POLYMERISATION OF CHLORO - OLEFINES AT HIGH PRESSURE.

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by

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ABSTRACT.

The effects of pressures up to 3000 atmospheres on the polymerisation of styrene, systems containing styrene with vinylidene chloride, technical and trans-dichloroethylene, or trichloroethylene; and of systems containing vinyl acetate with vinylidene chloride or trichloroethylene have been investigated. Rates of reaction have been measured. Composition and limiting viscosity number of the polymers have been determined.

The chlorine contents of the polymers formed in the styrene-chloro-olefine systems (except vinylidene chloride) are low and are believed to arise mainly from transfer reactions. The order of reaction of [styrene] $\rangle$ 1 except at highest pressures, and of [initiator] is about 0.5 and independent of pressure.

The rate coefficients R_{1000}/R_1 are similar in magnitude in the systems styrene and styrene-chloro-olefines. The volume of activation $\Delta V_o^{\neq}$ for the systems is styrene-trichloroethylene $\rangle$ styrene-trans dichloroethylene $\rangle$ styrene - technical dichloroethylene. The chain transfer constants of trichloroethylene $\rangle$ trans-dichloroethylene $\rangle$ technical dichloroethylene at low pressures, but at higher pressures, the activities of trichloroethylene and trans-dichloroethylene are similar. An explanation in terms of the varying polarity

of the initial reactants and the transition state, together with resonance stabilization of the transition state is suggested. Technical-dichloroethylene is unreactive due to its high energy of activation.

The monomer reactivity ratios in the copolymerisation of vinylidene chloride with styrene or vinyl acetate are independent of pressure. The molecular weights of copolymers formed from vinyl acetate and trichloroethylene are low and practically independent of pressure up to a feed composition of about 80 mole % vinyl acetate.

Solidified trans-dichloroethylene and technical dichloroethylene were unchanged when subjected to pressures of 27 Kb and 37 Kb. Trichloroethylene decomposed when subjected to similar pressures and heated.

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CONTENTS.

		Page
ABSTRACT.		2
ACKNOWLEDGEMENTS.		4
SECTION I.	ELEMENTARY PROCESSES IN HOMOGENEOUS LIQUID-PHASE ADDITION POLYMERISATION.	
1.1.	Introduction.	9
1.2.	Reaction in Radical Chain Processes.	
	(a) Initiation.	10
	(b) Propagation.	11
	(c) Termination.	11
	(d) Chain Transfer.	13
1.3.	General Kinetics of Free-Radical Polymerisation.	
	(a) Postulates.	14
	(b) The Kinetic Equation.	15
	(c) Rate Constants and Kinetic Chain Length.	18
	(d) General Chain Transfer Equation.	21
	(e) Summary.	23
1.4.	Modification of the Simple Kinetic Scheme.	
	(a) Modification of the Rate Equation.	25
	(i) The Monomer-Initiator Complex Theory.	25
	(ii) The Solvent Cage Theory.	25
	(iii) Retardation due to Solvent Transfer.	26
	(iv) Transfer to Initiator.	29
	(v) Transfer to Monomer.	31
	(b) Modified Chain Transfer Equation.	32

Page

SECTION II. BULK COPOLYMERISATION.

2.1. Introduction. 35

2.2. Reaction Scheme and Copolymer Composition Equation. 36

2.3. Monomer Reactivity Ratios. 38

2.4. The Rate of Copolymerisation. 40

2.5. Chemical Structure and Reactivity in Copolymerisation. 41

(a) Resonance Effects. 41

(b) Steric Effects. 43

(c) The Alternating Phenomenon and the Alfrey-Price Equation. 45

SECTION III. RADICAL POLYMERISATION UNDER HIGH PRESSURE.

3.1. Introduction. 49

3.2.

i) The Overall Rate of Radical Polymerisation under Pressure.

(a) The Collision Theory. 50

(b) The Transition State Theory. 51

ii) Effects of Pressure on the Individual Processes of the Polymerisation.

(a) Initiation. 55

(b) Propagation. 55

(c) Termination. 55

3.3. Chain Transfer. 56

3.4. Copolymerisation at High Pressure. 58

Page

SECTION IV. APPARATUS.

4.1. (a) High Pressure Equipment I 60
(b) High Pressure Equipment II. 61

4.2. Distillation Apparatus. 66

4.3. Apparatus for Determination of Molecular Weight. 66

SECTION V. MATERIALS USED AND EXPERIMENTAL PROCEDURE.

5.1. Materials used. 73

5.2. Experimental Procedure.
(a) Preparation of Samples. 75
(b) Polymerisation of Samples. 77
(c) Analysis of the Polymers. 80
(d) Determination of Molecular Weight. 81

SECTION VI. CALCULATIONS. 87

SECTION VII. RESULTS AND DISCUSSION OF THE EFFECT OF PRESSURE ON THE GENERAL KINETICS OF POLYMERISATION OF HALO-OLEFINES WITH STYRENE, AND STYRENE.

7.1. Summary of Some Previous Research. 91

7.2. Kinetic Investigations on the Bulk Polymerisation of Styrene. 94

7.3. Composition of the Polymers from Styrene/Chloro-Olefine Mixtures. 98

7.4. Kinetic Investigations on Polymerisation of Styrene with Trans-Dichloroethylene. 102

7.5. Kinetic Investigations on Polymerisation of Styrene with Trichloroethylene. 121

7.6. Kinetic Investigations on Polymerisation of Styrene with Technical-Dichloroethylene 139

7.7. General Conclusions. 140

			Page
SECTION VIII.		RESULTS AND DISCUSSION OF THE EFFECT OF PRESSURE ON THE KINETICS OF COPOLYMERISATION OF HALO-OLEFINES WITH STYRENE, AND WITH VINYL ACETATE.	
	8.1.	Summary of some Previous Research.	143
	8.2.	Kinetic Investigations on Copolymerisation of Vinylidene Chloride and Vinyl Acetate.	144
	8.3.	Kinetic Investigations on Copolymerisation of Vinylidene Chloride with Styrene.	156
	8.4.	Kinetic Investigations on Copolymerisation of Trichloroethylene with Vinyl Acetate.	159
	8.5.	General Conclusions.	161
SECTION IX.		POLYMERISATION OF CHLORO-OLEFINES UNDER VERY HIGH PRESSURE.	
	9.1.	Summary of some Previous Research.	166
	9.2.	Calibration of the Press.	167
	9.3.	Polymerisation of Trans-Dichloroethylene.	174
	9.4.	Polymerisation of Technical Dichloroethylene.	174
	9.5.	Polymerisation of Trichloroethylene.	174
	9.6.	Gneral Conclusions.	175

SECTION I.

Elementary Processes in Homogeneous Liquid-Phase Addition Polymerisation.

1.1. Introduction.

Sections I and II contain a review of the kinetic aspects of polymerisation and copolymerisation reactions. Deviations from the simple kinetic scheme, and the theories put forward to explain them, are discussed. Pressure is a significant variable in chemical reactions and its effects in relation to the kinetic scheme for radical polymerisations are discussed in Section III. This is necessary for the interpretation of the results obtained.

1.2. Reactions in Radical Chain Processes.

Polymerisation reactions have been known for over a century and were first described as "polymerisations" by Berthelot [1] in 1866. The present recognition of the macromolecular structure of polymers is due to Staudinger [2], who proposed that the polymerisation reaction can be written as

$$n\ CH_2 = CHR \qquad (-CH_2-CHR-)_n \qquad (1)$$

The process is a chain reaction in the kinetic as well as the structural sense. The chain grows by successive additions until a termination reaction occurs and growth ceases.

The polymerisation process can be resolved into the fundamental stages of initiation, propagation, termination and chain transfer.

(a) Initiation.

Initiation in radical polymerisation may be brought about by heat, radiation, or free radicals derived from the thermal breakdown of a number of compounds. The mechanism of thermal initiation, though many views have been put forward, is not very clear [3-6]. The same is the case with radiation polymerisation [7-10]. A large number of organic and inorganic compounds generate free radical intermediates on thermal decomposition and are effective catalysts for polymerisation. These compounds include the acyl peroxides, azo compounds, persulphates, etc. It involves the decomposition of an initiator I, to form radicals.

$$I \xrightarrow{\text{energy}} 2\,Z^* \qquad (2)$$

These radicals are frequently unstable species, and in the presence of a monomer, M, the following reaction takes place:

$$Z^* + M \longrightarrow M_1^* \qquad (3)$$

(b) Propagation.

In the propagation process, a polymerizable monomer, once activated to the free radical state, can add further monomer molecules. The normal chain growth may be represented by the successive series of reactions :

$$M_1 + M \longrightarrow M_2^* \quad (4a)$$

$$M_2 + M \longrightarrow M_3^* \quad (4b)$$

$$M_n^* + M \longrightarrow M_{n+1}^* \quad (4c)$$

The activation energy of this reaction is much lower than that of the initiation reaction. The average lifetime of the growing chains is very small, of the order of 10^{-3} to 10^{-2} sec. for a chain length of about 1000 molecules. The propagation reaction probably occurs when the active centre of the molecule collides with the active end of the radical in a particular way, and only if the necessary activation energy is available.

(c) Termination.

The termination of a kinetic chain in a radical polymerization may be due to

(i) reaction of the free radical end of one chain with a similar grouping in another chain;

(ii) addition of an initiator radical to the active chain end;

(iii) termination by impurities such as oxygen,

inhibitors, etc.

It is not easy to decide which is the predominant mechanism except in special cases, but extensive kinetic studies have shown that the most general termination reaction is bimolecular and probably of type (i). Two such types of bimolecular termination occur :

1. The union of the radicals by a coupling or combination mechanism

$$R - CH_2\overset{*}{C}HX + R-CH_2-\overset{*}{C}HX \longrightarrow R-CH_2CHX - CHXCH_2-R \qquad (5a)$$

2. The transfer of an atom, giving a saturated molecule together with the formation of a molecule having an unsaturated terminal group, by a dsproportionation mechanism

$$R - CH_2 - \overset{*}{C}HX + R - CH_2\overset{*}{C}HX \longrightarrow R-CH_2CH_2X + R-CH=CHX \qquad (5b)$$

A distinction between these two reactions is possible experimentally if it can be established accurately that the polymer molecule contains one or two catalyst fragments or that half the molecules have unsaturated end groups. Further, the disproportionation mechanism would lead to a lower average molecular weight than the combination mechanism. From a detailed examination of the polymerization of methylmethacrylate initiated by hydroxyl

radical [11], it has been shown that combination is the main process for this reaction.

(d) Chain Transfer.

Although bimolecular termination is the main process which stops the growth of a chain radical, its activity may be transferred by other phenomena. This concept was first introduced by Flory [12], and is termed chain transfer. The reactions are accompanied by the transfer of a monovalent atom, either from the molecule to the polymer radical or to an active monomer or other free radicals from a polymer molecule. In the latter case the activity may be transferred to any position along the chain and may lead to branching or cross linking [13]

$$Rn^* + Y \longrightarrow Rn + Y^* \qquad (6a)$$

Here Y represents a monomer, polymer, solvent, initiator or any other molecule present in the system, and Y* is a derived radical capable of initiating another chain.

Chain transfer may not greatly affect the overall rate of polymerisation, since the active centre is maintained, but the average molecular weight is reduced, the effect increasing as the reactivity of Y increases.

However, if the new radical Y* is not as effective in propagating a chain as Z*, it may lose its activity by terminating a growing chain or by combining with

another radical including Y* radicals.

$$Y^* + Rn^* \longrightarrow Rn + Y \qquad (6b)$$

$$Y^* + Y^* \longrightarrow \text{Product} \qquad (6c)$$

When Y* takes part in reactions such as (6b) or (6c), the overall rate of polymerisation is retarded as a result of transfer reaction, and the phenomenon has been called "degradative chain transfer" by Nozaki and Bartlett [14].

1.3. General Kinetics of Free-Radical Polymerisation.

(a) Postulates.

In order to develop a kinetic rate equation certain simplifying assumptions are needed. They are

(i) Only the initial stages of polymerisation are considered so that the concentrations of reactants may be taken as unchanged.

(ii) The activity of a growing radical is independent of its chain length.

(iii) The chains are long so that the rate of consumption of monomer is equal to the rate of chain propagation.

(iv) A "steady-state" is attained, that is the rate of change of concentration of an intermediate present in very low concentration is small compared to its rates of formation and disappearance. For all practical purposes the rate of change of free radical concentration is taken to be zero.

(b) Kinetic Equation:

Bearing the above postulates in mind, as an illustration of the general kinetic problem let us consider the following reactions.

Initiation	$M \longrightarrow M_1^*$	k_i	(7)
Propagation	$M_1^* + M \longrightarrow M_2^*$ $M_2^* + M \longrightarrow M_3^*$ $M_n^* + M \longrightarrow M_{n+1}^*$	k_p	(8)
Termination	$M_n^* + M_m^* \longrightarrow M_{n+m}$	k_t	(9)

The overall rate of monomer consumption

$$-\frac{dM}{dt} = V_{init.} + V_{prop.} = V_{init.} + k_p C^* M \qquad (10)$$

where M = monomer concentration and
C^* = total concentration of radicals.

Also for a very long chain, the growth reaction is much faster than that of initiation, and the first term in equation (10) is negligible, so that

$$-\frac{dM}{dt} = k_p\, C^*\, (M) \qquad (11)$$

In the steady state, $\frac{d_{C^*}}{dt} = 0$, and the velocity of initiation equals the velocity of termination. Since $V_{init.} = V_{term.} = k_t C^{*2}$,

$$C^* = \sqrt{\frac{V_{init}}{k_t}} \qquad (12)$$

Hence, $$-\frac{dM}{dt} = R_o = k_p M \sqrt{\frac{V_{init}}{k_t}} \quad (13)$$

Defining $\delta = k_t^{\frac{1}{2}}/k_p$, equation (13) can be written as

$$R_o = \delta^{-1} [M] \sqrt{V_{init}} \quad (14)$$

The overall rate of polymer formation may be derived by introducing the appropriate value for V_{init}. The following possibilities may be considered.

(i) The rate of initiation is dependent on the concentration of initiator and independent of monomer concentration :-

$$V_{init} = k_i (I) \quad (15)$$

$$-\frac{dM}{dt} = R_o = \frac{k_i^{\frac{1}{2}} k_p}{k_t^{\frac{1}{2}}} \cdot M \cdot (I)^{\frac{1}{2}} \quad (16)$$

In the case of an initiator like benzoyl peroxide which decomposes to form two radicals, if k_d is the rate constant for decomposition of the initiator, and "f" the efficiency of the radicals in starting chains, then

$$V_{init} = R_i = k_i(I) = 2f\, k_d(I) \quad (17)$$

and $$R_o = \delta^{-1} (2fk_d)^{\frac{1}{2}} M (I)^{\frac{1}{2}} \quad (18)$$

(ii) Initiation might occur by a bimolecular reaction between the initiator and the monomer.

$$V_{init} = k_i M (I) \quad (19)$$

$$-\frac{dM}{dt} = R_o = \frac{k_i^{\frac{1}{2}} k_p}{k_t^{\frac{1}{2}}} M^{3/2} I^{\frac{1}{2}} \quad (20)$$

The above kinetic scheme is known to be observed in several benzoyl peroxide-catalysed polymerisations.

(iii) Second order initiation.

$$V_{init} = k_i M^2 \qquad (21)$$

$$-\frac{dM}{dt} = R_o = \frac{k_i^{\frac{1}{2}} k_p}{k_t^{\frac{1}{2}}} M^2 \qquad (22)$$

This is the case in the polymerisation of styrene in the bulk and in solution without initiator.

(iv) First order initiation.

$$V_{init} = k_i M \qquad (23)$$

$$-\frac{dM}{dt} = R_o = \frac{k_i^{\frac{1}{2}} k_p}{k_t^{\frac{1}{2}}} M^{3/2} \qquad (24)$$

(v) Photochemical initiation.

$$V_{init} = f(I) M \qquad (25)$$

where I = intensity of absorbed light

$$-\frac{dM}{dt} = R_o = \left(\frac{f(I)}{k_t}\right)^{\frac{1}{2}} \cdot k_p \cdot M^{3/2} \qquad (26)$$

The validity of the simple kinetic equation (16) or (18) have been examined by kinetic investigations of polymerisation in a number of monomer-initiator systems. In most cases the order with respect to initiator [15-20] concentration is 0.5 which shows that the kinetic chains

end by mutual termination of radicals.

The dependence of polymerisation rate upon monomer concentration is less clear cut and there are complications arising from the dilution of the monomer. In the case of d-sec-butyl-α-chloracrylate catalysed by benzoyl peroxide in dioxane [16], the order with respect to monomer is first order. In other systems the order of reaction varies and different orders of reaction are obtained under different conditions [21-25]. The origin of this variation in the order of the polymerisation reaction with respect to monomer is still rather uncertain. However, it appears that at least three factors may be involved:-

(i) the variation of k_d and f with change in medium;

(ii) the presence of adventitious retarders;

(iii) the occurrence of degradative chain transfer between polymer radical and solvent.

(c) Rate Constants and Kinetic Chain Length.

Rate Constants: The simple kinetic equation can be rewritten as

$$k_p^2 / k_t = (R_o/M)^2 / R_i \qquad (27)$$

Since R_o and M are directly measurable and R_i may be determined, it is evident that the ratio k_p^2/k_t can, in principle, be determined for any polymerizing system obeying

the simple kinetic scheme. A comparison of the k_p^2/k_t ratios gives the relative rates of polymerisation of different monomers at a given rate of initiation. A comparison of the different determinations of k_p^2/k_t ratios [26-28] for styrene shows the genefal reproducibility and reliability of polymerisation kinetics. The evaluation of the individual rate constants by steady state methods involves the estimation of C*, which makes the measurement almost impossible because of the exteremly low concentration of the radicals and since radical production may be abruptly started and stopped. The application of the non-steady state techniques has, however, made it possible to evaluate the individual rate constants. The sector technique and the special interference method which have mostly been used for the measurement of individual velocity coefficients, belong to the so-called 'pseudo stationary state'. The propagation and termination rate constants for a number of monomers at 25°C are given below.

Monomer	k_p (l./mol.sec)	$k_t^{\frac{1}{2}} \times 10^{-3}$ (l./mol.sec)	$k_t^{\frac{1}{2}}/k_p$
Methyl acrylate	1500	7.4	4.9
Butyl acrylate	13.1	0.13	10.2
Styrene	39.5	2.81	71.3
Methyl methacrylate	275	5.0	18.1
Vinyl acetate	750	22.3	30

Kinetic Chain Length : The kinetic chain length, ν is the average number of monomer molecules consumed by every radical which starts a polymerisation chain. This quantity is given by the ratio of R_p to R_i (or R_t) :

$$\nu = R_p/R_i = R_p/R_t \qquad (28)$$

from equations (11) and (12) this becomes,

$$\nu = k_p M/2k_t C^* \qquad (29)$$

or eliminating radical concentrations,

$$\nu = k_p^2 M^2/2k_t R_p \qquad (30)$$

Equations 29 and 30 illustrate an important general property of radical chain processes involving bimolecular propagation and termination.

(i) The inverse relationship between chain length and either the radical concentration or the overall reaction rates.

(ii) The chain length is independent (at constant reaction rate) of the means of initiating the reaction, but is a characteristic of the particular monomer system involved.

When chain termination is by disproportionation $\nu = \bar{P}$, and when it is by recombination $2\nu = \bar{P}$, [29-30] ($\bar{P}$ is the average degree of polymerisation).

(d) General Chain Transfer Equation.

In non-degradative transfer reactions, termination of growth takes place without stopping the chain. In any system the reciprocal of the degree of polymerisation is given by the ratio of the rate of all chain-ending processes to the rate of polymerisation (for small amounts of reaction)

$$\frac{1}{\bar{P}} = \frac{\text{rate of chain termination by all processes}}{\text{rate of chain growth}} \qquad (31)$$

$$= \frac{k_t (C^*)^2 + k_{tm} M C^* + k_{ts} C^* S + k_{ti} C^* I}{k_p C^* M} \qquad (32)$$

k_{tm}, k_{ts}, k_{ti} are the rate constants for chain transfer to monomer, solvent and initiator respectively. The transfer to polymer is assumed to be negligible at fairly low conversion.

$$\text{Now} \quad C^* = \left(\frac{V_{init.}}{k_t} \right)^{\frac{1}{2}}$$

Taking the general case of chemical initiation, in which the rate of initiation is only proportional to initiator concentration,

$$C^* = (k_i I / k_t)^{\frac{1}{2}}$$

Let the chain transfer constant with a molecule X be defined as C_x, when $C_x = k_{tx}/k_p$. Substituting in equation (32) it follows that

$$\frac{1}{\bar{P}} = \frac{(k_i k_t)^{\frac{1}{2}} I^{\frac{1}{2}}}{k_p M} + \frac{k_{tm}}{k_p} + \frac{k_{ti}}{k_p} \frac{I}{M} + k_{ts}/k_p \frac{S}{M} \qquad (33)$$

$$\frac{1}{\bar{P}} = \frac{(k_i k_t)^{\frac{1}{2}} I^{\frac{1}{2}}}{k_p M} + C_m + C_I \frac{I}{M} + C_s \frac{S}{M} \qquad (34)$$

If the transfer to monomer and initiator is negligible, then the equation reduces to

$$\frac{1}{\bar{P}} = \frac{(k_i k_t)^{\frac{1}{2}} I^{\frac{1}{2}}}{k_p M} + C_s \frac{S}{M} \qquad (35)$$

Taking the general case of a bimolecular initiation reaction between the catalyst and the monomer, where $V_{init} = k_i M.I$, equation (35) becomes,

$$\frac{1}{\bar{P}} = \frac{(k_i k_t)^{\frac{1}{2}} I^{\frac{1}{2}}}{k_p M^{\frac{1}{2}}} + C_s \frac{S}{M} \qquad (36)$$

For the uncatalysed (thermal) reaction which is second order, the first term in equation (33) reduces to $(k_i k_t)^{\frac{1}{2}}/k_p$. In the absence of solvents the last term is zero, and the average degree of polymerisation in a pure monomer is given by

$$\frac{1}{\bar{P}_o} = \frac{(k_i k_t)^{\frac{1}{2}}}{k_p} + \frac{k_{tm}}{k_p} \qquad (37)$$

In the general case of an uncatalysed reaction, equation (37) becomes

$$\frac{1}{\bar{P}} = \frac{1}{\bar{P}_o} + C_s \, S/M \qquad (38)$$

which is Mayo's equation [31]. Equations (35) and (38) show a linear dependence of $1/\bar{P}$ on S/M, and have been widely used for the determination of chain transfer constants for many

solvents in the initiated and thermal polymerisation of various monomers [32-35]. A chain transfer constant of 0.02 means that a growing chain adds to its own monomer fifty times as readily as it attacks the solvent molecule. It has been found that the transfer constant for any one solvent increases in the order styrene < methylmethacrylate < acrylonitrile < vinyl acetate.

(e) Summary.

In initiated polymerisation the rate and efficiency of initiation are not always independent of monomer concentration, as has been assumed in developing the kinetic equation (18).

The dependence of the polymerisation rate on the square root of the initiator concentration has been found in bulk and solution polymerisation.

The kinetic equations suggest that the polymerisation rate should be proportional to the square root of the rate of initiation ($V_{init}^{\frac{1}{2}}$), irrespective of the initiation process. This is observed in the photochemical process of vinyl acetate and methyl methacrylate [36-37] and in several benzoyl peroxide initiated polymerisations. In addition a number of other monomers show similar behaviours. These observations support the generality of bimolecular/biradical termination processes in free radical polymerisations yielding high polymers

The interpretation of the dependence of the overall rate on the monomer concentration is not very satisfactory. In the benzoyl peroxide initiated polymerisation of styrene in toluene at 80°C, Horikx and Hermans [24] found that the apparent order with respect to monomer increased from 1.18 at [M] = 1.8 moles/litre to 1.36 at [M] = 0.4. Vinyl acetate and other common monomers also give an apparent order of reaction which is greater than one.

In chain transfer studies, some workers use an equation in which the first term of equation (35) is a function of I/M instead of $I^{\frac{1}{2}}/M$. But this does not cause noticeable discrepancy in the results obtained with a strong chain transfer agent [38]. It also can be seen that the exact form of the term containing I/M in the transfer equation will depend on the nature of initiation reaction.

1.4. Modification of the Simple Kinetic Scheme.

We have seen that in a number of systems the steady-state rate equations do not hold good. In a system having a monomer, an initiator, a solvent, a polymer and the derived radicals processes other than the simple initiation, propagation, termination and chain transfer can take place. Participation of these other processes or any change caused by a physical phenomenon going on in the system, may cause

a marked deviation in the kinetic order of the reaction. Some of the suggestions and modifications are discussed below.

(a) Modification of the Rate Equation.

(i) The Monomer-Initiator Complex Theory.

This theory was proposed by Schulz and Huseman [39], Mark and Josefowitz [40] and Kamenkaya and Medvedev [41]. They considered the formation of a monomer-initiator complex and the rate of initiation was assumed to be equal to the rate of decomposition of the complex. Schulz and Huseman [39] derived the equation :

$$-\frac{dM}{dt} = k_p \left(\frac{k_c k_d [I]}{k_t}\right)^{\frac{1}{2}} M^{3/2} (1 + k_c [M])^{-\frac{1}{2}} \qquad (39)$$

where k_c = rate constant for the formation of the complex and k_d its rate constant for decomposition.

No evidence of the formation of a monomer-initiator complex has been found by Mayo and others [21], and the hypothesis at present seems to be without foundation.

(ii) The Solvent-Cage Theory.

An alternative explanation was put forward by Matheson [42], using the "Solvent-Cage" theory of Frank and Rabinowitch [43]. He proposed that primary radicals are confined within cages of monomer or solvent molecules, and that some trapped radicals recombine instead of

initiating a polymer chain. The rate equation based on this theory is :

$$-\frac{dM}{dt} = k_p \left(\frac{r\, k_d\, [I]}{k_t} \right)^{\frac{1}{2}} M^{3/2} \left(1 + r\,[M]\right)^{-\frac{1}{2}} \qquad (40)$$

where k_d = rate constant for catalyst decomposition, r is equal to the ratio of the rate constant for reaction of an initiator radical with a monomer to that for reaction between two initiator radicals.

Horikx and Harmans [24] have supported the "cage" theory. However, it has been discounted by Flory [44], and Jenkins [45] has shown that the "cage" effect cannot satisfactorily explain the retardation, and the variation of the order of the reaction with monomer concentration.

(iii) Retardation due to Solvent Transfer.

In early work and in the cage theory, the solvent is taken as a diluent and assumed to have only a physical effect in surrounding the radicals, and not to undergo any chemical reaction. When the efficiency of re-initiation is very low, the substance is better considered as a retarder than a degradative chain transfer agent, but the distinction between them is one of degree only.

The reaction involving the solvent and the radicals generated by chain transfer, may be written as :

Transfer	$P^* + S \longrightarrow P + S^*$	k_s
Re initiation	$S^* + M \longrightarrow SM^*$	k_p'
Cross termination	$P^* + S^* \longrightarrow$ Product	k_t'
Mutual termination	$S^* + S^* \longrightarrow$ Product	k_t''

The order with respect to initiator [46], if "f" is the efficiency of re-initiation is given by

$$\frac{1 - f}{2} \left(1 - \frac{R_p}{R_{p_o}}\right) + 0.5$$

where R_p = rate of polymerisation in presence of transfer agent
R_{p_o} = rate in its absence.

This leads to the overall polymerisation being of the order of between 0.5 and 1 with respect to initiator.

$$f = \frac{k_p' [S^*] [M]}{k_p' [S^*][M] + k_t' [P^*][S^*] + k_t''[S^*][S^*]} \quad (41)$$

Kice [47] has shown that cross termination is usually favoured. Hence,

$$f = \frac{k_p' [S^*] [M]}{k_p'[S^*] [M] + k_t' [P^*] [S^*]} \quad (42)$$

The stationary concentration of polymer radicals is given by

$$R_p = k_p [P^*] [M] \quad (43)$$

$$1/f = 1 + \frac{k_t' R_p}{k_p' k_p} [M]^2 \quad (44)$$

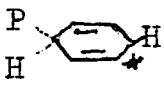
Burnett and Loan [48] developed a kinetic treatment to explain the dependence of rate of polymerisation upon monomer concentration when polymerisation is retarded by solvent transfer. There is, however, an inconsistency in the detailed treatment since the rate of radical displacement is put equal to the rate of re-initiation.

Jenkins [49] has shown that transfer constants may be calculated from rate measurements only if transfer is of the degradative type. His treatment seems best when retardation is pronounced and the efficiency of re-initiation is low. The derived equation is

$$R = \delta^{-1} [M] (R_i)^{\frac{1}{2}} \frac{(R_i k_t)^{\frac{1}{2}}}{k_{fs}[S] + (R_i k_t)^{\frac{1}{2}}} \qquad (45)$$

in which k_{fs} is the rate constant of transfer reaction.

The solution polymerisation of acrylonitrile has been examined by Thomas, Gleason and Pellon [50]. The pronounced retarding effect of benzene upon vinyl acetate might be attributed to the formation of phenyl radicals from the diluent, which fail to re-initiate the polymerisation. This would conflict with the results of work with benzoyl peroxide and vinyl acetate which show that these radicals initiate effectively. It must be recognized that radicals can interact with aromatic substances by mechanisms not yet fully understood. In this connection, the demonstration that

benzene can co-polymerise with vinyl acetate [51] is of great significance; the retardation is quite likely to be due to inertness of the radical  towards the relatively unreactive monomer.

(iv) Transfer to Initiator.

Transfer to initiator can properly be regarded as an induced decomposition of that substance since it leads to consumption by a process other than dissociation to radicals. Transfer to initiator can be studied by molecular weight methods and also by end-group analysis. Some of the di-aroyl peroxides are rather susceptible to transfer, and it is for this reason that azoisobutyronitrile is commonly preferred as an initiator. The radical displacement most probably can be represented as :

$$P^* + (RCO.O)_2 \xrightarrow{k_i'} P.O.CO.R + R.CO.O^{\cdot} \qquad (46)$$

The radical produced in equation (46) or one derived from it by loss of CO_2, initiates efficiently since it is identical with the radical produced by dissociation of the initiator. Such transfer to initiator leads to an abnormal relationship between the rate of polymerisation and the kinetic chain length [52]

$$R_{i\ (apparent)} = R_{i\ (true)} + 2k_i' [P^*] [I] \qquad (47)$$

Since $R_p = k_p [P^*] [M]$,

$$R_{i\ (apparent)} = R_{i\ (true)} + \frac{2k_i'[I]}{k_p[M]} \cdot R_p \quad (48)$$

For a fixed concentration of initiator, the rate of polymerisation can be varied by adding to the system a second initiator. Then a plot of $R_{i(apparent)}$, determined as the rate at which fragments of the first initiator enter the polymer, against the rate of polymerisation, should be linear; from the slope k_i'/k_p can be determined, and the true rate of initiation by the first initiator can be found from the intercept [53-54].

When degradative chain transfer with initiator[55] takes place, the order of reaction with respect to initiator concentration becomes less than 0.5. Taking an extreme case where all the termination reactions are with initiator molecules and they are degradative in nature(as with certain sulphides e.g. $P^* + (C_6H_5.S)_2 \longrightarrow P.C_6H_5 + C_6H_5.S.S^*$), then:

$$R_t = k_t\,(C^*)\,(I) = R_i = k_d\,(I)$$

$$R_p = k_p\,C^*\,M, \qquad C^* = \frac{k_d}{k_t}$$

Hence $$R_p = \frac{k_p.k_d}{k_t}\,M \quad (49)$$

The order of reaction with respect to the initiator can also change because of Primary Radical Termination [56]. The reactions are

$$R^* + Z^* \longrightarrow \text{Product} \quad (50)$$

$$Z^* + Z^* \longrightarrow \text{Product} \quad (51)$$

As the concentration of Z* increases it will participate more and more in these two termination reactions.

Bamford et al. [59] extended this theory and derived the following rate equation :

$$R = \delta^{-1} [M] (R_i)^{\frac{1}{2}} \left(\frac{k'_M}{k'_M + R_i^{\frac{1}{2}}} \right) \qquad (52)$$

where $k' = k_i/2(k_t)^{\frac{1}{2}}$

Equation (52) gives good correlation with the rate data obtained from those systems where there is no marked retardation by solvent. The relation between polymerisation rate and $(I)^{\frac{1}{2}}$ is linear at lower initiator concentration, but at higher initiator concentration the rate tends to level off, as the apparent order of reaction with respect to initiator concentration tends to zero. This is the case in the polymerisation of styrene at constant monomer concentration in N,N-dimethyl formamide, at 60°C, and with concentrations of AIBN between 0.02 and 0.659 mole/litre.

(v) Transfer to Monomer.

If transfer to monomer molecules is accompanied by retardation or if the monomer molecules take part in the termination reaction, the kinetics of polymerisation are changed. In an extreme case, when all the termination reactions are with monomer molecules, and initiation is due to generated monomer radicals, then,

$$R_t = k_t [C^*] [M] = R_i = k_d [I]$$

$$C^* = \frac{k_d [I]}{k_t [M]}, \qquad R_p = k_p C^* [M]$$

$$= \frac{k_p k_d [I] M}{k_t M} \tag{53}$$

$$= \frac{k_p k_d}{k_t} I \tag{54}$$

which shows that rate of polymerisation is directly proportional to rate of initiation. The kinetic order with respect to [I] and [M] will be 1 and zero respectively. The function k_p/k_t is the kinetic chain length ν, equation (54) gives $R_p = \nu R_i$ (55)
Equation (55) is obeyed by the polymerisation of allyl acetate [56].

(b) Modified Chain Transfer Equation.

Mayo's equation (38), page22 is satisfactory for the determination of chain transfer constant in the general case of thermally initiated polymerisation reaction. However, a number of workers have used the equation for the determination of chain transfer constants in the chemically initiated polymerisation of styrene, methylmethacrylate, vinyl acetate and acrylonitrile [57-61]. The transfer constants obtained [58] were compared with the figures obtained from thermal polymerisation. Taking the initiation

processes in the above systems to follow the simple kinetic scheme, (that is the rate of initiation is proportional only to the initiator concentration), then $I^{\frac{1}{2}}/M$ should be kept constant, (equation 33, page 21). But it was found that keeping I/M constant and changing [S]/[M] was equally satisfactory.

