowly at temperatures of 50°C. to 150°C with release of free radicals as follows :



There are other classes of compounds which are effective polymerisation initiators at temperatures where they undergo slow thermal decomposition by mechanisms which involve the release of free radicals. Of special interest are the aliphatic azonitriles such as azo-bis-isobutyronitrile (AIBN), which has been used in many kinetic investigations because of the freedom of its decomposition from side reactions.

Kinetics of Addition Polymerisation.

The kinetics of addition polymerisation have been described by various authors [53, 65, 66, 67]. In its simplest form this process may be represented in three distinct steps : initiation, propagation and termination.

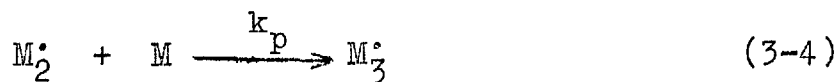
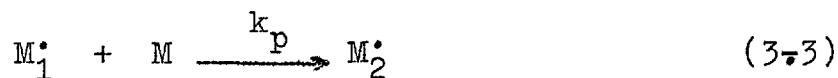
In the presence of initiator, I, the reaction proceeds first with the decomposition of initiator into free radicals $R^\bullet$



Then the addition of a monomer molecule to an initiator fragment $R^\bullet$ forms an active radical, $M_1^\bullet$



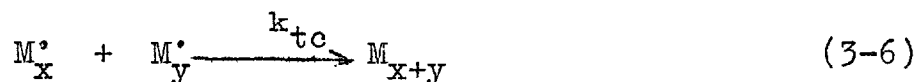
The successive steps in propagation involve the addition of monomer molecules to the growing polymer radical, and the rate of propagation is $k_p [M][C^*]$, where C^* is the concentration of all polymer radicals. If long chains are formed, the rate of propagation must be much greater than termination. Propagation steps may be shown as under



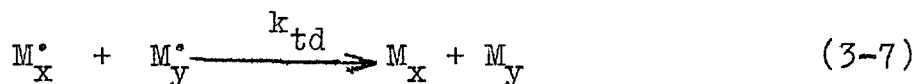
or in general



The termination involves the destruction of radicals in pairs, either by combination



or by disproportionation, with the transfer of a hydrogen atom and the formation of an unsaturated end group,



The rate equations of the three steps are :

Rate of initiation

$$\begin{aligned} v_i &= (d [M^\bullet] / dt)_i \\ &= 2f k_d [I] \end{aligned} \quad (3-8)$$

where f represents the fraction of the radicals formed by equation (3-1) which are successful in initiating chain by equation (3-2).

The concentration of free radical becomes constant very early in the reaction, as radicals are formed and destroyed at the identical rate. Since under steady-state conditions $v_i = v_t$ and equation (3-8) and (3-12) may be equated to solve for $[M^\bullet]$

$$[M^\bullet] = (f k_d [I] / k_t)^{\frac{1}{2}} \quad (3-9)$$

The rate of monomer disappearance in polymerisation is essentially the overall rate of propagation. When chains are long the amount of monomer used in the initiation step is very small compared to that used in the propagation reaction,

$$v_p = -d [M] / dt = k_p [M] [M^*] \quad (3-10)$$

Substituting from equation (3-9)

$$v_p = k_p (f k_d [I] / k_t)^{\frac{1}{2}} [M] \quad (3-11)$$

Rate of termination

$$\begin{aligned} v_t &= -(d [M^*] / dt)_t \\ &= 2k_t [M^*]^2 \end{aligned} \quad (3-12)$$

So the overall rate of polymerisation should, in the early stages of the reaction, be proportional to the square root of the initiator concentration and, if f is independent of $[M]$, to the first power of the monomer concentration. This will certainly be true if the efficiency of the initiator is high. The proportionality of the overall rate to the square root of the initiator concentration has been confirmed experimentally in a large number of cases [68, 69, 70].

Other possible reactions which are not included in the simple kinetic scheme include: Chain transfer, Degree of Polymerisation, Degradation and Depolymerisation.

1.5. Non-radical Polymerisation [12,66,67,72].

Polymerisation is known to occur by several mechanisms other than those involving free radicals discussed in the previous section. These include reactions in which the chain carriers are :

- (i) Carbonium ions (Cationic Polymerisation)
- (ii) Carbanium ions (Anionic Polymerisation).

In addition to these polymerisation may take place by mechanisms involving co-ordination compounds between the monomer, or possibly the growing chain, and a catalyst, usually a solid,

- (iii) Co-ordination Polymerisation.

The mechanisms of these polymerisations are less thoroughly understood than that of radical polymerisation, for several reasons. The reaction systems are often heterogeneous, if an inorganic catalyst is involved (the word catalyst is preferred to initiator in reference to ionic polymerisation since the agent often exerts its influence throughout the growth of the chain, rather than in the initiation only). Also, large effects may be produced by a third component (co-catalyst) present in very low concentration. According to investigation by some workers [73-78] the presence of a co-catalyst is usually

necessary for initiating reaction. Thus iso-butene in hexane will not polymerise with titanichloride as initiator at -80°C . in the absence of moisture, but passage of moist air is sufficient to initiate a rapid reaction [73, 76, 78]. In spite of this fact some cases are known where co-catalysts are not [79, 80] necessary and moreover their presence has no accelerating effect on the polymerisation.

Monomers with electron-donating groups attached to the double-bonded carbon atoms form stable carbonium ions and polymerise best with cationic catalysts. Conversely, monomers with electron-withdrawing substituents form stable anions and require anionic catalysts. Many monomers can polymerise by more than one mechanism [81], including co-ordination polymerisation.

Initiation of ionic polymerisation usually involves the transfer of an ion or an electron to or from the monomer, with the formation of an ion pair. It is thought that the counter ion of this pair stays close to the growing chain end throughout its lifetime, particularly in media of low dielectric constant. In contrast to radical polymerisation, termination never involves the reaction between two growing chains, but usually involves the unimolecular reaction of a chain with its counter ions or a transfer reaction which leaves a species too unreactive

to propagate. An agent which retards radical polymerisation, such as oxygen, often has little influence on ionic polymerisation, but impurities that neutralize the catalysts prevent the reaction, and many aromatic, heterocyclic, olefinic or acetylenic compounds retard or terminate polymerisation.

I.5. (i) Cationic Polymerisation.

The catalysts for cationic polymerisation are Friedel-Crafts catalysts such as AlCl_3 , AlBr_3 , BF_3 , SnCl_4 , H_2SO_4 and other strong Lewis acids. All these are strong electron acceptors. Most of them, excepting possibly the strong protonic acids, require a co-catalyst to initiate polymerisation [73-78]. The co-catalyst supplies H^+ , which is presumed to be the effective initiator. High rates of polymerisation at low temperatures are a characteristic of ionic polymerisations and it is often difficult to establish uniform reaction conditions before the reactants are consumed. The polymerisation of isobutylene [82] by AlCl_3 or BF_3 takes place within a few seconds at 100°C , producing polymer molecules ranging up to 10^5 in degree of polymerisation. Temperature coefficients are low, and they may in some cases be negative, the rate actually decreasing with rise in temperature [78,83]. As in polymerisations propagated by free radicals, the average degree of polymerisation

decreases with rise in temperature. Molecular weights obtained at room temperature and above are much lower than those for radical polymerisation. Thomas and co-workers [82] have studied the relationship between the molecular weights of polyisobutylenes and the polymerisation temperature.

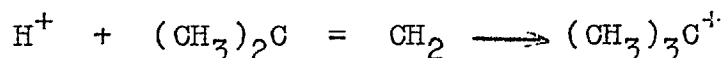
The Mechanism of Cationic Polymerisation.

The most satisfactory theory developed for Friedel-Crafts polymerisation involves the carbonium ion [77, 84-86]. Eley and co-workers [80,87] have shown that triphenyl - methyl chloride is a catalyst for the polymerisation of vinyl ethers in m-cresol, in which the catalyst ionises to yield the triphenylcarbonium ion $(C_6H_5)_3C^+$. Secondly, Evans and Hammann [88] showed that 1,1-diphenyl - ethylene develops an absorption band at 4340 Å in the presence of boron trifluoride (and adventitious moisture) or of stannic chloride and hydrogen chloride. This band is characteristic of both the triphenylcarbonium ion and the diphenyl-methyl carbonium ion.

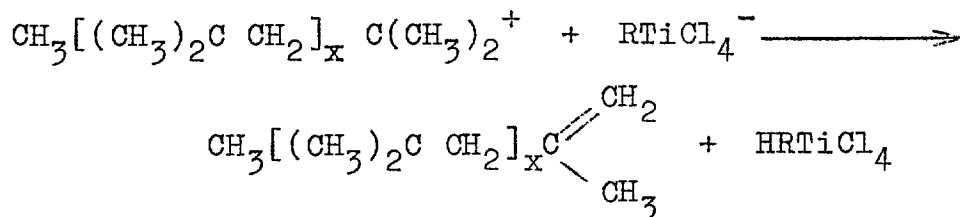
Polanyi et al. [73,74] based their theory of the carbonium ion reaction on a study of the polymerisation of iso-butene in the liquid and gaseous phases. According to this theory in the polymerisation of isobutylene with $TiCl_4$ catalyst, the first step in the reaction of catalyst and co-catalyst to form a complex acid,



which donates a proton to an isobutylene molecule to give a carbonium ion,

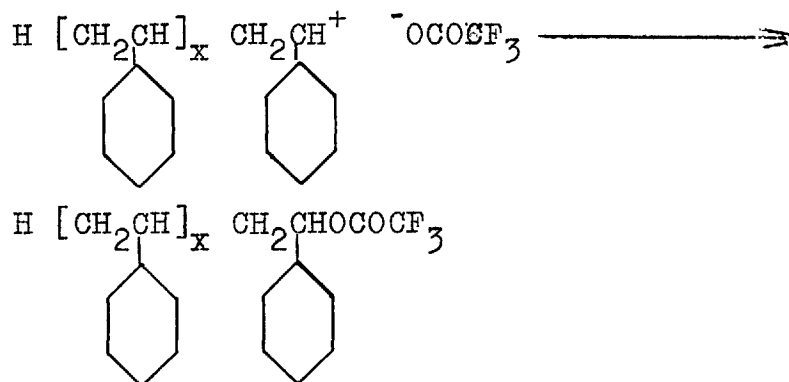


This ion then reacts with monomer with the formation of a carbonium ion at the end of each step. A "head to tail" addition of monomer to ion is required for energetic reasons. As the reaction is usually carried out in a hydrocarbon medium of low dielectric constant, the anion, TiCl_4R^- , cannot be separated from the growing cationic end to any appreciable distance; and they will form an ion pair. The nature of the anion may be expected, therefore, to influence the speed of the growth reaction and the incidence of other processes such as chain termination and transfer. The termination reaction can take place by the rearrangement of the ion pair to yield a polymer molecule with terminal unsaturation, plus the original complex,

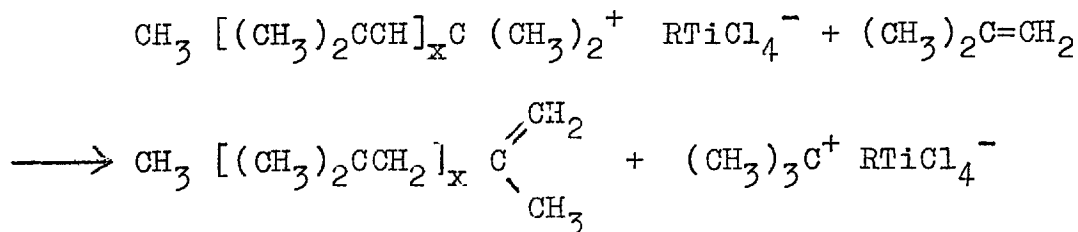


An alternative mechanism, in which the catalyst or co-catalyst combines with the growing chain, is unlikely in this example,

but can take place with formation of a covalent bond, as in the polymerisation of styrene with trifluoroacetic acid [89] :



Chain transfer to monomer can also take place :



Colclough [90] and Evans and Meadows [77] have shown that many polymer chains are formed for each catalyst molecule present. Chain transfer to polymer is known and leads to branched polymers [91,92].

The catalyst efficiency in propagation is dependent on the acid strength of the catalyst-co-catalyst complex. The efficiency of the catalyst as a terminator,

should also be related to the base strength of the complex anion. Thus the more active a molecule is as a catalyst, the less active it is as a terminator.

Though the requirements of the isobutylene - TiCl_4 system are fully satisfied by the mechanisms given above, generalizations of the scheme need to be made with caution.

I.5.(ii) Anionic Polymerisation.

Although research into anionic polymerisation is not within the scope of this work, a brief resume is included to complete the introductory remarks on ionic polymerisation.

Monomers with electronegative substituents are readily susceptible to a polymerisation which takes place in the presence of reagents capable of generating carbanions. This type of polymerisation was carried out on a commercial scale for many years [94], before the nature of the polymerisation was recognised, e.g. in the production

of the buna-type synthetic rubbers in Germany and Russia by the polymerisation of butadiene with sodium or potassium catalyst. The first anionic-type chain reaction to be so identified was the polymerisation of methylacrylonitrile by sodium in liquid ammonia at -75°C . [95]. Typical catalysts for anionic polymerisation include alkali metals, alkali metal alkyds, compounds such as sodium naphthalene, triphenyl methyl sodium and Grignard reagents. Acrylonitrile [96] and methyl methacrylate [95] are also polymerised by sodium in liquid ammonia.

I.5.(iii) Co-ordination Polymerisation.

It has been found that catalysts obtained by the reduction of transition metal halides with organo-metallic reducing agents will polymerise ethylene and substituted α -olefines to high molecular weight crystalline polymers. These catalysts [97,98] give rise to stereospecificity, and the process is frequently called stereospecific polymerisation or stereoregular polymerisation. The term co-ordination polymerisation is used here to suggest the essential feature of a co-ordination complex or a directing force which governs the orientation with which a monomer approaches the growing chain end.

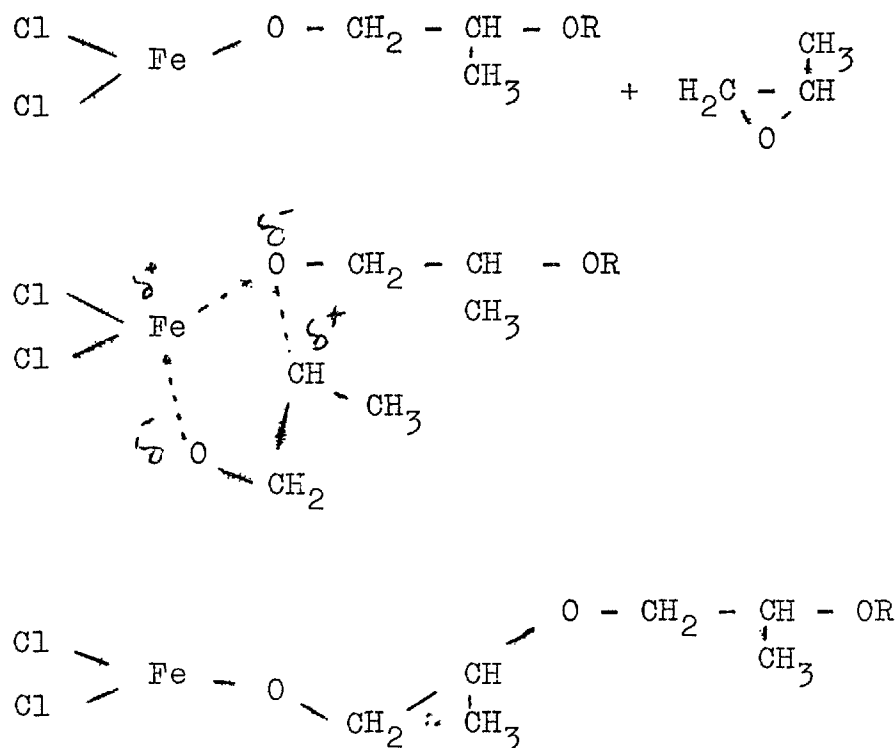
The original discovery by Ziegler et al. [97] related to a catalyst for the low-pressure polymerisation of ethylene which was prepared by adding a solution of triethylaluminium to a solution of titanium tetrachloride in hydrocarbon solvents such as heptane or hexane. The product of this reaction is a brown-black insoluble compound. Ethylene on co-ordination polymerisation yields products shown to be less highly branched than those resulting from the usual free radical synthesis.

The patent literature [103] now covers a vast number of variations on the original catalyst and it appears that catalytic activity can be obtained by mixing metal alkyls or aryls from Groups I to III in the Periodic Table, e.g. (RM_xY , where R = alkyl or aryl, M = metal and x = halogen, alkoxy etc.) with compounds (usually halides or esters) of the transition metals in Groups IV-VI. Thus titanium tetrachloride and titanium tetra-alkoxides and vanadium tetrachloride are typical examples, and in all these cases the solvent is preferably an aliphatic hydrocarbon.

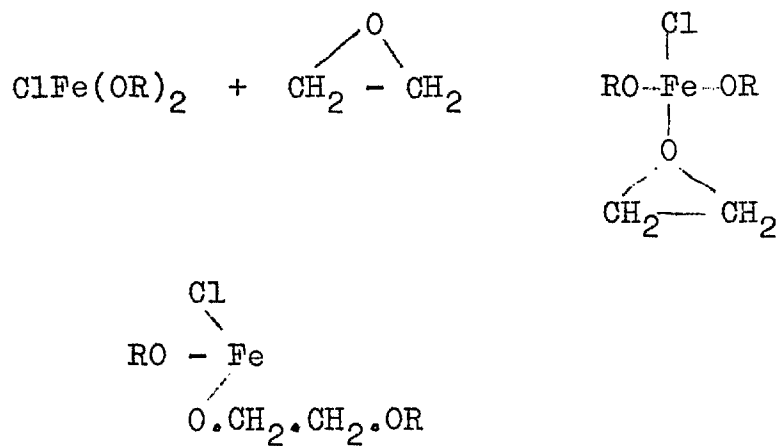
Natta and co-workers [99,100] developed the use and scope of the so-called "Ziegler catalysts" and utilized them to polymerise α -olefines. They proposed the system of nomenclature (isotactic, syndiotactic, atactic, etc. [101]

now accepted to describe the types of structure obtained.

For the polymerisation of propylene oxide with the FeCl_3 -propylene oxide complex, Price and Miller [102] proposed a mechanism of "co-ordinate complex polymerisation" in which the addition of each monomer molecule is formulated by the following scheme :



Gee and co-workers [15] suggested a related mechanism for the polymerisation of ethylene oxide with the same catalyst



Price and Miller's mechanism involves a transition state which contains a five-membered ring formed by co-ordination.

II.1. (1) HIGH PRESSURE EQUIPMENT AND ANCILLARY APPARATUS.

Experiments at high pressure were carried out in two high pressure vessels, both basically of the same design, with similar auxiliary equipment. The details of the constructions of one of the pressure vessels are indicated in Fig.1. This vessel can be used at pressures up to 15,000 atm.

The reaction chamber V is an autofrettaged monobloc of "Vibrac" V-45 steel (Fig.2). It is capable of withstanding internal pressure up to 20,000 atm. and is sealed at the top with a rubber Poulter packing.

A hand-operated two-stage pump A was used for the generation of pressure. Liquid paraffin B.P., supplied from the reservoir R, was used as the hydraulic fluid throughout the experiments and the pump was connected with the intensifier and reaction chamber by stainless steel tubing (3/8" o.d. by 1/8" i.d.).

An initial 'priming' pressure can be developed in the high pressure chamber through the side injection hole (0.016" diameter) via valve B, and the pressure is transmitted to the low pressure piston of the intensifier via valve C.

