THE POLYMERISATION OF ALKYL VINYL ETHERS AT HIGH PRESSURES

Thesis Submitted for the

DEGREE OF DOCTOR OF PHILOSOPHY

in the

FACULTY OF ENGINEERING

in the

UNIVERSITY OF LONDON

by

ISAAC NAHUMY, B.Sc.,

Department of Chemical Engineering,
Imperial College of Science and Technology,
LONDON, S.W.7.

January, 1962.

ABSTRACT

The free radical and ionic bulk polymerisations of some alkyl vinyl ethers have been studied at pressures up to 10000 atm. using benzoyl peroxide, azo-bis-isobutyronitrile and iodine as initiators. The overall rate of polymerisation and the molecular weight of products have been measured. The apparatus and procedures involved in the experimental work are described.

Iso-butyl vinyl ether was the monomer studied in greatest detail. In both types of polymerisation the overall rate of reaction was found to increase with pressure, reach a maximum and then slowly decrease with pressure. The main possible explanation for this retardation in the rate above a certain pressure is that iso-butyl vinyl ether has been found to pass through a second order transition, probably to an amorphous or glassy state, in the region of the pressure at which the maximum in rate is occurring.

The investigation into the dependence of the rate of polymerisation on the order with respect to iodine concentration was carried out at several pressures and temperatures. The change in order has been explained in terms of changes in the mechanism of initiation and termination.

The effect of pressure and temperature on the molecular weight of poly-iso-butyl vinyl ether was investigates. In the benzoyl peroxide-initiated polymerisation, the molecular weight was found to increase with pressure and temperature while in the iodine-initiated polymerisation, the molecular weight is almost independent of pressure and decreases with increase in temperature. An explanation is put forward in terms of the different effects of pressure and temperature on the individual reactions in the polymerisation with the two types of initiators. Only fairly low molecular weights were obtained, and very low values resulted at high concentrations of benzoyl peroxide, when the reaction yielded addition products as well as low polymers.

In the course of this study a patent was published on the use of hydrated ferric sulfate to initiate the polymerisation of alkyl vinyl ethers, yielding high molecular weight products at normal temperature and pressure. This was repeated successfully and the high molecular weight obtained is explained in terms of the elimination of the molecular chain termination by transfer.

The results of this work are compared with the results of previously published work where possible.

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Dr. K.E. Weale for his advice and help throughout the course of this research, and to Mr. A.M. Alger and the Departmental Workshop Staff for their help in maintaining the high pressure equipment.

The author also thanks the Scholarship Fund Committee, B'nai B'rith Leo Baeck Lodge (London) for the award of a Post-graduate Scholarship held during the course of this work.

Thanks are due to Miss Rawbone for her help in the preparation of this thesis.

CONTENTS

		Page
SECTION I		
I.1:	Introduction	1
I.2:	Reactions in Free Radical Polymerisation	3
I.3:	Ionic Vinyl Polymerisations	8
	(i) The Carbonium ion Theory	11
	(ii) The Carbanium ion Theory	16
	(iii) Summary on Ionic Polymerisation	18
I.4:	The Effect of Pressure on Liquid-Phase Polymerisations	18
	(i) The Effect of Pressure on Liquid-Phase Reactions	18
	(ii) The Overall Effect of Pressure on Polymerisation	23
I.5:	Previous Work on the Polymerisation of Vinyl Ethers	26
I.6:	Scope of the Work	34
SECTION II		
II.1:	Apparatus	37
	(i) High Pressure Equipment	37
	(ii) Atmospheric Pressure Equipment	44
II.2:	Materials	45
II.3:	Procedure	46
	(i) Preparation of Reaction Mixtures	46
	(ii) Polymerisation Procedure	47
	(iii) Separation of Polymer	48

			Page
II.3:	(iv)	Molecular Weight Determination	50
	(v)	Determination of the Compression Curve for Iso-Butyl Vinyl Ether at 75°C	52
	(vi)	Experiments with the Hydrated Ferric Sulfate Initiator	53
SECTION III		Experimental Results and Calculations	
III.1.		Polymerisation with Free Radical Initiation	54
	(i)	The Effect of Initiator Concentrations	54
	(ii)	The Effect of Temperature	59
	(iii)	The Effect of Pressure	60
III.2:		Polymerisation with Ionic Initiation	62
	(i)	The Effect of Iodine Concentration on the Rate of Polymerisation	68
	(ii)	The Effect of Pressure on the Rate of Polymerisation	72
	(iii)	The Effect of Temperature on the Rate of Polymerisation	74
III.3:		Supplementary	75
	(i)	Freezing Pressure of Iso-Butyl Vinyl Ether	75
	(ii)	The Spectrum of Iodine Solution	76
	(iii)	The Use of Hydrated Ferric Sulfate as Initiator	78

SECTION IV: Discussion

		Page
IV.1:	Polymerisation with Free Radical Initiators	80
	(i) The Effect of Initiator Concentration	80
	(ii) The Effect of Temperature	84
	(iii) The Effect of Pressure	86
IV.2:	Polymerisation with Iodine Initiation	92
	(i) The Effect of Iodine Concentration on the Rate of Polymerisation	92
	(ii) The Effect of Pressure on the Rate of Polymerisation	102
	(iii) The Effect of Temperature on the Rate of Polymerisation	107
	(iv) Molecular Weight of the Product in Ionic Polymerisation	110
Conclusion		117
Bibliography		119

I.1: INTRODUCTION

The theory that vinyl polymerisation is a chain reaction involving the rapture of the ethylenic linkage gained acceptance in the nineteen thirties. Since then a large amount of work has been devoted to investigate and develop the theory of polymerisation, as a result of which it is now generally accepted that vinyl polymerisation, (a term loosely used to describe the polymerisation of substituted ethylenes), is a chain reaction which takes place in three distinct basic stages:

a. Initiation, in which an activated monomer molecule is produced.

b. Propagation, usually a rapid reaction in which the activated molecule grows by a chain mechanism involving the incorporation of more monomer molecules.

c. Termination, a process in which the growth of the chain comes to an end.

Vinyl polymerisation can be initiated by thermal, chemical or photo-chemical means, and it is susceptible to retardation and inhibition by relatively small amount of certain substances.

Thermal initiation is not a universal property of vinyl monomers. It is most significant with styrene and methyl methacrylate, and even here its significance, compared with the effect of chemical initiators (even at very low concentrations) is negligible. A variety of mechanisms has been postulated for thermal initiation including a bi-molecular process producing diradicals(1)

$$2CH_2{=}CHR \longrightarrow {}^{*}CHR{-}CH_2{-}CH_2{-}{}^{*}CHR$$

a ter-molecular process producing two resonance-stabilised mono radicals (2)

$$3CH_2{=}CHR \longrightarrow CH_3{-}{}^{*}CH + CH_3{\cdot\cdot}CR{=}CH{-}{}^{*}CHR$$

and a disproportionation between two monomer molecules which also gives a pair of resonance stabilised mono radicals (3)

$$2CH_2{=}CHR \longrightarrow CH_3{-}{}^{*}CHR + CH_2{=}{}^{*}CR$$

Vinyl polymerisation initiated by chemical means may take place through free radical or ionic mechanisms, depending on the nature of the initiation process. In this work both free radical and ionic initiators were used.

I.2 : REACTIONS IN FREE RADICAL POLYMERISATION

Evidence that vinyl polymerisation may take place by free radical mechanisms includes the direct introduction of radicals to promote polymerisation (triphenyl methyl radicals with styrene), the use of substances which are known to decompose to free radicals, as effective vinyl polymerisation initiators; and, conversely, the introduction of inhibitors which destroy free radicals in order to retard polymerisation.

Many authors (3-7) have described in detail the reactions through which free radical vinyl polymerisation proceeds. The simplest reaction scheme is outlined below:

Initiation in the presence of initiator I may be considered in two steps. First, the decomposition of the initiator into free radicals, R^*,

$$I \xrightarrow{k_d} 2\,R^*$$

and second, the addition of a monomer unit to form a chain radical, M_1^*

$$R^* + M \xrightarrow{k_a} M_1^*$$

This is followed by the successive steps of propagation,

$$M_1^* + M \xrightarrow{k_p} M_2^*$$

$$M_2^* + M \xrightarrow{k_p} M_3^*$$

or, in general, $M_{n-1}^* + M \xrightarrow{k_p} M_n^*$

which are all assumed to have the same rate constant k_p, sinceradical reactivity is presumed to be independent of chain length.

The termination step involves the mutual annihilation of the activity of two radicals. This can take place in two ways. The two chains may terminate by combination.

$$M_x^* + M_y^* \xrightarrow{k_{tc}} M_{x+y}$$

Alternatively, they may undergo disproportionation, with the transfer of a hydrogen atom and the formation of an unsaturated end group,

$$M_x^* + M_y^* \xrightarrow{k_{td}} M_x + M_y$$

for example,

$$-CH_2-\overset{*}{C}HR + RHC\overset{*}{}-CH_2- \text{ -- } -CH_2-CH_2R + RHC{=}CH-$$

The rate of the three steps may be written in terms of the concentrations (shown in parenthesis) of the species involved and the rate constants. The rate of initiation is

$$v_i = \frac{d(M^*)}{dt} = 2fk_d(I) \quad \text{---------- (1)}$$

where the factor f represents the fraction of the radicals formed by the decomposition of the initiator which are successful in initiating chains (most of the usual initiators have efficiencies between 0.6 and 1.0 for common monomer systems). The rate of termination is

$$v_t = -\frac{d(M^*)}{dt} = 2k_t(M^*)^2 \quad \text{---------- (2)}$$

In all cases of interest, the concentration of free radicals becomes constant very early in the reaction, as radicals are formed and destroyed at identical rates. In this steady state cordition $v_i = v_t$ and Eqs. (1) and (2) may be equated to solve for (M^*)

$$(M^*) = \left(\frac{fk_d\ (I)}{k_t}\right)^{\frac{1}{2}} \text{---------- (3)}$$

The rate of propagation is essentially the same as the overall rate of disappearance of monomer, since the number of monomer molecules used in the initiation step to produce the chain radical M_1^* is small compared to that used in the propagation of the polymer chains. Therefore

$$v_p = \frac{-d(M)}{d_t} = k_p\ (M)(M^*) \text{ ---------- (4)}$$

or, substituting in Eq. (3)

$$v_p = k_p \left(\frac{fk_d(I)}{k_t}\right)^{\frac{1}{2}} (M) \text{ ----------(5)}$$

This proportionality of the overall rate to the square root of the initiator concentration has been confirmed for a variety of monomers and initiators, e.g. styrene with benzoyl peroxide (8)

Degree of Polymerisation and Chain Transfer

The kinetic chain length L is defined as the number of monomer units consumed per active centre. It is

therefore given by $v_p/v_i = v_p/v_t$

$$L = \frac{k_p}{2k_t}\frac{(M)}{(M^*)} \quad \text{---------- (6)}$$

or eliminating the radical concentration by means of Eq. (3)

$$L = \frac{k_p}{2(fk_dk_t)^{\frac{1}{2}}}\frac{(M)}{(I)^{\frac{1}{2}}} \quad \text{---------- (7)}$$

If no reactions take place other than those already discussed, the kinetic chain length should be related to P, the degree of polymerisation:

for termination by combination $P_c = 2L$

for termination by disproportionation $P_d = L$

This is found to be true for some cases, but for other systems wide variations are observed. The direction of the deviation is such that a greater number of polymer molecules is formed than that predicted from the kinetic chain length.

The mechanism which explains the production of additional molecules is that of the transfer of the activity of a growing chain to another molecule called the transfer agent. The latter becomes a free radical capable of adding monomer units.

A prominent mechanism of chain transfer is the removal by a chain radical of a hydrogen (or other) atom from another molecule. This may be a solvent molecule,

a monomer, an initiator or a polymer molecule.

The degree of polymerisation may now be expressed:

$$P = \sum \frac{\text{Rate of growth}}{\text{Rates of termination by all processes}}$$

$$= v_p \Big/ \Big\{ fk_d(I) + k_{tr,M}(M)(M^*) + k_{tr,S}(S)(M^*) + k_{tr,I}(I)(M^*) \Big\} \quad \text{---------- (8)}$$

where $k_{tr,M}$, $k_{tr,S}$, $k_{tr,I}$, are the rate constants for the different possible equations. If transfer constants are defined by:-

$$C_M = k_{tr,M}/k_p \qquad C_S = k_{tr,S}/k_p \qquad C_I = k_{tr,I}/k_p$$

then, assuming termination by combination,

$$\frac{1}{P} = \frac{k_t}{k_p^2} \frac{v_p}{(M)^2} + C_M + C_S \frac{(S)}{(M)} + C_I \frac{k_t}{fk_p^2 k_d} \frac{v_p^2}{(M)^3} \quad \text{---- (9)}$$

The above analysis assumes that the radical formed in the transfer process is approximately as reactive as the original chain radical.

Two other termination reactions involving primary initiator radicals may also take place.

$$M^* + R^* \longrightarrow P$$

$$R^* + R^* \longrightarrow RR^1$$

These processes exert an effect on the reaction kinetics only when the monomer concentration is low and the initiator concentration is high.

Other possible reactions which are not included in the simple kinetic scheme include:

Degradation; consisting of chain fracture and the production of two smaller units, one of which is unsaturated.

Depolymerisation; the reverse of the propagation reaction.

Re-initiation; the attacking of a dead polymer chain by a primary radical which extracts a small radical group and leaves a centre on the polymer molecule which is capable of propagation, leading to branching and cross-linking.

1.3. Ionic Vinyl Polymerisations

The basic difference between the ionic and the free radical mechanisms is best shown by one of the most familiar of ionic polymerisations - that of isobutene induced by boron trifluoride. This mononer is quite unaffected by the presence of free radicals, while the rate of polymerisation by the metal halides is very rapid, even at temperature as low as -120°C. The reaction has a negative temperature coefficient. A free radical mechanism is therefore ruled out on energetic grounds and the generally accepted theory is that the reactions proceed by an ionic mechanism. Pepper (9) has provided evidence of the ionic nature of the reactions by showing

that the initial rate of polymerisation and the molecular weight of the product in the polymerisation of α-methyl styrene initiated by stannic chloride are both dependent on the dielectric constant of the medium.

The characteristics of ionic or polar-type polymerisations have received little attention in comparison with the free radical induced polymerisations of vinyl monomers. The detailed investigations of ionic reactions has been hampered by very unusual experimental difficulties which make the accurate reproduction of results, and hence the measurement of polymerisation rates and the formulation of kinetic mechanism, almost impossible. This is due in some cases to the development of heterogenous systems involving inorganic initiators and organic monomers, and in other cases to the abnormally large effects produced by a third component (the co-catalyst) when present even in very small concentration. The presence of a co-catalyst is often necessary for initiating the reaction (10-14). Polanyi et al showed that a trace of some substance other than the initiator (usually water), is necessary for the dimerisation of di-isobutene (10). The polymerisation of isobutene in hexane solution with titanic chloride as initiator will not proceed at -80°C in the absence

of moisture, while passage of a stream of moist air through the solution is sufficient to initiate a rapid reaction (10) (11). On the other hand cases are known (15) (16) where co-catalysts are not necessary and their presence have no accelerating effect. The use of iodine as initiator, by Chalmers (15) and later by Eley and Richards (17) in the polymerisation of octyl vinyl ether, partly removed the difficulties associated with a third component, but because of the complexes formed by iodine with different organic solvents (18) (19) (20), new problems were introduced.

Vinyl polymerisation through ionic mechanism can be classified into two groups:- Those in which initiation is produced through a carbonium ion (cationic) by strong acids and Friedel Crafts (Lewis acid) type initiators such as BF_3, $AlCl_3$, $TiCl_4$, $SnCl_4$, H_2SO_4, I_2, (monomer responding best to cationic mechanism are those which contain groups promoting the release of electrons at the double bond, such as vinyl ethers), and those in which initiation is produced through a carbonium ion (anion) by strong (Lewis) basis such as butylmagnesium bromide, triphenilmethylsodium or sodium with liquid ammonia (21). Methacrylonitrile is a suitable monomer for anionic polymerisation since it contains the highly negative

cyano group to facilitate nucleophilic attack. The major portion of the work reported in the literature about ionic polymerisation is concerned with the carborium ion mechanism.

I.3.i. The Carbonium - ion Theory

Although the carbonium - ion theory had been applied to Friedel-Crafts polymerisation before the discovery of co-catalysis, the mechanism of the initiation step of the reaction was always uncertain (22) (23). In all cases it was assumed that the halide alone associates with the double bond and polarizes it sufficiently to start the ionic chain reaction. Houtman (24) was of the opinion that only in the case of the less active initiators would the intervention of a co-catalyst be essential.

Polanyi et al (11) (12) based their theory of the carbonium-ion reaction on the experimental data derived from the study of the polymerisation of isobutene both in solution and in the gas phase. According to this theory the first step is the formation of an acid complex between catalyst and co-catalyst.

$$TiCl_4 + RH \longrightarrow TiCl_4\ R^-H^+$$

where RH is the co-catalyst. This acid complex then

donates a proton to the monomer (isobutene) to form a carbonium ion:

$$TiCl_4R^-H^+ + (CH_3)_2\ C{=}CH_2 \longrightarrow (CH_3)_3\ C^+ + TiCl_4R^-$$

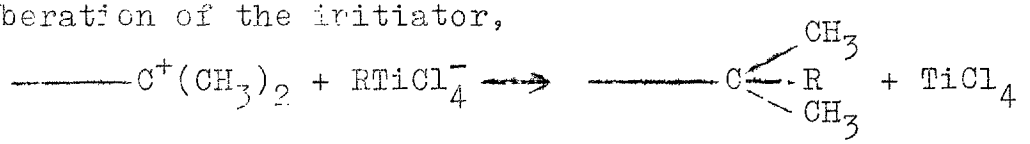
This ion then reacts with further monomer molecules, each addition bringing about a shift in the position of the positive charge. It has been clearly shown (12) that a head-to-tail addition of monomer to the ion is the only one possible for energetic reasons. Since the reaction is in general carried out in a hydrocarbon medium of low dielectric constant, the anion, $TiCl_4R^-$, cannot be very much separated from the growing cationic end, and it has been suggested that they form an ion pair. Thus, the specific initiator employed retains a marked effect on chain growth and termination, unlike a free radical which loses its identity and function as soon as it adds to a double bond.

Several different termination processes (25-28) have been suggested among which two are prominent. The ion pair could rearrange to yield a polymer molecule with unsaturated terminal, plus the original complex

$$\text{-----}\ {}^+C(CH_3)_2 + RTiCl_4^- \longrightarrow \text{----}C\!\!\diagup\!\!\!\diagdown \begin{matrix} CH_2 \\ CH_3 \end{matrix} + HRTiCl_4$$

Alternatively the ion pair may decompose in such a way that R^- combines with the carbonium ion with the

liberation of the initiator,



Infrared evidence (29) favours the former mechanism; the initiator does not appear to combine with the polymer.

As in the radical polymerisation, there is also the probability of a transfer reaction. Many polymer chains are formed for each initiator molecule present (14) (30), and it has recently been shown (31) that chain transfer to polymer can lead to branched polymers.

Present information on carbonium ion polymerisations does not permit the assumption of a steady state with any degree of certainty (6), but it may be predicted that the overall rate of polymerisation will, to a first approximation, be a function of $k_i\ k_p/k_t$, and that the molecular weight will be proportional to k_p/k_t, where k_i, k_p and k_t are the reaction rate constants for initiation, propagation and termination. A very troublesome feature of the results of rate measurements has been the report of high orders of reactions with respect to monomer. The overall order of reaction is apparently dependent on the monomer concentration and, in some cases, on the co-catalyst concentration. Dainton (32) has found that for the polymerisation with stannic

chloride, the following equation describes the reaction rate:

$$-\frac{d(M)}{dt} = k(SnCl_4)^{\frac{3}{2}}(M)^y \quad \text{---------- (10)}$$

when y increases from unity at low concentrations to higher values at higher concentrations, in the case of the polymerisation of alpha methylstyrene. Eley and Richards (16), using stannic chloride, silver perchlorate or triphenylmethyl chloride to initiate the polymerisation of 2- ethyl hexyl vinyl ether, found that the results of their work fit into a simple kinetic scheme, developed from that originally given by Eley and Pepper (33).