Toohey and Weale [62], in order to investigate the whole situation studied the polymerisation of styrene in toluene, ethyl benzene and trimethyl amine, using AIBN and benzoyl peroxide as initiator at 60°C. They found that keeping I/M and $I^{\frac{1}{2}}/M$ constant in the toluene-benzoyl peroxide system C_s values were 11.0 $x10^{-5}$ and 2.6 $x10^{-5}$ respectively and the latter value compared well with the thermal value of 1.25 $x10^{-5}$. In the case of triethylamine, a relatively active solvent, no significant difference was noticed in the value of C_s by changing I/M ratio to $I^{\frac{1}{2}}/M$. In both cases, the values were close to thermal values.

Mayo's equation for the determination of C_s can also be used for systems where retardation or degradative chain transfer occur. The chain length of the polymers should not be very low [63-64]. In an extreme case, when mutual termination is completely replaced by monoradical degradative chain transfer, the transfer equation can be written as :

$$\frac{1}{\bar{P}} = \frac{\text{rate of chain termination by all processes}}{\text{rate of chain growth}}$$

$$\frac{1}{\bar{P}} = \frac{k'_t\ C^*M}{k_p C^*M} + \frac{k'_{tm}\ C^*M}{k_p\ C^*M} + \frac{k'_{tI}\ C^*I}{k_p\ C^*M} + \frac{k'_{ts}\ C^*S}{k_p\ C^*M} \quad (56)$$

where k'_t is the rate constant for monoradical termination with monomer, resulting in formation of stable radicals; which can be equated with k'_{tm}. Hence,

$$\frac{1}{\bar{P}} = 2C'_m + C'_I\ I/M + C'_s\ [S]/[M] \quad (57)$$

where C'_m, C'_I and C'_s are the transfer constants with monomer, initiator and solvent, respectively, for degradative chain transfer. Thus in the extreme case of degradative chain transfer, provided the $\bar{P}$ is not too small, a plot of $1/\bar{P}$ against S/M gives the value of C_s.

SECTION II.

Bulk Copolmerisation.

2.1. Introduction.

From both the theoretical and practical standpoints, copolymerisation constitutes a very important branch of the study of polymerisation processes generally. When two or more monomers are polymerised together, they may copolymerise to yield macromolecules containing units of different monomers linked together. The process of copolymerisation is very important industrially. This technical interest in the reaction of copolymerisation has led to its intensive study and it was early recognized that the composition of a copolymer might be quite different from that of the monomer mixture or feed from which they are formed [65-66]. Although most copolymerisation reactions involve monomers, both of which can independently polymerise, other 'monomers' can be used which do not themselves form high polymers. Thus maleic anhydride, which is difficult to homopolymerise, readily polymerises with other monomers such as styrene, vinyl acetate, etc. [67-69]. The extreme case in which neither of the original monomers are capable of polymerising alone, but will copolymerise, is also known. Thus maleic anhydride will react with stilbene to give a copolymer [70].

2.2. Reaction Scheme and Copolymer Composition Equation.

If the two monomers are M_1 and M_2, and M_1^* and M_2^* designate the propagating radicals, then the reaction scheme is :

<u>Initiation</u>

$$M_1 \longrightarrow M_1^* \qquad M_2 \longrightarrow M_2^* \tag{58}$$

<u>Propagation</u>

$$M_1^* + M_1 \xrightarrow{k_{11}} M_1^* \qquad M_1^* + M_2 \xrightarrow{k_{12}} M_2^*$$
$$M_2^* + M_2 \xrightarrow{k_{22}} M_2^* \qquad M_2^* + M_1 \xrightarrow{k_{21}} M_1^* \tag{59}$$

<u>Termination</u> The termination reaction may involve mutual destruction by combination or disproportionation of any of the radical chains ending in M_1^* and M_2^*. Chain transfer reactions may also have to be considered.

This complicates the situation and was the main reason for the slow progress in the study of copolymerisation kinetics. In 1944 Alfrey and Goldfinger[71], Mayo and Lewis [72] and Wall [73], made kinetic investigations and derived the copolymerisation equation.

From equation (59) the rates of disappearance of M_1 and M_2 are given by :

$$-\frac{dM_1}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] \tag{60}$$

$$-\frac{dM_2}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2] \tag{61}$$

The radical concentrations are low, and since the chains are long the major reaction by which radicals M_1^* and M_2^* are formed and destroyed is by interconversion of one into the other. Then assuming steady-state conditions, we may write

$$\frac{dM_1^*}{dt} = k_{21}\,[M_2^*]\,[M_1] - k_{12}\,[M_1^*]\,[M_2] = 0 \qquad (62)$$

If we define $r_1 = \frac{k_{11}}{k_{12}}$ and $r_2 = \frac{k_{22}}{k_{21}}$,
then dividing equation (60) by (61) and eliminating radical concentrations with the help of equation (62), yields

$$\text{copolymer}\quad \frac{[dM_1]}{[dM_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1\,[M_1] + [M_2]}{M_1 + r_2\,[M_2]} \qquad (63)$$

This is the copolymerisation equation which gives the composition of the copolymer being formed at any instant from a polymerising mixture of monomers at concentrations $[M_1]$ and $[M_2]$, r_1 and r_2 are termed the "monomer reactivity ratios" of monomer M_1 and M_2 respectively. A similar derivation has subsequently been obtained by Melville, Noble and Watson [74] and Goldfinger and Kane [75] using statistical methods, and without assuming the steady state conditions. To prepare a copolymer of composition of $\left[\frac{M_1}{M_2}\right]_{\text{copolymer}} = x$, the starting monomer mixture $\frac{M_{1o}}{M_{2o}} = y$ will be given by

$$y = \frac{x-1 + [(x-1)^2 + 4r_1r_2 \cdot x]^{\frac{1}{2}}}{2\,r_2} \qquad (64)$$

The initial copolymer formed from a monomer mixture determined by the above equation has the desired composition. If it is desired to produce a uniform copolymer then the monomer ratio must be maintained at y throughout the reaction by continuous addition of the more reactive monomer.

2.3. Monomer Reactivity Ratios.

From the definition of the monomer reactivity ratio in the previous page it can be seen that it is "the ratio of the reactivity of a monomer radical towards its own molecule to that towards another molecule". A value of $r > 1$ indicates that an active centre should react more readily with its own type of monomer, whereas $r < 1$ indicates that it will prefer the other species. If we copolymerise different monomers with a particular monomer (radical), then the reciprocal of their monomer reactivity ratios will give the "relative reactivity" of the monomers towards that monomer (radical). Thus if we copolymerise monomer M and V with S, and if $r_1 = \frac{k_{ss}}{k_{sm}}$, $r_2 = \frac{k_{ss}}{k_{sv}}$, then $1/r_1$ and $1/r_2$ are the relative reactivities of M and V towards S.

There are three important types of copolymerisation depending on the values of r_1 and r_2 :

(a) The product of r_1 and r_2 is unity.

(b) The product is less than unity and one ratio greater than unity.

(c) The product is less than unity and both ratios are

less than unity.

If the product is unity, the monomers have the same relative reactivities towards both radical types and the copolymerisation is random. This is approximately correct for the copolymerisation of styrene and butadiene (0.78, 1.39). With all monomer mixtures, butadiene enters the chain at a relatively faster rate [76]. This has been called "ideal copolymerisation" by Wall [73].

If the product of r_1 and r_2 is less than unity, and r_1 is greater than unity, there is an alternating tendency and the relative rates at which the monomers enter the chain will depend on their initial composition. The monomer corresponding to the higher monomer reactivity ratio will enter the chain at a faster relative rate, irrespective of the monomer mixture. An example is methyl methacrylate and vinyl acetate (20, .015).

If both the ratios are less than unity, each monomer prefers the opposite radical and there is a tendency for the units to alternate in the polymer chain. There is a single monomer mixture in which the two monomers enter the copolymer in exactly the same proportions as in the monomer mixture; hence their relative concentrations do not change as conversion increases to 100%. This mixture, called a constant polymerising mixture (or azeotropic mixture), is given by :

$$\frac{M_1}{M_2} = \frac{r_2 - 1}{r_1 - 1} \qquad (65)$$

Typical examples are styrene-acrylonitrile [77] and styrene-diethylfumerate [78].

2.4. The Rate of Copolymerisation.

To derive an equation for the overall rate of copolymerisation presents difficulties because of the many rate constants which have to be considered. The equation has been worked out by various schools [74,79,80,81]. Assuming that a steady state condition is set up, so that the rate of initiation is equal to the rate of termination, we have :

$$R_i = 2k_{t_{11}} [M_1^*]^2 + 2k_{t_{12}} [M_1^*] [M_2^*] + 2k_{t_{22}} [M_2^*] \quad (66)$$

where k_t is the rate constant for each bimolecular radical termination, as denoted by subscripts. By summing equation (60) and (61) and eliminating radical concentration with the help of equation (62) and (66), the expression for the overall rate becomes :

$$-\frac{d([M_1] + [M_2])}{dt} = \frac{(k_{21}k_{11}[M_1]^2 + 2k_{12}k_{21}[M_1][M_2] + k_{22}K_{12}[M_2]^2) R_i^{\frac{1}{2}}}{(2k_{t_{11}}k_{21}^2[M_1]^2 + 2k_{t_{12}}k_{t_{21}}[M_1][M_2] + 2k_{t_{22}}k_{12}^2[M_2]^2)^{\frac{1}{2}}} \quad (67)$$

Taking $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, and introducing the ratios,

$$\delta_1^2 = 2k_{t_{11}}/k_{11}^2, \qquad \delta_2^2 = 2k_{t_{22}}/k_{22}^2 ,$$

$$\phi = k_{t_{12}}/2\,(k_{t_{11}}k_{t_{22}})^{\frac{1}{2}} ,$$ and substituting them in equation (67), the rate equation becomes :

$$\frac{-d([M_1]+[M_2])}{dt} = \frac{R_i^{\frac{1}{2}}\,(r_1[M_1]^2+2[M_1][M_2]+r_2[M_2]^2)}{(r_1^2\delta_1^2\,[M_1]^2+ 2\phi r_1 r_2\,\delta_1\delta_2\,[M_1]\,[M_2] + r_2^2\,\delta_2^2\,[M_2]^2)^{\frac{1}{2}}} \qquad (68)$$

In equation (68) δ is related reciprocally to quantities like k_p^2/k_t and can be obtained from rate measurements on individual monomers, the reactivity ratios may be determined from copolymer composition studies, and R_i can be determined, or rendered constant by using an initiator such as azoisobutyronitrile. The value of ϕ can therefore be obtained. ϕ is a measure of the ratio of the cross-termination rate constant to the geometric mean of the rate constants for symmetric termination.

2.5. Chemical Structure and Reactivity in Copolymerisation.

(a) Resonance Effects.

A detailed discussion of the effect of resonance-stabilisation of radicals, monomers and transition states has been given by Evans [82-83]. If the monomer or the radical is resonance-stabilised, the reactivity is less, whereas if the transition state is resonance-stabilised the reactivity is enhanced. Evans et al. [83] correlated the

increase in activation energy, $\triangle E$, corresponding to the decrease in resonance energy, $\triangle q$, by the expression,

$$\triangle E = 0.4 \triangle q \qquad (69)$$

It has been found that the radical addition occurring most readily is that involving the formation of the most stable radical, and also that the rate of reaction depends wholly on the energy of activation. This apparent paradox was resolved by Wheland [84] who explained that the resonance which stabilises the radicals may also stabilise the transition state complex.

Radicals associated with comparatively high resonance energy make their parent molecule more reactive, since the conversion of molecule to active molecule will require a low activation energy. The radicals however will be comparatively stable and will require a high activation energy to react. However, whereas the stabilisation of the monomer may amount to 2-4 Kcal./mole, stabilisation of the radical may be as much as 15 Kcal./mole. Since the resonance contribution to the transition state will be derived from both, it is reasonable to expect that the situation will be intermediate between the two.

Thus the two effects of resonance are in apparent opposition, but by far the most important effect is the stabilisation of the radical; for example the vinyl

acetate radical will attack the vinyl acetate molecule more than 1000 times faster than the styrene radical is capable of doing. The effect of substitution in the 1-position in enhancing the reactivity of a monomer are in the order $-C_6H_5 > -CH=CH_2 > -COCH_3 > -CN > -COOR > -Cl > -CH_2X > -OCOCH > -OR$.

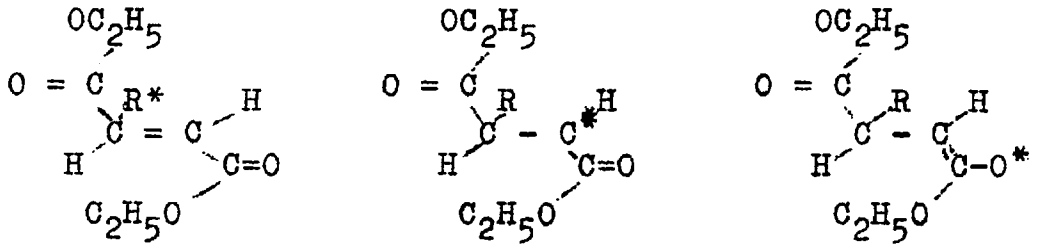
(b) Steric Effect.

The steric effect can be due to steric inhibition of resonance or to steric hindrance at the point of radical attack.

The difference in the behaviour of cis and trans isomers was first pointed out by Marvel and Schertz [85] and the investigation on geometric isomers was carried out by Lewis and Mayo [86]. If it is assumed that the radical is either planar or an easily reversible pyramid, the addition of the same radical to either geometric isomer will produce the same radical adduct and if this conversion is simultaneous with addition then, the more energy rich isomer, (i.e. the less stable) should be the more reactive of the pair. This is the case with dichloroethylenes and various other isomers. However, although the ratio of maleonitrile to fumaronitrile in equilibrium is about 3 [86], these isomers show very little difference in reactivity. Here it is most likely that the structure of the monomers decides

the transition state configuration, and conversion to the same radical takes place later, if at all.

The most obvious anomaly occurs in the diethyl esters of maleic and fumaric acids. Here the more stable fumarates are many more times reactive than the maleates, a result which can be ascribed to the steric inhibition of resonance. In the fumaric ester either or both ester groups can be coplanar with the double bonds, on the other hand, with the maleates the ester groups interfere and the molecule cannot be coplanar. Thus only in the fumarate can resonance-stabilisation of the transition state for radical addition occur.



A similar argument holds for cis and trans stilbenes, where the more reactive cis form cannot be planar because of interference between the phenyl groups.

As an illustration of steric hindrance due to the presence of substituents at the point of radical attack, the copolymerisation of styrene with chloro-olefines can be considered. In vinylidene chloride, the introduction of a chlorine atom in the 1-position of vinyl chloride increases

the reactivity by a factor of about 10, which is in accord with the effect of resonance on reactivity. If the second atom is introduced in the 2-position the reactivity decreases about 5-fold for the trans isomer and about 30-fold for the cis compound. The difference between the reactivities of these two molecules is adequately accounted for by steric inhibition of resonance, but the decrease in reactivity relative to vinyl chloride can be explained only on the grounds of steric hindrance due to the additional substituent being located at the site of reaction. With trichloroethylene the presence of the third chlorine atom has the effect of counterbalancing the decreased reactivity of cis-trans isomers, and this molecule is almost as reactive as vinyl chloride, while with tetrachloroethylene there is again a diminution in reactivity.

(c) The Alternating Phenomenon and the Alfrey-Price Equation.

The product of the monomer reactivity ratios can be taken as a measure of the tendency for monomers to alternate in the copolymer, the tendency increasing as $r_1 r_2$ decreases. The cause of this has been subject to considerable investigation. Lewis, Mayo and Hulse [87] suggested that in some instances it is due to steric effects and in others to some dipole interaction. Bartlett and

and Nozaki [88] suggested a theory based on electron donor and acceptor properties, and it is now believed that alternation is largely polar in origin.

The polar theory has been developed by Price [89] in terms of the electrostatic interaction between permanent charges, and an attempt to place the concepts of radical stabilisation and polar effects on a quantitative basis in order to predict monomer reactivity ratios has been made by Alfrey and Price [90]. According to them the rate constants may be written as :

$$k_{11} = P_1 Q_1 e^{-e_1^2}$$

$$k_{12} = P_1 Q_2 e^{-e_1 e_2}$$

$$k_{22} = P_2 Q_2 e^{-e_2^2}$$

$$k_{21} = P_2 Q_1 e^{-e_2 e_1}$$

where P_1 and Q_1 are the reactivity of the radical and monomer respectively and e_1 and e_2 the quantities of charge for the particular monomer-radical pair. It is assumed that the charge on the radical and the parent monomer is the same. From these equations, the monomer reactivity ratios can be derived as :

$$r_1 = (Q_1/Q_2)\, e^{-e_1 (e_1 - e_2)} \qquad (70)$$

$$r_2 = (Q_2/Q_1)\, e^{-e_2 (e_2 - e_1)} \qquad (71)$$

and $$r_1 r_2 = e^{-(e_1 - e_2)^2} \qquad (72)$$

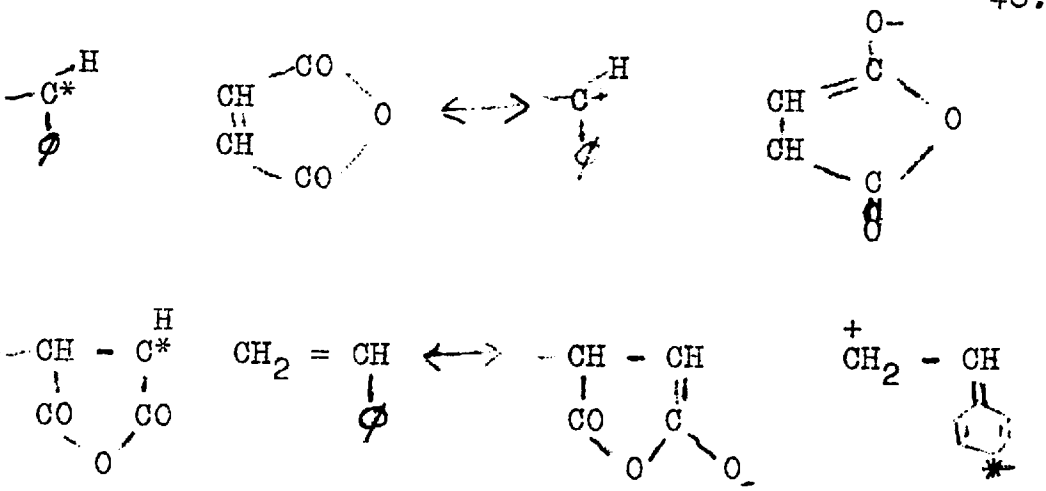
The validity of the above expressions has been questioned on three points

i). The alternating effect may not arise from electrostatic interaction between fixed charges only; because monomer reactivity ratios are not sensitive to the dielectric constant of the media.

ii). The charges on the monomer and the derived radical may not be equal.

iii). Q and e values are derived for a standard monomer which is arbitrarily chosen. (Q and e were chosen for styrene as 1 and -1, subsequently Price [91] has changed this base to 1 and -0.8).

Hence it is more realistic to consider the Alfrey-Price equation as an empirical expression, which has utility in correlating data and predicting monomer reactivity ratios for monomers where data are not available. The lack of sensitivity of monomer reactivity ratios to dielectric constants does not necessarily mean that a polar effect is not responsible for alternation, it may imply that alternation does not arise from the interaction of fixed charges but is instead due to the rearrangement of electric charge in the transition state of the monomer-radical system. For the attack of styrene on maleic anhydride such structures may be



SECTION III.

Radical Polymerisation under High Pressure.

3.1. Introduction.

Pressure is a significant variable in chemical reactions. Acceleration in the rate of gaseous reaction due to pressure is well known and is generally a Mass Action effect. High Pressure also affects liquid-phase reactions and this cannot be explained simply on the basis of changes in the concentration of the reactants. Kinetic investigation of liquid-phase reaction under high pressure started at the beginning of this century and at present a number of schools, including those of Walling (U.S.A.); Hamann (Australia); Gonikberg (U.S.S.R.); Weale (U.K.); and Laidler and Whalley (Canada); are working in this field.

Early work on liquid-phase polymerisation has been reviewed by Bridgman [92] and Perrin [93] has published an extensive summary of work by his group on the influence of pressure on reaction velocities of liquid-phase chemical reactions. The effect of pressure on rate of polymerisation and on molecular weight has been studied by a number of workers [94-100]. Weale has recently reviewed the effect of pressure on addition polymerisation [101].

3.2.i. The Overall Rate of Radical Polymerisation under Pressure.

The effect of pressure on the overall rate of chemical reactions can be explained by either the Collision Theory or the Transition State Theory.

(a) The Collision Theory.

According to this theory, the rate is accelerated by pressure because of changes in the E and PZ factor in the Arrhenius rate equation. The Arrhenius rate equation can be written as :

$$k = PZ\ e^{-E/RT} \qquad (73)$$

where k is called the velocity constant or rate constant or the specific reaction rate, P = probability factor, Z = frequency of collision, E = activation energy.

It is well known that application of moderate pressure produces important effects in gas reactions. Ammonia synthesis is favoured by the application of pressure of several hundred atmospheres and this can be accounted for satisfactorily by the increase in concentration and by the reduction in volume taking place during the reaction. But in the case of liquid phase chemical reaction, the effect of pressure cannot be explained by "mass action" effect and it is likely that the application of considerably higher pressure can produce results of more fundamental importance.

Bimolecular liquid phase chemical reactions can be divided into "normal" and "slow" reactions. The rates of "normal" reactions are increased by pressure to a relatively small extent. The value of PZ is not greatly affected by pressure, in fact it shows a tendency to decrease, and the increase in rate is due to a decrease in the value of the activation energy E. In the "slow" reactions increase in pressure causes a large increase in the numerical value of PZ. This more than compensates for an increase in E, and the net effect is a large increase in the rate of reaction. Pressure has a relatively small effect on the rate of collision between molecules in solutions, especially dilute solutions, and this is ccmpensated by the increased time between collisions of those molecules which are widely separated.

The large increase in the 'PZ' factor for slow reactions can therefore be attributed to the increase in the "probability factor" which for these reactions is much less than one. In the case of "normal"reactions, 'P' is approximately unity and pressure has only a small effect.

(b) <u>The Transition State Theory</u>.

The transition state theory can satisfactorily explain the effect of pressure on the overall rate of radical polymerisation. In the transition state theory, it

is assumed that a transition state is formed which is intermediate between the reactants and the products and in equilibrium with the reactants.

Reactants $\rightleftharpoons$ Activated complex $\longrightarrow$ Products

$aA + bB \rightleftharpoons (aA \ldots\ldots bB) \longrightarrow$ Products

It has been found possible to derive an equation for the rate constant of any reaction as

$$k = \frac{RT}{Nh} K^{\neq} \tag{74}$$

where k = rate constant, h = Planck's constant, and $K^{\neq}$ is the equilibrium constant of the equilibrium between activated complex and the reactants, N is Avogadro's Number. From equation (74)

$$K^{\neq} = \frac{Nh}{RT} k ,$$

$$-RT \ln K^{\neq} = -RT \ln \frac{Nh}{RT} k = \Delta F^{\neq}$$

$$\frac{\delta(\Delta F^{\neq})}{\delta P} = -RT \frac{\delta}{\delta P} \ln K^{\neq} = -RT \frac{\delta}{\delta P} \ln k$$

$$\frac{\delta(\Delta F^{\neq})}{\delta P} = \Delta V^{\neq}$$

Hence $$-RT \frac{\delta}{\delta P} \ln k = \Delta V^{\neq}$$

$$\text{or } \frac{\partial \ln k}{\partial P} = -\Delta V^{\neq}/RT \tag{75}$$

where $\Delta V^{\neq}$ = (Partial molar volume of transition state) - (partial molar volume of reactants). The above equation (75) using the transition state theory was derived by Evans and Polanyi [102].

In ionic reactions, solvation of the ions may account for a large part of this volume change, but the effect is unimportant in non-polar polymerisations. The effect of pressure on the rate of polymerisation can be expressed by an equation of the form of (75) although the process is complex and the rate equation includes several different rate constants. The overall effect of pressure will depend on the combined effect of initiation, propagation and termination processes on $\triangle V^{\neq}$.

$$R_p = k.M.I^{\frac{1}{2}} = \frac{k_p\, k_d^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} M.(2f\ I)^{\frac{1}{2}}$$

Assuming pressure does not change the monomer and initiator concentration and the reaction is first order; if equation (75) is applied to each of the individual rate constants, the overall volume of activation $\triangle V_o^{\neq}$ can be expressed as

$$\triangle V_o^{\neq} = \triangle V_p^{\neq} + \tfrac{1}{2} \triangle V_d^{\neq} - \tfrac{1}{2} \triangle V_t^{\neq} \qquad (76)$$

where $\triangle V_p^{\neq}$, $\triangle V_d^{\neq}$ and $\triangle V_t^{\neq}$ are the volumes of activation associated with the transition states of propagation, dissociation of initiator, and termination respectively, and $\triangle V_o^{\neq}$ is the overall volume change of transition.

Another approach can be made to the "transition state" theory from the theory of rate process .

$$\triangle F^{\circ} = -RT \ln K^{\neq} \quad \text{and} \quad \triangle F^{\circ} = \triangle H^{\circ} - T \triangle S^{\circ}$$

Therefore $K^{\neq} = e^{-\triangle F^{\circ}/RT} = e^{\triangle S^{\circ}/R}\ e^{-\triangle H^{\circ}/RT}$.

If the corresponding result for the equilibrium constant $K^{\neq}$ is inserted in the above equation then

$$k = \frac{RT}{Nh} e^{-\Delta F^{\neq}/RT} \quad (77)$$

$$= \frac{RT}{Nh} e^{\Delta S^{\neq}/R} e^{-\Delta H^{\neq}/RT} \quad (78)$$

$$= A e^{\Delta S^{\neq}/R} e^{-\Delta H^{\neq}/RT} \quad (79)$$

where $\Delta F^{\neq}$, $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are the standard free energy, entropy and heat of activation respectively; these quantities represent the difference between the values of the respective thermodynamic functions for the activated complex and the reactants, all the substances being in their standard state of unit activity which for gases is chosen as the ideal gas at 1 atmosphere, and for dilute solutions it is the hypothetical ideal solution of unit concentration, i.e. 1 mole (or 1 gram ion) per litre, or of unit molality (1 mole per 1000 grams of solvent).

The entropy change appears to be related to $\Delta V^{\neq}$ which usually tends to decrease or increase in the same direction as entropy. For bimolecular reactions the sub-dvision into 'normal' and'slow' reactions depends on the magnitude of the decrease in entropy $\Delta S^{\neq}$ in relation to the heat of activation $\Delta H^{\neq}$, which can be approximately identified with 'E', the energy of activation in Arrhenius's equation(73). Polymerisation reactions which are accompanied by considerable loss of entropy and large negative volume of activation are accelerated by pressure [103].

3.2.ii). Effect of Pressure on the Individual Processes of the Polymerisation.

(b and c) The Pressure Dependence of k_p and k_t.

$k_p/k_t^{\frac{1}{2}}$ can be determined by measurement of the steady state rate of polymerisation. The individual values of k_p and k_t have been obtained by photochemical polymerisation at high pressure under conditions of intermittent illumination. k_p increases exponentially with pressure, so that the propagation reaction, which is accompanied by a considerable loss of entropy has a large negative volume of activation [104-105]. $\triangle V_p^{\neq}$ for chain growth in the polymerisation of styrene by photochemical initiation at 30°C, has been calculated to be -13.4 cc./mole between the pressures 1-3000 atm; whereas $\triangle V_o^{\neq}$ is about -18 cc./mole. Hence $\triangle V_p^{\neq}$ is by far the largest factor contributing to $\triangle V_o^{\neq}$. k_t decreases rapidly up to 1000 atm, and then more slowly. $\triangle V_t^{\neq}$ for bimolecular termination by recombination should have a small negative value, but if it becomes diffusion-controlled it may change sign. Hence the decrease in k_t is probably due to the increase of viscosity with pressure.

(a) The Pressure Dependence of k_d.

The thermal decomposition of benzoyl peroxide in carbon tetrachloride over the pressure range of 1-3000 atm.

has been studied by Nicholson and Norrish [106]. The effect of pressure on other homolytic dissociations has been investigated by Ewald [107] and Walling et al [108]. Two mechanisms are distinguishable. The first is a radical-induced chain decomposition which is accelerated by pressure but is ineffective in initiating polymerisation, and is suppressed in the presence of monomer, and the second is the unimolecular decomposition corresponding to the simple kinetic equation. All the unimolecular decompositions are retarded by pressure, so that $\triangle V_d^{\neq}$ is always positive, but there are significant variations with solvents [107-109].

3.3. Chain Transfer.

The volume of activation accompanying the transfer reaction [110], $\triangle V_{tr}^{\neq}$, is related to the chain transfer constant by theequation,

$$\frac{d \ln C_{tr}}{dP} = - (\triangle V_{tr}^{\neq} - \triangle V_p^{\neq}) /RT \qquad (80)$$

Transfer reactions are accelerated by pressure. Walling and Pellon [111] found that the chain transfer constant is almost independent of pressure in the polymerisation of styrene in carbon tetrachloride at 60°C up to 6000 atm. Hence k_{tr} is increased to nearly the same extent as k_p; and $\triangle V_{tr}^{\neq}$ for this transfer is about -11 cc./mole.

Toohey and Weale [112] found that $\triangle V^{\neq}_{tr}$ for polystyryl radicals and trimethylamine is about -1 or -2 cc./mole. The abstraction of an atom from a neutral molecule may occur with a contraction in volume due to the formation of a bimolecular transition state, but the contraction should be less than in chain-growth, because bond-breaking occurs simultaneously. But if with some substrates, the polar structure suggested by Walling [113] takes place and contributes to the transition state an additional contraction due to solvation may occur. A study of the variation of $\triangle V^{\neq}_{tr}$ with the structure of the attacked molecule could be important in the behaviour of allylic monomers.

Merrett and Norrish [98] in the polymerisation of styrene with benzoyl peroxide as initiator up to 5000 atm. at 60°C found that molecular weight is approximately tripled between 1 and 3000 atm., but increases only slightly at higher pressures. The levelling-off of polymer molecular weight is due to an alteration in the balance between the termination and the transfer reactions. At 1 atm. most termination is by combination, and an increase in pressure at first causes an increase in molecular weight by slowing down this reaction. At higher pressure the accelerated transfer reaction determines the molecular weight.

3.4. Copolymerisation at High Pressure.

In spite of its industrial importance, fundamental studies of copolymerisation at high pressure have been rather neglected. Coffman et al. [114] found that an interesting copolymer can be formed from ethylene and carbon monoxide at 1000 atmospheres with t-butyl peroxide as initiator. The products with molecular weight less than 2000 are liquids or crystalline solids and are polyketones. Those with the highest carbonyl content have a structure $[-CO-C_2H_4-]_n$. Cairns et al. [115] obtained an unusual copolymer from carbon monoxide, an olefin and an alcohol at 2000-8000 atm. The product from carbon monoxide, ethylene and methanol contains α-hydroxy-ester groups and at the highest pressure the structure tends to $[-CCH_3(CO_2CH_3).CH_2.CH_2-]_n$.

Lamb and Weale [116] have studied the copolymerisation of styrene and methyl methacrylate with benzoyl peroxide as initiator at 60°C and pressures up to 4000 atm. The overall rate and molecular weight increased with pressure, the latter levelling off at the highest pressure. The monomer reactivity ratios were independent of pressure. If $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, then this indicates that $\Delta V^{\neq}_{11} \simeq \Delta V^{\neq}_{12}$ and $\Delta V^{\neq}_{22} \simeq \Delta V^{\neq}_{21}$. ϕ was found to vary little with pressure, where $\phi = k_{t_{12}}/(k_{t_{11}}.k_{t_{22}})^{\frac{1}{2}}$.

In equimolar mixture of styrene and methyl methacrylate $\emptyset \simeq 25$, and hence cross-termination is strongly favoured. This preference for cross-termination is not in accordance with the assumption of diffusion-control of the termination at high pressure. Since both types of radicals should diffuse at similar rates $\emptyset$ should approach unity with pressure. However the question of diffusion control is complicated [117] and no detailed study of the effect in copolymerisation has been reported. Gonikberg et al. have [118] copolymerised vinyl acetate with trichloroethylene and tetrachloroethylene with AIBN at pressures up to 4000 atm. According to them, more sterically hindered a reactant, the greater is the effect of pressure, hence the addition of a tetrachloroethylene molecule to the growing chain leads to a greater acceleration of this reaction by pressure than that of the addition of trichloroethylene molecules.

In the present work experiments have been carried out with styrene and vinylidene chloride, vinyl acetate—vinylidene chloride, and vinyl acetate and trichloroethylene.

SECTION IV.

Apparatus

4.1. (a) High Pressure Equipment I.

A photograph and a line diagram of the reaction vessel and ancillary high pressure equipment are shown in Figure 1 and Figure 2 respectively.

P is a hand operated "Blackhawk" hydraulic pump which can generate pressure up to 3,000 atmospheres, and has a by-pass valve C. The pump is connected to the low pressure side of the intensifier D, and the pressure gauge G through valve A, by means of stainless steel tubing of I.D. 1/8" and O.D. 3/8". The top-side of the intensifier, which is the high pressure side, is connected with the pressure vessel V by means of Vibrac steel tube of I.D. 1/16" and O.D. 1/2". The pressure vessel itself is made up of two high-tensile-strength molybdenum steel cylinders shrunk together and has O.D. of 4" and I.D. of 0.7". The vessel is 15.5" long, and is designed to withstand pressures of up to 5,000 atmospheres. It is immersed in an oil-bath, which is heated by an electric immersion heater of 1,400 watts, and stirred with a motor-driven stirrer. The temperature of the bath was kept constant at 60 $\pm$ 0.1°C by means of a mercury-toluene thermoregulator R and a Sunvic relay system. The

pressure is developed in the intensifier via two pistons (Figure 3), the lower one of diameter 1.5" and the upper one of 0.651". The lower piston, sealed by a Bridgman unsupported-area packing, is contained in the lower cylinder, and is connected with the upper piston through a thrust block and a copper washer to correct for any disalignment. The upper piston is sealed with a Poulter packing which travels with the piston in the upper high pressure cylinder, which is made of two Vibrac steel cylinders shrunk together. The two cylinders are joined by a screwed sleeve, and the upper cylinder is connected with the Vibrac steel tube via a screwed connector. From the ratio of the areas the pressure intensification should be 5.3-fold, but it was found that,

$$P_V = 5.12\ P_G - 120.$$

The loss in pressure can be accounted for by friction in the packing and the pistons, and a small change in area of the pistons due to pressure.