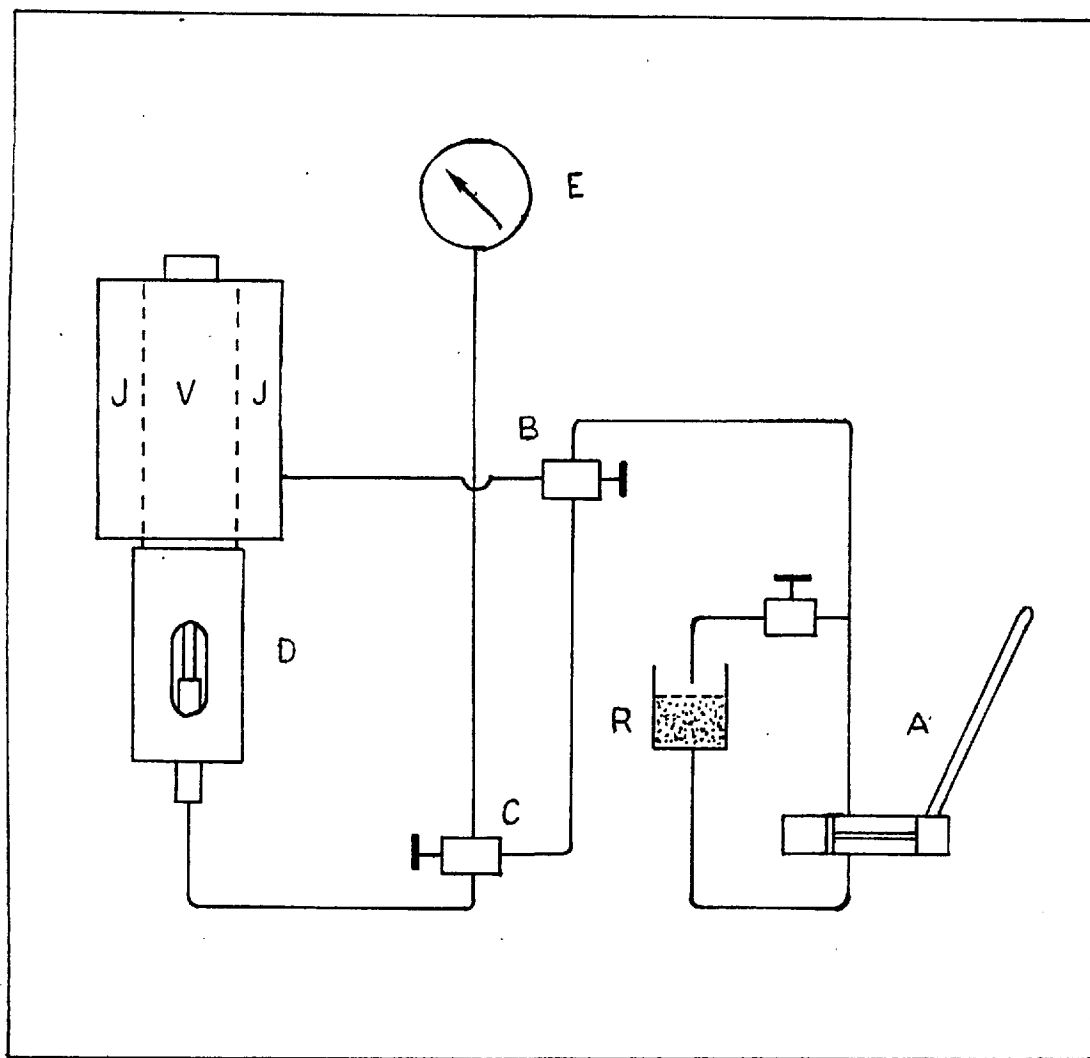


FIG. 1 GENERAL LAYOUT OF HIGH PRESSURE SYSTEM

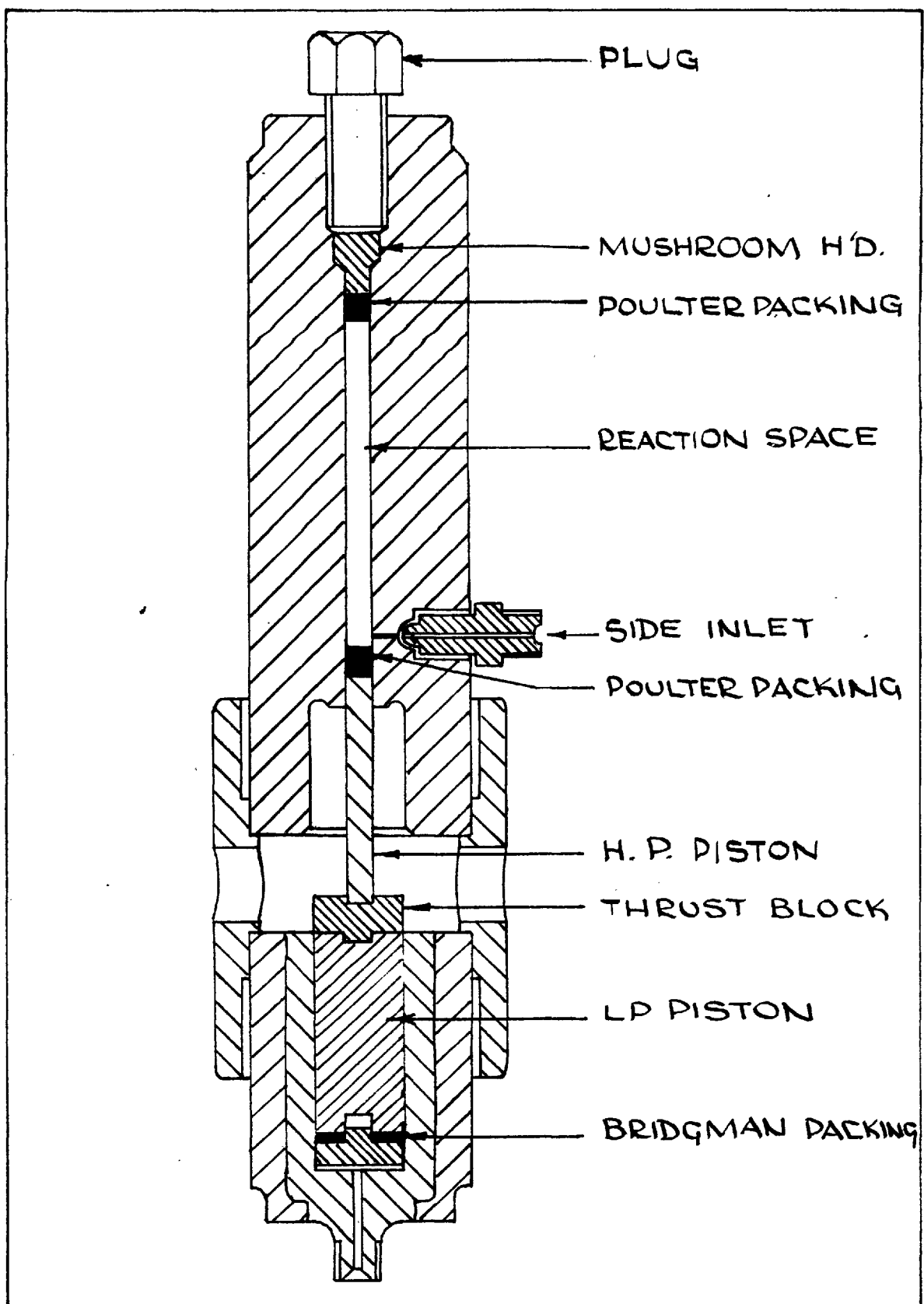


FIG. 2 VESSEL & INTENSIFIER

The final pressure is obtained by the use of the intensifier D. The pressure is applied to the bottom of the low pressure piston which is sealed with a Bridgman packing and the pressure is transmitted through a thrust block and a thin copper washer to the high pressure piston, sealed with a Poulter packing. The two pistons in the intensifier are of different cross-sectional area, and the intensifier increased the pressure delivered by the pump by a factor of approximately 15. The intensifier pistons and thrust blocks were made from oil-hardened C.R.C. quality race steel bar.

The top end of the reaction chamber V is closed by means of a steel "mushroom-head", which keeps the Poulter packing in position in the bore of the vessel and, in turn, is retained in place by a screw plug.

When the intensifier is used the high pressure piston moves up into the high pressure chamber, isolating the injection holes and compressing the contents of the chamber. Pressures up to 12,000 could be obtained without utilising the full travel of the intensifier piston.

Two types of reaction tubes were used (Fig.3). For some reactions below 3000 atm., Pyrex tubes of about 15 cm. in length and 0.8 cm. inside diameter were employed. Each tube was fitted with a ground glass stopper at the top and had a 3 mm. diameter hole at the lower end to allow

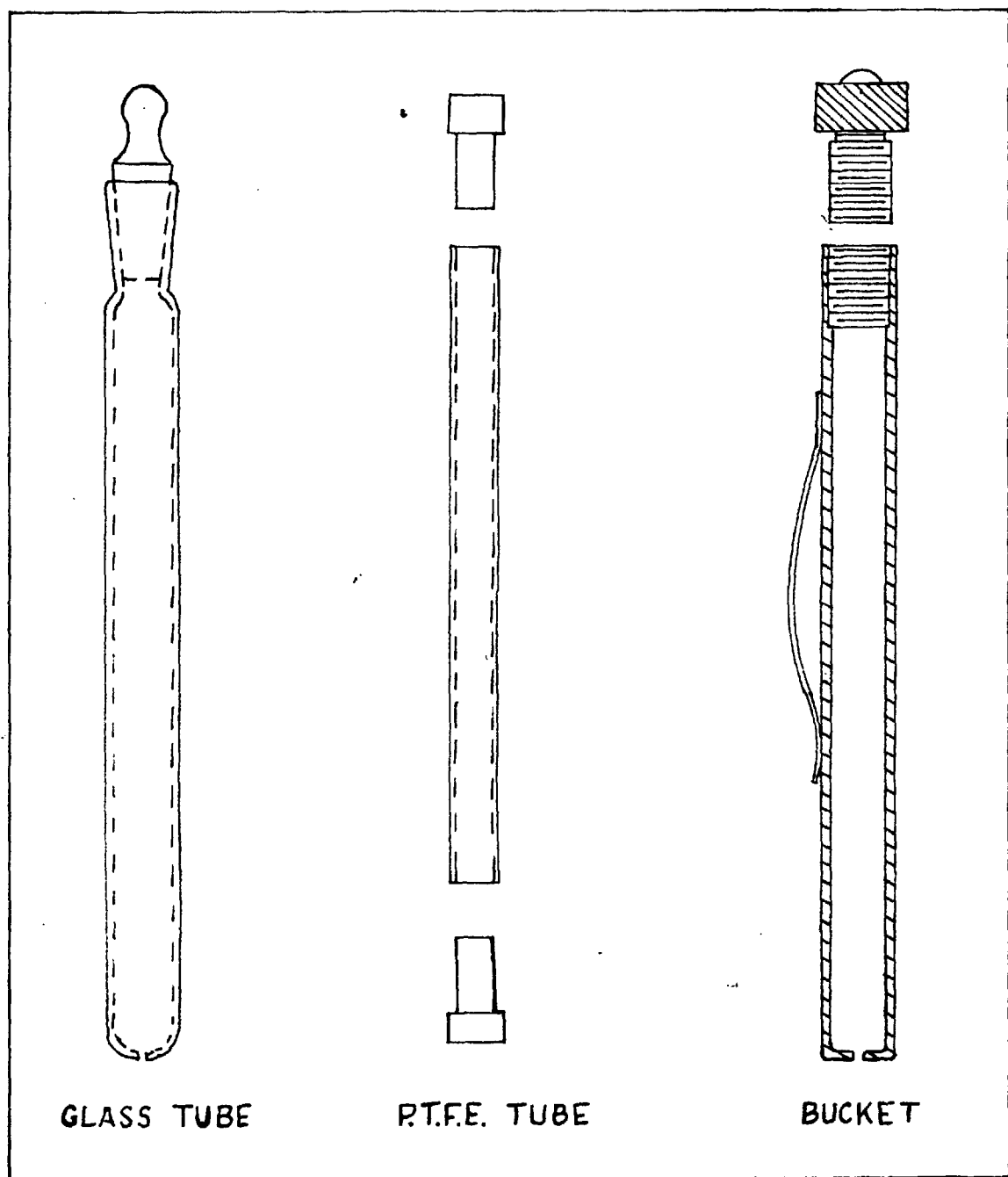


FIG. 3 REACTION TUBES & BUCKET

pressure equalisation. In order to avoid direct contact and contamination of the reagents with liquid paraffin the tube contained a small amount of mercury, and floated on mercury contained in a steel bucket.

Most of the reactions in this work, especially at the higher pressures (above 2,000 atm.), were carried out in P.T.F.E. tubes of about 5" length, 1/4" o.d. and 1/32" wall thickness. The tube ends were closed by plugs made to size from P.T.F.E. rod, with brass retaining rings on both ends. The pressure is transmitted through the flexible tube walls. The tube is held in the reaction vessel in a steel bucket having retaining screws at each end, and a hook to assist removal. Sufficient clearance is left between the reaction tube and the bucket wall to allow rapid transmission of pressure and the bucket is fitted with a bowed sprung steel attachment to hold it at any desired position in the reaction vessel.

The pressure on the low pressure side of the intensifier was measured on a standard Bourdon tube gauge E (Fig.1). The pressure recorded by the gauge E is approximately 1/15 of the pressure in the upper cylinder of the intensifier. The intensifier factor was determined by comparing the recorded pressure on gauge E with the pressure

in the upper cylinder measured on a 10,000 atm. factory-calibrated Bourdon gauge (Budenberg No. 8435900). The ratio was determined from 1,000 to 6,000 atm. and used for pressures up to 12,500 atm.

The vessel V is surrounded by an electrical heating jacket, J. Temperature control to $\pm 0.1^{\circ}\text{C.}$ in the high pressure chamber was achieved by the use of an adjustable-contact thermometer situated between the jacket and the vessel, which controlled a Sunvic hot wire vacuum switch relay.

A temperature gradient was observed at the lower end of the reaction vessel, due to loss of heat to the intensifier and the supports of the vessel.

The upper part of the reaction vessel was found to have a suitably constant temperature, and the reaction tube was placed in this section.

II. 1. (2) Atmospheric Pressure Apparatus.

Reactions at one atmosphere were carried out in a stirred oil bath heated with a 150 watt electric bulb and controlled by a mercury-toluene thermoregulator and Sunvic hot wire relay.

Amber glass ampoules of about 10 ml. capacity were used for monomers of higher boiling points (above 60°C.), while for low boiling monomers, thick walled Pyrex glass

reaction tubes $3/4$ " x 7" were used. The temperature control in this apparatus was better than $\pm 0.05^{\circ}\text{C}$.

II. 1. (3) Equipment for Conductivity Measurements at High Pressure.

The cylindrical steel vessel used for these measurements was closed by a specially designed screw plug of which the details are given in Fig.4. The plug was machined from "Vibrac V-30" steel and fitted with two insulated electrodes to which the high pressure conductivity cell could be attached. The electrodes were mounted on $1/2$ " centres and electrical insulation from the plug was provided by hollow ebonite cones, machined to a thickness of about $1/16$ ", and tightened into position.

The screw plug and electrodes withstood pressures up to 3,000 atm. (80°C .) with no leakage or electrical shorting.

The conductivity cell for high pressure work (Fig.5) was made from a B.10 "Quickfit" cone and socket glass connector. The approximate size of the platinum electrodes was 0.6 cm. x 0.6 cm. by 0.006" thick, and the distance between the two electrodes was approximately 1 cm. They were welded to 0.03" diameter wires and these were fused through the top of the cell into wells containing mercury which served to make contact with the wires from the plug

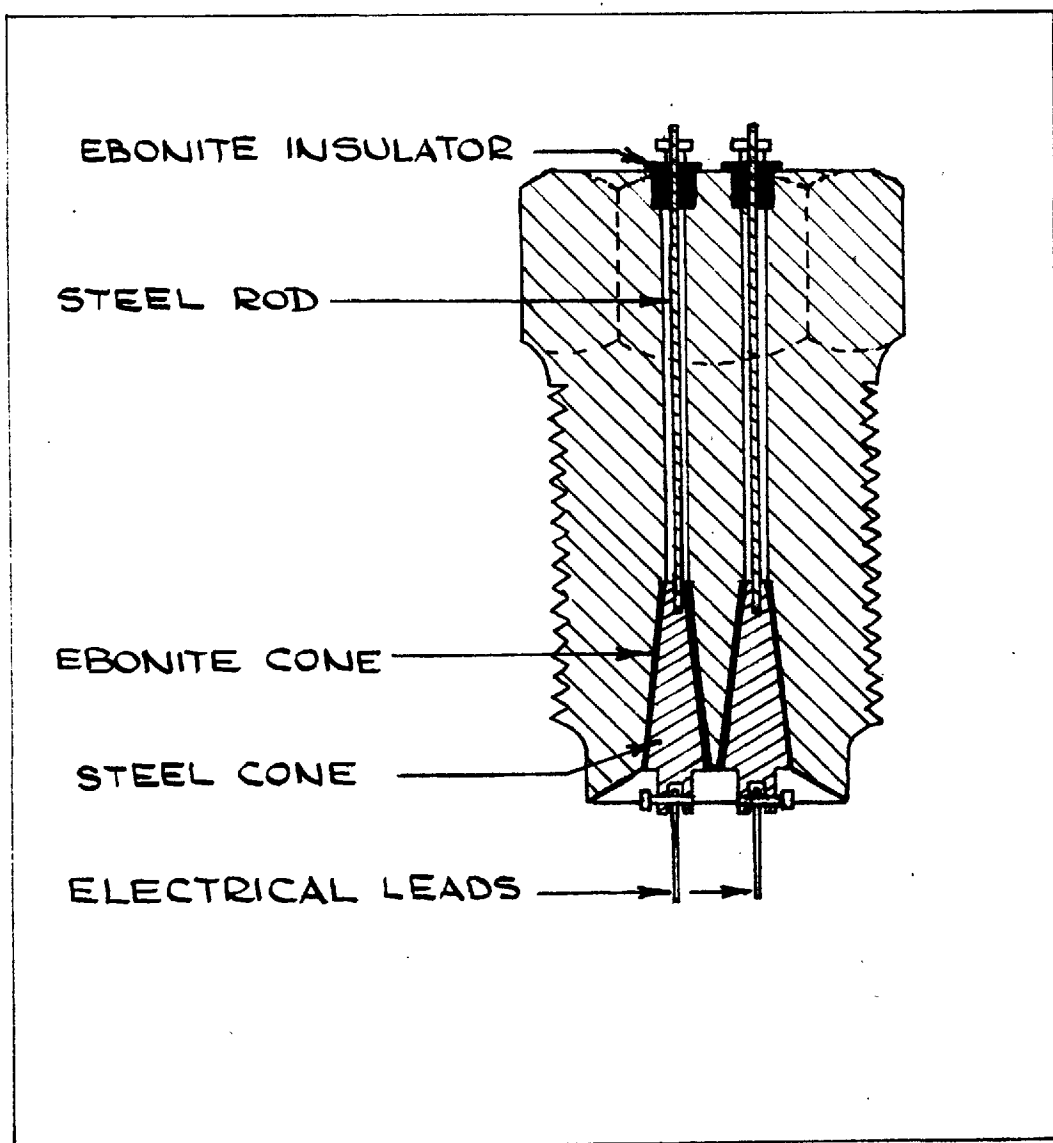


FIG 4 - ELECTRICAL LEADS THROUGH
VESSEL PLUG

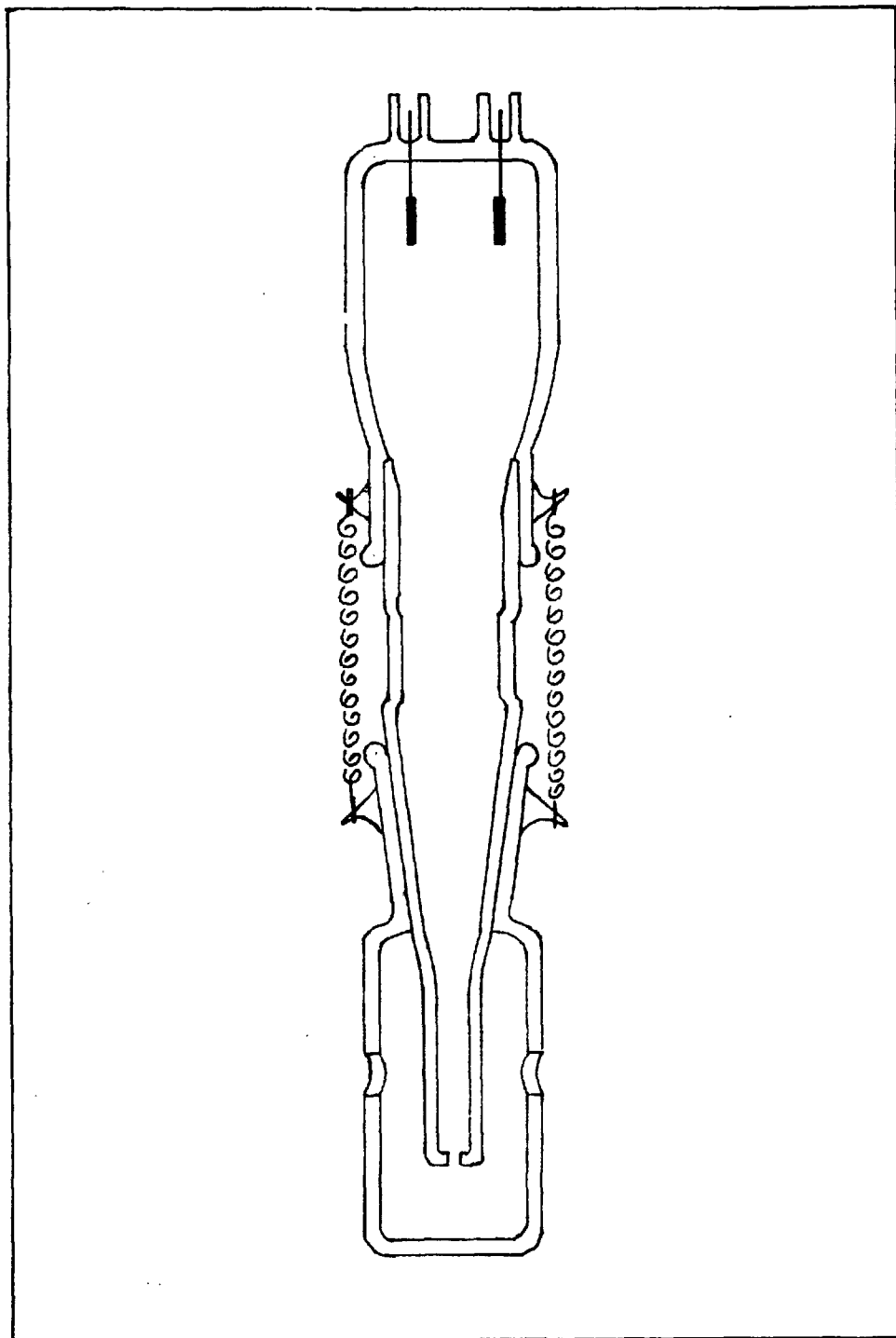


FIG. 5 CONDUCTIVITY CELL (HIGH PRESSURE)

electrodes. The whole cell was suspended in a brass holder attached to the plug.

To prevent contamination of the solutions by liquid paraffin, a mercury seal was provided in a glass container, which had side holes to allow pressure equalisation.

Spring connectors were used in order to hold the parts of the cell firmly together. The platinum electrodes were platinised lightly with a solution of chloroplatinic acid and a Wayne-Kerr B.221 Universal Bridge was used for conductance measurements. The bridge operated at 1592 C.P.S. (10,000 rads/sec.) and could be used to measure conductance in the range 10^{-1} to 10^{-8} mhos to four significant figures with an accuracy of better than $\pm 0.2\%$. Balancing was effected by two "magic eyes" of different sensitivities.

II. 2. Purification and Properties of Monomers, Solvents and Initiators.

(1) Monomers.

(i) Propylene Oxide.

Propylene oxide (freezing point $-112^{\circ}\text{C}.$) supplied by Messrs B.D.H. was dried over calcium hydride and fractionated in a column packed with rings. The first

fraction was rejected and the middle fraction (about 60%) collected at $33.5 - 34^{\circ}\text{C}/760 \text{ mm.}$ and stored over dried calcium chloride in absence of air.

(ii) Styrene Oxide.

Styrene oxide (L.Light & Co.) was thoroughly dried over dried calcium chloride, distilled under reduced pressure and the main fraction (60%) B.pt. $77.5 - 78.5/12 \text{ mm.}$ collected and stored in sealed tubes under nitrogen at -5°C.

(iii) Cyclohexene Oxide.

Cyclohexene oxide supplied by K & K Laboratories Ltd. Inc. New York, was fractionated and the middle fraction (about 70%) collected at $27.5^{\circ}\text{C}/11 \text{ mm Hg}$ in sealed tubes each of 20 ml. capacity, and stored below -5°C.

(iv) Tetrahydrofuran.

Tetrahydrofuran (B.D.H.) was dried [104] over calcium hydride, refluxed over lithium aluminium hydride for at least two hours and fractionated prior to use. The middle fraction (about 60%), boiling at $65.5 - 65.7^{\circ}\text{C.}$, was kept over dried calcium chloride.

(v) 3,3'-bis-(chloromethyl) Oxacyclobutane.

3,3'-bis-(chloromethyl) oxacyclobutane supplied by Imperial Chemical Industries (Reference 153/91E) had a

boiling point $83^{\circ}\text{C.}/11\text{ mm.}$ and a melting point 18.75°C.
As this sample was about 25 grams, it was used as received without any attempt at purification.

(vi) 1,2-epoxy-4-Vinylcyclohexane.

1,2-epoxy-4-vinylcyclohexane was supplied by L.Light & co. (B.pt. $169^{\circ}\text{C}/760\text{ mm.}$, freezing point -100°C.) and was distilled under reduced pressure. The middle fraction (about 70%) was collected at $70 - 70.5^{\circ}\text{C}/2\text{ mm. Hg.}$

(vii) 1,3,5, Trioxane.

Supplied by L.Light & Co. as crystals (melting point 64°C.) and was used as received.

(2). Solvents.

(i) Di-ethyl Ether.

The chief impurities in commercial ether are water and ethyl alcohol. In addition samples which have been exposed to air and light for some time form "ethyl peroxide" which should be removed before distillation. The presence of the peroxide was detected by the liberation of iodine when the sample was shaken with an equal volume of 2% KI solution and a few drops of dilute HCl. The peroxide was removed by shaking with a concentrated solution of a ferrous salt. The ether was then dried over anhydrous calcium chloride for 24 hours and fractionated.