Initiation	$C + M \longrightarrow CM \equiv M^*$	k_2
Propagation	$M^* + M \longrightarrow M_2^*$ $M_{r-1}^* + M \longrightarrow M_r^*$	k_3
Termination	$M_n^* \longrightarrow M_r + C$	k_4
or	$M_n^* + M \longrightarrow M_n + M^*$	k_5

They assumed that the stationary state conditions can safely be applied here and concluded that the overall rate of polymerisation is:

$$-\frac{dM}{dt} = \frac{k_2 k_3}{k_4}(C)(M)^2 \quad \text{---------- (11)}$$

and the average molecular weight is:

$$M.W. = \frac{k_3(M)}{k_4 + k_5(M)} \quad \text{---------- (12)}$$

In their work with iodine as initiator the initiation steps are assumed to be,

$$2\ I_2 \longrightarrow I^+ + I_3^- \qquad k_1$$

$$I^+ + M \longrightarrow I^+M \equiv M^* \qquad k_2$$

which leads to an overall rate of polymerisation depending on the square of the iodine concentration:

$$-\frac{d(M)}{dt} = \frac{k_1 k_3}{k_4} (I_2)^2 (M) \text{ --------- (13)}$$

In cationic polymerisation the efficiency of the initiator is dependent on the acid strength of the initiator - co-catalyst complex, while the efficiency of the initiator as terminator should be related to the base strength of the complex anion. The interesting conclusion from this is that the more active a molecule is as initiator the less active it is as terminator.

Some investigators (34) have suggested that polymerisation also occurs by carbonium chains initiated by the anion of the initiator complex. This concept was introduced to explain the high early rates of initiation occurring in some cases. This is of dubious validity owing to the fact that the charge separation necessary for independent growth of oppositely charged chains appears much too great to occur in media of low dielectric constant. The importance of the solvent media

is shown by the fact that changing the dielectric constant of the solvent from 6.5 to 18.4 increases the rate of polymerisation of styrene initiated by $SrCl_4$ by a factor of 1400.

I 3 ii <u>The Carbonium - ion Theory</u>

From the very little detailed work on vinyl polymerisations initiated by Lewis bases, the most probable mechanism seems to be that formulated by Anderson and Hauser (35). For the polymerisation of styrene, methyl methacrylate and acrylonitrile induced by potassium amide in liquid ammonia (36), they write

Initiation $NH_2^- + CH_2{=}CHR \longrightarrow NH_2CH_2\bar{C}HR$

Propagation $NH_2(CH_2CHR)_{n-1}\,CH_2\bar{C}HR + CH_2{=}CHR \longrightarrow NH_2(CH_2CHR)_nCH_2\bar{C}HR$

Termination $NH_2(CH_2CHR)_n\,CH_2\bar{C}HR + NH_3 \longrightarrow NH_2(CH_2CHR)_nCH_2CH_2R + \bar{N}H_2$

The rate of the reaction was experimentally found to be of the form (37),

$$-\frac{dM}{dt} = k(M)^2(KNH_2)^{\frac{1}{2}} \qquad \text{---------- (14)}$$

while the molecular weight is relatively unaffected by the concentration of the initiator and increases with increase of monomer concentration, up to a limit where (M) = 0.3 mole/litre. In further work on the same

reaction (38), it is shown that the efficiency of the base as initiator is dependent on the base strength and that the reactivity of the monomers corresponds to the order of their strength as Lewis acids:

Acrylonitrile > methyl methacrylate > styrene

Alkali metals can also act as polymerisation initiators and were used to polymerise butadiene in the early method of producing synthetic rubber (39). The reaction mechanism is likely to be that of an anionic chain process. This is supported by comparison of the results obtained from alkali metal - liquid ammonia initiation with those obtained using known anionic initiators. Higginson and Wooding (40) show that the rate of polymerisation of styrene in liquid ammonia using potassium metal as initiator, is proportional to the square of the monomer concentration and the square root of the initiator concentration, as expected from the kinetic expression derived in the work with potassium amide initiation. In the metal-initiated reactions, it is suggested that the initial step is the formation of the amide (NH_2^-) ion which is the true initiator

$$2\ K + 2\ NH_3 + CH_2{=}CHR \longrightarrow 2\ K^+ + CH_3CH_2R + 2\ NH_2^-$$

I.3.iii Summary on Ionic Polymerisation

From the above evidence, one can conclude that ionically initiated polymerisations, unlike free radical polymerisations, do not exhibit a very well defined scheme of mechanism and kinetics. The steady state condition which is usually assumed with great reliability for free radical polymerisation to solve the kinetic equations can be assumed only in some cases, and then with reservations. Owing to the large influence of co-catalysts and the formation of different complexes the formulation of individual kinetic schemes for different polymerisations is preferable to attempts to apply a general theory covering all ionic polymerisations.

I.4: The Effect of Pressure on Liquid-Phase Polymerisation.

I.4. i The Effect of Pressure on Liquid-Phase Reactions

When a liquid system is compressed, many of its physical properties (density, viscosity, dielectric constant) are altered. Concentrations expressed per unit volume in a multi-component system also change; and since all these factors influence the rates of chemical reactions, it is to be expected that the application of an external hydrostatic pressure will have an

overall effect on reactions rates.

During the nineteen thirties, Fawcett, Gibson, Perrin and Williams (41-45) studied the effect of pressure on the rates of a number of organic reactions. They summarised their results by grouping reactions into three kinetic classes:

1. "Slow" reactions, where the reactants had a low collision factor A (10^6-10^9) in the Arrhenius equation $k=Ae^{-E/RT}$, and which were greatly accelerated by pressure.
2. "Normal" reactions, where the reactants had normal collision factors (A about 10^{12}). These were slightly accelerated by pressure.
3. Unimolecular reactions, with A about 10^{18}, which were retarded by pressure.

Many theories were formulated to explain this pressure effect on the rate of reactions, among which were the suggestion that very high pressures enhance chemical activity by causing a change in electronic configurations (45), and the suggestion that the potential energy gained by a system as a result of an isothermal compression may be available as part of the activation energy necessary for a reaction (41).

The first satisfactory formulation, made on the

basis of the "transition state" theory of rate processes (47), was by Evans and Polanyi (48) (49) (50), who derived the following relationship to explain the effect of pressure on liquid-phase reactions:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^*}{RT} \qquad \text{---------- (15)}$$

The theory of "transition state" states that a complex of definite geometry and free energy, in equilibrium with the reactants and intermediate between the reactant and product states, is formed; k is the rate constant of the reaction and ΔV^*, the volume of activation, is the change of volume per mole occurring when the initial reactants pass to the transition state. Evans and Polanyi divided ΔV^* into two parts; ΔV_1^*, the intra-molecular volume change determined by the configuration of the transition state, and ΔV_2^*, the inter-molecular volume change determined by the interaction between the solvent and the transition state. Assuming the solvent as a continuous dielectric medium to which the theory of electro-striction be applied (51), it can be shown that the decrease in volume accompanying the development of a single electronic charge on a small spherical molecule is 10-30 c.c. /mole for most solvents. It is therefore

quite possible that ΔV_2^* will be numerically greater than ΔV_1^*, in reactions involving appearance or disappearance of ionic charges. The question whether ΔV_1^* or ΔV_2^* is the dominating term for a particular reaction will depend on how highly developed the electrical charges in the transition state are and also on the complexity of the reactants. Because of the interaction of the reactants in the transition state with the solvent, reactions do not normally respond to pressure simply according to their kinetic order, but are grouped into:

1 Reactions whose rate determining step involves the creation of ionic charges. These are greatly accelerated by pressure.

2. Reactions whose rate determining step involves the loss of ionic charges. These are retarded by pressure.

3. Reactions whose rate determining step involves no charge change. These are generally slightly accelerated by pressure.

It is therefore possible to predict the effect of pressure on a reaction from a knowledge of ΔV_1^*, and ΔV_2^* and the expected behaviour for different types of reactions is listed overleaf:

TABLE 1

Expected Volume of Activation for Some Reactions

Reaction	Charge Changes	ΔV_1^*	ΔV_2^*	Expected ΔV^*
Unimolecular dissociations				
1. $A \longrightarrow X + Y$	0	+	0	+
2. $A \longrightarrow X^+ + Y^-$	increase	+	-	-
Bimolecular associations				
3. $A + B \longrightarrow X$	0	-	0	-
4. $A^+ + B^- \longrightarrow X$	decrease	-	+	+
Bimolecular exchanges				
5. $A + BC \longrightarrow AB + C$	0	-	0	-
6. $A + BC \longrightarrow AB^+ + C^-$	increase	-	-	-
7. $A^- + BC \longrightarrow AB^- + C$	0	-	-	-
8. $A^{2-} + BC \longrightarrow AB^- + C^-$	0	-	+	+
Double decompositions				
9. $AB + CD \longrightarrow AC + BD$	0	-	0	-
10. $AB + CD \longrightarrow AC + B^+ + D^-$	increase	+	-	-

Pressure may also affect the reaction rate by increasing the viscosity of a liquid-phase system. In a diffusion controlled rate process, the rate constant k_d is dependent on the diffusivity D of the reactants. In an ideal case of spherical molecules, the diffusivity is inversely proportional to the viscosity of the medium.

To the majority of liquids not containing OH groups the viscosity is exponentially dependent on the pressure and hence the approximate proportionality ($k_d \propto e^{-P}$) is derived.

From the above considerations it is seen that although the chemical reaction rate may be increased by increasing the pressure, the physical rate process of diffusion is reduced so that a transition may occur to diffusion control. This had been experimentally confirmed by Hamann for the alkaline etherification of ethyl bromide under very high pressures (52). The increase in the concentrations of the reactants due to increase in pressure also increases the rate of reactions. Liquid compressibilities are small - compressibilities of the order of 10^{-4} atm^{-1} which decreases with increasing pressure are usual - so that this effect is relatively slight. Most liquids contract on freezing and increase of pressure therefore favours the production of the solid phase. This will lead generally to the stoppage of reactions.

I.4. ii <u>The Overall Effect of Pressure on Polymerisation</u>

It was first observed by Bridgman and Conant (53) that high pressures increase the rate of polymerisation of olefins. Further work (54-57) on the thermal

polymerisation of some vinyl compounds confirmed this finding but the effects reported were sometimes surprisingly large, e.g. an acceleration of the rate of polymerisation of styrene by a factor of 2×10^6 at 1500 atm (55). Much of the earlier work was only qualitative or semi-quantitative in nature because of poor purification techniques, failure to maintain isothermal conditions, the presence of oxygen and because reactions were taken to very high conversions, sometimes up to 100%, all of which led to irreproducible results. However, during the last decade accurate work has been carried out in order to explain the overall effect of pressure in terms of its effect on the individual reaction steps (58) (59) (60). Merrett and Norrish (58) studied the polymerisation of styrene initiated by benzoyl peroxide at $60^{\circ}C$ and pressures up to 5000 kg/cm^2. They summarised their findings as:

1. The overall rate of polymerisation is approximately proportional to the square root of the initiator concentration, the index of the power decreasing to about 0.40 at 3000 kg/cm^2, thereafter, apparently, rising very slightly.

2. For a constant initiator concentration, the logarithm of the rate of the reaction is almost directly proportional to the pressure over the range 3000-5000 kg/cm^2, but the relation is more complex at low pressures. With 0.043 mole benzoyl peroxide, the overall rate is increased by about fifteen fold at 5000 kg/cm^2.
3. The molecular weights of the polymers produced are increased by two to three fold, up to about 3000 kg/cm^2, thereafter remaining approximately constant.

The explanation of these effects accords with the general theory of the effect of pressure on liquid phase reactions:

1. The rate of initiation, a non-polar uni-molecular dissociation, is retarded by pressure.
2. The rate of propagation which involves bi-molecular associations is accelerated by pressure.
3. The rate of mutual termination which depends on collision between large molecules is reduced by pressure because it becomes diffusion-controlled as a result of the increase in viscosity.

Almost all the work carried out on the effect of pressure on polymerisation has been on those initiated

by free radicals. In the case of ionic polymerisation, the difficulties in developing techniques which will give reproducible results at atmospheric pressure has already been mentioned. Because these difficulties are increased at high pressures, investigations into the effect of pressure on ionic polymerisations have not previously been made. One of the very few exceptions appears to be recent unpublished work by Hamann (61) on the polymerisation of iso-amyl vinyl ether initiated by iodine. Hamann has verified Eley's kinetic results for a similar polymerisation at atmospheric pressure (17) (33) (overall rate of polymerisation dependent on the square of the initiator concentration) but found apparent discrepancies at higher pressures. In bulk polymerisation under pressure the rate is found to be directly proportional to the initiator concentration and only an insignificant increase occurs in the molecular weight.

I.5 Previous Work on the Polymerisation of Vinyl Ethers

Almost all the previous work on the polymerisation of vinyl ethers, including the alkyl vinyl ethers, has been carried out at atmospheric pressure.

Shostakovskii et al found that alkyl vinyl ethers can polymerise by either radical or ionic chain

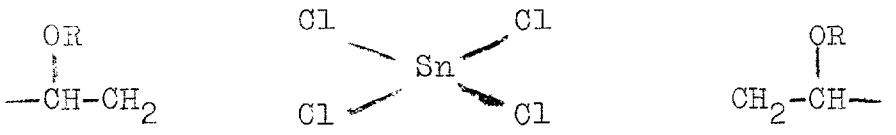
mechanism (62). Using benzoyl peroxide as initiator at 60° and 80°C, they showed that with very high initiator concentration (10-50 wt%), the benzoyl peroxide mainly plays the part of an adding agent reacting at the double bond of the vinyl ethers (63). The products were of the acylal structure $C_6H_5COO(CH_2CHOR)OCOC_6H_5$. They showed (64) that by reducing the benzoyl peroxide concentration to (5-10 wt%) addition and polymerisation reactions occur simultaneously while with still lower concentrations (lower than 2%) low yields of viscous liquid polymers of low molecular weights, ranging from about 400 to 1100, are obtained. Other workers (65) (66) (67) using ionic initiators of the Friedel-Crafts type, tried to obtain high molecular weight, rubber like or crystalline polymers, by carrying out the polymerisation at very low temperatures (down to -100°C). The low temperature was usually obtained by carrying out the polymerisation in liquified organic gases such as propane, or in liquid SO_2 which acts as an initiator as well as diluent. It has also been claimed recently that high molecular weight polymers may be obtained at about room temperatures by using a ferric sulphate with overall composition of $Fe(SO_4)_3 . H_2SO_4 . xH_2O$, where

x is equal to 3 or 4 (68). In an extensive investigation of ionic polymerisation Eley et al used vinyl ethers, (mainly alkyl vinyl ethers) initiated by various cationic initiators. The results of their two first papers (16) (17) in which the polymerisation of 2- ethyl hexyl vinyl ether initiated by iodine, stannic chloride, silver perchlorate and triphenyl methyl chloride, in solution with ether or ethylene dichloride, was studied at atmospheric pressure, can be summarised as follows:

1. Effect of Monomer and Initiator Concentrations

This was already partly mentioned on pages 14 and 15. In the iodine initiation the molecular weight was found almost independent of monomer and initiator concentrations, which suggests that the transfer process is the most important mechanism for ending molecular chains and that $k_5(M) \gg k_4$ in Eq. 12. In the case of the other three initiators the molecular weight was independent of the initiator concentration but increased with monomer concentration, slightly when $AgClO_4$ was used as initiator and in direct proportion with $SnCl_4$ as initiator. In the latter case molecular weights up to 20,000 were obtained, becoming constant above a value of monomer concentration of 0.87 mole/litre.

These markedly high molecular weights were partly attributed to the fact that the coordination number of tin is six and hence it is possible that $SnCl_4$ may start two chains simultaneously,



This is supported by the analytical result which shows that each polymer molecule contains two double bonds. But owing to the fact that the molecular weights are much more than twice those obtained with iodine or silver perchlorate, a large part of the increase in molecular weight is thought to be due to the reduced importance of transfer effects, i.e. $k_4 \gg k_5(M)$ in Eq. 12.

2. Effect of Temperature: Eley and co-workers also found that the rate of polymerisation increased with temperature as shown overleaf:

TABLE 2

Effect of Temperature on the Rate of Polymerisation of 2- ethyl hexyl vinyl ether at one atm.

	Temperature $\frac{1}{T} \times 10^3$	Log Rate	Activation Energy Kcal/Mole
Iodine Initiation			
1. In ethylene dichloride solution	3.19	-.2.40	
	3.00	- 1.65	16
2. In petrol ether solution	3.45	- 2.80	
	3.10	- 2.04	10
$SnCl_4$ initiation in petrol ether solution	3.32	- 2.80	
	2.80	- 1.60	10

The molecular weights however decreased with increasing temperature:

TABLE 3

Effect of Temperature on the Molecular Weights of 2- ethyl hexyl vinyl ether at one atm.

	Temperature ^oC	Molecular Weight
Iodine Initiation		
1. In ethylene dichloride solution	25	1050
	56	640
2. In petrol ether solution	25	1800
	48	1000
$SnCl_4$ initiation in petrol ether solution	25	6000
	60	1000

Effect of Dielectric Constant of Solvent: A most marked increase in the rate constant resulted when the dielectric constant of the solvent was increased. The relationship is approximately exponential:

TABLE 4

Effect of Dielectric Constant on the Rate of Polymerisation of 2- ethyl hexyl vinyl ether initiated by iodine at one atm.

Dielectric Constant	Rate Constant
2 D	0.3×10^9 $l^2 mole^{-2}$ min^{-1}
10 D	147×10^9 " "

Effect of Added Inhibitors: This was investigated with iodine initiation and it was found that the addition of peroxides, such as benzyl or vinyl ether peroxide, lead to a marked induction period and the lowering of molecular weight of the product from runs taken to 100 % conversion. Butyl alcohol in amounts up to 0.2 m.mole/litre had a similar effect but above this concentration the induction period decreased to zero and a very rapid reaction set in. Such a combination of increase in rate and decrease in molecular weight suggested that butyl alcohol acts as a transfer agent from growing chain to a monomer.

Effect of Addition of Water: The addition of water was found to have no effect on the reaction initiated by $SnCl_4$,

while a marked acceleration resulted in the case of $AgClO_4$ initiation, especially at low initiator concentrations.

TABLE 5

Effect of Addition of Water on the Rate of Polymerisation of 2- ethyl hexyl vinyl ether initiated by $AgClO_4$ at one Atm.

Initiator Concentration m.mole/litre	Monomer Concentration mole/litre	H_2O m.mole/litre	Rate x 10^3
36.3	3.6	0	1.11
0.066	0.3	0.26	94
0.088	0.3	0.35	158

This was attributed to the simultaneous initiations:

$AgClO_4 + ROCH=CH_2 \longrightarrow ROCH=CH_2AgClO_4$

$H_2O.\ AgClO_4 + ROCH=CH_2 \longrightarrow RO^+CH-CH_3 + HOAgClO_4^-$

Two main points were investigated in the third paper (69). The first was the effect of the side chain, R, in $CH_2=CHOR$, on the rate constant of iodine-initiated polymerisation. The following results were obtained:

TABLE 6

Side Chain -R	Rate Constant
1. Cyclo-hexyl	22,000
2. Iso-butyl	1,900
3. 2- ethyl hexyl	1,000
4. n - butyl	1,800
5. ethyl	1,900
6. 2- chloroethyl	90

It seems clear that the rate is greatly increased (up to 244 times) by an increase in the electron-repelling properties of the side chain in the series 2- chloro ethyl - cyclo-hexyl. The exact order of the middle group, the members of which lie rather close together so far as their inductive effect goes, may be influenced by sterric factors. In the same series it was found that the molecular weight also increases by a factor of 3-4 which is negligible compared to the increas in rate constant.

The second point investigated, which is of most importance to this work, was the dependence of the rate on (M), the monomer concentration, as this approaches its highest values. As previously stated, for the lower values of (M), the rate follows the relationship, Rate = $k(M)(I_2)^2$, almost without deviation and the rate then reaches a maximum value at a certain value of (M). Eley et al have assumed that a part of the iodine is bound in a complex with the monomer which is inactive in initiating polymerisation. Two such complexes were postulated, the one between the iodine and the ether oxygen atom, and the second, between iodine and the ethylenic double bond. The concentration of the inactive complexes is assumed to increase with (M) and with an increase in the electron repelling properties of the group.