(b) High Pressure Equipment II.

For pressures above 25 Kb (1 Kb = 1000 bars = 987.1 atm.) the tetrahedral anvil equipment as devised by Hall [123] and as modified by Lloyd et al. [124] was used. A photograph of the apparatus and a line diagram of the anvils used and ancillary equipment, are shown in Figure 5 and Figure 6 respectively. The apparatus consists

essentially of three lower anvils and a top anvil contained in a steel ring with a conical inner surface. The pressure is applied by a Denison hydraulic press of 300 tons capacity. Three types of anvils made of different materials of construction are used [125]. The anvils used in this work have a triangular loading face of 3/4" edge length and are made of a 1½" diameter core of Edgar Allen 'Stag Major' high speed steel hardened and tempered to 800-900 DPN. This inner core is fitted, with 0.006" interference, in a binding ring of Ni-Cr-Mo steel, EN.26, hardened and tempered to 400-420 DPN. The binding ring contains a carbide backing block which is supported in turn by a steel backing-block. The anvils have an annular ring for cooling and the overall diameter of the anvil is 3.45". The containing steel-ring has an O.D. of 14.3" and an I.D. of 9.8" tapering at the base to 4.7". The cooling rings in some of the anvils leaked and they were sealed with Araldite. The top anvil had a flat base and the three bottom anvils had bases of the same curvature as the inner surface of the supporting ring. Pyrophyllite tetrahedrons of 0.85" and 0.94" length were used.

The edges of the triangular faces of the anvils were painted with an acetone-rouge mixture and the three bottom anvils were placed in the containing ring in their numbered sequence. They were separated from each other with 0.1" teflon buttons placed near the tetrahedron. The

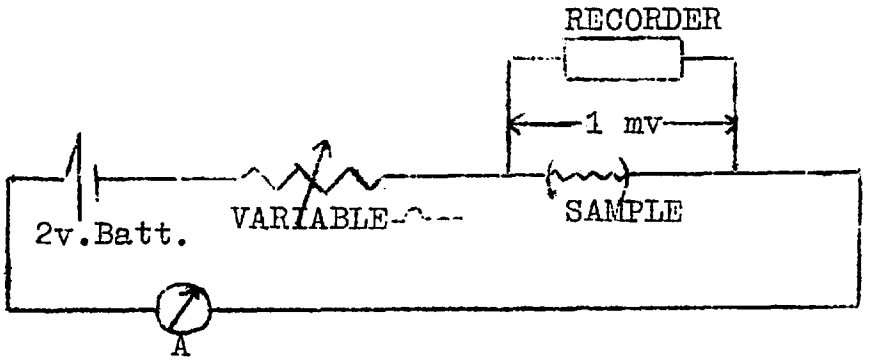
top anvil had six buttons to separate it from the bottom anvils. This helps to provide symmetrical positioning of the four anvils aroung the over-sized tetrahedron inserted in the cavity, and also separates the two 'heating'anvils (the top and one of the bottom ones) from the other two. A piece of teflon 0.002" thick sandwiched between two polythene sheets of the same thickness was placed between the bottom anvils and the conical ring. This acts as a lubricant and overcomes the effects of excessive friction between the anvils and the ring; and also provides electrical insulation.

Samples were inserted in a hole drilled in the pyrophyllite tetrahedron in either the "edge to edge" or "base to apex" directions (shown in Figure 6). Calibration of the press was done for both "edge to edge" and "base to apex" arrangements, with a pyrophyllite sample holder of 0.94" long. The results by both methods were quite concordant.

Pressure Calibration.

Measurements of pressure were made by means of the 'fixed point' transitions of bismuth and thallium, which were detected by changes in their electrical resistance. 0.005" diameter wires of these materials were placed in an AgCl tube, contained in a graphite tube. Electrical connections to the samples were made by strips of nickel foil (0.003") through specks of indium pressed over the ends

of the wire (Figure 6). The electrical connection for the calibration is shown.

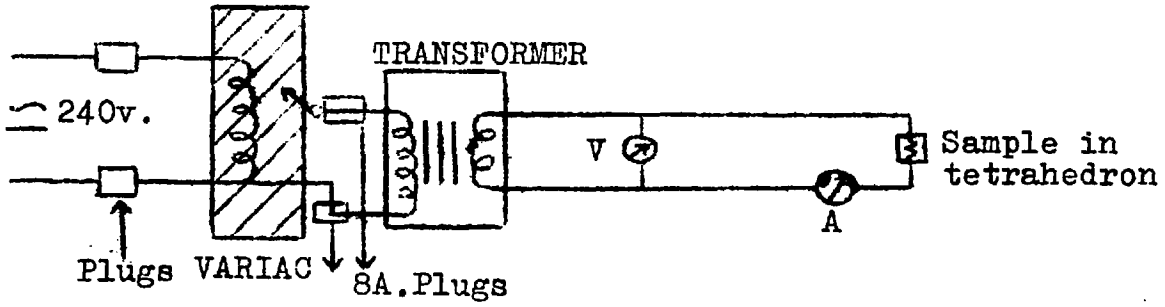


Graphs of resistance against load applied were plotted and from the known fixed points, (namely 25.6 Kb and 27 Kb for the first and second bismuth transition points, and 36.8 Kb for the thallium transition), the press was calibrated. The AgCl tube was contained in the graphite tube, because in subsequent experiments, graphite sleeves were used for heating the samples.

Runs with Samples.

As the monomers used were liquids, only the "base to apex" arrangement of the sample in the pyrophyllite tetrahedron could be used. The samples were taken in a teflon bottle (I.D. 0.177", O.D. 0.1875") which was a'push fit' in the carbon heating tubes (I.D. 0.1875", O.D. 0.228") (see Figure 6). Samples with low B.P. were cooled in "dry ice" before they were loaded in the small teflon bottles (trans DCE), the anvils were pre-cooled with "dry ice" and the sample was subjected to pressure. As the anvils have to attain room

temperature before heating can be done, which would require the press to be operated overnight. Samples which had to be strongly cooled were not heated under pressure. With monomers such as trichloroethylene, having a higher B.P., the sample could be loaded at room temperature and it was heated under pressure. An approximate 15° rise of m.p./Kb was assumed and the sample was heated to about that temperature under the corresponding pressure. The heating circuit is shown



The transformer used was a 'Harmsworth Townly' of P V - 240, S.V. - 24 and maximum current capacity of 500 amp. A 'Ferranti clip up' ammeter was used to measure the current. The temperature of the sample was measured with the help of chromel-alumel thermocouple in a stainless steel sheath having 0.5 mm. outside diameter. The two heating anvils were cooled with a water-soluble oil mixture.

4.2. Distillation Apparatus.

The apparatus used was standard Quickfit laboratory glassware. Monomers were distilled under a nitrogen atmosphere and/or under vacuum before use.

4.3. Apparatus for Determination of Molecular Weight.

(a) Beckmann's Apparatus.

The Beckmann apparatus for measuring the depression of the freezing point consisted of a tube containing the solution, fitted with a Beckmann thermometer and a stirrer. The tube is supported by a ring of rubber inside a wide tube which serves as an air-mantle separating the tube containing the solution from the freezing-bath. This ensures a slower and more uniform rate of cooling. The freezing mixture is contained in a glass jar which is fitted with a cork. The cork had a central hole to take the wide tube and also holes for a stirrer and a thermometer.

(b) Viscometer.

The viscosity measurements were done with a U-tube micro-viscometer, M2/BS/U/M. It was placed in a water bath with glass walls, which was fitted with a stirrer and a heating and cooling system. The temperature of the bath was controlled to better than $\pm$ 0.1^{o}C. Viscosities were measured at 25^{o}C.

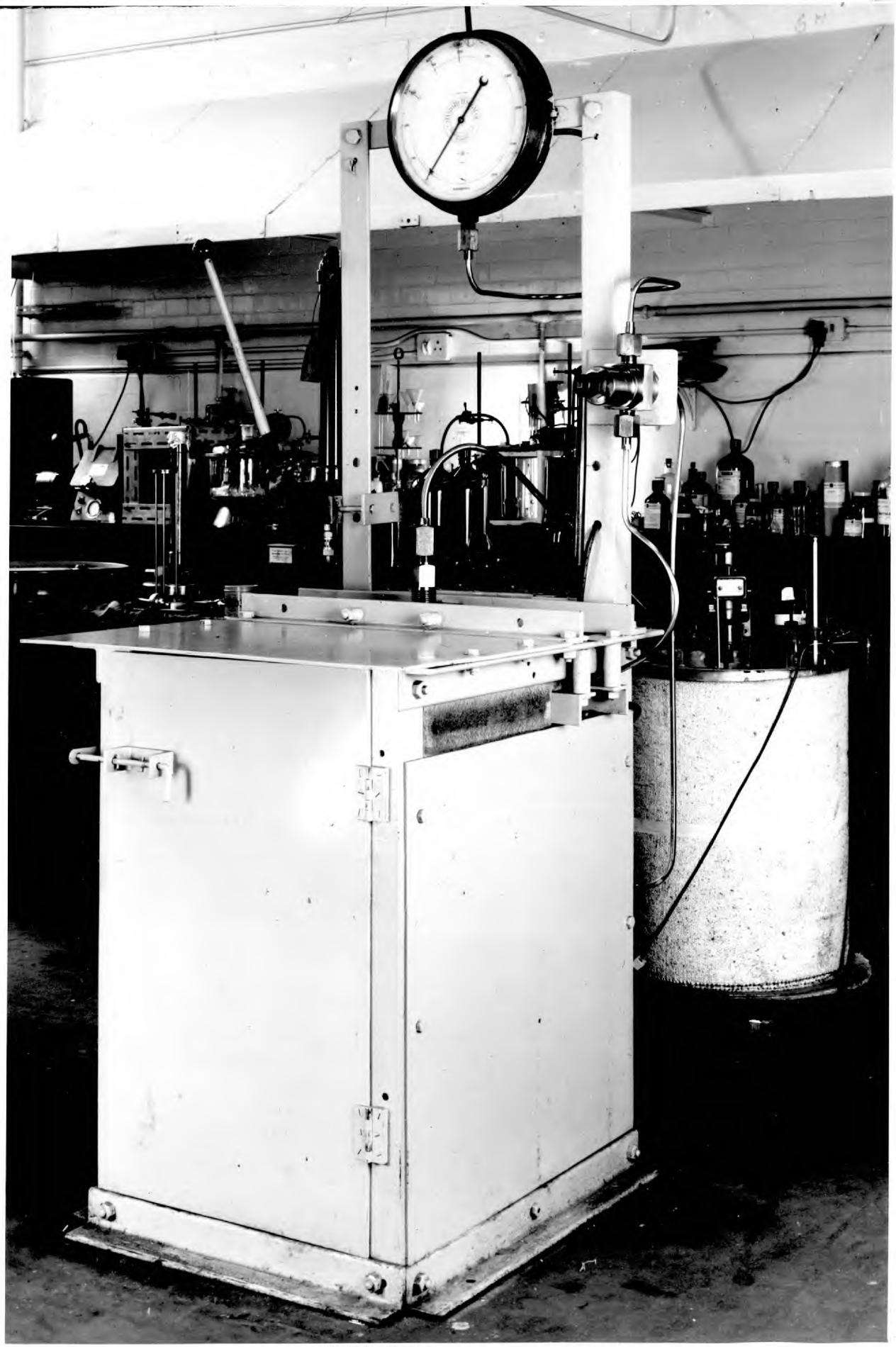


FIGURE 1

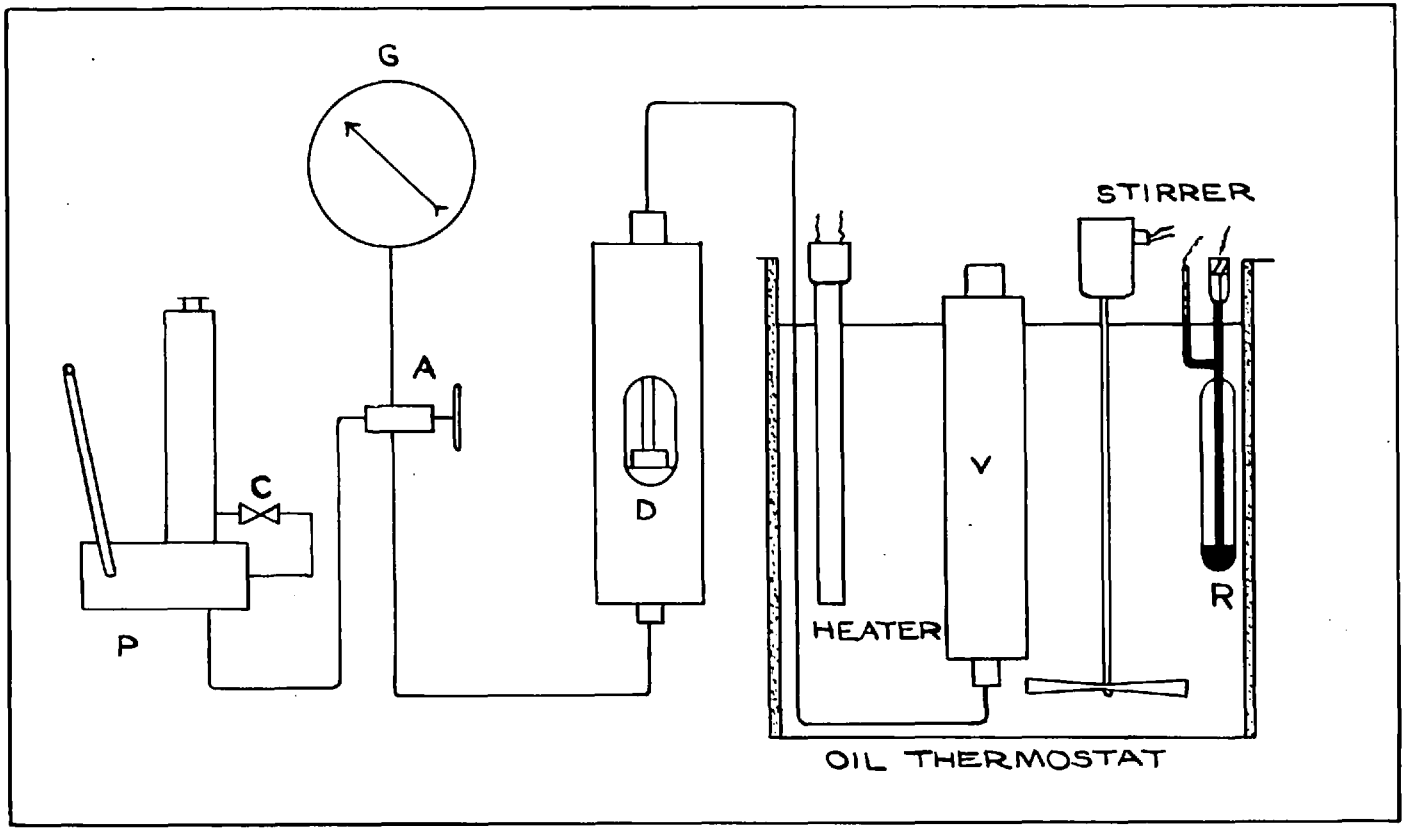


FIGURE 2

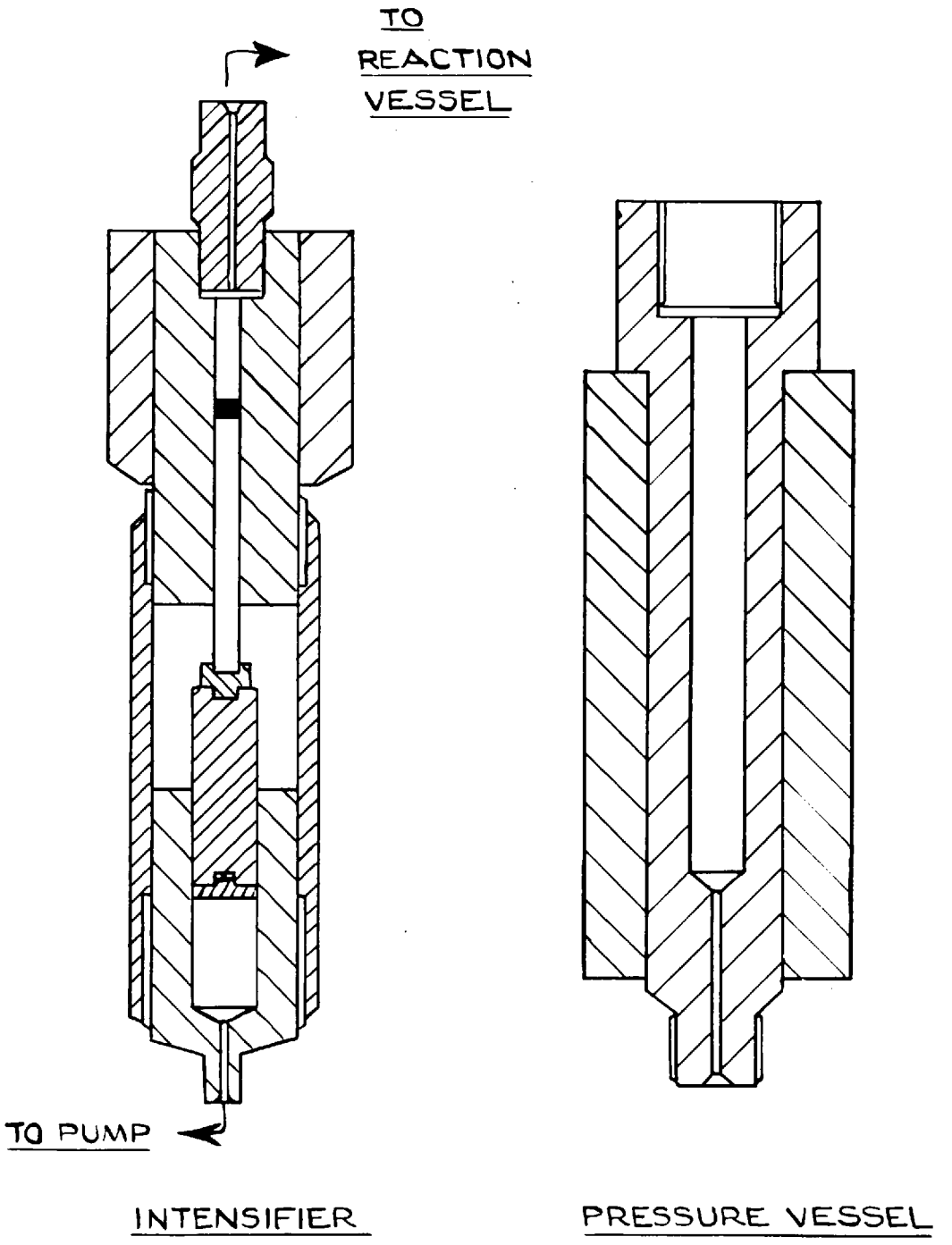
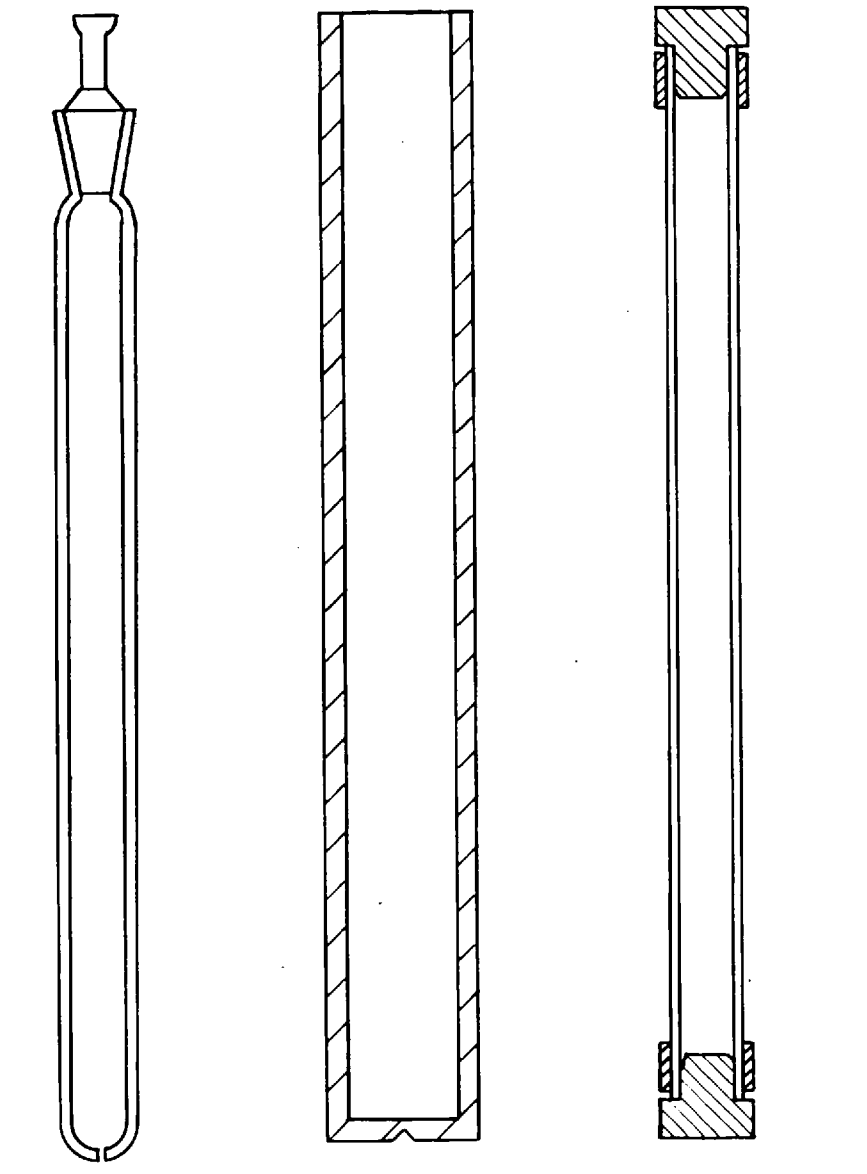


FIGURE 3


PYREX TUBE
BUCKET
P.T.F.E. TUBE

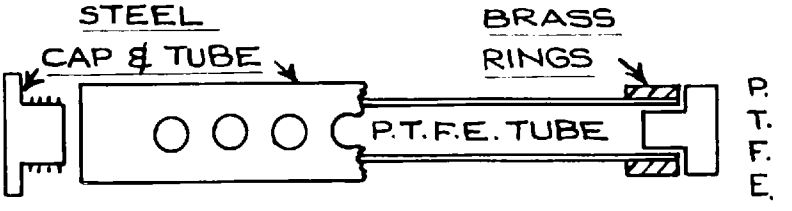
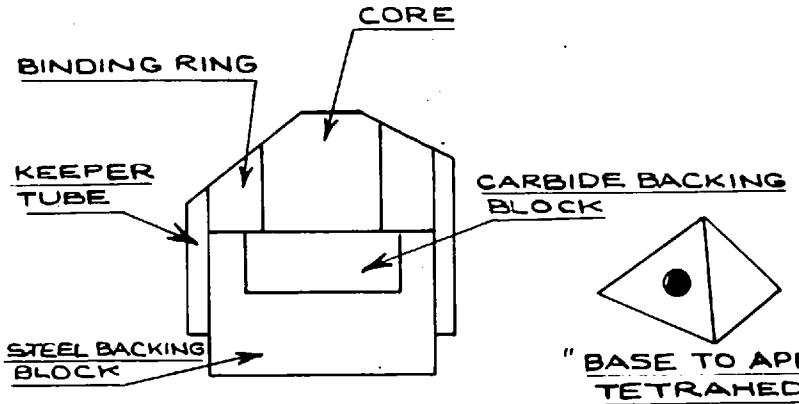

STEEL
CAP & TUBE
BRASS
RINGS
P.T.F.E. TUBE
P.
T.
F.
E.

FIGURE 4



FIGURE 5

THE TETRAHEDRAL ANVIL APPARATUS

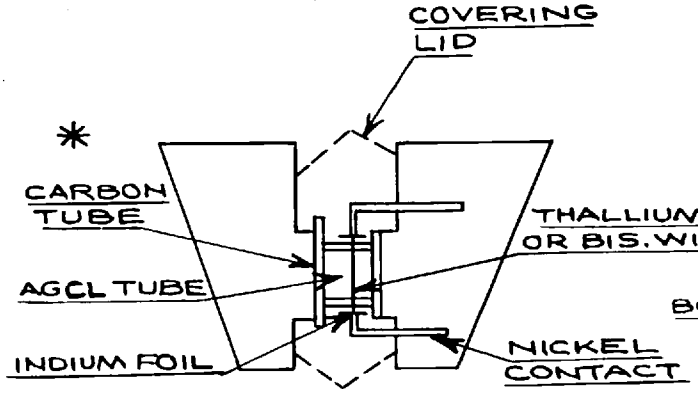


DESIGN OF ANVIL

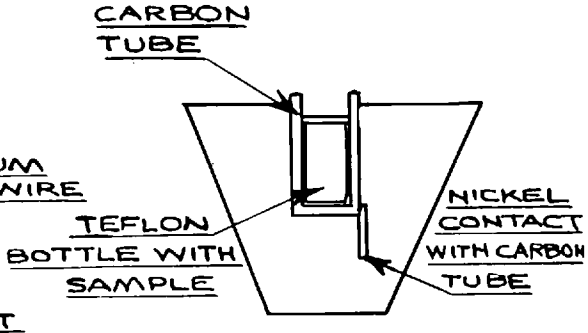
"BASE TO APEX" TETRAHEDRON



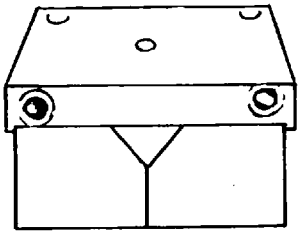
"EDGE TO EDGE" TETRAHEDRON



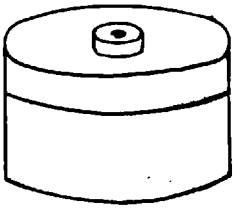
SECTION OF SAMPLE FOR "EDGE TO EDGE" CALIBRATION



"BASE TO APEX" SAMPLE FOR RUN



HOLDING BLOCK FOR MAKING "EDGE TO EDGE" HOLE



HOLDING BLOCK FOR MAKING "BASE TO APEX" HOLE

* NOTE THE 'WIRE' IS IN A SOLID AGCL TUBE FITTED IN A CARBON TUBE, THE WIRE IS IN CONTACT WITH INDIUM FOILS AND THE NICKEL FOILS IN CONTACT WITH INDIUM FOILS.

FIGURE 6

SECTION V.

Materials Used and Experimental Procedure.

5.1. Materials Used.

i). Styrene.

The styrene monomer (B.D.H.) contained t-butyl catechol as inhibitor. This was removed by shaking 250 ml. of crude styrene with 100 ml. of 10% NaOH three times in a separating funnel. Excess alkali was removed by three distilled water washes and the monomer was stored over calcium chloride in the dark under vacuum for 24 hours. It was then distilled under vacuum in a nitrogen atmosphere, and the middle fraction was collected. The sample was stored in a deep-freeze under vacuum. Fresh samples were prepared from time to time. A typical sample had refractive index $\eta_D^{25^\circ} = 1.5450$. B.P. 145°C at 760 mm.

ii). Technical Dichloroethylene.

Technical dichloroethylene, (Cis/Trans ≃ 3.5) was used as supplied. The sample was kept in a dark cool place.

iii). Trans-Dichloroethylene.

Supplied by the Koch-Light Laboratories and distilled under vacuum. The sample was kept under vacuum in the cold. A typical sample had a B.P. of 47.5°C at 760 mm.

iv). Trichloroethylene.

Supplied by Koch-Light Laboratories and distilled under vacuum. The sample was kept under vacuum in the cold. A typical sample had B.P. 87.5°C at 760 mm. pressure.

v). Vinyl Acetate.

Supplied by Koch-Light Laboratories and was distilled under vacuum in a nitrogen atmosphere. The sample was kept under vacuum in the cold. A typical sample had a B.P. of 72.5°C at 760 mm. pressure.

vi). Benzoyl Peroxide.

Benzoyl peroxide (B.D.H.) was re-precipitated from chloroform, dried under vacuum and kept in a dark bottle in a vacuum desiccator. Fresh samples were prepared from time to time. A typical sample had M.P. 104.5°C.

vii). Benzene.

For molecular weight determinations mol.wt. benzene as supplied by British Drug Houses was used. Benzene for use as a diluent was supplied by May and Baker Ltd. under the label "Benzene, Pure, Crystallizable".

viii). 1-2Epoxypropane.

This was used without further purification as supplied by B.D.H.

ix). Methanol.

Methanol, employed as a precipitant, was used as supplied.

x). Petroleum Ether.

Petroleum ether with 60-80°C B.P. range, was used as a precipitant as supplied.

xi). Vinylidene Chloride.

Supplied by Koch-Light Laboratories, and was distilled under vacuum. The sample was kept under vacuum in the cold. A typical sample had B.P. 32°C. at 760 mm. pressure.

5.2. Experimental Procedure.

a). Preparation of Samples.

The concentration of reaction mixtures are all expressed in mole-fraction or as mole percent. This has the advantage that concentration is independent of pressure. The amounts of styrene and vinyl acetate were determined by weighing. Technical dichloroethylene, trans-dichloroethylene, trichloroethylene and vinylidene chloride were added by volume (calculated from known densities) from a micro-burette. Precautions were taken to avoid loss of any solvent by evaporation. The weighed amount of benzoyl peroxide was

added before adding the chloro-olefines. For runs in the tetrahedral-anvil apparatus volatile samples were cooled in "dry-ice" so that they could be contained in the small bottles. Random checks showed that additions of the reactants by volume were accurate. This has the advantage that a desired composition of reaction mixture can be prepared and effects of pressure on rates and other properties at given concentration can be known.

For high pressure runs (1-4000 atm.) stoppered glass tubes containing about 1/2" mercury were used (Figure 4). The tube was filled with reaction mixture through a hole at its lower end and re-inverted taking care that no air bubbles were present. It was floated on mercury in a steel bucket which was then immersed in oil inside the reaction vessel, which was maintained at a constant temperature. The vessel was just filled with liquid paraffin, both valves were kept open, a rubber bung (Poulter packing) was inserted manually, the vessel closed at the top by a steel screw plug, and pressure applied at a controlled rate.

For high pressure runs in the tetrahedral-anvil apparatus, the three bottom anvils, arranged in a clockwise sequence in accordance with the marking (A,B,C) were lowered together in the steel ring, taking care that there was no disalignment. The anvils were separated from the steel ring by two sheets of polythene with a sheet of

teflon in between them (each 0.002" thick). The borders of the tungsten carbide triangle of the bottom anvils were painted with acetone-rouge mixture, and they were separated from each other by teflon studs 0.1" thick. The sample tube, contained in a pyrophillite tetrahedron, was then placed in the triangular cavity. The top anvil, which was similarly painted, was then placed on top. It was separated from the bottom set of anvils by means of the teflon studs. The steel ring containing the anvils was placed in position in the press and pressure applied at a controlled rate.

For atmospheric pressure runs the reaction mixture was transferred to amber-coloured ampoules which were flushed with oxygen-free nitrogen. The ampoules were sealed, and pushed into wire-gauze tubes which were immersed in the oil bath, kept at the required constant temperature.

(b) Polymerisation of Samples.

The time of polymerisation was recorded as the sum of the time the material was under the required pressure, plus half the time for generating and releasing pressure.

For runs with trans-dichloroethylene and vinylidene chloride the mercury-sealed glass tubes could not be used because of their high vapour pressures at the reaction temperature ($60^{\circ}C$). Teflon "squeeze" tubes (Figure 4) of

about 4.85" long and 3/8" diameter with 1/5" plugs to push-fit at both ends were used instead. There was a copper ring at each end to give additional support. They were placed in a steel holder which had a screw plug to be tightened on the "squeeze" tubes and openings in the walls to admit the pressure transmitting oil.

At the end of the run, the reaction tube was taken out and the reaction mixture transferred to a pre-cooled, previously weighed, stoppered flask.

The reaction mixture was diluted with its own volume of "diluent", and transferred to a beaker with three or four washings till about twice to two-and-a-half times the volume of diluent was added. Precipitant was slowly added to the mixture with stirring until a volume ratio (precipitant to solution) of between three and five had been added. The precipitate was covered and after allowing to stand for some time it was filtered under vacuum using a sintered glass crucible of porosity 4. In some cases the precipitate was left to stand overnight in the cold, and allowed to attain room temperature before filtration.

For mixtures of styrene and technical dichloroethylene benzene was used as a diluent. With reaction mixtures containing trans-dichloroethylene and trichloroethylene, benzene gave a "colloidal" precipitate, hence 1-2 epoxy propane was used. Even then the polymer,

after standing for 24 hours in the cold, was very difficult to filter. It was found that by adding a few drops of saturated solution of sodium chloride in methanol, this difficulty could be overcome. 1-2 epoxy propane was used as a diluent for reaction mixtures containing vinylidene chloride.

For the vinyl acetate-vinylidene chloride system, addition to the reaction mixture of a mixture of 1:1 (by volume) of acetone and chloroform gave practically no precipitate. On further addition of petroleum ether a white colloidal precipitate was obtained which could not be filtered. Petroleum ether alone (B.P. range 60-80°C) was found to be a satisfactory precipitant for systems containing vinyl acetate.

In the vinyl acetate-vinylidene chloride system, with runs containing high proportions of vinylidene chloride, there was precipitation in the reaction tube, and as all the precipitate could not be mechanically removed rate measurements were not possible. The precipitates could be filtered after being allowed to stand for three to four hours.

In the vinyl acetate-trichloroethylene system, the precipitate, after having been left overnight, got "stuck" to the beaker and could not be removed. It was dissolved in 1:1 acetone-chloroform mixture, re-precipitated

from petroleum ether, but the colloidal solution could not be filtered. Fitration of the precipitate was done after allowing the precipitate to settle for 15-20 minutes, even then there was a tendency for the precipitate to stick to the beaker. This difficulty could not be overcome, and hence the "rates" for the system as measured are not very accurate.

The polymer samples were washed and dried at 60°C in a vacuum oven for 24 hours at 1 cm. Hg. Where petroleum ether was used as a precipitant, it was dried at 68°C. The samples were cooled in a desiccator under vacuum before weighing.

c). Analysis of the Polymers.

