CHAIN TRANSFER TO THE SOLVENT

IN THE POLYMERISATION OF

STYRENE AT HIGH PRESSURES

A thesis submitted for the Degree of
DOCTOR OF PHILOSOPHY

in

CHEMICAL ENGINEERING

in the

UNIVERSITY OF LONDON

by

KHAWAJA SALAHUDDIN

Department of Chemical Engineering
and Chemical Technology,
Imperial College of Science and Technology,
London, S.W.7.   January, 1965.

ABSTRACT

The object of the work described in this thesis
was to study the effect of pressure on chain transfer
to the solvent, tetrachloroethylene, in the polymerisation
of styrene; and to investigate whether tetrachloroethylene
copolymerises with styrene.

The rate of polymerisation in this solvent is found
to be of half order with respect to initiator concentration
and of order 3/2 with respect to monomer concentration.

Pressure has an accelerating effect on the rate of
polymerisation of styrene in tetrachloroethylene, and
increases it 5 to 6-fold in the pressure range 1 to 2680
atmospheres.

The molecular weight of polystyrene prepared in
solution increases up to about 1030 atmospheres, beyond
which there is no pronounced change up to 3000 atmospheres.
However, in experiments with mole ratios of solvent to
monomer $\geq$ 3.04 the molecular weights are almost constant
up to 2680 atmospheres.

The solvent-transfer constants of tetrachloroethylene
with styrene have been determined at several pressures.
C_S is 29.0×10^{-4} at 1 atmosphere and 27.4×10^{-4} at
2680 atmospheres and so is almost independent of pressure.

This result is compared with previous work on chain transfer at high pressures.

While tetrachloroethylene is found to be an active chain transfer agent for polystyrene radicals the chlorine content of the polymers is very low and there is no evidence of copolymerisation with styrene at 1 atmosphere or higher pressures. Gonikberg's claim that tetrachloroethylene copolymerises with vinyl acetate and Doak's assumption that styrene and tetrachloroethylene form copolymers are critically discussed and considered to be incorrect.

Tetrachloroethylene was not found to homopolymerise in bulk or in solution at temperatures up to $100^{\circ}C$ and pressure up to 7000 atmospheres, in the presence of azobisisobutyronitrile, benzoyl peroxide, di-tertiary butyl peroxide or tertiary butyl perbenzoate.

Tetrachloroethylene was found to give low yields of apparently polymeric substances with boron trifluoride diethyl etherate at low temperatures but this was not investigated in detail.

Polymers obtained in a few experiments with methyl methacrylate in tetrachloroethylene contained very low percentages of chlorine, so that copolymerisation appears not to occur in this system.

ACKNOWLEDGEMENTS

The author also thanks Mr. Moulder for preparing the photographs of the equipment, and Mrs. MacGarry and Miss Smart for their assistance in the preparation of this thesis.

It is appropriate to acknowledge the contributions of the vast army of scientific workers who preceded us. As D'Alelio puts it, they "by their persistent and diligent research efforts gave us the foundations to build and we should be humble when we add stones to pyramids whose excavations and bases are the work of others".

Khawaja Salahuddin.

D E D I C A T E D

TO

THE MEMORY OF

PROF. TAJ MOHAMMAD KHIYAL

VICE-CHANCELLOR OF THE

UNIVERSITY OF THE PANJAB,

LAHORE, WEST PAKISTAN,

WITHOUT WHOSE PERSUASION

AND KINDNESS THIS WORK

WOULD NEVER HAVE BEEN

UNDERTAKEN

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SECTION IV: GENERAL DISCUSSION AND CONCLUSIONS

GENERAL DISCUSSION

I.1: Introduction

Following the pioneer work of Conant and Bridgman
(1-3), the effects of high pressures on the rates of chemi-
cal reactions have been studied by chemists and chemical
engineers in different parts of the world.   Early work
has been reviewed by Bridgman (4).   Perrin (5) in 1938
published a summary of work of his group on typical organic
reactions.   The pressure effects can be as great and as
varied as those caused by temperature.   According to the
law of mass action, pressure will exert its maximum influence
when one or more of the reactants is a gas which will be com-
pressed and so produce large changes in the concentration of
the components.   However, the kinetics of many gas-phase
and heterogeneous systems at high pressures are generally
complex and the mechanisms obscure (6-8).

The kinetics of homogeneous liquid phase reactions at
high pressures are much better understood and have been ex-
tensively studied from the stand point of heats of reaction
and mechanism of chain initiation, propagation, transfer
and termination.   Free radical vinyl polymerisations have
been studied at high pressures in more detail than those of
almost any other type of reactions.

The present work was started with a view to studying

the effect of high pressures on the chain transfer to the
solvent in the polymerisation of styrene.   The solvent
used throughout was tetrachloroethylene and the initiator
azo-bis-iso-butyronitrile.   Experiments were generally
performed at 60°C. and at pressures up to 3000 atmospheres
and at atmospheric pressure.

Understandably, for the interpretation of experimental
results in a system containing monomer, solvent, initiator
and polymer molecules, it is necessary to study in detail
the kinetic scheme and the validity of the various assump-
tions.   Vinyl polymerisation is not the result of a single
reaction but a composite series of reactions based on un-
stable intermediates which will eventually terminate.
Such polymerisations occur through a 'kinetic chain reac-
tion' to produce polymer chains.   The idea of formation
of 'macro molecules' as a chain mechanism was first con-
ceived by Staudinger (9).   Flory (10) in 1937 showed that
in the kinetics of vinyl polymerisation there are three
distinct stages in the process: the activation or initiation
stage in which free radicals are produced, the propagation
stage which occurs more rapidly and leads to the develop-
ment of long chains, and the termination stage in which
the chain radicals are self-terminated.

Any process by which one polymer chain is terminated and another free radical generated is known as a chain transfer because the new radical can usually propagate a new chain.   Some of the salient features of the mechanism of each of the above steps will be discussed below.   Such kinetic schemes have been described in detail and discussed by a number of workers.   (11-17). Work on "Addition Polymerisation at High Pressures" has recently been reviewed by Weale (18), and a report on "Homogeneous Liquid-Phase Polymerisation" has also appeared (19).

I.2   <u>General Review of Radical Addition Polymerisation</u>

(i)   <u>Chain initiation</u>.

(a)   Polymerisation may occur in
the presence or absence of any added initiators - chemical
substances known to decompose and giving rise to free radi-
cals when mixed with certain monomers at proper conditions.
Styrene and some other monomers are known to undergo poly-
merisation without the help of any initiator by radical
processes.   This is known as <u>thermal initiation</u> and its
mechanism is not very clear.   According to Flory (10)
the mechanism is a bimolecular process leading to the
formation of diradicals:

$$2 \; CH_2 = CH.C_6H_5 \longrightarrow \overset{\text{x}}{C}H.C_6H_5 - CH_2 - CH_2 - \overset{\text{x}}{C}HR$$
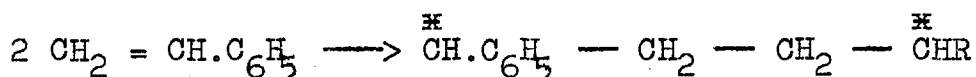
but the reaction suffers from the fact that the diradicals
have a great tendency to cyclize, thus retarding the growth
of long chains(20).   Some further studies have been made
but the mechanism still remains obscure (21-22) (11).

Since it is impossible to exclude the last traces of
air in the high pressure experimentation, reproducible
results cannot be obtained with thermal initiation.   All
polymerisations throughout this work are 'catalysed' (or
chemically initiated) reactions.

(b) <u>Chemical initiation</u>.   In this type of poly-merisation, free radicals are obtained by thermal (or photochemical) decomposition of compounds such as organic peroxides, and azo and diazo compounds.   These are known as initiators.

Chemical initiation may be regarded as occurring in two steps.   The initiator, C, decomposes to give two primary radicals Z^* .   The Z^* radicals react with the double bond of the olefinic monomer, M, producing a chain radical R_1^* .   In the case of Azo-bis-isobutyro-nitrile (AIBN), the decomposition into free radicals, Z^* :

$$NC - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - N = N - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CN \longrightarrow 2 \ CH - \underset{\underset{CH_3}{|}}{\overset{\overset{CN}{|}}{C^*}} + N_2$$

$$C \longrightarrow 2 \ Z^* \qquad\qquad (1)$$
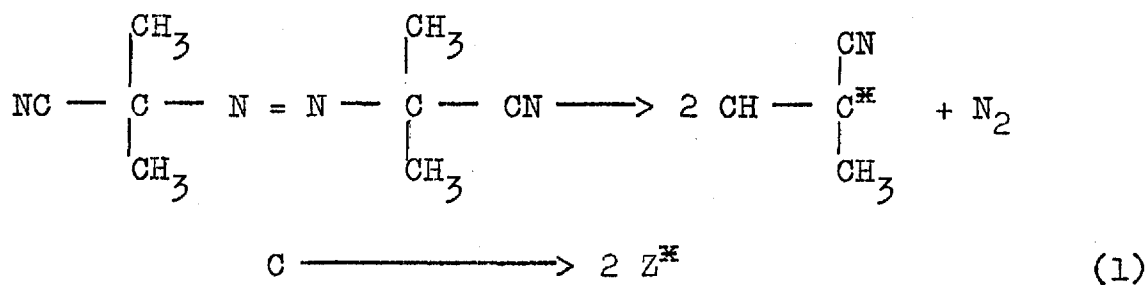
is followed by the formation of a chain radical:

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CN}{|}}{C^*}} + CH_2 = CHX \longrightarrow CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CN}{|}}{C}} - CH_2 - \underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C^*}}$$

$$Z^* + M \longrightarrow R_1^* \qquad\qquad (2)$$
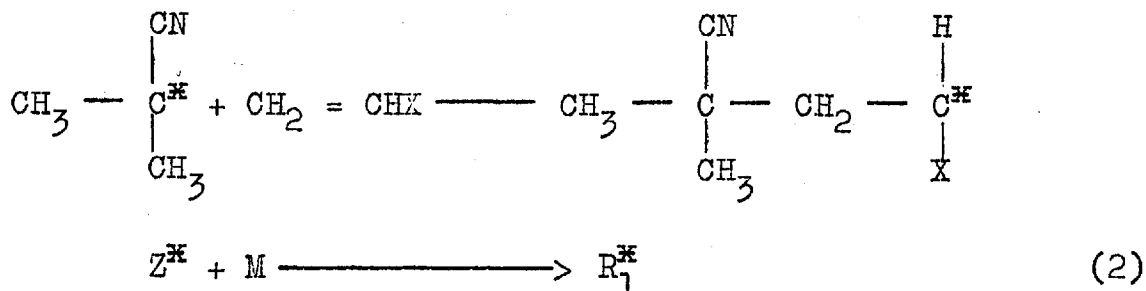
The fragments of the initiator are always found incorpo-rated in the polymer (23-38).

(ii) <u>Chain Propagation</u>.   The chain radical, R_1^* , produced during the initiation stage, because of its high reactivity adds on other monomer molecules at the double bond.   This regenerates an active centre at the end of the chain, thus preserving its reactivity and resulting in the growth of polymer chains,

$$CH_3 - \overset{\overset{\displaystyle CN}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C^*}} + CH_2 = CH\ X \longrightarrow CH_3 - \overset{\overset{\displaystyle CN}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}} - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C^*}}$$

$$R_1^* + M \longrightarrow R_2^*$$

followed by, $R_2^* + M \longrightarrow R_3^*$

and in general,

$$R_n^* + M \longrightarrow R_{n+1}^* \tag{3}$$
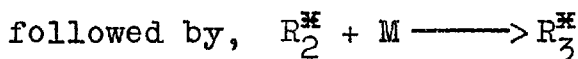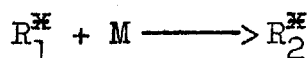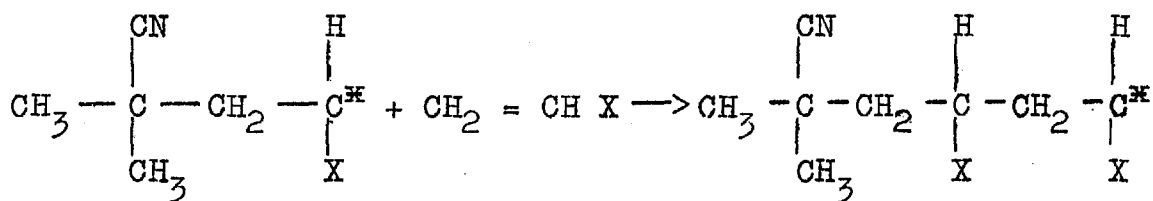
It is usually assumed that the rate of propagation is independent of the length of the growing chain.

Large amounts of energy are liberated in this process. As the propagation reaction requires much lower energies than the initiation step, the rate of propagation $k_p[M][R^*]$ is much more rapid and the maximum chain length is achieved in a fraction of the total time of polymerisation.

(iii) <u>Chain Termination</u>. The disappearance of the active centres is preceded by self-termination of the chain radicals by one of the two bimolecular processes:

(a) <u>Coupling or combination</u> of two chains giving one inactive polymer molecule P :

$$R_n^{*} + R_m^{*} \longrightarrow P_{m+n} \tag{4a}$$
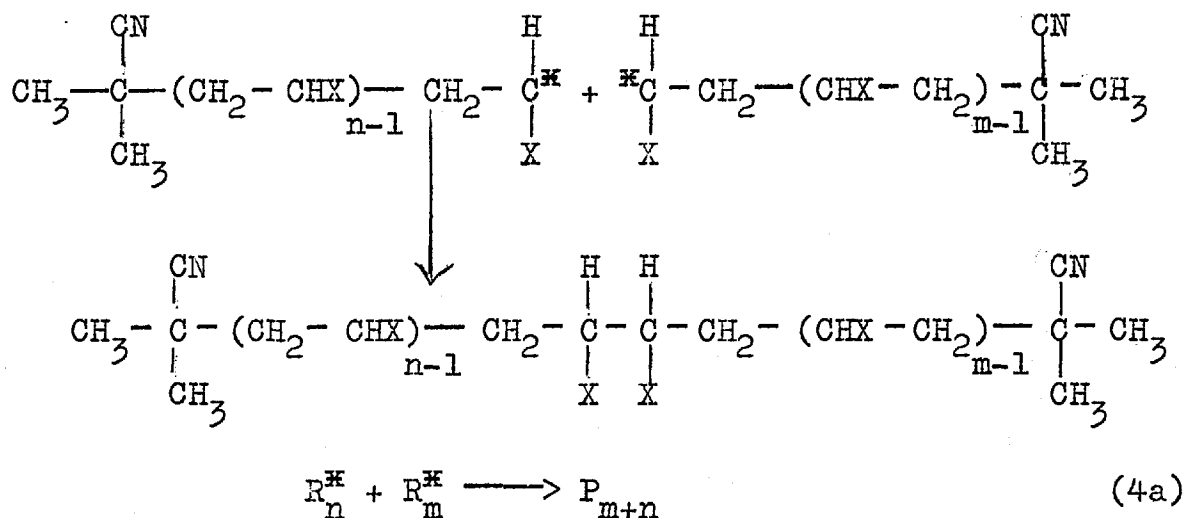
(b) <u>Disproportionation</u>. This involves the migration of a hydrogen atom along the chain or during a collision which causes the saturation of the free chemical valencies, with the production of two inactive polymer molecules P_m and P_n .

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CN}{|}}{C}} - (CH_2 - CHX) \underset{n-1}{} - CH = CHX \quad +$$

$$CH_2X - CH_2 - (CHX - CH_2) \underset{m-1}{} - \underset{\underset{CH_3}{|}}{\overset{\overset{CN}{|}}{C}} - CH_3$$

$$R_n^{\ast} + R_m^{\ast} \longrightarrow P_n + P_m \tag{4b}$$
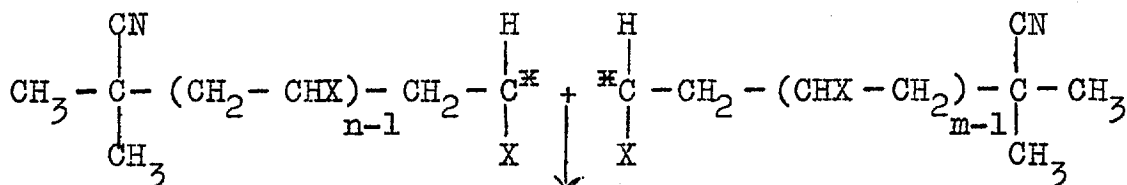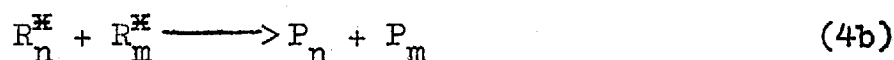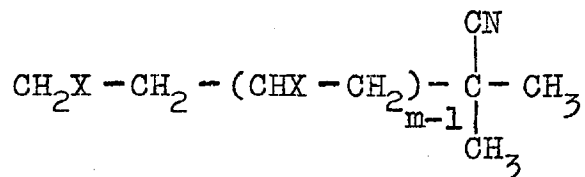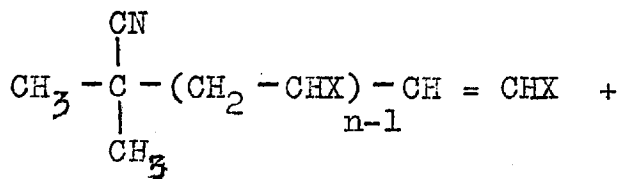
It is difficult to say which of the two types of termination is involved in a particular system. There is considerable evidence to show that termination by combination is the predominant one for the polymerisation of styrene at atmospheric pressure while in the case of methyl methacrylate termination occurs predominantly by disproportionation. (10, 12, 35, 39).