I.6: Scope of the Work

It is clear that in general there have been relatively few kinetic measurements on ionic polymerisation, in marked contrast to the wealth of data available for free radical polymerisation. The polymerisation of vinyl alkyl ethers has been investigated by several workers at atmospheric pressure with free radical as well as ionic initiators, but very little information has been published about the influence of high pressures on this polymerisation.

The object of the work described in this thesis was to investigate the general effect of high pressures on the free radical and ionic polymerisations of alkyl vinyl ethers, and to find out the changes occurring, if any, in the kinetics of the ionic mechanism.

With free radical initiation, a preliminary investigation into the polymerisation of alkyl vinyl ethers under pressure was carried out. This included changes in monomer (ethyl, n-butyl, iso-butyl), in initiator (benzoyl peroxide, AIBN), in initiator concentration (8, 3, 0.1 wt. %), in temperature (75°, 50°C) and in time (ranging from 2 to 25 hours). Iso-butyl vinyl ether initiated by benzoyl peroxide at 75°C was used to study the effect of pressure

between 1 and 10,000 atm. on the rate of polymerisation. Molecular weights were measured to study the effect of changes of temperature, pressure and initiator concentration on the molecular weight.

In the ionic polymerisation iso-butyl vinyl ether initiated by iodine was used to study the dependence of rate on pressure and on initiator concentration (at 10,000 and 5,000 atm. at 75°C and at one atm. at 75°, 35° and 0°C). This part of the work also included a spectroscopic study of complex formation in the iso-butyl-iodine-benzene system; an examination of a new initiator, patented by the Goodyear Tyre and Rubber Company, with which high molecular weight, rubber-like polymers are obtained from alkyl vinyl ethers at atmospheric pressure, and an investigation of whether iso-butyl vinyl ether freezes at 75°C in the pressure range employed in this work.

Choice of Monomer for Kinetic Studies

From the three monomers used in the preliminary investigation, the iso-butyl vinyl ether was chosen for detailed study for the following reasons:

1. It has a boiling point of 82.9°C in between that of ethyl- (35.5°C) and n-butyl- (93.5°C) compounds. The low boiling point of the ethyl vinyl ether

would have caused difficulties in handling in the high pressure runs at 75°C, and the higher temperature of the n-butyl vinyl ether would have made it more difficult to evaporate the monomer from the reaction mixture at the end of a run.

2. It is known (70) that alkyl vinyl ethers with branched groups yield polymers of higher molecular weight than those with unbranched groups.

3. The rate of polymerisation is convenient to follow at the conditions used.

Choice of Iodine as Initiator

Previous work on the kinetics of the ionic polymerisation has shown that iodine initiation gives satisfactorily reproducible results. The iodine, which causes a very rapid polymerisation if added as solid, is usually used in solution, preferably in the same solvent in which the polymerisation is taking place. However, owing to the limited volume of the high pressure reaction chamber, the investigation was confined to bulk polymerisation, without a solvent. The iodine was added in benzene solution, as benzene is known to have no effect on the polymerisation of n-butyl vinyl ether (33). The amount of benzene present did not usually exceed 0.5% by weight of the reaction mixture.

SECTION II

II 1. Apparatus

II 1. i. High Pressure Equipment

The high pressure reaction vessel used in this work and its ancillary equipment are shown diagrammatically in Fig 1.

The high pressure reaction chamber C is an auto-frettaged monobloc of Vibrac V45 steel capable of withstanding internal pressures up to 20,000 atm, sealed at both ends by hard rubber Poulter packings. Pressures up to about 1000 atm can be generated inside the reaction chamber by direct transmission from a hydraulic hand pump through the side inlet S (Liquid Paraffin (B.P.) is used throughout as the pressure transmitting fluid). For higher pressures an intensifier I is used. Pressure is then transmitted to a piston of 2.5" diameter, moving in the intensifier cylinder, and obturated by a Bridgman unsupported-area packing. The thrust on this piston is passed through a thrust block and a thin copper washer to a 0.6" diameter piston which moves in the lower part of the reaction chamber and is obturated by the lower Poulter packing. The thrust block and washer serve to take up any slight difference in alignment between the two pistons. The ratio of the cross-sectional areas of the two intensifier pistons is 17.23:1

giving an approximately sixteen fold pressure intensification after allowance is made for losses due to friction of the piston packings and the very small changes in the relative areas of the pistons due to elastic compression. The upper end of the reaction chamber is closed by means of a steel "mushroom-head" hold down on top of the sealing rubber packing by a screw plag. The reaction chamber and the intensifier cylinder are connected together by means of a sleeve and both are shown in detail in Fig. 2. The main dimensions of the vessel are as follows:

Length of reaction chamber	19.8"
Overall length	30.6"
Outside diameter	6.0"
Bore	0.6"

Connections to the pump amd to a pressure gauge are with $\frac{3}{8}$" x $\frac{1}{8}$" dia. stainless steel tubing.

The reactants are contained in a P.T.F.E. tube of about 5" length, $\frac{1}{4}$" O.D. and 1/32" wall thickness. The ends are closed by plugs turned down to size from a rod of the same material. The pressure is transmitted directly through the tube walls. This tube is held inside the reaction chamber in a steel bucket with sufficient clearance to allow rapid transmission of

pressure. The bucket is fitted with a bowed sprung-steel attachment to hold it firmly at any desired height within the reaction chamber and with a hook at the top to assist removal. The bucket and the reactants tube are shown in Fig. 3.

The experimental pressure is measured on the low pressure side of the intensifier by a standard Bourdon tube test gauge G. The readings of this instrument and the intensifier ratio were checked against a primary free piston gauge in order to determine the true working pressures. The recorded pressures taken from the gauge readings, and allowing also for the slight fluctuations in pressure during a run, are estimated to be accurate within 1% at about 5000 atmospheres. This is adequate in view of the magnitude of the effect measured.

The reaction vessel is heated by a 440 Watt radiant heating jacket. Two separate windings are arranged to give more uniform heat distribution along the length of the reaction chamber by compensating for heat losses into the intensifier. The heating element is controlled by a sliding contact mercury regulator and a Sunvic hot-wire relay. This arrangement gives a temperature control of about $\pm$ 0.1°C. In addition, the whole apparatus is enclosed within a boiler-plate steel cabinet, which

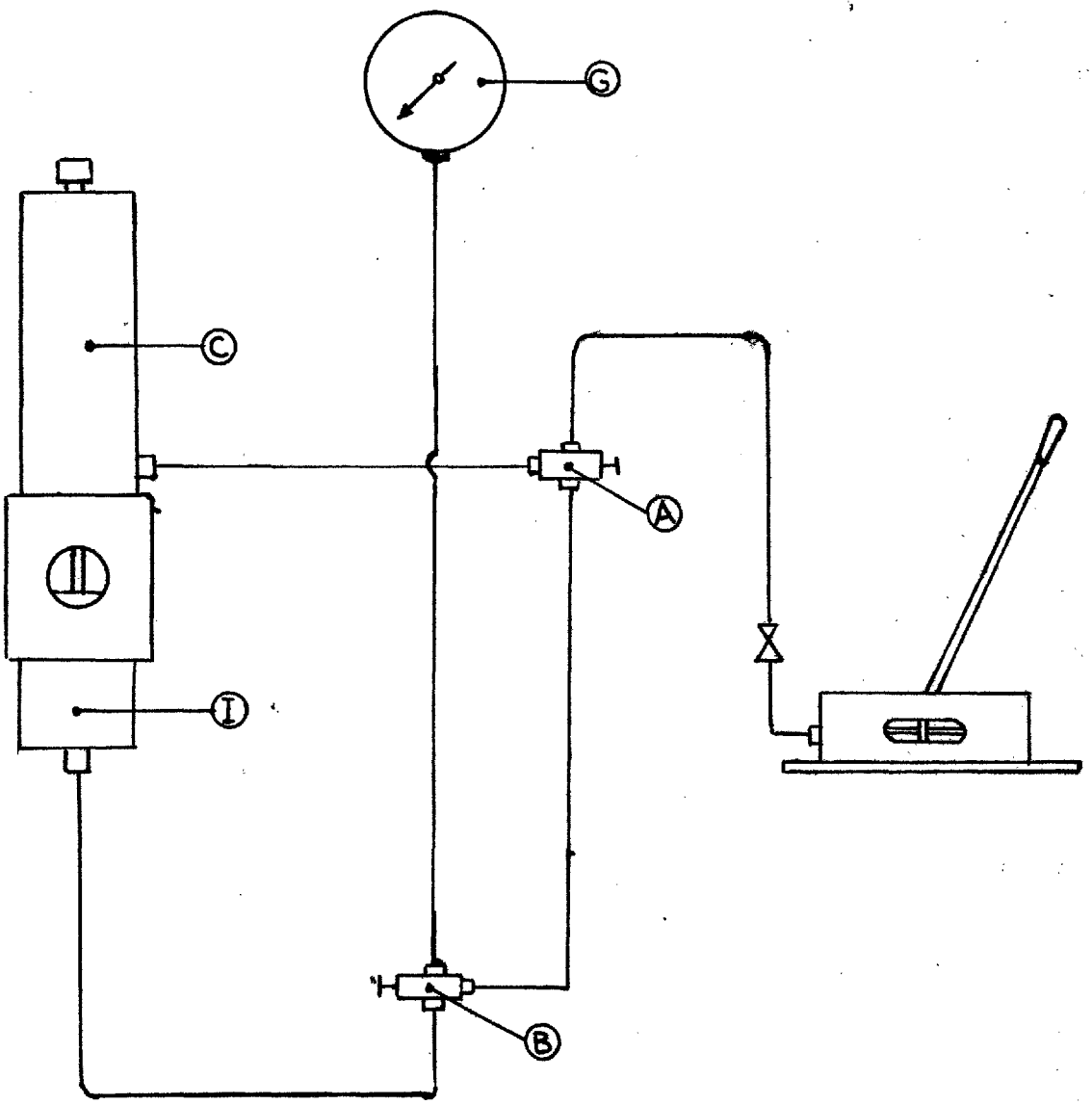


FIGURE 1

GENERAL LAYOUT OF APPARATUS

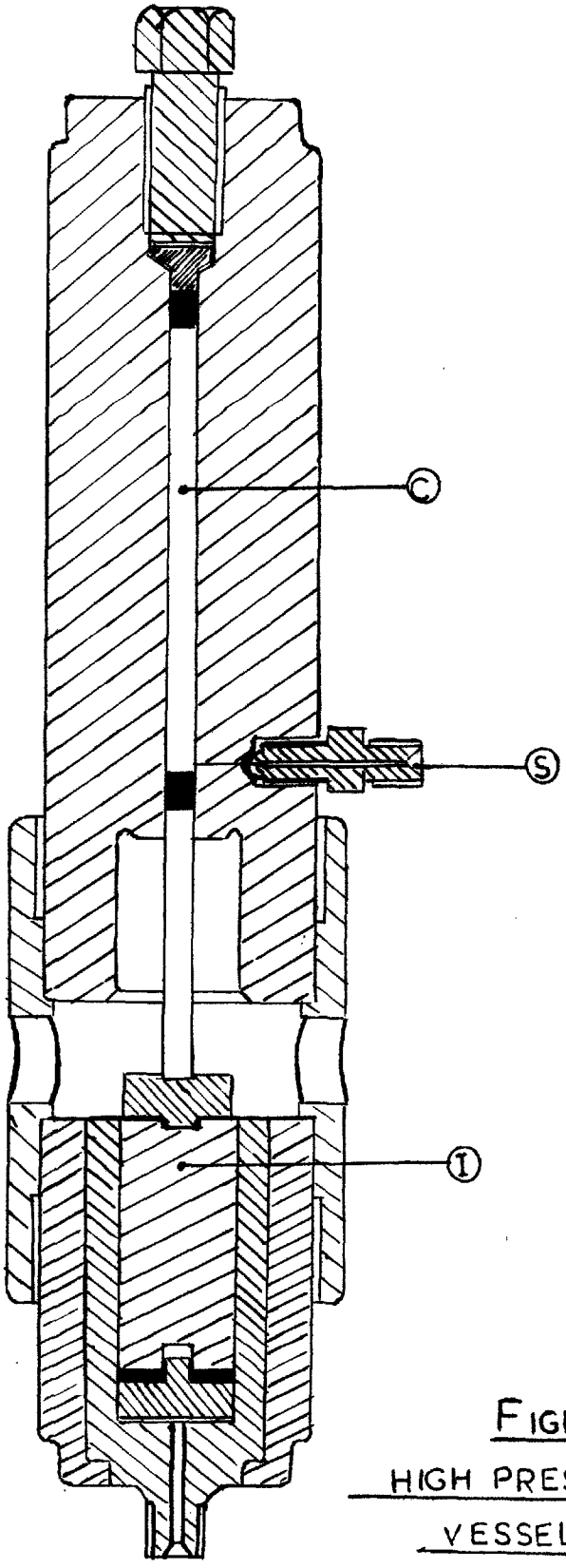


FIGURE 2

HIGH PRESSURE VESSEL

SCALE – 1/4 FULL SIZE

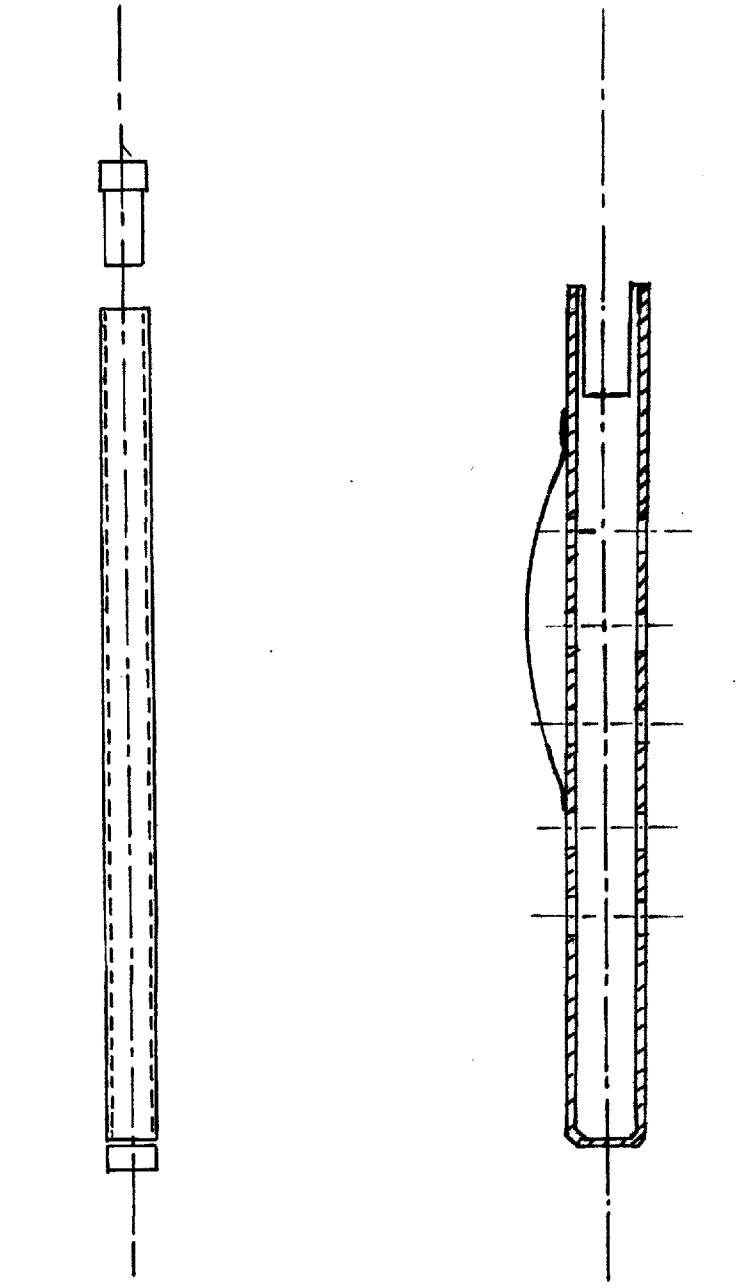


FIGURE 3

FULL SCALE

although designed primarily to protect against possible failure of parts of the equipment, helps to minimise the effect of changes occurring in the external temperature. A temperature gradient exists along the length of the reaction chamber owing mainly to the losses from the chamber to the intensifier block. The inaccuracy caused by this gradient in the desired fixed temperature was reduced to a negligible minimum by selecting that section of the reaction chamber along which the smallest gradient exists. It is estimated that the overall error in temperature measurement was $0.2^{\circ}C$ and whenever the difference in the working temperature before and after a run exceeded this value, the results of that run were considered unreliable.

The major source of trouble in the high pressure equipment was the moving Poulter packing which seals the piston. While the packing is passing the side inlet (S) it tends to extrude and a deep groove is formed on its surface. After a few runs (about six in the beginning of this work and about three at the end), the groove stretches along all the length of the packing, causing a pressure leak. This necessitated dismantling all the apparatus after few runs to change

the packing. The use of moulded instead of extruded packings and lapping the interior surface of the cylinder helped to prolong the useful life of the packings.

II.1.ii Atmospheric Pressure Equipment

Experiments at atmospheric pressure were carried out in 10 ml. amber glass ampoules. After the ampoule was charged with the reactants it was sealed and placed in a thermostat at the appropriate temperature. Two sorts of thermostats were used. The first, for experiments carried out at 0°C, was a large Dewar thermos flask inside which the temperature is controlled by the use of a mixture of pure distilled water and crashed ice. A stirrer was used to ensure a uniform temperature throughout. The second thermostat, for experiments at higher temperatures, was a constant temperature, stirred oil bath. The bath was heated by a 100 Watt electric lamp controlled by a conventional mercury thermo-regulator and a Sunvic hot-wire relay. This arrangement gave a temperature control of ± o.1°C.

II.2 Materials

Alkyl Vinyl Ethers

Ethyl, n-butyl and iso-butyl vinyl ethers were supplied by Eastman Kodak. Before use they were washed free of inhibitor (t-butyl catechol) by shaking them in a separating funnel with an equal volume of alkalined water of a PH greater than 8 (distilled water with KOH). The washing was repeated several times until the volume of the ether remained constant. The washed monomer was then dried by storing in contact with solid KOH for 24 hours. Traces of alcohols and other impurities were removed by heating under reflux with metallic sodium wire. The ether was distilled in an atmosphere of oxygen-free nitrogen, n-butyl and iso-butyl were distilled under vacuum (51 mm Hg, 77 mm Hg at 25°C respectively) and the more volatile ethyl ether under atmospheric pressure at 35.5°C, and the first and the last 20% were rejected. The vinyl ethers were stored at 0°C and usually used within five days from their distillation, otherwise fresh batches were prepared.

Benzoyl Peroxide (Bz_2O_2):

Benzoyl peroxide was supplied by (B.D.H) and was purified by precipitation from chloroform solution

with cold methanol. The precipitated benzoyl peroxide was filtered off, dried under vacuum, and then kept in the dark in a vacuum desiccator. Fresh material was prepared at regular intervals.

Azo-bis-isobutyronitrile (AIBN)

This initiator was supplied by Eastman Kodak and purified by fractional crystallisation from a saturated solution in chloroform. The crystalline product was filtered, dried and kept under vacuum.

Iodine

Resublimed iodine was supplied by Hopkin and Williams Ltd. No further purification was carried out.

Benzene

Benzene for use in molecular weight determination and as a solvent for iodine was supplied by Hopkin and Williams Ltd. No further purification was carried out.

II.3. Procedure

II.3.i. Preparation of Reaction Mixtures

Reaction mixtures having the desired (C)/(M) ratio were prepared by weight in a suitable weighing flask. With free radical initiators an approximate amount was accurately weighed in the flask and the amount of monomer needed to make up the desired concentration was

added. In the case of iodine which is a very fast initiator for bulk polymerisation of the vinyl ethers the most suitable method of addition was in benzene solution. At the lower ratios of (C)/(M) (0.001-0.030 m.mole I_2/mole monomer) a 1% by weight solution of iodine in benzene was used, while at the higher ratios (0.125-0.600 m.mole I_2/mole monomer) a 10% wt. solution was used.