For elemental analysis and spectroscopic work the copolymers and the polymers were re-precipitated, filtered and dried again. The purified samples were sent to the Organic Micro-Analytical Laboratory of Imperial College for elemental analysis. For styrene-vinylidene chloride system, C, H, and Cl analyses were done and they were corrected for 100% total percentage composition. For the vinyl acetate-vinylidene chloride system only chlorine analysis was done. Infra-red spectra of styrene-trans-dichloroethylene and styrene-trichloroethylene systems were done in Nujol with sodium chloride cell. A few samples

from the vinyl acetate-trichloroethylene system were sent to Germany for elemental analysis.

d). Molecular Weight Determination.

Polymers normally have a wide molecular size distribution and any method of measurement of molecular weight gives an average value. The molecular weight so derived depends on the method used. Three types of molecular weight averages are of considerable importance.

i). Number-average Molecular Weight : Designated by $\bar{M}n$, where the molecular weight of each species is weighted by the mole fraction of the particular species in the polydisperse system. Mathematically,

$$\bar{M}n = \sum XiMi = \sum NiMi / \sum Ni ,$$

where Xi is the mole fraction of the species, i, Mi the molecular weight, Ni the number of molecules of the species, and the summation is carried out over all values of i.

ii). Weight-average Molecular Weight : Designated by $\bar{M}w$, where the molecular weight of each species is weighted by the weight fraction of the species in the polydisperse system. Mathematically,

$$\bar{M}w = \sum WiMi = \sum NiMi^2 / \sum NiMi$$

where Wi is the weight fraction of the species in the polydisperse system.

iii). Viscosity-average Molecular Weight.

The physical property Pi of a solution of monodisperse material is related to the molecular weight Mi, and the concentration Ci, by

$$Pi = K\, Mi^{\alpha} Ci ,$$

then for a polydisperse system,

$$P = \sum Pi = \sum K\, Mi^{\alpha} Ci .$$

The average molecular weight which would be measured by using this particular property would be

$$M_P = (P/K \sum Ci)^{1/\alpha}$$

$$= \left(\frac{\sum Ci\, Mi^{\alpha}}{\sum Ci} \right)^{1/\alpha}$$

The concentration, Ci, is proportional to NiMi, so that

$$M_P = \left(\frac{\sum NiMi^{\alpha+1}}{\sum NiMi} \right)^{1/\alpha} \qquad (81)$$

a). Now when $\alpha = 1$, equation (81) is the same as that for weight-average molecular weight. In light scattering measurement, the turbidity of a solution is directly proportional to the molecular weight, so that $\alpha = 1$, hence it gives the weight-average molecular weight.

b). When $\alpha = -1$, equation (81) is the same as that for number-average molecular weight. Now osmotic pressure is inversely proportional to the molecular weight, and $\alpha = -1$. Hence measurement of the "colligative" properties give the number-average molecular weight.

c). The viscosity of linear macromolecular solutions gives α usually between 0.5 and 1, so that the viscosity average molecular weight can be defined as :

$$M\bar{v} = \left(\frac{NiMi^{\alpha+1}}{NiMi} \right)^{1/\alpha}, \quad 0.5 < \alpha < 1$$

The viscosity average lies between a weight average and number average, the order being $M\bar{w} > M\bar{v} > M\bar{n}$.

Molecular weights were determined by the depression of the freezing point or by viscosity measurements. Both the measurements were made in "molecular-weight" benzene.

For depression of the freezing point a Beckmann thermometer was used. It is graduated in 0.01° and could be quite accurately read to 0.005° with the aid of a lens. It does not indicate absolute temperatures, but merely differences of temperature. Before using the Beckmann thermometer it was "set", that is the amount of mercury in the bulb was adjusted so that for the particular experimental temperature it remained on the scale. The solvent and the solutions were supercooled to about $0.2\text{-}0.5^{\circ}$ and then stirred which caused the temperature to rise; and the highest constant temperature reached was noted in every case after tapping the thermometer with the finger. The average of four to five readings were taken. The solutions used had a concentration of 1-2% by weight of solute. Precautions were taken so that the temperature of the cooling bath was

not too low (not more than 5° below the freezing point of the solvent), the amount of supercooling did not exceed $0.2-0.3^{\circ}$, the stirring was not too rapid and as uniform as possible.

The molecular weight of the sample was determined from the formula :

$$\Delta T_f = K_f \frac{w_2}{M_2 w_1} \qquad (82)$$

where ΔT_f = freezing point depression,

M_2 = molecular weight of the solute,

w_2 and w_1 = weight of solute and solvent in grams,

K_f = cryoscopic constant for benzene and is 5120.

The measurement of viscosity is a well-established method of determining the molecular weight of high polymer. A solution of polymeric material has a higher viscosity than the pure solvent, and this increase depends on (a) the size and shape of the polymer molecule; (b) the concentration of the polymer; (c) the polymer-solvent interaction; and (d) the orientation of the large molecules in the moving solvent. The original law due to Staudinger [119] states

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = K\,M.c \qquad (83)$$

where η_o and η are the viscosities of solvent and solution respectively, K is a constant for a particular polymer-solvent system at a given temperature whose value is independent of molecular weight. If the effects of mechanical and structural interference are to be separated

from the effects due to the molecular size of the solute, the experimental data must be extrapolated to infinite dilution, and equation (83) can be written as :

$$[\eta] = (\eta_{sp}/c)_{c \to o} = KM$$

The above equation was modified by Huggins [120] by using the results due to Kuhn [121] and Eyring [122] as

$$[\eta] = (\eta_{sp}/c)_{c \to o} = KM^{\alpha} \qquad (84)$$

where $[\eta]$ is the limiting viscosity number, α is dependent on the shape of the solute molecule and ranges in value from zero for perfect spheres to 2 for rigid rods. K and α can be determined for a particular polymer-solvent system at a given temperature by an absolute method on the monodisperse phase, and then it can be used in equation (84) for a polydisperse phase.

The viscosity measurements were made on benzene solutions at 25°C. The concentration of the polymer was kept in the range 0.1 to 0.4 gm./100 ml. of solution. The solution was allowed to attain the temperature of the bath and the flow of liquid across the etched marks on the viscometer was observed through a lens, and the time recorded with a stop-watch. The stop-watch was graduated in divisions of 0.1 second, and readings to 0.05 second could be taken. The average of three concordant readings was used and from the time of flow of the solution and the solvent, the

intrinsic viscosity was found from :

$$[\eta] = \eta - \eta_o / \eta_o c = \frac{t - t_o}{t_o c} ;$$

where η and η_o are the dynamic viscosities. Since dynamic viscosity = $\frac{\text{flow time}}{\text{density}}$, and as the solutions were very dilute, $d \simeq d_o$. "c" is the concentration in gm./100 ml. For each polymer sample, the quantity η_{sp}/c was plotted against "c", and the straight line was extrapolated to zero concentration. The numerical value of the intercept on the η_{sp}/c axis is the value of $[\eta]$.

All the viscosity measurements were done with the same viscometer. Because of the low rate of flow no kinetic energy corrections were needed.

SECTION VI.

Calculations.

(a) Concentration of Reactants.

As the concentrations of the reactants are expressed in mole fraction or mole % no pressure correction is necessary.

(b) Reaction Rate and Rate Constant.

Reaction rates were calculated as weight % of polymer produced per unit time. The units of time were fixed durations of the runs or per hour

$$\text{wt.\% Polymer} = p/R \times \frac{W}{w} \times 100$$

where 'p' is the weight in grams of the polymer obtained from R grams of reaction mixture; W is the weight of the reaction mixture containing w grams of monomer.

For runs with pure styrene, and for calculating weight % copolymer, the rate is calculated as

$$\text{wt.\% polymer} = p/R \times 100.$$

Rate Constant.

In the kinetic equation, $R = k[M]\,[In]^{\frac{1}{2}}$, the overall rate constant k, for different initiator concentrations in the polymerisation of styrene was

calculated as follows :

$$R = k [M] [In]^{\frac{1}{2}}$$

If 'R' is measured in moles/litre.sec., [M] and [In] are monomer and initiator concentrations in mole/litre, then the dimensions of k is in litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec.$^{-1}$.

$[M] = \frac{\rho .1000}{W}$, where ρ is the density of monomer in gm./cc., W its molecular weight. R is also equal to $\frac{x.\rho .1000}{W}$, where 'x' is the fraction of the initial monomer converted to polymer per second. Therefore,

$$R = k [M] [In]^{\frac{1}{2}} = x [M],$$

and $$k = x [In]^{-\frac{1}{2}}.$$

If 'P' is the rate of conversion in wt.% per hour, then

$$x = P/3600 \times \frac{1}{100} .$$

Hence, $$k = \frac{P}{3600 \times 100} \times [In]^{-\frac{1}{2}} \text{ (litre/mole)}^{\frac{1}{2}}\text{sec.}^{-1}$$

It only remains to calculate [In] in mole/litre and the value of k can be obtained. For example, when In used is 0.1 mole %, [In] = 1 mole/1000 mole of styrene

= 1 mole per ($\frac{1000 \times 104}{868.9}$) litre at 60°C.

(c) Volume of Activation for Overall Rate of Polymerisation ($\triangle V_o^{\neq}$), and for Chain Transfer ($\triangle V_{tr}^{\neq}$).

The volumes of activation for overall rate of polymerisation were calculated from equation (75), page 52, and equation (80) page 56, respectively. The values of R and T were :

$$R = 82.06 \text{ cc-atm. (gm-mole)}^{-1}\ {}^{o}K^{-1},$$

$$T = 333.2^{o}K.$$

$\triangle V_p^{\neq}$ for styrene was taken as -13 cc./mole.

(d) Copolymer Composition.

In calculating the composition of the copolymer corrected values of %C were used where possible, (i.e. when all elements present were determined, as in the case of styrene and vinylidene chloride). Otherwise values were taken as determined. If two monomers M_1 and M_2 are copolymerised, and C_1 and C_2 are percentages of carbon in the monomers respectively, then their percentages in the copolymer are :

$$\% M_2 = \frac{\%C - C_1}{C_2 - C_1} \times 100$$

$$\% M_1 = \frac{\%C - C_2}{C_1 - C_2} \times 100$$

(e) Monomer Reactivity Ratios.

The monomer reactivity ratios were calculated by using equation (63) page 37, in the following linear form.

$$r_2 = \frac{[M_1]}{[M_2]} \left[\frac{d[M_2]}{d[M_1]} \left(\frac{[M_1]}{[M_2]} \cdot r_1 + 1 \right) - 1 \right]$$

[M] and d[M] were expressed in mole %. The values of r_2, corresponding to various assumed values of r_1, were calculated and plotted. r_1 and r_2 were obtained from the region of intersection of the lines.

SECTION VII.

Results and Discussion of the Effect of Pressure on the General Kinetics of Polymerisation of Halo-Olefines with Styrene, and Styrene.

7.1. Summary of some Previous Research.

An early attempt to measure the acceleration of the polymerisation of styrene [126] gave the huge factor of 2.24 $\times 10^6$ at 140°/1500 atm. A re-investigation by Gillham [127] showed that it was considerably less, the error being due to failure to carry out the experiments isothermally. Further measurements on styrene were made by Merrett and Norrish [98] up to 5000 atm. at 60°C, using benzoyl peroxide as initiator. With improved techniques, they obtained reproducible kinetic results which have been confirmed by later workers. They found log (overall rate) to be nearly a linear function of pressure. The polymer molecular weight tripled between 1 and 3000 atm., but increased only slightly at higher pressure. The reaction order with respect to initiator concentration was found to be 0.5 at 1 atm., but decreased a little with increase in pressure. $-\Delta V_o^{\neq}$ was found to be about 18 cc./mole and $\Delta V_p^{\neq}$ = -13 cc./mole. Walling and Pellon [111] found that $\Delta V_{tr}^{\neq}$ in the system styrene and CCl_4 was about -11 cc./mole.

Tri-, tetra-, and 1,2 disubstituted ethylenes (except $CF_2 = CF_2$ and $CFCl = CF_2$) polymerise much less readily than styrene, if at all; but a few attempts to produce polymers at high pressure have suceeded. Holmes-Walker and Weale [128] examined a number of these monomers up to 10,000 atm., generally using benzoyl peroxide as initiator. Weale [129] found 1,2 dichloroethylene forms a solid polymer of low yield and unknown molecular weight. Attempts to polymerise tri- and tetra-chloroethylenes have been unsuccessful. Klaassens and Gisolf [130] found that at 150° under a pressure of 10,000 atm., trichloroethylene undergoes "explosive" decomposition accompanied by carbonization. Gonikberg and Zhulin [131-132] have found that tetrachloroethylene does not polymerise even at pressures up to about 30,000 atm. Results of investigation with larger quantities of tri- and tetra-chloroethylenes have been reported by Gonikberg and Zhulin [133-134].

Copolymerisation of styrene with cis and trans dichloroethylene and trichloroethylene was tried under atmospheric pressure, using benzoyl peroxide as catalyst [135], but without success. Doak studied the copolymerisation of chloro-ethylenes with other monomers [136] and found the data to give the reactivity series vinylidene chloride > vinyl chloride > trichloroethylene > trans dichloroethylene > cis dichloroethylene > tetrachloroethylene. Mayo and Lewis [86]

compared some cis and trans isomers and found that steric inhibition of resonance, when it occurs, seems to determine the relative reactivities of geometrical isomers, and that relative stability has only a qualitative relation to reactivity in other cases.

Alfrey and Greenberg [137] have reported results for the copolymerisation of cis and trans dichloroethylenes and trichloroethylene with vinyl acetate and styrene. The monomer reactivity ratios of chloro-olefines with styrene were $\simeq 0$. Trans dichloroethylene was found to be much more reactive than cis-; and trichloroethylene a little more reactive than the trans isomer - a result in agreement with those of Doak.

Recently Asai [138-139] has reported some high pressure copolymerisation of styrene and the chloroethylenes. The monomer reactivity ratios of the halo-olefines were $\simeq 0$. The relative reactivity of the chloroethylenes were in agreement with Doak's reactivity series.

Chain transfer studies and other aspects of kinetic investigation studied in the system styrene and the chloro-olefines under pressure have not been done before.

7.2. Kinetic Investigations on the Bulk Polymerisation of Styrene.

Kinetic investigations of the benzoyl peroxide polymerisation of styrene at 60°C at different initiator concentrations and pressures were carried out. Table I gives the rate as wt.% conversion in 4 hrs. at different catalyst concentrations and pressures of 1 and 1000 atm. The overall rate constant k, expressed in litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec.$^{-1}$ is shown for the different catalyst concentrations at corresponding pressures.

In the bulk polymerisation of styrene, the order of reaction, calculated from the plot of log (Rate) against log of initiator concentration (Figure 7) is found to be 0.5 at 1 atm. and 0.46 at 1000 atm. This is in good agreement with previous works. The decrease in the order of reaction with the initiator concentration at high pressure may be due to some primary radical chain termination or to an increased amount of thermal polymerisation [143].

The overall rate constant k is given by

$$R_o = k\,[I]^{\frac{1}{2}}[M] = \frac{k_p(fk_d)^{\frac{1}{2}}}{k_t^{\frac{1}{2}}}\,[2I]^{\frac{1}{2}}\,[M]\,,$$

where k_p, k_d and k_t has the same significance as explained previously, and 'f' is the efficiency of the initiator, where 'f' is given as $\frac{\text{rate of initiation}}{\text{rate of decomposition}}$.

The overall rate constant k slightly decreased with increase

Table I.

Polymerisation of Styrene with Benzoyl Peroxide at 60°C.

[I] (mole%)	Conversion (wt% in 4hr.)	Log R	'K' x 10^4 (litre$^{\frac{1}{2}}$mole$^{-\frac{1}{2}}$sec.$^{-1}$)	$[I]^x$
	P = 1 ATM.			
0.1	6.71	0.827	0.492	
0.2	9.51	0.978	0.488	x = 0.5
0.3	11.2	1.049	0.470	
0.4	12.99	1.114	0.440	
	P = 1000 ATM.			
0.1	13.15	1.119	0.954	
0.2	16.13	1.207	0.860	
0.3	19.58	1.292	0.840	x = 0.46
0.4	23.21	1.366	0.840	

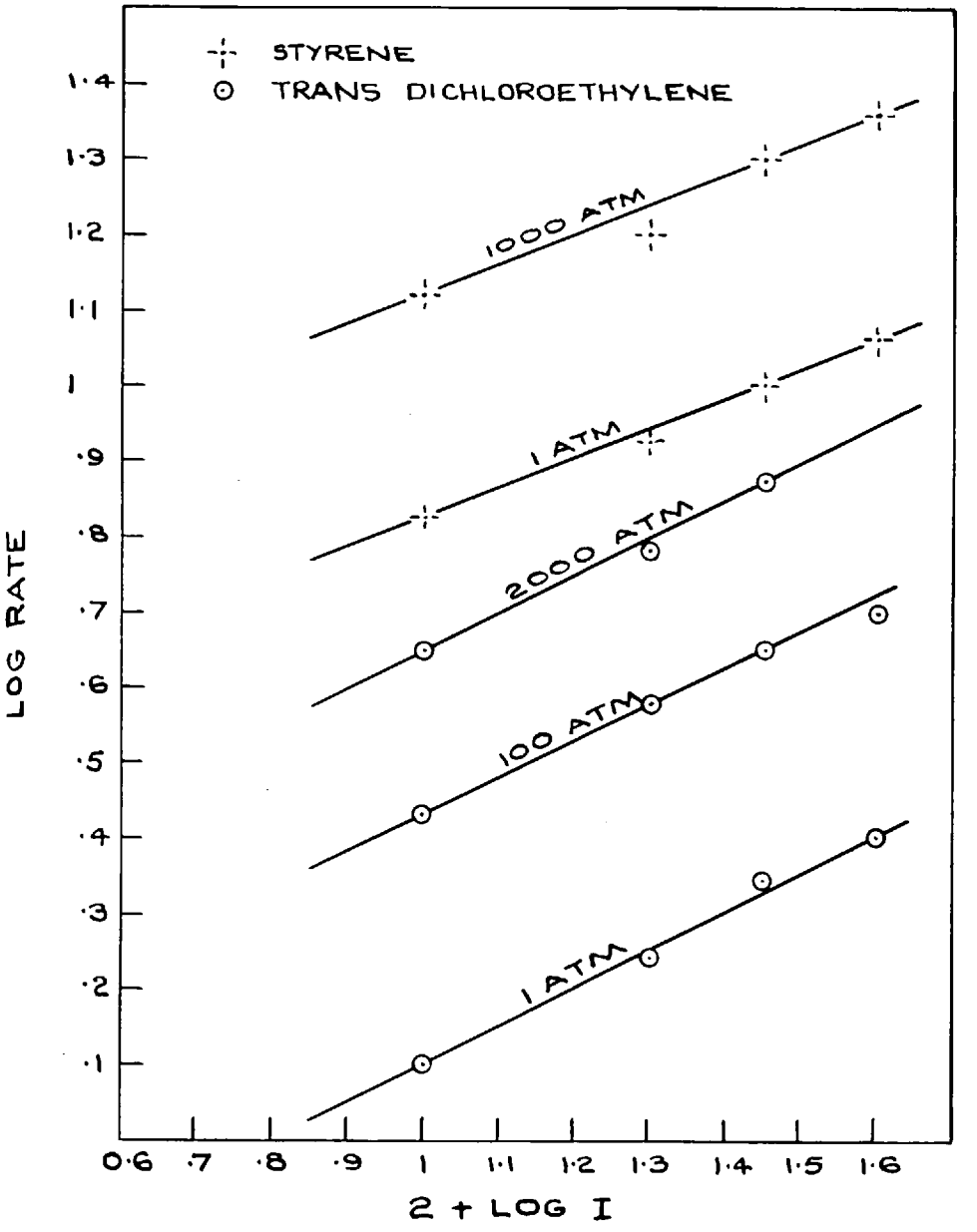


FIGURE 7 EFFECT OF INITIATOR CONCN. ON POLYMERISATION RATE. TABLE I AND III.

in initiator concentration at constant pressure and temperature. This decrease in the value of k at 1 atm. can be attributed to a decrease in 'f' with an increase in the initiator concentration. In calculatingthe value of k (page 88) the monomer and the initiator concentrations were expressed in mole/litres. Hence if pressure has any effect on them, it would increase at higher pressure. The ratio k_p^2/k_t for the polymerisation of styrene increases with pressure, hence the decrease in the value of k with increase in initiator concentration at 1000 atm., which is more pronounced than that at 1 atm. is due to a decrease in f and k_d.

A comparison of the absolute rates with previous results shows good agreement. Toohey [38] gives the rate at 60°C, 1 atm., and initiator concentration of $10^4[I]$ = 35.4 mole/litre as 0.97% hr. Table I gives the rate as 1.68% hr. for $10^4[I]$ = 87.2 mole/litre. If the result is corrected to the value of the initiator concentration [I], by the relation $[I]^{.5}$ then the rate calculated is = $1.68\ [35.4/87.2]^{.5}$ = 1.07% hr. The overall rate increased with initiator concentration, and the acceleration factor or the pressure coefficient of the overall rate, R_{1000}/R_1 was calculated for different initiator concentrations (Table III).

7.3. Composition of the Polymers from Styrene/Chloro-Olefine Mixtures.

Elemental analyses of the polymers formed in styrene/chloro-olefine mixtures (Table II) were done. The purpose was to investigate the amount of chlorine present in the polymer, and hence the analyses of samples with lowest value of M/S ratio (which was 1:1) prepared at constant initiator concentration of 0.05 mole % (on the reactants) under different pressures were carried out. Weight % compositions of the polymers formed in styrene-trans-dichloroethylene, styrene-technical dichloroethylene and styrene-trichloroethylene are shown in Table II.

It can be seen that the chlorine content is very low. Although the analyses for such small amounts of chlorine are not very accurate, it is clear that practically no copolymerisation occurs even at the highest pressure. Molecular weights of the polymers were determined, and from the weight % composition, average number of units of styrene monomer and the corresponding halo-olefines per molecule were calculated.

The infra-red spectra of polymers formed in 1:1 styrene/trichloroethylene at 3000 atm., and 1:1 styrene/trans-dichloroethylene at 2500 atm. were done with "Nujol" as solvent and using sodium chloride cell (Figures 8 and 9). The spectra were similar to that of pure styrene polymer.

Table II.

Composition of Polymers formed in Styrene/Chloro-olefine Mixtures.

	P (Atm)	M/S (Molar Ratio)	Wt% Compos^{n}. C	H	Cl	M.W.x10^{-3}	Average Number of units/molecule M	S
trans DCE	1500	1	> 90	7	1	33.6	320	3
	2500	1	> 90	7	1	37.8	360	4
tech. DCE	1000	1	> 90	7	1	48.7	464	5
	3000	1	> 90	7	1	113	1076	12
trichloro-ethylene	1	1	> 90	7	1	18.2	180	2
	3000	1	> 90	7	1	44.7	427	5

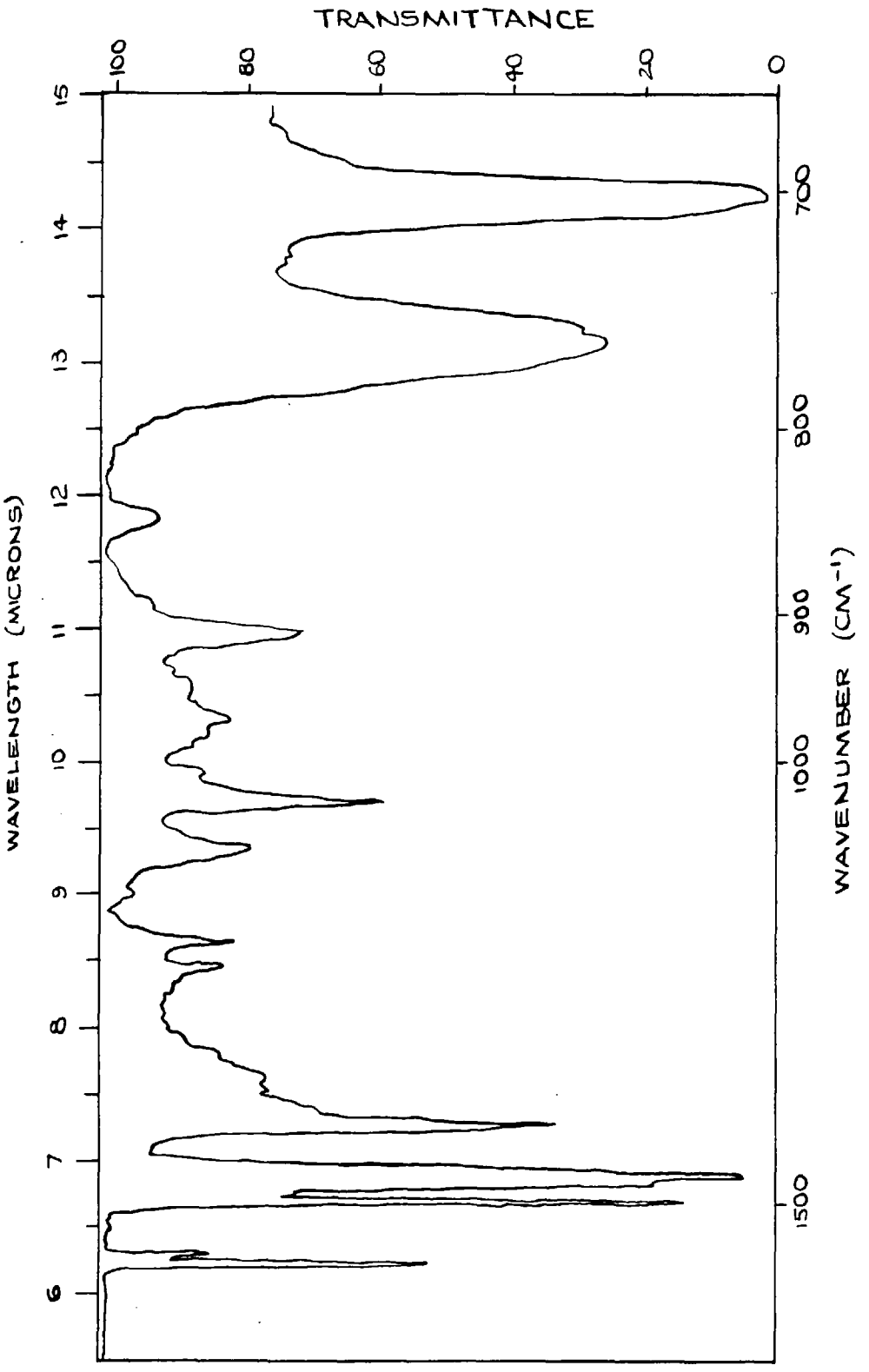


FIGURE 8 INFRA-RED SPECTRA OF STYRENE - TRICHLOROETHYLENE POLYMER PRESSURE - 3000 ATM.

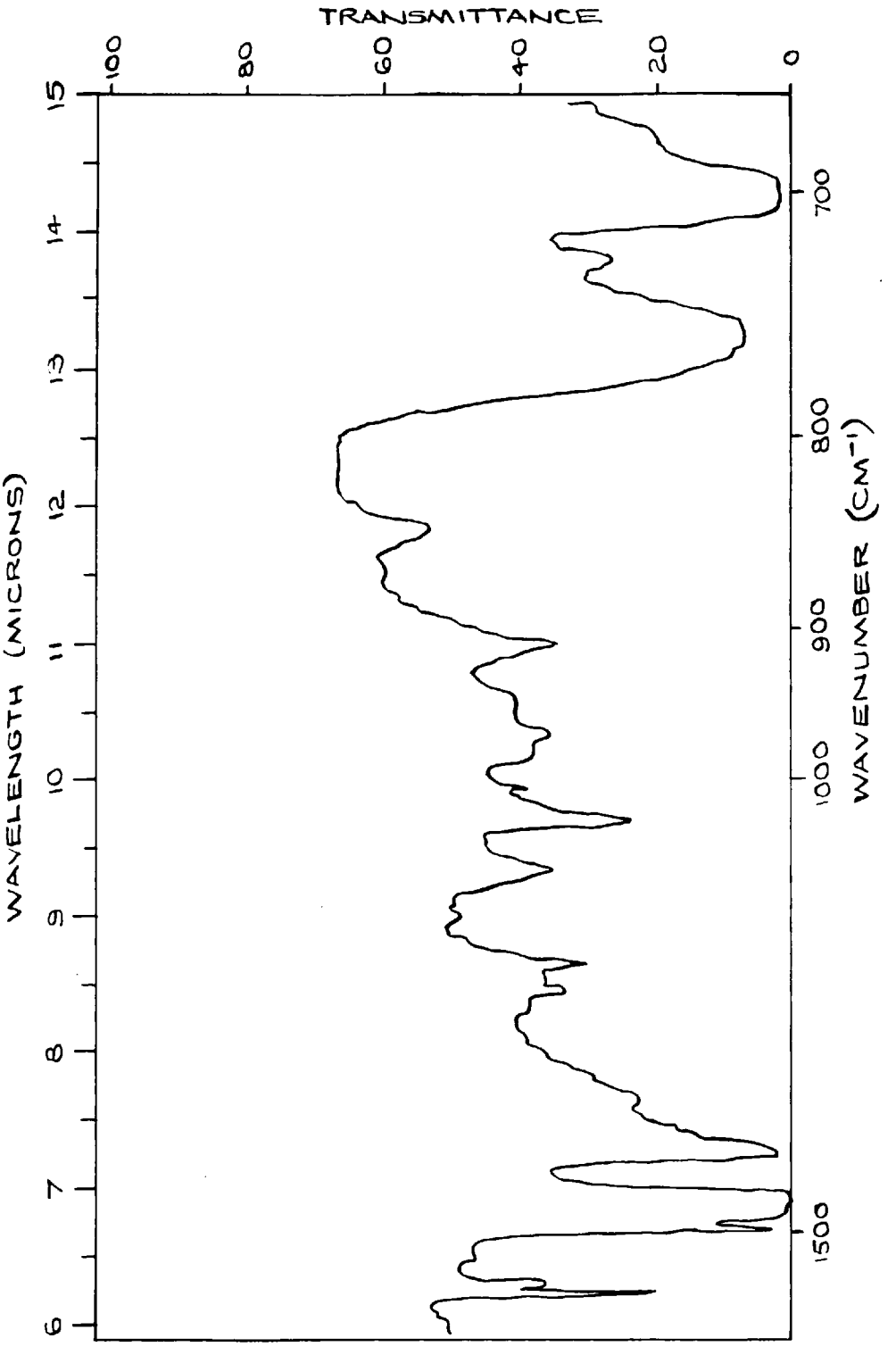


FIGURE 9 INFRA-RED SPECTRA OF STYRENE - TRANS DICHLOROETHYLENE POLYMER PRESSURE - 2500 ATM.

C-Cl absorption could not be identified because polystyrene itself has "bands" in the C-Cl absorption region (12-14 μ).

7.4. Kinetic Investigations on Polymerisation of Styrene with Trans Dichloroethylene.

Table III gives the rates of polymerisation of styrene with trans dichloroethylene at different initiator concentrations and pressures. At 1 atm., styrene/dichloroethylene is 0.972 molar ratio and at 1000 and 2000 atm. styrene/dichloroethylene is 0.675 molar ratio. By comparing the results in Table I with those of Table III and from Figure 7 it can be seen that trans dichloroethylene retards the polymerisation of styrene, although the pressure coefficient of the rate R_{1000}/R_1 is similar to those for styrene at different initiator concentrations. The exact pressure coefficient of the rate cannot be obtained as the M/S ratios for runs at 1000 atm. and 1 atm. are not the same, but the results show that the effects of pressure on the rate ratios are similar. Asai [138] observed a rate ratio of $R_{1000}/R_1 = 2.39$ with a 1:1 molar ratio and with an initiator concentration of 3.04×10^{-3} mole/litre of AIBN at $60^{\circ}C$. As the runs at 1000 and 2000 atm. are with a lower M/S ratio than that at 1 atm., the calculated rate ratios of 2.17, 2.16, 2.03 at 0.1, 0.2, 0.3 mole % catalyst concentration respectively seem to compare well with that of Asai.

The slowing down of the rate is mainly due to degradative chain transfer, though occasional incorporation of unreactive chloroethylene units in the polymer may occur. The order of reaction with respect to initiator [I] was found to be about 0.49 at 1 atm., and 0.48, 0.46 at 1000 and 2000 atm. respectively (Figure 7, Table III). Within the experimental accuracy it can be said that the order of reaction with respect to initiator is independent of pressure.

Table IV gives the rate of polymerisation at constant initiator concentration of 0.05 mole % at different M/S ratios for various pressures. The order of reaction with respect to monomer (styrene) concentration obtained by plotting log (rate) against log of monomer concentration has been investigated (Tables IV and VI, Figure 10). The order of reaction with respect to monomer is 1.8 at 1 atm., it decreases with increasing pressure and attains a value of about 1 at 2500 atm. (Figure 11). This indicates that inactive radicals formed by transfer become reactive at higher pressure. This conclusion can be supported (Figure 12) as it can be seen that for a fixed M/S ratio, there is a sharper increase in rate at higher pressure. This is attributed to either the CHCl = CH* or the $\overset{P}{\sim}$CH-CHCl-CHCl* radicals becoming more active at higher pressure and, as transfer is thought to be the main process of chlorine incorporation, the reason is probably that the reactivity of the CHCl=CH* radical increases at higher pressure.

Table III.

Order of Reaction (x) with respect to initiator in the system Styrene + Trans-dichloroethylene at 60°C. At 1 atm. Styrene/DCE = 0.972 molar ratio at 1000 and 2000 atm. Styrene/DCE = 0.675 molar ratio.

P (Atm.)	[I] (mole %)	2+log[I]	R (wt.% in 4 hr.)	log R	x
1	0.1	1.000	1.25	0.094	
1	0.2	1.301	1.75	0.242	0.49
1	0.3	1.477	2.22	0.346	
1	0.4	1.602	2.52	0.40	
1000	0.1	1.000	2.7	0.431	
1000	0.2	1.301	3.77	0.576	0.48
1000	0.3	1.477	4.5	0.653	
1000	0.4	1.602	4.87	0.688	
2000	0.1	1.000	4.43	0.646	
2000	0.2	1.301	6.05	0.781	0.46
2000	0.3	1.477	7.35	0.86	

The pressure-acceleration factor R_{1000}/R_1 was found to be similar in magnitude to that for pure Styrene.

Styrene + trans DCE	R_{1000}/R_1	2.17	2.16	2.03	1.94
	[I]	0.1	0.2	0.3	0.4
Styrene	R_{1000}/R_1	1.96	1.64	1.75	1.79
	[I]	0.1	0.2	0.3	0.4

Table IV.