(ii) Di-iso-Propyl Ether.

This was dried and distilled as described above and the middle fraction (67.5 - 67.7°C.) was stored over dried calcium chloride.

(iii) Toluene (Analar).

Supplied by Hopkin & Williams Ltd., and was dried over calcium chloride and kept in the dark.

(3). Initiators,

(i) Benzoyl Peroxide (Bz_2O_2)

Benzoyl peroxide (B.D.H.), supplied as a wet paste, was dried in vacuo. A saturated solution in chloroform was prepared, and the Bz_2O_2 was reprecipitated as a crystalline solid in cold methanol. The purified material was filtered off and dried under vacuum and was kept in the dark in a vacuum desiccator. Fresh material was prepared at regular intervals.

(ii) Azo-bis-isobutyronitrile (AIBN).

AIBN (Eastman Kodak) was purified by fractional crystallization from saturated solution in absolute ether. The crystalline product was filtered, and dried and stored in vacuo.

(iii) Anhydrous Ferric Chloride.

Anhydrous ferric chloride (Hopkin and Williams) was used as received.

(iv) Boron Trifluoride Diethyl Etherate.

Boron trifluoride diethyl etherate (Mol.Wt. 141.94, Boiling point $123^{\circ}\text{C}.$, melting point $-60.4^{\circ}\text{C}.$) was supplied by B.D.H. No further purification was carried out.

II. 3, EXPERIMENTAL PROCEDURES.

(1). Preparation of Ferric Chloride/Propylene Oxide and Ferric Chloride/Styrene Oxide Complexes.

A weighed amount of anhydrous ferric chloride was transferred in a previously weighed weighing bottle to a dry-box having a dry nitrogen atmosphere. The ferric chloride was dissolved in purified di-ethyl ether (18 times by weight) and purified propylene oxide (6 times by weight) was added drop by drop. During this process the solution was cooled in an ice-salt bath and stirred continuously. In the case of styrene oxide the complex was made from equal quantities of the epoxide and a solution of ferric chloride in 15 times its weight of di-ethyl ether.

At the beginning the mixture became cloudy and as the addition proceeded a dark brown oil separated. When

all the monomer had been added the reaction mixture was allowed to come to room temperature and the mixture stirred for 15-20 mins. The volatile part was then distilled off at room temperature below 20 mm. Hg and the residue was left for 1-2 hours under vacuum (1-2 mm.Hg). This catalyst complex was stored under nitrogen (O_2 -free) at $-20^{\circ}C$.

(2) Preparation of Reaction Mixtures.

In the free radical polymerisations the amount of initiator was accurately weighed in a flask and the exact amount of monomer needed to make the desired concentration was added. The same procedure was adopted when the catalyst was the $FeCl_3$ -propylene oxide or $FeCl_3$ -styrene oxide complex, and this stock solution was kept under nitrogen at $-20^{\circ}C$. In the case of tetrahydrofuran, a known volume of boron trifluoride ethyl ether complex was added to a known volume of monomer. Unless other wise stated the reactions were carried out in bulk, without any solvent, but the polymerisation of 3,3-bis-(chloromethyl) oxacyclobutane was carried out in toluene solution. Solutions of the desired concentration were prepared by weight in a weighing flask and the correct weight of BF_3 /ethyl ether complex was added.

(3). General Technique of Polymerisation.

For reactions at atmospheric pressure and monomers of low boiling points, pyrex glass tubes of diameter 3/4" and wall thickness 1/16" and about 6 to 7 in. long were used. Amber glass ampoules (10 ml.) were used for monomers having boiling points above 100°C. These tubes were flushed with nitrogen, filled with weighed quantities of reaction mixture and sealed. The tubes were then placed in a constant temperature bath at 60 or 80°C. (Working of one atmosphere bath is described in Section II.1.(2)). The tubes were removed from the bath after appropriate times and for ionic polymerisations were quenched in a dry-ice-acetone bath to stop polymerisation.

(4). Separation of Polymers.

Two methods of separation of the various polymers were used. Wherever possible the polymer was precipitated from solution by addition of methanol, as a very convenient method of obtaining polymer-free of unreacted monomer.

However, in most cases the polymers were moderately or highly viscous liquids which were readily soluble in most organic solvents. These were freed from unreacted monomer and other volatile substances by prolonged treatment under vacuum.

Although styrene oxide also gave viscous liquid or semi-solid polymers, when polymerised with a free radical initiator its high boiling point ($191-2^{\circ}\text{C}.$) made it difficult to pump off monomer under vacuum. It was however found possible to precipitate the product from methanol (10-15 vols.) cooled to -10 to $-20^{\circ}\text{C}.$ The polymer was immediately separated in weighed filter crucibles and washed with methanol cooled to -10 to $-20^{\circ}\text{C}.$, and dried at $35^{\circ}\text{C}.$ and 1-2 mm. Hg. In the experimental section III, particular methods of separation used for each monomer have been mentioned separately.

(5). Separation of FeCl_3 Catalyst from Propylene Oxide and Styrene Oxide Polymers.

A sufficient amount of benzene was added to the crude polymer of propylene oxide and styrene oxide to give a clear solution. The amount varied from 50-200 ml. depending on the molecular weight of the polymer formed and the degree of conversion. The catalyst (FeCl_3) was then removed by adding 10% aq. HCl (50 to 100 ml.) and shaking thoroughly. The colourless solution of polymer in benzene was washed three to four times with water, then with a dilute aqueous solution of sodium bicarbonate solution, and finally with successive amounts of distilled water till the water was neutral to litmus. The benzene solution was

then frozen to -78°C . in a dry ice-acetone bath and was freeze-dried under vacuum (2-3 mm.Hg). 24 hours drying at room temperature was found quite sufficient to give constant weight of polymer.

(6). Fractionation of Polypropylene Oxide Polymer.

Purified polymer obtained as described above, was dissolved in hot acetone to make a 1-3% solution and chilled to -30°C . for 1 hour. Solid polymer crystallized from solution, and was separated by filtration. The white solid had a melting point of $68-70^{\circ}\text{C}$.

(7). Methods of Molecular Weight Determination.

Polymers ranging from viscous syrups to tough solids have been obtained during this study of the polymerisation of cyclic ethers. Most of the polymers were found to be of low molecular weight (Mol.wt. 6000) although polytetrahydrofuran was of high molecular weight. The lower molecular weights were determined by means of the freezing-point depression in benzene [105-106]. For polytetrahydrofuran, intrinsic viscosities were determined in benzene solution.

(i) Freezing-Point Depression Method.

Normally a plot of the molecular weights (calculated from the freezing point depression) vs. concentration yields a straight line, and extrapolation to zero concentration gives the correct value of the molecular weight. This method was tried in the present study but most samples of polymer did not give a linear relationship. Presumably this is due to a random distribution of molecular weight in the sample. It was therefore considered that a sufficiently accurate indication of the molecular weights could be obtained by measurement at a single concentration (0.5-0.6% w/w) in benzene.

The freezing point apparatus consisted of an inner freezing tube fitted with a Beckmann thermometer and a stirrer, an air-jacket surrounding the inner tube to ensure a slower and more uniform rate of cooling of the liquid, and a thermos flask, with stirrer, containing melting ice. The temperature of the charged cryoscopic tube fell at a rate of $0.2 - 0.5^{\circ}\text{C.}$ per minute, which is quite a satisfactory temperature differential. A weighed amount of benzene was placed in the cryoscopic tube, the stirrer and thermometer were inserted and the tube placed in the channel of the cold reservoir. The freezing point of the benzene and of solutions of known concentration was then determined.

The difference of freezing points of pure solvent (t) and polymer solution (t_1) give the depression of freezing point $\Delta T (= t_1 - t)$ and the molecular weights were calculated from the formula :-

$$\text{Molecular weight} = \frac{1000 K_w}{\Delta T W}$$

where w = weight of polymer,

W = weight of solvent (benzene)

K = cryoscopic constant.

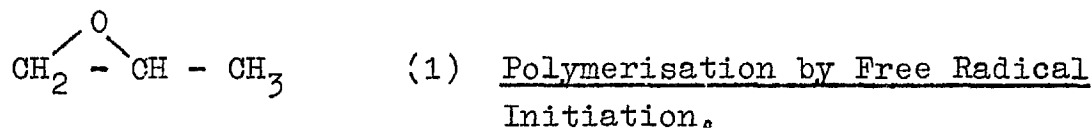
The value of K was determined by using a solute (dipheyl) of known molecular weight and was found to be 5.631.

(ii) Viscosity Method.

An M.2 standard viscometer was used for viscosity determinations on benzene solutions in a constant temperature bath at $30^\circ \pm 0.1^\circ\text{C}$. The efflux time (t) needed for a given volume of polymer solution to flow through a capillary tube was compared with the corresponding efflux time (t_0) for the solvent. The flow time (t) for each polymer solution was determined at four different polymer concentrations, and concentrations, C , were expressed as g/100 ml. (benzene). The intrinsic viscosity $[\eta]$ was calculated from t , t_0 and C by the following relationships :

Relative viscosity	$\eta_r = t/t_0$
Specific viscosity	$\eta_{sp} = \frac{t - t_0}{t_0}$
Reduced viscosity	$\eta_{red} = \eta_{sp}/C$
Intrinsic viscosity	$[\eta] = (\eta_{sp}/C)_{C=0}$

The intrinsic viscosity $[\eta]$, which is independent of concentration by virtue of the extrapolation to $C = 0$, is the quantity usually correlated with the molecular weight.

SECTION III.RESULTS AND DISCUSSION.1. Polymerisation of Propylene Oxide.

In the light of the previous work [3] on cyclic ether polymerisation, it was decided to study the effect of pressure on the polymerisation of propylene oxide. Benzoyl peroxide was usually used as initiator but in some runs 2,2' azo-bis-isobutyronitrile (AIBN) was also used. Most of the reactions were carried out at 60°C. A series of runs were made up to 10,000 atm. and for a maximum period of 68 hours.

The presence of non-volatile residue after heating the product on a water bath was taken to be a positive criterion of polymerisation as the normal boiling point of the monomer is 34°C. Any remaining unreacted monomer or other volatile substances were removed by heating at 35°C. and 1-2 mm. Hg.

In most cases very small traces of non-volatile residue were found but never more than 0.8 to 1.2%. As it appeared that no appreciable polymerisation occurred

under these conditions, further work with the free radical initiators was abandoned and it was decided to proceed with different initiators.

(2) Ionic Initiation.

In these experiments the anhydrous ferric chloride-propylene oxide complex, obtained as described in Section II, was used as the catalyst. The polymerisation of propylene oxide was carried out at various pressures and catalyst concentrations, and the rate of polymerisation and the molecular weight of the product were determined. All runs were carried out at 80°C. and the percentage of catalyst given in Table 1 represents the weight of complex present in 100 g. of monomer. No solvent was used although a few experiments were attempted in di-ethyl ether as solvent. It was found that in this solvent the solubility of the complex was very poor and it was difficult to keep for more than a few hours, even at -20°C., without the appearance of a brown precipitate. On the other hand, the catalyst complex is much more stable in propylene oxide and can be stored easily for 4 to 5 days at -20°C. under dry nitrogen (oxygen-free). Hence all the polymerisation reactions were carried out in bulk.

A single batch of propylene oxide - ferric chloride complex of known composition was prepared and used for each set of experiments.

The results obtained with each batch are shown in Tables 1 to 5 and Figs. 6 and 7. The methods of separation and fractionation of polymers are given in Section II.

TABLE 1.

POLYMERISATION OF PROPYLENE OXIDE.

Initiator : FeCl_3 - Propylene oxide complex.Temperature 80°C .

Batch A.

Initiator concentration : 2.5 wt.%.
.

Run No.	Pressure (atm)	Time (hrs)	Conversion (wt.%)	Mol.Wt. of Polymer *
1	1	4	13.78	690
2	1	8	24.47	880
3	1	17	33.41	1050
4	1	37	54.71	1990
5	1	72	76.34	1860
6	4000	4	21.33	790
7	4000	10	32.20	1620
8	4000	17	49.33	1680
9	4000	39	81.65	2300
10	4000	72	95.62	2790

* Determined cryoscopically in benzene

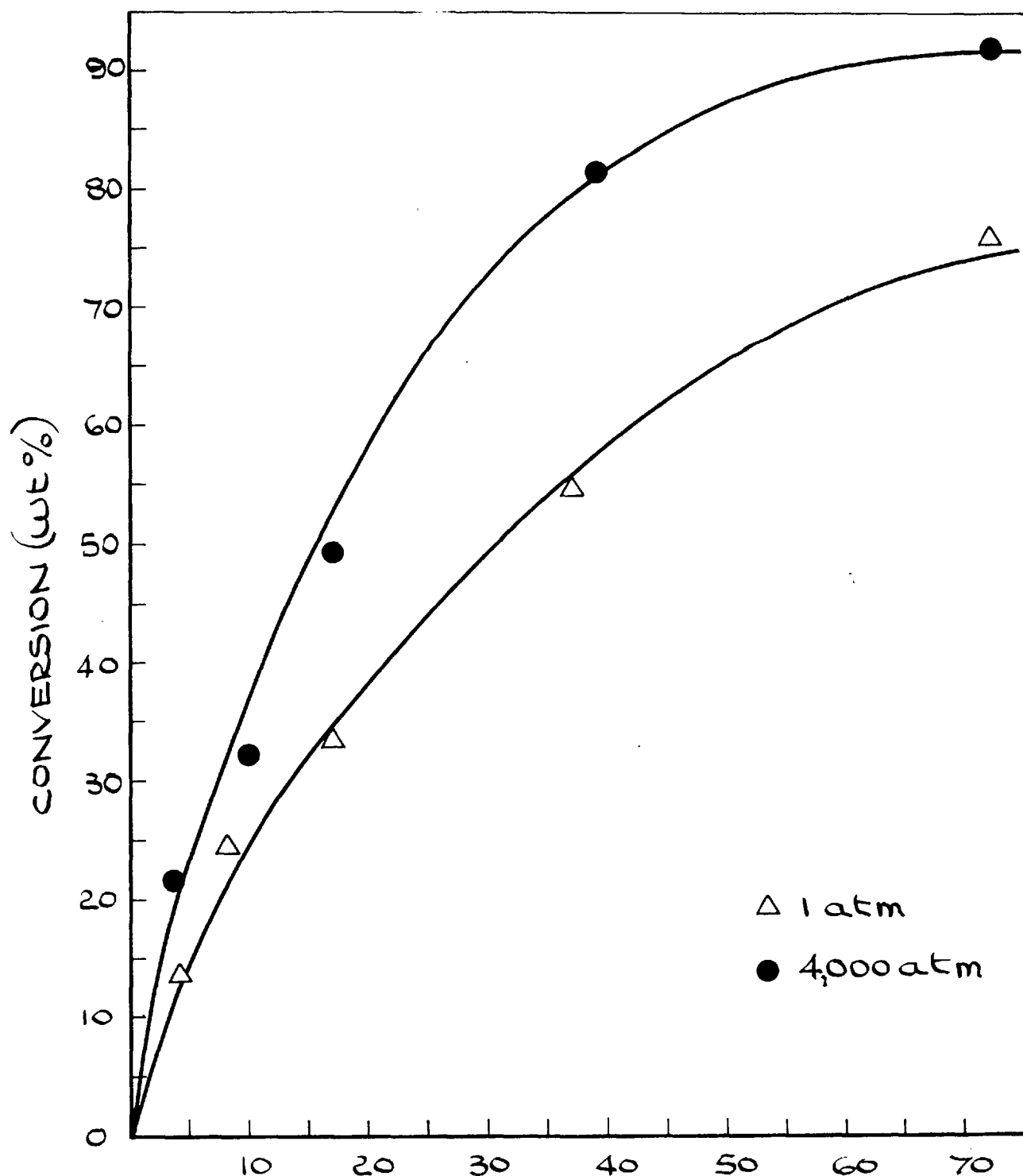


FIG 6
TIME (HRS)
POLYMERISATION OF PROPYLENE OXIDE (80°)
INITIATOR (PROPYLENE OXIDE- FeCl_3 COMPLEX)
= 2.5 (wt%)

TABLE 2.

POLYMERISATION OF PROPYLENE OXIDE.

Initiation : FeCl_3 -Propylene oxide complex.Temperature 80°C .

Batch B.

Initiator concentration : 2.05 wt.%

Run No.	Pressure (atm)	Time (hrs.)	Conversion (wt.%)	Molecular Weight of Polymer *
11	500	5	11.41	450
12	500	8	13.28	560
13	500	11.5	20.47	-
14	500	20	33.08	630
15	500	45	44.14	-
16	500	73	70.17	1030
17	4000	5	26.09	960
18	4000	15	30.91	1220
19	4000	45	57.26	1320
20	4000	75	85.62	1530

* Determined cryoscopically in benzene.

TABLE 2(a).

DEPENDENCE OF THE RATE OF POLYMERISATION
OF PROPYLENE OXIDE ON PRESSURE.

Initiator Concentration : 2.05 wt. %

(Propylene oxide- FeCl_3 Complex).

Pressure (atm.)	Rate of Polymerisation Wt.% Polymer/hr.	
500	2%	Initial rate of polymerisation at approximately equal
4000	4%	conversion (20%)

TABLE 3.

POLYMERISATION OF PROPYLENE OXIDE.

Batch C.

Initiator Concentration : 1.2 wt.%

Run No.	Pressure (atm.)	Time (hrs.)	Conversion (wt.%)	Molecular Weight of Polymer *
21	1	4	2.9	-
22	1	8	10.2	1120
23	1	18	14.0	-
24	1	35	17.2	2320
25	1	60	23.9	2460
26	4000	4	8.3	1500
27	4000	7	16.7	-
28	4000	17	28.1	2730
29	4000	35	48.5	3450

* Determined cryoscopically in benzene.

TABLE 3(a)

DEPENDENCE OF THE RATE OF POLYMERISATION OF
 PROPYLENE OXIDE ON THE INITIATOR CONCENTRATION.

Initiator : FeCl_3 -Propylene Oxide Complex.

Initiator (Wt.%)	Pressure (atm.)	Rate of Polymerisation (Wt.% Polymer/hr.)	
1.2	1	1	Initial Rate of Polymerisation based on approximately equal conversion (10%)
1.2	4000	2	
2.5	1	3	Initial Rate of Polymerisation based on approximately equal conversion (15%)
2.5	4000	~ 5	

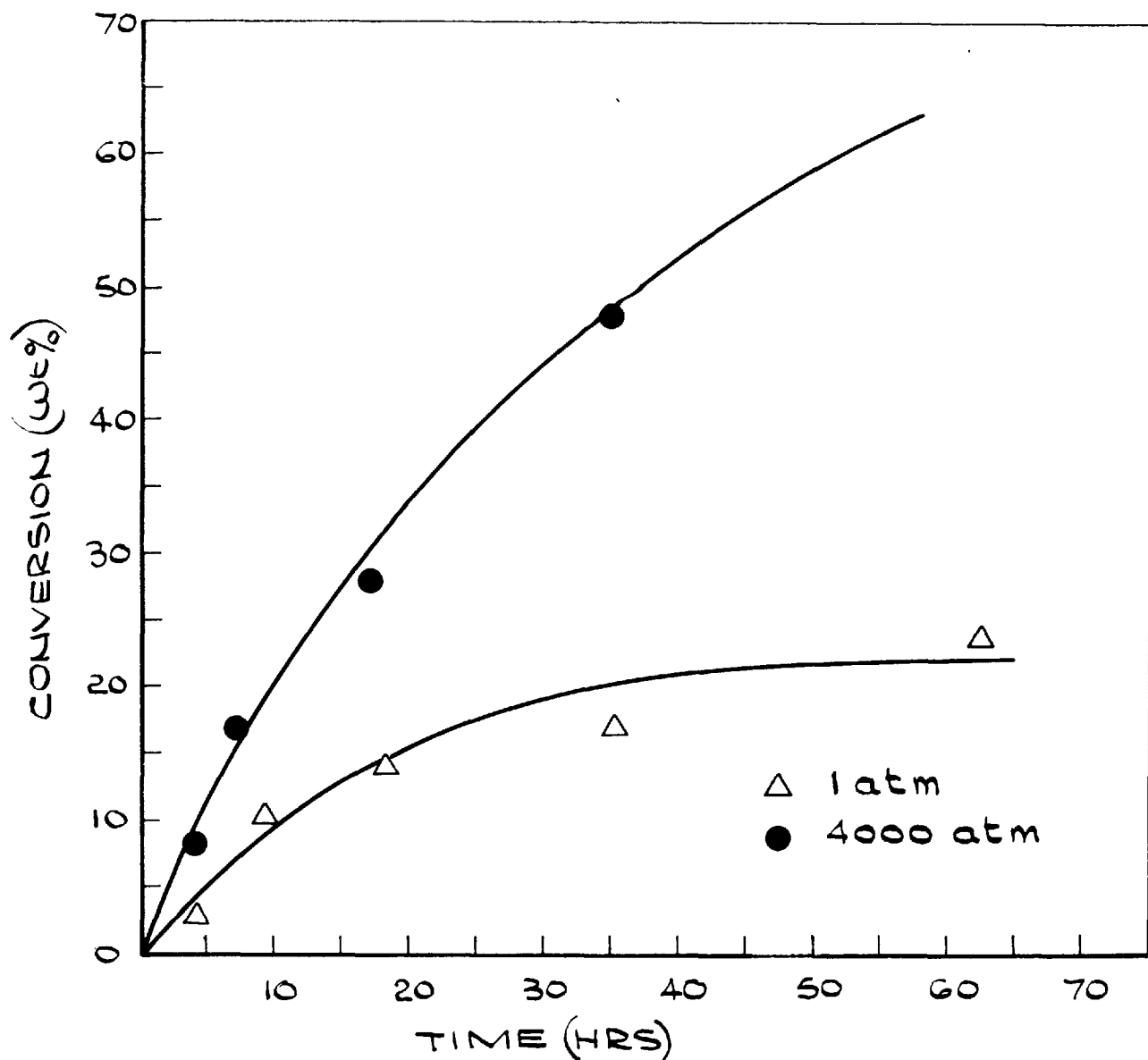


FIG 7 POLYMERISATION OF PROPYLENE OXIDE (80 °C)
 INITIATOR (PROPYLENE OXIDE -
 - FeCl_3 COMPLEX) = 1.2 (wt%)

TABLE 4.

THE VARIATION OF MOLECULAR WEIGHT WITH
CONVERSION IN THE POLYMERISATION OF
PROPYLENE OXIDE AT 3,000 ATM.

Initiator : FeCl_3 -Propylene oxide Complex.

Temperature 80°C .

Batch D

Initiator Concentration : 2.72 wt.%

Run No.	Pressure (atm.)	Time (hrs.)	Conversion (wt.%)	Molecular Weight of Polymer *
30	3000	5	12.1	630
31	3000	8	14.8	820
32	3000	15	20.17	-
33	3000	45	49.25	1880
34	3000	75	81.16	2370

* Determined cryoscopically in benzene.

TABLE 5.