II.3.ii Polymerisation Procedure (Operation of the High Pressure Apparatus.

After thorough mixing of the reaction mixture, a sample was poured into the reaction tube and the stopper inserted. After a check to ensure the absence of an air bubble, the reaction tube was placed in the steel bucket and both inserted into the high pressure reaction chamber, which was already filled with oil and at the required temperature. With valve A (Fig. 1) opened and valve B closed the hard rubber Poulter packing was inserted into the bore of the vessel, the mushroom-head set in position on top of it and the screw plag turned down until hand tight. After noting the time, pumping was begun. After reaching a pressure of about 1000 atm. the intensifier was brought into

operation by closing valve A and opening B. Pumping was continued at a controlled rate until the desired experimental pressure was reached. Valve B was then closed and the time required for pumping recorded.

At the conclusion of the run and after noting the time, the vessel pressure was slowly released, first through valve B, to restore the intensifier piston to its original position, and then through valve A. Time was again noted; the steel screwed plag was removed with a spanner, and the Poulter packing ejected by pumping it out with a few strokes of the pump (valve A opened, B closed). The bucket was removed and the temperature checked 15 minutes later.

II.3.iii Separation of Polymer

After removal from the reaction vessel, the reactants were poured into a weighed 25 ml Erlenmeyer flask which was re-weighed. To purify the polymers, attempts were made first to precipitate them. This was found to be most difficult since they were viscous liquids readily soluble in most organic solvents. Consequently, a method of applying vacuum to pump off the remaining unreacted monomer or other volatile substances was used. In the case of free radical

initiation, vacuum was applied immediately to remove the unreacted monomer, first at 60°C and 15 mmHg pressure for 2 hours and then at room temperature and 2-3 mmHg pressure for 24 hours, (a period found to be enough to bring the polymeric residue to constant weight). In the case of iodine initiation, it was first necessary to destroy the remaining iodine. This was done by mixing and shaking the reactants with N/100 sodium thiosulphate solution. The polymer solution was separated by sucking out the thiosulphate solution with a very fine pipette. It was found that greater accuracy was achieved in this operation if the polymer solution was diluted to about twice or three times its volume (depending on the expected molecular weight) with benzene, before being mixed with the thiosulphate solution. The removal of the unreacted monomer and the added benzene was carried out, as in the case of free radical initiation, by vacuum.

II.3.iv Molecular Weight Determination

Except for products of polymerisation at atmospheric pressure initiated by hydrated ferric sulfate, all polymerisation products were viscous liquids with low molecular weights. These were determined cryoscopically by the method outlined by Bonnar et al (71). This involves the measurements of the depression of the freezing point of "Molecular Weight" Benzene solvent containing a known amount of polymer, the determination operation being repeated with different concentrations of polymer. A plot of the calculated molecular weights vs. concentration usually yields a straight line, the extrapolation of which to zero concentration gives the true value of the molecular weight. In this study it was found that a non-linear relationship was obtained, presumably because of the random distribution of the molecular weight in the sample, and it was decided that a sufficiently accurate indication of the molecular weight could be obtained by measurement at a single concentration of polymer in the benzene solution.

The cold reservoir was adjusted to the operating temperature which generally is about $5^{\circ}C$ below the

freezing point of the pure solvent. With benzene as solvent, this temperature was conveniently attained by filling the reservoir with chopped ice with water sufficient to cover the ice. This gave an adequate temperature differential so that at the freezing point of the solvent the temperature of the charged cryoscope tube dropped at a rate of 0.2 - 0.25°C per minute.

The cryoscope tube was charged with a known weight of solvent, followed by about 1 gr. of desiccant; the stirrer and the thermometer were inserted and the tube placed in the channel of the cold reservoir. When the temperature had fallen down to about 0.5 - 1.0°C above the freezing point, continuous observation of the thermometer was begun and the cooling rate noted. As soon as the temperature had fallen to 0.5°C below the freezing point, the solvent was seeded by contact with a chilled pointed wire, and the maximum temperature attained during freezing was recorded. The solvent was remelted and warmed to about 1 - 1.5°C above the observed freezing point to ensure that all crystals of the solvent are melted and that no local cold spots remain and the procedure was then repeated until three successive results not differing by more than 0.003°C

were obtained. The freezing points of polymer-benzene solutions of a known concentration were determined similarly. The freezing point depression, θ, ($\theta = {}^{t}o - t$, where ${}^{t}o$ is the initial freezing point of the solvent and t is that of the solution) was then used to calculate the molecular weight, from the formula

$$\text{Molecular Weight} = \frac{1000\ Kw}{\theta\ W}$$

where w and W are the weights of the polymer sample and benzene respectively and K is the cryoscopic apparatus constant, determined from measurements with a standard solute of known molecular weight, in this case diphenyl. This constant was found to be equal to 5.75.

II.3.v Determination of the Compression Curve for iso-Butyl Vinyl Ether at 75°C.

In an attempt to find an explanation for the reduced rate of polymerisation above about 6000 atm. (see results and discussion), it was decided to investigate the possibility of pressure-freezing in the system. The monomer examined was iso-butyl vinyl ether, a sample of which was enclosed in a P.T.F.E. tube inside the pressure vessel at 75°C. Quinol was added (0.2 mole%) to the monomer to prevent thermal polymerisation. Small

increments of pressure were then applied by pumping through the intensifier, and the position of a fiducial mark on the intensifier thrust block was observed through a cathetometer. Sufficient time was allowed to elapse for the heat of compression to be dissipated before the pressure and the corresponding intensifier height were observed.

II.3.vi Experiments with the Hydrated Ferric Sulphate Initiator.

The initiator, $(Fe_2SO_4)_3 \cdot H_2SO_4 \times H_2O$, where x is equal to 3 or 4, was prepared by heating for 4.5 hours at 80°C, 20 grams of ferric sulfate hexahydrate with 100 ml of concentrated sulfuric acid. The mixture was then cooled and the initiator precipitated with diethyl ether. The solid was filtered, washed with diethyl ether and dried under vacuum at room temperature. This initiator was used with iso-butyl vinyl ether in solution in pentane in the following proportions: Initiator - 0.034 gram; Monomer - 50 ml; Solvent - 200 ml The reactants were kept at 34°C, at atmospheric pressure, in a flask with reflux and were stirred continuously for 20 hours. The rubber-like polymer was then separated by precipitation with a water-methanol mixture and dried under vacuum at room temperature.

SECTION III

Experimental Results and Calculations

III. 1 Polymerisation with Free Radical Initiation

III.1.i The Effect of Initiator - Concentrations:

High concentrations of Benzoyl peroxide, (8 and 3 wt.%), were used to initiate the polymerisation of n-butyl and iso-butyl vinyl ethers at 10,000 atm. and 75°C. The results are shown in Table 7. Comparatively, fairly high conversions to sticky liquid products of low molecular weight resulted. Higher molecular weights and lower conversions were obtained when the concentration of benzoyl peroxide was reduced to 0.1 wt.%. The results for ethyl vinyl ether, (table 8), and iso-butyl vinyl ether, (table 9), show that the molecular weights tended to increase with time, and that molecular weights of up to 9400 were obtained.

AIBN (0.1 wt %) was also used to initiate the polymerisation of ethyl and iso-butyl vinyl ethers, (tables 8 and 9). Almost similar results to those with benzoyl peroxide were obtained with ethyl vinyl ether, but lower conversions and higher molecular weights resulted in the case of iso-butyl vinyl ether. Fig. 4 shows these results graphically.

TABLE 7

Monomer - Runs 1-10, n-butyl vinyl ether.

- Runs 11-14, iso-butyl vinyl ether

Initiator - Benzoyl Peroxide.

Pressure - 10,000 atm.

Temperature - 75°C

Run No.	Initiator Conc. Weight %	Time Hours	Conversion Weight %	Molecular Weight
1	8	5	17.95	397
2	8	10	25.10	465
3	8	15	27.32	419
4	8	20	27.15	484
5	8	25	29.16	437
6	3	5	6.38	375
7	3	10	9.11	391
8	3	15	14.05	462
9	3	20	14.24	499
10	3	25	16.28	484
11	8	5	16.76	455
12	8	10	18.72	489
13	8	15	21.96	381
14	8	25	25.88	433

TABLE 8

Monomer - Ethyl vinyl ether

Initiator - Runs 15-20 Benzoyl peroxide

Runs 21-26 AIBN

Initiator Conc - 0.1 wt %

Pressure - 10,000 atm.

Temperature - Runs 20, 26 at 50°C

All others at 75°C

Run No.	Time Hours	Conversion Weight %	Molecular Weight
15	5	5.34	1547
16	10	9.48	3208
17	15	9.60	3540
18	20	10.80	4422
19	25	10.70	6026
20	25	2.99	1341
21	5	6.27	2093
22	10	8.78	2818
23	15	10.40	4454
24	20	10.47	5767
25	25	11.71	8080
26	25	1.06	410

TABLE 9

Monomer - Iso-butyl viryl ether

Initiators - Runs 27-32 AIBN

Runs 33-50 Benzoyl peroxide

Initiator Conc. - 0.1 wt. %

Temperature - Runs 32, 37 at 50°C

All others at 75°C

Run No.	Pressure Atm.	Time Hours	Conversion Weight %	Molecular Weight
27	10000	5	3.64	1888
28	10000	11	6.48	2164
29	10000	15	7.90	6265
30	10000	20	11.15	7645
31	10000	25	13.39	9434
32	10000	25	0.89	831
33	10000	2.5	3.52	1256
34	10000	5	6.31	1670
35	10000	7.5	9.65	2410
36	10000	10	13.71	2968
37	10000	25	1.36	485
38	7000	2	3.71	915
39	7000	4	6.50	1403
40	7000	6	10.46	1362
41	5000	2	2.76	1042
42	5000	4	5.70	985
43	5000	6	9.65	1257
44	2500	4	2.02	743
45	2500	6	3.26	896
46	2500	8	4.32	875
47	2500	10	4.87	1108
48	1	5	0.50	466
49	1	10	1.32	540
50	1	20	2.62	623

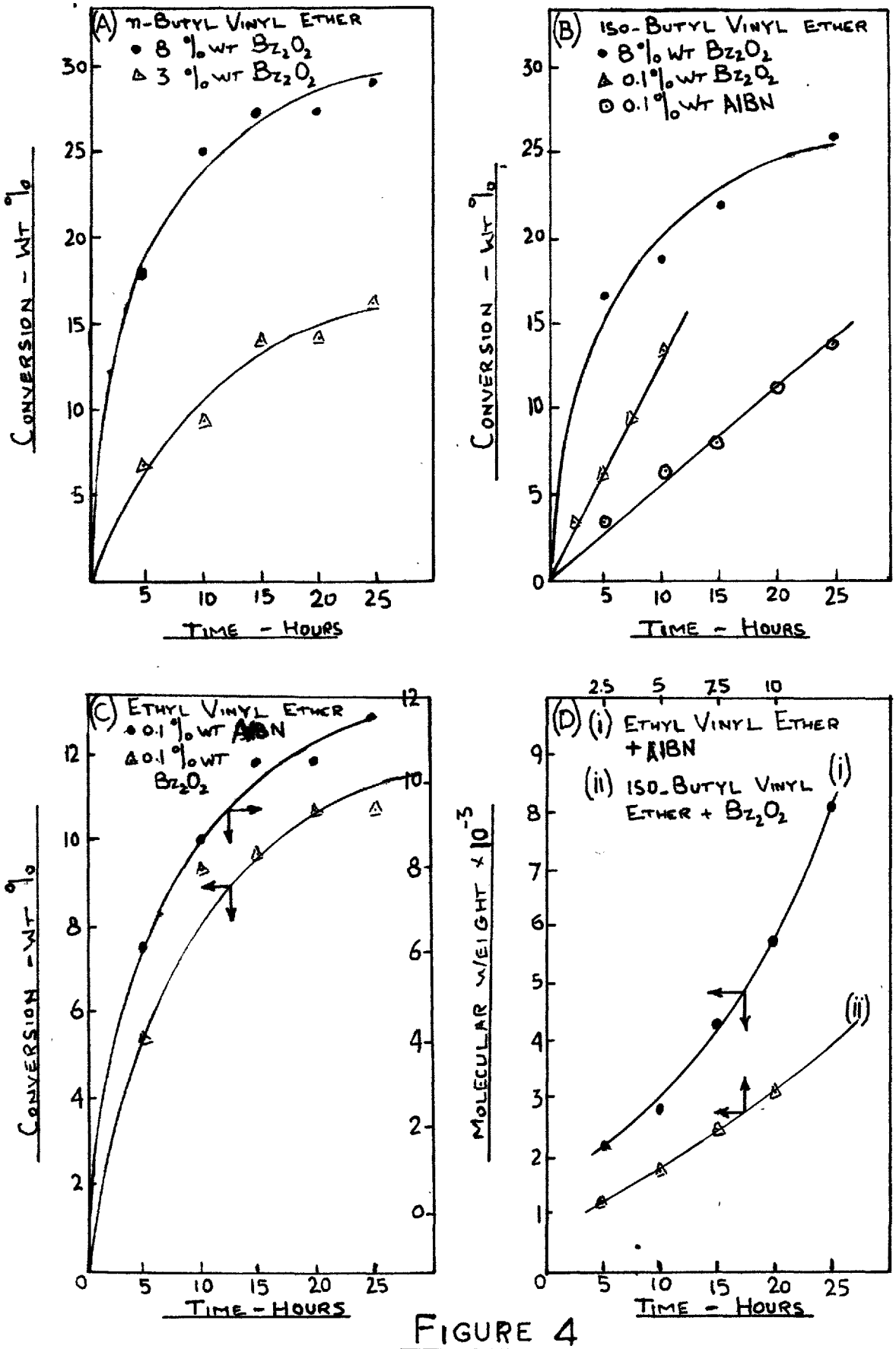

(A) n-Butyl Vinyl Ether
• 8 % wt Bz_2O_2
△ 3 % wt Bz_2O_2
Conversion - wt %
Time - Hours
(B) Iso-Butyl Vinyl Ether
• 8 % wt Bz_2O_2
△ 0.1 % wt Bz_2O_2
⊙ 0.1 % wt AIBN
Conversion - wt %
Time - Hours
(C) Ethyl Vinyl Ether
• 0.1 % wt AIBN
△ 0.1 % wt Bz_2O_2
Conversion - wt %
Time - Hours
(D) (i) Ethyl Vinyl Ether + AIBN
(ii) Iso-Butyl Vinyl Ether + Bz_2O_2
Molecular Weight $\times 10^{-3}$
Time - Hours

FIGURE 4

III.1.ii The Effect of Temperature

The effect of temperature on the polymerisation was studied by reducing the temperature from 75° to 50° C. At 50°C the rate of polymerisation of ethyl vinyl ether (initiated by benzoyl peroxide) and the molecular weight of the product were only about one quarter of the values at 75°C (Run 20). A greater decrease, to less than one tenth of the rates and molecular weights at 75°C occurred in the polymerisation of the same monomer initiated by AIBN (Run 26) and in the polymerisation of iso-butyl vinyl ether initiated by benzoyl peroxide (Run 37) and AIBN (Run 31 and 32). From these runs and the corresponding ones at 75°C, the following approximate overall activation emerges and frequency factors (A in the Arrhenius equation $k=Ae^{-E/RT}$) at 10,000 atm. were calculated.

Table 10

Approximate Activation Energies and Frequency Factors of the Overall Polymerisation Reaction at 10000 atm.

Monomer	Initiator	Activation Energy Kcal/mole	Frequency Factor
Ethyl Vinyl Ether	Bz_2O_2	19	4×10^{7}
Ethyl Vinyl Ether	AIBN	30	4×10^{14}
Iso-butyl Vinyl Ether	Bz_2O_2	28	5×10^{13}
Iso-butyl Vinyl Ether	AIBN	24	3×10^{10}

III.1.iii The Effect of Pressure

The effect of pressure on the rate of polymerisation and the molecular weight of the product was investigated for iso-butyl vinyl ether with benzoyl peroxide as initiator (0.1 wt %) at 75°C. From table 9 graphs of the % conversion vs. time were constructed and rates of polymerisation obtained from the slopes. These rates, and the molecular weights from polymerisations lasting 5 hours, (some of which are interpolated values, shown with star), are shown in table 11 and Fig. 5. The molecular weight is almost directly proportional to the pressure, while the rate of polymerisation at first increases almost exponentially with pressure, but passes through a maximum at about 6000 atm at which it is about 16 times greater than at 1 atm, and then decreases with pressure.

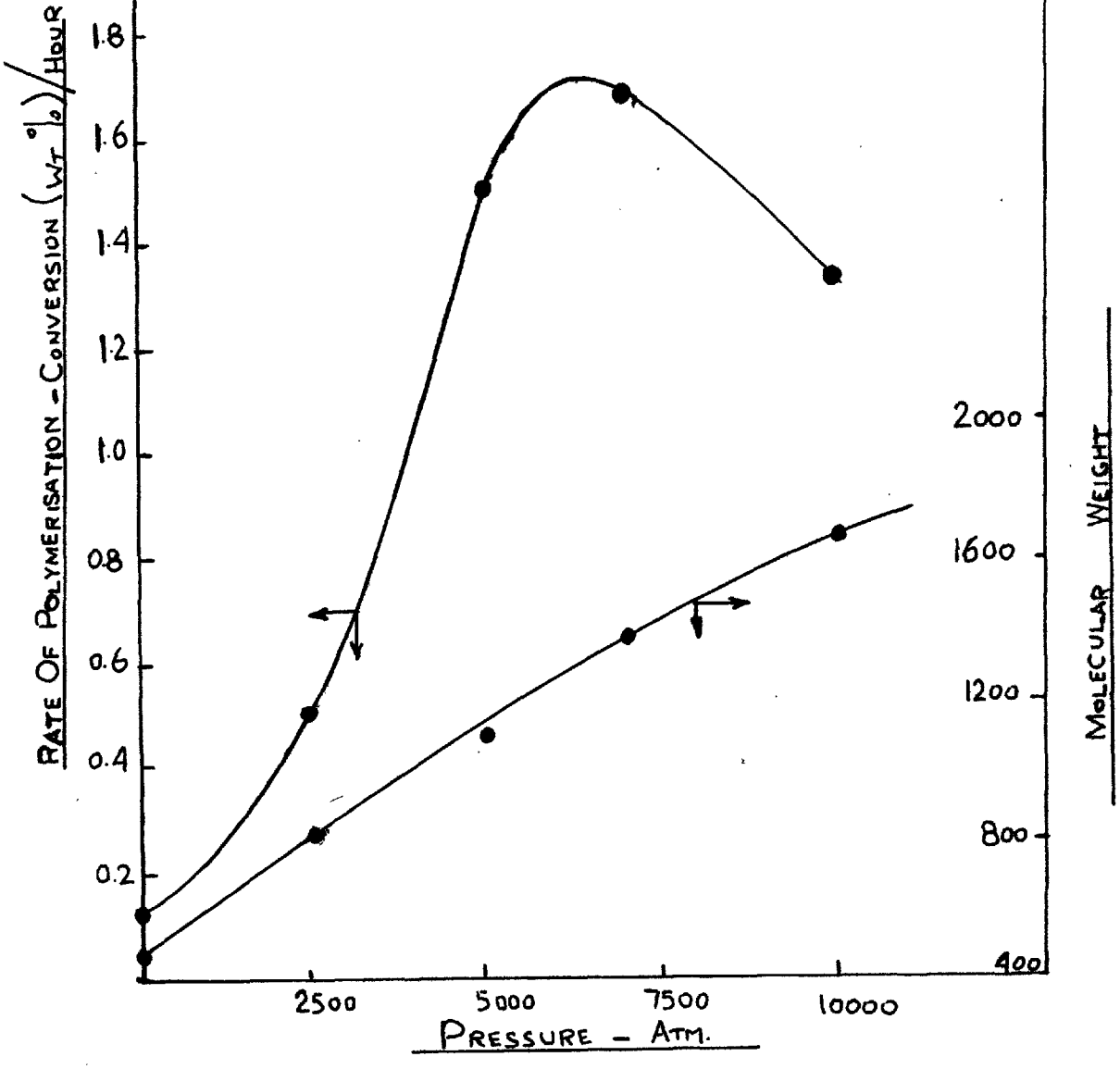
Table 11

Effect of Pressure on the Polymerisation of Iso-Butyl Vinyl Ether Initiated by Benzoyl Peroxide at 75°C.