The rates of polymerisation in the system Styrene + Trans dichloroethylene at 60°C and at various pressures and [M]/[S] ratios. Catalyst concentrations = 0.05 mole %.

P (Atm)	M/S Molar ratio	[M] mole%	(log M)-1	R (wt.% in 4 hr.)	log R
1	1:1	50	0.699	1.9	0.28
1	1.5:1	60	0.778	2.73	0.433
1	2.0:1	66.7	0.824	3.25	0.51
1	4:1	80	0.903	4.13	0.62
875	1:1	50	0.699	3.21	0.507
875	1.5:1	60	0.778	4.4	0.644
875	2:1	66.7	0.824	5.38	0.731
875	2.5:1	71.4	0.854	6.0	0.778
1500	1:1	50	0.699	4.29	0.633
1500	1.5:1	60	0.778	5.33	0.727
1500	2:1	66.7	0.824	6.34	0.802
2000	1:1	50	0.699	6.36	0.804
2000	1.5:1	60	0.778	7.63	0.883
2000	2:1	66.7	0.824	8.8	0.945
2500	1:1	50	0.699	7.50	0.875
2500	1.5:1	60	0.778	9.5	0.978
2500	2:1	66.7	0.824	10.04	1.002

Table V.

The effect of pressure and of the [M]/[S] ratio on the molecular weight and intrinsic viscosity of polymers from Styrene + Trans-dichloroethylene at 60°C, and with 0.05 mole% catalyst concentration, on monomer.

P (Atm.)	M/S Molar ratio	$[\eta]$ at 25°C.	M.W. at 10^{-3} A	B
1	1	0.304	23.0	20.0
1	1.5	0.357	30.1	26.0
1	2	0.415	37.8	31.6
1500	1	0.380	33.6	28.4
1500	1.5	0.500	50.2	43.05
1500	2	0.571	61.6	52.7
2000	1	0.405	35.0	31.7
2000	1.5	0.575	55.4	53.2
2000	2	0.606	67.5	57.6
2500	1	0.416	37.8	32.6
2500	1.5	0.583	63.6	54.3
2500	2	0.653	75.7	64.5

A calculated for $K = 4.4 \times 10^{-4}$

$\alpha = 0.65$

B calculated for $K = 4.37 \times 10^{-4}$

$\alpha = 0.66$

Table VI.

The effect of pressure on the order of reaction with respect to monomer concentration [M], initiator concentration [I], and on the chain transfer constant, Cs, in the polymerisation of Styrene + Trans-dichloroethylene at 60°C.

$$R = k[M]^y [I]^x \qquad Cs = k_{tr}/k_p$$

P (Atm.)	y	x	Cs x 10^4
1	1.8	0.49	33
875	1.85	0.48 (at 1000)	-
1500	1.3	-	29
2000	1.0	0.46	28.5
2500	1.0	-	26

Table VII (a)

The effect of the pressure on the volume of activation $\Delta V_o^{\neq}$, for polymerisation, and the volume of activation $\Delta V_{tr}^{\neq}$ for chain transfer in the polymerisation of Styrene + Trans-dichloroethylene at 60°C, with 0.05 mole % catalyst concentration, at various [M]/[S] ratios.

P (Atm.)	M/S Molar ratio	$-\Delta V_o^{\neq}$ cc/mole	$-\Delta V_{tr}^{\neq}$ cc/mole
1-500	1:1	16.1	
500-1500		16	11.3
1500-2000		16	
1-500	1.5:1	14.1	
500-1500		14	11.3
1500-2000		14	
1-500	2:1	12	
500-1500		12	11.3
1500-2000		12	

Table VII (b)

Polymerisation of Styrene + Tech-dichloroethylene at 60°C with 0.05 mole % catalyst concentration.

P (Atm.)	M/S Molar ratio	$-\Delta V_o^{\neq}$ cc/mole	Cs x 10^4
1-500	1:1	10.4	
500-1500		10.7	1.6
1500-3000		10.7	

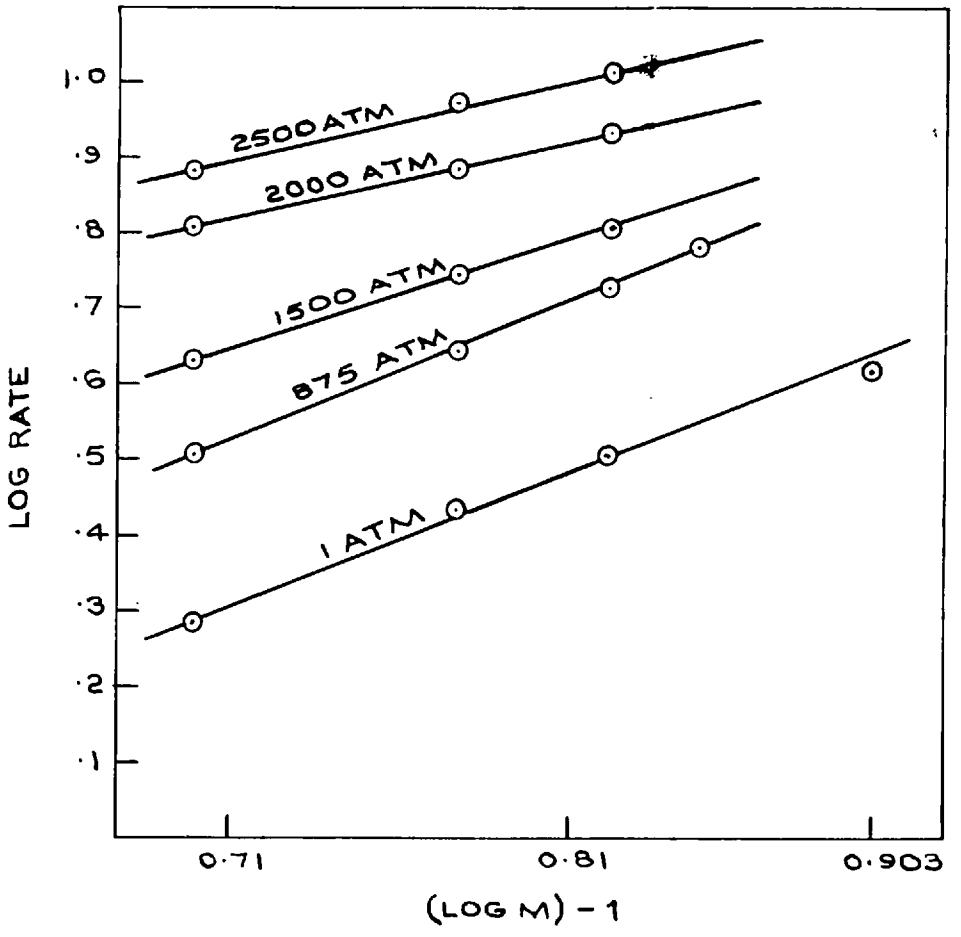


FIGURE 10 EFFECT OF MONOMER CONC.N ON POLYMERISATION RATE OF STYRENE AND TRANS DYCHLOROETHYLENE. TABLE IV

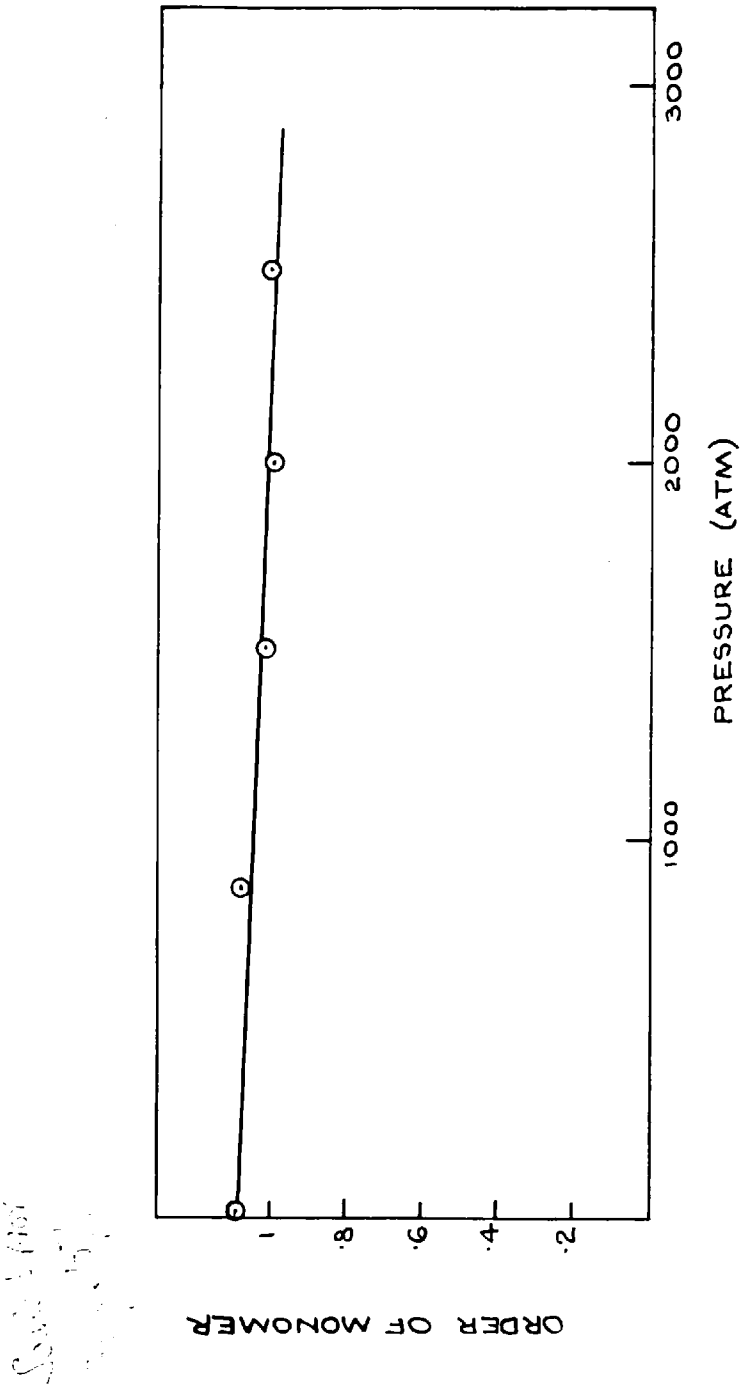


FIGURE 11 EFFECT OF PRESSURE ON ORDER OF REACTION WITH RESPECT TO MONOMER IN POLYMS.N OF STYRENE AND TRANS DICHLOROETHYLENE.

TABLE VI

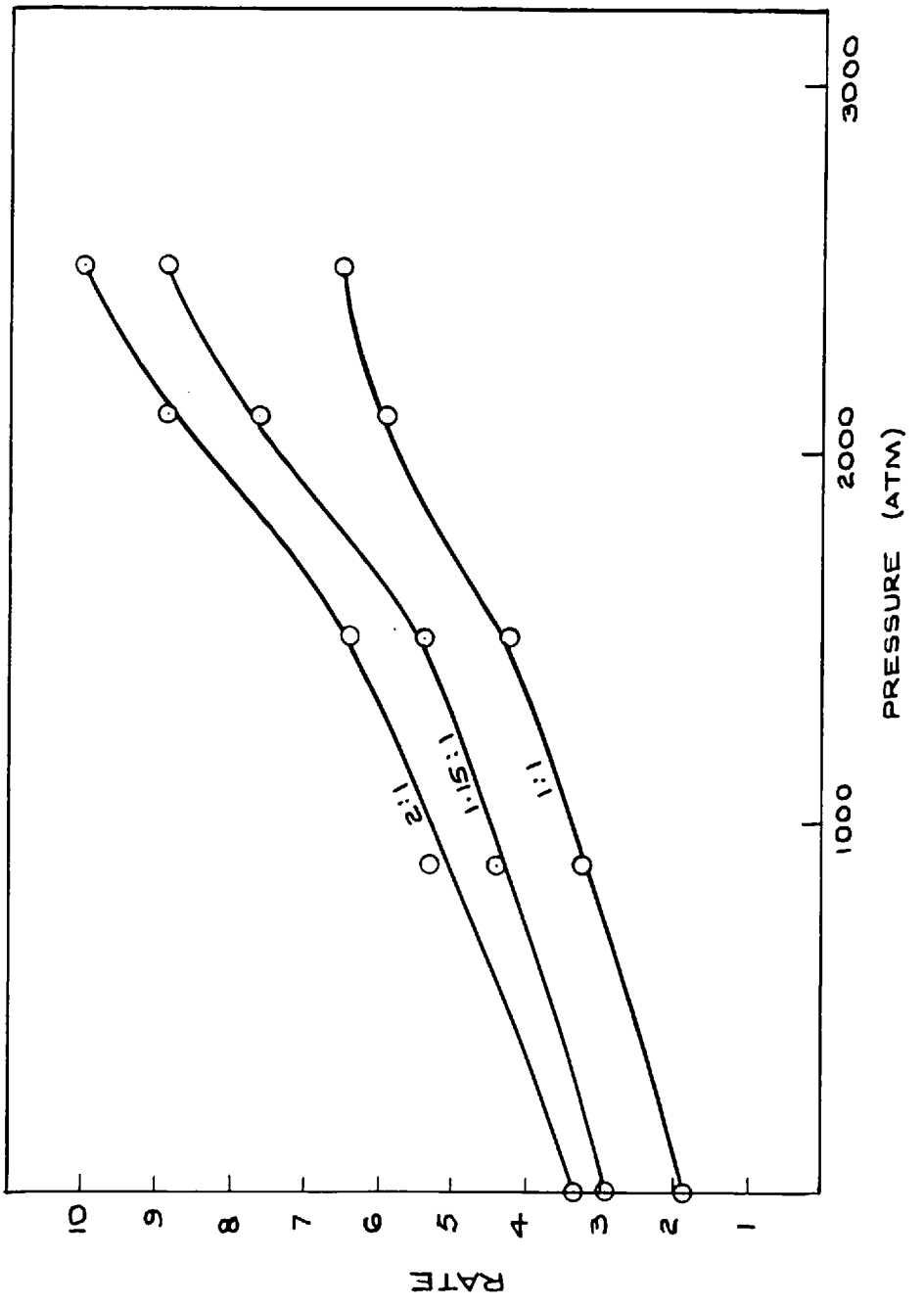


FIGURE 12 EFFECT OF RATE ON PRESSURE IN POLYMERISATION OF STYRENE AND TRANS DICHLOROETHYLENE AT DIFFERENT [M]/[S] RATIOS. TABLE IV.

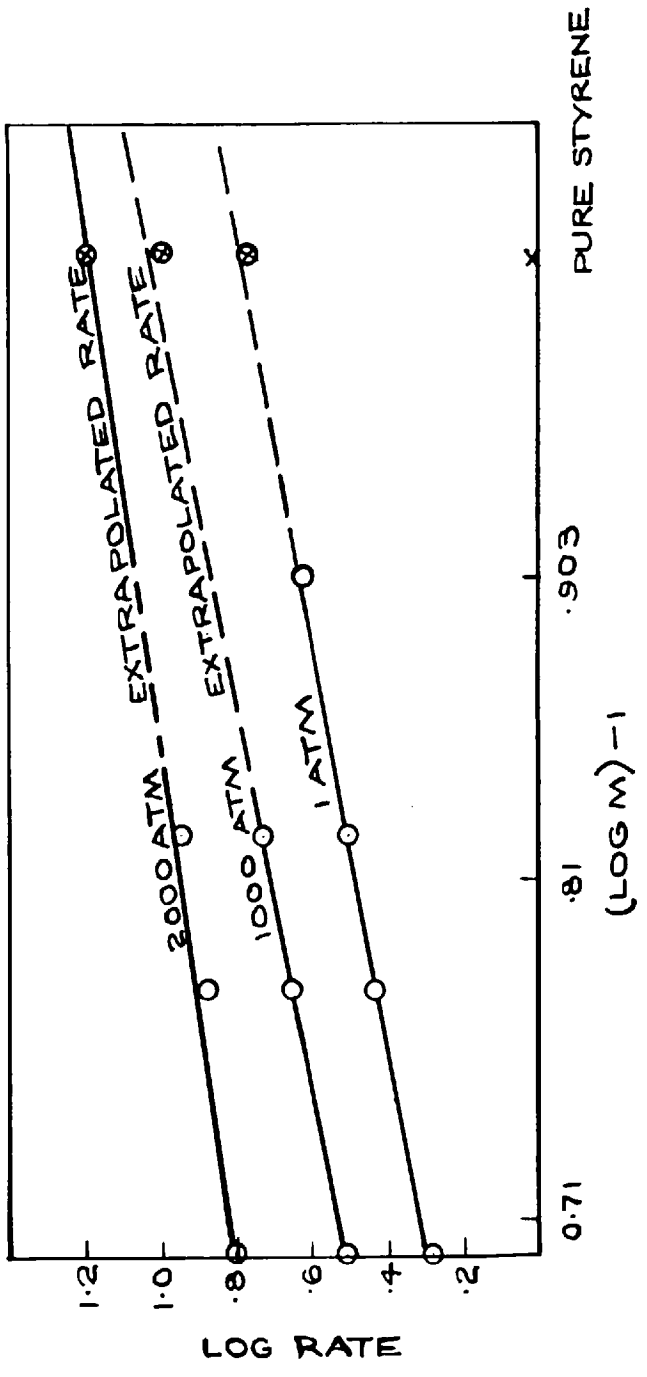


FIGURE 13 EFFECT OF CONC^{N} OF STYRENE ON RATE OF POLYMERISATION IN TRANS DICHLOROETHYLENE AT 1,000 AND 2000 ATM. RATES CORRECTED FOR USING THE FACTOR I^{x}, $x = 0.5$.

⊗ CALCULATED RATE FOR PURE STYRENE.

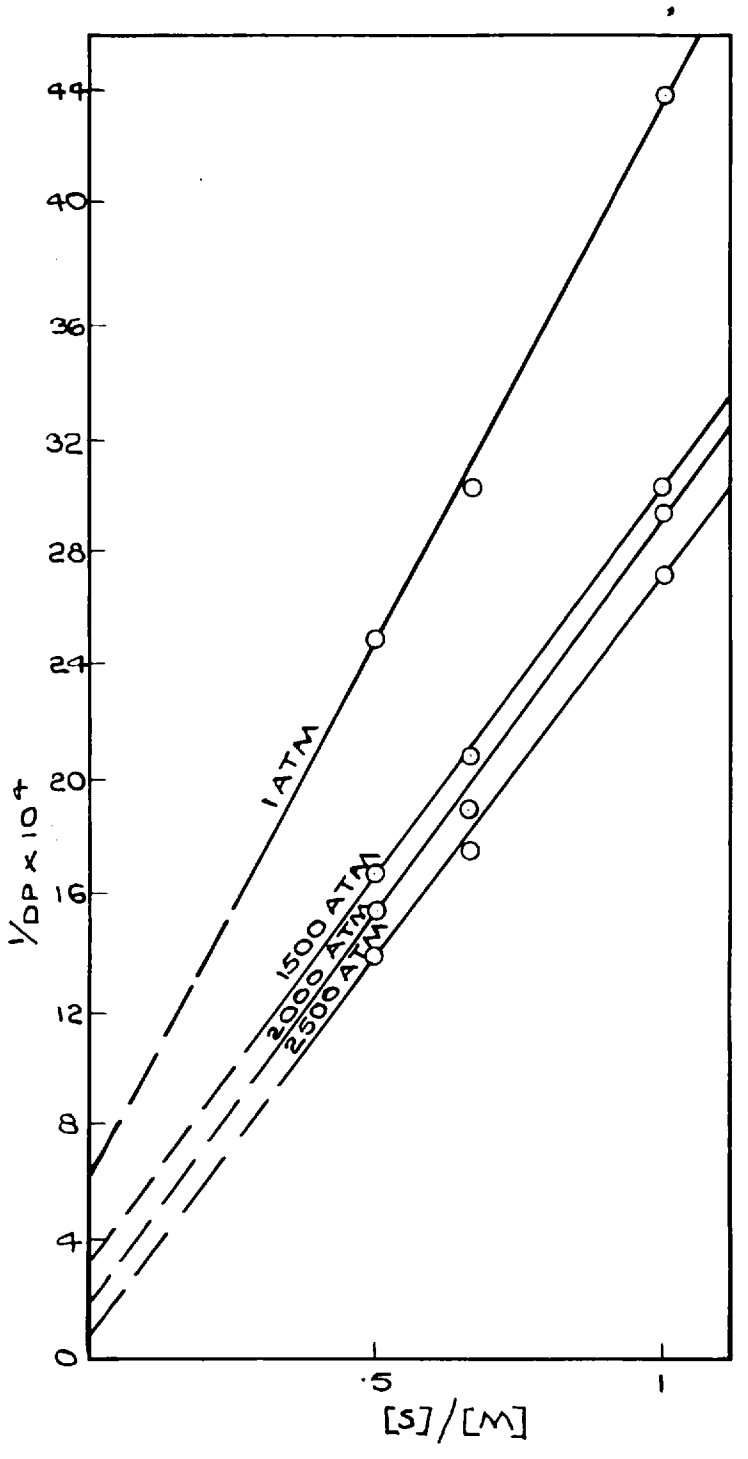


FIGURE 14 EFFECT OF PRESSURE AND MONOMER CONCⁿ ON 1/DP IN POLYMERISATION OF STYRENE [M] AND TRANS DICHLORO-ETHYLENE [S].

TABLE V.

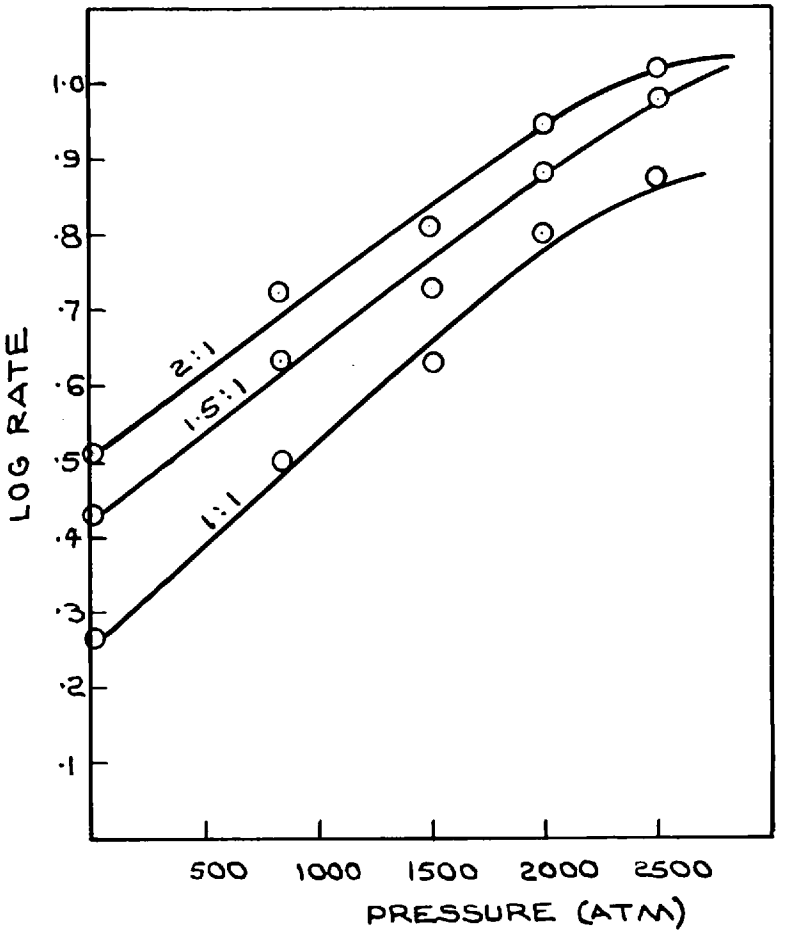


FIGURE 15 PLOT OF LOG RATE AGAINST PRESSURE IN THE POLYMERISATION OF STYRENE AND TRANS DICHLORO-ETHYLENE AT DIFFERENT [M]/[S] RATIOS.

TABLE IV.

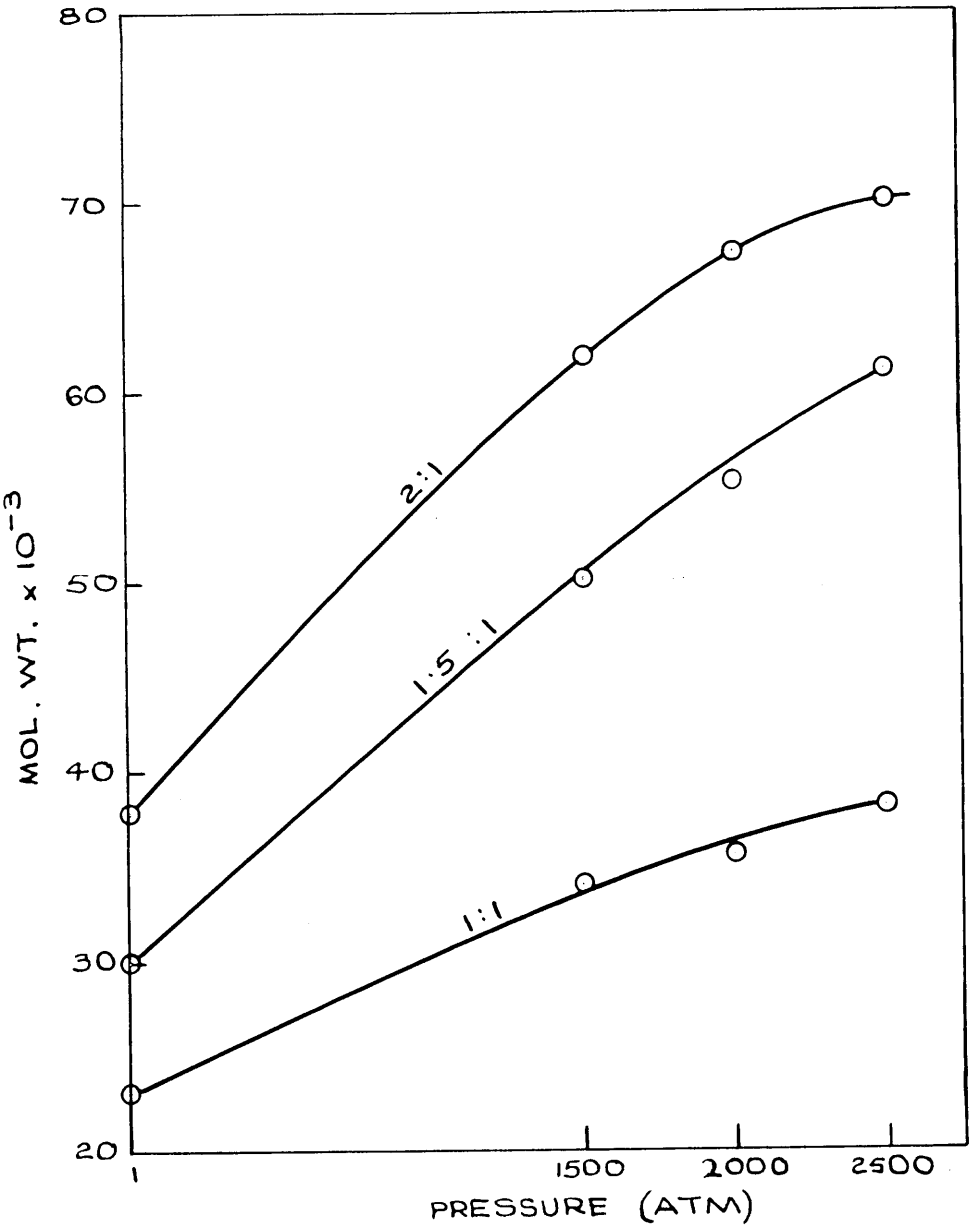


FIGURE 16 EFFECT OF PRESSURE ON MOL. WT. OF POLYMERS AT DIFFERENT [M]/[S] RATIOS, IN POLYMERISATION OF STYRENE [M] AND TRANS DICHLOROETHYLENE [S].

TABLE V

By plotting log (rate) against log (styrene concentration), at 1, 1000 and 2000 atm. (Figure 13), and extrapolating the curves to values for pure styrene, the extrapolated rates are in good agreement with calculated rates for pure styrene, the agreement being best at 2000 atm. This accords with the observation that the order of reaction with respect to monomer concentration attains a value of about 1 at higher pressure. The overall rate of polymerisation at a given initiator concentration increased with increasing M/S ratio at a given pressure (Table IV, Figure 10) and also with increasing pressure at a given initiator concentration and M/S ratio (Table IV, Figure 12). The rates for pure styrene at 1 and 1000 atm. were obtained from Table I, that for 2000 from Toohey's thesis [38].

From the composition of the polymers, the incorporation of the small quantity of chlorine atoms in the polymer molecules formed in the styrene-trans dichloroethylene system is considered due to chain-transfer, and the effect of pressure on this kinetic parameter has been studied. The transfer constant is obtained by plotting 1/DP against S/M (Figure 14). The molecular weights were determined from measurements of viscosities in benzene solution at 25°C (Table V), and DP was calculated using the set of constants A. Polymers were prepared with a constant I/M ratio. The chain transfer constant Cs x 10^4 changed from 33 at 1 atm.

to 26 at 2500 atm. (Table VI). It can be concluded that the chain transfer constant is practically independent of pressure - the value slightly decreasing at higher pressure. This means that the effect of pressure on k_{tr} and k_p are similar in magnitude and they both increase with pressure, and also that $\Delta V^{\neq}_{tr} \simeq \Delta V^{\neq}_{p}$. The volume of activation for chain transfer was calculated (equation 80, page 56) at a given M/S ratio for pressure ranges between 1-500 atm., 500-1500, and 1500-2000 atm. (Table VIIa). The pressure is divided in the three ranges so as to divide the graph of log Cs against pressure in best possible straight lines or to get the tangent. Taking $\Delta V^{\neq}_{p}$ for styrene as -13 cc./mole, $\Delta V^{\neq}_{tr}$ was found to be about -11.3 cc./mole for different M/S ratios in the pressure ranges mentioned above. $\Delta V^{\neq}_{tr}$ is similar in magnitude to $\Delta V^{\neq}_{p}$, but slightly less negative as both bond formation and bond-breaking takes place; and the value is close to the value for the active transfer agent CCl_4.

Asai [139] has carried out polymerisation of the chloro-olefines with styrene and has calculated their monomer reactivity ratios. The reactivity of the halo-olefines have been found to be $\simeq 0$. The table of his relative reactivity is given below.

Relative reactivity of chloroethylenes (60°C.)

Monomer	Pressure (Kg./cm²)	Relative Reactivity
Tetrachloroethylene	1	0.005
	100	0.005
	1000	0.004
Trichloroethylene	1	0.07
	100	0.06
	1000	0.06
Cis-dichloroethylene	1	0.005
	100	0.005
	1000	0.005
Trans-dichloroethylene	1	0.03
	100	0.03
	1000	0.03

If $r_1 = \frac{k_{S*S}}{k_{S*TCE}}$, then the relative reactivity $\frac{1}{r_1} = \frac{k_{S*TCE}}{k_{S*S}}$

If chain transfer is the main process by which chlorine atoms are incorporated in the molecule, then $\frac{1}{r_1}$ or the relative reactivity of the trichloroethylene monomer can approximately be taken to be equal to the chain-transfer constant. Hence

$$\frac{1}{r_1} = \frac{k_{S*TCE}}{k_{S*S}} \simeq Cs .$$

From the values of Asai, Cs $\times 10^4$ at 1, 100 and 1000 will be 700, 600, 600 respectively. In chain transfer both bond formation and bond-cleavage takes place, hence the value of k_{S*TCE} (transfer) will be less than k_{S*TCE}. Even if the

value of k_{S*TCE} (transfer) is taken as half of k_{S*TCE}, Cs $x10^4$ at 1, 100 and 1000 will be 350, 300, 300 respectively. The values seem rather high for the system - monomer reactivity ratios calculated in such cases are likely to be of very uncertain accuracy. The 'monomer reactivity ratios' are almost independent of pressure, slightly decreasing at higher pressure, in a way similar to that found with the chain transfer constants.

The overall volume of activation for polymerisation $\triangle V_o^{\neq}$ was calculated by plotting log (rate) against pressure (equation 75, page 52). Volumes of activation at a given M/S ratio for the experimental pressure ranges were calculated (Table VIIa, Figure 15). $-\triangle V_o^{\neq}$ is between 12 and 16 cc./mole, and it decreases with increasing M/S ratio. The decrease in $\triangle V_o^{\neq}$ with increasing M/S ratio may be due to lesser "steric effect" of chain transfer on the system or to the formation of the inactive P-$\dot{C}$H-CHCl-CHCl* radical becoming more probable with increasing M/S ratio, so bringing degradative chain transfer on to the kinetic pattern. The contribution of the latter case, in accordance with the previous idea should be very small, and hence it is thought to be due to lesser "steric effect" of transfer on thesystem. With decrease in M/S ratio the system is

more sterically hindered in the sense that the rate is more retarded at 1 atm. due to increasing chain transfer with the formation of inactive CHCl=CH* radicals, andthe effect of pressure on rate ratio is pronounced, giving a higher value of $\Delta V_o^{\neq}$.

The molecular weights of the polymers (Table V, Figure 16) at different pressures and constant M/S ratio, increase with pressure, the rate of increase being less at higher pressure. This is due to an increased amount of transfer with monomer at higher pressure. At constant pressure, the molecular weight increases as the M/S ratio increases. Asai [139] has reported for styrene-trans-dichloroethylene polymers prepared at 1,1000 Kg./cm^2 with 3.04 x10^{-3} mole/litre of AIBN at 60^{o}C the values of intrinsic viscosity determined in toluene at 30^{o}C as 0.225 and 0.387 respectively, the polymers are said to have a styrene content of 99.3 mole %. Viscosities of polymers prepared from 1:1 molar styrene-trans dichloroethylene with 0.05 mole % benzoyl peroxide at 60^{o}C were determined in benzene (Table V) at 25^{o}C, and the values at 1 and 1500 atm. are 0.304 and 0.380 respectively. The values of the intrinsic viscosities are comparable.

7.5. Kinetic Investigations on Polymerisation of Styrene with Trichloroethylene.

Table VIII gives the rate of polymerisation of styrene with trichloroethylene at different initiator concentrations and pressure, the M/S ratio being 1.17 molar. A comparison of the results with those for styrene and styrene-trans dichloroethylene, shows that the pressure-coefficient of the rate is of similar magnitude, but is less dependent on the initiator concentration.