RESULTS OF THE FRACTIONATION OF PROPYLENE OXIDE
POLYMER *

Initiator FeCl_3 -Propylene oxide Complex.
Temperature 80°C .

Run No.	Initiator Concn. (wt.%)	Time (hrs)	Pressure (atm.)	Cryst. (wt.%)	Molecular Weight of Polymer *	
					Crystalline	Amorphous
6	2.5	4	4000	14.8	-	-
7	2.5	10	4000	11.1	2250	670
8	2.5	17	4000	9.5	-	-
9	2.5	39	4000	28.1	5630	670
10	2.5	72	4000	57.6	-	-
2	2.5	8	1	11.5	-	-
5	2.5	72	1	13.4	963	520

* The method of fractionation is described in Section
II-3(6)

* Determined cryoscopically in benzene.

Discussion of the Results for Propylene Oxide.

The Effect of Pressure on the Rate of Polymerisation.

The polymerisation of propylene oxide with FeCl_3 - propylene oxide catalyst complex becomes heterogeneous, by separation of polymer, at low conversions ($<10\%$), the interpretation of the kinetic data would thus in any case be complicated but, in addition, the unusual experimental problems make the determination of accurately reproducible results extremely difficult and this difficulty is greater at high pressures.

The data in Tables 1, 2 and 3 indicate that the rate of polymerisation does increase with increasing pressure. In Tables 2(a) and 3(a), the rates of polymerisation calculated on the basis of polymer obtained in one hour. These are the initial rates which are based approximately on equal conversion. These initial rates can be obtained only very approximately, but the increase is about 2-fold in the range 1-4,000 atm.

Price and co-workers [16] and Gee and co-workers [15] have made a detailed kinetic study of the polymerisation of propylene oxide with the FeCl_3 -propylene oxide complex.

Price et al. concluded that the rate of polymerisation is directly proportional to the catalyst

concentration : that the rate of polymerisation in solution is independent of the propylene oxide concentration over a considerable range; and that the molecular weight depends on catalyst concentration and conversion.

The results of the present work seem to show that catalyst concentration has some effect on the pressure-dependence of the rate of polymerisation. At the higher catalyst concentrations used (Fig.6), the initial rate of polymerisation at 4,000 atm. is only about twice that at 1 atm. At the lowest concentration (Fig.7), the initial rate increases approximately three times.

Moreover this difference may be within the experimental error and also a co-catalyst (water or HCl) may be present in variable amounts in the different batches of catalyst. The presence of different amounts of co-catalyst might affect the change of rate with pressure. Gee et al. [15] summarised the effects of water when present in this type of reaction as (a) an increase in the overall rate, (b) a reduction or eventual elimination of the acceleration period observed with dry propylene oxide at 90°C., (c) reduction in the yield of polymer, and (d) an increase in crystalline/amorphous ratio of the propylene oxide polymer.

The results for the initial rate of polymerisation given in Tables 2(a) and 3(a) although not very accurate, show that the reaction is accelerated at high pressure, but the increase in rate is relatively small compared with free radical polymerisation. As mentioned earlier no free radical polymerisation could be achieved, even at 10,000 atm.

The Effect of Pressure on the Molecular Weight of Polypropylene Oxide.

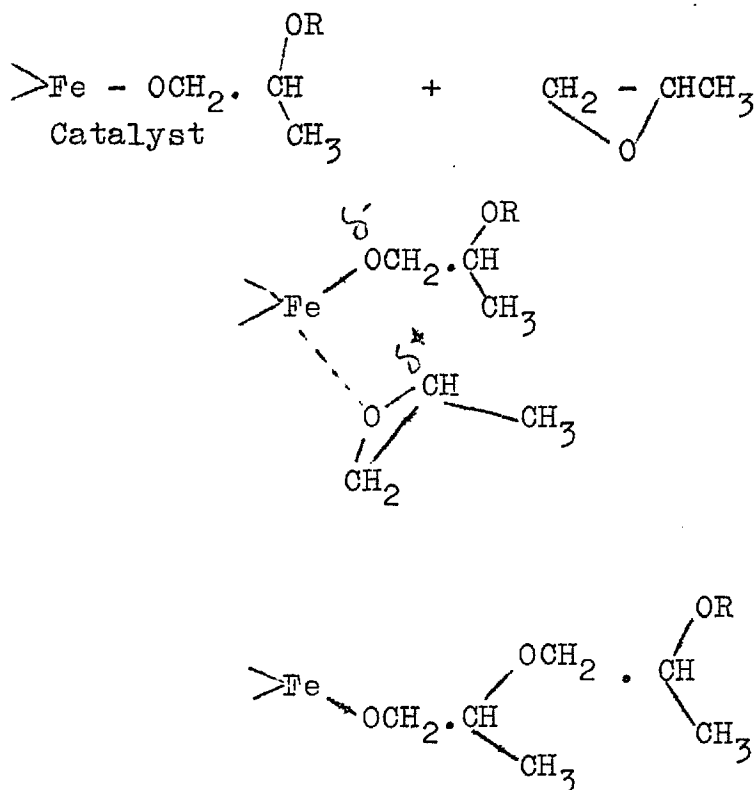
The increase in pressure seems to have no large effect on the molecular weight of the polymer. However, it can be seen from Tables 1, 2 and 3 that there is a slight tendency for the molecular weight to increase with increasing pressure. The effect is partly obscured by the increase in molecular weight definitely with increase in conversion, but from Table 1, runs 3 and 7 at 1 and 4000 atm., of approximately equal conversion, the molecular weight increases from 1050 to 1620. This increase in molecular weight with pressure is not as high as that obtained by Merret and Norrish for the free radical polymerisation of styrene [58]. They found an approximately three-fold increase in the molecular weight in the range 1 to 3000 atm., which was attributed to a decrease in the rate of the termination reactions relative to the rate of chain

propagation. In the case of the propylene oxide polymerisation there seems to be no such pronounced effect on the relative rates.

The Effect of Catalyst Concentration on the Rate of Polymerisation and the Molecular Weights.

The effect of catalyst concentration on the rate of polymerisation is large and the rate seems to be approximately proportional to this concentration. Although some of their results show a direct dependence of initial rates on catalyst concentration, Price et al.[16] suggested that the rate of polymerisation is actually not dependent on the catalyst concentration but on the catalyst sites available at heterogeneous surfaces.

The type of propagation mechanism suggested involves insertion of an incoming monomer at the catalyst via a co-ordination complex :

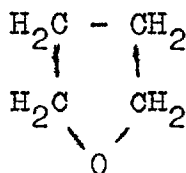


If this is the correct mechanism pressure would be expected to shift the equilibrium towards the charged complex but to retard the disappearance of the charges in the final step. This could possibly account for the small overall effect of pressure on the reaction rate.

The Effect of Pressure on the Formation of
Crystalline and Amorphous Polymers.

In this work the polymers obtained at high pressure contained a greater percentage of crystalline materials and this was especially so at higher conversions (Table 5). At 4,000 atm. polymers obtained in 72 hours give 57.6% crystalline polymer whereas at 1 atm. under similar conditions only 13.4% crystalline polymer. This may be partly an effect of the higher conversion and higher molecular weight obtained under pressure. It is possible that on fractionation (as described in Section II-3(6)) while the higher molecular weight polymer precipitated out more of the low molecular weight material remains in the solvent. The presence of moisture plays a very important part in these reactions and the formation of crystalline polymer depends on its presence. Colclough [40] and his co-workers have found that the production of crystalline polymer is associated with the presence of water in the reaction mixture and that no crystalline polymer is obtained when the FeCl_3 , propylene oxide and diluents are anhydrous. In this work great care was taken to use as dry conditions as possible, but it was still not possible to exclude moisture completely from the reacting system.

2. The Polymerisation of Tetrahydrofuran.



(1). Free Radical Initiation.

As in the case of propylene oxide free-radical initiators were found to be ineffective in the polymerisation of this monomer. Benzoyl peroxide and 2,2' azo-bis-isobutyronitrile were used as concentrations up to 2% and 1% by weight, respectively. Several runs were carried out at pressures up to 10,000 atm., at 60°C., for maximum periods of three days. Unreacted monomer and volatile material were pumped off under vacuum (2-3 mm.Hg) at room temperature. Negligible quantities of non-volatile residue (0.5-1%) were obtained and they were not examined further.

2. Ionic Initiation.

Since the radical initiators were ineffective, the BF_3 /ethyl ether complex was used as catalyst. The stock solution was made as described in Section II.

The effect of pressure on the polymerisation of tetrahydrofuran was studied at several catalyst concentrations.

and for each set of experiments a single batch of known catalyst concentration was used. The results obtained at various pressures and catalyst concentrations are given in Tables 6 and 7, and are shown in Figures 8 and 9.

TABLE 6.THE EFFECT OF PRESSURE ON THE POLYMERISATION
OF TETRAHYDROFURAN.Initiator : $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ Temperature : 60°C .

Run No.	Pressure (atm.)	Time (hrs.)	Conversion %	Molecular Weight (cryoscopic)	$[\eta]$ in Benzene
35	1000	6	1.31	-	-
36	1000	18	1.82	-	-
37	1000	26	1.61	-	-
38	1000	68	2.91	700	0.08
39	1750	6	1.41	-	-
40	1750	11	2.21	710	0.07
41	1750	16	5.13	-	-
42	1750	24	5.22	1600	0.1
43	2500	5	4.53	4230	0.25
44	2500	8	5.81	-	-
45	2500	10	7.64	-	-
46	2500	16	14.1	-	0.49
47	4000	2	5.21	-	1.17
48	4000	3.5	10.8	-	-
49	4000	5	14.2	-	-
50	4000	7	18.3	-	2.03

TABLE 6 (continued)

Run No.	Pressure (atm.)	Time (hrs.)	Conversion %	Molecular Weight (cryoscopic)	[η] in Benzene
51	5400	1	7.9	-	2.13
52	5400	2	18.56	-	-
53	5400	4	27.50	-	-
54	5400	6	31.3	-	2.2
55	1	48	0.5	-	-
56	1	68	0.52	-	-

TABLE 6(a).THE DEPENDENCE OF THE RATE OF POLYMERISATION OF
TETRAHYDROFURAN ON PRESSURE.

Initiator $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ 2% V/V
Temperature $60^\circ\text{C}.$

Pressure (atm.)	Rate Conversion (wt.%/hr.)
1	< 0.01
1750	0.17
2500	0.86
4000	2.8
5400	9.3

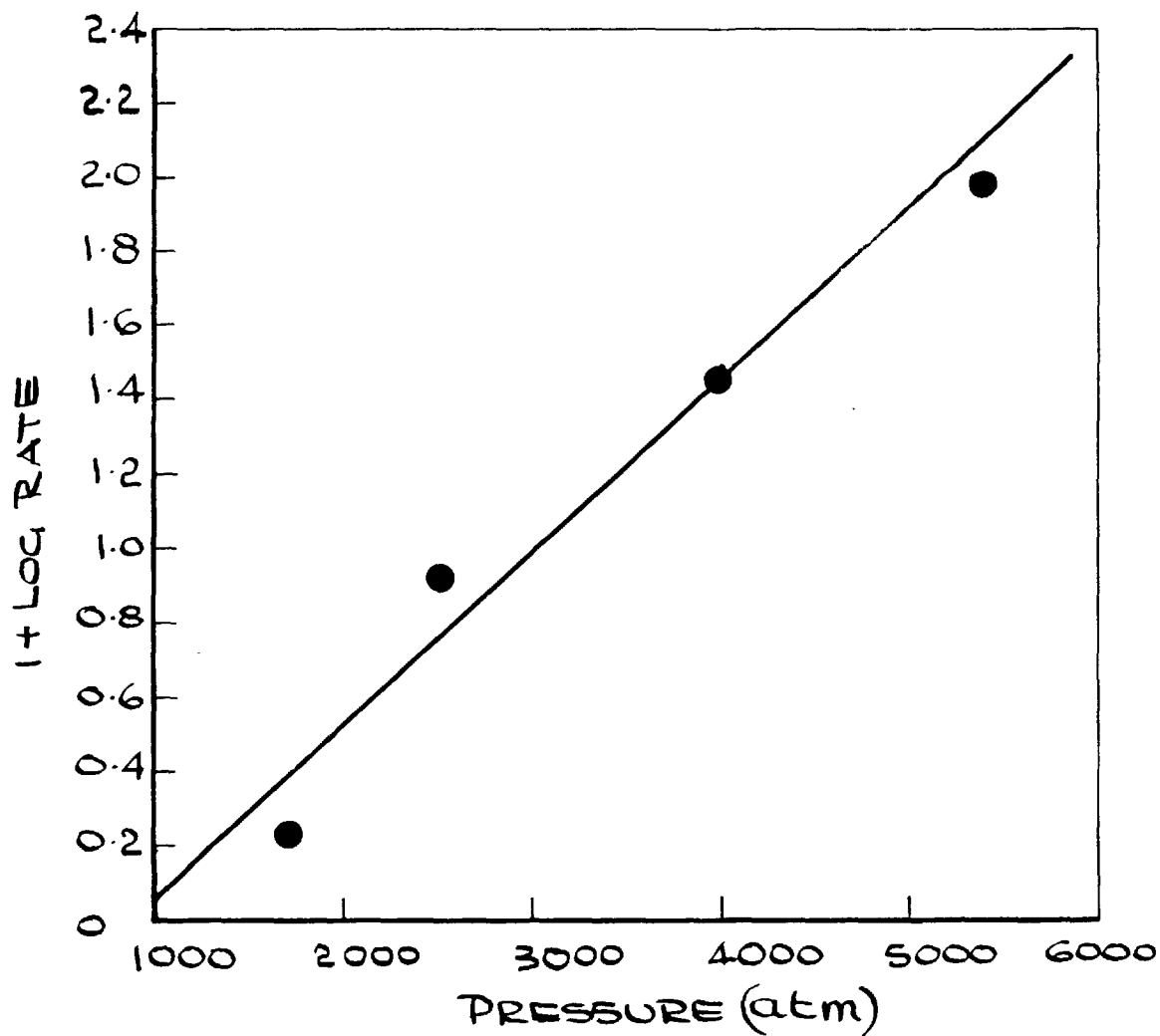


FIG 8 PRESSURE EFFECT ON THE RATE
OF POLYMERISATION OF TETRAHYDROFURAN(60°)

$\text{BF}_3 (\text{C}_2\text{H}_5)_2\text{O} = 2\% (\text{V/V})$

TABLE 7.THE EFFECT OF INITIATOR CONCENTRATION ON THE
POLYMERISATION OF TETRAHYDROFURAN.

Pressure : 5400 atm.

Temperature: 60°C.

Run No.	BF ₃ /Ethyl Ether (% V/V)	Time (hrs.)	Conversion %	[η] in benzene
57	0.5	16	1.5	0.32
58	0.5	24	3.21	0.68
59	0.5	63	5.62	-
60	0.5	45	5.10	-
61	1.0	2	3.34	2.87
62	1.0	5	4.40	-
63	1.0	8	7.3	3.01
64	1.0	18	19.5	3.32
51	2.0	1	7.9	2.13
52	2.0	2	18.56	-
53	2.0	4	27.5	-
54	2.0	6	31.3	2.2
65	3.0	1	11.9	1.2
66	3.0	3	27.5	1.58
67	3.0	5	41.5	1.6

TABLE 7(a).THE DEPENDENCE OF THE RATE OF POLYMERISATION OF
TETRAHYDROFURAN ON INITIATOR CONCENTRATION.Initiator : $\text{BF}_3 (\text{C}_2\text{H}_5)_2\text{O}$

Pressure : 5400 atm.

Temperature: 60°C .

Initiator Concentration % (V/V)	Rate of Polymerisation Wt.% Polymer/hour
0.5	0.11
1	1.1
2	9.3
3	13.3

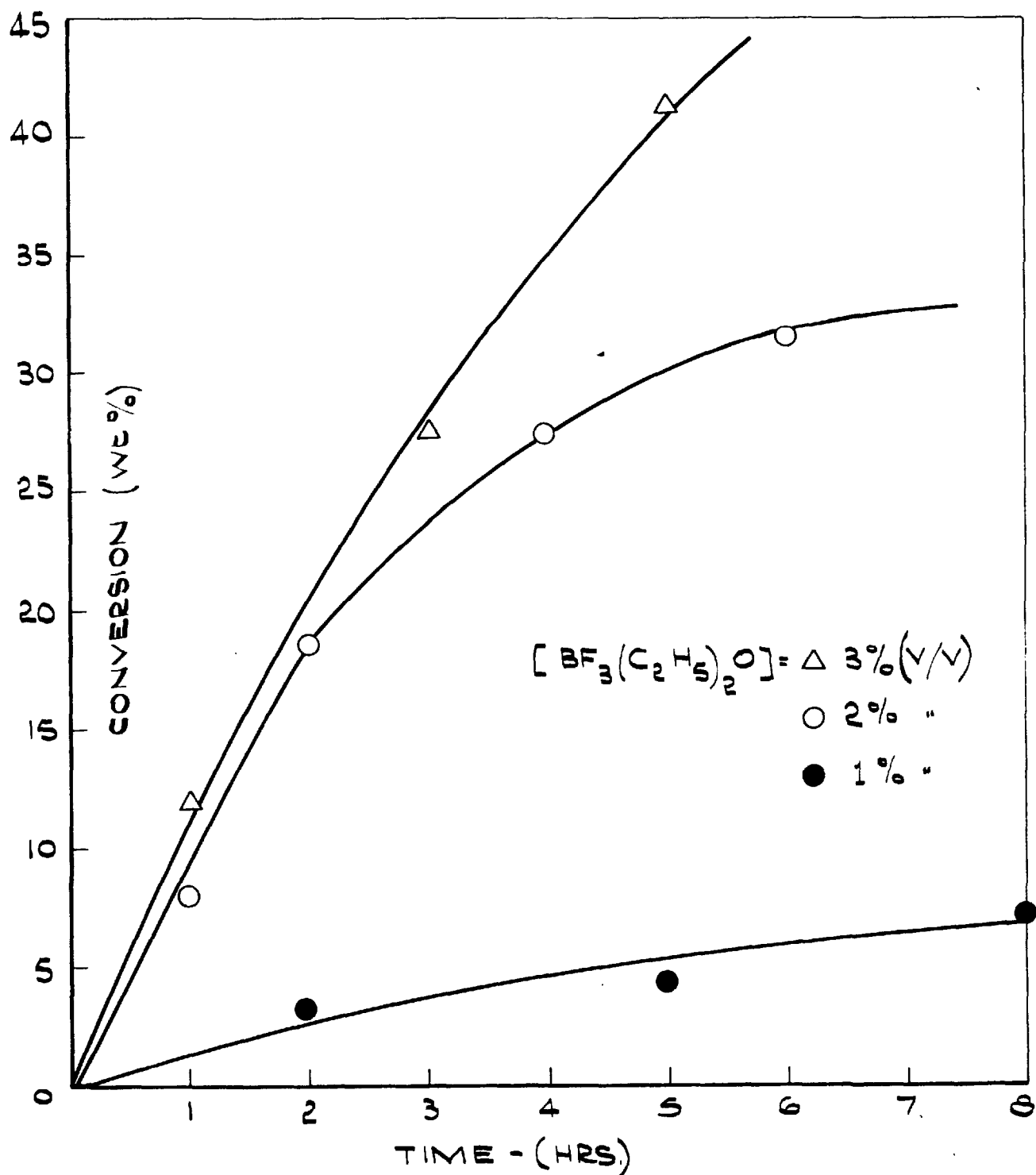


FIG. 9 EFFECT OF INITIATOR $(BF_3(C_2H_5)_2O)$ CONCENTRATION ON THE POLYMERISATION OF TETRAHYDROFURAN. (60°) . AT 5400 atm

The Depolymerisation of Polytetrahydrofuran.

Two samples of the polymer obtained at 8360 atm. and 60°C., with different catalyst concentrations were stored for prolonged periods at room temperature and re-examined in order to investigate the stability of the polymer. The results are given in the following table.

TABLE 8.

Run No.	$\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ % (V/V)	Storage Time (weeks)	Solubility of Polymer in benzene.	[η] in benzene
68	0.5	0	Swells	-
		11	soluble	1.76
		29	soluble	
69	2.0	0	Swells	-
		4	soluble	0.11
		24	soluble	0.08
		33	soluble	0.065

The Effect of Pressure on the Conductivity of Boron Trifluoride Diethyl Etherate in Di-iso-propyl ether at 60°C.

In order to obtain some indication of possible effects of pressure on ionic equilibrium involving the initiator the conductance of solutions of boron trifluoride ethyl etherate in di-iso-propyl ether was measured up to 2700 atm.

Freshly made solutions of known concentrations of boron trifluoride ethyl etherate in di-iso-propyl ether were used for each run. In order to calculate the specific conductivity, the conductivity cell was standardised with 0.1 N KCl solution, which has the known equivalent conductivity of $128.96 \text{ ohm}^{-1} \text{ cm}^2$ at 25°C. [107]. The cell constant was calculated and found to be 0.6846 cm^{-1} .

The assumption that the cell constant is independent of pressure has been confirmed by Strauss [108], who has calculated that the change in cell dimensions in a glass conductivity cell with pressure has an insignificant effect on the cell constant for pressures below 3000 atm. The range of temperature used in this work has a negligible effect on the cell constant [109]. The conductances for various concentrations of boron trifluoride diethyl etherate in di-iso-propyl ether, at a number of pressures, are given

in the following tables. The conductance and pressure relationships at various $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ concentrations are given in Table 9 and shown in Fig.10.

TABLE 9.MOLAR CONDUCTANCE OF BORON TRIFLUORIDE DIETHYL
ETHERATE IN DI-ISO-PROPYL ETHER AT 60°C.Units : (mhos cm² mole/litre) x 10⁻³

Concentration (moles/litre)	0.156	0.2345	0.318
Pressure (atm.)			
1	0.22	0.56	1.31
300	0.26	0.64	-
470	-	0.65	1.49
710	0.29	0.69	1.55
875	0.32	0.74	1.65
1200	0.34	0.79	1.73
1440	0.36	0.83	1.83
1680	0.38	0.88	1.92
1920	0.41	0.92	1.99
2160	0.42	0.96	2.08
2400	0.44	1.00	2.15
2650	0.45	1.04	2.23

(Concentration uncorrected for compressibility;
corrected for temperature).