Pressure atm	Rate Conversion (wt%)/hour	Molecular Weight After 5 hours
1	0.11	466*
2500	0.51	810*
5000	1.53	1100*
7000	1.70	1380*
10000	1.34	1670

FIGURE 5

RATES AND MOLECULAR WEIGHTS OF Bz_2O_2 – INITIATED POLYMERISATION OF ISO-BUTYL VINYL ETHER AT 75°C.



III.2. Polymerisation With Ionic Initiation

The polymerisation of iso-butyl vinyl ether initiated by iodine was used in a study of the effect of pressure on the ionic polymerisation of alkyl vinyl ethers. Results obtained at high pressures are classified in tables 12, 13, 14, and those of atmospheric pressure runs are classified in tables 15, 16, 17.

Table 12

Monomer - Iso-butyl Vinyl Ether
Initiator - Iodine
Pressure - 10000 atm.
Temperature - 75°C.

Run No.	Iodine Conc. m. mole/ mole monomer	Time Hours	Conversion Weight %	Molecular Weight
51	0.030	1	5.32	982
52	0.030	1.5	6.48	949
53	0.030	2	10.03	1291
54	0.030	3	12.14	1140
55	0.015	1	3.54	1024
56	0.015	2	5.61	1058
57	0.015	3	8.02	1212
58	0.015	4	9.52	1456
59	0.015	5	12.81	1132
60	0.005	1	2.18	1081
61	0.005	2	3.21	1504
62	0.005	3	4.22	1448
63	0.005	4	6.27	1965
64	0.005	6	8.00	1607
65	0.005	8	10.05	1366
66	0.001	1	1.36	2014
67	0.001	2	1.98	2193
68	0.001	3	2.88	1847
69	0.001	4	3.16	1964
70	0.001	6	4.68	1753
71	0.001	8	6.22	2204
72	0.001	10	7.03	2315

TABLE 13

Monomer - Iso-butyl vinyl ether

Initiator - Iodine

Initiator Conc. - 0.015 m. mole/mole monomer

Temperature - 75°C

Run No.	Pressure atm.	Time Hours	Conversion Weight %
73	7000	1	4.74
74	7000	2	7.73
75	7000	3	9.95
76	7000	3.5	11.12
77	2500	1	3.42
78	2500	2	5.91
79	2500	3	7.68
80	2500	4	10.62
81	2500	5	13.63

TABLE 14

Monomer - Iso-butyl vinyl ether
Initiator - Iodine
Pressure - 5000 atm.
Temperature - Runs 86, 87, 92, 93 at 50°C
All others at 75°C

Run No.	Iodine Conc. m. mole/ mole monomer	Time Hours	Conversion Weight %	Molecular Weight
82	0.015	1	4.24	858
83	0.015	1.5	6.35	950
84	0.015	2	8.52	1210
85	0.015	2.5	11.38	1058
86	0.015	5	4.85	1655
87	0.015	10	8.92	1830
88	0.010	2	4.11	887
89	0.010	3	6.75	992
90	0.010	4.5	9.31	1250
91	0.010	6	11.48	1218
92	0.010	5	3.48	1683
93	0.010	10	6.53	1794
94	0.005	2	1.80	862
95	0.005	3	2.32	1026
96	0.005	4	3.61	1213
97	0.005	5	3.95	1561
98	0.005	6	5.68	2068
99	0.005	7	5.56	1609
100	0.005	8	6.34	1985

TABLE 15

Monomer - Iso-butyl vinyl ether

Initiator - Iodine.

Pressure - Atmospheric

Temperature - 75°C

Run No.	Iodine Conc. m. mole/ mole monomer	Time Hours	Conversion Weight %	Molecular Weight
101	0.025	2	3.42	-
102	0.025	4	5.71	-
103	0.025	6	8.68	-
104	0.025	8	10.03	-
105	0.015	2	1.26	798
106	0.015	4	2.17	934
107	0.015	6	2.81	1228
108	0.015	8	4.17	1484
109	0.015	10	4.38	1356
110	0.015	15	7.51	1640
111	0.015	20	10.35	1522
112	0.005	10	0.82	1235
113	0.005	15	1.04	886
114	0.005	20	1.62	1652
115	0.005	40	2.88	1972

TABLE 16

Monomer - Iso-butyl vinyl ether

Initiator - Iodine

Pressure - Atmospheric

Temperature - 35°C

Run No.	Initiator Conc. m.mole/mole	Time Hours	Conversion Weight %
116	0.400	1.5	5.13
117	0.400	2	8.27
118	0.400	3	11.34
119	0.300	2.5	5.22
120	0.300	3.5	8.20
121	0.300	5	11.21
122	0.300	3	2.61
123	0.200	5	4.39
124	0.200	7	6.23
125	0.200	8	6.78

TABLE 17

Monomer - Iso-butyl vinyl ether

Initiator - Iodine

Pressure - Atmospheric

Temperature - 0°C

Run No.	Iodine Conc. m. mole/ mole monomer	Time Hours	Conversion Weight %
126	0.600	2	6.16
127	0.600	2.5	7.35
128	0.600	3	10.51
129	0.550	2	4.80
130	0.550	3	7.85
131	0.550	4	9.47
132	0.500	3	5.05
133	0.500	4	7.24
134	0.500	5	8.81
135	0.500	6	9.82
136	0.375	4	3.89
137	0.375	5	5.21
138	0.375	6.25	6.33
139	0.375	8	8.12
140	0.250	4	1.84
141	0.250	7	3.30
142	0.250	9	4.01
143	0.250	11	4.72
144	0.250	13	5.91
145	0.125	11	1.47
146	0.125	13	1.51
147	0.125	15	1.85
148	0.125	17	2.20
149	0.125	19	2.23

III.2.i. The Effect of Iodine Concentration on the Rate of Polymerisation.

From the preceding tables graphs of the % conversion vs time were constructed and rates of polymerisation obtained from the slopes. The following table shows the changes occurring in the rate of polymerisation when the iodine concentration is varied at several pressures.

TABLE 18

Pressure atm.	Temperature °C	Iodine Conc. m.mole/ mole monomer	Rate Conversion (wt%)/hour
10000	75	0.001	0.67
10000	75	0.005	1.22
10000	75	0.015	2.24
10000	75	0.030	3.80
5000	75	0.005	0.86
5000	75	0.010	1.92
5000	75	0.015	3.85
1	75	0.005	0.075
1	75	0.015	0.43
1	75	0.025	1.25
1	35	0.200	0.87
1	35	0.300	2.24
1	35	0.400	3.85
1	0	0.125	0.12
1	0	0.250	0.45
1	0	0.375	1.02
1	0	0.500	1.76
1	0	0.550	2.42
1	0	0.600	3.15

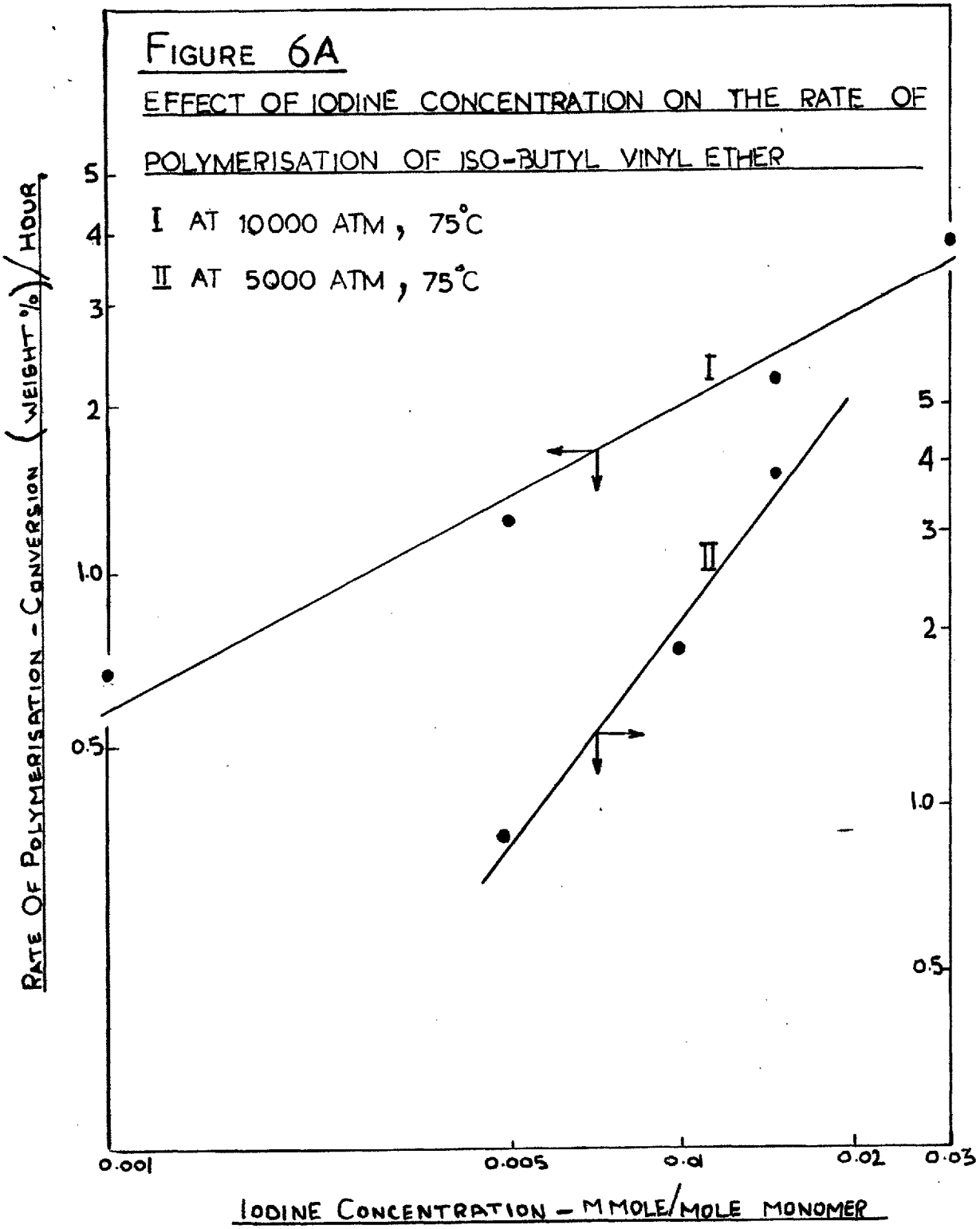
These results are shown in Fig. 6 A,B, as graphs of log (rate of polymerisation) vs. log (iodine concentration). The plots are straight lines whose slopes give the exponent x of the iodine concentration in the equation Rate of Polymerisation = $K(I_2)^x$. It will be seen that x varies considerably with pressure and to a lesser extent with temperature. The values obtained are given in the table below.

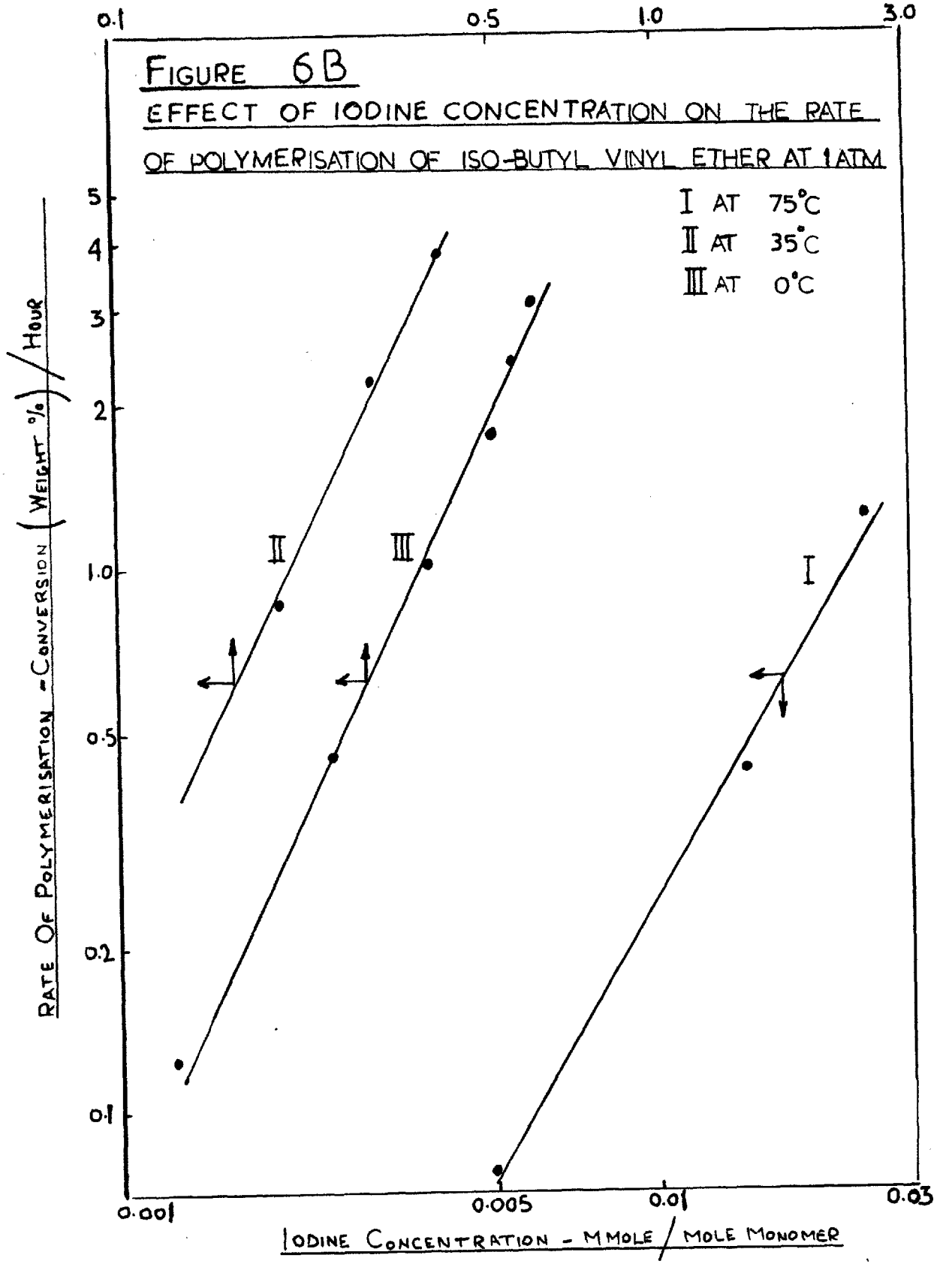
TABLE 19

Variations in Exponent x of the Iodine Concentration in the Eq. Rate = $K(I_2)^x$ with Pressure and Temperature.

Pressure atm.	Temperature ^oC	x
10000	75	0.52
5000	75	1.35
1	75	1.75
1	35	2.08
1	0	2.06

The effect of the changes of iodine concentration on the molecular weights of the products of the ionic polymerisation are smaller and less systematic than in the case of the radical polymerisation, but can be summarized as a slight trend towards increased molecular weights at lower initiator concentrations.


FIGURE 6A
EFFECT OF IODINE CONCENTRATION ON THE RATE OF POLYMERISATION OF ISO-BUTYL VINYL ETHER
I AT 10000 ATM, 75°C
II AT 5000 ATM, 75°C
RATE OF POLYMERISATION - CONVERSION (WEIGHT %)/HOUR
IODINE CONCENTRATION - M MOLE/MOLE MONOMER
0.001
0.005
0.01
0.02
0.03
0.5
1.0
2
3
4
5
I
II


FIGURE 6B
EFFECT OF IODINE CONCENTRATION ON THE RATE OF POLYMERISATION OF ISO-BUTYL VINYL ETHER AT 1 ATM
I AT 75°C
II AT 35°C
III AT 0°C
RATE OF POLYMERISATION - CONVERSION (WEIGHT %) / HOUR
IODINE CONCENTRATION - M MOLE / MOLE MONOMER
0.1
0.5
1.0
3.0
5
4
3
2
1.0
0.5
0.2
0.1
0.001
0.005
0.01
0.03
I
II
III

III.2.ii The Effect of Pressure on the Rate of Polymerisation

The effects of pressure on the rate of the iodine-initiated polymerisation bore a general similarity to the radical polymerisation. When pressure is increased, the rate increases with pressure up to about 6000 atm, (at which the rate is about 9 times greater than at 1 atm), and afterwards decreases with pressure. The rates of polymerisation at 75°C at various pressures (iodine concentration 0.015 m.mole/mole monomer) are classified in table 20 and shown graphically in Fig. 7.

TABLE 20

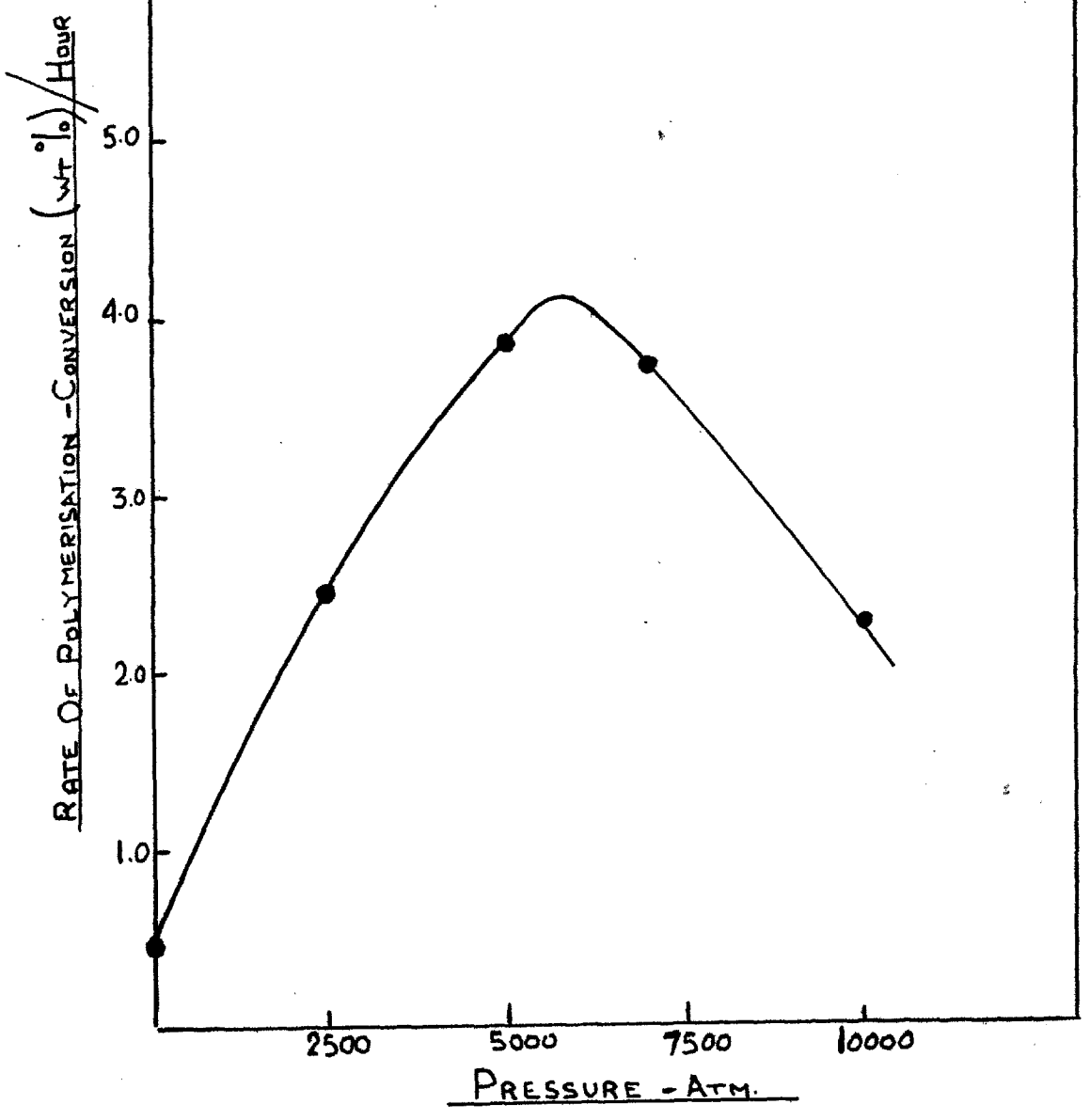
Effect of Pressure on Iodine-Initiated Polymerisation of Iso-butyl Vinyl Ether at 75°C

Pressure atm	Rate Conversion (wt %)/hour
1	0.43
2500	2.46
5000	3.85
7000	3.72
10000	2.24

A trend towards slightly higher molecular weights at higher pressures is observed, in comparison to the 3-4 times increase in the molecular weight in radical polymerisation when pressure is increased from 1 to 10000 atm.