Whether the self-termination is by combination or by disproportionation, the rate of disappearance of chain radicals in both cases will be

$$k_t \ [R^{\ast}]^2$$

where $k_t = (k_{tc} + k_{td})$.

If x denotes the fraction of termination reactions which occur as a result of disproportionation, the following

relationship is obtained: $x = k_{td} / (k_{tc} + k_{td})$.

Two other radical termination processes may also take place, involving primary radicals:

$$R^x + Z^x \longrightarrow \text{products} \qquad (5)$$
$$Z^x + Z^x \longrightarrow \text{products} \qquad (6)$$

These processes have a profound effect on the polymerisation kinetics if the initiator concentration is very high and/or the momomer concentration is very low. In such cases the initiator radicals also participate in this step.

(iv) <u>Chain Transfer</u>.   According to the older concept it was assumed that the degree of polymerisation was equal to the kinetic chain length and that the degree of polymerisation should be proportional to the square root of monomer concentration when the catalyst was present.   It was observed by a number of workers that in many polymerisation systems the degree of polymerisation was lower than that predicted by the above kinetic scheme.   This indicated that some side reaction was also going on which terminated the polymer chain without destroying the activity for growth.   (40-41).

In order to explain this deviation, Flory (10) intro-
duced the concept of "chain transfer". He assumed that
the activity of a growing polymer chain may be transferred
to a monomer, polymer, initiator or solvent molecule, which
may grow by successive addition of monomer molecule, al-
though the original polymer chain has ceased to grow.
The chain transfer reaction usually involves the transfer
of a hydrogen atom or other labile atom or group.

There are two possible reactions in case the chain
transfer takes place with monomer. With styrene, for
example it proceeds:

$$R.CH_2.\overset{\text{x}}{CH}.C_6H_5 + CH_2 = CH.C_6H_5 \longrightarrow R.CH = CH.C_6H_5 + CH_3.\overset{\text{x}}{CH}C_6H_5$$

$$(7a)$$

$$R.CH_2.\overset{\text{x}}{CH}C_6H_5 + CH_2 = CHC_6H_5 \longrightarrow R.CH_2 - CH_2.C_6H_5 + CH_2 = \overset{\text{x}}{C}.C_6H_5$$

$$(7b)$$

or in general

$$R^{\text{x}} + M \longrightarrow P + M^{\text{x}} \tag{7}$$
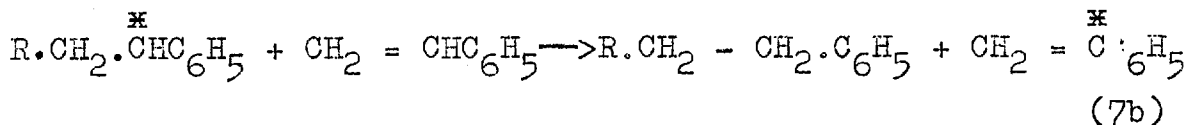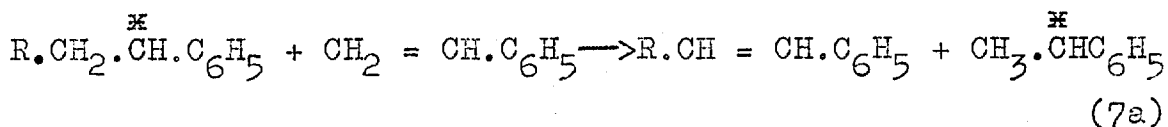
When the transfer to monomer and/or polymer is rapid,
branched structures may result leading to cross-linkings:

$$R^{\text{x}} + R - CH_2 - CH(C_6H_5) - R \longrightarrow RH + R - CH_2 - \overset{\text{x}}{C}(C_6H_5) - R$$
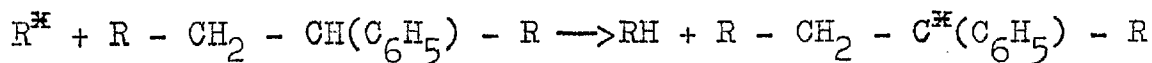
which can be generalised to

$$R_m^{\ast} + P_n \xrightarrow{\text{kp}} P_m + R_n^{\ast} \tag{8}$$

There has been considerable interest in chain transfer studies with halogen-containing compounds and of these carbon tetrachloride has been thoroughly studied. The following mechanism has been suggested by Walling (11) to explain the unusual reactivity of carbon tetrachloride:

$$\sim \overset{\overset{\text{H}}{|}}{\underset{\underset{C_6H_5}{|}}{C}}\cdot \quad Cl-CCl_3 \longleftrightarrow \sim \overset{\overset{\text{H}}{|}}{\underset{\underset{C_6H_5}{|}}{C}}{}^+ \dots\cdot \overset{\cdot}{Cl} \dots \overset{-}{C}Cl_3$$

or

$$\overset{\ast}{R} + CCl_4 \longrightarrow RCl + \overset{\ast}{C}Cl_3$$

In general,

$$R^{\ast} + S \xrightarrow{\text{ks}} P + S^{\ast} \tag{9}$$
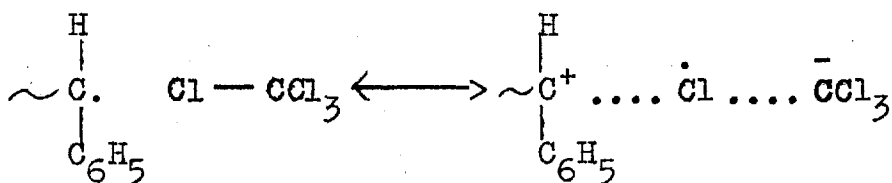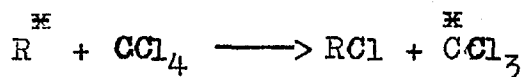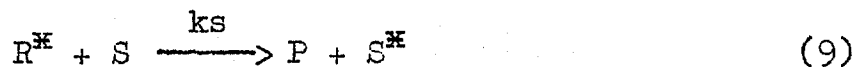
where S represents a substance, which may be a monomer, polymer, solvent, initiator or any other molecule present in the system and S^X is a derived radical which is capable of initiating further. Since the molecular weight is dependent on the nature and reactivity of S and the overall rate of polymerisation depends on the

reactivity of S^{*} radicals with the monomer molecules, it is obvious that if the reactivity of the radicals formed is equal to that of the chain radicals, then transfer will not affect the overall rate.

It may be pointed out that Walling's explanation has not been considered satisfactory and the question will be taken up in some detail while discussing the effect of pressure on the numerical values of the kinetic constants.

I.3   Kinetic Scheme for Liquid Phase Polymerisations

(a)   General Properties of the Polymerisation Reactions

Free radical polymerisation reactions have been the subject of systematic study and possess a number of characteristic features.   Firstly, out of the large variety of substituted olefins, only a limited number satisfy the structural requirements and yield polymers of high molecular weight.   It will be apparent from Table I, that the majority of the monomers falling into this category possesses the structure $CH_2 = C<$, which is of considerable importance:

Table I

Some Common Polymerisable Monomers

Name	Structural Formula
Ethylene	$CH_2 = CH_2$
Vinyl chloride	$CH_2 = CH.Cl$
Vinyl acetate	$CH_2 = CH.COO\ CH_3$
Vinylidene chloride	$CH_2 = C\ Cl_2$
Tetrafluoroethylene	$CF_2 = CF_2$

Name	Structural Formula
Acrylonitrile	$CH_2 = CH.CN$
Methyl acrylate	$CH_2 = CH.COO.CH_3$
Methyl methacrylate	$CH_2 = C(CH_3).COO.CH_3$
Styrene	$C_6H_5-CH = CH_2$
Butadiene	$CH_2 = CH - CH = CH_2$

Secondly, the rate of polymerisation is enhanced by heat, light and a very wide variety of substances including organic peroxides, azo compounds, metallic sodium, strong bases, strong acids etc. Zeigler, Natta and others (42-43) have developed a new technique of heterogeneous polymerisation involving the growing polymer chain as a nucleophilic species.

Thirdly, a significant property of free radical polymerisation is that the process producing each completed polymer molecule is over in a fraction of the time which is required for conversion of the whole system to polymer, i.e. the % conversion of the polymer increases with time but the molecular weight remains constant over a considerable extent of reaction. This characteristic feature is of great importance in the study of overall reaction.

(b) (i) <u>Assumptions for the Kinetic Scheme</u>

For setting up a kinetic scheme to include the various reactions considered above, it is necessary to introduce the following simplifying assumptions (11-14):

(a) that the chain length of the polymer is fairly long so that the propagation reaction consumes almost all the monomer,

(b) that the radical reactivity is independent of the length of the growing polymer radicals and that a single rate constant is applicable to all reactions involving large radicals. The validity of this assumption has been confirmed by Matheson (44) in the case of styrene.

(c) that the concentrations of all reactants may be taken as virtually constant (almost equal to their initial values). To ensure this the polymerisation reaction is allowed to proceed only to a low degree of conversion,

(d) that the rate of change of concentration of free radicals is so small as compared to their rates of formation and destruction that it may be assumed to be Zero, i.e. a 'stationary" or "steady state" is attained in the system.

(ii) Simplified Kinetic Scheme

Taking the simplest case and without considering the transfer reactions, a simplified reaction scheme is represented below:

1. $C \ \text{--------->} \ 2 \ Z^{\ast}$ k_d

2. $Z^{\ast} + M \longrightarrow R^{\ast}$ k_i

3. $R^{\ast} + M \longrightarrow R^{\ast}$ k_p

4. $R^{\ast} + R^{\ast} \longrightarrow P(+P)$ k_t
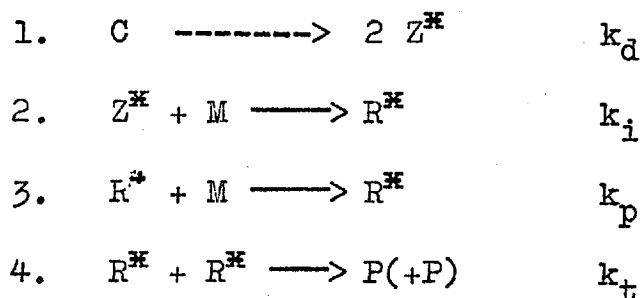
Assuming the steady state condition, the rate of initiation, I , is

$$I = k_t [R^{\ast}]^2 = 2 \ f \ k_d [C]$$

or $$R^{\ast} = (I/k_t)^{\frac{1}{2}} = \left\{ 2 \ f.k_d[C]/k_t \right\}^{\frac{1}{2}}$$

The rate of propagation, V , is

$$V = - \ d[M]/dt = k_p [M][R^{\ast}] + k_i [M][Z^{\ast}]$$

where k_d , k_i , k_p and k_t are the rate constants for the initiator decomposition, initiation, propagation and bimolecular termination respectively.   The letter f

denotes the efficiency of radicals Z^* in starting the chain and is defined mathematically as

$$f = \frac{\text{Rate of initiation of chain radicals}}{2(\text{rate of initiator decomposition})}$$

The value of f varies usually between 0.5 and 1.0, that is to say, between 50 and 100% of all the radicals produced ultimately initiate polymerisation.

Assuming that the rate of initiation, I , is independent of monomer concentration and that the initiator efficiency is quite high, the overall rate of polymerisation for long chains to grow is given by:

$$V = k_p[M][R^*]$$

$$= k_p[M](I/k_t)^{\frac{1}{2}} \tag{9A}$$

$$= d^{-1}[M]I^{\frac{1}{2}}$$

$$= d^{-1}(2\,f\,k_d)^{\frac{1}{2}}\,[M][C]^{\frac{1}{2}} \tag{10}$$

where d , also denoted by $\delta = k_t^{\frac{1}{2}} / k_p$.

In the case of thermal polymerisation, for simple diradical initiation

$$I = k_i [M]^2 , \text{ and}$$

$$V_{th} = d^{-1} k_i^{\frac{1}{2}} [M]^2$$

where V_{th} indicates the rate of thermal polymerisation.

For catalytic and thermal initiation,

$$V^2 = V_{th}^2 + \frac{(2fk_d)}{d^2} [M]^2[C]$$

The rate of thermal initiation usually varies with monomer concentration and the overall rate of polymerisation is thus proportional to $[M]^2$. Initiation rates are significantly low as compared to those obtained in the presence of an initiator.

(iii) The Transfer Equation

The average degree of polymerisation, $\overline{DP}$, which is represented by the number of monomer units in a given polymer molecule is given by

$$\overline{DP} = - \frac{d[M]}{dt} \bigg/ \frac{d(\overline{DP})}{dt}$$

Adopting assumption (a), the monomer consumption may be equated to the rate of propagation:

$$V = - d[M]/dt = k_p [M][R^{\ast}]$$

Both termination by combination and transfer reactions result in the formation of a single polymer molecule, whereas in the case of termination by disproportionation two molecules of polymer are produced. Hence

$$1/\overline{DP} = \frac{(k_{tc}/2 + k_{td})[R^{\ast}]^2 + k_M [R^{\ast}][M] + k_s [S][R^{\ast}] + k_I [C][R^{\ast}] + k_p [P][R^{\ast}]}{k_p [M][R^{\ast}]}$$

where k_M , k_s , k_I and k_p are respectively the rate constants of chain transfer to monomer, solvent, initiator and polymer.

It follows from Section I.2, (iii), that

$$k_{tc}/2 + k_{td} = k_t (1+x)/2$$

so by introducing chain transfer constants, and on simplifying the above equation, we get:

$$1/\overline{DP} = (1+x) \frac{k_t}{2k_p} \frac{[R^{\ast}]}{[M]} + C_m + C_s \frac{[S]}{[M]} + C_I \frac{[C]}{[M]} + C_P \frac{[P]}{[M]} \quad (11)$$

In the simplest case, the following relationship has been shown to hold good:

$$R^{\ast} = V/k_p[M] = (I/k_t)^{\frac{1}{2}} = [2fk_d[C]/k_t]^{\frac{1}{2}}$$

and, also

$$[C] = k_t V^2/2fk_d k_p^2[M]^2$$

Assuming transfer to polymer to be negligible at low conversions, equation (11) can be rewritten as:

$$1/\overline{DP} = (1+x)\frac{k_t^{\frac{1}{2}}}{k_p}\left(\frac{fk_d}{2}\right)^{\frac{1}{2}}\frac{[C]^{\frac{1}{2}}}{[M]} + C_m + C_I\frac{[C]}{[M]} + C_s\frac{[S]}{[M]} \qquad (12)$$

or

$$1/\overline{DP} = (1+x)\frac{k_t}{2k_p^2}\cdot\frac{V}{[M]^2} + C_I\frac{k_t}{(2fk_d)k_p^2}\cdot\frac{V^2}{[M]^3} + C_m + C_s\frac{[S]}{[M]} \qquad (13)$$

If the transfer to monomer and initiator is negligible as in the styrene-azo-bis-iso-butyro nitrile (hereafter abbreviated to AIBN) system and Methyl Methacrylate-AIBN system , the above equation simplifies to:

$$1/\overline{DP} = (1+x)\frac{k_t}{2k_p^2}\frac{V}{[M]^2} + C_s\frac{[S]}{[M]} \qquad (14)$$

In the case of purely thermal polymerisations,

$$1/\overline{DP} = 1/\overline{DP}_o + C_s\frac{[S]}{[M]} \qquad (15)$$

where $1/\overline{DP}$ denotes the degree of polymerisation in bulk in the absence of any solvent, $[S] = 0$.

Equation (15) is known as Mayo's equation (45). C_S may be determined from a simple plot of $1/\overline{DP}$ versus $[S]/[M]$. Gregg and Mayo (46) utilised this relationship in calculating the transfer constants for styrene with various solvents, the results for each solvent giving good linear plot; and all extrapolating to the value of $\overline{DP}_0$.

The value of C_S depends upon the nature of monomer and solvent and the temperature of polymerisation but is independent of $[S]/[M]$ ratios in a set of experiments.

(iv) Absolute Reaction Rate Constants

For the comparison of radical reactivity of the monomers involved, the function k^2_p/k_t (denoted by δ^{-2}) can be determined by using any of the equations (9A), (10) and (14), although it must be pointed out that considerable experimental error is involved in the determination of k^2_p/k_t and therefore in derived values of k_p and k_t . For styrene and methyl methacrylate at 60°C, the values of δ^{-2} are 0.0007 and 0.028 respectively.

Methyl methacrylate is thus more reactive than styrene.
(36, 39). The basic parameters for the determination
of k_p and k_t are rate of initiation I , and the
rate of polymerisation, V , and τ_S , a quantity which
is equal to the radical concentration at the steady state
divided by the rate of disappearance of radicals. Any
small error in τ_S will give considerably lower values
of k_p and k_t but increasing the error in k_t .
Similar situation will arise when a positive error is
introduced in I , which will lower the values of k_p
and k_t . There is considerable difficulty in the
exact determination of τ_S .