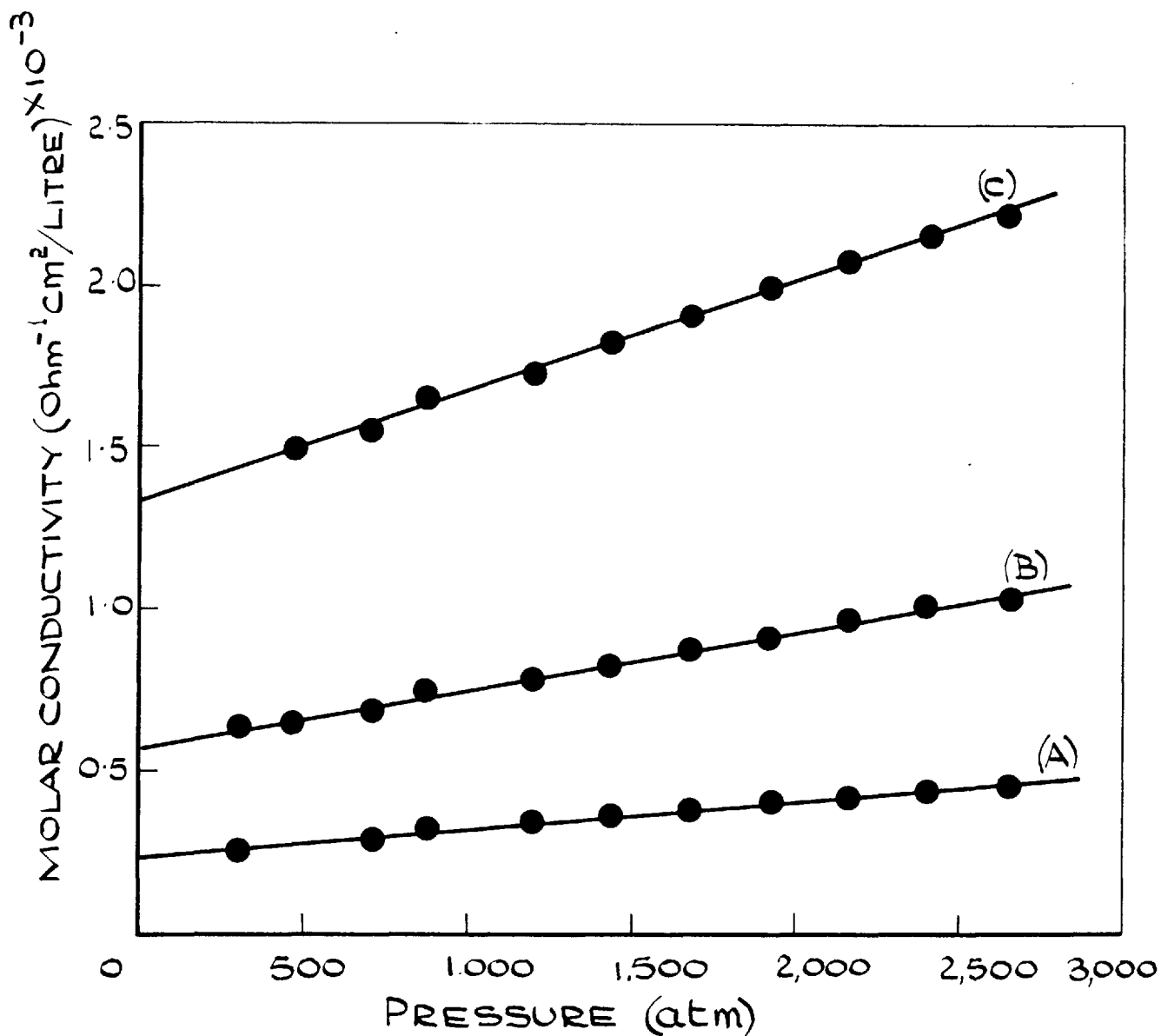


FIG 10 EFFECT OF PRESSURE ON THE CONDUCTIVITY OF $\text{BF}_3 (\text{C}_2\text{H}_5)_2\text{O}$ IN DI-ISO PROPYL ETHER AT 60°

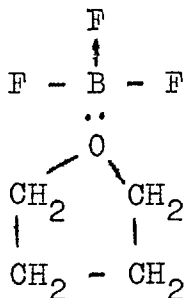
$[\text{BF}_3 (\text{C}_2\text{H}_5)_2\text{O}]$ (MOLE/LITRE) = (A) 0.156;
 (B) 0.2345; (C) 0.318;

Discussion.

The Polymerisation of Tetrahydrofuran at 1 atmosphere.

A few runs were carried out at 1 atm. and 60°C. with tetrahydrofuran in the presence of boron trifluoride diethyl ether. Runs were made at different durations. The results of two experiments of 48 and 68 hours duration respectively, are shown in Table 6 (Runs 55 and 56). Only a minute non-volatile residue was obtained after pumping-off the unreacted monomer and other substances. Boron trifluoride diethyl etherate is thus not a catalyst for the polymerisation under these conditions.

Tetrahydrofuran and boron trifluoride are known to form an addition compound [111]. This addition compound was prepared by reaction of 35.0 cc. of tetrahydrofuran with 35 cc. of BF_3 at the temperature of liquid nitrogen. This addition product melts to a colourless liquid at 8-10°C., which boils [104] at 69°C./4 mm., and probably has the structure :



The rigidity of the five-membered ring of tetrahydrofuran greatly reduces the possibility of steric strain and the tetrahydrofuran-boron trifluoride complex is far more stable than boron trifluoride diethyl etherate and boron trifluoride di-iso-propyl etherate. Although it seems rather unlikely that this complex could have been formed in the reaction system used in this work, the possibility has not been eliminated, and it would be expected that the complex would be an ineffective catalyst for the polymerisation of tetrahydrofuran.

The Polymerisation of Tetrahydrofuran at High Pressure.

Although the rate of reaction is negligibly small at 1 atm., at high pressures the rate of polymerisation of tetrahydrofuran with boron trifluoride diethyl etherate (Table 6a) becomes conveniently measurable. Pressures up to 5400 atm. were used, and the results of runs carried out for different periods of time at 60°C. were plotted as wt.% conversion vs. time and the initial slopes of the lines are taken as the overall rate of polymerisation at each particular pressure and are given in the table.

There is about a 10.8-fold increase in the rate of polymerisation between 2500 atm. and 5400 atm., but the

acceleration is less in the upper part of the pressure range. Between 4000 and 5400 atm. the rate increases about 3.8-times.

Merrett and Norrish [58] reported similar behaviour for the free radical polymerisation of styrene. They found that the logarithm of the rate of polymerisation was directly proportional to the pressure in the range 3000 - 5000 atm. The logarithm of the rate of polymerisation of tetrahydrofuran (Fig.8) at constant catalyst concentration, and at 60°C., is also nearly directly proportional to the pressure in the range 2500 - 5400 atm. The relationship is not clear at lower pressures. At lower pressures low percentage conversions were obtained and the conversion vs. pressure results are erratic. There is evidence (Table 8) that at 1 atm. the polymer slowly depolymerises and it seems that for low conversions this process may affect the results significantly.

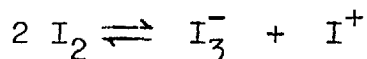
The acceleration factor of ~ 10.8 in the range 2500 to 5400 atm. shows that the effect of pressure is larger than in the free radical polymerisation of styrene, for which factors of 15 and 13.5 have been reported [58,104] for the range 1 to 5000 atm.

Equation 1 (page 24) can be applied to the results to calculate an apparent volume of activation for the polymerisation reaction. For the tetrahydrofuran

polymerisation the value of ΔV^* is found to be -30 cc/mole in the range 1750 to 5400 atm. This value is considerably higher than the corresponding volumes of activation for free-radical vinyl polymerisation. Typical values [57] for these are : styrene -18 cc/mole; methyl methacrylate -19 cc/mole; -methyl styrene -17 cc/mole. The quantity ΔV^* so obtained is composite and contains terms attributable to each stage of the reaction, but in the vinyl polymerisations the dominant term is known to be ΔV_p^* , the volume of activation for chain growth. In these reactions also, ΔV_p^* (and the apparent ΔV^*) are less negative than the overall volume difference, ΔV , between monomer and polymer, which indicates that the contraction accompanying formation of the transition state for chain growth is lower than the total contraction for the reaction. In contrast with this the measured ΔV for tetrahydrofuran polymerisation is 17.1 cc/mole, which is only about half the apparent ΔV^* .

This difference suggests that in the ionic polymerisation the term for chain-growth may not be the largest component of ΔV^* . The effect of pressure on the ionic polymerisation of isopentyl vinyl ether catalysed by iodine was investigated by Hamann and Teplitsky [9], and on the iodine-catalysed polymerisation of isobutyl vinyl ether by Nahumy. [8]. In both cases it is pointed out that

part of the observed increases in rate may be due to a shift of the equilibrium



to the right at high pressures.

Pressure enhances the ionisation of weak electrolytes [48] (because the solution of the ions is accompanied by a volume contraction) and lowers the free energy of the ions, with respect to that of the unionised molecules. The ionisation of carboxylic acids in water involves a contraction of about 12 cc/mole and that of amines in water a contraction of about 28 cc/mole.

The conductivity measurements on $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ in iso-propyl ether show that there is an appreciable increase of conductivity with pressure (Fig.10). There appear to have been no studies of the nature of such solutions even at 1 atm., and it is not known whether they can be treated as weak electrolytes or to what extent association to ion-pairs and higher complexes occurs. It is also not known whether free ions or ion pairs and higher associations are the most effective catalyst for polymerisation.

The results also show an increase in molar conductivity with an increase in concentration. This type

of behaviour is usually found only with electrolytes in solvents of low dielectric constant, and, as in the case of quaternary ammonium salts in benzene [80,93] is believed to indicate a high degree of ion association.

In these circumstances it is not justifiable to treat the results as a normal effect of pressure on a simple type of ionic dissociation. However it is reasonable to suppose that the increase with pressure of the ionic character of the solution favours the polymerisation and contributes to the observed acceleration. The increase in molar conductivity with pressure is between 1.5 and 2.0 times in the range 1 to 2000 atm. Very few results have been reported for the effect of pressure on the conductivity of non-aqueous solutions but Hamann and Strauss [87] found a similar increase with pressure for the conductivity of piperidine in methanol, and it has been calculated [108] that the corresponding volume change on ionisation is

-27 cc/mole. It is therefore quite possible that the change in the initiator equilibrium may contribute a substantial part of the observed ΔV^* of -30 cc/mole for the overall polymerisation.

The Effect of Pressure on the Molecular Weight of Tetrahydrofuran Polymers.

Low molecular weight polymers were obtained (Table 6) in the lower pressure range (1000-1750 atm.), and the molecular weights of these were determined cryoscopically. The intrinsic viscosities of solutions in benzene of these polymers, and of the higher polymers obtained, were also determined. These results show that pressure has a large effect on the molecular weight of the polymer. For example, the polymer obtained at 1000 atm. in 68 hours (Run 38, Table 6) has an intrinsic viscosity of 0.08, whereas polymer obtained at the highest pressure (5400 atm.), in two hours reaction time at the same temperature and catalyst concentration, has an intrinsic viscosity of 2.13. This indicates that as well as causing a general increase in reaction rate pressure produces an increase in the rate of chain propagation relative to that of chain termination, as is the case in radical polymerisation.

In the radical reactions the major effect is the acceleration of chain growth, but the mutual termination of the chains is somewhat retarded at high pressures as the process is diffusion-controlled. In the tetrahydrofuran

polymerisation the increase in the rate of initiation with pressure which is believed to occur (see above) will not much affect the molecular weight of the polymer and the main effect is probably also an acceleration of chain-growth. Diffusion-controlled mutual termination does not occur in ionic polymerisation but it is possible that pressure may retard the ionic termination process. It is likely that in the weakly ionising medium the counter-ion will remain close to the cation of the growing chain. Termination may occur by a reaction between the two ions which neutralise their ionic charges, and this process would be retarded at high pressures as it involves an increase in volume due to desolvation.

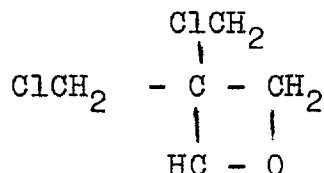
The Effect of Catalyst Concentration on the Rate of Polymerisation of Tetrahydrofuran.

At constant pressure (5400 atm.), the rate of polymerisation increases with increase in catalyst concentration (Table 7a). Thus if the concentration of catalyst is increased from 1 to 3% (V/V), the rate of polymerisation increases 13-fold.

It appeared that these results are only a quantitative indication of a strong effect of catalyst concentration on the rate of reaction. The relation

between the concentration of catalyst and the concentration of ions which are effective in initiating polymerisation is not known. It is also possible that at the lowest catalyst concentrations, for which low yields and low molecular weights were obtained, some depolymerisation of the product may have caused the apparent reaction rates to be too low.

3. The Polymerisation of 3,3,Bis-(Chloromethyl)-
Oxacyclobutane.



A brief investigation of this monomer was carried out to study the effect of pressure on the polymerisation of the oxetane ring in the presence of radical and ionic initiators. More extensive measurements were not made because only a small quantity of monomer was available, and it was evident from the insolubility of the polymer that the kinetics would be complicated.

1. Free Radical Initiation.

A few runs were carried out at pressures from 3000 to 10,000 atm. at 60°C. and for a maximum period of 20 hours, in toluene as solvent ($[S]/[m] = 4.25$) and with benzoyl peroxide (concentration 0.0413 mole.litre⁻¹) as initiator.

No polymerisation reaction could be detected under these conditions and it appears that benzoyl peroxide is not an effective initiator, even at high pressures.

2. Ionic Initiation.

Boron trifluoride diethyl etherate was used as initiator and toluene as solvent. Four runs were carried out at different pressures and the results are given in Table 10 and Fig.11.

As the polymer was insoluble, the weighed amount of reactants was immediately transferred to a flask containing an excess of methanol with a small amount of ammonia (to stop polymerisation). The polymer was filtered on a glass filter, washed with methanol, and dried to constant weight under vacuum at room temperature.

TABLE 10.

THE EFFECT OF PRESSURE ON THE POLYMERISATION OF
3:3'-BIS-(CHLOROMETHYL)-OXACYCLOBUTANE.

Initiator $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$: 0.0123 mole.litre⁻¹
 Temperature : 60°C.
 Concentration of Monomer
 in Toluene : 1.85 mole.litre⁻¹
 Time : 6 hours.

Run No.	Pressure (atm.)	Conversion (wt.%)
70	1	3.3
71	1500	7.5
72	3000	20.5
73	5400	68.2

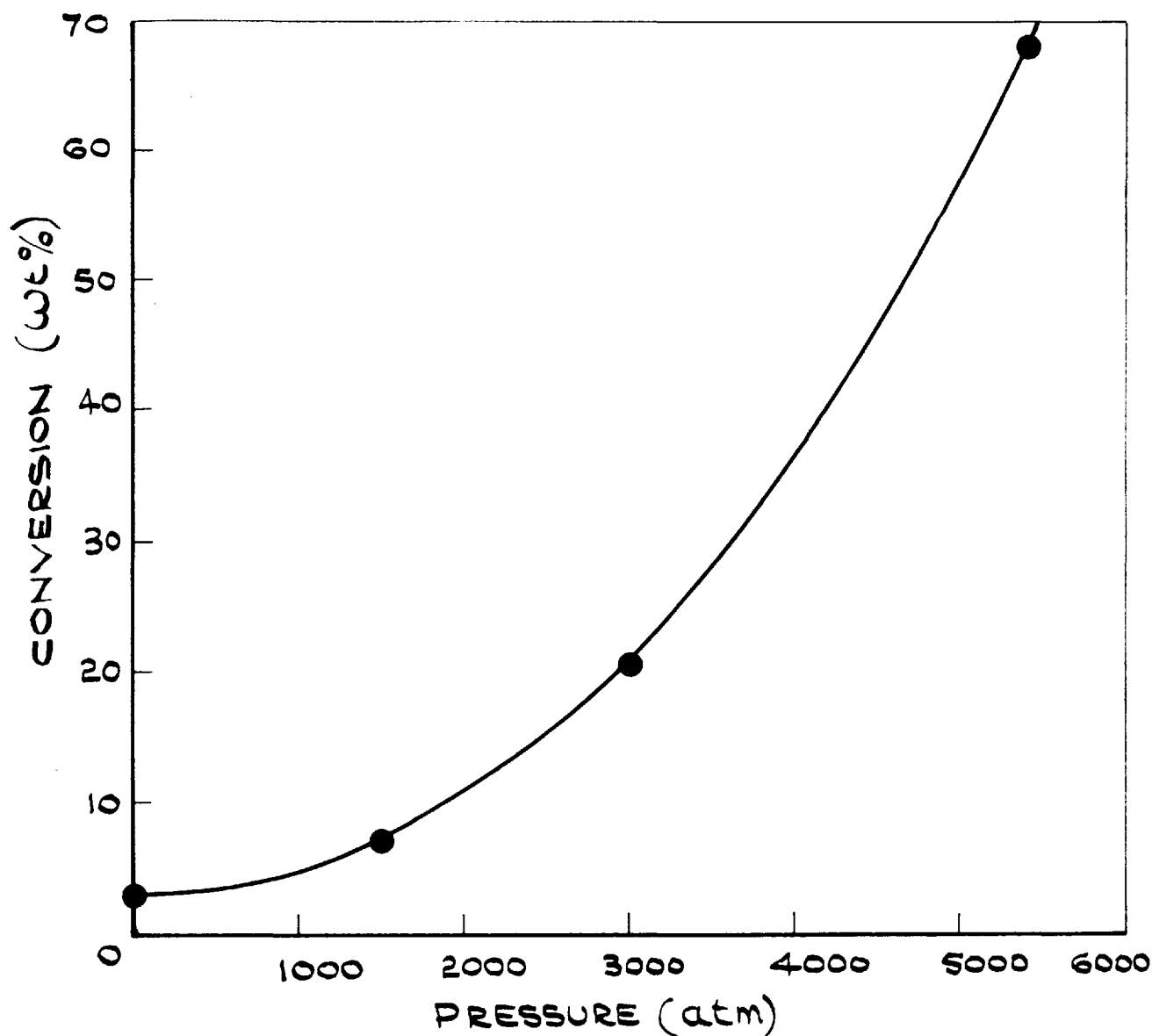
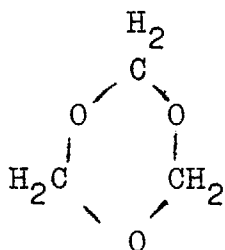


FIG. 11 PRESSURE - CONVERSION CURVE FOR
POLYMERISATION OF 3,3'-BIS-(CHLOROMETHYL)
OXACYCLOBUTANE IN PRESENCE OF
 $\text{BF}_3 (\text{C}_2\text{H}_5)_2\text{O}$, IN TOLUENE AT 60°C

Discussion of the Results for 3,3-Bis-(Chloromethyl)-
Oxacyclobutane.

In contrast with tetrahydrofuran, 3,3-bis-(chloromethyl)-oxacyclobutane polymerises very rapidly and exothermally in the presence of boron trifluoride ethyl etherate. Because of the difficulty of controlling the bulk polymerisation it was necessary to use a solvent (toluene) in this work at 1 atm. pressure and high pressure. The runs were carried out at 60°C. with a duration of 6 hours, at different pressures. It can be seen from the results in Table 10 that the rate of polymer formation increases very considerably with increase in pressure. Between 1 and 1500 atm. the rate of polymerisation increases by 2.27 times, and between 1 and 5400 atm. there is a 22.6-fold increase in rate.

The polymers obtained in this work were white solids, which did not melt sharply, but softened at 183-185°C. They were found to be insoluble in the common organic solvents, and even in more powerful solvents such as dimethyl formamide and formic acid.

4. The Polymerisation of 1,3,5, Trioxane.

This monomer was investigated briefly to study the effect of pressure on the polymerisation of a cyclic ether containing a six-membered ring.

1. Free Radical Initiation.

The runs were carried out at pressures from 1 to 10,000 atm. at 60°C., in toluene as solvent ($[S]/[M] = 5.04$) and with benzoyl peroxide (concentrations from 0.05 to 0.15 mole.litre⁻¹) as initiator.

No polymerisation occurred and it appears that benzoyl peroxide is not an effective initiator in this case.

2. Ionic Initiation.

Boron trifluoride diethyl etherate was used as initiator, and toluene as solvent. Runs were carried out at various pressures and the results are classified in Table 11. As the polymer separates out of the reaction medium, during polymerisation, the weighed amount of reactants was transferred to methanol and filtered, washed several times with methanol, and dried under vacuum at room temperature. The polymers thus obtained were insoluble in benzene, chloroform, and di-methyl formamide, and melted at 175 - 180°C.

TABLE 11.THE POLYMERISATION OF 1,3,5, TRIOXANE.

Initiator $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$: 0.015 mole.litre⁻¹
 Temperature : 60°C.
 Concentration of monomer
 in Toluene : 1.85 mole.litre⁻¹

Run No.	Pressure (atm.)	Time (hrs.)	Conversion (wt.%)
74	1	5	8.2
75	1	17.5	19.2
76	1	39.5	79.9
77	1	48	79.8
78	1000	5	86.8
79	5400	5	89.4

Discussion of the Results for 1,3,5, Trioxane.

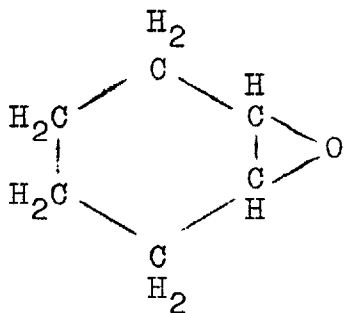
As in the case with 3,3-bis-(chloromethyl) oxacyclobutane the polymer of 1,3,5, trioxane is insoluble in the reaction medium and the polymer settles down in the bottom of the reaction tube. The separation of polymers can be expected to make the reaction kinetics complicated and a detailed study was not attempted in the present work.

The stock solution, in toluene, at a trioxane concentration of 1.85 mole/litre and a $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ concentration of 0.015 mole/litre, remained clear (without any sign of polymer separation) for approximately one hour at room temperature, and a measured amount of reaction mixture was immediately transferred to the reaction tubes or ampoules (for 1 atm. runs). The results obtained are shown in Table 11, and it can be seen that with increase in pressure the rate of polymerisation increases very rapidly. In runs of five hours duration, 8.2% of polymer was obtained at 1 atm., but the conversion was 86.8% at 1000 atm. and 89.4% at 5400 atm. As runs of shorter duration were not carried out at 1000 and 5400 atm. the effect of pressure on the overall rates is not known in detail.

It has been reported [112] that an induction period exists in the polymerisation reactions at 30°C . in dry

conditions at 1 atm., with trioxane concentrations of 3.9 and 5.3 mole/litre and boron trifluoride concentrations of 0.012 - 0.018 mole/litre. During this period no polymer is formed but monomeric formaldehyde appears and reaches an equilibrium concentration (0.06 mole/litre, 30°C.). The existence of this induction period followed by a rapid polymerisation after the equilibrium concentration of formaldehyde has been established, was explained in terms of the slowness of initiation, and an absence of termination leading to a steady increase in the concentration of growing chains. Further work [113] on the polymerisation of trioxane supports the view that no direct polymerisation of trioxane takes place.

It is therefore likely that the high pressure polymerisation is also not a ring-opening chain reaction of the same kind as that which occurs in the cyclic ethers which have three-, four- and five-membered rings, but that a preliminary depolymerisation is involved.

5. THE POLYMERISATION OF CYCLOHEXENE OXIDE.(1) Free Radical Initiation.

Benzoyl peroxide (1-2%) was used to initiate the polymerisation of this monomer at pressures from 8,000 at 12,500 atmospheres. The results are shown in the following tables. All the polymers were isolated by precipitation in methanol and the molecular weights of the polymers were determined cryoscopically in benzene.

TABLE 12.

POLYMERISATION OF CYCLOHEXENE OXIDE.

Initiator : Benzoyl peroxide

Pressure : 11,300 atm.