FIGURE 7

RATES OF IODINE-INITIATED POLYMERISATION OF ISO-BUTYL VINYL ETHER AT 75°C.



III.2.iii The Effect of Temperature on the Rate of Polymerisation

The effect of temperature was studied at 5000 ard 1 atm. Changes in temperature were found to exert a lesser effect on the rate of ionic polymerisation than on that of free radical polymerisations of iso-butyl vinyl ether. The following approximate activation energies and frequency factors (A in the Eq. $k=Ae^{-E/RT}$), were calculated.

TABLE 21

Approximate Activation Energies and Frequency Factors of the Overall Iodine-Initiated Polymerisation of Iso-Butyl Vinyl Ether.

Pressure atm.	Activation Energy kcal/mole	Frequency Factor A
5000	13	3×10^8
1	10	2×10^7

The molecular weight of the polymer increases by a factor of about 1.5, when the temperature is reduced from 75°C to 50°C at 5000 atm.

III.3 Supplementary

III.3.i Freezing Pressure of Iso-Butyl Vinyl Ether

The results of the attempt to determine the freezing pressure of iso-butyl vinyl ether at 75°C were as follows:

TABLE 22

Gauge Reading atm.	Intensifier Height cm.	Gauge Reading atm.	Intensifier Height cm.
325	0.178	550	1.348
350	0.376	575	1.452
375	0.533	600	1.553
400	0.684	625	1.663
425	0.834	650	1.736
450	1.005	675	1.840
475	1.105	700	1.938
500	1.134	725	2.020
525	1.234		

These results are plotted in Fig 8, from which it can be seen that at about a gauge pressure of 450 atm corresponding to a true pressure of 6400 atm, a small discontinuity is occurring in the graph with a change of slope thereafter. This is suspected to be caused by a second order transition of the iso-butyl vinyl ether to an amorphous or glassy state.

III.3.ii The Spectrum of Iodine Solution

Results of the study of the absorption spectrum of the complex formed in the iso-butyl vinyl ether-iodine-benzene system are shown in table 23, (the background absorption of the iso-butyl vinyl ether and cell were subtracted). The solution inspected contained 0.015 m.mole iodine/mole iso-butyl vinyl ether, the iodine being added in 1% wt solution in benzene. These results are shown graphically in Fig. 9, together with results on the absorption spectrum of iodine-benzene complex in n-heptane solution (concentration of iodine = 1.2×10^{-3} mole/litre, concentration of benzene 1.6×10^{-1} mole/litre), measured by Ham (19) at 2000 atm. It is shown that in both cases a peak in the absorption in the region of the near ultraviolet is occurring. This is attributed to the charge transfer absorptions of the iodine complexes (18).

TABLE 23

Absorption Spectrum of the System Iso-butyl Vinyl Ether - Iodine - Benzene.

Wave Length mμ	Optical Density D
302	1.71
305	1.08
308	0.95
310	0.98
315	1.31
318	1.42
320	1.37
325	1.18
330	0.92
340	0.53
350	0.37

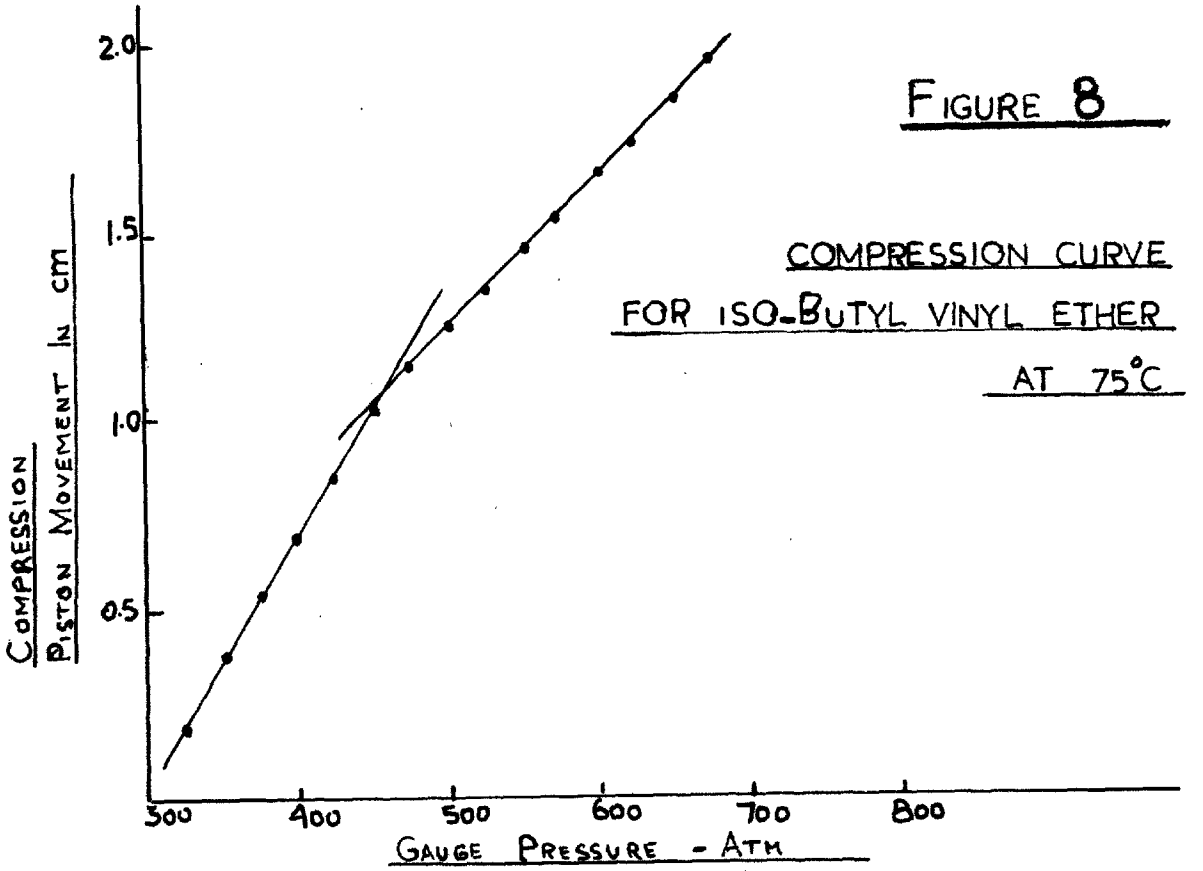


FIGURE 8

COMPRESSION CURVE FOR ISO-BUTYL VINYL ETHER AT 75°C

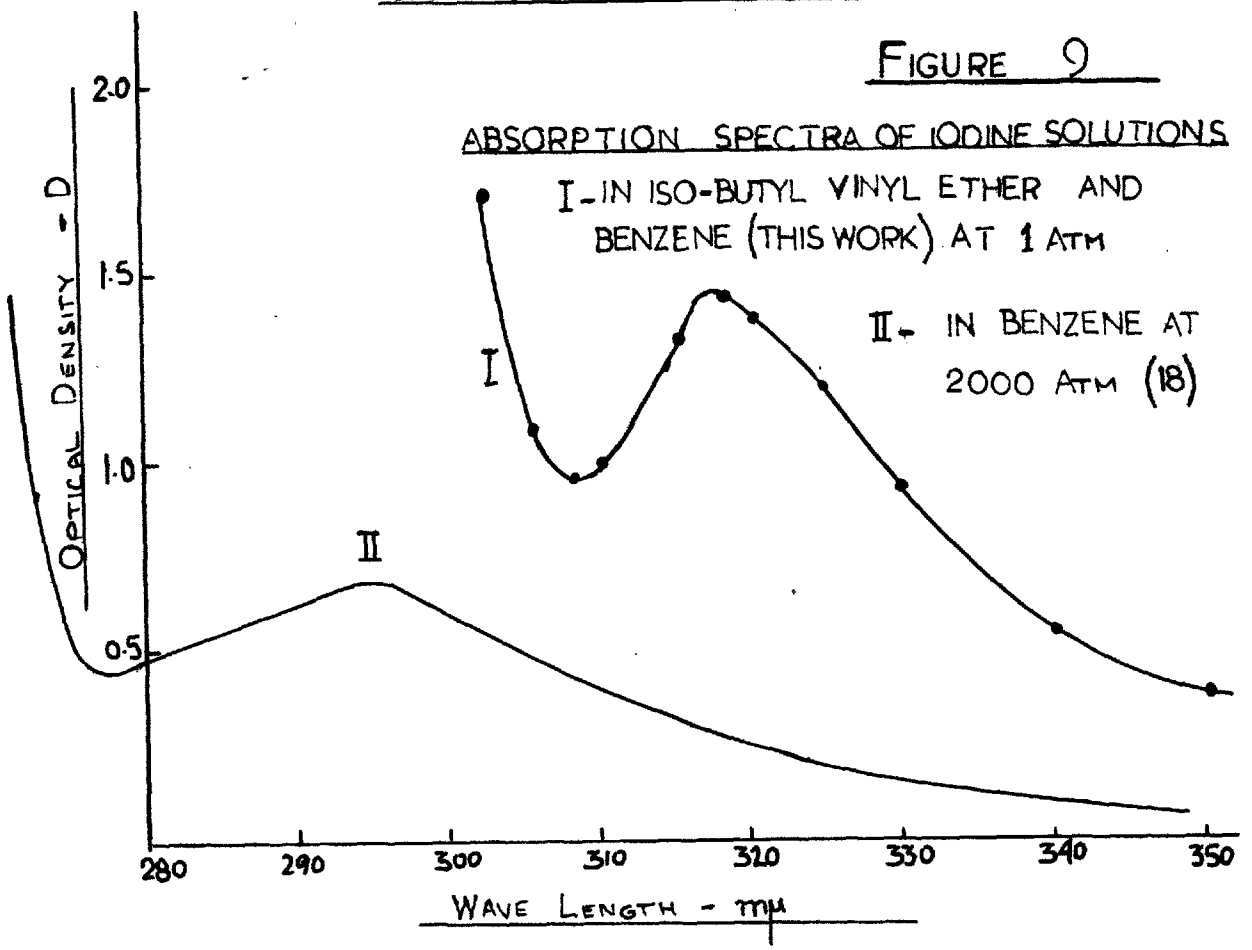


FIGURE 9

ABSORPTION SPECTRA OF IODINE SOLUTIONS

I - IN ISO-BUTYL VINYL ETHER AND BENZENE (THIS WORK) AT 1 ATM

II - IN BENZENE AT 2000 ATM (18)

III.3.iii The Use of Hydrated Ferric Sulfate as Initiator.

The result of the experiment using this patented initiator (described in II.3.vi) gave a rubber like, high molecular weight polymer. The relative viscosity at 30°C of a solution of 0.5 gm polymer in 100 ml Benzene was found to be·

$$\frac{\eta}{\eta_0} = \frac{\text{Viscosity solution}}{\text{Viscosity Benzene}} = 4.39$$

The yield was less than that stated in the patent

Yield stated	3	gms
Actual yield	0.95	gms

SECTION IV

Discussion

It was the purpose of this work to study the polymerisation of alkyl vinyl ethers and to examine the effect of pressure on the kinetics and the polymer molecular weight. From the experimental results it is found that although the effects of some changes in the conditions of the polymerisation resemble in some ways those observed in the polymerisation of styrene, in other respects the vinyl ethers behave in an unexpected way. Two general reasons can be cited for these differences in behaviour.

1. The electron-repelling nature of the ether group increases the electron density at the double bond and causes it to be much less reactive towards free-radical initiators and in radical chain propagation than are other monomers, such as styrene, and to be more readily polymerised by ionic initiators (compare activation energies in tables 10 and 21)

Iso-butyl vinyl ether undergoes a volume transition (apparently of second order), at a pressure

of about 6400 atm, and this appears to affect the kinetics of the polymerisation of this monomer at higher pressures.

IV.1. Polymerisation With Free Radical Initiators

IV.1.i. The Effect of Initiator Concentration

The use of high concentrations of benzoyl peroxide to initiate the polymerisation of n-butyl and iso-butyl vinyl ethers at 10000 atm. gave similar products (table 7) to those obtained by Shostakovskii et al with this initiator in the atmospheric pressure. Fairly large yields of a mixture of addition product and low molecular weight polymers were obtained. The analysis of the products of Runs 12 and 36 together with the theoretical composition of two possible products are given in the following table:

TABLE 24

Reaction	C wt %	H wt %	O wt % (by difference)
Run No. 12 - initiated by 8% Bz_2O_2	71.09	9.27	19.64
Run No. 36 - initiated by 0.1% Bz_2O_2	71.61	11.91	16.48
Addition product - $C_6H_5COOCH_2CH(OC_4H_9)OCOC_6H_5$	70.17	6.43	23.40
Polymer product - $C_6H_5COO(CH_2CH\text{-}OC_4H_9)_{30}$	71.93	11.69	16.38

The decrease in the oxygen content in the product of Run 36 indicates a decrease in the number of benzoyloxy groups per mole of product. The molecular weight of the products obtained with both 8 and 3% wt of benzoyl peroxide was about 450, indicating the formation of either a low polymer (trimer), or a mixture of addition product, e.g. the acylal structure $C_6H_5COOCH_2CH(OR)OCOC_6H_5$ which has a molecular weight of 342 when R is a butyl group, plus a low polymer containing about 5 to 6 monomer units. The process can probably be represented as follows: the benzoyloxy radicals formed by the decomposition of benzoyl peroxide react at the double bond of the alkyl vinyl ether and initiate polymerisation. The resulting chain raction is slow and gives short polymer chains of $C_6H_5COO(CH_2\text{-}CHOR)_n$ because it is not much faster than the termination process with its lower activation energy. With increase in benzoyl peroxide concentration n decreases and in the extreme case the process will give rise to an addition product in which one monomer molecule combines with both benzoyloxy groups resulting from the decomposition of a benzoyl peroxide molecule. When the benzoyl peroride concentration was reduced to 0.1% wt, molecular weights

of up to 3000, corresponding to n ≈ 30, were obtained, indicating that at this concentration the benzoyl peroxide acted principally as a chain initiator and not an adding agent.

The dependence of the overall rate of polymerisation on the initiator concentration was not investigated in detail but the data obtained follow the anticipated trend to higher rates at higher concentrations of benzoyl peroxide. This initiator is known to decompose rapidly in ethers (72); and as the chain propagation reaction is slow (only relatively low molecular weight products are formed), the rate of consumption of monomers is only about 1 wt %/hour, i.e. only 3 times faster than that of the initiator, when the initiator concentration is 0.1 wt %. With AIBN instead of Bz_2O_2 as initiator (tables 8 and 9), the polymerisation rate of iso-butyl vinyl ether was lower and the molecular weight of the product higher. These results indicate that this monomer is less reactive to AIBN than to Bz_2O_2, and that transfer to Bz_2O_2 initiator is important as a chain-ending process. At 10000 atm. iso-butyl vinyl ether is believed to exist in an amorphous or glassy state so that

termination by combination or disproportionation involving the movement of large molecules is extremely unlikely. Molecular chain termination will probably be by transfer to initiator or to monomer and kinetic chain termination by reaction with primary radicals. Benzoyl peroxide is known (73) to undergo both spontaneous and induced decomposition in contrast with the strictly first order decomposition, with no evidence of induced decomposition, found for AIBN (74). A higher concentration of primary radicals and a greater degree of chain transfer to the initiator would explain the lower molecular weight obtained when using benzoyl peroxide. Although it is difficult, from the experiments carried out to be certain of the reason for the effect of the change in initiator on the polymerisation of isobutyl vinyl ether, it seems clear that the change in the physical state of this monomer above a pressure of about 6400 atm has a large influence. In contrast the polymerisation of ethyl vinyl ether, (the compression curve of which was not investigated), was found to be almost unaffected by a change of initiators.

IV.1.ii The Effect of Temperature

The effect of temperature on the rate of polymerisation by radical mechanism is shown by the results at 50°C and 75°C (table 10). Over this range values of temperature coefficients, defined as k_{t+10}/k_t where k_t is the rate constant at t°C and k_{t+10} at 10°C higher, were found to be between 2.3 and 3.7, which is near the estimate (75) of 2 to 3 made for homogenous processes. These results were slightly higher than values found by Shostakorskii et al (64) in the polymerisation of n-butyl vinyl ether initiated by 0.2 wt % benzoyl peroxide at 1 atm whose results are given below:

TABLE 25

Effect of Temperature on the Polymerisation of n-Butyl Vinyl Ether at 1 atm. (64)

Temperature °C	Time of Reaction Hours	Yield Wt %	Molecular Weight
60	140	1.34	920
80	120	2.77	1200

If the Arrhemius equation $k=Ae^{-E/RT}$ is applied to the results for iso-butyl vinyl ether, a very approximate value for the overall activation energy of 28 kcal/mole is found, which is somewhat higher than the values of

about 26 kcal and 20 kcal/mole found for styrene at 1 and 3000 atm respectively (76).

As well as increasing the rate of reaction -, a rise in temperature is also found to increase the molecular weight of the product in the free radical initiated polymerisation of alkyl vinyl ethers (tables 8 and 9, compare also Shostakovskii's results in table 25). This is unusual for vinyl polymerisation processes (76) (77), as generally the molecular weight decreases with an increase in temperature. The decrease is usually attributed to a greater increase with temperature in the rate of transfer than in the rate of chain propagation, which leads to a reduction in the molecular weight. The explanation is satisfactory for vinyl monomers which have a high rate of propagation so that the molecular weight is controlled by the transfer and termination processes. However, the slow rate of the free-radical initiated polymerisation of alkyl vinyl ethers, and the relatively low molecular weight of products makes it probable that the polymer molecular weight is controlled by the slow rate of chain propagation. Therefore an increase in temperature which causes an increase in the propagation rate will also result in a polymer of higher molecular weight (See Eq. 9).

IV.1.iii The Effect of Pressure

The overall rate of the polymerisation of iso-butyl vinyl ether initiated by benzoyl peroxide was found to increase considerably with pressure up to about 6000 atm (Table 11, Fig. 5). The acceleration is probably due to the combined effects of an increase in the rate of the chain propagation reaction and a retardation in the mutual chain radical termination reaction, as suggested for styrene polymerisation by Merrett and Norrish (58) and confirmed by the work of Nicholson and Norrish (59). Although in the termination process the formation of the transition state is almost certainly accompanied by a decrease in volume, so that it should be accelerated by pressure, Norrish and his co-workers suggest that the reaction becomes diffusion controlled as a result of the increase of viscosity with pressure.

The relative effect of pressure on the overall rate of polymerisation is shown by the ratio of the rates (conversion (wt %)/hour) at high pressures to the rate at one atmosphere. A comparison between the results for iso-butyl vinyl ether and those obtained in studies of styrene polymerisation at

60°C with an almost identical concentration of benzoyl peroxide, is given below.

TABLE 26

Acceleration Factors for High Pressure Polymerisation.

	Rate 2500 atm / Rate 1 atm	Rate 5000 atm / Rate 1 atm
Iso-butyl vinyl ether at 75°C (This work)	4.6	13.9
Styrene (58) at 60°C	5.6	15.0
Styrene (78) at 60°C	5.0	13.5

The overall polymerisation rates for iso-butyl vinyl ether and styrene are thus similarly affected by an increase in pressure, although the rates of the two polymerisations differ considerably at atmospheric pressure, (about 1 wt % conversion/hour for styrene at 60°C (58) in comparison with only 0.11%/hour found for iso-butyl vinyl ether with almost the same concentration of benzoyl peroxide). These results suggest that the volume changes occurring in the transition state formation are much the same in both polymerisations. As these accelerations are in accordance with the proportionality of log k to

pressure, then if Eq. 15 is applied to the results of this work, an average $\triangle V^* = -15$ c.c./mole is found which is near the value of $\triangle V^* = -17$ c.c./mole found by Merrett and Norrish (58) for styrene.