A table of the rate ratios, for various compositions at a catalyst concentration of 0.05 mole% for the two systems styrene-trans DCE and styrene-TCE (Tables IV and IX) is given below :

	M/S	Rate Ratios R_p/R_1				
	(Molar)	875	1500	2000	2500	
Styrene	1:1	1.69	2.26	3.35	3.94	
+	1.5:1	1.65	1.95	2.79	3.48	
trans DCE	2:1	1.61	1.95	2.70	3.08	
		1000	1500	2000	2500	3000
Styrene	1:1	2.23	2.87	4.4	5.64	6.46
+	1.5:1	2.04	2.43	3.55	4.79	5.45
TCE	2:1	2.00	2.38	3.49	4.61	5.43

The pressure coefficient of the rate at a particular value of R_p/R_1 increases as M/S ratio decreases, and it is more pronounced at higher values of R_p/R_1. This can be due to

Table VIII.

Order of reaction (x) with respect to initiator concentration in the system Styrene + Trichloroethylene at 60°C. Styrene/TCE = 1.17 (molar ratio).

P (Atm.)	[I] (mole%)	2+log[I]	R (wt% in 4 hr)	log R	x
1	0.1	1.000	2.19	0.3404	
1	0.2	1.301	3.02	0.4800	
1	0.3	1.477	3.81	0.5809	0.52
1	0.4	1.602	4.50	0.6532	
1000	0.1	1.000	4.08	0.6106	
1000	0.2	1.301	5.64	0.7512	0.50
1000	0.3	1.477	6.92	0.8401	
1000	0.4	1.602	8.10	0.9084	

The pressure-acceleration factor R_{1000}/R_1 was found to be similar in magnitude to that of Styrene and Styrene + Trans-dichloroethylene system, but to be less dependent on [I].

Styrene + TCE	R_{1000}/R_1	1.85	1.86	1.82	1.84
	[I]	0.1	0.2	0.3	0.4
Styrene	R_{1000}/R_1	1.96	1.64	1.75	1.79
	[I]	0.1	0.2	0.3	0.4

Table IX.

The rates of polymerisation in the system Styrene + Trichloroethylene at 60°C and at various pressures and [M]/[S] ratios. Catalyst concentration = 0.05 mole%.

P (Atm.)	M/S Molar Ratio	[M] mole%	(log M)-1	R (wt.%4 hr.)	log R
1	1:1	50	0.699	1.38	0.1398
1	1.5:1	60	0.778	2.09	0.3201
1	2:1	66.7	0.824	2.56	0.408
1	4:1	80	0.903	3.47	0.5452
1000	1:1	50	0.699	3.08	0.4885
1000	1.5:1	60	0.778	4.27	0.6304
1000	2:1	66.7	0.824	5.13	0.7102
1500	1:1	50	0.699	3.97	0.5987
1500	1.5:1	60	0.778	5.09	0.7062
1500	2:1	66.7	0.824	6.10	0.7850
2000	1:1	50	0.699	6.09	0.7840
2000	1.5:1	60	0.778	7.43	0.8709
2000	2:1	66.7	0.824	8.93	0.9503
2500	1:1	50	0.699	7.79	0.8915
2500	1.5:1	60	0.778	10.01	1.004
2500	2:1	66.7	0.824	11.81	1.072
3000	1:1	50	0.699	8.92	0.950
3000	1.5:1	60	0.778	11.40	1.057
3000	2:1	66.7	0.824	13.91	1.143

Table X.

The effect of pressure and of the [M]/[S] ratio on the molecular weight and intrinsic viscosity of polymers from Styrene + Trichloroethylene at 60°C, with 0.05 mole % catalyst concentration on monomer.

P (Atm.)	M/S Molar ratio	$[\eta]$ at 25°C.	M.W. x 10^{-3} A	B
1	1	0.262	18.2	16
1	1.5	0.318	23.9	21.2
1	2	0.352	29.2	26.5
1000	1	0.311	23.9	19.4
1000	1.5	0.372	34.4	31.5
1000	2	0.482	47.5	43.0
1500	1	0.357	30.5	36.2
1500	1.5	0.482	47.5	42.0
1500	2	0.564	61.0	52.0
2000	1	0.407	36.3	31.6
2000	1.5	0.529	55.2	45.0
2000	2	0.664	75.0	64.2
2500	1	0.450	41.7	35.5
2500	1.5	0.607	65.5	53.0
2500	2	0.706	87.5	76.0
3000	1	0.466	44.7	39.8
3000	1.5	0.664	75.0	64.2
3000	2	0.782	104.0	82.1

A calculated for: $K = 4.4 \times 10^{-4}$ B calculated for $K = 4.37 \times 10^{-4}$

$\alpha = 0.65$ $\alpha = 0.66$

Table XI

Effect of pressure on the order of reactions with respect to monomer [M], initiator [I], and on the chain transfer constant Cs, in the polymerisation of Styrene + Trichloroethylene at 60°C.

$R = k[M]^y [I]^x$ $\quad\quad$ $Cs = k_{tr}/k_p$

P (Atm)	y	x	Cs x 10^4
1	2.4	0.52	42
1000	1.7	0.50	38
1500	1.4		30
2000	1.2		26
2500	1.3		26
3000	1.25		25

Table XII.

The effect of pressure on the volume of activation, $\Delta V_o^{\neq}$, for polymerisation and the volume of activation for chain transfer, $\Delta V_{tr}^{\neq}$, in the polymerisation of Styrene + Trichloroethylene at 60°C, with 0.05 mole % catalyst concentration, at various [M]/[S] ratios.

P (Atm.)	M/S (Molar ratio)	$-\Delta V_o^{\neq}$ cc./mole	$-\Delta V_{tr}^{\neq}$ cc./mole
1-1500	1:1	18.8	10
1500-3000		16.6	
1-1500	1.5:1	16.6	10
1500-3000		16.1	
1-1500	2:1	16.5	10
1500-3000		14	

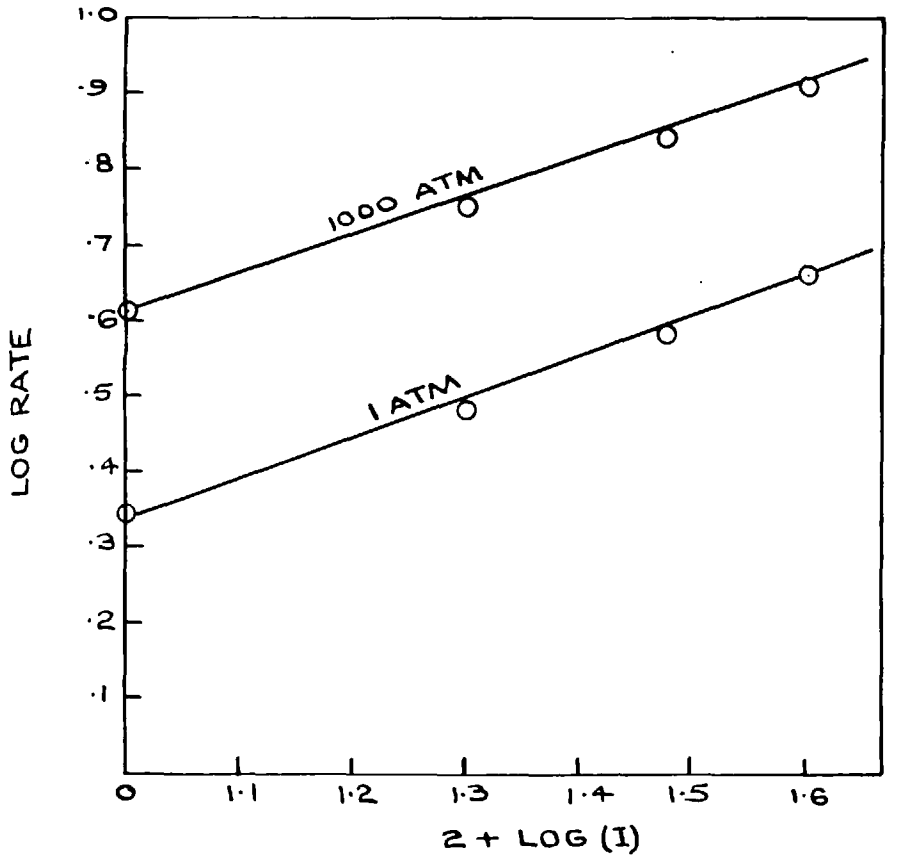


FIGURE 17 ORDER OF REACTION WITH RESPECT TO INITIATOR IN THE POLYMERISATION OF STYRENE AND TRICHLOROETHYLENE.

TABLE VIII

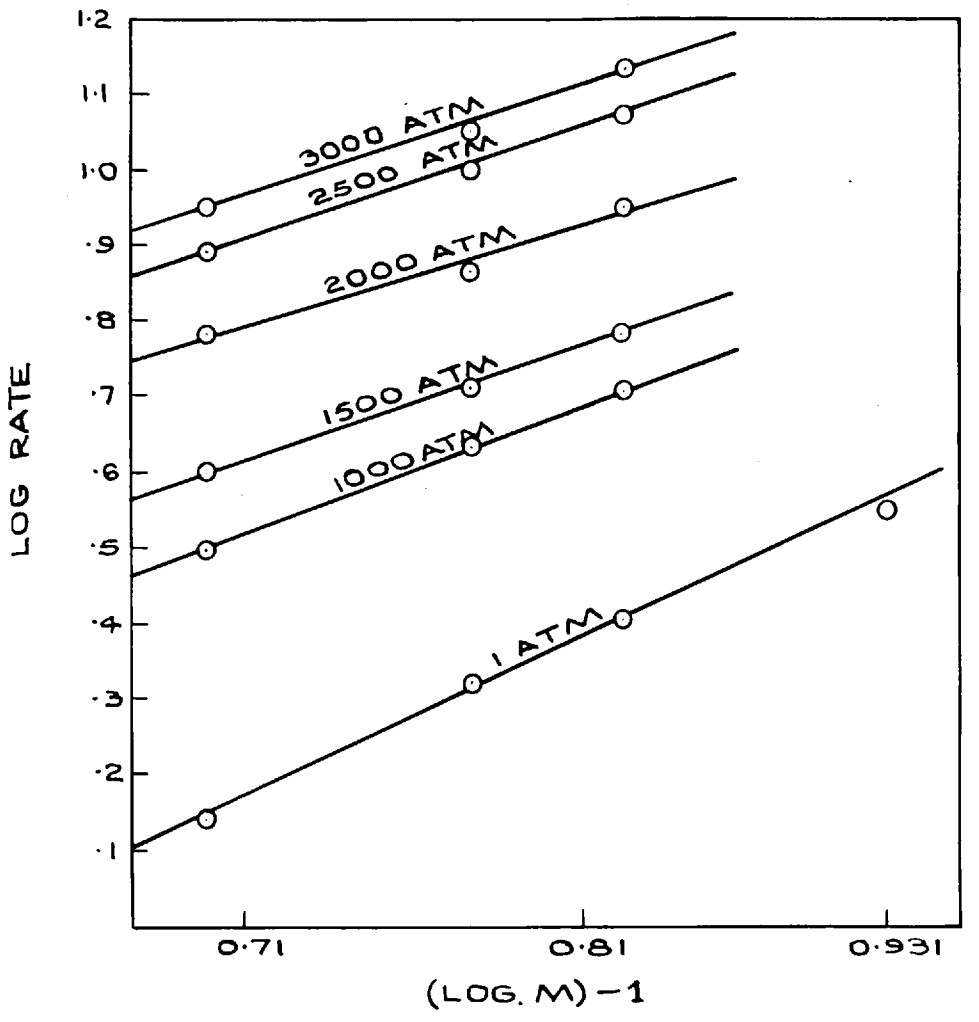


FIGURE 18 EFFECT OF MONOMER CONC.N ON POLYMERISATION RATE OF STYRENE AND TRICHLOROETHYLENE. TABLE IX.

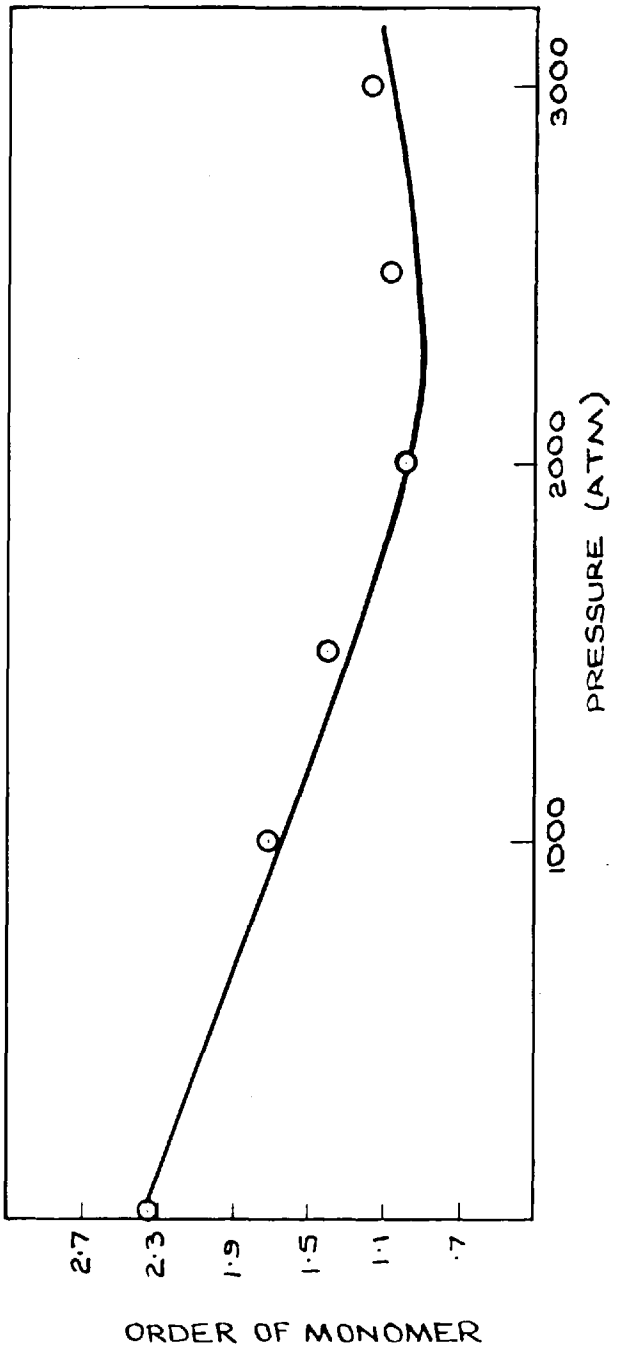


FIGURE 19 EFFECT OF PRESSURE ON ORDER OF REACTION WITH RESPECT TO MONOMER IN POLYMERISATION OF STYRENE AND TRICHLOROETHYLENE.
TABLE XI.

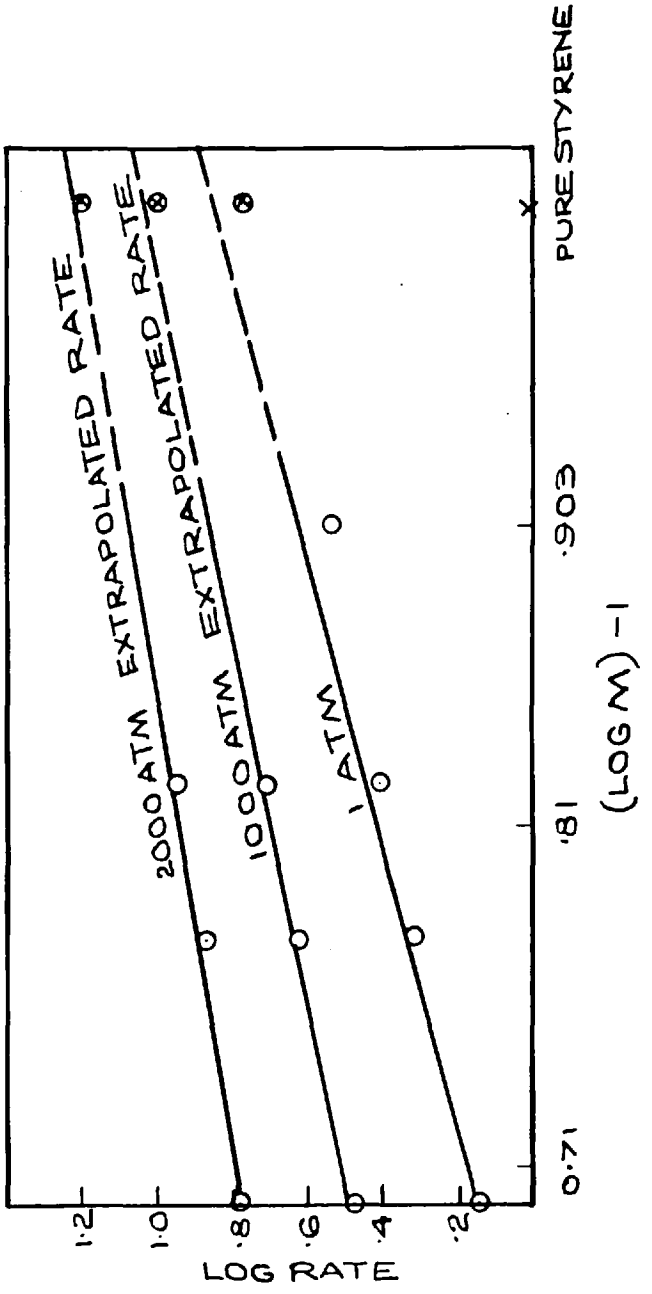


FIGURE 20 EFFECT OF CONC^{N} OF STYRENE ON RATE OF POLYMERISATION IN TRICHLOROETHYLENE AT 1,1000 AND 2,000 ATM. RATES CORRECTED FOR USING FACTOR 1^{x}, $x = 0{\cdot}5$.

⊗ CALCULATED RATE FOR PURE STYRENE.

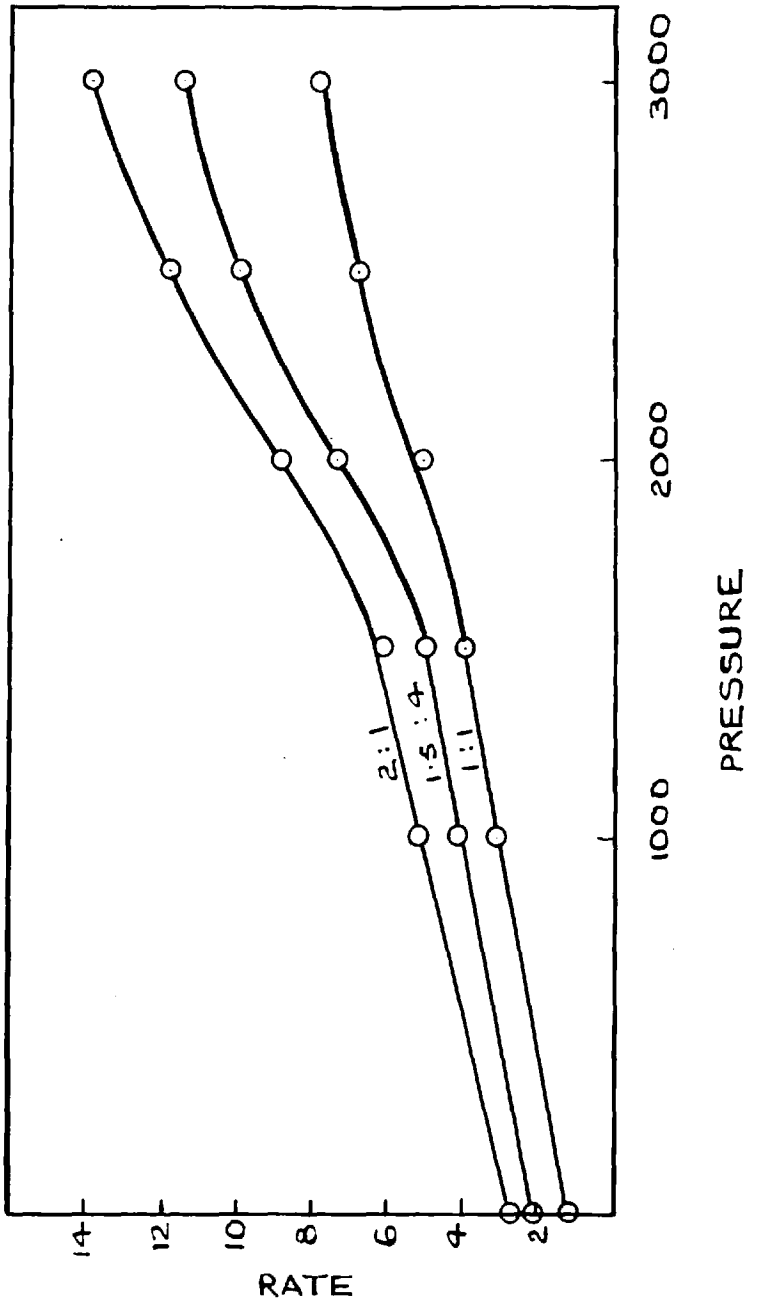


FIGURE 21 EFFECT OF PRESSURE ON RATE IN POLYMERISATION OF STYRENE AND TRICHLOROETHYLENE AT DIFFERENT [M]/[S] RATIOS.

TABLE IX.

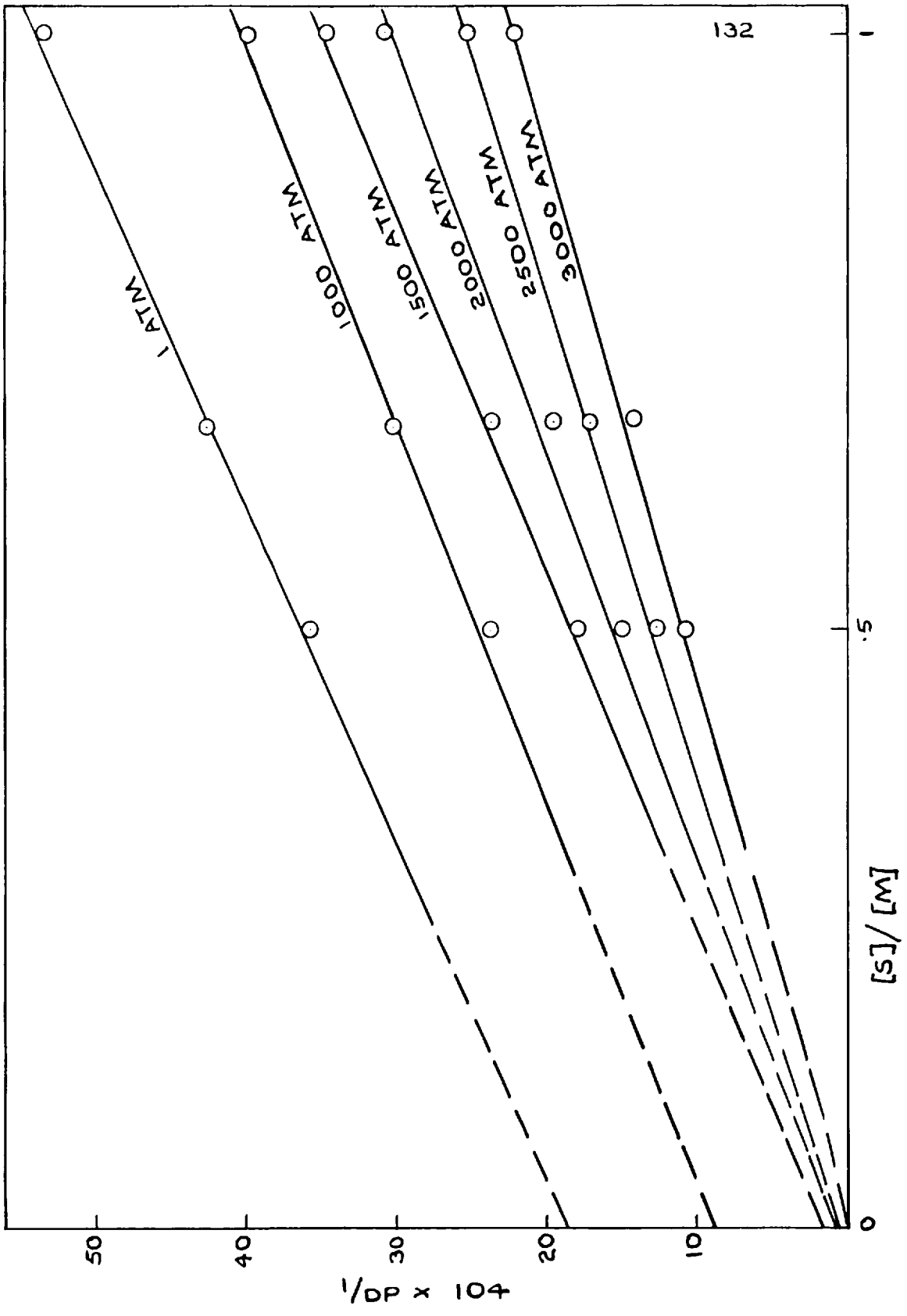


FIGURE 22 EFFECT OF PRESSURE AND MONOMER CONCS ON 1/DP IN POLYMERISATION OF STYRENE [M] AND TRICHLOROETHYLENE [S].
TABLE X

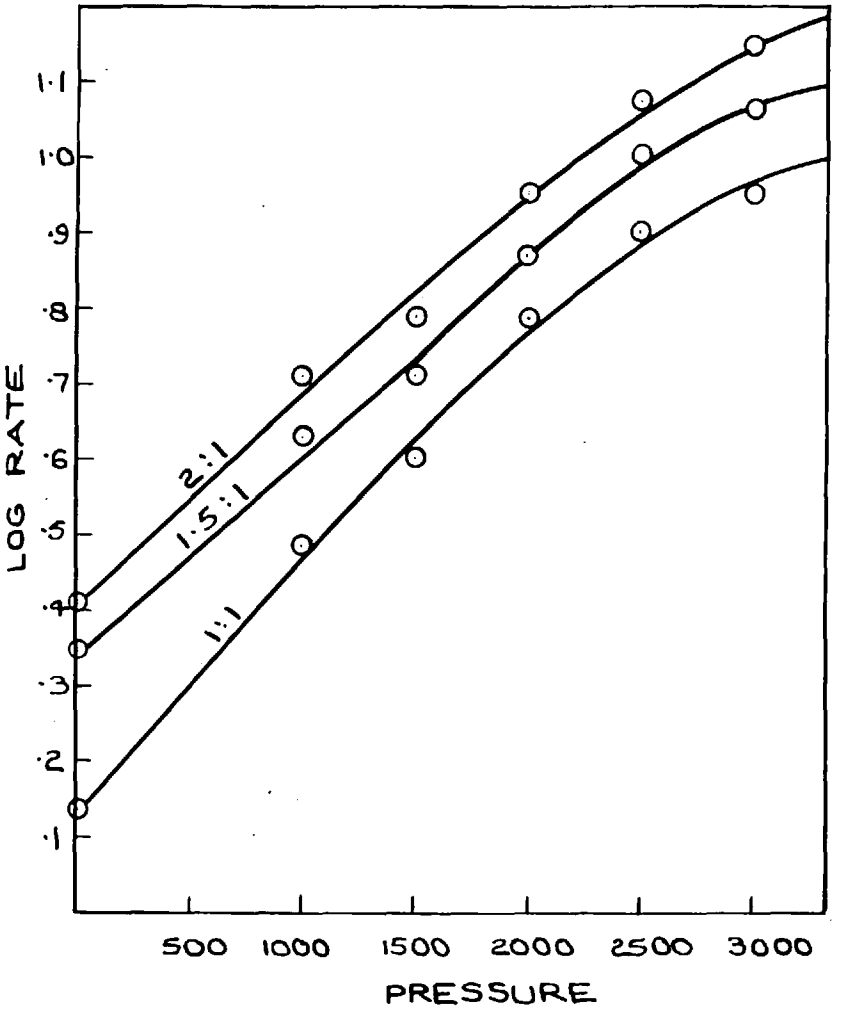


FIGURE 23 PLOT OF LOG RATE AGAINST PRESSURE IN THE POLYMERISATION OF STYRENE AND TRICHLOROETHYLENE AT DIFFERENT [M]/[S] RATIOS.

TABLE IX

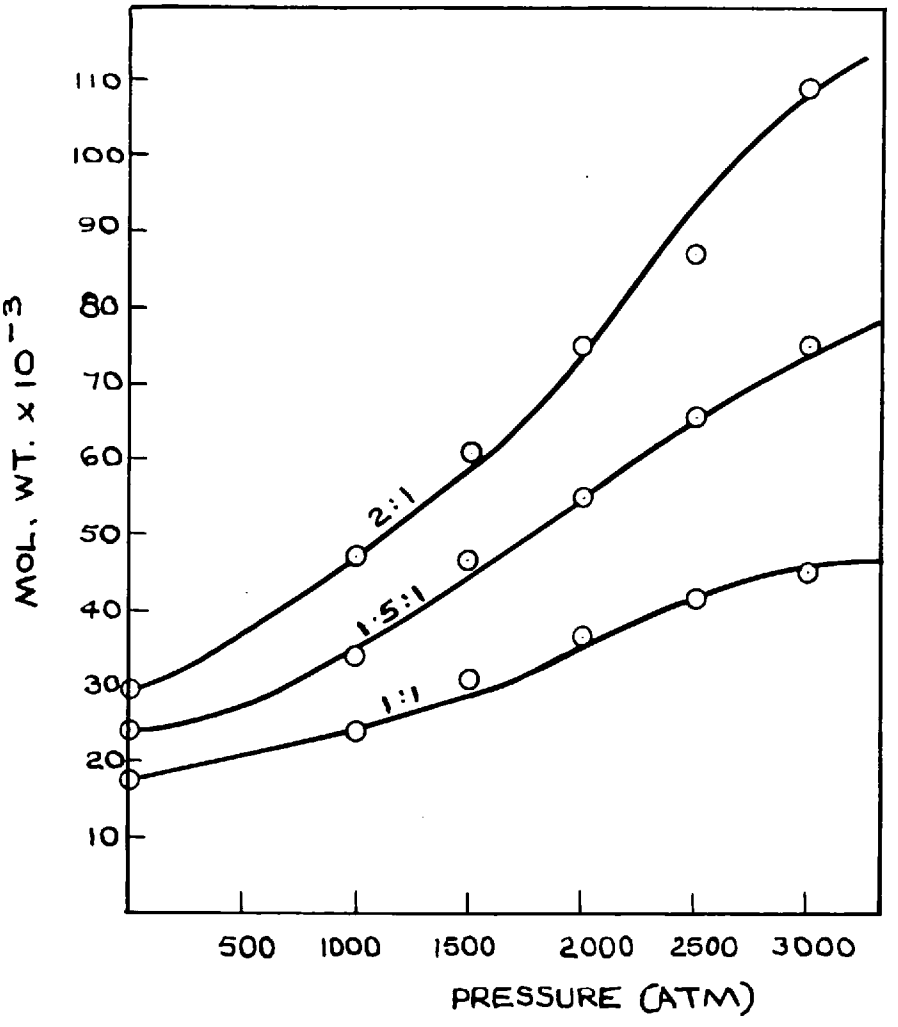


FIGURE 24 EFFECT OF PRESSURE ON MOL. WT. OF POLYMERS AT DIFFERENT [M]/[S] RATIOS IN POLYMERISATION OF STYRENE [M] AND TRICHLORO-ETHYLENE [S].

TABLE X.

the "steric effect" on the rate of the system due to transfer increasing, as the M/S ratio decreases, the effect being more overcome the higher the pressure. Also for the same M/S ratio, the rate ratios for the trichloroethylene system are higher than those of trans-dichloroethylene, a result which can again be explained in terms of "steric effect". Asai also noted similar behaviour. From the results of Table VIII it can be seen that trichloroethylene is also a retarder in styrene polymerisation.

The order of reaction with respect to initiator [I] (Table VIII, Figure 17) was found to be 0.52 and 0.50 at 1 and 1000 atm. respectively. Within experimental error it can be concluded that the order of reaction with respect to initiator is independent of pressure.

The order of reaction with respect to monomer (Table IX and Table XI, Figures 18 and 19) is 2.4 at 1 atm. It decreases with increasing pressure and attains a value of about 1 at the highest pressure, a behaviour similar to that of trans-dichloroethylene. At 1 atm., the order of reaction is higher than that for styrene-trans-dichloroethylene system, and Tables IV and IX show that trichloroethylene is a more efficient retarder than trans-dichloroethylene at the lower pressures.

Plots of log (rate) against log (styrene concentration), at 1, 1000 and 2000 atm. (Figure 20), were

extrapolated to the values for pure styrene, and gave good agreement. The agreement is least good at 1 atm., probably because of the rather high order of [M] at 1 atm.

The overall rate of polymerisation at a given initiator concentration increased with increasing M/S ratio at a given pressure (Table IX, Figure 18), and also with increasing pressure at given M/S ratio (Table IX, Figure 21).

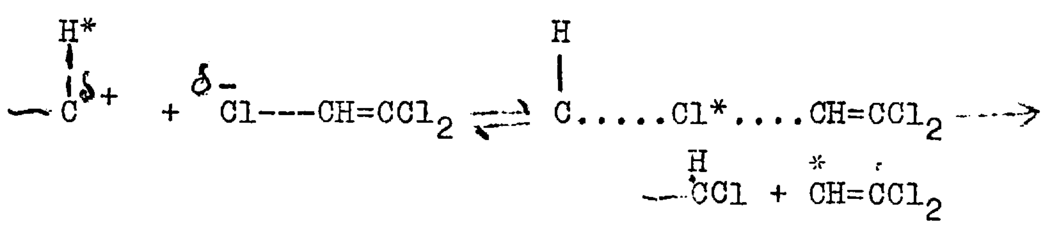
The order of reaction changes from 2.4 at 1 atm. to about 1 at higher pressure, indicating that inactive radicals formed at lower pressure becoming active at higher pressure, which is mainly due to $CH=CCl_2$* radical becoming active at higher pressure. This conclusion is supported by the fact that at a fixed M/S ratio, there is a sharper increase of rate at higher pressure (Figure 21), an observation similar as in the case of styrene-trans-dichloroethylene system.