Temperature 60°C.

Run No.	Initiator Concentration (Wt.%)	Time (hrs.)	Conversion (Wt.%)	Molecular Weight
80	2.0	4	2.81	-
81	2.0	6	4.90	1710
82	2.0	10	8.71	2670
83	2.0	14	11.95	2850
84	1.5	6	3.60	-
85	1.5	10	6.21	3030
86	1.5	18	10.63	3280
87	1.5	25	12.70	3630
88	1.0	6	1.80	-
89	1.0	10	3.40	3750
90	1.0	15	4.60	3870
91	1.0	20	7.10	4010

TABLE 12(a)

DEPENDENCE OF THE RATE OF POLYMERISATION OF
CYCLOHEXENE OXIDE ON INITIATOR CONCENTRATION.

Pressure 11,³~~7~~00 atm.

Temperature 60°C.

Initiator Concentration (wt. %)	Rate of Polymerisation x 10 (wt. % Polymer/hr.)
2.0	0.5 8.3
1.5	5.7
1.0	3.5

TABLE 13.POLYMERISATION OF CYCLOHEXENE OXIDE.

Initiator : Benzoyl Peroxide

Initiator concentration : 2.0 wt.%

Temperature : 60°C.

Run No.	Pressure (atm.)	Time (hrs.)	Conversion (wt.%)	Molecular Weight
92	8360	6	1.14	670
93	8360	12	2.11	-
94	8360	22	3.51	1850
95	9100	7	1.37	-
96	9100	10	2.21	-
97	9100	14	3.1	2850
98	9100	22	4.39	3280
99	10000	5	2.32	970
100	10000	8	3.12	1580
101	10000	11	4.8	-
102	10000	16	6.98	2830
103	10000	24	10.5	3240
104	12500	4	5.01	-
105	12500	6	7.48	5640
106	12500	8	9.51	6150
107	12500	10	12.1	6700

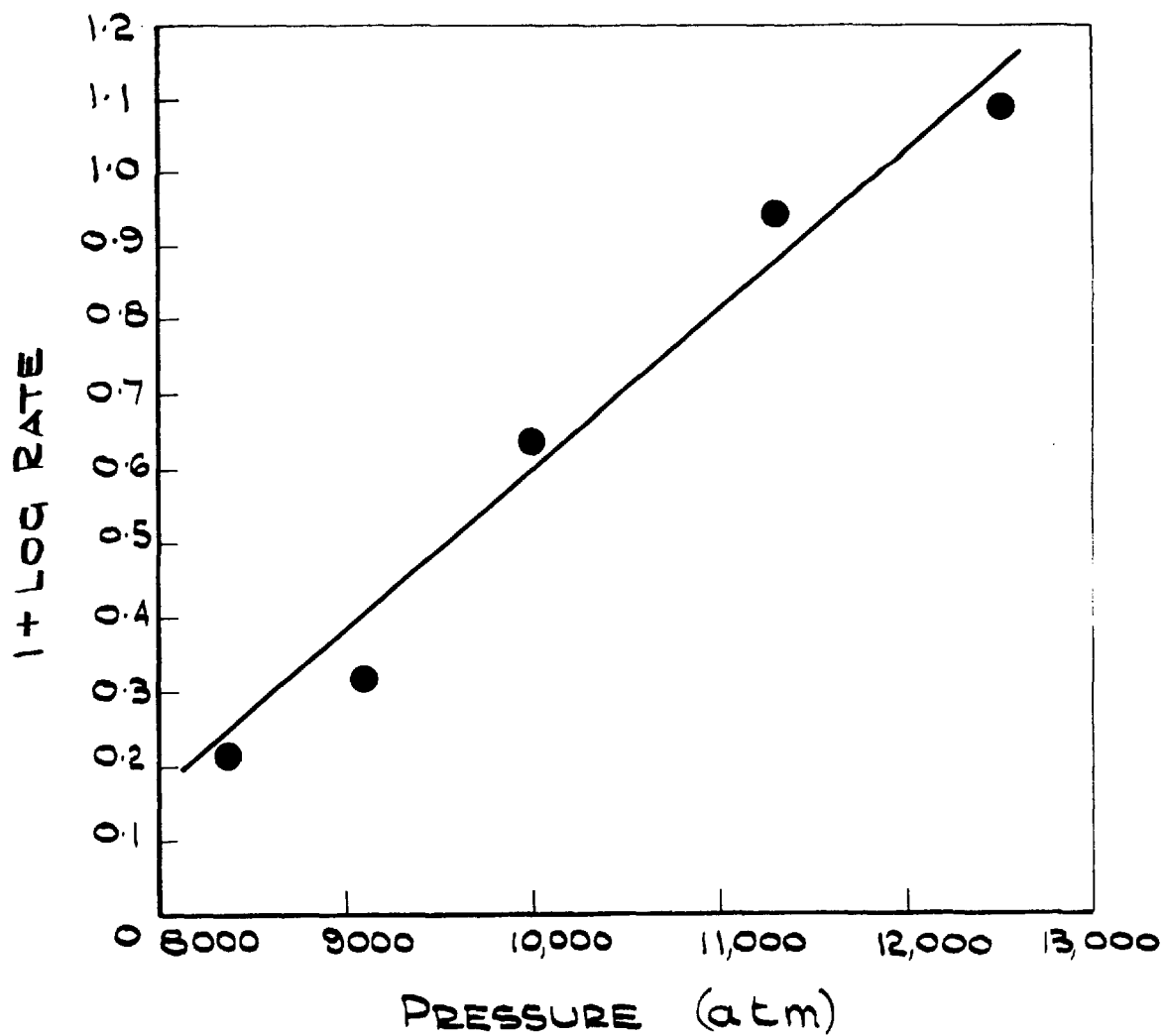


FIG. 12 PRESSURE EFFECT ON THE RATE OF
POLYMERISATION OF CYCLOHEXENE
OXIDE AT 60° BENZOYL PEROXIDE 2%

TABLE 13(a)DEPENDENCE OF THE RATE OF POLYMERISATION OF
CYCLOHEXENE OXIDE ON PRESSURE.

Initiator Concentration : 2.0 wt.%

Temperature : 60°C.

Pressure (atm.)	Rate of Polymerisation x 10 (wt.% Polymer/hr.)
8360	1.67
9100	2.14
10,000	4.3
11,300	8.3
12,500	12.5

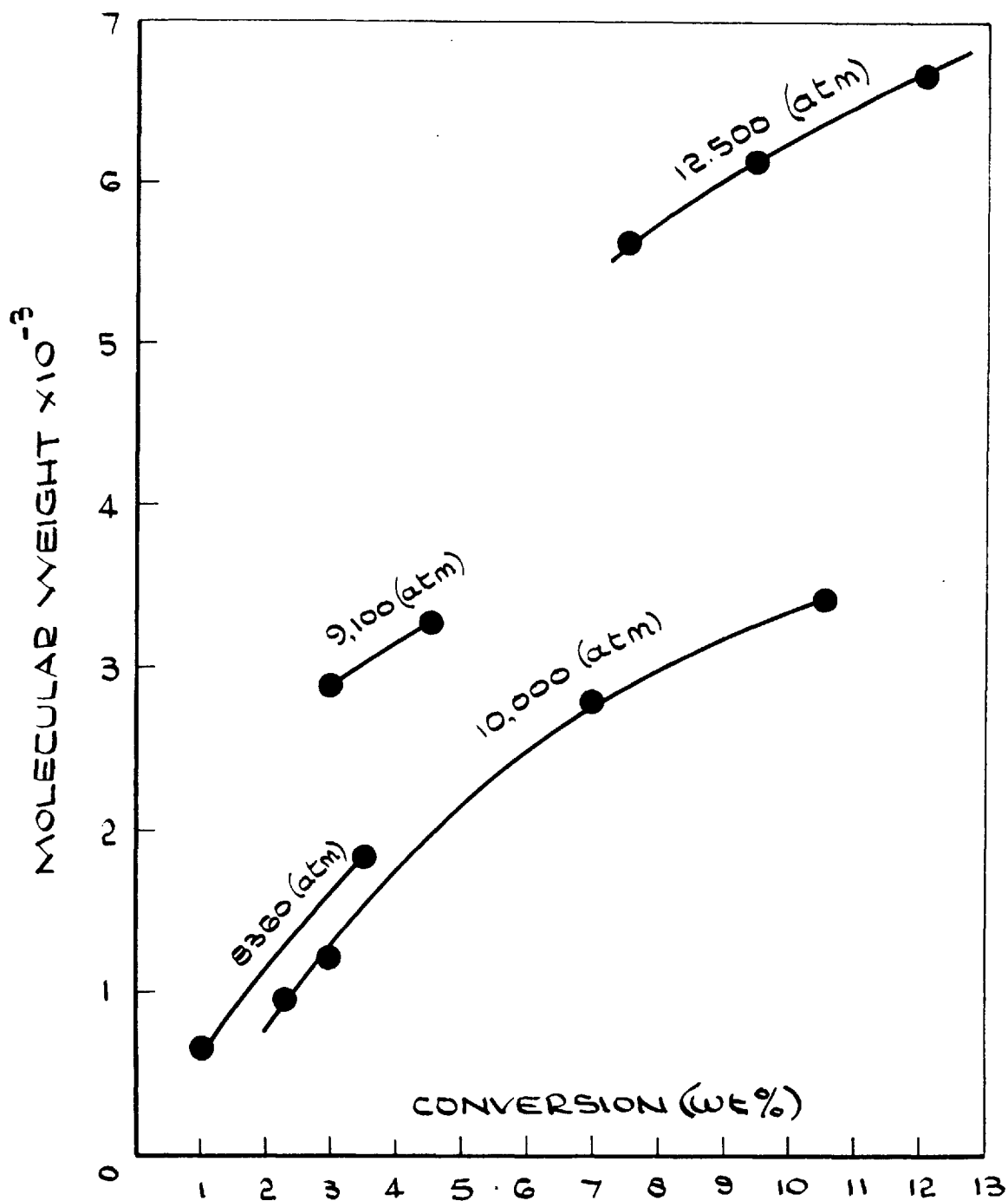


FIG 13 CYCLOHEXENE OXIDE POLYMER
MOLECULAR WEIGHT - CONVERSION
CURVES AT DIFFERENT PRESSURES

TABLE 14.

THE DIFFERENCE BETWEEN THE MOLAR VOLUME OF
CYCLOHEXENE OXIDE MONOMER AND THE APPARENT
MOLAR VOLUME OF CYCLOHEXENE OXIDE POLYMER
IN SOLUTION IN THE MONOMER.

Density of Monomer (20°) at 1 atm. = 0.9576 gm/cc.

Density of Solution of 22.11% (by Wt.) of
 Polymer in Monomer (20°) at 1 atm. = 1.0014 gm/cc.

The volume of 100 gms. of the polymer solution
 = 99.86 cc.

The volume of 77.89 gm. of pure monomer = 81.34 cc.

Therefore the apparent volume of 22.11 gm. of polymer
 in solution = 18.55 cc.

and of 1 gm. polymer in solution = 0.8389 cc.

The difference between the volume of 1 gm. monomer and
 apparent volume of 1 gm. dissolved polymer = 0.2053

The difference in volume per mole = 98.1×0.2053
 = 20.14

i.e. $\Delta V_s = 20.14$ at 1 atm. and 20°C.

(2). Polymerisation of Cyclohexene Oxide, initiated by Benzoic Acid.

Two runs were carried out at constant temperature (60°C.) and 2% (w/w) benzoic acid (a possible impurity in benzoyl peroxide). The results are given in Table 15.

TABLE 15.

Run No.	Pressure (atm.)	Time (hrs.)	Conversion (wt. %)	Molecular Weight
108	6850	67	3.83	750
109	9850	67	5.79	-

(3). Polymerisation initiated by AIBN.

A few runs were carried out in an attempt to polymerise cyclohexene oxide at pressures up to 11,300 and at 60°C., for a maximum duration of 65 hours, in the presence of AIBN 0.5 to 1% (w/w). No polymerisation took place under these conditions and it appears that AIBN is not an effective initiator in this case.

(4). Polymerisation of Cyclohexene Oxide in presence of finely powdered KOH, at room temperature.

Following the work of Price and Osgan [16], who reported that propylene oxide can be polymerised at room temperature in the presence of finely powdered KOH, a single run was carried out under similar conditions with cyclohexene

oxide as monomer. The run was carried out for two weeks in the presence of finely powdered KOH (6%w/w) with constant stirring at room temperature. Samples were withdrawn at regular intervals and tested for the presence of polymer. In all, seven samples were withdrawn and no evidence of polymerisation was found. The last sample was distilled and more than 75% was recovered at 130-140°C, some traces of residue remaining. The substance which was collected at 130-140°C. gave analyses : C = 74.40%, H = 9.47% and O = 14.9, corresponding to the molecular formula of the monomer, $C_6H_{10}O$.

(5). Thermal Polymerisation of Cyclohexene Oxide.

A single run was carried out to investigate the effect of pressure on the thermal polymerisation of cyclohexene oxide at 60°C. The results are given in Table 15(a).

TABLE 15(a).

THERMAL POLYMERISATION OF CYCLOHEXENE OXIDE AT HIGH PRESSURE (60°C.).

Run No.	Pressure (atm.)	Time (hrs.)	Conversion * (wt. %)
110	10,000	72	0.45

* Polymer isolated by precipitation in methanol. The yield is very low and was not sufficient for a molecular weight determination.

DISCUSSION OF THE RESULTS FOR CYCLOHEXENE OXIDE.The Effect of Pressure on the Rate of Polymerisation of Cyclohexene Oxide.

The polymerisation of cyclohexene oxide was carried out at pressures from 8,000 to 12,500 atm. A few runs were made in the lower pressure range from 5,000 - 7,000 atm., for a maximum duration of 68 hrs. (60°C.), but a negligible quantity of solid product was obtained (< 0.5%) and it was difficult to isolate such small amounts of polymer by precipitation in methanol.

The results obtained in the range 8,000 - 12,500 atmospheres are classified in Tables 12 and 13 and are plotted as wt.% conversion vs. time at different initiator concentrations and pressures. The slope of each line gives the overall rate of polymerisation, and the rate of polymerisation increases with increase in pressure. From Table 13(a) it can be seen that there is about a 7.48-fold increase in the rate of polymerisation between 8360 and 12500 atm., and a 2.9 -fold increase between 10,000 and 12,500 atm. As Fig.12 shows, the logarithm of the rate of polymerisation is approximately a linear function of the pressure between 8,000 and 12,500 atm., at constant temperature (60°C.) and initiator concentration.

Following Evans and Polanyi's treatment [50], the effect of pressure on the rate can be related to the volume change ΔV^* on going from the reactants to the transition-state by means of equation 1 (page 24).

Since the polymerisation is accelerated by pressure, ΔV^* is negative, and from the above equation an average ΔV^* of -15 cc/mole for the range 8000-12,500 atm. is obtained. In polymerisation reactions ΔV^* obtained from the overall rate of reaction is a composite quantity containing terms due to the initiation, propagation and termination reactions. From the density measurements the overall change in volume for polymerisation of cyclohexene oxide in solution in monomer at 1 atm. is -20.14 cc/mole. Although the volume of activation ΔV^* and the overall volume change, ΔV , refer to different pressures it seems likely that the polymerisation of cyclohexene oxide resembles free radical vinyl polymerisations in that ΔV^* is less than, or is comparable in magnitude to, ΔV .

Furthermore the value (-15 cc/mole) of ΔV^* is similar to the value of -17 cc/mole found by Merrett and Norrish [58] for the polymerisation of styrene.

The Effect of Initiator Concentration on the Rate of Polymerisation of Cyclohexene Oxide.

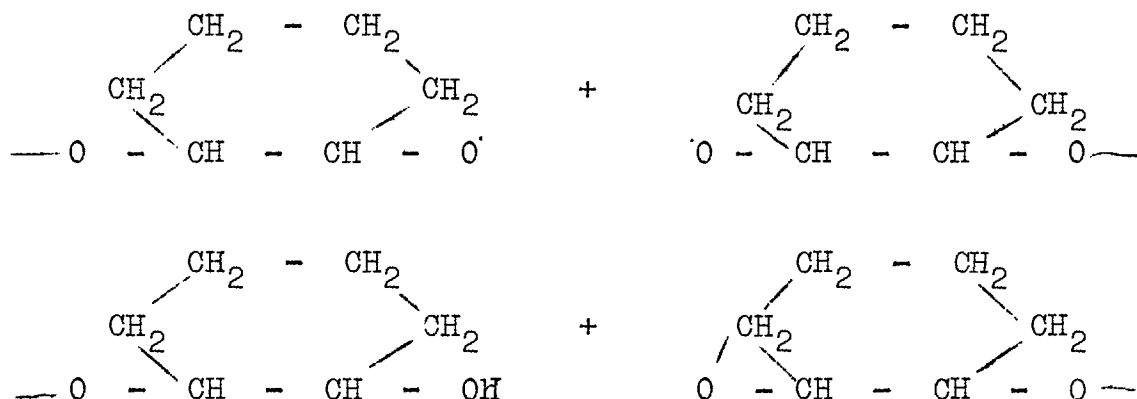
The rate of polymerisation increases with increase in initiator concentration, at constant temperature (60°C.) and pressure (11,300 atm.) as shown in Table 12(a). When the initiator concentration is increased from 1 to 1.5 wt.%, the rate increases by 1.45 times, while an increase in initiator concentration from 1 to 2 wt.% increases the rate by a factor of 2.38.

In view of the difficulty of making accurate rate measurements at these pressures it appears that the rate of polymerisation is approximately proportional to the concentration of the initiator, $[I]$. This behaviour is in contrast to free-radical vinyl polymerisations in which the rate is usually approximately proportional to $[I]^{0.5}$ at 1 atm., and at high pressures. In these reactions the power index 0.5 arises from the mutual termination of the growing radical chains either by coupling or by disproportionation.

The proportionality to the first power of $[I]$ in the polymerisation of cyclohexene oxide implies that each growing chain is terminated by reaction with another component of the system. This component cannot be the

initiator as in this case the power of [I] in the overall rate expression would be zero, and so is probably either the monomer or an impurity, such as moisture.

The absence of mutual chain termination is to be expected since radical coupling would involve the formation of an -O-O- bond, while disproportionation would require the re-formation of an epoxide ring :-



The Effect of Pressure on the Molecular Weight of Cyclohexene Oxide Polymers.

The polymers obtained at the various pressures and initiator concentrations were white solids. They melted in the range 70°-75°C., and on cooling become hard clear solids. They were, however, not of very high molecular weight. This was usually between 1,000 and 3,000 with a maximum value of 6,700 (Run 107) at the highest pressure and highest percent conversion. Conant and

Peterson [3] report a molecular weight of 565 (determined cryoscopically in p-chlorotoluene) for polymer obtained at 12,000 atm. at room temperature, in 168 hours, which was isolated by evaporating the unpolymerised monomer in vacuo at 100°C. It is possible that during the prolonged evaporation of the monomer at high temperature the product may have undergone some thermal degradation. In the present work the polymer was isolated by precipitation in methanol.

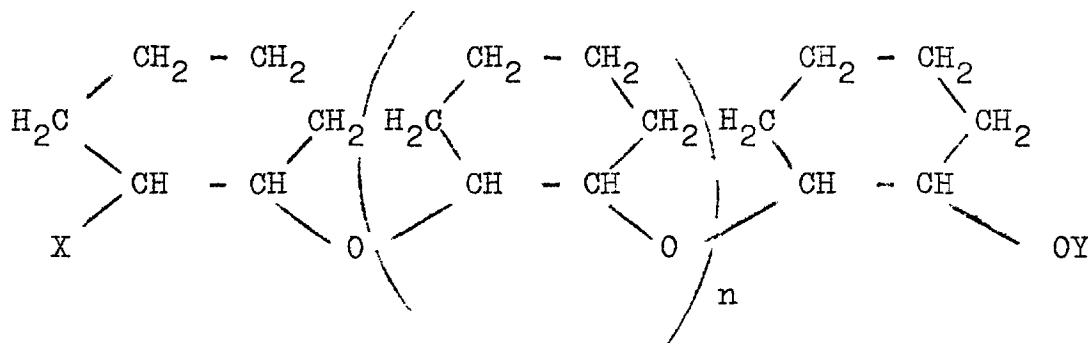
At constant pressure the molecular weights of the products tend to increase with the duration of reaction and the amount of conversion to polymer, (Fig.13). The dependence of molecular weight on pressure is less clearly defined but the polymers obtained at 12,500 atm. had a molecular weight about twice as great as those formed at 10,000 atm. in runs taken to a similar percent conversion.

It is probable that (as in free-radical vinyl polymerisation) the rate of chain initiation decreases slightly with increasing pressure. The two-fold increase of molecular weight, over a pressure range in which the overall rate increases by a factor of 2.9, therefore probably indicates that the principal effect of pressure is an acceleration of chain-growth relative to chain termination.

The effect of initiator concentrations on the molecular weight was not studied in detail but some results are given in Table 13. The molecular weight increases in the initial stages of polymerisation with decrease in initiator concentration.

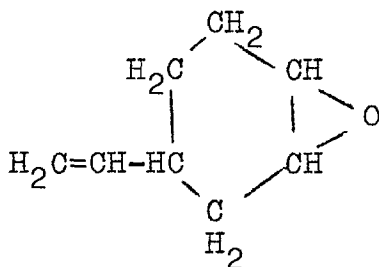
The Mechanism of the Polymerisation of Cyclohexene Oxide.

Conant and Peterson [3] in a discussion of the mechanism of polymerisation of butaldehyde at high pressure (12,000 atm.) pointed out that peroxide catalysis appears to be essential and suggested an energy-chain mechanism. Bevington [114] in a more recent review, considers that the evidence favours a free radical mechanism. Conant and Peterson considered that the polymerisation of cyclohexene oxide is very similar to that of the aldehyde except that the polymer is stable at atmospheric pressure, and suggested the following structure for the polymer :



where X and Y are unknown terminal groups.

The data obtained in the present work supports the view that the reaction proceeds through a free radical mechanism.

6. The Polymerisation of 1,2-Epoxy-4-Vinyl Cyclohexane.

An investigation of the polymerisation of the monomer was carried out at pressures up to 10,000 atm. for comparison with cyclohexene oxide and to see whether simultaneous polymerisation by vinyl addition and by ring-opening would occur.

(1) Free Radical Initiation.

Benzoyl peroxide (1-3% w/w) was used as initiator and the reactions were carried out at pressures from 1 to 9850 atm. (60°C.). The polymer obtained at pressures below 6000 atm. was not precipitated by agents such as methanol so the method of pumping off the unreacted monomer under vacuum was adopted. Polymers obtained above 6000 atm. were usually isolated by precipitation in methanol. The results are shown in the following tables. The molecular weights of the polymers were determined cryoscopically in benzene.

TABLE 16.POLYMERISATION OF 1,2-EPOXY-4-VINYLCYCLOHEXANE.

Initiator : Benzoyl Peroxide

Temperature : 60°C.