The decrease in the overall rate of polymerisation at pressures above 6000 atm (Fig. 5), which also was found to occur in the iodine-initiated reaction (Fig. 7), has not been observed for styrene, but a maximum in the rate vs. pressure curve was found by Kilroe and Weale (79) in the polymerisation of alpha methyl styrene, the maximum being shifted to higher pressure when the medium was diluted with solvents. They suggested that the decrease in rate is probably due to a large increase in viscosity or a phase separation, both of which would be affected by dilution. Subsequent work by Elroy (80) has established that the rate maximum occurs at the freezing pressure of alpha methyl styrene. The maximum in the overall rate of polymerisation of iso-butyl vinyl ether observed in this work at 75°C and about 6000 atm is much less sharp than that which occurs with alpha methyl styrene. The investigation of the pressure-volume curve of iso-butyl vinyl ether at 75°C gave the results plotted

in Fig. 8. The pressure-volume curve changes in slope at about 6400 atm but there appears to be no abrupt change in volume at this pressure. This indicates that a first order change of phase from liquid to solid (as found with alpha methyl styrene) is not occurring, and the effect observed is a second order transition to an amorphous or glassy state which is presumably accompanied by a large increase in the viscosity of the medium above this pressure. A large increase in the viscosity could affect the rate of chain propagation and cause the maximum observed in the rate curve. In an investigation of the role of viscosity in bimolecular reactions at high pressures, Hamann (52) measured the rate of etherification of ethyl bromide at 25°C in a range of solvents and at pressures up to 40000 atm. In methyl alcohol the reaction is accelerated but less rapidly at higher pressures. In an iso-propyl alcohol-eugenol mixture the viscosity of which increases much more rapidly with pressure, the reaction was strongly retarded above a pressure of about 14000 atm, corresponding to an increase in viscosity of about 10^{10} fold, as estimated by Hamann on the basis of the Einstein-Smoluchowski theory of

diffusion. Although the polymerisation process is too complex for these theoretical calculations to be applied, it is to be expected that reactions involving relatively large polymer chain radicals will be retarded by much smaller increases in viscosity. It is also possible that a second reason for the retardation of the polymerisation by pressure is the effect the pressure has on the decomposition of the initiator. The decomposition of Bz_2O_2 in CCl_4 at 60^o, 70^o and 80^oC, at pressures up to 3000 kg/cm^2 was studied by Nicholson and Norrish (81). It was found that under these conditions the spontaneous and induced decompositions which took place are retarded and accelerated respectively by pressure:

$$(C_6H_5COO)_2 \longrightarrow 2C_6H_5COO^* \quad \text{retarded by pressure}$$

$$C_6H_5COO^* + (C_6H_5COO)_2 \longrightarrow C_6H_5COOC_6H_5 + CO_2 + C_6H_5COO^* \quad \text{accelerated by pressure}$$

The decomposition of Bz_2O_2 under pressure in allyl acetate and acetophenone at 80^oC has been investigated by Walling and Pellon (82) who found that although the actual rate of decomposition of Bz_2O_2 was at first reduced and then strongly accelerated as the pressure was increased, the rate of the initiation step was

retarded by pressure. These results show that a rapid, pressure induced chain decomposition of Bz_2O_2 can occur, which represents a wastage of initiator without any increase in the free radical concentration and the rate of initiation.

Pressure also causes an increase in the molecular weight of the polymer, although at higher pressures, the increase is less rapid. From table 11 it can be calculated that the molecular weight at 5000 atm is 2.4 times that of one atmosphere while the molecular weight at 10000 atm is only 1.5 that of 5000 atm. Merrett and Norrish (58), in their work on styrene, found an approximately three-fold increase in the molecular weight when the pressure was increased from one to 3000 atm, while at higher pressures the molecular weight remained almost constant. They explained the initial increase of molecular weight with pressure as due to a decrease in the mutual termination reaction and a parallel increase in the rate of propagation. At higher pressures, the molecular weight is determined largely by transfer reactions which are known (83) to be accelerated by pressure. The initial increase in the molecular weight of poly-iso-butyl vinyl ether

with pressure can probably be ascribed to the same reasons, but at 10000 atm, the system is above the observed volume transition point and it is uncertain to what extent the various steps will be affected by viscosity changes.

IV.2. Polymerisation with Iodine Initiation

IV.2.i The Effect of Iodine Concentration on the Rate of Polymerisation

The exponent x of the iodine concentration in the equation Rate = $K(I_2)^x$ was found to vary considerably with pressure, from 1.75 at one atmosphere and 75°C to about 0.5 at 10000 atm and 75°C. The exponent varies to a lesser extent with temperature at 1 atm, increasing from 1.75 at 75°C to about 2 at 35° and 0°C (table 19). This exponent is dependent on the initiation and termination processes of the polymerisation and the kinetics of these two processes are influenced to a very large extent by such factors as type of monomer, initiator and co-catalyst (in contrast with radical polymerisation in which a value of $x \simeq 0.5$ is usually obtained). It is therefore necessary to discuss the possible mechanisms of the initiation and termination steps in relation to the

changes in the exponent x. The nature of the propagation step is usually little affected by the factors mentioned and need not be considered.

The initiation step in a cationic polymerisation is generally agreed to be the formation of a carbonium ion. To produce the carbonium ion, the initiator generally needs a co-catalyst (See I.3). In the case of Friedel Crafts catalytic halides, this is supplied by the solvent or an acid, organic or inorganic, e.g:

Solvent (84)

$$RCl + TiCl_4 \longrightarrow R^+ + (TiCl_5)^-$$
$$R^+ + M \longrightarrow RM^+$$

Water (85)

$$SnCl_4 + SnCl_4.2H_2O \longrightarrow 2\ SnCl_4.OH_2$$
$$SnCl_4.OH_2 + R_1R_2C{=}CH_2 \longrightarrow SnCl_4OH^- + R_1R_2C^+-CH_3$$

Trichloroacetic acid (86)

$$TiCl_4 + CCl_3COOH \longrightarrow (TiCl_4.OOCCCl_3)^-H^+$$
$$XA^-H^+ + R_1R_2C{=}CH_2 \longrightarrow R_1R_2C^+-CH_3 + XA^-$$

A few cases are known in which apparently no co-catalyst is required, as in the polymerisation of styrene by $AlCl_3$ in CCl_4 solution (87). This is attributed to the possibility that a strongly electrophilic molecule may attach itself directly to the monomer and thus polarise the double bond.

$$Al\ Cl_3 + Ph\ CH{=}CH_2 \longrightarrow Cl_3Al\bar{C}H_2-\dot{C}HPh$$

In the polymerisation of alkyl vinyl ethers by iodine, the initiation could occur in two different ways. Eley et al (17) (33) (69) postulated that the iodine acts as its own co-catalyst:

$$2I_2 \longrightarrow I^+ + I_3^-$$
$$I^+ + M \longrightarrow IM^+$$

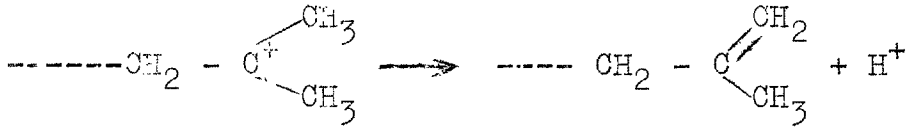
The rate of production of the carborium will then be proportional to $(I_2)^2$, so that x=2 as observed by Eley in solution polymerisation and in this work for pure monomer at 1 atm. Alternatively, as Harmann (61) suggested to account for the value of x=1 found in his work on iso-amyl vinyl ether in the range 1 - 10000 atm, since I^- ions are known to form strong complexes with olifinic compounds (88) it is possible that at higher monomer concentration than that used by Eley the I^- ion will form a complex with a monomer molecule instead of existing as I_3^-

$$I_2 + M \longrightarrow I_2M$$
$$I_2M + M \longrightarrow IM^+ + IM^-$$

Here the rate of production of the carbonium ion will be proportional to (I_2), leading to a value of x=1.

The chain termination process, in which a positively charged growing chain is converted into an electrically neutral polymer may involve the expulsion

of the positive charge, (usually a proton), leaving an unsaturated end in the polymer.



In this termination process the rate of disappearance of the carbonium ion depends on its own concentration only. Alternative method of termination is the neutralisation of the positive charge by combination with the balancing charge which has been formed in the initiation step (89). Infra red analysis indicates the existence of part of the gegen ion in the product of the polymerisation of isobutene by $TiCl_4$-Cl_3CCOOH (90) while with the iodine initiation of the polymerisation of 2- ethyl hexyl vinyl ether (17) an analysis of the product for double bond showed the existence of only one double bond for every two molecules. When termination is accompanied by charge neutralisation, the rate of disappearance of the carbonium ion depends on the concentration of both types of ions and would lead to x=1 or x = 0.5 according as the negative ion is I_3^- or I^-. Chain transfer has no effect on the magnitude of x and hence it is not considered.

It is clear from the foregoing discussion, that in ionic polymerisation there is not a single universal kinetic pattern and that there are alternative processes for the formation and extinction of ions in these systems. Consequently, one of the alternatives may be favoured by changing such factors as pressure, temperature and concentrations.

The value of about 2 found for the exponent x at atmospheric pressure, at 35° and 0°C agrees with the value found by Eley et al (17) (69) in the solution polymerisations of alkyl vinyl ethers at atmospheric pressure and 25°C, in which it is believed that the initiation step is $2I_2 \longrightarrow I^+ + I_3^-$ and that termination is by the expulsion of a proton, $M_n^+ \longrightarrow M_n + H^+$ This value of x is twice that found by Hamann (61) in the iodine-initiated bulk polymerisation of iso-amyl vinyl ether at one atmosphere and 0°C. As discussed previously, Hamann has suggested in this case that although the termination process is similar to that postulated by Eley, the initiation step involves co-catalysis by MI^- instead of I_3^- which would give $x = 1$. The difference between the results for iso-butyl and iso-amyl vinyl ethers at 0°C and one atmosphere may result from the different concentrations

used in the experiments. A summary of the concentration ratios of I_2 to monomer used in the three sets of experiments is given below,

Eley et al, at atmospheric pressure (17)

$$\frac{3.66 - 18.16 \text{ m.mole } I_2}{\text{mole 2- ethyl hexyl vinyl ether}}$$

This work a. at atmospheric pressure, at 35° and 0°C

$$\frac{0.125 - 0.6 \text{ m. mole } I_2}{\text{mole iso-butyl vinyl ether}}$$

b. at 1, 5000, 10000 atm. and 75°C

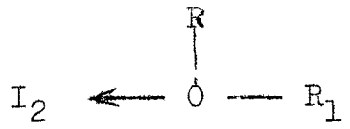
$$\frac{0.001 - 0.030 \text{ m. mole } I_2}{\text{mole iso-butyl vinyl ether}}$$

Hamann, at 1-10000 atm (61)

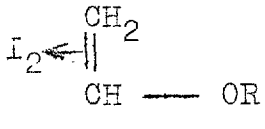
$$\frac{0.15 \text{ m. mole } I_2}{\text{mole iso-amyl vinyl ether}}$$

These I_2 concentrations are the overall concentrations which will differ from the effective concentrations because of the formation of inactive iodine complexes. Such complexes may be formed between iodine and monomer in all the three cases and also between iodine and the solvent in the first case. Eley et al (69) discuss two possible inactive complexes. In the first, it is assumed that I_2 forms a weak coordinate link (I) with the ether oxygen atom (91). In the second,

they postulate a complex with the ethylenic bond (II), by analogy with the complex I_2 .... C_6H_6 found spectroscopically for benzene by Benesi and Hildebrand (18).



(I)



(II)

The equilibrium constants for these complexes, and so the iodine concentration effective in initiating polymerisation are not known, but it should be pointed out that in Eley's experiments, the effective iodine concentration will probably be reduced appreciably due to the presence of almost 1.6 litres of solvent for each mole of monomer, the solvent being an ether or ethylene dichloride which might form inactive complexes. It is also possible that the inactive complexes formed between iodine and monomer may be weaker in the case of iso-butyl vinyl ether which has a bulkier side chain than the iso-amyl vinyl ether. The result of this would be to increase the effective concentration of iodine in the experiments carried out in this work at one atmosphere and the two low temperatures relative to that used by Hamann and probably bring it nearer to that used by Eley. An indication that this

may be so is the almost instantaneous disappearance of the iodine colour in iso-amyl vinyl ether (and in experiments on iso-butyl vinyl ether with 0.001-0.030 m.mole I_2/mole monomer). The iodine colour did not disappear in iso-butyl vinyl ether at higher concentrations of the iodine.

At 10000 atm and 75°C, x was found to be equal to about 0.5. The influence of pressure on liquid phase reactions was dealt with in general in Sec. I.4.i from which the conclusion can be drawn that the sum of ΔV_1^*, the intramolecular volume change and ΔV_2^*, the intermolecular volume change, determines whether an increase of pressure will accelerate a reaction by a particular mechanism (or alter the position of an equilibrium). In the iso-butyl vinyl ether-iodine system, with iodine concentrations much lower than those used by Hamann (0.001-0.030 m.mole I_2/mole monomer) the increase of pressure to 10000 atm can be expected to favour the overall initiation process $I_2 + 2M \longrightarrow IM^+ + IM^-$ rather than the process $2I_2 \longrightarrow I^+ + I_3^-$ In the first process there is a reduction in the number of molecules and so a negative ΔV_1^*, while in the second mechanism there is no change. Furthermore, in the first

process twice as many ions are formed from each molecule of iodine added so that there will be a larger negative ΔV_2^* resulting from solvation. This change in the initiation process alone can only account for a change in x from 2 to 1. The value of $x \simeq 0.5$ found at the highest pressure suggests that the termination process is also changed from proton expulsion to that which involves the neutralisation of the positive charge by the acquisition of a negative charge. In this process two ions combine and the charges disappear so that ΔV_1^* will be negative while ΔV_2^* will be positive. If this reaction is to be favoured by pressure it must be concluded that numerically $\Delta V_1^* > \Delta V_2^*$. Although for some reactions at 1 atm the reverse of this relationship holds, in the present case the system is highly compressed and has passed through a volume transition to what is presumably an amorphous or glassy state. Because of this, the expansion in volume due to the release of solvated molecules will be small and may well be less than the contraction due to the bond-forming process. At lower pressures, a termination process which involves the disappearance of ions will be less favoured than that in which they are preserved.

This will lead to values of x between 1-2 depending on the kinetics of the initiation step.

In this work values of 1.35 and 1.75 were found for x at 75°C and 5000 and 1 atm respectively, indicating mixed-order kinetics under these conditions. Dainton et al (32) found that x = 1.5 in the polymerisation of alpha methyl styrene in ethyl chloride solution, initiated by $SnCl_4$, and formulated the dibasic proton acid initiator complex, $3SnCl_4.2H_2O$ to explain it. In the case of iso-butyl vinyl ether-iodine system at 5000 atm, it seems more likely that the initiation step is a combination of the two initiation processes already mentioned. On the other hand, the decrease in x from 2 at 35°C and 0°C to 1.75 at 75° at atmospheric pressure seems attributable to the lower concentration of iodine which had to be used at the higher temperature, and the effect of temperature on the stability of the inactive complexes formed. It is not possible, from the data at hand, to decide the quantitative effects of these factors on the value of x.

IV.2.ii The Effect of Pressure on the Rate of Polymerisation

The change in the overall rate of iodine-initiated, ionic polymerisation of iso-butyl vinyl ether due to change in pressure is similar to that occurring in the benzoyl peroxide initiated polymerisation of the same monomer. The rate increases with pressure up to about 6000 atm (table 20, Fig.7) and the ratios of the rates at higher pressures to the rate at one atmosphere found in this work are similar, over this range, to the values found by Hamann (61) in the iodine-initiated polymerisation of iso-amyl vinyl ether, as shown below:

Iso-Butyl Vinyl Ether		Iso-Amyl Vinyl Ether	
$\frac{\text{Rate 2500 atm}}{\text{Rate 1 atm}}$	= 6	$\frac{\text{Rate 2000 atm}}{\text{Rate 1 atm}}$	= 5
$\frac{\text{Rate 5000 atm}}{\text{Rate 1 atm}}$	= 9	$\frac{\text{Rate 3000 atm}}{\text{Rate 1 atm}}$	= 7

These marked accelerations follow the relationship that log K (the constant of the overall polymerisation equation) is proportional to the pressure (48) (49) (50). In the ionic, as well as the radical polymerisation, the overall rate constant is a function of the rate constants of the individual processes in the polymerisation:

$$K = f\left\{ \frac{k_{\text{initiation}} \cdot k_{\text{propagation}}}{k_{\text{termination}}} \right\}$$

With iodine as initiator, another factor, the equilibrium constant K_e for the reaction,

$$I_2 + CH_2 = CHOR \rightleftharpoons \text{inactive complex}$$

ought to be introduced. If (I_2) and (M) denote the total initial concentration of iodine and monomer respectively, x the concentration of the inactive complex formed, then,

$$K_e = \frac{x}{(M)((I_2)-x)}$$

and therefore the concentration of iodine free to initiate polymerisation is

$$(I_2)f = (I_2) - x = \frac{I_2}{1+K_e(M)}$$

The initiation process in which the carbonium ion is produced will be accelerated by pressure. Hamann and Teplitsky (92) found that the rate determining step in the addition of iodine to olefins in solvents of low dielectric constant

$$2I_2 + R_2C{=}CR_2 \longrightarrow R_2CI\text{-}\overset{+}{C}R + I_3^-$$

is accelerated by a factor of about 3 at 1000 atm, corresponding to a $\Delta V^* = -25$ c.c./mole

The bond forming process in the propagation step must also be associated with a negative ΔV^*, as it is in the radical polymerisation, and hence will be

accelerated by pressure. There is very little data on the values of the constants of the individual reactions in ionic polymerisations. The unusual experimental difficulties make the determination of accurately reproducible results, from which these constants are calculated, almost impossible, and the difficulties are greater at high pressures. In the benzoyl peroxide initiated polymerisation of styrene at 60°C, Nicholson and Norrish (59) found that $k_{propagation}$ increases by factors of 1.5, 2.8, 5.5 when the pressure is increased from one atmosphere to 1000, 2000 and 3000 atm, respectively. As the propagation step in ionic polymerisation involves no changes in electrical charges, the transition state volume change might be as high as that in free radical propagation and consequently the effect of pressure on this step would be similar to that found by Nicholson and Norrish.

The termination step in ionic polymerisation can be expected to be almost unaffected by pressure. In free radical polymerisation, termination by either combination or disproportionation involves the movement and meeting of two growing chains. As the pressure increases, so does the viscosity, making the movement of large molecules more difficult. Nicholson

and Norrish (59) found that the rate of termination is retarded 2.6 times when the pressure is increased from one to 3000 atm. In ionic polymerisation mutual termination of chains carrying like charges is unlikely, and as there is no simultaneous initiations by positive and negative charges, termination is either by expulsion of a proton or by neutralisation through acquisition of the negative charge in the gegen ion. The polymerisation takes place in a medium of low dielectric constant in which the gegen ion will not be much separated from the positive charge on the growing chain, and as both termination mechanisms involve a small molecule it is concluded that the rate of termination will not be much affected by any increase in viscosity caused by the increase in pressure.

An estimate of the increase in the overall rate based on these considerations leads to a higher value than that actually found. The difference may be due to the effect of pressure on the concentration of iodine complexes. In this work the absorption spectrum of the iso-butyl vinyl ether-iodine-benzene system was measured at atmospheric pressure (Fig. 9) and a peak was found at about 315 m μ. Benesi and Hildebrand (18)

attributed similar peaks observed in the spectra of solutions of iodine in aromatic hydro carbons at atmospheric pressure in the region 280 - 400 mμ to the formation of iodine complexes. Ham (19) measured the absorption spectra of dilute solutions of iodine and aromatic compounds in heptane and observed increases in the absorption of the charge transfer bands with pressure which were attributed to an increased concentration of the complex formed. The concentrations of complexes inactive in polymerisation such as those involving the I_2 .... ether oxygen and I_2.... ethylenic bond associations should also be increased with pressure.