The composition of the polymers were similar to those in the system styrene-trans-dichloroethylene; hence the incorporation of the small quantity of chlorine atom is considered due to chain transfer, and the effect of pressure on this kinetic parameter has been studied. The transfer constant has been calculated keeping I/M constant as explained previously. The value of the chain transfer constant Cs $x10^4$ changed from 42 at 1 atm. to 25 at 2500 and 3000 atm. (Table XI, Figure 22). The corresponding values

for trans dichloroethylene at 1 and 2500 atm. are 33 and 26. Hence trichloroethylene is a stronger chain transfer agent than trans dichloroethylene at 1 atm., but both are about equally effective at higher pressure. The greater decrease in the chain transfer constant of trichloroethylene in comparison to trans dichloroethylene at the highest pressures indicates a difference in the values of $\Delta V^{\neq}_{tr}$, the value for trans dichloroethylene being more negative than that for trichloroethylene. The decrease in the chain transfer constant for both the systems at higher pressure may be explained in terms of bimolecular reactions of the type

$$A^{\delta -} + {}^{\delta +}BC \rightleftharpoons A \ldots\ldots BC \longrightarrow AB + C^{*}$$

in which the initial reactants are considered to have a weak polarity arising from the existence of permanent dipole moments. The dipole moment of trans dichloroethylene $\simeq 0$, that of cis dichloroethylene = 1.9×10^{-18} esu., and trichloroethylene will have a greater dipole moment than cis dichloroethylene. Taking trichloroethylene as an example, the transition state can be written as



The denser "cis" form is more favoured under pressure, hence there will be some induced "polarization" in trans-

dichloroethylene under pressure. In the transition state as shown above, some release of solvating molecules is expected to occur because of cancellation of the weak partial charges. Since trichloroethylene has a greater dipole moment than trans dichloroethylene, stronger charges on A and BC will be developed and consequently a greater neutralisation of charges should take place in transition state with a larger release of solvent. This reaction should therefore be less-accelerated by pressure, but the transition state of bimolecular association for chain transfer in the styrene-trichloroethylene system is more resonance stabilised than in styrene-trans dichloroethylene. The net effect is that the two substances become equally effective as chain transfer agents at high pressure. At lower pressures the trichloroethylene is a more reactive transfer agent. $-\Delta V^{\neq}_{tr}$ was found to be about 10 cc./mole.

The overall volume of activation $\Delta V^{\neq}_{o}$ was calculated as before. The volumes of activation for different M/S ratios on the various pressure ranges are given (Table XII, Figure 23). $-\Delta V^{\neq}_{o}$ is between 14 to 18 cc/mole, and it decreases with increasing M/S ratio. The explanation is similar to that in the case of trans dichloroethylene. For a given M/S ratio, the volume of activation in the styrene-trichloroethylene system is bigger than in styrene-trans dichloroethylene. This may be due to the latter

system being more "hindered", as explained previously.

The molecular weights of the polymers (Table X, Figure 24) prepared at constant I/M ratio at different pressures and constant M/S ratios, increases with pressure, the rate of increase being less at higher pressure. At constant pressure the molecular weight increases as the M/S ratio increases. The observations are similar to those for the styrene-trans dichloroethylene system. Asai [139] has reported values of intrinsic viscosity determined in toluene at 30°C to be 0.270 and 0.571 for polymers prepared at 1, and 1000 Kg./cm^2 respectively, with 3.04 x10^{-3} mole/l. of AIBN at 60°C, the styrene content of the polymer is said to be 99.3 mole %. Viscosities of polymers prepared from a 1:1 molar mixture of styrene-trichloroethylene with 0.05 mole % benzoyl peroxide at 60°C were determined in benzene at 25°C (Table X). The values at 1 atm. and 1500 atm. are 0.262 and 0.311 respectively.

7.6. Kinetic Investigations on Polymerisation of Styrene with Technical-Dichloroethylene.

Kinetic investigations on the polymerisation of styrene with technical dichloroethylene, (Cis/Trans ≃ 3.5) with initiator concentration of 0.05 mole % at 1:1 M/S ratio at different pressures were done. The chain transfer constants Cs x10^4 at 1 atm. and 1500 atm. were found to be

about 1.6. This shows that both trichloroethylene and trans-dichloroethylene are more reactive than technical dichloroethylene. The volume of activation for overall rate of polymerisation $\Delta V_o^{\neq}$ with 1:1 molar ratio was found to be (VII b) -10 to 11 cc./mole. This is less than forthe systems styrene-trans dichloroethylene or styrene-trichloroethylene. The difference in reactivity in the cases of cis and trans dichloroethylene cannot be explained in terms of steric effect or steric inhibition of resonance. It is probably due to the difference in the free energy of activation.

7.7. General Conclusions.

In the bulk polymerisation of styrene the measured rates, and the order of reaction with respect to initiator concentration, are in good agreement with previous work at 1 atm. and 1000 atm. The decrease in the rate constant k with increasing initiator concentration and pressure can be attributed to a decrease in 'f' and k_d.

At all pressures the polymers formed in the styrene-chloroethylene systems have a low Cl content which is believed to arise mainly from transfer reactions; although some incorporation of chloroethylene units in the polymer chain is not excluded. The molecular weights of the polymers are greatly reduced by the presence of chloro-ethylenes in the reacting system (factor $\simeq$ 0.1). The order of reaction

with respect to [styrene] is $>$ 1 except at the highest pressures, i.e. the rate of polymerisation is reduced more by addition of chloroethylene than it would be by dilution with an inert solvent. The order of reaction with respect to initiator is about 0.5, and it is independent of pressure.

The pressure-coefficient of the rates R_{1000}/R_1 are similar in magnitude for the systems styrene, styrene-trans dichloroethylene, and styrene-trichloroethylene; although the actual value for trichloroethylene is $>$ dichloroethylenes. This can be explained in terms of "hindrance" of reaction due to transfer. The overall volume of activation $\Delta V_o^{\neq}$ for the system is styrene-trichloroethylene $>$ styrene-trans dichloroethylene $>$ styrene-cis dichloroethylene. For the system styrene-trichloroethylene and styrene-trans dichloroethylenes, this can be attributed to a "steric effect" with stabilization of the trichloroethylene radical $CH{=}CCl_2{}^*$, whereas in the case of the dichloroethylenes it is due to the difference in their reactivity because of the difference in their free energy of activation.

At a given pressure the rate of polymerisation increases as the M/S ratio increases and also at a given M/S ratio there is a sharper increase in rate at higher pressure. This is considered to be due to the radicals $CHCl{=}CH^*$ or $CHCl{=}CCl^*$ becoming more reactive at higher pressure. The molecular weight increases with pressure at a

given M/S ratio, the rate of increase being lower at higher pressure. It also increases as the M/S ratio increases at a given pressure.

There is some tendency towards reduced chain transfer under pressure, and the reaction order in [styrene] falls towards 1, but there is no marked increase in the Cl content of the polymers. The order of reactivity in chain transfer is found to be trichloroethylene > trans dichloroethylene > "technical" dichloroethylene at low pressures, but at higher pressures the activities of the trichloroethylene and trans dichloroethylene are similar. The latter phenomenon can be explained by cancellation of weak partial charges in the transition state in bimolecular reactions of the type

$$A^{\delta-} + {}^{\delta+}BC \rightleftharpoons A.....BC \longrightarrow AB + C^*$$

in which the initial polarity is associated with the dipole moments of the chloro-olefines; and also by resonance stabilization of the transition state complex. Technical dichloroethylene is very unreactive due to its high free energy of activation.

SECTION VIII.

Results and Discussion of the Effect of Pressure on the Kinetics of Copolymerisation of Halo-Olefines with Styrene, and with Vinyl Acetate.

8.1. Summary of some Previous Research.

Fundamental kinetic investigations of copolymerisation under pressure have not been attempted extensively. Doak [136] has investigated the copolymerisation of chloroethylenes with other monomers at 1 atm. Gonikberg [118] has done some work on copolymerisation of vinyl acetate and trichloroethylene under pressure. Mayo et al. [140] studied the copolymerisation of vinyl acetate at 1 atm. An extensive list of monomer reactivity ratios of styrene with other monomers is given in Boundy's [135] and in Ham's book [144]. Alfrey and Greenberg [137] have reported results for the copolymerisation of cis-and trans-dichloroethylenes and trichloroethylene with vinyl acetate and styrene.

Kinetic investigations on copolymerisation of styrene, and vinyl acetate with vinylidene chloride under pressure have not been reported. Extensive investigations of copolymerisation in vinyl acetate - trichloroethylene system under pressure has not been done before. Results of some work on copolymerisation under pressure are tabulated at the end [33, 141, 142, this work].

8.2. Kinetic Investigations on Copolymerisation of Vinylidene Chloride and Vinyl Acetate.

Mixtures of vinylidene chloride and vinyl acetate, with different initial compositions, were copolymerised at various pressures, with 0.05 mole % benzoyl peroxide, at 60°C. The results are tabulated in Table XIII. The composition of the copolymers were calculated from the analyses of the chlorine content of the polymer, which clearly shows that there is copolymerisation. Monomer reactivity ratios were calculated by the equation on page 90. Values for monomer reactivity ratios at 1000 atm., obtained by plotting r_2 against values for r_1 are shown in Figure 25. No rate measurements were done, because of the precipitation of the copolymer (especially with higher vinylidene chloride content in the feed) and also because of the difficulty of removing the precipitate.

Values for reactivity ratio of vinyl acetate (r_1) and vinylidene chloride (r_2) at different pressures are shown in Table XV. The values of monomer reactivity ratios obtained at 1 atm. as $r_1 = 0.025 \pm 0.01$, $r_2 = 3.2 \pm 0.1$ are comparable with those of Doak [136] who found $r_1 = 0.03 \pm 0$, $r_2 = 3.6 \pm 0.5$ at 60°C, with 0.1 mole % benzoyl peroxide at 1 atm.

From Table XV it can be seen that r_1 and r_2 are independent of pressure.

$$r_1 = \frac{k_{Va^* Va}}{k_{Va^* Vc}}, \qquad r_2 = \frac{k_{Vc^* Vc}}{k_{Vc^* Va}}.$$

Table XIII.

Copolymerisation of Vinyl Acetate and Vinylidene Chloride at various pressures with 0.05 mole % Benzoyl Peroxide at 60°C.

M_1 = Vinyl Acetate.

P (Atm.)	M_1/M_2 Initial mole ratio in feed	%Cl in Copolymer	Mole of Vinylidene Chloride	Mole of Vinyl Acetate	dM_1 mole% in Copolymer
1	3.5:1	48.39	.6814	.3941	36.65
1	2.1:1	52.36	.7374	.2998	28.91
1	1.6:1	55.69	.7842	.2784	26.20
1000	2.7:1	51.63	.7271	.3426	32.03
1000	1.51:1	56.68	.7969	.2641	24.90
1000	1:1.01	60.52	.8251	.2019	19.16
1000	1:2.1	65.52	.9228	.1224	11.72
1000	3:10	68.01	.9578	.0830	7.97
1500	2.73:1	50.75	.7147	.3567	33.3
1500	1.50:1	56.64	.7968	.2640	24.9
1500	1:2.4	66.34	.9343	.1094	10.49
1500	3:9.4	67.56	.9515	.0901	8.76
2000	2:1.01	53.64	.7555	.3108	29.15
2000	1.3:1	58.17	.8193	.2389	22.58
2000	1:1.38	62.72	.8834	.1668	15.89
2500	3.5:1	48.12	.6777	.3984	37.02
2500	1.36:1	57.22	.8059	.2540	23.97
2500	1:1.38	62.66	.8825	.1677	15.97
2500	1:2.4	66.02	.9299	.1144	10.96

Table XIII (b)

Values of r_1 and r_2 calculated for various pressures.

1 Atm.			1000 Atm.			1500 Atm.	
	r_1	r_2		r_1	r_2		r_1	r_2
(3.5:1)			(2.7:1)			(2.73:1)		
	0.1	4.66		0.1	4.57		0.1	4.23
	0.2	6.78		0.15	5.35		0.15	4.97
	0.3	8.9		0.2	6.12		0.2	5.72
(2.1:1)			(1.51:10)			(1.5:1)		
	0.1	4.07		0.1	3.70		0.1	3.7
	0.15	4.69		0.15	4.04		0.15	4.03
	0.2	5.23		0.2	4.38		0.2	4.37
(1.6:1)			(1:1.01)			(1:2.4)		
	0.1	3.61		0.1	3.64		0.1	3.28
	0.2	4.34		0.2	4.06		0.2	3.43
	0.3	5.06		0.3	4.48		0.3	3.58
			(1:2.1)	0.1	3.44	(3:9.4)	0.1	3.11
				0.2	3.64		0.2	3.21
				0.3	3.83		0.3	3.32
			(3:10)	0.1	3.26			
				0.2	3.37			
				0.3	3.48			

2000 Atm.			2500 Atm.		
	r_1	r_2		r_1	r_2
(2:1.01)	0.1	3.83	(3.5:1)	0.1	4.54
	0.2	4.8		0.2	6.62
	0.3	5.77		0.3	8.705
(1.3:1)	0.1	3.74	(1.36:1)	0.1	3.59
	0.2	4.32		0.2	4.13
	0.3	4.9		0.3	4.76
(1:1.38)	0.1	3.38	(1:1.38)	0.1	3.33
	0.2	3.65		0.2	3.63
	0.3	3.93		0.3	3.92
			(1:2.41)	0.1	3.11
				0.2	3.25
				0.3	3.39

Table XIV.

Copolymerisation of Styrene and Vinylidene Chloride at various pressures with 0.05 mole % Benzoyl Peroxide at 60°C.

M_1 = Styrene.

P (Atm)	M_1/M_2 Initial mole ratio in feed	M_1 mole % in feed	Rate wt.% in 4 hr.	% C in copolymer	dM_1 mole% in copolymer
1	1:1.01	49.75	1.09	78.0	77.3
1	1.501:1	60.09	1.89	81.23	82.8
1	2.5:1	71.43	2.61	84.59	87.7
1000	1:1	50	1.31	77.6	77.02
1000	1.5:1	60	2.92	82.06	83.84
1000	2.5:1	71.43	3.71	85.01	88.50
1500	1:1	50	1.90	78.16	77.89
1500	1.5:1	60	4.66	82.02	83.88
1500	2.5:1	71.43	5.46	84.58	87.88
2500	1:1	50	5.1	78.06	77.73
2500	1.5:1	60	9.36	81.21	82.62
2500	2.5:1	71.43	10.98	84.56	87.84

Table XIV(b)

Values of r_1 and r_2 calculated for various pressures.

	1 Atm.		1000 Atm.		1500 Atm.	
	r_1	r_2	r_1	r_2	r_1	r_2
(1:1)			(1:1)		(1:1)	
	3	0.175	3	0.193	3	0.135
	4	0.468	4	0.492	4	0.419
	5	0.762	5	0.789	5	0.702
(1.5:1)			(1.5:1)		(1.5:1)	
	3	0.215	3	0.134	3	0.085
	3.5	0.447	4	0.524	4	0.517
	4	0.681	5	0.958	5	0.950
(2.5:1)			(2.5:1)		(2.5:1)	
	2.5	0.0425	3	0.261	3	0.431
	3	0.480	3.5	0.666	3.5	0.862
	3.5	0.918	4	1.07	4	1.29

	2500 Atm.	
	r_1	r_2
(1:1)	3	0.146
	4	0.433
	5	0.719
(1.5:1)	3	0.235
	4	0.709
	5	1.182
(2.5:1)	3	0.442
	3.5	0.874
	4	1.31

Table XV.

Effect of pressure on monomer reactivity ratios at 60°C.

Vinylidene Chloride = M_2

Pressure (Atm.)	Monomer M_1	r_1	r_2	$r_1 r_2$
1	Vinyl acetate	0.025 ± 0.01	3.2 ± 0.1	0.080
1000	"	0.02 ± 0.005	3.2 ± 0.1	0.064
1500	"	0.025 ± 0.005	3.1 ± 0.1	0.0775
2000	"	0.03 ± 0.025	3.25± 0.1	0.0975
2500	"	0.035 ± 0.01	3.1 ± 0.1	0.1085
1	Styrene	2.55 ± 0.1	0.04± 0.02	0.102
1000	"	3.0 ± 0.3	0.165± 0.05	0.495
1500	"	2.5 ± 0.3	0.04± 0.02	0.100
2500	"	2.5 ± 0.01	0.01± 0	0.025

Table XVI.

Dependence of molecular weight on feed composition and pressure in the copolymerisation of Vinyl acetate and Trichloroethylene (with 0.1 wt.% Benzoyl peroxide) at 60°C.

P (Atm.)	Feed Composition (mole % Vinyl acetate)	Rate(wt.%) [24 hr runs]	Average ΔT_f (in benzene)	Average molecular weight.
1	16.82	1.17	0.0503	695
1	39.34	7	0.0473	1220
1	45.90	9.69	0.0369	1509
1	48.58	10.39	0.0320	1790
1	51.8	13.49	0.0310	1992
1	59.2	2.09($6\frac{1}{2}$hr.)	0.0452	1208
1	80.16	22.6	0.0100	5567
1	92.9	32.96	Negligible	High
1	40.21	1.4 (6hr.)	0.0491	920
		[6 hr runs]		
1000	41.07	1.46	0.0310	1575
1000	46.3	1.79	0.0160	2004
1000	55.17	2.56	0.0252	2400
1000	60.5	2.72	0.0198	2600
		[5 hr runs]		
2000	39.08	1.39	0.0335	1655
2000	49.13	1.91	0.0265	2200
2000	55.78	3.44	0.0172	2700

Table XVI(b)

P (Atm.)	Feed Composition (mole% Vinyl acetate)	% Cl_2 in copolymer.
1	51.8	37.59
1	59.2	36.74
2000	49.13	37.82

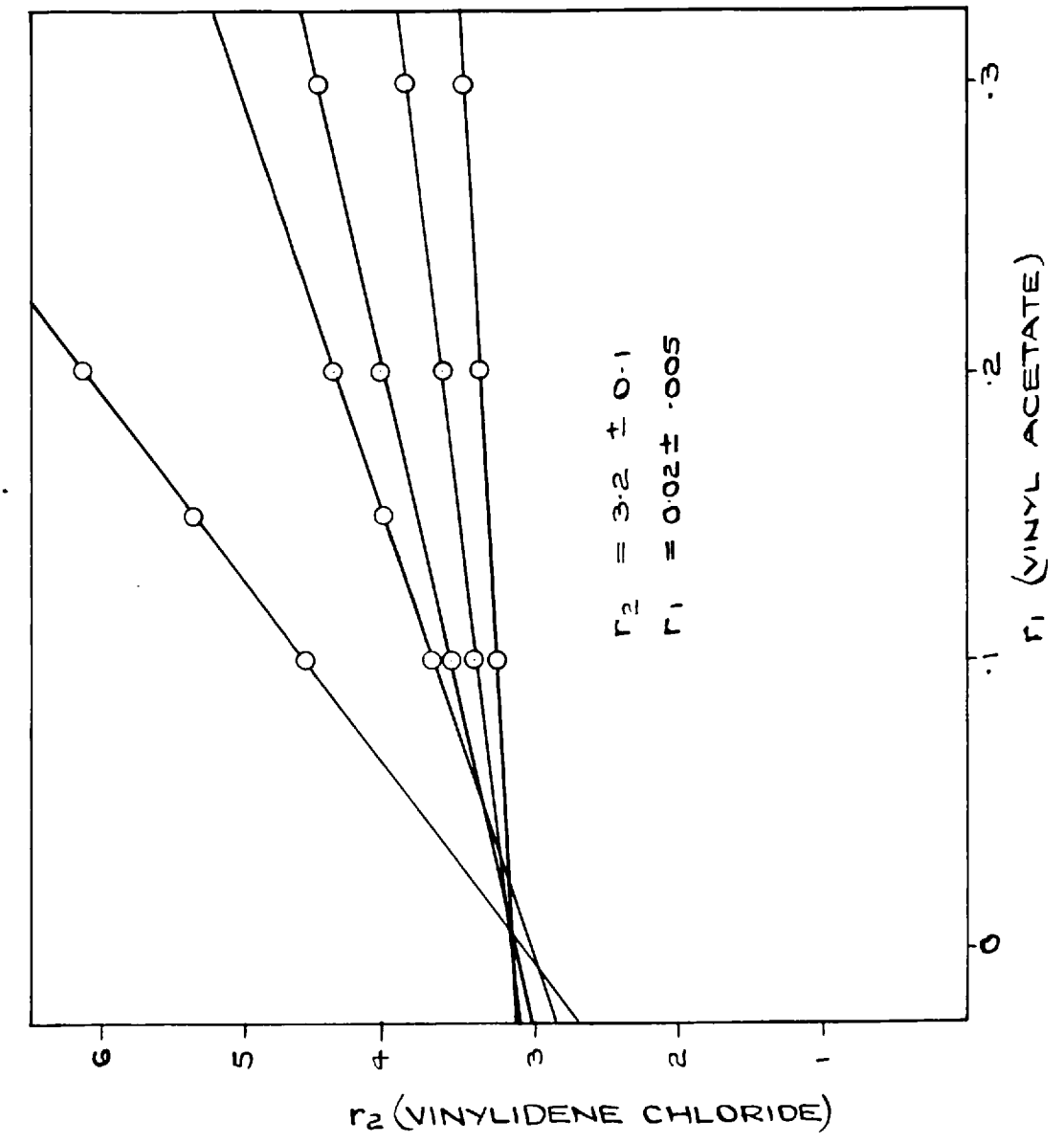


FIGURE 25 MONOMER REACTIVITY RATIOS OF VINYLIDENE CHLORIDE AND VINYL ACETATE.
P – 1000 ATM.
TABLE XIII.

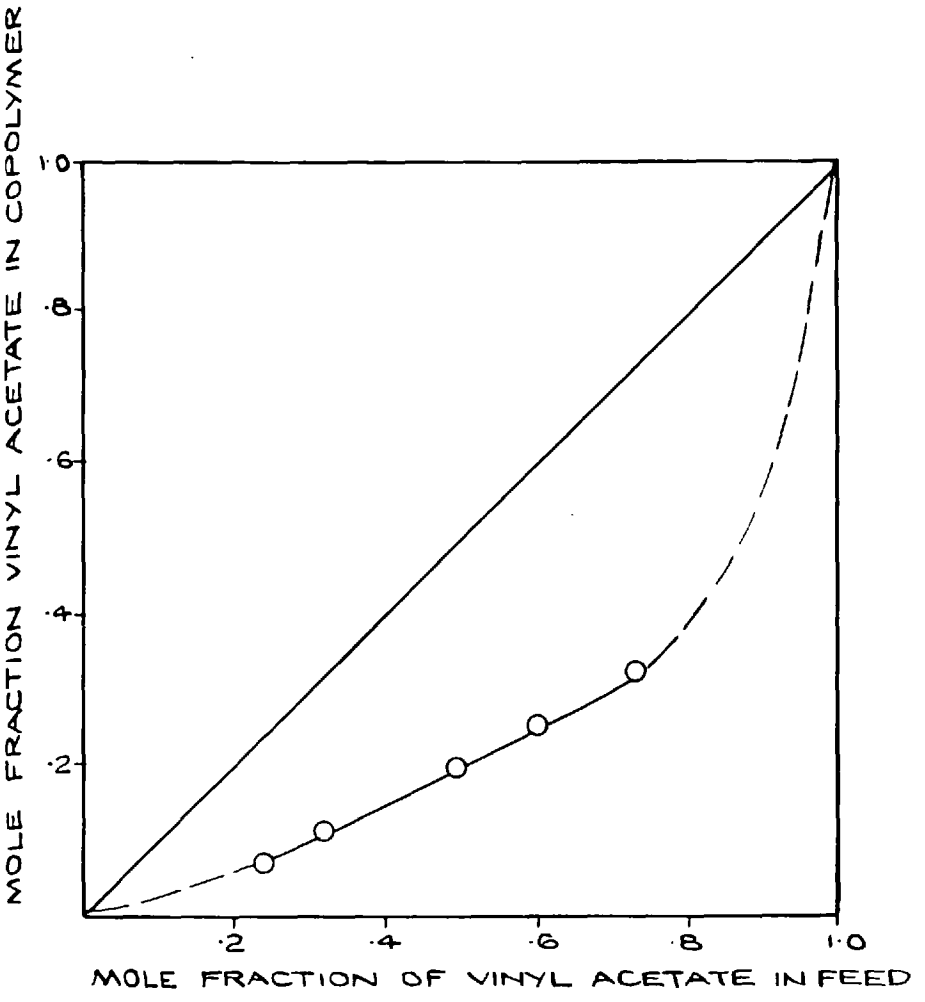


FIGURE 26 DEPENDENCE OF COPOLYMER COMPOSITION ON VINYL ACETATE CONTENT IN MONOMER FEED.
(P – 1000 ATM).
TABLE XIII.

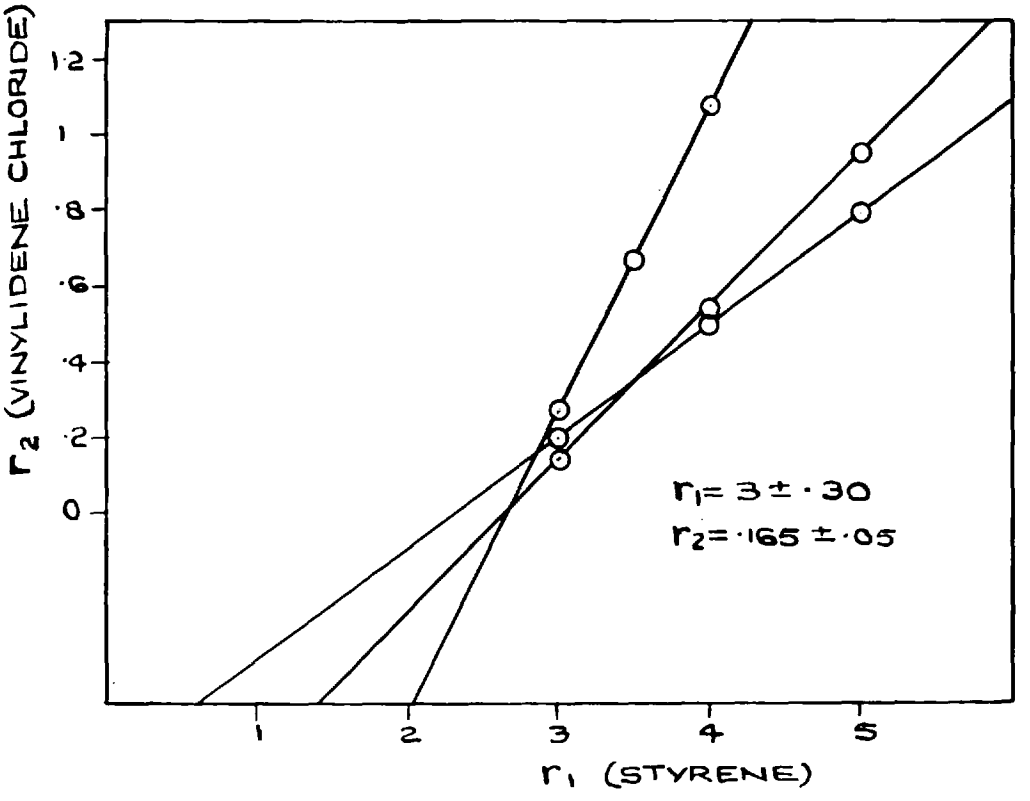


FIGURE 27 MONOMER REACTIVITY RATIOS OF STYRENE AND VINYLIDENE CHLORIDE P – 1000 ATM.

TABLE XIV

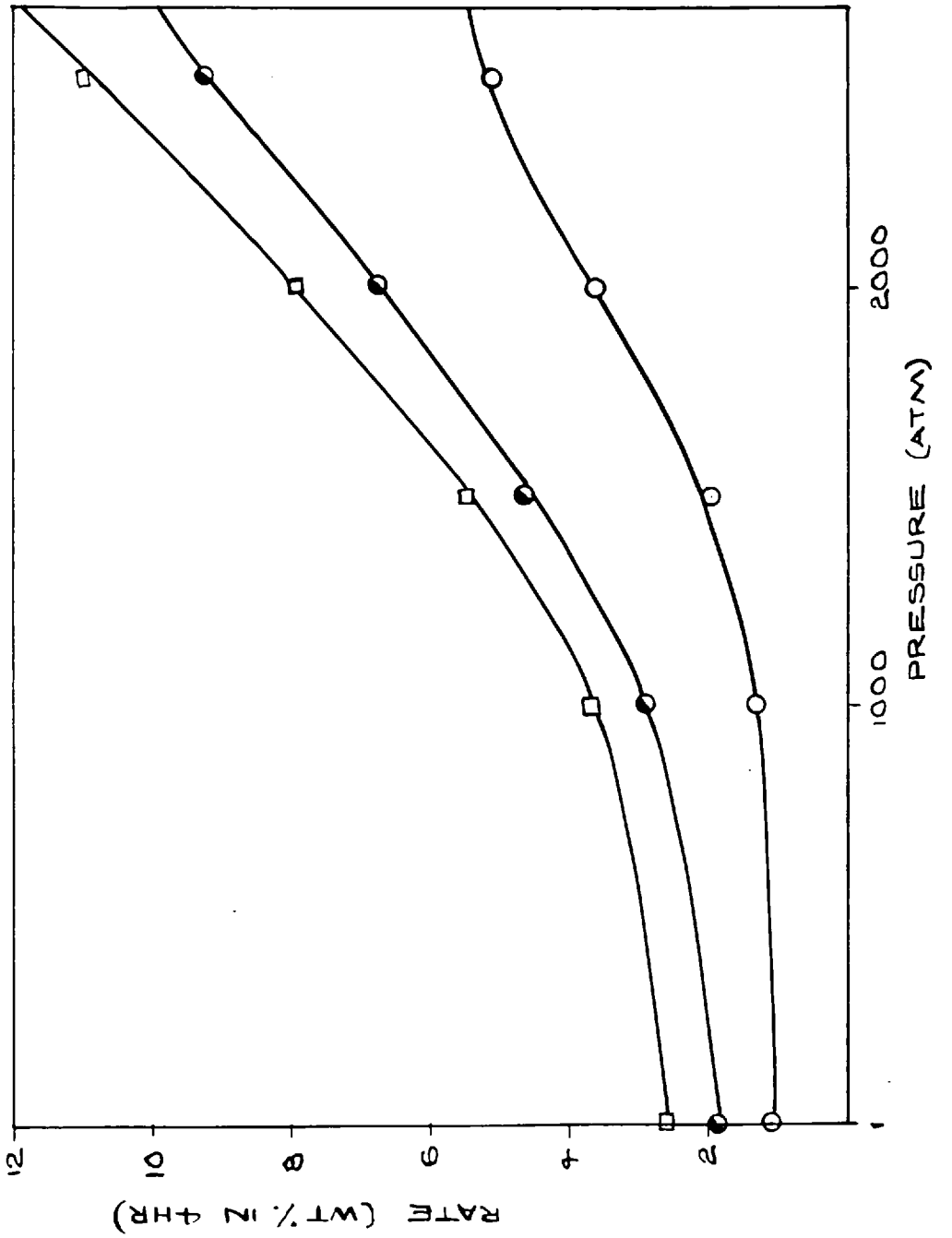


FIGURE 28 RATE OF COPOLYMERISATION OF STYRENE AND VINYLIDENE CHLORIDE AT DIFFERENT PRESSURES.

○ STYRENE 50 MOLE%

◐ STYRENE 60 MOLE%.

□ STYRENE 71·4 MOLE%.

TABLE XIV.

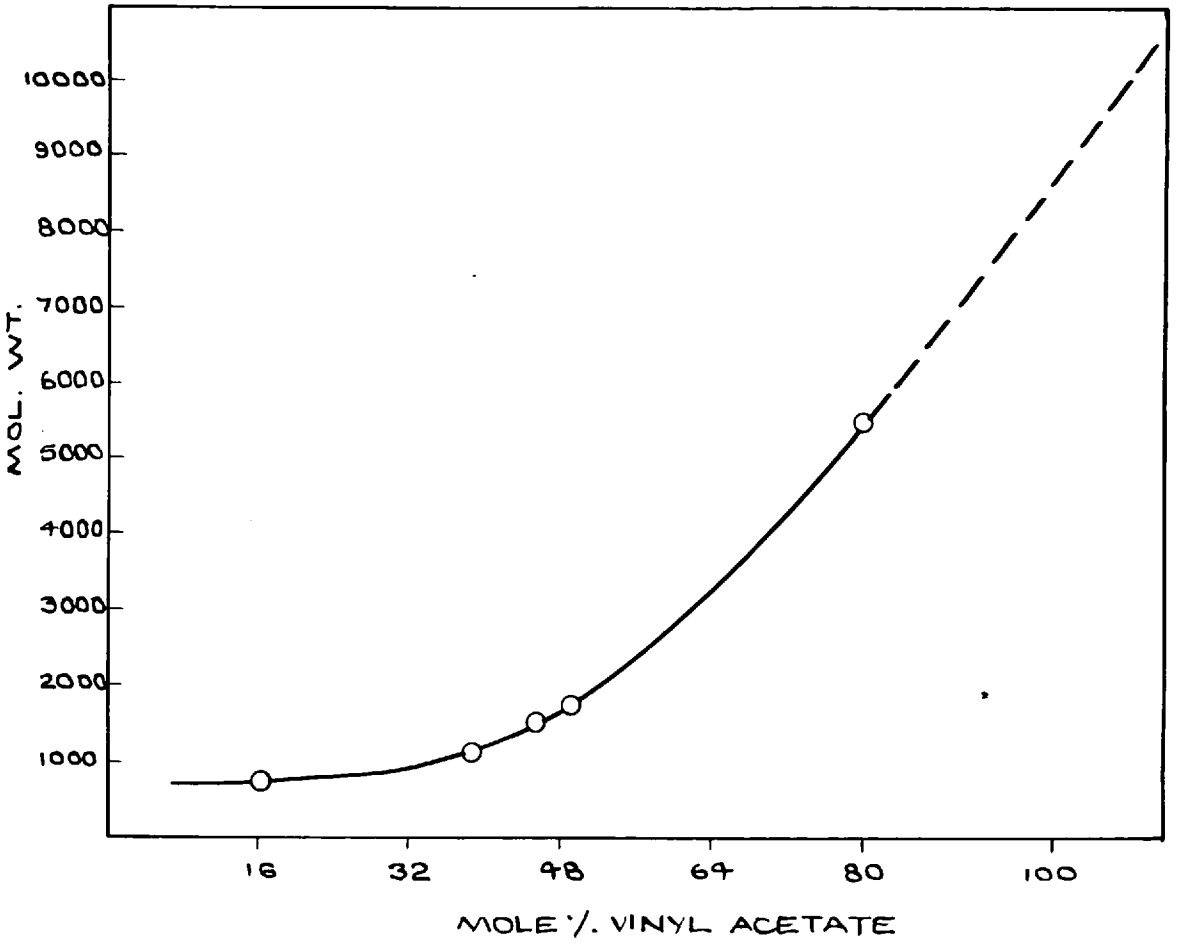


FIGURE 29 DEPENDENCE OF MOL·WT. ON FEED COMPOSITION IN THE COPOLYMERISATION OF VINYL ACETATE AND TRICHLOROETHYLENE WITH 0·1 WT. '/. BENZOYL PEROXIDE AT 1 ATM. PRESSURE. TABLE XVI.