Despite this uncertainty it is worthwhile to com-
pare some of the best values obtained for a few monomers
at a temperature of $60^{\circ}C$. (11).

Table I

Absolute Rate Constants for Chain Propagation
and Termination in Vinyl Polymerisation.

Monomer	k_p litre mole-second	E_p K cal	$K_t \times 10^{-7}$ litre mole-second	E_t K cal
Styrene	145	7.3	0.30	1.9
Methyl Meth-acrylate	705	4.7	1.8	1.2
Methyl acrylate	2090	~ 7.1	0.47	~ 5
Vinyl Acetate	2300	6.3	2.9	3.2
Vinyl Chloride	12300	3.7	2300	4.2

(v) Experimental Tests of Simplified Kinetic Scheme

The validity of equation (11) and the assumptions
made in deriving the general transfer equation have been
proved by examining a number of monomer-initiator systems
for the dependence of the overall rate of polymerisation
on the concentrations of monomer and initiator.   Assuming
the rate of initiation to be independent of the monomer
concentration, the rate equation (10) becomes

$$V = d^{-1}[M]I^{\frac{1}{2}}$$

It is apparent from the above equation that the overall
rate is proportional to the square root of the initiator
concentration.   This has been confirmed in the case of
the styrene-benzoyl peroxide system at $60^{\circ}C$. (47).   The
dependence of the rate on the square root of the initiator
concentration has also been proved in the case of Methyl
methacrylate polymerised at $50^{\circ}C$. with azobisisobutyro-
nitrile (48).   The above relationship has also been
found to hold good in the bulk and solution polymerisation
of Vinyl acetate (22, 49-52).   The kinetic orders for
different monomer-initiator systems have been reported by
a number of workers (53-59).

Deviations of the exponent from its square-root value have been reported in the literature (59-63, 84, 93). A lower value has been reported by Van Hook and Tobolsky (63) in bulk polymerisation with high initiator concentration. Similar results were obtained for lower monomer concentrations with moderate initiator concentrations.

The determination of the order of reaction with respect to the monomer concentration has proved to be comparatively difficult because of the complications involved by the introduction of a solvent in the system and it would appear that there is no general agreement on the value of this exponent. According to some workers (57, 64-67), the order depends on the monomer concentration and is represented by the following equation:

$$-\frac{d[M]}{dt} = k[M][C]^{\frac{1}{2}}E^{\frac{1}{2}} \qquad (16)$$

where $E = \frac{B[M]}{1 + B[M]}$ and B is a constant for a

particular system at a constant temperature. Accordingly, the order should lie between 1.0 and 1.5 depending

upon the magnitude of B[M] and most of the values so
far reported for styrene and methyl methacrylate lie in
this range.   Anderson, Burnett and Gowan polymerised
MMA with AIBN in the presence of halogenated benzenes
and naphthalene and reported an order of reaction with
respect to monomer concentration *of* less than unity (68).
The whole matter was fully investigated by Horikx and
Hermans (67) who used the new experimental technique
of the open system flow method.   They polymerised
styrene in toluene solution at 80°C using benzoyl
peroxide as an initiator.   They found that the order
of reaction with respect to monomer concentration in-
creases from 1.18 at [M] = 1.8 moles/litre to 1.36 at
[M] = 0.4 moles/litre.   These results are in accord with
equation (16), with B = 1.19 litres/mole.   In their
interpretation of the results, they preferred Matheson's
view (69) to that of Schulz and Husemann (64), according
to which a fraction of the radicals formed in pair from
the initiator recombine by a "cage" effect before
escaping from each other's proximity.   This will be
discussed in a subsequent section.

        In the bulk polymerisation of styrene, the order
of reaction with respect to monomer concentration is

low (70).   This has been attributed to the "gel-effect" (71), also known as "autoacceleration" or "Trommsdorff effect".   This effect is very pronounced in the case of methyl methacrylate and methylacrylate (72).   'It is independent of initiator and is due to a decrease in the rate at which the polymer molecules diffuse through the viscous medium, thus lowering the ability of two long-chain radicals to come together and terminate" (73).

In the case of vinyl acetate, it may be noted that the monomer is exceedingly difficult to purify and the polymer formed at high conversions tends to be insoluble. The kinetic measurements have therefore been confined mainly to low conversions.   The kinetic order with respect to initiator concentration is 0.5 in the pure monomer (51), in benzene (22, 74), and in toluene solution (52).   The dependence of rate on monomer concentration is rather complex (51, 74).   Burnett and Melville (75) reported a first order dependence on monomer concentration (1.5 to 4.5 molar) in ethyl acetate but Conix and Smets (57) found an order of 1.5 in the same solvent in the range of 5-10 molar.   Still greater deviation of the order with respect to monomer concen-tration was observed by Burnett and Loan in benzene

solution at 60°C (76). Such deviations in the case of other monomers have also been studied (87-93).

The determination of rates of initiation is a part of the determination of individual velocity coefficients and is of interest in calculating the efficiency of the initiator. This can be determined in a number of ways.

Following the method of Baysal and Tobolsky (77), Tobolsky and Mesrobian (78) found that the rate and efficiency of initiation are independent of monomer concentration down to values of [M] as low as 3 moles/litre. Bevington and co-workers (79-81) have shown that the rate of initiation and hence the efficiency is generally independent of monomer concentration over a wide range, for concentrations above 1 mole/litre. They report an efficiency of about 60% and almost 100% for azo-bis-isobutyronitrile and benzoyl peroxide respectively at 60°C in the case of styrene. Below the above monomer concentration, there was a rapid decrease in f with [M] (80, 79).

The rate of production of free radicals is usually found by estimating the rates of disappearance of inhibitors and retarders. Probably the most accurate method is that of Bamford, Jenkins and Johnston (82)

who use ferric chloride, which behaves as an ideal in-
hibitor or retarder in the polymerisation of several
vinyl monomers.   Collinson and co-workers (83) have
also applied this method to a few determinations.   The
method is based on the reduction of ferric chloride to
ferrous iron and hence there is no ambiguity in the
number of initiator radicals reacting with one ferric
ion.   The rate of initiation can be determined by esti-
mating the ferrous iron formed volumetrically.   Bamford,
Jenkins and Johnston (84) found that the rate of initiation
of styrene in dimethyl formamide in presence of AIBN,
at $60^{o}C$ was independent of the monomer concentration over
a range of 0.4 to 2.2 moles/litre and their results were
in agreement with the findings of Bevington (80).   The
ferric chloride method has not given accurate results
with vinyl acetate because of the high reactivity of
its radicals (12).

Another method involves the use of the stable free
radical of α-α diphenyl β-picryl hydrazyl (DPPH)
which is prominent among such retarders.   It can be
prepared in the pure state and gives brilliantly coloured
solutions.   The DPPH is supposed to halt radical
chains via the process (11)

$$M^{\text{x}} + (C_6.H_5)_2 .N - \overset{\text{x}}{N}\!-\!\!\left\langle\begin{array}{c} NO2 \\ \\ NO_2 \end{array}\right\rangle\!\! NO_2 \longrightarrow$$

$$M\!-\!\!\left\langle\quad\right\rangle\!\! N(C_6.H_5) - NH\!-\!\!\left\langle\begin{array}{c} NO2 \\ \\ NO_2 \end{array}\right\rangle\!\! NO_2$$
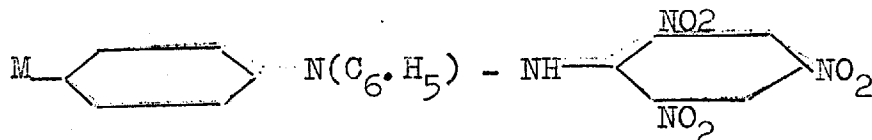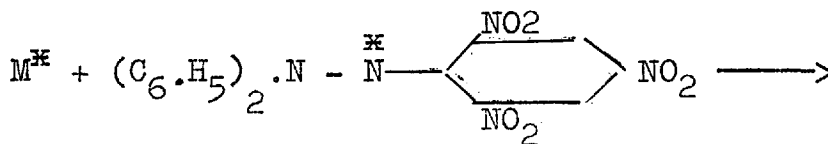
Reaction with a growing chain yields a colourless product which is probably due to the detachment of the hydrogen atom from the penultimate carbon atom.   At present the data on the interaction of radicals and DPPH is conflicting and the mechanism of the reactions is not clearly understood (85, 86).   The accuracy of this method is therefore questionable.

Duroquinone and benzoquinone have also been employed for determining. rates of chain initiation but the inhibition process is more complicated (11).

(vi) Modified Kinetic Schemes.

Several instances of departure from the simple scheme have been pointed out above.   Losheek and Co-workers (87) polymerised styrene in naphthalene at 60°C and noted a

variation in order of reaction with respect to monomer
concentration from 0.8 to 1.0.   George and Onyon (88)
studied the polymerisation of styrene in carbon tetra-
chloride at $60^{\circ}C$ with azo-bis-isobutyronitrile as an
initiator and their results when corrected for loss of
low-molecular-weight polymer led to orders of 1.29 and
0.53 in monomer and initiator respectively.   Anderson,
Burnett and Gowan (68) observed "some novel effects in
solution polymerisation" of methyl methacrylate initiated
by AIBN in the presence of halogenated benzenes and
naphthalene.   In each case they reported an order of
reaction with respect to monomer less than unity.
Burnett and Loan (76) have reported an order of reaction
greater than 10 in the polymerisation of vinyl acetate
in benzene at $60^{\circ}C$.   The photosensitized polymerisation
of vinyl chloride in tetrahydrofuran has been studied by
Burnett and Wright (89), using either AIBN or 1,1' azo-1
cyclohexane nitrile as initiator over the temperature
range 25°-$55^{\circ}C$ and an order of 1.46 with respect to
monomer concentration is reported.

The catalysed polymerisation of vinyl benzoate has
been investigated and the rate of polymerisation is stated
to be directly proportional to the initiator concentration

(90). This result has been challenged by Smets and Vrancken (91) who claim that the result is due to the presence of impurities in the monomer and that the kinetics of purified monomer are normal.

Bartlett and Altschul (92) studied the kinetics of allyl acetate in the presence of benzoyl peroxide and found that throughout the course of reaction, the rate of disappearance of monomer was directly proportional to the rate of consumption of initiator.

Cooper (93); Van Hook and Tabolsky (63); and Bamford, Jenkins and Johnston (84) have reported values lower than 0.5 for order of reaction with respect to initiator concentration.

In order to account for these departures, various modifications to the simple reaction scheme have been proposed and some of these are discussed below.

(a) The Monomer-Initiator Complex Theory

In view of the evidence from several investigations (64-66) that the order of the photochemical or catalysed reaction with respect to styrene concentration is intermediate between 1.0 and 1.5, an explanation was put forward by Schulz and Husemann (64) who proposed an equation

identical in form to equation (16). They assume that the catalyst (benzoyl peroxide in their case) forms a complex with the monomer with the result that the order of reaction with respect to monomer will be greater than unity, going as high as 3/2 for low values of monomer concentration. Assuming that the rate of initiation is equal to the rate of decomposition of the complex, the following equation was derived, similar to equation (16) in which B is equal to K_c , the equilibrium constant for the formation of complex and k_c stands for the rate constant for its decomposition:

$$\frac{-d[M]}{dt} = k_p \left[\frac{k_c \cdot K_c [c]}{k_t} \right] [M]^{\frac{3}{2}} \left[1 + K_c [M] \right]^{-\frac{1}{2}} \qquad (17)$$

Mayo et al (47) did not find the above explanation tenable as there was no experimental proof for the formation of monomer-initiator complexes in their melting point diagram of styrene-benzoyl peroxide mixtures. Another weakness of this theory is the increase in the value of B with temperature observed by Schulz and Husemann, whereas for a true equilibrium constant a decrease is to be expected.

(b)   The Cage-Effect Hypothesis.

This comparatively satisfactory explanation was proposed by Matheson (69) who took into account the views of Frank and Rabinowitsch (94).   This hypothesis assumes a physical effect of the solvent (and the monomer) on the surroundings of the radicals in that the primary radicals produced by the initiation are entrapped by the surrounding monomer and solvent molecules and some of the trapped radicals, instead of initiating a polymer chain, combine with each other within the "cage".   According to these ideas the decomposition proceeds according to the following scheme:

$$(C_6H_5.Coo)_2 \rightleftharpoons [2\ C_6H_5.Coo.] \longrightarrow [C_6H_5Coo\ C_6H_5 + Co_2]$$

or any other products

$$C_6H_5Coo\cdot + C_6H_5Coo\cdot$$

$$C_6H_5\cdot + Co_2$$

Brackets are used for substances within the cage. A corresponding scheme will represent the decomposition of other initiators.   A probable mechanism is considered below, where Z^{x} and R^{x} are primary and chain radicals,

Q represents the products of the recombination of the primary radicals trapped in 'cage' and the brackets denote species contained within a solvent cage:

1. $C \longrightarrow (2Z^{*})$ k_d

2. $(2Z^{*}) \longrightarrow Q$ k_R

3. $(Z^{*}) + M \longrightarrow R^{*}$ k'_p

4. $(Z^{*}) \rightleftharpoons Z^{*}$ k_D

5. $Z^{*} + Z^{*} \longrightarrow$ products   --

6. $Z^{*} + M \longrightarrow R^{*}$ --

7. $R^{*} + M \longrightarrow R^{*}$ k_p

8. $R^{*} + R^{*} \longrightarrow P$ k_t
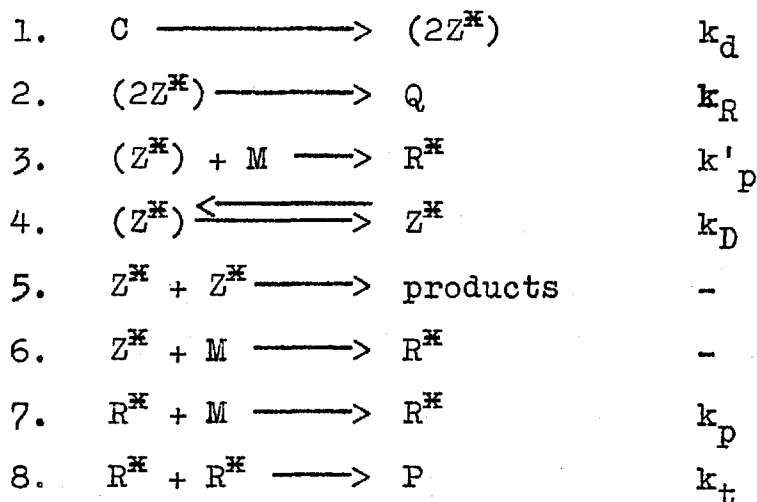
Steps 2, 3 and 4 are the alternatives available to a caged primary radical: (i) primary recombination, (ii) reaction with a monomer molecule in the "walls of the cage" and (iii) diffusion out of the cage. Steps 5 and 6, are similar to 2 and 3 and take place in the main body of the solution after reaction 4 has occurred, except that step 2 is a first order process because the radicals exist in pairs which are quite independent as a result of the 'cage' effect.

Applying the hypothesis of the stationary state (95) the following equation is obtained for long chains:

$$\frac{-d[M]}{dt} = d^{-1}k_d^{\frac{1}{2}}[M][C]^{\frac{1}{2}}\left[\frac{k_D + k_p'[M]}{k_R + k_D + k_p'[M]}\right]^{\frac{1}{2}} \qquad (18)$$

If k_D is much greater than $k_p'[M]$, the order of reaction with respect to monomer is unity. But if k_D is much smaller than $k_p'[M]$, the rate $\frac{-d[M]}{dt}$ would be proportional to

$$[M]\left[\frac{k_p'[M]}{k_R + k_p'[M]}\right]^{\frac{1}{2}}$$

so that the order of reaction with respect to monomer concentration varies from 1.5 to 1.0 as [M] increases.

Although Horikx and Hermans (67) have strongly supported the cage-effect hypothesis, Flory (14) regards this explanation as unrealistic. He observed that the rates of radical addition processes such as step 3 are invariably lower than those of the diffusion process, step 4. Flory's criticism has been supported by Jenkins (95) who fully investigated the situation and came to the conclusion that Matheson's hypothesis fails to offer a fully satisfactory explanation for retardation.

(c) <u>Solvent Retardation Theory</u>

Most of the early work has regarded the solvent as simply a diluent for the monomer, although its physical influence was realised as in the 'cage' hypothesis. While studying the polymerisation of vinyl acetate in toluene, Cuthbertson, Gee and Rideal (51) supported Flory's view (lo) that a solvent might ~~as well~~ participate in the polymerisation reactions. Burnett and Loan (76) also supported this view and explained the variation of order with respect to monomer concentration in terms of solvent transfer reactions.