In the last chapter, it was concluded that the fall in the value of x in Rate = $K(I_2)^x$ from 1.75 at one atmosphere to 1.35 at 5000 atm. is due to a change in the kinetics of the initiation step. As a lower value of x causes a higher overall rate of polymerisation and as the initiation step, by either mechanism, should be accelerated by pressure, it is possible that this step is the most important factor in the acceleration of the polymerisation between 1 - 6000 atm.

The maximum in the rate-pressure curve for the benzoyl peroxide-initiated polymerisation of iso-butyl vinyl ether (Fig. 5) was attributed to a considerable retardation in the rate of propagation caused by the second order transition of the monomer to an amorphous or glassy state above a pressure of about 6400 atm. This reason will also account for the maximum in the overall rate of the iodine-initiated polymerisation of iso-butyl vinyl ether at a pressure of about 6000 atm. In this case, part of the fall in the rate could also be due to an increase in the concentration of inactive iodine complexes, leaving a lower effective iodine concentration for initiating the polymerisation.

IV.2.iii The Effect of Temperature on the Rate of Polymerisation

An increase of rate with temperature, and consequently positive activation energies, were found for the iodine-initiated polymerisation of iso-butyl vinyl ether (table 21). A comparison between the results of this work and of other workers on the polymerisation of similar vinyl ethers is given as follows:

TABLE 27

Effect of Temperature on Ionic Polymerisation

	Monomer	Initiator	Medium	Activation Energy Kcal/mole
This work				
a. at 1 atm	iso-butyl vinyl ether	iodine	bulk	10
b. at 5000 atm	"	"	"	13
Hamann (61)	iso-amyl vinyl ether	iodine	in ether solution	8
Eley (16) (17)				
at 1 atm.	2-ethyl hexyl vinyl ether	iodine	in petrol ether	10
	"	$SnCl_4$	"	10

The changes in rate with temperature are dependent on the activation energies of the individual steps in the polymerisation. Thus if $E_{initiation} + E_{propagation} > E_{termination}$, the rate will increase with temperature. Since the propagation step in ionic polymerisations involves the approach of an ion to a neutral molecule in a medium of low dielectric constant, only a small activation energy is necessary. The termination step on the other hand requires the

rearrangement of an ion-pair and this involves a considerably larger activation energy. These conditions are exactly the reverse of these found in free radical polymerisation. Thus, as the rate of the iodine-initiated polymerisation of iso-butyl vinyl ether increases with temperature, it is possible to write, as a first approximation, that

$$E_{\text{initiation}} > E_{\text{termination}}$$

In some ionic polymerisations, this difference between E_i and E_t may result in a negative overall activation energy. With $TiCl_4$ - CCl_3COOH as initiator in the polymerisation of iso-butene in n-hexane solution, Plesch (84) found that E=-7.5 Kcal/mole, while with $SnCl_4$-H_2O as initiator for the polymerisation of the same monomer in EtCl solution Norrish and Russell (37) found that E=+7 Kcal/mole. Negative values of activation energies are not observed in the radical polymerisations, as $E_p + E_i$ are usually positive and far greater than E_t.

The greater effect of temperature on the radical polymerisations of iso-butyl vinyl ether at 10000 atm, compared with the ionic polymerisations at one and 5000 atm is probably due to the slow chain propagation

and high $E_{propagation}$ of the radical reaction compared with the fast chain growth in the ionic reaction. If, as previously suggested, the chain growth is the rate-determining factor, one would expect a greater effect of temperature on the overall rate of radical polymerisation.

IV.2.iv Molecular Weight of the Product in Ionic Polymerisation

Molecular weights were measured at one, 5000 and 10000 atm. The results (tables 12, 14, 15) show that viscous liquid products of low molecular weight, ranging from 800 to 2300 were obtained. These results were not very reproducible and do not appear related in any well-defined way to changes made in the conditions of polymerisation. Similar erratic tendencies in molecular weights were reported by Plesch (86) in the ionic polymerisation of styrene, and by Eley (17) in the iodine polymerisation of 2-ethyl hexyl vinyl ether.

Ionic polymerisations carried out at room or higher temperatures resulted generally in viscous products of low molecular weights (about 1000). By carrying out the reaction at low temperatures of about

-80°C, higher molecular weights ($\sim$>5000) were obtained and often the products were solid with a partially crystalline structure. It was mentioned earlier that one of the features of ionic polymerisation is the existence of negative activation energies due to the large activation energy associated with the termination step. The marked decrease of molecular weight with temperature in ionic polymerisation is generally to be associated with transfer reactions which also may have quite large energies of activation. By working at low temperatures one eliminates the transfer reaction which leads to low molecular weights. This is possible with some ionic initiators which require only small activation energies in the initiation step (about $<$10 Kcal/mole) in comparison with activation energies of about 30 Kcal/mole for free radical initiation.

Investigating the polymerisation of iso-butyl vinyl ether at one atmosphere, Schildknecht et al (67) showed that amorphous and crystalline polymers could be formed from the same monomer. If polymerised rapidly (actually a flash polymerisation) in liquid propane at about -40°C with BF_3, iso-butyl vinyl ether forms an amorphous, rubber like polymer. On the other hand, if BF_3-etherate is used dropwise at -60°C to -80°C, the polymerisation is quite

slow and the product is crystalline. This difference is not due to molecular weight differences but to the occurrence of stereo-specific polymerisation in the slow process which leads to the eutactic crystalline structure of the product.

Either or both of these effects of low temperatures i.e. higher molecular weights and stereo-regulation have been found in the polymerisation of many vinyl moromers by the use of Ziegler type catalysis at temperature of about 50^{o} - 100^{o}C and at atmospheric pressure. The Ziegler type catalyst (93) is formed from a halide of a transition element from the groups IV - VIII of the periodic table such as $TiCl_4$ and a metal hydride or alkyl such as AlH_3, which have been termed catalyst and co-catalyst respectively, by analogy with the nomenclature of cationic initiated polymerisation. The metal hydride or alkyl promotes the polymerisation of vinyl compounds through an addition or growth reaction involving insertion of a monomer unit at the metal-carbon bond, while the transition metal compound controls the degree of polymerisation by participating in a displacement reaction in which the growth of the chain comes to an end.

This type of polymerisation is very often a heterogenous process carried out on the surface of the catalyst. With these catalysts the transfer reaction is eliminated, as the active centre of the growing chain is not the free chain end but the metal-carbon bond from which the chain grows by insertion of monomer molecules.

During the course of this work a patent (68) was published describing the use of hydrated ferric sulfate to obtain rubber-like poly alkyl vinyl ethers with high molecular weights. This was tried (Sec.II.3.iv) with iso-butyl vinyl ether and a rubbery product was obtained with an estimated molecular weight $> 10^4$. The polymerisation was heterogenous, and although the exact mechanism of the initiation is not known it is likely that the high molecular weight results from the polymerisation being carried out heterogenously on the surface of the catalyst, with elimination of the transfer reaction. The molecular weights of the products were not as high as those obtained by Schildknecht at low temperatures. He found specific viscosities between 2 and 4 for benzene solutions with 0.1 gm polymer/100 ml benzene (corresponding to estimated molecular weights ranging from 65000 to 500000) while a specific viscosity of 3.39 was obtained

with 0.5 gm polymer /100 ml benzene in this work.

It has been suggested recently by Prof. C.E.H. Bawn in the Liversidge Lecture (1961) given in The Chemical Society, that the stereo-regularity of the poly-iso-butyl vinyl ether obtained by Schildknecht is due to the transition state in the chain growth reaction consisting of a six-membered ring complex in which the monomer being added has the trans-configuration. If this is so, successive monomer units will be added to the chain in the same way, since the bulky iso-butyl group hinders other arrangements. No such regularity has been found with benzoyl peroxide or iodine, and the present experiments show that pressure is not effective in producing stereo-regularity.

The decrease in molecular weight with increase in temperature found to occur at 5000 atm (runs 86, 87 92, 93) could be attributed to the increase in transfer with temperature. As discussed earlier, there is a reverse effect of temperature on the molecular weight of radical polymerisation, which was attributed to the acceleration in the slow chain growth which determines the molecular weight in the radical polymerisation of iso-butyl vinyl ether. The importance of transfer in determining the molecular weight in the ionic

polymerisations is shown by Eley's results on the iodine initiated polymerisation of 2-ethyl hexyl vinyl ether (17). The molecular weight was found to be independent on the monomer concentration which suggests that in Eq. 12 (Molecular Weight = $\frac{k_3(M)}{k_4 + k_5(M)}$), $k_5(M)$, the term of the transfer reaction is far greater than k_4, the rate constant for termination by expulsion of the charge. The same equation explains the negligible effect that change of iodine concentration was found to have on the molecular weights obtained in this work.

Molecular weights at the different pressures, showed a tendency to increase with pressure. In radical polymerisation a similar, although larger, increase was attributed to a simultaneous decrease in the mutual termination reaction because of the increase in viscosity, and an increase in the chain growth reaction which is favoured by pressure. In the section dealing with the effect of pressure on the overall rate of ionic polymerisation, it was argued that the kinetic chain termination is almost unaffected by pressure, compared with a marked retardation in the rate of termination in the radical polymerisation. It is possible that this explains the different effect of pressure on the molecular weight in the two different types of

polymerisation. However, pressure may also accelerate the transfer reactions to a different extent in each case and these are known (17) to be a very important factor in determining the molecular weights of poly alkyl vinyl ethers.

CONCLUSION

The main conclusions which have been reached in the course of this work are listed below:

1. It has been found that alkyl vinyl ethers can be polymerised by radical as well as cationic initiators in the range 1 to 10000 atm.

2. The overall rate of polymerisation of iso-butyl vinyl ether by either mechanism is accelerated by pressure and this is discussed with reference to work on other monomers.

3. Iso-butyl vinyl ether passes through a second order transition at about 6400 atm. and 75°C, probably to an amorphous or glassy state.

4. The rate-pressure curve of both types of initiation passes through a maximum in the region of the transition.

5. There is a change in the value of the exponent x of the iodine concentration in the equation, Rate of polymerisation = $K(I_2)^x$, from about 0.5 at 10000 atm. and 75°C to about 2 at one atm. and 35°C and 0°C, and it is shown that this can be accounted for by changes in the mechanism of initiation and termination.

6. The molecular weight of radical polymerisation of iso-butyl vinyl ether increases with pressure and temperature, while the molecular weight of the iodine-initiated polymerisation is almost independent of pressure and decreases with increase in temperature.

7. Both types of polymerisation of iso-butyl vinyl ether give viscous liquid products of relatively low molecular weight, and even at the highest pressures the polymer does not resemble the rubber-like product of high molecular weight obtained by using hydrated ferric sulfate as initiator at $34^{\circ}C$ and 1 atm.

BIBLIOGRAPHY

(1) P.J. Flory; J.Am. Chem. Soc., 59 (1937), 241.

(2) F.R. Mayo; ibid , 75 (1953), 6133.

(3) C. Walling; "Free Radicals in Solutions" John Wiley, New York, (1957), Chapter 5.1.

(4) Bamford et al; "The Kinetics of Vinyl Polymerisation by Radical Mechanisms" Butterworths, London, (1958).

(5) P.J. Flory; "Principles of Polymer Chemistry" Cornell University Press, New York, (1953).

(6) G.M. Burnett; "The Mechanism of Polymer Reactions" Interscience, New York, (1954)

(7) Billmeyer; "Textbook of Polymer Chemistry" Interscience, New York, (1957)

(8) F.R. Mayo; R.A. Gregg and M.S. Matheson; J. Am. Chem. Soc., 73 (1951), 1691.

(9) Pepper; Nature, 158, (1946), 789

(10) M. Polanyi et al; Nature, 157 (1946), 102.

(11) P.H. Plesch, M. Polanyi and H.A. Skinner; J. Chem. Soc., (1947), 252.

(12) A.G. Evans and M. Polanyi; ibid (1947), 257.

(13) A.G. Evans, G.W. Meadows and M. Polanyi; Nature, 160 (1947), 869.

(14) A.G. Evans and G.W. Meadows Trans. Far. Soc., 46 (1950), 327.

(15) W. Chalmers; Canada J. Research, B.7 (1932), 464.

(16) D.D. Eley and A.W. Richards; Trans. Far. Soc., 45 (1949), 436.

(17) D.D. Eley and A.W. Richards; ibid, 425.

(18) H.A. Benesi and J.H. Hildebrand;
J. Am. Chem. Soc., 71 (1949), 2703.

(19) Joe Ham; ibid , 76 (1954), 3875.

(20) F. Fairbrother; J. Chem. Soc., (1948), 1051.

(21) R.G. Beaman; J. Am. Chem. Soc., 70 (1948), 3115.

(22) W.H Hunter and R.N. Yoke; ibid, 55 (1933), 1248

(23) F.C. Whitmire; Ind. Eng. Chem., 26 (1934), 94.

(24) J.P.W. Houtman; J. Soc. Chem. Ind., London, 66 (1947) 102.

(25) J.J. Throssel et al;
J. Am. Chem. Soc., 78 (1956), 1122.

(26) F.S. Dainton and R.H. Tomlinson;
ibid , 75 (1953), 151

(27) R.E. Burk and H.P. Lankelma;
ibid , 67 (1945), 910.

(28) R.L. Meier; J. Chem. Soc., (1949), 3656

(29) F.S. Dainton and G.B.B. Sutherland
J. Polymer Sci., 4 (1949), 37

(30) R.O. Colclough; ibid , 8 (1952), 467.

(31) J.T. Atkins and F.W. Billmeyer; unpublished work

(32) F.S. Dainton et al; paper presented at Symposium on ionic polymerisation, Stafford, England (1952)

(33) D.D. Eley and Pepper;
Trans. Far. Soc., 43 (1947), 112.

(34) R.G.W. Norrish and K.E. Russell; ibid, 48 (1952), 91.

(35) J.J. Anderson and C.R. Hauser;
J. Am. Chem. Soc., 71 (1949), 1595

(36) M.G. Evans, W.C. Higginson and N.S. Wooding;
Rec. Trav. Chim., Pays-Bas, 68 (1949), 1069.

(37) W.C.E. Higginson and N.S. Wooding;
J. Chem. Soc., (1952), 760.

(38) W.C.E. Higginson and N.S. Wooding; ibid . p.774

(39) C. Harries; Liebigs Ann., 383 (1911), 213.

(40) W.C.E. Higginson and N.S. Wooding;
J. Chem. Soc., (1952), 1178.

(41) E.W. Fawcett and R.O. Gibson;
J. Chem. Soc., (1937), 386.

(42) R.O. Gibson, E.W. Fawcett and M.W. Perrin;
Proc. Roy. Soc., 150 A (1935) 223

(43) E.W. Williams, M.W. Perrin and R.O. Gibson;
ibid , 154 A (1936), 684.

(44) M.W. Perrin and E.W. Williams;
ibid , 159 A (1937), 162

(45) M.W. Perrin; Trans. Far. Soc., 34 (1938), 144.

(46) A. Michels; Proc. Roy. Soc., 127 A (1930), 258.

(47) S. Glasstone, K.J. Laidler and H. Eyring;
"The Theory of Rate Processes"
McGraw-Hill, New York (1941)

(48) M.G. Evans and M. Polanyi;
Trans. Far. Soc., 31 (1935), 875.

(49) M.G. Evans and M. Polanyi;
ibid 32 (1936), 1333

(50) M.G. Evans and M. Polanyi;
ibid 33 (1937), 448.

(51) S.D. Hamann; Physico-chemical Effects of Pressure,
9 (1957), 164.

(52) S.D. Hamann; Trans. Far. Soc., 54 (1958), 507.

(53) P.W. Bridgman and J.B. Conant;
Proc. Nat. Aca., Sci., 15 (1929) 680.

(54) H.W. Starkweather;
J. Am. Chem. Soc., 56 (1934), 1870

(55) G. Tamann and A. Page;
Z. Anorg. Allgem. Chem., 200 (1931), 113.

(56) R.C. Gillham; Trans. Far. Soc., 46 (1950), 497.

(57) R.H. Sapiro, R.P. Linstead and D.M. Newitt;
J. Chem. Soc., (1937), 1787.

(58) F.M. Merrett and R.G.W. Norrish;
Proc., Roy , Soc., A 206 (1951) 309.

(59) A.E. Nicholson and R.G.W. Norrish;
Dis. Far. Soc., 22 (1956), 104.

(60) C. Walling and J. Pellon;
J. Am. Chem. Soc., 79 (1957), 4776

(61) S.D. Hamann; unpublished work got through by
correspondence

(62) M.F. Shostakovskii et al;
Soedineniyam, Akad. Nauk. S.S.S.R.,
(1949) P.34-44.

(63) M.F. Shostakovskii, N.A. Gershtein and V.A. Neterman;
Proc. Acad. Sci., U.S.S.R. 103 No. 2.
265 (1954)

(64) M.F. Shostakovskii, E.S. Shapiro and F.P.Sidelkovskaya
Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.,
(1956) 351-4.

(65) Mueller, Cunradi, Martin and Pierdi, Kurt;
U.S. Patent, 206, 934 (Nov. 24 1936)

(66) Reppe, Walter and Kuehn, Eric
U.S. Patent, 2098108 (Nov 2, 1937)

(67) C.E. Schildknecht, S.T. Gross, H.R. Davidson,
J.M. Lambert and A.V. Zoss,
Ind. Eng. Chem., 40 (1948), 2104

(68) The Goodyear Tire and Rubber Company;
British Patent, 846690 (Feb. 11, 1959)

(69) D.D. Eley and J. Saunders;
J. Chem. Soc., (1952), 4167.

(70) Mueller-Cunradi, Martin and Pierdi, Kurt (to I.G. Farbenindustrie) U.S. Patent, 745030 (Feb. 24, 1944)

(71) R.U.Bonnar, M. Dimbat and F.H. Stross;
"Number Average Molecular Weights"
Interscience Pub-Inc., New York (1958)

(72) K. Nozaki and P.D. Bartlett;
J. Am. Chem. Soc., 68 (1946), 1686

(73) J.C. Bevington; Proc. Roy. Soc., A239 (1957), 420

(74) J.C. Bevington; Trans. Far. Soc., 51 (1955), 1392.

(75) S. Glasstone; "Textbook of Physical Chemistry"
MacMillan and Co. Ltd., London, page 1087.

(76) C.H. Bamford and Dewar;
Proc. Roy. Soc., A192 (1947-1948), 308

(77) F.R. Mayo; J. Am. Chem. Soc., 75 (1953), 6133

(78) J. Pellon; Ph.D., Thesis, Columbia University (1957)

(79) J.G. Kilroe and K.E. Weale;
J. Chem. Soc., (1960), 3849.

(80) I. Elroy; Ph.D., Thesis, University of London (1961)

(81) A.E. Nicholson and R.G.W. Norrish;
Dis. Far. Soc., 22 (1956), 97.

(82) C. Walling and J. Pellon;
J. Am. Chem. Soc., 79 (1957) 4782,4786

(83) C. Walling and J. Pellon; ibid , 4776

(84) P.H. Plesch; J. Chem. Soc., (1953), 1653

(85) R.G.W. Norrish and K.E. Russell;
Trans. Far. Soc., 48 (1952), 91

(86) P.H. Plesch; J. Chem. Soc., (1950), 543

(87) D.O. Jordan and A.R. Mathieson; ibid, (1952), 611.

(88) Kowser et al; J. Chem. Phys., 26 (1957), 1353

(89) P.H. Plesch; "Cationic Polymerisation and Related Complexes" W. Heffer and Sons Ltd. (1953) p 150.

(90) M. St.C. Flett and P.H. Plesch; J. Chem. Soc., (1952), 3355

(91) Kleinberg and Davidson; Chem. Reviews, 42 (1948) 601

(92) S.D. Hamann and D.R. Teplitsky; Dis. Far. Soc., 22 (1956), 114.

(93) N.G. Gaylord and H.F. Mark; "Linear and stereoregular addition polymers: Polymerisation with controlled propagation." Int. New York (1959) p 87.