Run No.	Pressure atm.	Initiator wt. %	Time hrs.	Conversion* wt. %	Molecular Weight.
111	1	1	24	4.2	-
112	1	1	120	6.2	930
113	1000	1	25	5.8	1560
114	4000	2	5	4.3	-
115	4000	2	25	6.4	1620
116	4000	3	5	6.7	-
117	4000	3	21	7.9	1410
118	9850	1	20	15.6	2090

* Polymer separated by pumping off the unreacted monomer at 60°C.

TABLE 17.THE POLYMERISATION OF 1,2-EPOXY-4-VINYL CYCLOHEXANE.

Initiator : Benzoyl Peroxide

Pressure : 9850 atm.

Temperature : 60°C.

Rxn No.	Initiator wt.%	Time hrs.	Conversion* wt.%	Molecular Weight
119	2	9	7.54	5320
120	2	14	10.6	-
121	2	24	18.98	6580
122	1.5	10	4.5	6320
123	1.5	14	6.97	-
124	1.5	20	10.6	7960

* Polymer separated by precipitation in methanol.

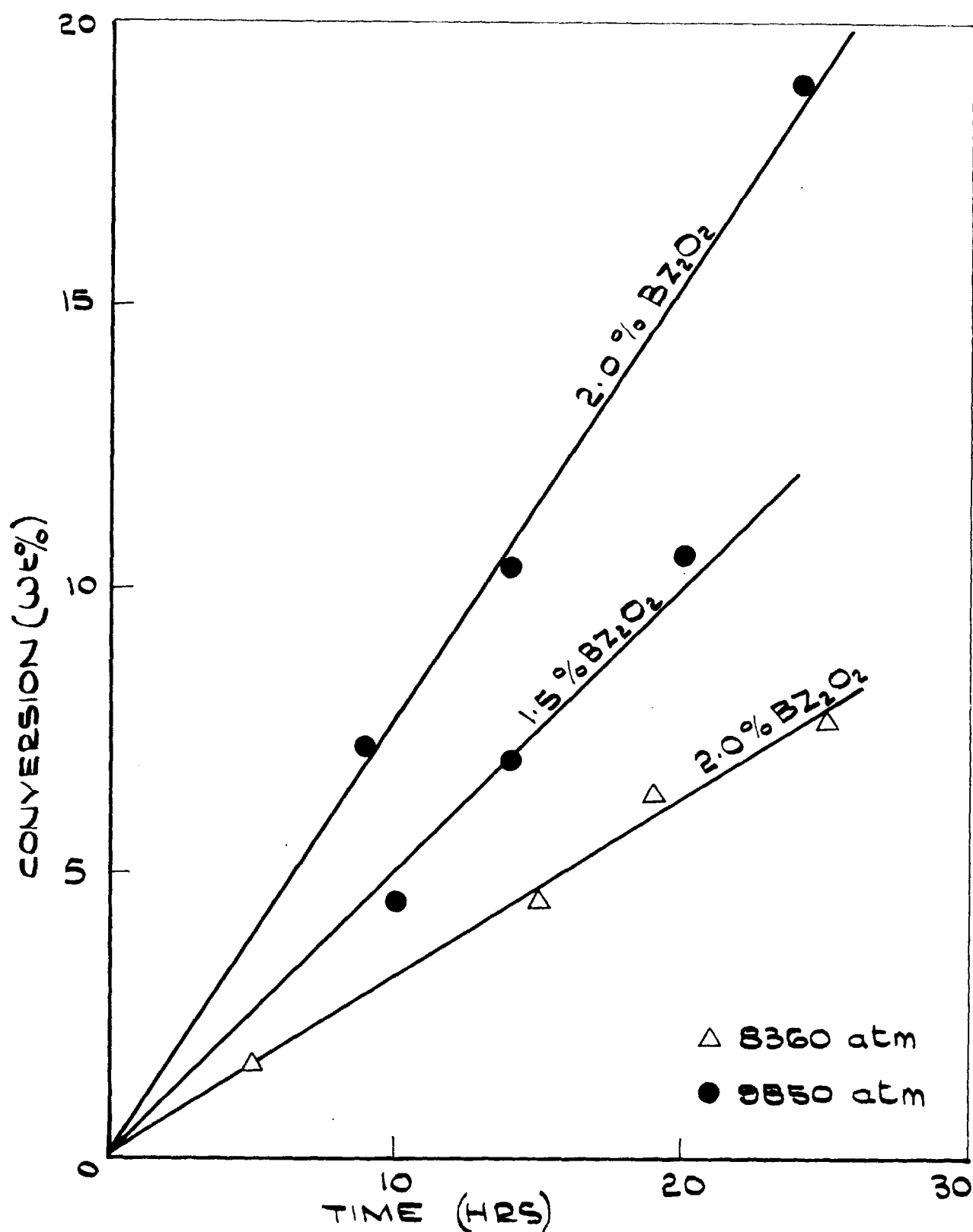


FIG. 14 POLYMERISATION OF 1,2-EPOXY-4-VINYLCYCLOHEXANE AT 60°C

TABLE 18.THE POLYMERISATION OF 1,2-EPOXY-4-VINYL CYCLOHEXANE.

Initiator : Benzoyl Peroxide

Pressure : 8360 atm.

Temperature : 60°C.

Run No.	Initiator wt.%	Time hrs.	Conversion* wt.%	Molecular Weight
126	2	5	1.6	3420
127	2	15	4.5	--
128	2	19	6.49	4210
129	2	25	7.7	4780

* Polymer obtained by precipitation in methanol.

TABLE 18(a)

DEPENDENCE OF THE RATE OF POLYMERISATION OF
1,2-EPOXY-4-VINYL CYCLOHEXANE ON PRESSURE.

Initiator : Benzoyl Peroxide

Temperature : 60°C.

Pressure atm.	Initiator Concentration wt.%	Rate of Polymerisation
		x 10. Wt.% Polymer/hr.
9850	2	7.9
8360	2	3.1
9850	1.5	5.1

(2) Ionic Polymerisation Initiated by Iodine.

A few runs were carried out to study the effect of iodine on the polymerisation of 1,2-epoxy-4-vinylcyclohexane at pressures from 1 to 8360 atm. An unsuccessful attempt was made to isolate the polymer by precipitating in methanol or petroleum ether, and the method of pumping off the unreacted monomer under vacuum at 60°C. (2 mm.Hg) was adopted. In each case approximately the same low yield of sticky residue was obtained. Results at various pressures and initiator concentrations are classified in the following table.

TABLE 19.POLYMERISATION OF 1,2-EPOXY-4-VINYLCYCLOHEXANE.

Initiator : Iodine

Temperature : 60°C.

Run No.	[I] (mole litre ⁻¹)	Pressure atm.	Time hrs.	Conversion %	Molecular Weight
130	0.0113	1	72	3.9	418
131	0.0113	2000	18	3.8	390
132	0.0113	8360	24	4.4	820
133	0.034	8360	24	4.2	760

(3) Polymerisation Initiated by Benzoic Acid.

As benzoic acid is a possible impurity in benzoyl peroxide a few runs were carried out with benzoic acid as initiator. The results are shown in Table 20.

TABLE 20.

Run No.	Initiator (wt.%)	Pressure (atm.)	Time (hrs)	Conversion (wt.%)	Molecular Weight
135	2	1	68	4.3*	510
136	2	1000	38	4.8*	480
137	2	6850	24	5.8**	1780
138	2	9850	45	12.8**	3040

* Polymer obtained by pumping-off unreacted monomer at 60°C. (2-3 mm.Hg)

** Polymer obtained by precipitating in methanol.

(4) Thermal Polymerisation.

A single run was carried out to investigate the extent to which thermal polymerisation occurs in 1,2-epoxy-4-vinyl cyclohexane at high pressure. The results are given in Table 20(a).

TABLE 20(a).

THERMAL POLYMERISATION OF 1,2-EPOXY-4-VINYLCYCLOHEXANE
AT HIGH PRESSURE (60°C.).

Run No.	Pressure atm.	Time hrs.	Conversion* wt. %	Molecular Weight
139	10,000	73.5	1.9	3780

* Polymer isolated by precipitation in methanol.

TABLE 21.INFRA-RED ABSORPTION BANDS OF CYCLOHEXENE OXIDE AND ITS POLYMER. OBTAINED AT 11,300 atm.

Substance	Wave No.	Attribution	Intensity
Cyclohexene oxide (monomer)	1080 -	Saturated Ether $\begin{array}{c} \text{C} \\ \diagdown \\ \text{CH-O-C} \\ \diagup \\ \text{C} \end{array}$	V.W.
	1100		
	1240 -	Epoxy	V.S.
	1260		
Cyclohexene oxide (polymer)	1080 -	Saturated Ether $\begin{array}{c} \text{C} \\ \diagdown \\ \text{CH-O-C} \\ \diagup \\ \text{C} \end{array}$	V.S.
	1100		
	1240 -	Epoxy	Nil
	1260		

W : Weak

S : Strong

V.W. : very weak

V.S. : very strong.

TABLE 22.

INFRA RED ABSORPTION BANDS OF 1,2-EPOXY-4-VINYL-
CYCLOHEXANE AND ITS POLYMER OBTAINED AT PRESSURES
(1-10,000 atm.).

Substance	Wave No.	Attribution	Intensity
1,2-epoxy-4-vinyl cyclohexane (Monomer)	1095	Saturated Ether $\begin{array}{c} \text{C} \\ \diagdown \\ \text{CH} - \text{O} - \text{C} \\ \diagup \\ \text{C} \end{array}$	V.W.
	1240-1260	Epoxy	S.
	1620-1640	- C = C -	V.S.
	1715	C = O	V.W.
* Polymer (at 1 and 4000 atm)	1080-1100	$\begin{array}{c} \text{C} \\ \diagdown \\ \text{CH} - \text{O} - \text{C} \\ \diagup \\ \text{C} \end{array}$	S.
	1260-1965	Epoxy	S.
	1620-1640	- C = C -	Nil
	1700-1720	C = O	V.S.
** Polymer (9850 atm.)	1080-1100	Saturated ether $\begin{array}{c} \text{C} \\ \diagdown \\ \text{CH} - \text{O} - \text{C} \\ \diagup \\ \text{C} \end{array}$	S
	1620-1630	- C = C -	V.S.
	1700	C = O	V.W.
	1260-1265	Epoxy	Nil

* Polymer obtained by precipitation in petroleum ether

** Polymer obtained by precipitation in methanol.

W = weak; S = strong; V.W. = very weak;
V.S. = very strong.

TABLE 23.

N.M.R. SPECTRA OF 1,2-EPOXY-4-VINYLCYCLOHEXANE
POLYMERS OBTAINED AT PRESSURES OF 1, 4,000 AND
9,850 atm. (60°C.).

Substance	τ (Tau)	Attribution
1,2-epoxy-4-Vinyl Cyclohexane		
* Polymer (1 and 4000 atm.)	6.9	Epoxide
** Polymer (9850 atm.)	4.2-5.08	Monosubstituted ethylene
	6.5	Ether linkage

* Polymer obtained by precipitation in petroleum ether

** Polymer obtained by precipitation in methanol.

Discussion of the Results for 1,2-Epoxy-4-Vinyl
Cyclohexane in the light of Previous Discussion on the
Polymerisation of Cyclohexene Oxide, under similar
conditions.

(1) Free-Radical Initiation.

The Effect of Pressure on the Rate of
Polymerisation of 1,2-Epoxy-4-Vinylcyclohexane.

Pressure Range 1-4000 atm.

The polymerisation of this monomer was carried out at various pressures between 1-4000 atm. and at different durations at 60°C. The results in Table 16 shows an approximately constant yield of polymer was obtained, although the runs were carried out at different conditions of pressures and initiator concentrations. The rate of polymer formation through vinyl addition appears to be slow and it seems probably this is due to the presence of the bulky cyclohexane ring in the molecule.

Pressures above 6000 atm.

The results in Tables 17 and 18 are plotted (Fig.14) as the wt.% vs. time at different initiator concentrations and pressures. The slope of each gives the overall rate of polymerisation, which increases with pressure. At pressures above 6000 atm., the results show that the

polymerisation of 1,2-epoxy-4-vinyl cyclohexane is similar to that of cyclohexene oxide, although the rate of polymerisation of 1,2-epoxy-4-vinyl cyclohexane is higher than that of cyclohexene oxide. For example, the rate of polymerisation of cyclohexene oxide at 8360 atm. is 1.67%/hr. and that of 1,2-epoxy-4-vinyl cyclohexane under the same conditions is 3.1%/hr. The rate of polymerisation of 1,2-epoxy-4-vinyl cyclohexane is thus about 1.8 times higher than that of cyclohexene oxide. The higher rate of polymerisation in the former case may be due to the polymerisation proceeding simultaneously through the vinyl and epoxy groups. To obtain further information regarding the structures of the polymers I.R. and N.M.R. spectra (Tables 22,23) were obtained.

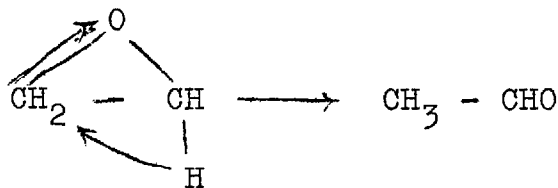
The N.M.R. spectra of the polymer made at the highest pressure (9850 atm.) show [115] that the mono-substituted ethylene groups is still present but the epoxy group has disappeared and has been replaced by absorption due to the saturated ether group. The reaction at this pressure therefore proceeds through breaking of the epoxy ring and formation of a polymer chain containing ether linkages as in the I.R. spectra of cyclohexene oxide polymer obtained at high pressure (Table 21).

On the other hand the N.M.R. and I.R. spectra show that at 1 and 4,000 atm. the vinyl group undergoes reaction and the peak at $\tau = 6.9$ in the N.M.R. spectra indicates [116] that a considerable proportion of the epoxy groups remain unaffected.

The I.R. spectra (Table 22) confirm the view that at lower pressures the reaction probably proceeds through the vinyl group, as the >C=C< peak is absent although it is very strong in polymer obtained at 9850 atm.

The I.R. spectra also show a very strong absorption attributable to the carbonyl group >C=O , in the polymers made at 1 and 4,000 atm., which is not present in the monomer or in the polymer formed at 9850 atm. Thus although these polymers still exhibit absorption due to the epoxy group a portion of them have presumably rearranged to give carbonyl groups.

Epoxides are known to rearrange on heating or in the presence of catalysts such as Lewis acids [117,118]. Even when an external nucleophilic reagent is not available, the substituent groups in the epoxide may take its place and migrate from one epoxide carbon atom to the other, as in the case of ethylene oxide:-



The mode of re-arrangement to carbonyls is not clear in epoxy compounds such as cyclohexene oxide and 1,2-epoxy-4-vinyl cyclohexane, in which the epoxy ring is condensed with the cyclohexane ring. It is known [118] that in such cases the attack at one epoxide carbon atom will give diaxial opening (the OH and the introduced group in axial positions).

From the results obtained in this work it appears that at the highest pressures the polymerisation substantially involves only the epoxide group and leads to a polyether structure. The reaction is therefore similar to that of cyclohexene oxide. At lower pressures and at 1 atm. the epoxide group appears not to participate in polymerisation but there is evidence for a partial rearrangement to carbonyl. Under these conditions the vinyl group reacts but the detailed structure of the polymer has not been investigated. The reason for the unreactivity of the vinyl group at the highest pressures is unknown, and it seems possible that its reactivity at the lower pressures may depend on a preliminary rearrangement of the molecules.

The Effect of Initiator Concentration on the Rate of Polymerisation of 1,2-Epoxy-4-Vinylcyclohexane.

The effect of initiator concentration on the rate of polymerisation of the monomer has not been studied in detail. A few runs have been carried out at 60°C. and 9850 atm. with different initiator concentrations. The rate of polymerisation increases 1.55 times when the concentration of initiator is increased from 1.5 to 2% (w/w). The acceleration in the rate of polymerisation of 1,2-epoxy-4-vinylcyclohexane between 8360 and 9850 atm. is comparable to the results obtained for cyclohexene oxide, discussed previously.

It is very difficult to study the effect of initiator concentration on the rate of polymerisation reaction at lower pressure range (1-4,000 atm.). It can be seen in Table 16 that at initiator concentrations between 1 and 3% (w/w) and in runs of different duration at constant temperature (60°C.), conversions from 4 to 8% were obtained. The polymer from these runs was separated by pumping off the unreacted monomer at 60°C. (2-3 mm.Hg). The reaction which takes place is not the same as at higher pressures, and the low molecular weight of the polymer appears to be formed through vinyl addition.

The Effect of Pressure on the Molecular Weight of
1,2-Epoxy-4-Vinylcyclohexane.

The polymer obtained at the lower pressures (1-4,000 atm.) and at initiator concentrations of 1-3% (w/w) had molecular weights between 900 and 1500 (Table 16). As described earlier these polymers were obtained by pumping off the unreacted monomer under a vacuum (60°C., 2-3 mm[Hg]). The possibility of thermal degradation, exists in this case, due to the prolonged evaporation at 60°C., but it is also possible that polymerisation by vinyl addition gives only products of very low molecular weight.

In the polymerisation reaction above 6,000 atm. (Tables 17,18), the polymer could be separated easily by precipitation in methanol. The molecular weight of the polymer tends to increase with the duration of reaction and with the amount of conversion. At higher pressures (8360-9850 atm.) the variation of molecular weight is less clearly defined (Tables 17,18), but there appears to be a slight tendency to an increase in molecular weight with pressure.

Discussion of the Results for 1,2-Epoxy-4-Vinyl
Cyclohexane in the presence of Initiators other
than Benzoyl Peroxide.

1. The Polymerisation Initiated by Iodine.

The iodine-initiated polymerisations of iso-vinyl ether [8] and isopentyl ether [9] have been reported to be accelerated by pressure. A few runs were carried out to investigate the effect of iodine on the polymerisation of 1,2-epoxy-4-vinylcyclohexane. It can be seen from the results in Table 19 that iodine is not an effective initiator in this case at concentrations from 0.0113 to 0.034 mole litre⁻¹ and at pressures up to 8360 atm. Higher concentrations of initiator have not been tried.

2. The Polymerisation Initiated by Benzoic Acid.

As stated earlier, benzoic acid may be present as an impurity in benzoyl peroxide. A few runs were therefore carried out to investigate the effect of benzoic acid on the polymerisation of 1,2-epoxy-4-vinylcyclohexane at pressures of 1 - 9850 atm. and at 60°C. The results in Table 20 show that at pressures of 1-1000 atm. low molecular weight polymer was obtained which was difficult to separate by precipitation in methanol. Polymers obtained between 6850 and 9850 atm. were easily separated by precipitation

in methanol and were similar to those obtained with benzoyl peroxide as initiator.

However the rate of polymerisation and molecular weight obtained is lower than when benzoyl peroxide is used as initiator. For example, at 60°C. and 9850 atm. in the presence of benzoic acid, 12.8% of polymer of molecular weight 3040 was obtained in 45 hours (Run 138) while with benzoyl peroxide under similar conditions of temperature and pressure, 18.98% of polymer (Mol.Wt. 6850) was obtained (Run 121).

The above results show that benzoic acid is an initiator for the polymerisation of this monomer, but is less effective than benzoyl peroxide.

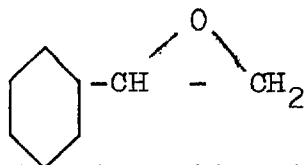
Cyclohexene oxide is also polymerised by benzoic acid (Table 15). The rate of conversion and molecular weight is low in comparison with 1,2-epoxy-4-vinylcyclohexane. For example, cyclohexene oxide on polymerisation (Table 15) at constant temperature (60°C.) and pressure (6580 atm.) yielded 3.83% polymer (Mol.Wt. 750) in 67 hrs., while 1,2-epoxy-4-vinylcyclohexane under similar conditions of pressure and temperature gave 5.8% conversion. (Mol.Wt. 1780) in 24 hours.

These results eliminate the possibility that an

appreciable amount of the polymerisation with benzoyl peroxide could be due to benzoic acid present as an impurity.

3. The Thermal Polymerisation of 1,2-Epoxy-4-Vinylcyclohexane (60°C.).

A very low yield (1.9%) of polymer (Table 20a) was obtained at 10,000 atmospheres in 73.5 hours and was isolated by precipitation in methanol. Cyclohexene oxide also gave only low yield (0.45%, Table 15(a)) of product (obtained by precipitation in methanol) when no initiator was added.

7. The Polymerisation of Styrene Oxide.

A brief investigation of this monomer was carried out in order to compare its reactivity under pressure with that of cyclohexene oxide.

(1) Free Radical Initiation.

In the presence of benzoyl peroxide (2%), styrene oxide was found to polymerise quite readily at 10,000 atm. Only a few runs were carried out as it was difficult to separate the polymer completely. The polymer was precipitated in methanol ($-20^{\circ}\text{C}.$), filtered immediately through a weighed filter crucible, washed with cold methanol ($-20^{\circ}\text{C}.$), and dried under vacuum at $35^{\circ}\text{C}.$

A semi-solid sticky product was obtained.

Molecular weights were determined cryoscopically in benzene.

The results are shown in Table 24 and Fig.15.

TABLE 24.POLYMERISATION OF STYRENE OXIDE.

Initiator : Benzoyl Peroxide 2%

Pressure : 10,000 atm.

Temperature : 60°C.