The reaction scheme may be summarised as:

Transfer	$R^* + S \longrightarrow P + S^*$	k_s
Re-initiation	$S^* + M \longrightarrow R^*$	k_p''
Cross-termination	$R^* + S^* \longrightarrow P$	k_t'
Mutual termination	$S^* + S^* \longrightarrow$ Product	k_t''
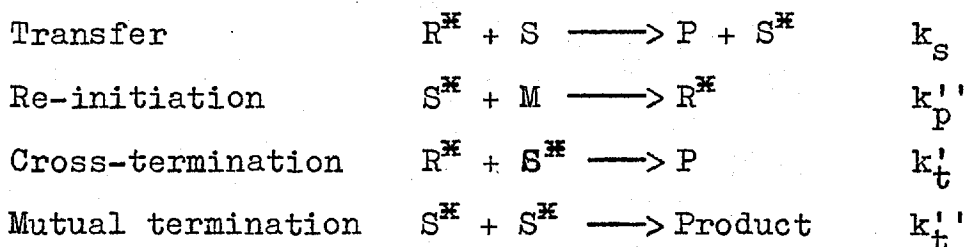
Burnett and Loan assumed that $k_s[R^*][S] = k_p''[S^*][M]$, that is, the rate of transfer to solvent was equal to the rate of initiation of the chains, and the same assumption was made by Thomas et al (96) in an identical kinetic scheme. They could not, however, offer any convincing proof of the validity of this theory which could account

for their results for the homogeneous polymerisation of acrylonitrile in solution.

The problem of retardation by solvent transfer was treated more thoroughly by Jenkins (97) who derived the following equation:

$$V = d^{-1}[M] \; I^{\frac{1}{2}} \; \frac{(I \; k_t)^{\frac{1}{2}}}{k_s[S] + (I \; k_t)^{\frac{1}{2}}} \qquad (19)$$

which predicts a variation of 0.5 to 1.0 in the kinetic order with respect to the initiation rate, depending upon the rate of initiation. This equation explains the observations of Burnett and Loan (76) and also makes it possible to calculate k_s. . But the calculated values for the styrene-toluene and the methyl methacrylate-benzene systems at $25^{\circ}C$ and $60^{\circ}C$ respectively were found to be much higher than those obtained from molecular weight measurements.

Burnett and Melville (52) investigated the vinyl acetate-toluene system using benzoyl peroxide and found the order with respect to initiator concentration to be approximately 0.5, whereas equation (19) predicts a higher exponent. Bevington et al (81) used tracer

technique for the determination of the order of reaction
in the polymerisation of vinyl acetate in benzene using
labelled benzoyl peroxide, and obtained similar results.
The retardation has been attributed to the inefficiency
of the phenyl radicals produced as a result of hydrogen
transfer to growing radicals, but this view has been
discounted by Bevington et al (81).   Benzoyl peroxide
decomposes in solution into benzoyloxy radicals:

$$C_6H_5CO.O.O.C_6H_5 \longrightarrow 2\ C_6H_5.CO.O.$$

which may lose carbon dioxide to give two phenyl
radicals of equal efficiency:

$$2\ C_6H_5.CO.O \longrightarrow 2\ C_6H_5. + 2\ CO_2$$
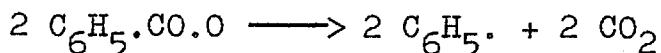
Using tracer technique, they found that the rate of
initiation was almost constant over a range of monomer
concentrations, indicating that the phenyl radicals
produced were not inefficient initiators.   But this
technique has a serious drawback in that differentiation
is not possible between the two labelled phenyl radicals,
namely, the one initiating the chain and the other which
enters a polymer chain by a termination process.

It has been reported that vinyl acetate copolymerises

with the solvent and the copolymer contains a small number of monomer units.   The mechanism of polymerisation of this monomer is therefore rather uncertain (98).

(d)   <u>Primary Radical Termination Theory</u>

According to Chapiro et al (99) the kinetics of polymerisation may be influenced by the participation of primary radicals in the termination reaction.   Thus

$$R^{x} + Z^{x} \longrightarrow P$$
$$Z^{x} + Z^{x} \longrightarrow products$$
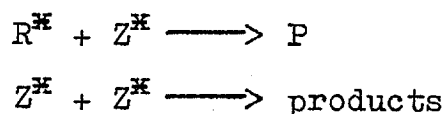
When the concentration of primary radicals $[Z^{x}]$, is large, these would participate more and more in the above two reactions; as a result of which the rate of initiation, I , and the rate of polymerisation will decrease.   By studying the γ-ray induced polymerisation of styrene in toluene at $19^{\circ}C$, Chapiro et al (99) found that the rate of polymerisation showed a tendency to become increasingly less dependent on the rate of radiation intensity (rate of initiation) and became almost independent at high rates of initiation.   Bamford, Jenkins and Johnston (84), using the same scheme, extended this theory.   By applying the geometric mean assumption to the three termination reactions:

$$k_5 = Z \, k_t$$

$$k_6 = Z^2 k_t$$

Writing $k_2/Z.(k_t)^{\frac{1}{2}} = K'$, the following equation is obtained:

$$V = k_p[M][R^{\divideontimes}] + k_2[M][Z^{\divideontimes}] \tag{20}$$

$$= d^{-1}[M].I^{\frac{1}{2}}\left[\frac{K'[M] + K'dI^{\frac{1}{2}}}{K[M] + I^{\frac{1}{2}}} \right] \tag{21}$$

For long chains:

$$V = k_p[M][R^{\divideontimes}]$$

$$= d^{-1}[M].I^{\frac{1}{2}}\left[\frac{K'[M]}{K'[M] + I^{\frac{1}{2}}} \right] \tag{22}$$

$$\frac{1}{V} = \frac{d}{[M]^2 K'}\left[1 + \frac{K'[M]}{I^{\frac{1}{2}}} \right] \tag{23}$$

In deriving the above equation, Bamford et al, assume
that the monomer concentration does not influence the rate
of initiation.   They verified this by polymerising styrene
in   N-N   dimethyl formamide at 60°C with AIBN, keeping the
monomer concentration constant and using fairly high con-
centrations of the initiator (0.02 to 0.659 moles/litre).
They did not study the effect of varying the monomer con-
centration.   The relationship between polymerisation
rate and initiator concentration was linear at low con-
centrations, as predicted by equation (23), but at higher
concentrations the slope slowly decreased, indicating
that an increase in initiator concentration gradually
lowered the exponent to zero.

The above findings are also in accord with the results
of Cooper (93) who investigated the styrene-nitrobenzoyl
peroxides systems.

The primary radical termination theory fails to give
a satisfactory explanation for the behaviour of the vinyl
acetate-benzene system in which small concentrations of
benzene.
~~some solvents~~ produce large retardations.   Bamford,
Jenkins and Johnston (84) have attempted to explain the
polymerisation of acrylonitrile in dimethyl formamide
on the basis of this theory but Thomas, Gleason and

Pellon (96) have observed a fairly pronounced effect of solvent on the rate of polymerisation. Obviously, the possibility of retardation by solvent transfer cannot be ignored. Further, the results of Bevington (79-80) and Van Hook (63) for styrene cannot be explained by the primary radical termination theory.

(vii) <u>Conclusions</u>

(a) <u>Modified Kinetic Schemes</u>

It would appear from the above survey that the kinetics of various monomer-solvent-initiator systems cannot be explained by any one scheme. The monomer-initiator complex theory fails in many respects and has therefore been abandoned. The solvent cage theory also falls short of offering clarification in a number of systems which have been studied. A satisfactory kinetic scheme for all systems should take into consideration the different reactions discussed in the solvent transfer retardation theory and the primary radical termination theory; and their contribution will depend upon the individual systems and the relative reactivities of the monomer, solvent and initiator. Such a kinetic scheme will be described subsequently.

(b) The Modified General Transfer Equation

(i) Solvent Cage theory

In interpreting the general transfer equation in the light of this theory, the first term in the equation becomes

$$d\ k_d^{\frac{1}{2}}\ \frac{[C]^{\frac{1}{2}}}{2[M]}\ \left[\frac{k_D\ +\ k_p'[M]}{k_R\ +\ k_D\ +\ k_p'[M]}\right]^{\frac{1}{2}}$$

It would appear that when k_D is much greater than $k_p'[M]$, the first term becomes a function of $[C]^{\frac{1}{2}}/[M]$. If k_D is much smaller than $k_p'/[M]$, the first term will become a function $[C]^{\frac{1}{2}}/[M]$ for larger concentrations of the monomer, and at lower concentrations will depend upon $[C]^{\frac{1}{2}}/[M]^{\frac{1}{2}}$.

(ii) Solvent Transfer Retardation Theory

In solvent transfer, the solvent radical termination reactions must be considered. Omitting the transfer terms for convenience,

$$1/\overline{DP}\ =\ \frac{k_t}{2k_p}\cdot\frac{[R^{\mathbf{x}}]}{[M]}\ +\ \frac{k_t'}{k_p}\frac{[S^{\mathbf{x}}]}{[M]}\ +\ \frac{k_t''}{2k_p}\frac{[S^{\mathbf{x}}]^2}{[M][R^{\mathbf{x}}]}\ +\ \text{etc.} \qquad (24)$$

$$R^{\mathbf{x}}\ =\ V/k_p[M]$$

$$=\ (I/k_t)^{\frac{1}{2}}\ (1\ +\ sF)^{-1}$$

where $[S^{\ast}] = F[R^{\ast}]$. The latter equalities, in which F is a function of rate constants, and initiation and monomer concentrations may be determined by applying "stationary states" and "geometric mean" assumptions(97).

If maximum retardation occurs, the first term takes the following form:

$$\frac{k_t}{2k_p} \cdot \frac{I}{[M]} \left[\frac{1}{k_s[S] + (I\,k_t)^{\frac{1}{2}}} \right]$$

This will be a function of $[C]/[M]$ if $k_s[S]$ is much greater than $(I\,k_t)^{\frac{1}{2}}$, but if the solvent concentration is very low, it will be proportional to $[C]^{\frac{1}{2}}/[M]$.

By using Burnett and Loan's relationship (76) and substituting $[R^{\ast}] = V/k_p[M]$, the general equation takes the following form when retardation is weak:

$$1/\overline{DP} = \frac{V}{[M]^2} \cdot \frac{d^2}{2} + \frac{k_t' \cdot k_s}{k_p^2 \cdot k_p'} \frac{[S]}{[M]} + \frac{k_t'' + k_s^2}{(k_p \cdot k_p')^2} \frac{[S]^2}{[M]^2} + \text{etc.} \quad (25)$$

Van Hook and Tobolsky (63) and Jenkins (97) arrive at the same result in the case of weak retardation, so that for normal values of the rate of initiation, I , $k_p'[M]$ is greater than $s(I\,k_t)^{\frac{1}{2}}$. Thus the first term takes the following form:

$$\frac{d}{2} \cdot \frac{I^{\frac{1}{2}}}{[M]} \cdot \frac{k_p[M]}{[M] + k_s[S]}$$

It would appear that the first term is a function of $[C]^{\frac{1}{2}}/[M]$, as $k_p[M]$ is greater than $k_s[S]$ for all but the lowest concentrations of the monomer.

(iii) <u>Primary Radical Termination Theory</u>

The general transfer equation takes the following form:

$$1/\overline{DP} = \frac{k_t}{2k_p} \cdot \frac{[R^*]}{[M]} + \frac{k_s}{k_p} \cdot \frac{[Z^*]}{[M]} + \frac{k_6}{2k_p} \cdot \frac{[Z^*]^2}{[M][R^*]} + \text{etc.} \qquad (26)$$

where $[Z^*]$ and $[R^*]$ are determined by assuming the stationary states attainment (84):

$$[R^*] = (I/k_t)^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}/K'M)$$

$$[Z^*] = (I/k_t)^{\frac{1}{2}}/Z(1 + K'M/I^{\frac{1}{2}})$$

(c) <u>Chain Transfer Studies</u>

It would appear from the equation

$$1/\overline{DP} = (1+x)\delta \cdot \left(\frac{fk_d}{2}\right)^{\frac{1}{2}} \frac{[C]^{\frac{1}{2}}}{[M]} + C_M + C_I \frac{[C]}{[M]} + C_S \frac{[S]}{[M]} \qquad (a)$$

that for the experimental determination of chain transfer constants, the ratio $[C]^{\frac{1}{2}}/[M]$ must be kept constant, whereas if the rate of initiation, I, is taken as

$$I = k_i[M][C]$$

the transfer equation becomes:

$$1/\overline{DP} = (1+x).\frac{\delta}{2}.(k_i\frac{[C]}{[M]})^{\frac{1}{2}} + C_M + C_I\frac{[C]}{[M]} + C_S\frac{[S]}{[M]} \qquad (b)$$

Equations (a) and (b) can be used for the determination of C_S, C_I and C_M and also for finding out the value of δ. Equation (b) suggests that C_S can be obtained from the slopes of lines relating to $1/\overline{DP}$ to $[S]/[M]$, by keeping $[C]/[M]$ constant, and is quite in agreement with the results of Basu et al (100) and other workers (101-105).

Toohey and Weale (106) polymerised styrene in toluene, ethyl benzene and triethylamine at 60°C, initiated by dibenzoyl peroxide and α-α' azo-bis-isobutyronitrile. Using equations (a) and (b) they obtained the C_S values 2.6 x 10⁻⁵ and 11.0 x 10⁻⁵ respectively in the toluene-benzoyl peroxide system. The former value, determined by keeping $[C]^{\frac{1}{2}}/[M]$

constant was not very far from the thermal value of 1.25×10^{-5}. In fact, none of the methods gives results in agreement with those from thermal polymerisation in the case of less active solvents like toluene. Equation (a) is however better than equation (b) in this respect. In the case of the styrene-triethylamine system the values of C_S obtained by keeping $[C]^{\frac{1}{2}}/[M]$ constant were not significantly different from those in which $[C]/[M]$ was kept constant. It should be noted that triethylamine is comparatively a more active solvent than toluene.

In view of the above conclusions, the ratio $[C]/[M]$ was kept constant throughout the present work, in which styrene was polymerised in tetrachloroethylene which is an active solvent. AIBN was chosen as initiator because it does not participate in the transfer reactions.

The most noteworthy effect of chain transfer is upon molecular weight and its study has engaged the attention of many workers. It gives particularly useful information on the relation between structure and reactivity in radical displacement reactions. The majority of determinations of transfer constants have

been for styrene polymerisations and some of the values
are given in Table II (46).

Table II

Transfer Constants of Hydrocarbons with Polystyrene Radicals at $60^{\circ}C$ and $100^{\circ}C$.

Substance	$C_S \times 10^4$		Activation energy
	$60^{\circ}C$	$100^{\circ}C$	k cal
Benzene	0.018	0.184	14.8
t-Butylbenzene	0.06	0.55	13.7
Toluene	0.125	0.65	10.1
Ethyl benzene	0.67	1.62	5.5
Isopropyl benzene	0.82	2.0	5.5
Triphenyl methane	3.5	8.0	5.1
Cyclohexane	0.024	0.16	13.4

Basu, Sen and Palit (108) have studied the polymer-
isation of methyl methacrylate in benzene, toluene and
halogen-containing solvents.   (Table IV).

Transfer constants for halogen-containing compounds

are of considerable interest and some of the transfer
constants for styrene and methyl methacrylate with
typical solvents are given in Tables III (45, 109-111)
and IV (108).

Table III

Transfer Constants of some Halides with
Polystyrene Radicals at $60^{\circ}C$ and $100^{\circ}C$.

Substance	$c_S \times 10^4$	
	$60^{\circ}C$	$100^{\circ}C$
n-butyl chloride	0.04	–
n-butyl bromide	0.06	–
n-butyl iodide	1.85	–
methylene chloride	0.15	–
chloroform	0.5	–
Ethylene dichloride	0.32	–
Tetrachloroethane	–	18
Carbon tetrachloride	92[*]	180
Carbon tetrabromide	13600	23500
Benzyl chloride	1.56	–
Benzal chloride	50	–
Benzo trichloride	57.5	–
chlorobenzene	–	approx. 0.5

[*] Compare values reported by George and Onyon (88) and
Walling and Pellon (112)

Table IV

Transfer Constants of Some Compounds with
Polymethyl methacrylate Radicals at $80^{o}C$.

substance	$C_S \times 10^4$
Benzene	0.075
t-Butyl benzene	0.26
Toluene	0.525
Ethylbenzene	1.35
iso-Propyl benzene	1.9
Butyl chloride	1.2
chloroform	1.4
methyl chloroform	0.6
Carbon tetrachloride	2.39
Chloro benzene	0.2

It has also been noted (113) that with halogen
containing transfer agents, styrene exhibits a higher
transfer constant at $80^{o}C$ than methyl methacrylate,
while the opposite order is found with hydrocarbon
transfer reagents.

In Table III, carbon tetrachloride possesses a very

high transfer constant, $C_S' = 180$ (100°C). This means that a growing styrene chain attacks carbon tetrachloride about one-fiftieth as readily as it adds another monomer to the chain.

The transfer constants of triethylamine with various polymer radicals are shown in the following table (106, 107).

Table V

Transfer Constants of Triethylamine with Various Polymer Radicals at 60°C

Polymerising monomer	$C_S \times 10^4$
Styrene	7.1
Methyl methacrylate	8.3
Methyl acrylate	400
Vinyl acetate	370
Acrylonitrile	5900

Carbon tetrabromide is a much more reactive substance and even traces of this material profoundly affect molecular weight. Some of the transfer constants are given in Table VI (107, 113).

Table VI

Transfer Constants of Carbon Tetrabromide
with Various Polymer Radicals at 60°C.

Polymerising monomer	C_S
styrene	2.2
p-chlorostyrene	5.2
Methyl methacrylate	0.27
Methyl acrylate	0.41
Vinyl acetate	> 39
Acrylonitrile	0.19

Many sulphur compounds possess high transfer reactivity which is apparent from the figures shown in Table VII (58, 114, 115).