Therefore $\Delta V_{Va*Va} \geq \Delta V_{Va*Vc}$ and $\Delta V_{Vc*Vc} \geq \Delta V_{Vc*Va}$. The energies of activation for the overall reaction of polymerisation for vinyl acetate and vinyl chloride are about 21.6 and 21.8 Kcal./mole respectively [14]. Vinylidene chloride is a more reactive monomer than vinyl chloride, hence it should have a lower energy of activation, and also a lower entropy of activation [i.e.$-\Delta S^{\neq}_{Vc}) - \Delta S^{\neq}_{Va}$]. The difference in the energy of activations is mainly due to the difference in the energy of activations of the radicals. Hence it can be said that $\Delta V_{Vc*Vc} > \Delta V_{Va*Va}$ and $\Delta V_{Vc*Va} > \Delta V_{Va*Vc}$.

The product of r_1 and r_2 is much less than 1. Hence the monomers have a tendency to alternation, and as $r_1 r_2$ is practically independent of pressure this phenomenon is unchanged under pressure. The dependence of copolymer composition on the vinyl acetate content of the feed for experiments at 1000 atm. is shown in Figure 26.

8.3. Kinetic Investigations on Copolymerisation of Vinylidene Chloride with Styrene.

Vinylidene chloride and styrene were copolymerised under various pressures with 0.05 mole % benzoyl peroxide at 60°C, having different initial feed compositions. The results are shown in Table XIV, together with the results of C, H and Cl estimations. At 1 atm.

pressure with 1:1 and 2.5:1 molar feed ratio of styrene to vinylidene chloride, the chlorine content of the polymer was 16.94 and 8.7 percent, respectively, by weight. For runs at 2500 atm. the corresponding values were 18.09 and 8.56 respectively. This clearly shows that copolymerisation takes place. The percent of C in the copolymer was corrected for 100% composition, and the mole % of the monomers in thecopolymer is calculated from the carbon content. Values for the monomer reactivity ratios at 1000 atm., obtained by plotting r_2 against values of r_1 are shown in Figure 27. A comparison of the measured rates with Table IV shows that vinylidene chloride retards styrene polymerisation, and is a more efficient retarder than trans-dichloroethylene. This is due to $\sim\!\!\sim CH(Ph)-CH_2-CCl_2^*$ being more stabilised than in $\sim\!\!\sim C(Ph)=CHCl-CHCl^*$ and also because $CH_2=CCl^*$ will be more stabilised than $CHCl=CH^*$. At a given styrene : vinylidene chloride ratio, the rate increases as pressure increases; and at a given pressure the rate increases as the styrene : vinylidene chloride ratio increases. With the 1:1 ratio at the highest pressure the rate is not very accurate because of precipitation of the polymer, and the difficulty in quantitative removal of the solid polymer from the reaction tube.

Values for the reactivity ratio of styrene (r_1)

and vinylidene chloride (r_2) at different pressures are given in Table XV. The values of monomer reactivity ratios obtained at 1 atm. are $r_1 = 2.55 \pm 0.1$ and $r_2 = 0.04 \pm 0.02$. The corresponding values obtained by Doak [136] and Lewis et al. [87] are 1.85 ± 0.05, 0.085 ± 0.01; and 2.0 ± 0.1, 0.14 ± 0.05, respectively. A graph of rate of copolymerisation for a given feed composition at different pressures is shown in Figure 28. At a given feed composition there is a sharper increase in rate at higher pressure which is attributed to the $\sim\overset{\overset{Ph}{|}}{C}H-CH_2-CCl_2^*$ and $CH_2=CCl^*$ radicals becoming more reactive at higher pressure, an observation similar to that for trans dichloroethylene and trichloroethylene.

From Table XV it can be seen that r_1 and r_2, within the experimental limits, are independent of pressure $r_1 = \frac{k_{S^*S}}{k_{S^*Vc}}$, $r_2 = \frac{k_{Vc^*Vc}}{k_{Vc^*S}}$. Therefore $\triangle V_{S^*S} \simeq \triangle V_{S^*Vc}$ and $\triangle V_{Vc^*Vc} \simeq \triangle V_{Vc^*S}$. The energy of activation for the polymerisation of styrene is about 40 Kcal./mole, hence its entropy of activation is greater than those of vinyl acetate and vinylidene chloride (i.e. $-\triangle S^{\neq}_{Vc^*} > -\triangle S^{\neq}_{Va^*} > -\triangle S^{\neq}_{S^*}$). Therefore $\triangle V_{Vc^*Vc} > \triangle V_{Va^*Vc} > \triangle V_{S^*S}$. Also $\triangle V_{Vc^*S} \simeq \triangle V_{Vc^*Vc} \simeq \triangle V_{Vc^*Va}$ and $\triangle V_{Vc^*S} > \triangle V_{Va^*Vc} > \triangle V_{S^*Vc}$. This shows that the effect of pressure

is about the same for the addition of a vinylidene chloride radical to its own monomer, or to styrene and vinyl acetate, whereas pressure has a small effect on the vinyl acetate radical, a smaller effect on the styrene radical and a comparatively larger effect on the vinylidene chloride radical.

The product of r_1 and r_2 is less than unity, which indicates that there is a tendency for alternation, and as $r_1 r_2$ is practically independent of pressure the above phenomenon does not change with pressure.

8.4. Kinetic Investigations on the Copolymerisation of Trichloroethylene with Vinyl Acetate.

Vinyl acetate and trichloroethylene, with different feed compositions, were copolymerised in the presence of 0.1 weight % benzoyl peroxide at 60°C, under different pressures. The results are given in Table XVI.

Measurements of rates of polymerisation showed that rates were not proportional to time. This may be due to non-steady state kinetics or due to transfer with polymer molecules. At a given pressure the rate increased with increase in vinyl acetate content in the feed, and with increase of pressure at a given composition.

Molecular weights of the polymers were determined. The molecular weights are low, and at 1 atm.

pressure they are practically independent of feed composition up to about 80 mole % vinyl acetate in the initial feed. The dependence of the molecular weight on feed composition at 1 atm. is shown in Figure 29, the extrapolated rate is probably much steeper. With increase in pressure for a given feed composition, there was not much change in the molecular weights of the polymers. Analyses of the polymers show that there is copolymerisation (Table XVIb).

The monomer reactivity ratios of trichloroethylene and vinyl acetate at 1 atm. [136] and 60°C are 0.01 ± 0.01 and 0.66 ± 0.04 respectively. The azeotropic feed composition $\frac{M_1}{M_2} = \frac{.01 - 1}{.66 - 1} = \frac{2.91}{1}$ or 74.6 mole % vinyl acetate. Due to r_1 and r_2 both being less then 1, there is a strong tendency for alternation. So the growing ends of the polymer chains will consist of $\sim CHCl-CCl_2^*$ or $\sim CHMe-CH_2^*$ radicals. Both trichloroethylene and vinyl acetate are efficient transfer agents. Radical chains with the $\sim CHMe-CH_2^*$ terminal group are more active than those ending in $\sim CHCl-CCl_2^*$; but the former undergo transfer reaction more rapidly, the latter, being less active, may not undergo transfer-phenomenon quickly, but its contribution to chain propagation is also less. When the feed composition with respect to vinyl acetate is in excess of its azeotropic composition, there is considerable increase in molecular weight (to about 5600 with 80% vinyl acetate in the feed).

This is due to the vinyl acetate molecules entering the chain at a relatively faster rate. With increase of pressure, (below the azeotropic feed composition with respect to vinyl acetate) there is no marked change of the system, showing that radical additions and radical displacements are facilitated to the same extent.

8.5. General Conclusions.

The monomer reactivity ratios in the copolymerisation of vinyl acetate and vinylidene chloride are independent of pressure. The values obtained at 1 atm. are comparable with previous results. $r_1 r_2 < 1$, indicating that there is a tendency for alternation, and this is also unaffected by pressure.

In the copolymerisation of styrene with vinylidene chloride, the latter is found to be a more efficient retarder of polymerisation than trans dichloroethylene. This may be due to $\sim CH(Ph)-CH_2-Cl_2^*$ and $CH_2=CCl^*$ being more stable than $\sim CH(Ph)-CHCl-CHCl^*$ and $CHCl=CH^*$ respectively. At a given styrene:vinylidene chloride ratio, the rate increases with increase of pressure, and at a given pressure rate increases with increase in styrene:vinylidene chloride ratio. The monomer reactivity ratios are independent of pressure. The values obtained at 1 atm. are comparable with previous work. $r_1 r_2 < 1$, indicating that there is a

tendency for alternation, the phenomenon being independent of pressure.

Defining r_1 and r_2 for the two pairs as :

$$r_1 = \frac{k_{Va*Va}}{k_{Va*Vc}} \qquad r_2 = \frac{k_{Vc*Vc}}{k_{Vc*Va}}$$ (Vinyl acetate and vinylidene chloride)

$$r_1 = \frac{k_{S*S}}{k_{S*Vc}} \qquad r_2 = \frac{k_{Vc*Vc}}{k_{Vc*S}}$$ (Styrene and vinylidene chloride)

$$\triangle V_{Va*Va} \simeq \triangle V_{Va*Vc}, \qquad \triangle V_{Vc*Vc} \simeq \triangle V_{Vc*Va}$$

$$\triangle V_{S*S} \simeq \triangle V_{S*Vc}, \qquad \triangle V_{Vc*Vc} \simeq \triangle V_{Vc*S}$$

The energy of activation for the polymerisation of styrene $>$ vinyl acetate $>$ vinylidene chloride. Therefore $-\triangle S^{\neq}_{Vc*} > -\triangle S^{\neq}_{Va*} > -\triangle S^{\neq}_{S*}$. Therefore from the above relationships, $\triangle V_{Vc*Vc} > \triangle V_{Va*Va} > \triangle V_{S*S}$. Also $\triangle V_{Vc*S} \simeq \triangle V_{Vc*Vc} \simeq \triangle V_{Vc*Va}$ and $\triangle V_{Vc*Va} > \triangle V_{Va*Vc} > \triangle V_{S*Vc}$. This shows that the effect of pressure is about the same for the addition of a vinylidene chloride radical to its own monomer, or to styrene or vinyl acetate, and pressure has a small effect on the activity of the vinyl acetate radical, a smaller effect on styrene radical and a comparatively larger effect on the vinylidene chloride radical.

In the copolymerisation of vinyl acetate and

trichloroethylene, the rate is found not to be proportional to time. This may be due to non-steady state kinetics or due to transfer with the polymer. The rate increased with increase of vinyl acetate content in the feed. The molecular weights of the polymers were low. They were practically independent of the pressure and the composition of the feed up to a vinyl acetate content of 80 mole %. The azeotropic feed composition is 74.6 mole % vinyl acetate. The low molecular weights of the polymers can be explained in terms of strong tendency to alternation, producing "lazy"—$CHCl-CCl_2$* radicals, and to chain transfer. Molecular weights are independent of pressure, which shows radical addition is facilitated to the same extent as radical displacement. The sharp increase in the molecular weight of the polymer above the azeotropic composition of vinyl acetate is attributed to an increase in the rate of addition of vinyl acetate due to the large excess of the monomer.

Monomers M_1	Monomers M_2	Solvent	$t^{\circ}C$	P (Atm)	r_1	r_2	$r_1 r_2$
Acenaph.	MMA	-	60	1	3.1±0.3	0.57±0.05	1.77
			"	880	2.2	0.58	1.28
			"	1900	1.9	0.60	1.14
			"	2880	1.8	0.54	$\simeq 1$
			"	3900	1.6	0.58	$\simeq 1$
	Mal Anhyd	-					
			"	1	0.43±.04	0.07±0.03	0.030
			"	2880	0.32±0.1	0.1 ±0.05	0.032
	Tetra CE	-	"	2880	270	0	$\simeq 0$
						Ref. [33]	
Styrene	MMA	-	60	1	0.52	0.46	0.24
			"	1000	0.53	0.47	0.25
			"	1500	0.50	0.48	0.24
			"	2000	0.53	0.45	0.24
			"	2500	0.53	0.48	0.25
			"	3000	0.57	0.54	0.31
			"	3500	0.59	0.50	0.26
	Diethyl Fumerate	-	"	1	0.30	0.07	0.021
			"	1000	-	-	
			"	1500	0.26	0.01	0.0026
			"	2000	-	-	
			"	2500	0.27	0.02	0.0054
			"	3500	0.30	0.02	0.006
MMA	Mal. Anhyd		"	1	2.1	0.0	$\simeq 0$
			"	2000	2.4	0	$\simeq 0$
						Ref. [141]	

Monomers M_1	Monomers M_2	Solvent	t°C	P Kg/cm^2	r_1	r_2	r_1r_2
Styrene	MMA	Benzene	50	1	0.52	0.45	0.23
			"	100	0.58	0.48	0.28
			"	1000	0.72	0.58	0.42
		Dichloro-ethane	50	1	0.49	0.46	0.23
				100	0.53	0.52	0.28
				1000	0.63	0.66	0.44
		Pyridine	50	1	0.44	0.50	0.22
				100	0.49	0.57	0.28
				1000	0.56	0.80	0.45
		Ethyl Alcohol	50	1	0.45	0.47	0.21
				100	0.49	0.52	0.25
				1000	0.59	0.62	0.37
				(Atm.)		Ref. [142]	
Vinyl Acetate	Vinylidene chloride	-	60	1	0.025±.01	3.2±0.1	0.08
			"	1000	0.02 ±.005	3.2±0.1	0.06
			"	1500	0.025±.005	3.1±0.1	0.077
			"	2000	0.03 ±.025	3.25±0.1	0.097
			"	2500	0.035±.01	3.1±0.1	0.108
Styrene	Vinylidene chloride		60	1	2.35± 0.1	.04±.02	0.102
			"	1000	3.0±0.3	.165±.05	0.49
			"	1500	2.5±0.3	.04 ±.02	0.10
			"	2500	2.5±0.01	.01 ± 0	0.025
						[This work]	

SECTION IX.

Polymerisation of Chloro-Olefines under very High Pressure.

9.1. Summary of some Previous Research.

The tetrahedral anvil apparatus as devised by Hall [123] and as modified by Lloyd et al. [124] was used. Gonikberg and Zhulin have investigated the effects of pressure on tetrachloroethylene and trichloroethylene [134, 133] to about 1870 Kg./cm^2 and 1200 Kg./cm^2. Klassens and Gissolf [130] attempted to polymerise trichloroethylene at about 10,000 atm., and Gonikberg et al. have investigated tetrachloroethylene [131, 132] at pressures up to 30,000 atm.

Trans-dichloroethylene and Technical Dichloroethylene appear not to have been studied at very high pressure. Trichloroethylene has also not previously been investigated at pressures as high as 37 Kb, and the effects of added initiators on the reactions of chloro-olefines under very high pressure have not been studied before.

9.2. Calibration of the Press.

The press was calibrated by means of the 'fixed point;' transitions of bismuth and thallium. The electrical connections are shown on page 64, section IV. The sample was prepared as shown in Figure 6. 'Edge to Edge' and 'Base to Apex' arrangements in a pyrophyllite tetrahedron of 0.94" edge-length were used. The results of the two arrangements were in good agreement. Tables XVII and XVIII give the data for 'Edge to Edge' calibration with bismuth and thallium, the corresponding plots for resistance against load are shown in Figures 30 and 31 respectively. Similar plots for 'Base to Apex' arrangements are shown in Figures 32 and 33. From the figures, the pressure co-relations of the press for the two arrangements are ,

45 tons $\simeq$ 25.6 Kb

52 tons $\simeq$ 27 Kb

83 tons $\simeq$ 36.8 Kb.

Table XVII.

Calibration of the Press with 0.005" diameter Bismuth wire in a pyrophyllite tetrahedron of 0.94" edge-length with 'edge to edge' assembly, at room temperature.

Load (Tons)	V (millivolt)	I (milliamp)	R (ohms)
32	0.317	3.2	0.099
40	0.328	"	0.102
44	0.334	"	0.104
45	0.336	"	0.105
46	0.220	"	0.068
47	0.181	"	0.056
50	0.161	"	0.050
52	0.161	"	0.049
52	0.194	"	0.061
58	0.195	"	0.061
60	0.195	"	0.061

Table XVIII.

Calibration of the Press with 0.005" diameter Thallium wire in pyrophyllite tetrahedron of 0.94" edge-length and 'edge to edge' assembly at room temperature.

Load (Tons)	V (millivolt)	I (milliamp)	R (ohms)
50	0.610	22	0.0278
60	0.598	"	0.0272
70	0.578	"	0.0267
80	0.579	"	0.0263
82	0.564	"	0.0257
83	0.558	"	0.0254
85	0.552	"	0.0251
86	0.551	"	0.02505
87	0.550	"	0.0250
90	0.549	"	0.02497
100	0.545	"	0.02482

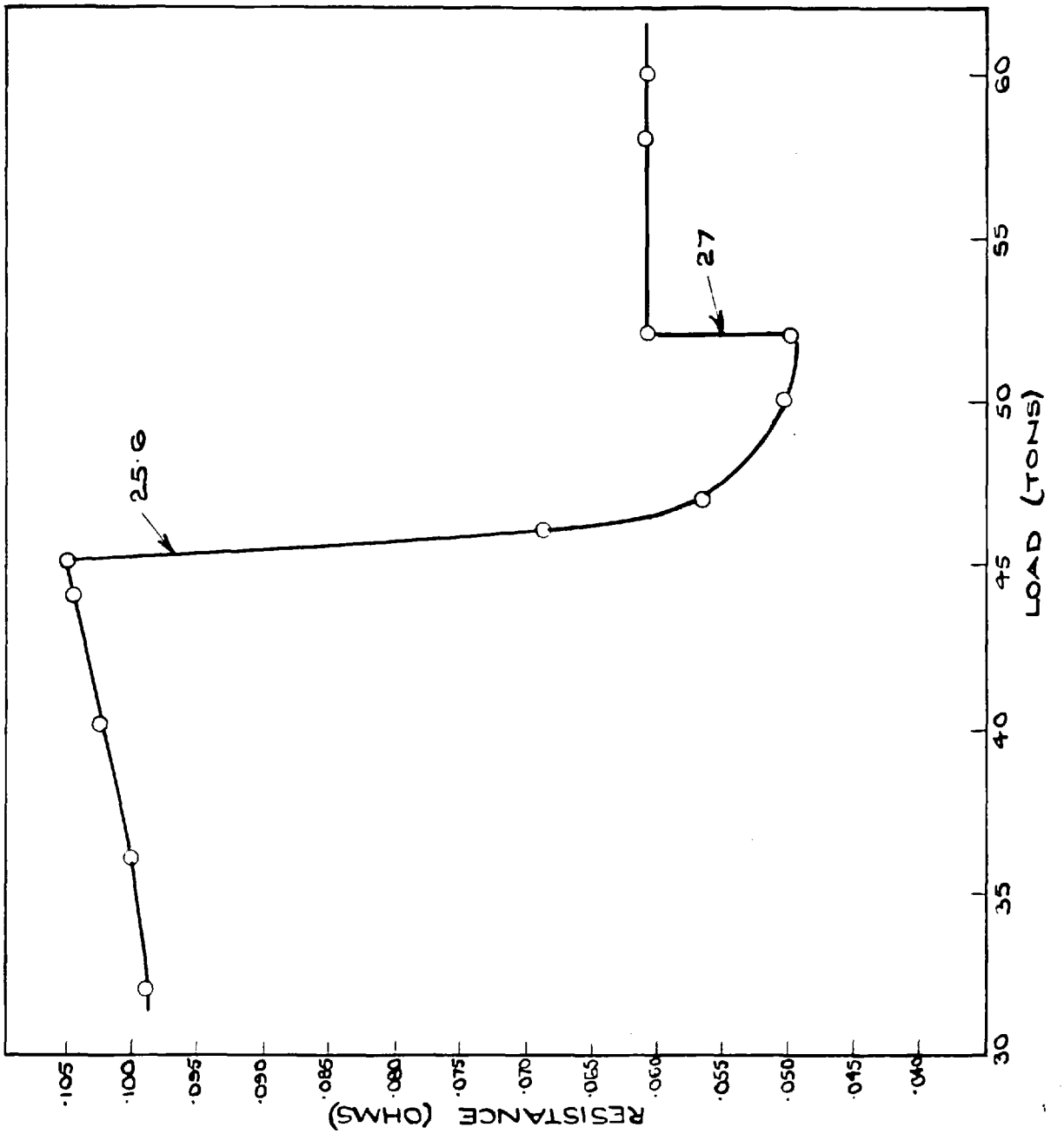


FIGURE 30 BISMUTH POINT WITH 'EDGE TO EDGE' SET UP.
·94" TETRAHEDRON.

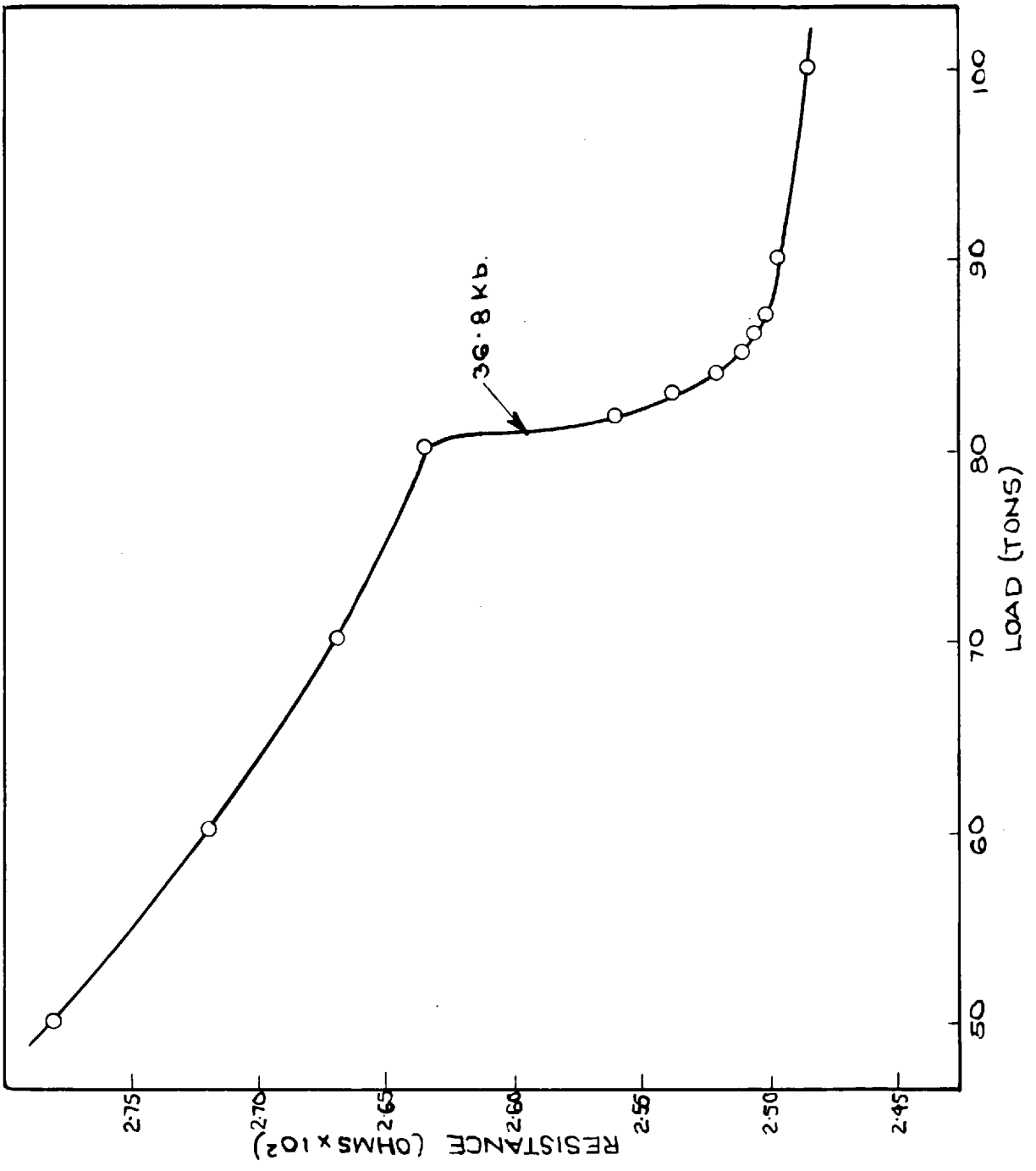


FIGURE 31 THALLIUM POINT WITH 'EDGE TO EDGE' SET UP.
0·94" TETRAHEDRON

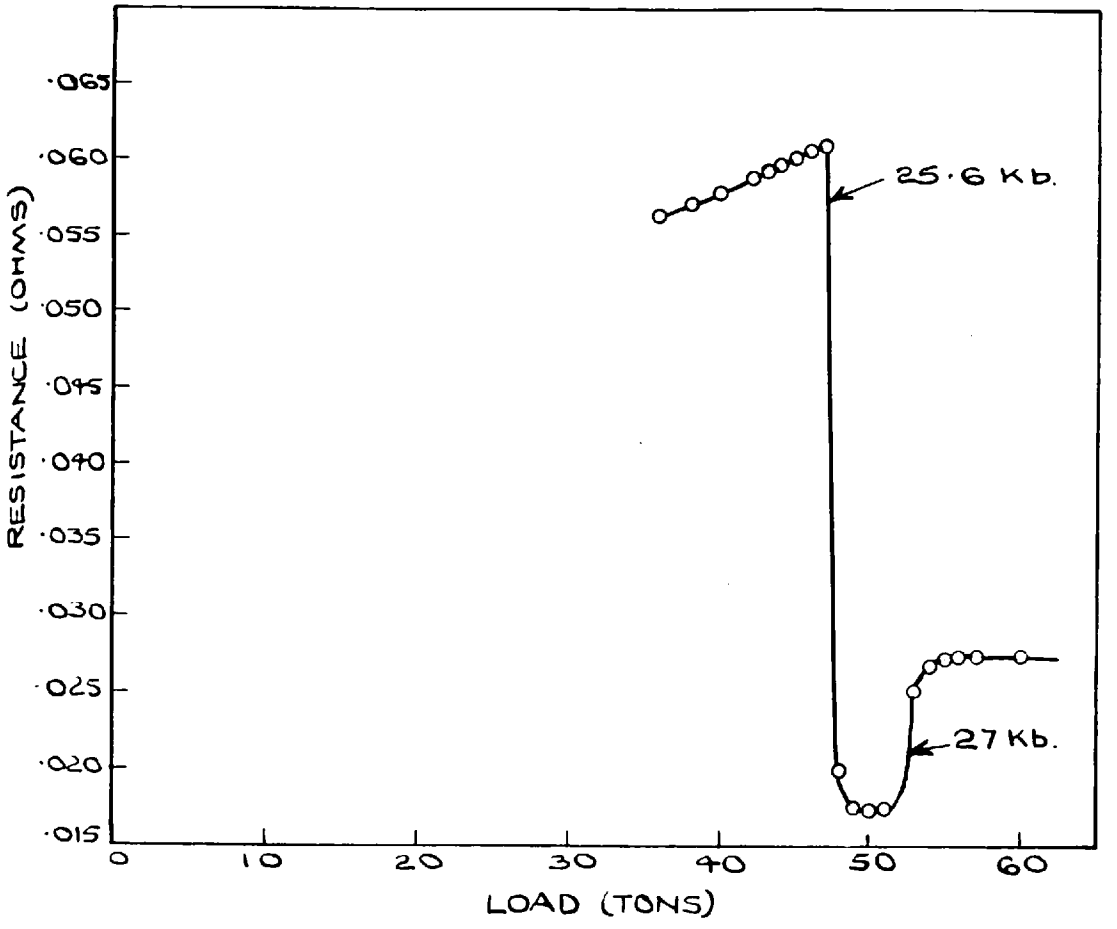


FIGURE 32 BISMUTH POINT WITH 'BASE TO APEX' SET UP.
·94" TETRAHEDRON.

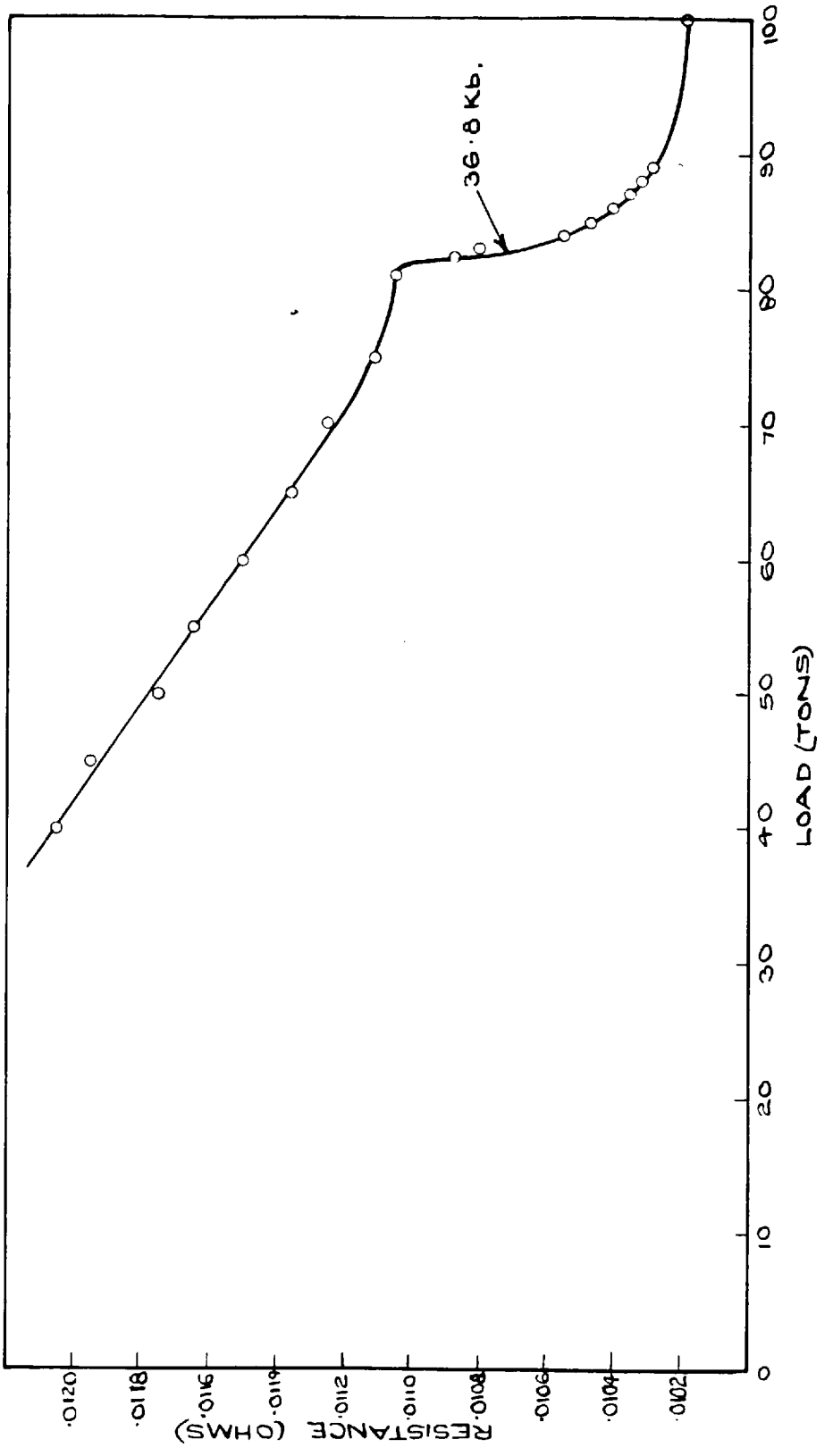


FIGURE 33 THALLIUM POINT WITH 'BASE TO APEX' SET UP
0·94" TETRAHEDRON.

9.3. Polymerisation of Trans Dichloroethylene.

Trans-dichloroethylene pre-cooled in "dry-ice" was subjected to pressures of about 27 Kb and 37 Kb, with and without benzoyl peroxide. As the anvils were pre-cooled, further heating of the sample was not carried out. The sample was held under the two pressures for 20 minutes. No apparent change and no polymerisation of the sample was observed.

9.4. Polymerisation of Technical Dichloroethylene.

Technical-dichloroethylene (Cis/Trans $\simeq$ 3.5) was subjected to the same pressures as trans-dichloroethylene. As the anvils were pre-cooled further heating of the sample was not carried out. Samples with and without benzoyl peroxide showed no apparent change or polymerisation.

9.5. Polymerisation of Trichloroethylene.

Trichloroethylene was subjected to pressures of about 27 Kb and 37 Kb. The sample was held at each pressure for 20 minutes. In the 27 Kb run, the sample was heated to a temperature of about 300°C, and in the 37 Kb run the sample was heated to a temperature of about 470°C. This was done to maintain the sample in the liquid state at the high pressures. (The m.p. of trichloroethylene is -88°C, and an increase in m.p. of about 15°C/Kb was assumed).

Apparent changes in the sample occurred. A portion of the sample had decomposed with the formation of black carbon particles and there was also some viscous yellow product. A sample subjected to pressures of 37 Kb and temperature of about 470°C contained a larger proportion of decomposed product, and the viscous yellow product. No apparent differences were noticeable between samples with or without benzoyl peroxide.

9.6. General Conclusions.

The calibration of the press showed that both the 'Edge to edge' and 'Base to Apex' assemblies give pressure co-relations in good agreement. Technical dichloroethylene and trans-dichloroethylene did not undergo polymerisation or any permanent physical change when subjected to pressures of 27 and 37 Kb, with or without benzoyl peroxide. Trichloroethylene, when subjected to the same pressures, and heated to temperatures of about 300°C and 470°C, respectively, underwent physical and chemical change. There was decomposition and formation of a yellow viscous product, both changes being more favoured at higher pressure and temperature. No apparent effect on the changes was produced if benzoyl peroxide was added.

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