Run No.	Time(hrs.)	Conversion (%)	Molecular Weight
140	2	5.2	785
141	3	10.4	850
142	4	12.2	-
143	6	18.6	1350

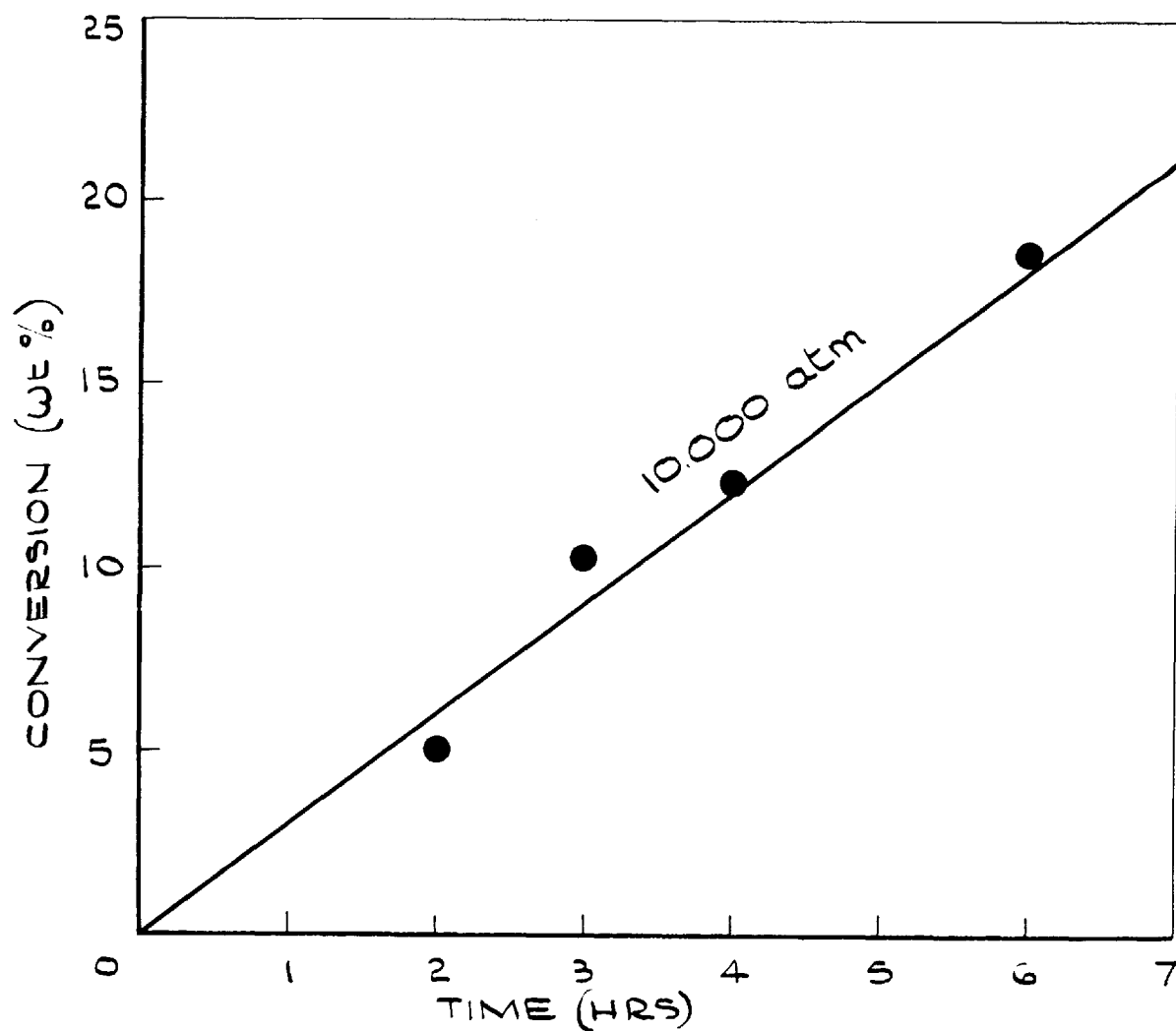


FIG 15 CONVERSION - TIME CURVE FOR
POLYMERISATION OF STYRENE OXIDE (60°).
BENZOYL PEROXIDE 2% (w_c/w_t)

(2) Ionic Initiation.

The styrene oxide - ferric chloride catalyst complex was used as a catalyst for the ionic polymerisation of styrene oxide. Runs were carried out at 1 atm. and 4100 atm. The polymerisation was carried out in bulk and the polymer isolated as described in Section II.

The results are shown in Table 25 and Fig.16. Molecular weights were determined cryoscopically in benzene.

TABLE 25.THE POLYMERISATION OF STYRENE OXIDE.Initiator : Styrene Oxide - FeCl_3 complex.

Initiator Concentration : 1.495 wt. %

Temperature : 80°C .

Run No.	Pressure (atm.)	Time (hrs.)	Conversion * (wt. %)	Molecular Weight
144	1	3	35.5	800
145	1	6	41.1	1110
146	1	10	44.6	-
147	1	24	48.3	1410
148	4100	2.5	58.3	1530
149	4100	9	69.5	-
150	4100	20	80.4	1730

* Polymer separated by pumping off the unreacted monomer at 60°C . (2-3 mm.Hg).

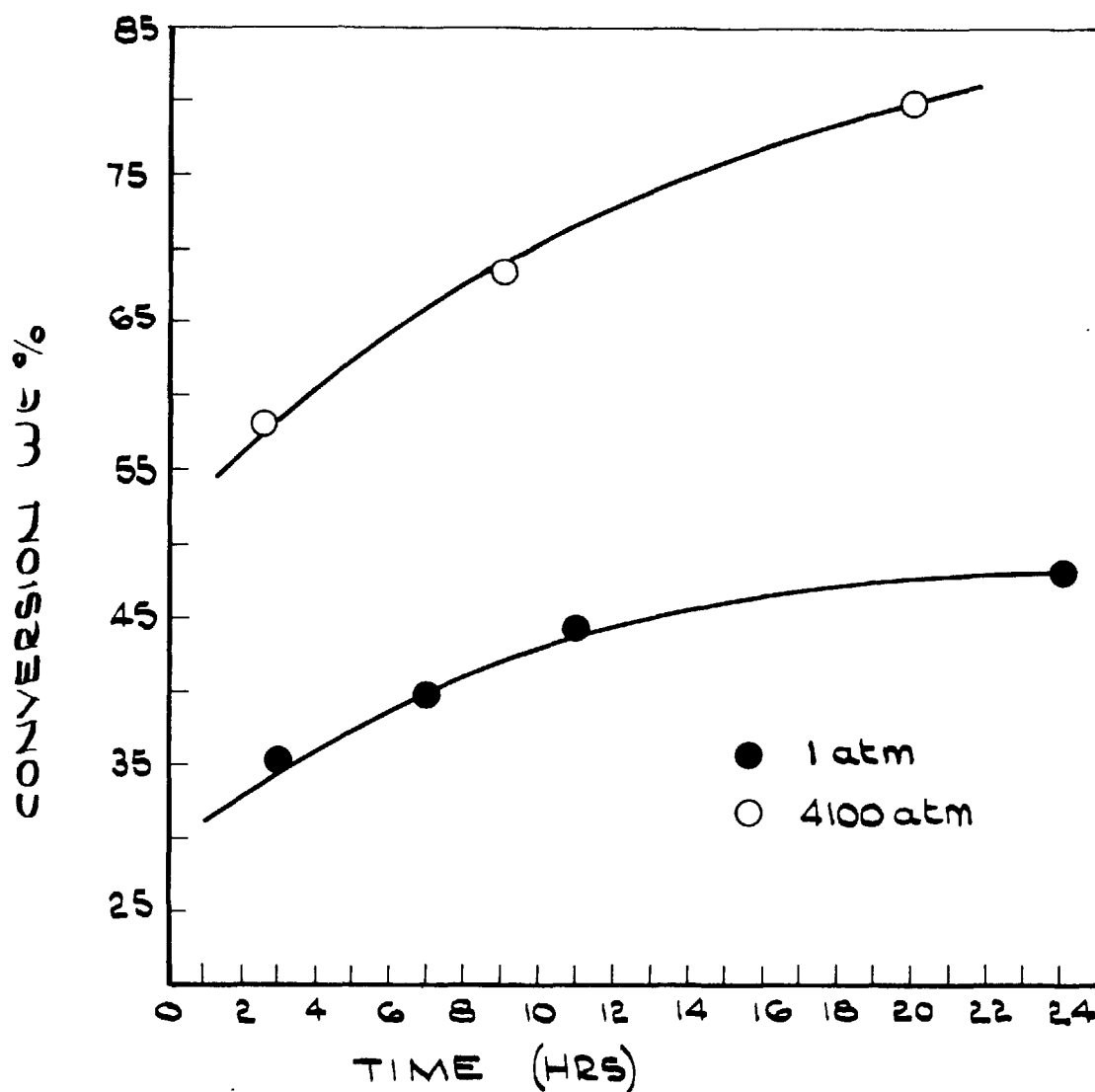


FIG. 16 CONVERSION - TIME, CURVES FOR
POLYMERISATION OF STYRENE OXIDE (80°)
STYRENE OXIDE - FeCl_3 CATALYST
COMPLEX 2% (Wt/Wt)

Discussion of the Results for Styrene Oxide in
Comparison with Cyclohexene Oxide.

1. Free Radical Initiation.

The rate of polymerisation of styrene oxide was investigated at 10,000 atm. only, as the sticky liquid or semi-solid character of the polymer made it very difficult to handle.

The results obtained at 10,000 atm. pressure (Table 24) are plotted as wt.% conversion vs. time in Fig. 15. The slope of the line obtained gives the overall rate of polymerisation, which under these conditions is found to be 3%/hour. The rate of polymerisation of styrene oxide under these conditions is about 6.9 times greater than that of cyclohexene oxide. The larger rate is probably due to the structural difference between the two monomers. The presence of the phenyl group will facilitate the break-up of the bond between the oxygen and carbon atoms [118], but in the case of cyclohexene oxide, the epoxide ring is fused with the cyclohexene ring and this structure cannot exert a comparable effect on the breaking of the C-O bond.

At approximately equal conversion the molecular weight of the styrene oxide was found to be lower than that of the cyclohexene oxide polymer. For example, under

similar conditions of pressure, temperature and initiator concentrations, 10.4% of styrene oxide polymer obtained in 3 hours had a degree of polymerisation (D.P.) of about 7 (Run 141) and 10.5% cyclohexene polymer (10.5% yield in 24 hours) had a D.P. of 33 (Run 103).

Polymerisation Initiated by the Styrene Oxide - Ferric Chloride Complex.

The polymerisation of styrene oxide in the presence of the styrene oxide-ferric chloride complex proceeds very rapidly. As shown in Table 25, at 1 atm. and 80°C., with a catalyst concentration of 1.495 wt.%, 35.5% conversion occurred in 3 hours, and at 4100 atm., 58.3% conversion occurred in 2.5 hours.

The rapid rate of reaction made it impossible to obtain accurate kinetic results for fairly low conversions in the equipment used. The results are plotted as wt.% conversion vs. time in Fig.16 and although these refer only to conversions between 35% and 80% they indicate that the amount of polymer formed in a given time at 4100 atm. is approximately 1.5 times greater than at 1 atm.

Molecular weights of polymer obtained at 1 atm. and at 4100 atm. are quite low and are more or less in the same range, but there appears to be a slight tendency for

the molecular weight to increase with increase in pressure, at least in the earlier stages of polymerisation.

The very low molecular weights of the polymers indicate that many moles of polymer have been produced per mole of catalyst used.

SECTION IV.

GENERAL DISCUSSION.

The results for each monomer have been discussed separately. The purpose of this section is to make a brief comparison of the results obtained with different types of cyclic ether studied.

1. Dainton et al. [41] measured the heats of polymerisation of styrene oxide (-24.3 Kcal./mole) and 3,3.bis (chloromethyl)-oxacyclobutane (-20.2 Kcal./mole), and further observed that if one or two hydrogen atoms on a carbon atom are replaced by a substituent in these compounds, the heats of polymerisation are only slightly affected by the nature of the substituents. These results show that the polymerisation of 2- and 3-membered cyclic ether rings are favoured thermodynamically, more than styrene.

Thermal data for the polymerisation of tetrahydrofuran (5-membered ring) and trioxane (6-membered ring) are not available, but with suitable catalysts, polymerised readily, so they also probably have fairly large heats of polymerisation. It can therefore be

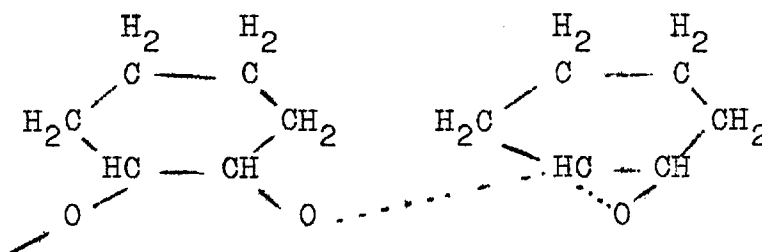
concluded that all the monomers investigated in this work are thermodynamically polymerisable.

The effects of pressure can be expected to arise from changes in the kinetics of the reactions, rather than from changes in a monomer/polymer equilibrium.

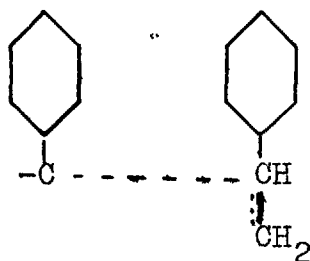
2. In practice, with the initiators used, very large differences in rates of polymerisation have been observed. The polymerisability of each monomer mainly depends on its activity towards initiators and in the series of monomers used in this work there is a wide difference in reactivities with the initiators.

3. Pressure affects all rates of polymerisation investigated. The rate of polymerisation of monomers with 4-membered and 6-membered rings could not be measured accurately because of the insolubility of the polymers in the reaction medium and the high rates of reaction. The three-membered ring molecules polymerised easily at high pressures in the presence of a radical initiator, while the 5-membered tetrahydrofuran ring polymerised in the presence of ionic initiators. In all cases the rate of polymerisation increased with increase in pressure.

4. In the case of the 3-membered cyclohexene oxide ring, no appreciable polymerisation takes place < 5000 atm. The values of ΔV^* (-15 cc/mole) and of ΔV_0 (-20 cc/mole) obtained, closely resembles the values for styrene so that the decrease in volume accompanying the opening of the 3-membered ring and simultaneous C-O bond formation



is similar to the contraction accompanying the opening of the double bond and C-C bond-formation in styrene polymerisation.



5. In the case of the 5-membered ring (tetrahydrofuran) the value of ΔV^* is -30 cc/mole, which is high in comparison to styrene, but as discussed previously a

considerable part of ΔV^* is probably due to a change in the ionic equilibrium of the catalyst.

6. Polymers of apparently high molecular weight could be obtained from the 4- and 5-membered ring cyclic ethers. The epoxides gave polymers of fairly low molecular weights and these were increased by pressure much less than the rates of polymerisation.

One or two general conclusions can be drawn from the results:-

(a) Even at high pressures most of the cyclic ethers are not active towards radical initiators.

(b) The effect of pressure on the chain growth rate is significant is probably similar to that for vinyl monomers.

(c) The molecular weights are not greatly increased by pressure, presumably because of transfer reactions which are not suppressed by pressure and may be considerably accelerated as in the case of allyl acetate polymerisation [51(b)].

BIBLIOGRAPHY.

1. Bridgman and Conant, Proc.Nat.Acad.Sci., (1929),
15, 680.
2. Conant and Tomberg, J.Am.Chem.Soc., (1930), 52, 1659.
3. Conant and Peterson, ibid., (1932), 54, 628.
4. Starkweather, J.Am.Chem.Soc., (1934), 56, 1870.
5. Toussaint and Harvey, U.S.Patent, 2,425,845., Aug. 1947
(Union Carbide Corporation).
6. Makoto and Okawara, J.Chem.Soc. Japan Ind.Chem.Soc.,
(1952), 55, 335.
7. Kilroe and Weale, J.Chem.Soc., (1960), 3849.
8. Nahumy, Ph.D.Thesis, London University, 1961.
9. Hamann and Teplitsky, J.Phys.Chem., (1961), 65, 1654.
10. Gee et al., J.Chem.Soc., (1959), 1338.
11. Gee et al., ibid., (1959), 1345.
12. Plesch, 'The Chemistry of Cationic Polymerisation',
Pergamon Press, London, (1963).
13. Pruitt and Baggett, U.S.Pat., 2,706,181 (Ap.12,1955).
14. Pruitt, Baggett and co-workers, U.S.Pat., 2,706,182
(ap.12,1955).
15. Gee et al., Polymer, (1962), 2, 231-41.
16. Price et al., J.Amer.Chem.Soc., (1956), 78, 4787.
17. Borkovec, U.S.Pat., 2,873,258 (Feb.1959).
18. Robinson, Tetrahedron, (1959), 5, 96.

19. Meerwein et al., J.Prakt.Chem., (1939), 83, 154.
20. Hamann, Angew.Chem., (1951), 63, 231.
21. Meerwein et al., Angew Chem., (1960), 72, 927.
22. Muettertities, U.S.Pat., 2,856,370 (Oct.14, 1958).
23. Hachihama and Shono, Technol.Reports Osaka Univ., (1959), 9, 337.
24. Bawn et al., Chem.Soc. Symposia, (1963).
25. Gresham, U.S.Patent, 2,394,910.
26. Murbach and Adicoff, Ind.Eng.Chem., (1960), 52, 772-5.
27. Farthing and Reynold, J.Poly.Sci., (1960), 45, 243-6.
28. Farthing, J.Chem.Soc., (1955), 3648.
29. Rose, J.Chem.Soc., (1956), 542, 546.
30. Hudy, U.S.Patent, 2,895,924.
31. Hatano and Kambara, J.Poly.Sci., (1959), 35, 275.
32. Etienne, Ind.Plast.Mod., (1957), 9, (4), 37.
33. Staudinger, Die Hochmolekularen Organischen Verbindungen-Springer, Berlin, 1932.
34. Schneider, U.S.Patent, 2,795,571 (June 11, 1957).
35. Bruni, U.S.Patent, 2,989,510 (June 20, 1961).
36. Kern et al., Angew Chem., (1961), 73, 177.
37. Okamura et al., J.Poly.Sci., No.4 (Symposia 1963), Part C, 827-38.
38. Bartleson, U.S.Patent, 2,792,375 (May 14, 1957).
39. Blanchette, U.S.Patent, 2,916,463, (Dec. 1959).

40. Colclough, Gee and co-workers, J.Poly.Sci., (1959),
34, 171-3.
41. Dainton et al., Trans.Farad.Soc., (1960), 56, 1784-92.
42. Baily and France, J.Poly.Sci., (1960), 45, 243-6.
43. Foster, U.S.Patent, 2,687,406 (August, 1954).
44. Foster, U.S.Patent, 2,687,404 (August, 1954).
45. Strain, U.S.Patent, 2,765,296 (Oct., 1956).
46. Hamann, Trans.Farad.Soc., (1958), 54, 507.
47. Michels, Proc.Roy.Soc., (1930), A.127, 258.
48. Hamann, Physico Chemical Effect of Pressure,
Butterworths, 1957.
49. Hirschfelder et al., Molecular Theory of Gases and
Liquids, Wiley, New York.
50. Evans and Polanyi, Trans.Farad.Soc., (1935), 31, 875.
51. Walling, Free Radicals in Solution, Wiley, New York,
(a) p.238; (b) p.236.
52. Stearn and Eyring, Chem.Revs., (1941), 29, 509.
53. Bridgman and Conant, Proc.Nat.Acad.Sci., (1929),
15, 680.
54. Starkweather, J.Am.Chem.Soc., (1934), 56, 1870.
55. Tamman and Pape, Z.anorg.Chem., (1934), 113, 200.
56. Gilham, Trans.Farad.Soc., (1950), 46, 497.
57. Weale, Quarterly Review Vol.XVI, No.3, (1962), 267-81.
58. Merrett and Norrish, Proc.Roy.Soc., (1951), A.206, 309.
59. Nicholson and Norrish, Disc.Faraday Soc., (1956),
22, 104.

60. Jacobson and Carothers, J.Amer.Chem.Soc., (1933),
55, 1624.
61. Newitt et al., J.Chem.Soc., (1937), 1784.
62. Holmes-Walker and Weale, J.Chem.Soc., (1955), 2295.
63. Weale, J.Chem.Soc., (1952), 2223.
64. Ostwald, J.Prak.Chem., (1878), 18, 328.
65. Bamford et al., The Kinetics of Vinyl Polymerisation
by Radical Mechanisms, Butterworths, 1958.
66. Flory, Principles of Polymer Chemistry, Cornell Univ.,
(1953).
67. Burnett, The Mechanism of Polymer Reaction,
Interscience, New York, (1957).
68. Arnett, J.Amer.Chem.Soc., (1952), 74, 2027.
69. Mayo et al., J.Amer.Chem.Soc., (1951), 73, 1691.
70. Schulz et al., Z.Physik.Chem., (1942), B5, 175.
71. Penczek and Penczek, Macromol.Chem. (in English),
(1963), 67, 203-18.
72. Schildnecht, Polymer Process, (Interscience, N.Y.),
(1956).
73. Plesch, Polanyi and Skinner, J.Chem.Soc., (1947), 257.
74. Evans and Polanyi, ibid., (1947), 252.
75. Evans, Meadows and Polanyi, Nature, (1947), 160, 869.
76. Polanyi et al., Nature, (1946), 157, 102.
77. Evans and Meadows, Trans.Farad.Soc., (1950), 46, 327.

78. Plesch, J.Chem.Soc., (1950), 543.
79. Chalmers, Canada J.Research, B.7, (1932), 464.
80. Fuoss et al., J.Amer.Chem.Soc., (1933), 55, 21, 3644.
81. Schildknecht,, Ind.Eng.Chem., (1958), 50, 107.
82. Thomas and co-workers, J.Am.Chem.Soc., (1940), 62, 276.
83. Plesch, Research, (1949), 2, 267.
84. Dainton and Sutherland, J.Poly.Sci., (1949), 4, 37.
85. Norrish and Russel, Trans.Farad.Soc., (1932), 48, 91.
86. Whitmore, Ind.Eng.Chem., (1934), 26, 94.
87. Hamann and Strauss, Disc.Farad.Soc., (1956), 22, 70.
88. Evans and Hamann, Sci.Proc.Roy.Dublin Soc., (1950),
25, 139.
89. Throssell et al., J.Amer.Chem.Soc., (1956), 78, 1122.
90. Colclough, J.Poly.Sci., (1952), 8, 467.
91. Atkins and Billmeyer, Jr., J.Phys.Chem., (1959),
63, 1966.
92. Overberger and Endres, J.Amer.Chem.Soc., (1953), 75,
6349; (1955), 77, 2201;
J.Poly.Sci., (1955), 16, 283.
93. Fuoss et al., J.Amer.Chem.Soc., (1934), 56, 2017.
94. Ziegler, Angew.Chem., (1936), 49, 455, 499.
95. Beaman, J.Am.Chem.Soc., (1948), 70, 3116.
96. Foster, J.Am.Chem.Soc., (1952), 74, 2299.
97. Ziegler et al., Angew.Chem., (1955), 67, 426, 541.

98. Ziegler et al., Makromol.Chem., (1956), 18/19, 186.
99. Natta and co-workers, J.Am.Chem.Soc., (1955), 77,
1708.
100. Natta, J.Poly.Sci., (1955), 16, 143.
101. Natta, Plastics, (1956), 34, No.4, 170.
102. Price and Miller, J.Poly.Sci., (1959), 34, 161.
103. Gaylord and Mark, Linear and Stereoregular Addition
Polymers, (Interscience, N.Y.) 1959.
104. Osthoff et al., J.Am.Chem.Soc., (1951), 73, 5480.
105. Bonnar, Dimbat and Stross, Number Average Molecular
Weights (Interscience, N.Y.) 1958.
106. Findlay, Practical Physical Chemistry, (Longmans).
107. Glasstone, Text Book of Physical Chemistry,
Van Nostrand & Co., 2nd Edn. 1946.
108. Strauss, M.Sc.Thesis, Univ. of Melbourne, (1956).
109. Robinson and Stokes, Electrolytic Solutions, 2nd Edn.,
Butterworths, (1939).
110. Pellon, Ph.D.Thesis, Columbia Univ., (1957).
111. Brown and Adams, J.Am.Chem.Soc., (1942), 64, 2557.
112. Kern and Jaaks, J.Poly.Sci., (1960), 48, 399.
113. Wilson and Hay, Chem. and Ind., (1962), 412.
114. Bevington, Quarterly Reviews, (1952), 6, 153.
115. Pople, Schneider and Bernstein, High Resolution
Nuclear Magnetic Resonance (McGraw Hill)
(1959) p.238.

- 116. Jackman, N.M.R.Spectrography, (Pergamon Press),
1959, p.55.
- 117. Elderfield, Heterocyclic Compunds, (Wiley & Sons),
1950, Vol.1, 47.
- 118. Parker and Isaacs, Chem.Reviews, (1959), 59, 772.