Table VII

Transfer Constants of Sulphur Compounds
with Various Polymer Radicals at 60°C

Polymerising monomer	Transfer agent	C_S
Styrene	n-butyl mercaptan	22
Styrene	n-dodecyl mercaptan	19
Styrene	t-butyl mercaptan	3.6
Methyl methacrylate	n-butyl mercaptan	0.67
Methyl methacrylate	iso-propyl mercaptan	0.38
Methyl methacrylate	t-butyl mercaptan	0.18
Vinyl acetate	n-butyl mercaptan	48

A comparison of the rather scattered data on transfer constants with solvents for other monomers than styrene is given below (11):

Table VIII

Comparison of C_S for Different Monomer-Solvent Systems at 60°C. (All x 10^4)

Solvent	Styrene	MMA	Methyl acrylate	Vinyl acetate
Benzene	0.018	0.075	0.045	3
Toluene	0.125	0.525	2.7	21
Carbon tetra-chloride	90	2.4	1.25	$> 10^4$
Carbon tetra-bromide	13600	3300	4100	> 39 x 10^4

In general, the transfer constants for any one solvent increase in the order styrene > methyl methacrylate > acrylonitrile > methyl acrylate > vinyl acetate (11).

I.4.   Studies in Chain Transfer at Atmospheric
        Pressure.

(i) Introduction.

It has been noted by a number of workers that the
presence of certain solvents in vinyl polymerisation
reactions resulted in the a considerable decrease in the
molecular weight even though the overall rate was
unaffected (40, 41, 116, 64). Flory (10) attributed
this decrease to a side reaction which he termed "chain
transfer" as it involved the transfer of activity from
a growing polymer chain to a solvent, monomer, initiator
or polymer molecule. The chain transfer results in
the termination of growing polymer chains without
destroying the overall activity in growth. Shortly
after these results were published, some German workers
reported their observations on the thermal polymerisation
of styrene (40, 41, 116) and tried to explain their
results without taking notice of this new concept.
Bamford (117) and Walling (114) independently obtained
further direct evidence in support of Flory's views.
Mayo (45) as a result of his exhaustive researches on
chain transfer, and employing the kinetic scheme of
Flory (16), derived the following equation:

$$\frac{1}{DP} = \frac{1}{DP_o} + C_s \frac{[S]}{[M]}$$

in which $\overline{DP}_o$ is the value of $\overline{DP}$ in the absence of solvent and C_s is the ratio of the rate constants for the solvent transfer and propagation reactions. This is known as Mayo's equation and is in fact a simplified form of the general equation in the absence of an initiator. Mayo applied this equation to the work of the German authors (40, 41, 116) mentioned previously and by plotting $1/\overline{DP}$ against $[S]/[M]$ obtained C_s from the slope of the straight line, while the intercept corresponded to the reciprocal of $1/\overline{DP}$.

Medvedev et al (118) independently derived an equation similar to Mayo's.

(ii) The Determination of Transfer Constants.

The following transfer equations are generally used in the determination of chain transfer constants to solvent, monomer, initiator and polymer:

$$1/\overline{DP} = (1+x).d.(\frac{fk_d}{2})^{\frac{1}{2}}.\left[\frac{C}{M}\right]^{\frac{1}{2}} + C_I\left[\frac{C}{M}\right] + C_m + C_s\left[\frac{S}{M}\right] \quad ...(27)$$

$$1/\overline{DP} = (1+x).\frac{d^2}{2}.\frac{V}{[M]^2} + C_I\frac{d^2}{(2fk_d)}.\frac{V^2}{[M]^3} + C_m + C_s\left[\frac{S}{M}\right]$$
$$...(28)$$

$$1/\overline{DP} = 1/\overline{DP}_o + C_s\left[\frac{S}{M}\right]$$

It is obvious that the various general methods for the determination of transfer constants are mostly based on the measurements of the $\overline{DP}$ of the polymer, as the most noteworthy effect of chain transfer is upon the molecular weight of the polymer. It is therefore reasonable that molecular weight measurements should be employed to evaluate the competition between transfer and chain propagation processes.

Some of the more important conditions which must be satisfied and the precautions to be observed in the accurate determination of transfer constants are summarised below:

(1) It is very important that conversions must be kept low, particularly with substances of high transfer constants.

(2) The transfer agent should not affect the rate of polymerisation.

(3) Care should be exercised in the choice of an initiator when determining the transfer constants other than monomer or initiator. The initiator selected should not be susceptible to a transfer reaction or should have only a low transfer constant.

(4) The thermal rate of initiation, in the case of catalysed polymerisation, should be low as compared

to that arising from catalyst decomposition.

(5) If the transfer agent copolymerises with the monomer, measurements of $\overline{DP}$ and the results based thereon will not be valid.

(6) Initiator efficiency should not vary in the range of monomer concentration investigated, nor should a change in [S]/[M] lead to a change in the physical state of the polymer (for example, when a solvent also acts as a precipitant for the polymer).

(7) If viscosity measurements or indirect methods are applied in the determination of $\overline{DP}$, the correct relationship between the molecular weight and the limiting viscosity number must be chosen.

In many systems, due to a phase change or abnormal rates of polymerisation, the above conditions may not be fulfilled and the number of classes of compounds for which transfer constants may be determined becomes limited. However, Bamford and White (107) have been able to determine transfer constants under such conditions, by introducing certain plausible assumptions.

(a) Use of Mayo Equation.

The Mayo equation (15) is applicable in all thermally-initiated polymerisation for determining the solvent transfer constant by plotting the values of $1/\overline{DP}$ against

a range of [S]/[M] values. The slope of the straight line is equal to the transfer constant.

Although this method has been widely used, particularly by Mayo (21, 109, 115, 46) in the case of styrene and by Basu et al (108) for methylmethacrylate, it suffers from a serious drawback in that repoducible results are very difficult to obtain in the absence of initiator. Traces of oxygen are always present in high pressure experiments.

(b) Method of Relative Rates.

This method is particularly suitable for systems containing polymerisation regulators (like mercaptans which are very reactive transfer agents). It is not conveniently applicable to less reactive solvents. C_S may be derived by any of the following equations by measuring the relative rates of consumption of the monomer and transfer agent:

$$\frac{-d[M]/dt}{-d[S]/dt} = \frac{k_p[M][R^*]+k''_p[M][S^*]}{k_s[S][R^*]} \quad \ldots(29)$$

$$= \frac{[M]}{C_s[S]} + 1$$

The above relationships assume that solvent retardation is almost negligible and that $k''_p[M][s^*]$ becomes equal to $k_s[S][R^*]$.

However, if the reaction yeilds high polymer, $[M]/C_s[S] \gg 1$, the following simpler form of equation is valid:

$$\frac{d \log [S]}{d \log [M]} = C_s \quad .$$

The quantity d[s] can be determined by measuring the rate of inclusion of the regulator in the polymer or its rate of disappearance.

(c) <u>Dilution Method.</u>

In this method the ratios of the solvent and monomer concentrations are varied, keeping $[C]/[M]$ constant, using an inert diluent. It is thus possible to keep all terms on the right hand side of the transfer equation, constant, with the exception of the solvent transfer term. Gregg and Mayo (111) applied this method in their studies of the benzoyl peroxide initiated polymerisation of Styrene in carbon tetrachloride, using benzene $(C_s = 0.2 \times 10^{-5}$ at $60^{\circ}C)$ as an inert solvent. The value of C_s obtained was quite close to that obtained from the Mayo equation applied to thermal polymerisation. Fuhrman and Mesrobian (113) also employed this method in investigating the transfer constants of six vinyl mono-mers with carbon tetrabromide.

In the case of comparatively active solvents, the

solvent transfer term in the general transfer equation *may* be greater than the sum of all other terms. It is also very desirable in such cases to keep a narrow range of [S]/[M] values. Walling and Pellon (112) determined the transfer constants for $CC\ell_4$ with styrene using this procedure. Bamford (107) used this method for tertiary amines.

(d) Transfer Constants from overall Rates of Polymerisation.

Some of the methods described in this section are based on the experimental determination of $\overline{DP}$ (the degree of polymerisation) and V (the overall rate). Obviously these methods are less accurate than those in which only one experimental measurement is involved.

It is apparent from the general transfer equation:

$$\frac{1}{\overline{DP}} = (1+x) \frac{d^2}{2} \frac{V}{[M]^2} + C_I \frac{d^2}{(2fk_d)} \cdot \frac{V^2}{[M]^3} + C_m + C_s \left[\frac{S}{M}\right]$$

that if the reaction rate, and the reciprocal of the degree of polymerisation, are determined in bulk and solution polymerisation, it is possible to determine the values of C_s, C_m, C_I and $(1+x)d^2$ from the graph.

If the initiator transfer constant is negligible, as for AIBN with styrene and methylmethacrylate, or benzoyl peroxide with methylmethacrylate, a straight line

will be obtained by plotting the values of $1/\overline{DP}$ versus rate for bulk polymerisation, having a slope equal to $(1+x)d^2$ and an intercept equal to C_m on the $1/\overline{DP}$ axis. Although the value of C_I for benzoyl peroxide and styrene is not negligible, Tobolsky et al have used this method in the determination of C_m, by keeping the initiator concentration low (50, 119).

For solution polymerisations, with constant $[C]/[M]$, C_s may be found by plotting $(1/P-d^2V/2[M]^2)$ against $[S]/[M]$ which will give a straight line having a slope equal to C_s. This method has been applied by Palit et al (120-121) to determine the transfer constants to various solvents in the polymerisation of styrene and methyl methacylate. They report a fair agreement between values obtained from catalysed and uncatalysed experiments.

Another method based on the following modified transfer equation has been used by Breitenbach and Schindler (122):

$$\frac{[M]^2}{V}\left[1/\overline{DP} - C_m - C_I\left[\frac{C}{M}\right]\right] = (1+x)\frac{d^2}{2} + C_s\frac{[S][M]}{V}$$

$$...(30)$$

They polymerised styrene with benzoyl peroxide and AZO-bis-iso butyro nitrile in various chlorinated hydrocarbons at $70^\circ C$.

By plotting the left hand side of this equation
against $[S][M]/V$, they determined C_S from the slope
of the straight line, whose intercept was equal to
$(1+x) \cdot \dfrac{d^2}{2}$.

Palit et al (120) have suggested several other
methods for determining the transfer constants based
on the observed values of $1/\overline{DP}$ and V. They claim that
by the direct application of the modified transfer
equation, the transfer constant can be determined for
any monomer by single measurements of $\overline{DP}$ and reaction
rate; and further, that the values of the transfer
constants are in agreement with the values already
reported

As pointed out earlier, the methods described in
this section are less accurate than those based on the
$\overline{DP}$ measurements only. Moreover, the experimental results
of Palit and co-workers have been criticised by Tooltey
(123) and shown to be unsatisfactory in many aspects.
These authors purified methyl methacrylate by distilling
this monomer at $100^{\circ}C$, apparently in contact with air.
Further, they did not take into account the reactivity
of the solvent, i.e. whether normal (such as benzene)
or reactive (like ethyl benzene, chlorinated hydrocarbons etc.)

Tookey (123) and Bamford et al (12) consider that in
the determination of C_s for normal (less active) solvents
by plotting $1/\overline{DP}$ against $[S]/[M]$, more accurate results
are obtained by keeping the ratio, $[C]^{1/2}/[M]$, constant,
instead of $[C]/[M]$.

(iii)   <u>Effects of structure on Reactivity in Transfer.</u>

The data in Tables II - VIII give some information
about the relation between structure and reactivity
but this information is largely inferential. It is
evident from these tables that some solvents are
efficient chain transferring agents and considerably
reduce the degree of polymerisation, while others are
quite weak in this respect. The question naturally
arises as to the reason for the variation in chain
transferring activity. An examination of the transfer
constants for a series of related compounds suggests
that some atoms will undergo transfer more readily than
others. This is attributed to factors such as differences
in bond energy, and steric effects, as a result of which
the transfer activity of a solvent will generally be
displayed by one atom, that is the activity resides in
that atom. If there is more than one reactive atom in

the molecule, the most active in transfer will be the one attached to the most highly substituted carbon atom.

Mayo (45), using the observations of Price and Tate (25) attempted to correlate the magnitude of transfer constant with molecular structure. The work was elaborated by Gregg and Mayo (46) who investigated the thermal polymerisation of styrene. Their choice of solvents was confined to cyclic compounds only, due to the insolubility of polystyrene in aliphatic hydro-carbons (Table II). The values discussed below illustrate the reactivity of the benzyl hydrogen and the effect of substitution on the alpha-carbon atom.

In benzene and cyclohexane, the transfer constants for styrene polymerisation are low, (0.018×10^{-4} and 0.024×10^{-4} respectively), apparently because of the absence of any active hydrogen atoms. In toluene, however, the side-chain hydrogen atoms are very reactive owing to their attachment to a carbon atom linked directly to the electron-attracting phenyl nucleus. Consequently the side-chain hydrogen atoms can readily take part in the transfer reactions and the transfer constant of toluene is 0.125×10^{-4}. In ethyl benzene and isopropyl benzene, the increased reactivity, ($C_s = 0.67 \times 10^{-4}$

and 0.82 x 10^{-4} respectively), is due to the presence
of secondary and tertiary hydrogen. It is a well-known
fact that the reactivity of the hydrogen atom increases
in the order normal < Secondary < tertiary (124). In
the case of tertiary butyl benzene, there is no alpha-
hydrogen and consequently the transfer constant falls
back to a very low value, 0.06 x 10^{-4}, intermediate
between those of benzene and toluene. It may also be
noted that in the case of hydrocarbons listed in Table II,
the increasing activity is accompanied by decreasing
activation energy.

Gregg and Mayo (109) studied a number of oxygen-
and halogen-containing transfer agents and on the basis
of their observations concluded that the substituents
on the conjugate carbon atom had an activating effect
decreasing in the following order:

> Phenyl > carbo alkyloxy, carboxyl, carbonyl > halogen
> > hydroxyl, alkyl > hydrogen.

The above order is according to expectation on the basis
of stabilisation of the resulting transfer radical and
is almost in agreement with the earlier results of Mayo
and Walling (125), deduced from copolymerisation
experiments.

Basu, Sen and Palit (108) studied chain transfer
in the polymerisation of methylmethacrylate with seven
chlorinated hydrocarbons. These solvents differed widely
among themselves in their transfer activity which was
in the following order:

carbon tetrachloride > chloroform > Butylchloride

> Propylene chloride > 1:1:1 trichloroethane

> tetrachloroethane and chlorobenzene.

They further report that despite such wide difference
in their chlorine content, these solvents obey Mayo's
equation, justifying the correctness of the assumptions
involved. Mayo (45) assumed that the transfer activity
of a chloro-compound was a function of the chlorine
content in the molecule, but the above order shows that
this interpretation is not tenable in the case of compounds
having chlorine atoms attached to different carbon
atoms (86). For example, tetrachloroethane and propylene
chloride have lower transfer constants than that of
butyl chloride, and tetrachloroethane is as much resistant
to free radical attack as chlorobenzene.

The transfer constants for halogeno-benzenes are
generally close to those of benzene and the polymers are
almost free of halogen (21, 126, 127).

Of the various halogen-containing solvents, carbon tetrachloride has been thoroughly studied (47, 112, ~~113~~). Breitenbach and Maschin (126) studied the polystyrenes formed over a wide range of [S]/[M] ratios in this solvent and the polymer was found to contain four chlorine atoms per molecule. Breitenbach and Schindler (122) polymerised styrene in a variety of halogen-containing solvents. They obtained chlorine-free polymers in 1:2 dichloroethane with an [S]/[M] ratio of about 3, but in the case of 1:1:2:2: tetra-chloro-ethane, there were six atoms of chlorine per molecule, which is a surprisingly high figure.

It is at first surprising that the chain transfer reactivity of carbon tetrachloride - an apparently rather inert molecule, should be so high. The unusually high value is attributed to its ready decomposition under free radical attack. This view has been supported by the fact that a large variety of compounds capable of generating free radicals by decomposition invariably react with carbon tetrachloride and aliphatic chloro compounds. Hey and Waters (128) were able to prove that benzoyl peroxide on decomposition reacted with carbon tetrachloride giving chlorobenzene and hexachloroethane, that is to

say, the $.CCl_3$ radicals generated were destroyed by mutual combination. In the polymerisation reactions the growing polymer chain also attacks the carbon tetrachloride molecule, leading to the sequence of chain reactions. The $.CCl_3$ radicals generated propagate a new reaction chain, instead of being destroyed by mutual combination. Breitenbach and Maschin (126) and Mayo (129) proved the existence of $Cl_3.C$ $(-CH_2-CH(\phi)-)_n.Cl$ molecules in the polystyrene obtained in carbon tetrachloride. Such polystyrenes, prepared over a wide range of [S]/[M] ratios, contain four chlorine atoms per molecule, thus establishing the radical displacement mechanism.

Walling (11) has attempted to explain the high reactivity of carbon tetrachloride by ascribing it to the resonance stabilisation of the $.CCl_3$ radical produced in the transfer process (12k cal/mole from bond dissociation data) and to the comparative weakness of $C-Cl$ bonds. Less activation energy is therefore required for processes in which they are broken and formed. "It may be helped" says Walling (11) "by the additional strength of the Benzyl $C-Cl$ bond formed, due to overlap between the orbitals of the Cl and the benzene ring, and by the contributions of a polar effect. Similar arguments

must apply to the still higher reactivity of carbon tetrabromide". Walling's explanation has been criticised by Romani (130) who finds it unsatisfactory in accounting for the lower reactivity of chloroform with polystyryl radicals ($C_S = 0.4 \times 10^{-4}$). This will be discussed in Part III of this work.

It would appear from the above statement that a prediction of the C_S value in the case of chloro-compounds is not a simple matter, either on the basis of high chlorine content or from any structural considerations. In the case of hydrocarbons the active hydrogen hypothesis often works well. Most probably the bond energy of the C-Cℓ linkage plays an important role in the chloro-compounds in determining their susceptability to free radical attack. Dewar (131) suggested this idea in 1949. The values of the force constants of C-Cℓ bonds in different chlorine-containing compounds have been obtained by Raman spectra and are found to be in the order $CC\ell_4$ > $CHC\ell_3$ > Propylene dichloride (132).

Bamford and White (12) and Toohey and Weale (106) have investigated polymerisation reactions in tertiary amines and the values for some of the transfer constants

are given in Table ᛁᚼᛁ. V.

The mercaptans are particularly reactive transfer agents, with transfer constants greater than unity. This high reactivity is certainly due to the cleavage of the S-H bond. This view is supported by the fact that thiol-regulated polymers generally contain one sulphur atom per molecule, present as an organic sulphide, and also among the polymers obtained are β-phenyl-ethyl alkyl sulphides. Many sulphur compounds possess high transfer activity as may be seen from Table VII. It is interesting to note that unlike the behaviour of many compounds and particularly the hydrocarbons, they show a decrease in the value of transfer constant with increase in temperature.

As previously stated, Toohey and Weale (106) found it preferable to keep $[C]^{1/2}/[M]$ constant rather than $[C]/[M]$, in determinations of C_s via $\overline{DP}$ for inactive solvents such as toluene. Bamford and his colleagues (12) are also of the same view. In the course of the present work, however, the ratio $[C]/[M]$ was kept constant, in view of the comparatively more reactive nature of tetrachloroethylene.

I.5.   The Effect of Pressure on Reaction Rate.

(i)   Introduction.

Some of the earliest work on polymerisation under pressure is due to Bridgman and Conant (1-3) who in 1929 polymerised styrene, vinyl acetate, iso prene and 2:3 dimethyl butadiene at pressures ranging between 9000 and 12000 atmospheres, and noted a considerable increase in the rate of reaction.

Subsequently a number of workers (18, 19, 112, 133-143) have confirmed the accelerating effect of pressure. More recently much research on the effects of pressure on the rates of polymerisations and of other types of reaction has been carried out. Among those now active in this field are Weale (U.K.); Hamman, Ewald (Australia); Whalley, Laidler (Canada); Gonikberg (Russia); and Walling, Ehrlich, Le Noble, Brower, Wall (U.S.A.) (144).

(ii) The Theory of Reaction Rates at High Pressures.

The two theories of reaction kinetics which are equivalent but quite different in method of approach (145) have been used in explanation of the effects of pressure on reaction rates, namely the collision theory and the transition state (or activated complex) theory.

The latter permits greater insight into the details of the reaction process.

(a) The Collision Theory.

According to this theory when the reactions are bimolecular, the rate of reaction cannot exceed the collision rate of the molecules which comprise the activated complex. The classical collision theory leads to the following expression for the velocity constant, k, in the case of a bimolecular reaction

$$k = PZe^{-E/RT} \qquad \qquad ...(31)$$

where Z represents the collision rate. E is the activation energy, i.e., the minimum thermal energy per mole which colliding molecules need in order to react ("fruitful collision"), and P is a probability factor less than unity. The observed values of P cover a wide range and a unified treatment of the observed P values does not seem to be possible. This is a weakness of this theory.

The application of equation (31) to reactions under pressure only allows a determination of the separate effects of pressure on PZ and on E. For many reactions the analysis of the experimental data shows that both E and PZ are changed by pressure and may also be influenced

by different solvents (146). Such reactions can be best
interpreted on the basis of the transition state theory.

(b)   The Transition State Theory.

In the collision theory, detailed study of the
structure of the reacting molecules and the nature of
the activated condition is seldom required; and the
emphasis is generally on the collision rates and energy
of activation. In the transition state theory the
approach is different. The method requires the calculation
of the changes in energy and configuration of the system
as it passes from the reactants to products in the
activated complex, and the evaluation of the rate
constant by means of statistical mechanics. A general
reaction of the type

$$aA + bB + \ldots \longrightarrow X^{\ddagger} \longrightarrow \text{Products} \quad \ldots(32)$$
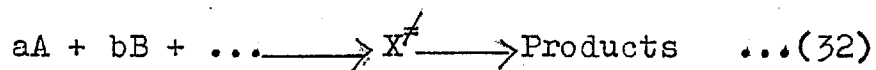
is assumed to proceed through a transition state X.
The transition state and the activated complex are often
used as synonymous terms, but strictly speaking, the
former refers to the set of coordinates and the latter
to the groups of atoms having this set of coordinates.
The rate constant is derived in the following form by
the application of statistical mechanics to the energetics
of the reaction (147,148):

$$k = \kappa \frac{KT}{h} (K^{\neq}) \qquad \dots (33)$$

where k is the rate constant usually defined in terms
of the concentrations of the reactions, κ is a transmission
coefficient representing the probability of the passing
over of the transition state to the products, rather
than reverting to the original reactants, aA, bB,..., K
is Boltzman's constant, h is Planck's constant, T is
temperature on the absolute scale and $K^{\neq}$ is the equi-
librium constant for the equilibrium between the reactants
and the activated complex.

The value of the transmission constant, κ, is
generally assumed to be close to unity and independent
of the temperature and pressure. Equation (33) can be
put in the following form:-

$$k = \frac{KT}{h} \cdot e^{-\Delta F^{\neq}/RT} \qquad \dots (34)$$

or

$$k = \left(\frac{KT}{h}\right) e^{\Delta S^{\neq}/R} e^{-\Delta H^{\neq}/RT} \qquad \dots (35)$$

or, assuming the activation energy to be equal to the
heat of activation (149),

$$k = (\frac{KT}{h})\ e^{\Delta s^{\neq}/R}\ e^{-E/RT} \qquad \ldots(36)$$

where the superscripts $\Delta F^{\neq}$, $\Delta H^{\neq}$ and $\Delta s^{\neq}$ represent the changes in these thermodynamic quantities when the transition state is formed from the initial reactants.

The following relationship may be derived from equation (34) after taking the logarithms, differentiating with respect to pressure and using the identity $\frac{dF}{dP} = V$:

$$\frac{d\ \ell n \kappa}{dP} = -\ \frac{\Delta V^{\neq}}{RT} \qquad \ldots(37)$$

or

$$-\Delta V^{\neq} = \frac{RT\cdot d\ \ell n \kappa}{dP} = \frac{RT\cdot d\ \ell n \kappa^{\neq}}{dP} \qquad \ldots(38)$$

Equations (37) and (38) were originally proposed by Evans and Polanyi (150). They link the pressure and the rate constant with the volume of activation, $\Delta V^{\neq}$, which denotes the change in volume when the transition state is formed from the initial reactants. Small correction terms will be introduced in this equation if the equilibrium constant $K^{\neq}$ is based on the molar scale, when the equation (38) takes the following form:

$$(\frac{d\ RT\ \ell n\ k_C}{dP})_{C=0} = -(\Delta V^{\neq})^{\infty} + (1-a-b\ldots)RT\kappa_s \qquad \ldots(39)$$

in which κ_s represents the compressibility of the solvent. This can be avoided if $K^{\neq}$ is expressed in terms of the molal concentration scale or the mole fractions (144, 151). Equation (39) will be reduced to equation (38) in the case of a first order reaction, when a = 1, and b = 0. In high pressure measurements of rate constants there is an uncertainty of a few Cm^3/mole due to experimental errors, which is generally greater than the factor $RT\kappa_s$ in equation (39).

$\Delta V^{\neq}$ can be determined from the experimental results by means of equation (37), but for a theoretic calculation a complete knowledge of the structural and electrical properties of the initial reactants, solvent and transition state would be essential. This involves the methods of statistical and quantum mechanics. However, it is often possible to predict the sign and order of $\Delta V^{\neq}$.

According to equation (37) if $\Delta V^{\neq}$ is negative, an increase of pressure will accelerate the rate. A positive value of $\Delta V^{\neq}$ implies that the reaction is retarded by pressure.

Although the "volume of activation" most often considered is the volume change at one atmosphere, it is necessary in order to clearly define it to state the

pressure. This is because $\Delta V^{\neq}$ changes with pressure
and occasionally the change is rapid.

Fawcett and Gibson in collaboration with Perrin
and Williams (152-155) published a series of papers on
the effect of pressure on the rates of Menschutkin
reactions. Their results have been summarised by Perrin
(5) who observed that pressure has an accelerating effect
on "slow reactions" in which the value of the entropy
of activation, $\Delta S^{\neq}$, is negative. This is true in the
case of polymerisation reactions. $\Delta V^{\neq}$ is related to
the free energy of activation, $\Delta G^{\neq}$,

$$\Delta V^{\neq} = \frac{d\ \Delta G^{\neq}}{dP} \qquad\qquad ...(4C)$$

where $\Delta G^{\neq}$ may either be equal to $-RT\ \ell n(\frac{kh}{KT})$ or $-RT\ \ell n\ K^{\neq}$
(145). Thus the value of $\Delta V^{\neq}$ may be found if the figures
for $\Delta G^{\neq}$ at different pressures are known.

(iii) Division of the Volume of Activation into Two Terms.

Evans and Polanyi (150) suggested that it is
convenient to split up $\Delta V^{\neq}$, a composite function, into
two terms: $\Delta V_1^{\neq}$, which is the change in volume of the
initial reactants aA, bB ... when they form the activated
complex; and $\Delta V_2^{\neq}$ which is the corresponding volume change of

surrounding solvent resulting from changes in electro-
striction (rearrangement of the solvent molecules).
Any marked change in the intermolecular forces when the
transition state is formed is likely to increase the
value of $\Delta V^{\neq}$. In the case of non-polar reactions there
is probably an insignificant contribution from $\Delta V_2^{\neq}$
and $\Delta V_1^{\neq}$ is the dominating term.

In the case of polar reactions it has been generally
found that the acceleration or retardation by pressure
is dependent on their electrical nature i.e. $\Delta V_2^{\neq}$ is
important. This is a conclusion which could not have
been arrived at on the basis of collision theory,
according to which reactions of the types

$$L_+ M \longrightarrow A, \ a \quad \ldots \ldots (i)$$

$$L^+ + M^- \longrightarrow A, \quad \ldots \ldots \ldots (ii)$$
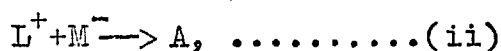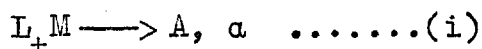
would both be accelerated by pressure, whereas in the
latter reaction retardation occurs (156).

(iv) The Overall Effect of Pressure on Polymerisation.

The accelerating influence of pressure on the rates
of polymerisation was studied by Conant and his collabora-
tors (1-3). They found a 10-fold increase in the rate
of polymerisation of isoprene at room temperature between

6000 and 12000 atm. They further observed that dissolved oxygen present in their high pressure experiments acted as a catalyst (initiator) through the formation of unstable peroxides. Shortly after these experiments, Tamman and Pape (133) studied the rates of polymerisation of five liquid olefins, including styrene, at pressures up to 3000 atm. and obtained the astonishing acceleration factor of 2.24×10^6 at $140^{\circ}C$ at 1500 atmospheres. However, on reinvestigation Gillham (138) discovered a number of serious shortcomings in their technique; and it is now clearly established that the actual figures should be less than 10 (138, 141). In Gillham's experiments the conversions to polymer were often between $20^{\circ}/o$ and $100^{\circ}/o$ and the results are not suitable for detailed kinetic analysis (157).

Another investigation of the kinetics of free radical polymerisation of styrene was made by Kobeko et al (137) but unfortunately the results are most inadequately presented. Very illuminating and detailed studies were however undertaken by Norrish and his collaborators (141-142) on the kinetics of styrene polymerisation at high pressures. Merrett and Norrish (141) in 1950 studied the catalysed polymerisation of styrene, using

benzoyl peroxide as initiator and at pressures up to 5000 Kg/cm² at 60°C. Their results, which represent the combined effects of pressure on the initiation, propagation and termination reactions show that:

(a) The overall rate of polymerisation is proportional at 1 atmosphere to the initiator concentration raised to the index 0.5. This drops at 3000 Kg/cm² to 0.4 and thereafter rises very slightly.

(b) Between a range of 2000 - 3000 Kg/cm², the rate increases exponentially with pressure but in the range of 3000 - 5000 Kg/cm² it is almost directly proportional to the pressure, for a constant initiator concentration. The overall rate is increased by 15-fold at 5000 Kg/cm², with 0.043 mole per cent of benzoyl peroxide.

(c) The molecular weights of the polymers increase with pressure up to about 3000 Kg/cm², becoming almost tripled between 1 and 3000.

Although the enhanced rate and the increase in polymer molecular weights have been shown to be mainly due to the accelerating effect of pressure on k_p and hence on $k_p/k_t^{1/2}$, there are other factors which may

affect the overall rate constants and the $\overline{DP}$.

A subsequent study of the photosensitized poly-merisation of styrene using the same initiator and pressure range at $30^{\circ}C$ was undertaken by Nicholson and Norrish (142) which enabled these authors to determine k_p and k_t separately at high pressures. They also investigated the effect of pressure on the rate of decomposition of benzoyl peroxide and their results show that:

(d) The initiation step is retarded by pressure.

(e) The rate of propagation is accelerated in a roughly exponential manner by pressure.

(f) The rate of termination is considerably retarded by pressure due to increased viscosity at high pressures.

The polymerisation of methyl methacrylate has also been studied at high pressure (158) and the rate of reaction is proportional to the square root of the initiator concentration. The increase in the rate of polymerisation and in the polymer molecular weight, (which levels off at high pressures) are similar to those found for styrene.

In addition to these kinetic studies, much work has been done on the pressure effect on the polymerisation

of styrene and other monomers and the structures of
the polymers. Detailed studies have been made by
Gonikberg and his collaborators (159), Jacobson and
Carothers (139), Starkweather (134), Walling (11,12),
Ehrlich and Pittilo (160), Sapiro, Linstead and Newitt
(135), Holmes-Walker and Weale (143), El Roy (55),
Mehdi (161) and Romani (130).

(v) The Kinetic Equations at High Pressures.

It has been pointed out above that in the general
rate equation (10), pressure has a great accelerating
effect on $k_p/k_t^{1/2}$. But the overall rate also depends
upon $[M]^{1.0}$ and $(2fk_d[C])^{0.5}$. Since it has become
customary to express the composition of a solution in
terms of the molar concentrations of its components,
the small increases due to compression, in the concentrations
of the monomer and initiator affect the calculated values
of rate constants.

(a) Pressure Effects on Initiation Processes.

As pointed out earlier (57, 60, 64, 74, 84), the
rates of vinyl polymerisations often show departures
from the simple kinetic scheme, depending on such factors
as low monomer concentration, high rates of initiation,

the type of initiator, the nature of the solvent and
monomer, and the temperature (106, 162-163). Toohey
and Weale (106), and Norrish and his coworkers (141-142)
have investigated the dependence of the exponent of the
initiator concentration on pressure. Their results
are summarised below:

System	Temp $^{\circ}$C	Pressure(atm)	Exponent of [C]	Reference
1. Styrene-Benzoyl-peroxide	60	3000	0.4	141
2. Styrene-Benzoyl-Peroxide (Photosensitized)	30	3000	0.45	142
3. Styrene-Benzoyl peroxide	60	4400	0.44	106
4. Styrene-Benzoyl Peroxide (Toluene)	60	4400	0.44	106

At 1 atmosphere, the order of reaction with respect to [C] was found to be 0.5 in each system. The decrease at high pressures has been attributed to termination by primary radicals.

Walling and Pellon (112) studied the effect of pressure on the decomposition of benzoyl peroxide and confirmed the findings of Norrish and Coworkers (141-142) that pressure retards the dissociation of the initiator. Their results are tabulated below:-

Substance (and reference)	Solvent	Temperature	Method	$k_d \times 10^5$ (1 atm) sec^{-1}	$k_d \times 10^5$ (1500 atm) sec^{-1}	$\Delta V^{\ddagger}$ (1 atm) cc/mole
Benzoyl peroxide (141-142)	CCl_4	60°C	Direct	0.14	0.078	+10
Benzoyl peroxide (112)	aceto-phenone	80°C	Direct	5.6	4.6	+5

Ewald (164) studied the dissociation of AIBN in toluene at 62.5°C at pressures up to 10,000 atmospheres and observed retardation in the rate of decomposition from 1 atm. to 1500 atm. His figures for k_d obtained by the scavenger technique and the direct method showed

a decrease from 0.89×10^{-5} to 0.55×10^{-5} and 1.87×10^{-5} to 1.52×10^{-5} respectively, the former value indicating a wastage of free radicals. Ewald employed iodine as a scavenger but Bawn and Mellish (165) used diphenyl picrylhydrazyl (DPPH) for studying the decomposition of benzoyl peroxide and azo-bis-isobutyronitrile at 1 atmosphere mainly in aromatic solvents. Assuming that in the retardation reaction each DPPH radical reacts with one other radical, they obtained results fairly close to those calculated from the volumetric measurement of nitrogen evolved or from direct spectroscopic measurement of the azo-bis-isobutyronitrile concentration. The D.P.P.H. method has been criticised by Walling (166). Hammond, Sen and Boozer (85) have produced experimental evidence to show that the value of D.P.P.H. as a "counter" is doubtful as it does not capture the decomposition products quantitatively, particularly in the case of azo-bis-isobutyronitrile in which several (instead of one) initiator radicals react with one D.P.P.H. radical. In their view the probable mechanism is

$$(CH_3)_2 \cdot \overset{\text{x}}{C} \text{-CN} + DPPH \longrightarrow CH_2 = C(CH_3) \cdot CN + H\text{-}DPPH$$

$$H\text{-}DPPH + (CH_3)_2 \cdot \overset{\text{x}}{C} \text{-CN} \rightarrow (CH_3)_2 \cdot CHCN + DPPH$$
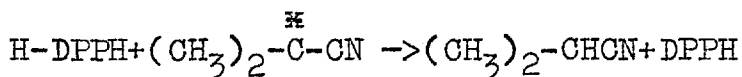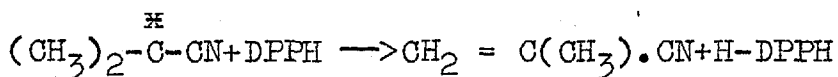
which is responsible for regeneration of the D.P.P.H.
This type of double transfer had been suggested by
Burnett and Cowley (167). The findings of Hammond et
al have been confirmed by Bawn and Verdin (168). Ewald
(164) and Walling (166) suggested that the difference
in the values obtained by the "scavenger" technique
and the "direct" method for the decomposition of azo-
bis-isobutyronitrile was due to a "cage" effect. The
value of $\Delta V^{\neq}$ by the scavenger technique is larger than
that obtained by the direct method. This is obviously
due to the radicals diffusing out of their "cages"
prior to their reacting with the molecules of scavenger.
Talat-Erben and Bywater (169) determined the rate of
decomposition of azo-bis-isobutyronitrile in toluene
at $70^{\circ}C$ at 1 atmosphere and the rate constant (0.4×10^{-4})
was much lower than that obtained by Ewald. Although
they do not agree with Walling's above explanation based
on the "cage" effect, the low efficiency of initiation
in carbon tetrachloride as observed by Lewis and Matheson
(170), Hammond et al (85) and Bawn and Mellish (165)
is still explained by some workers on this hypothesis
(12). According to Flory (14) 'Matheson's widely accepted
explanation in terms of the cage effect appears to

be based on an unrealistic interpretation of the rates of the processes involved.'

It has been pointed out in Section I(v) that inorganic ions possessing chain terminating properties have also been employed for this purpose. Bamford, Jenkins and Johnston (82, 82a, 171) and Dainton and his coworkers (83, 172) have shown that hydrated ferric chloride in dimethyl formamide or methyl ethyl ketone behaves as an ideal inhibitor of styrene polymerisation and retards the polymerisation of acrylonitrile. But to the writer's knowledge the method has not yet been used for high pressure studies.

It has been pointed out earlier that the nature of the various reactions in the decomposition of azo-bis-isobutyronitrile still remains uncertain. It is supposed to decompose into nitrogen and two isobutyronitrile radicals by either simultaneous or successive cleavage of C-N bonds:

$$(CH_3)_2 \cdot C \cdot (CN)-N = N-(NC) \cdot C \cdot (CH_3)_2 \longrightarrow$$
$$(CH_3)_2 \cdot C \cdot (CN)-N = N^x + NC-\overset{x}{C} \cdot (CH_3)_2 \longrightarrow$$
$$N_2 + NC-\overset{x}{C}(CH_3)_2$$
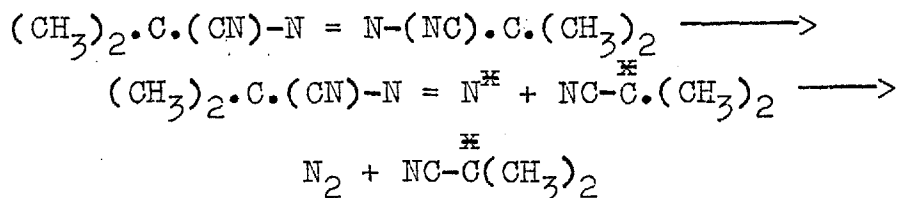
Bevington (173) analysed the expected products of combination and disproportionation from the primary products and found that relative amount of each reaction was dependent on the extent of decomposition. Higher conversions favour the formation of the combination product, namely, tetramethyl succinodinitrile. The formation of an unstable intermediate, ketene-imine,

$$(CH_3)_2 \; C = C = N(CH_3)_3$$
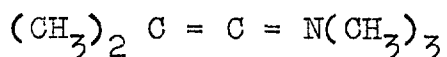
has been proved by Talat-Erben and Bywater (169).

It would appear from the above discussion that pressure slightly retards the rate of decomposition of initiator and hence the rate of initiation is also reduced.

(b) <u>Pressure Effects on Propagation and Termination.</u>

Merrett and Norrish (141) made a number of inferences from their results which were subsequently confirmed by Nicholson and Norrish (142) for the pressure effects on k_d, k_p and k_t for styrene. By using a "rotating sector" technique they showed that k_p in styrene, between 1 and 2900 atm. at $30^\circ C$, increased by a factor of 5.5 and obtained a value of $-13.4 \; cm^3/mole$ for $\Delta V^{\neq}$. Shortly afterwards, Walling and Pellon (112)

employed a different technique (emulsion polymerisation) for measuring the same rate constant and found an increase by a factor of 3.9 between 1000 and 3700 atmospheres at $40^{\circ}C$ which corresponds to an activation volume $\Delta V^{\neq}$ = -11.5 cm^3/mole, comparing well with the value of Nicholson and Norrish.

Nicholson and Norrish (142) also found that the rate of the termination step, (another bimolecular reaction), decreased rapidly up to 1000 atmospheres and then more slowly. Walling and Pellon (112) reached the same conclusion independently. This anomaly is probably due to the large increase in the viscosity of styrene under high pressure with a corresponding decrease in the diffusion rate. The correctness of this explanation is yet to be established, although Hamman (174) has shown that viscosity does play some role in high pressure bimolecular reactions.

The viscosity effect may be minimised in processes which are diffusion-controlled by using diluents of low transfer values.

The viscosity effect at high pressures is very similar to the behaviour of methyl methacrylate when the polymerisation is carried to high conversions. The

rate is almost unaffected by the extent of polymerisation up to about $10^{\circ}/o$, beyond which it rises rapidly as the increasing viscosity is accompanied by a decrease in the rate of termination. At very high conversions the rate of propagation is retarded and it is reduced almost to zero at about $90^{\circ}/o$ conversion.

(c) <u>The Transfer Equation at High Pressures.</u>

Since the transfer reactions generally involve a bimolecular reaction between a small molecule and a large radical, it is expected that pressure will have an accelerating effect. The increased importance of the various transfer reactions in the termination of the growing chain radicals causes a trend of the molecular weights at high pressures to an almost constant values.

Chain transfer in vinyl polymerisation can occur either by the attack of a polymer radical in a monomer molecule:

$$\overset{\text{x}}{R-CH_2} + CH_2 = CHX \longrightarrow RCH_3 + CH_2 = \overset{\text{x}}{CX}$$
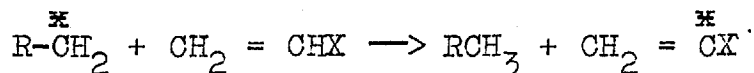
or by attack on a solvent molecule, for example,

$$\overset{\text{x}}{R-CH_2} + CC\ell_4 \longrightarrow RCH_2C\ell + \overset{\text{x}}{CC\ell_3}$$
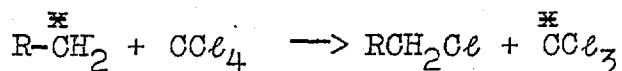
Acceleration in both these reactions is to be

expected under high pressures, and this has been confirmed
by Walling and Pellon (112). They investigated the
styrene-carbon tetrachloride system using benzoyl
peroxide at $60^\circ C$ and keeping the [C]/[M] ratios constant.
From graphs of $1/\overline{DP}$ values versus [S]/[M] they found a
value of $C_s = 98 \times 10^{-4}$ (1 atmosphere) which is quite
close to the value of $C_s = 93 \times 10^{-4}$ as reported by
Gregg and Mayo (111) at one atmosphere and not very
far from the uncorrected value of George and Onyon (88).
The C_s values obtained by Walling and Pellon at higher
pressures are given below:-

Pressure (Kg/cm²)	1	2000	3950	5980
$C_s \times 10^4$	98	90	84	59

They conclude that the transfer constant is almost
independent of pressure, decreasing by about $15^\circ/o$ at
4000 atmospheres, and that the increase in the rate
constant for transfer is very nearly identical with
that for the chain propagation reaction. The results
indicate a value of $\Delta V_{tr}^{\neq} \cong -11$ cm³/mole at pressures
between 1000 and 3700 atmospheres.

Toohey and Weale (106) investigated the styrene-

Triethylamine system, using benzoyl peroxide at 60°C
and up to a pressure of 4400 atmospheres. They found a
decrease in $C_s = 6.7 \times 10^{-4}$ at one atmosphere to
3.2×10^{-4} at 1810 atmospheres, falling to 1.4×10^{-4} at 4400
atmospheres. It would appear that there is a marked
contrast between these findings and those of Walling
and Pellon (112).

If the transfer equation (12) is considered an
increase in pressure will have a marked effect on
$(k_t^{1/2}/k_p)$, generally represented by δ, (lowering its
value and so affecting the value of $1/\overline{DP}$). Other factors
of the first term, namely, 'X'; $(\frac{fk_d}{2})^{1/2}$, $\frac{[C]^{1/2}}{[M]}$

and the transfer reactions to monomer, initiator, polymer,
etc., also affect the molecular weight. The reduction
in the value of δ, under pressure has been reported
by Nicholson and Norrish (142) and the rate of initiation
is retarded slightly. The value of $(fk_d)^{1/2}$ is also
affected to a small extent. A small reduction will be
caused by pressure in the value of $[C]^{1/2}/[M]$. Thus
there will be a large overall decrease in the value of
the first term.

Taking the simplest case of ordinary homogeneous

polymerisation of styrene and considering the general rate equation

$$V = k_p(k_t)^{-1/2} [M] I^{1/2} \qquad \ldots(41)$$

$\Delta V^{\neq}_{overall}$ may be written as:

$$\Delta V^{\neq}_{overall} = \Delta V^{\neq}_p + \frac{1}{2} \Delta V^{\neq}_i - \frac{1}{2} \Delta V^{\neq}_t \quad \ldots(42)$$

or $$-\Delta V^{\neq}_{overall} = -(\Delta V^{\neq}_p + \frac{1}{2} \Delta V^{\neq}_i - \frac{1}{2} \Delta V^{\neq}_t) \quad \ldots(43)$$

where $\Delta V^{\neq}_p$, $\Delta V^{\neq}_i$ and $\Delta V^{\neq}_t$ respectively denote the volumes of activation during the processes of propagation, initiation and termination. Bukhart and Zutty (175) obtained the following relationship between the transfer constant, C_y, and the volume of activation associated with the transfer reaction, $\Delta V^{\neq}_{fy}$,

$$\frac{d \ln C_y}{dP} = -(\Delta V^{\neq}_{fy} - \Delta V^{\neq}_p)/RT \qquad \ldots(44)$$

Since $\Delta V^{\neq}_p$ is much the largest term in this equation as is evident from the work of Nicholson and Norrish (142)

and Walling and Pellon (112), it suggests that the
value of $\Delta V^{\neq}_{overall}$ can serve as a useful approximate
guide to its variation with the monomer structure (18),
and for the increase in the rate of polymerisation at
high pressures. Qualitatively, $\Delta V^{\neq}_{p}$ and $\Delta V^{\neq}_{fy}$ must be
negative. $\Delta V^{\neq}_{t}$ should be negative if the rate is controlled
by the rate constant and positive if the reaction is
diffusion-controlled. $\Delta V^{\neq}_{i}$ has a small positive value
when it relates to the unimolecular dissociation of an
initiator and hence pressure retards the rate of
initiation to a small extent.

SECTION II

II.1.   Apparatus.

(a) Two high pressure vessels have been used in this work,
one for pressures up to 3500 atmospheres and the other
for higher pressures.

(b) Photographs of the assembled apparatus and intensifier
are shown in Figures 1 and 2. A line diagram of the
high pressure vessel for generating pressures up to
3500 atm. is shown in Figure 3.

V is a compound-cylinder high pressure vessel con-
structed of two Vibrac high tensile steel cylinders
shrunk together. A vertical section is shown in Figure
4a. The hand-operated hydraulic pump P, is connected
to V through valve A by Vibrac tubing, $\frac{1}{2}$" O.D., $\frac{1}{16}$" I.D.
A pressure of about 1000 atm. can be generated in the
vessel by direct pumping with the valve B closed. A
satisfactory fluid for transmitting pressure is liquid
paraffin B.P.

The intensifier D is used for the generation of
higher pressures and is connected to the system by stain-
less steel tubing, $\frac{3}{8}$" O.D., $\frac{1}{8}$" I.D. By closing valve
A and opening valve B, pressure is transmitted to a
piston 2.047" in diameter which is supported in the upper

FIG: 1

110
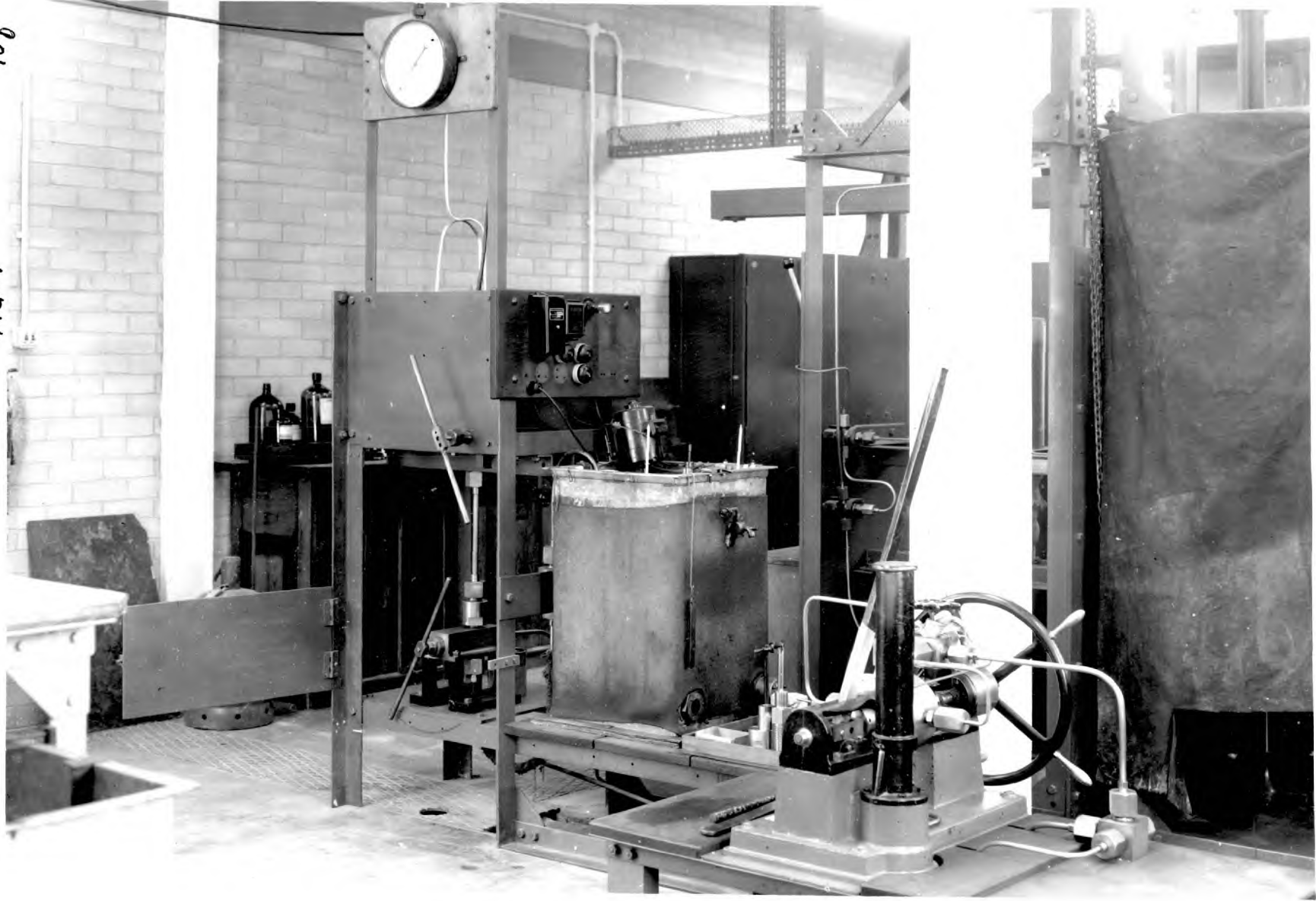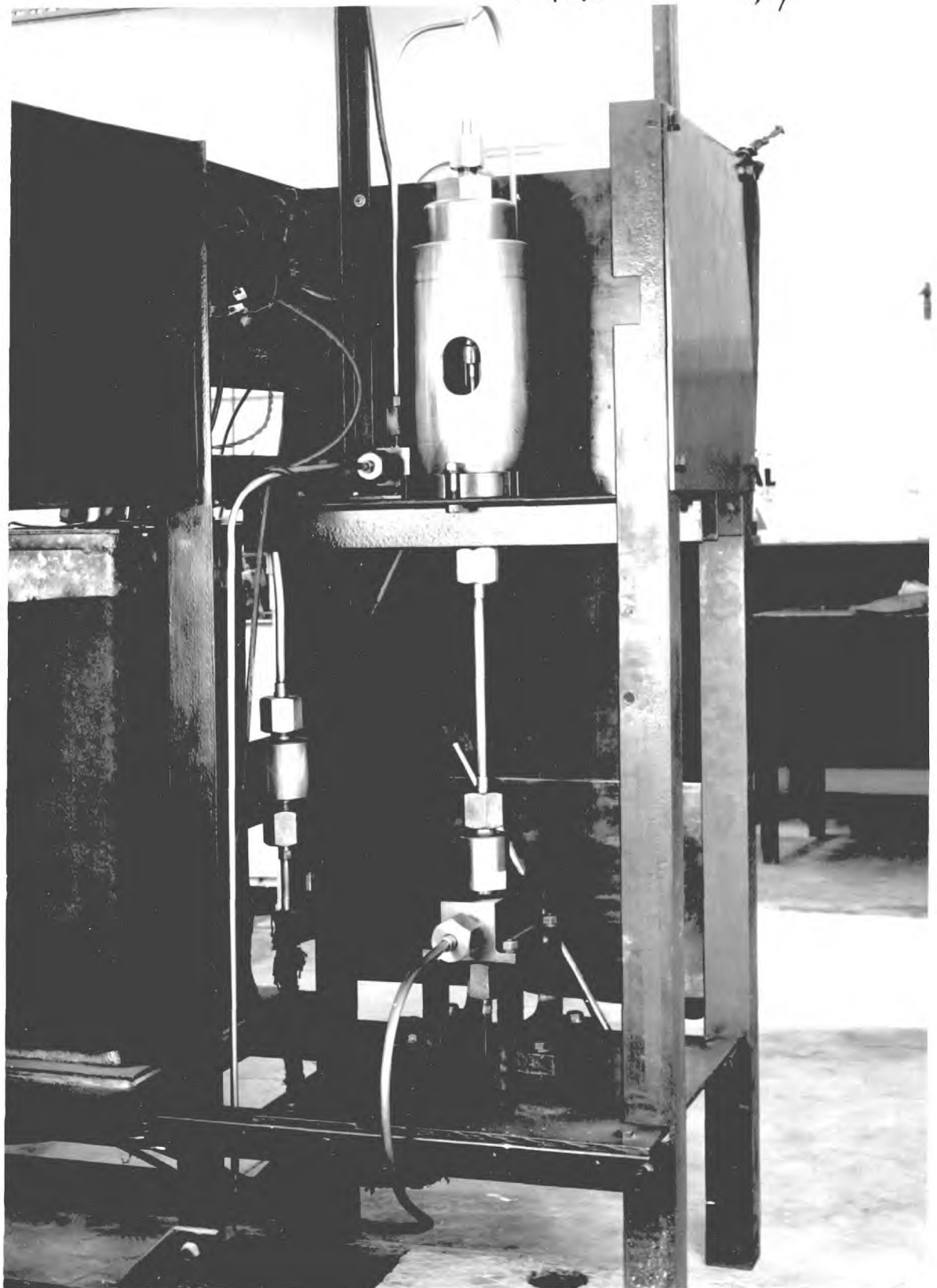
FIGURE 3

FIGURE: 4 A

FIGURE: 4 B

PYREX
TUBE

P.T.F.E
TUBE

STEEL
BUCKET
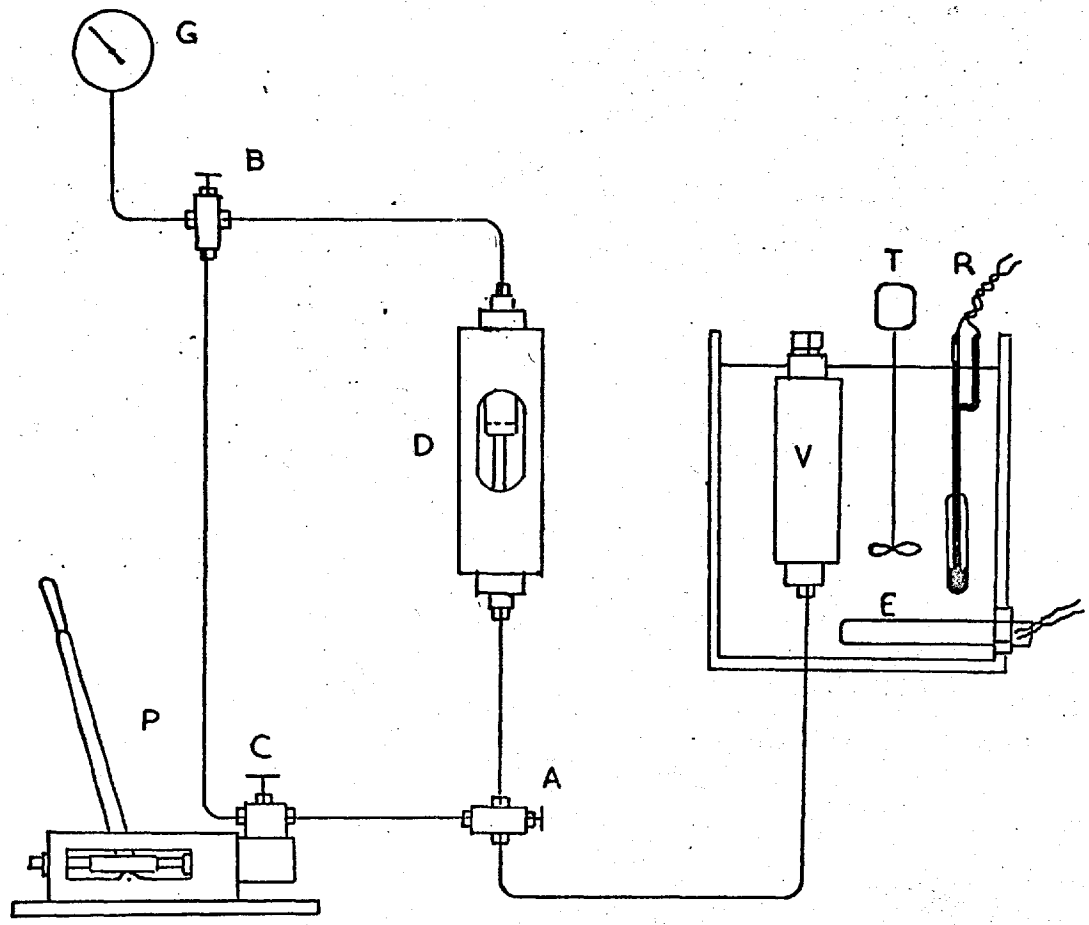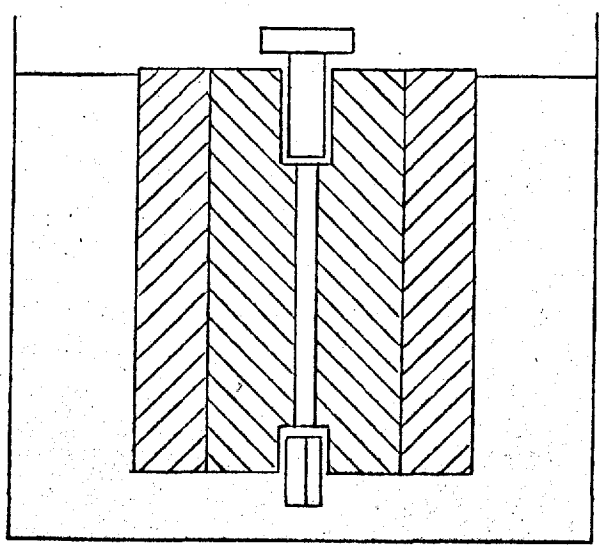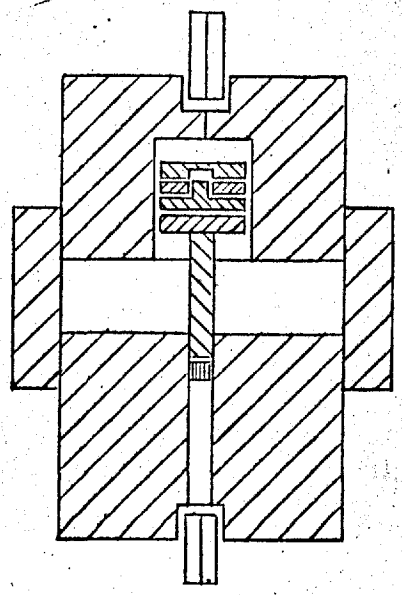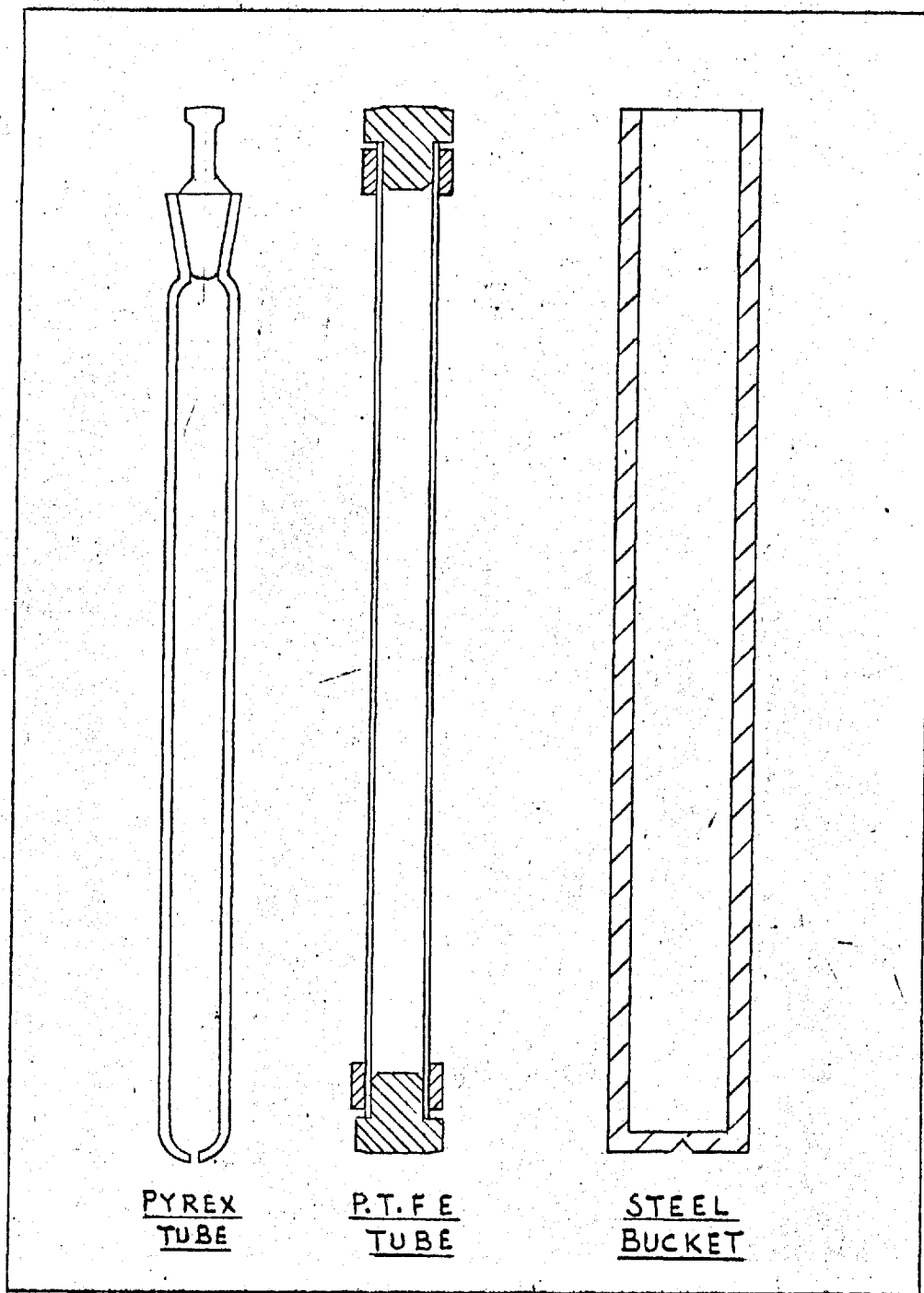
block of the intensifier, and obturated with a Bridgman
unsupported-area packing. Through a thrust block and
thin copper washer, the thrust on this piston is trans-
mitted to a piston, 0.652" diameter, obturated by a
hard rubber Poulter packing and moving in the lower
block of the intensifier D. The thrust block and
washer serve to correct any non-alignment of the two
pistons. The intensification of pressures by the intensi-
fier is theoretically 9.86 fold, that is, the ratio of
the cross-sectional areas of the bottom and top pistons.
However in actual practice it gives approximately a
nine-fold intensification ratio when allowance is made
for the losses due to friction in packing and the pistons,
coupled with very small changes in the cross-sectional
areas of the pistons and cylinders due to compression.
A vertical section of the intensifier is shown in Figure
4b.

The vessel has the following dimensions:

overall length	13.625"
Bore	0.75"
External diameter	4.125"
Length of reaction space	9"

The upper end of the reaction vessel V is sealed
with a hard Poulter packing backed by a screw plug (Fig. 4a).

Since the valve A is exposed to the full pressure
of the vessel, it was difficult to stop leakage altogether
and it caused trouble occasionally. A shaped hard
rubber packing fitted with rubber O-rings at each end
proved fairly satisfactory. At high pressures it was
always necessary to pump occasionally in order to main-
tain the pressure. The line for direct pressurisation
up to about 1000 atm, including the valve A, is essential
as the pistons of the intensifier D can travel only to
a limited extent.

The pressure, on the low pressure side of the
intensifier, was measured by a standard Bourdon test
gauge G. This was calibrated against a primary free
piston gauge, connected to the high pressure side of
the intensifier, at intervals of 10 atmospheres (gauge)
up to a pressure of 1000 atm (vessel), the maximum
pressure measurable with the free piston gauge. The
vessel pressure P was found to vary linearly with the
gauge pressure p according to the following relationship:

$$P = 8.650p + 79$$

This was assumed to hold good up to a pressure of
4500 atmospheres. The recorded pressures taken from the
gauge readings are considered accurate within 1°/o and
in view of the magnitude of the effect measured this is

a reasonable assumption.

(c) The reacting solutions were placed in two types
of containers and these reaction tubes are shown in
Figure 5. For pressures up to 3000 atmospheres, glass
reaction tubes with ground glass stoppers at the top,
and having a small hole at the bottom to allow the
transmission of pressure, were used. These had a capacity
of about 5 ml, and were about 17 cm. long and 9 mm. O.D.
Contact between the liquid paraffin which fills the vessel
and the reactants was avoided by filling the lower $\frac{3}{4}$ "
part of the glass tube with distilled mercury. The
reaction tube, filled with the reactants, was introduced
into a stainless steel bucket (Figure 5) fitted with a
hook at the top and containing sufficient mercury to
allow the reaction tube to float. Since the liquid
paraffin is more viscous at high pressures, it is necessary
to provide sufficient clearance between the vessel and
the bucket, and between the bucket and the reaction tube,
to allow rapid transmission of pressure changes.

For higher pressures. P.T.F.E. tubing of $\frac{1}{4}$ " O.D.
and wall thickness of about $\frac{1}{32}$ " was used. Each end of
the tube was fitted with brass sleeves and closed by
plugs made of P.T.F.E. This type of reaction tube has
the advantage of avoiding direct contact with any other

fluid as the pressure is transmitted through the flexible walls.

(d) The pressure vessel V is immersed in an oil bath which is heated by an electric immersion heater E of 1400 watts. In order to have a uniform temperature throughout the bath a stirrer T was employed with a synchronous motor (not shown in the diagram) at 200 r.p.m. A mercury-toluene thermoregulator R with a Sunvic hot-wire relay system was used for controlling the temperature to $\pm$ 0.1°C in the oil-bath and $\pm$ 0.01°C within the vessel, generally at 60°C and very occasionally at 80°C.

(e) For studies at higher pressures (> 4000 atm), another pressure vessel designed for pressures up to 20,000 atm. was used. The upper part of the intensifier constitutes the reaction chamber and the pressure is generated by a pump and transmitted by liquid paraffin through tubes to the low pressure side and via the intensifier piston to the high pressure side. The vessel and the intensifier are heated by a 440 watt radiant heating jacket and the temperature is controlled to within $\pm$ 0.5°C by using a sliding-contact mercury regulator and a Sunvic hot-wire relay.

A complete description of this equipment has been given by Kilroe (176) and also by Lamb (177).

(f) The bath used for atmospheric pressure runs was
filled with liquid paraffin. It was well lagged and
fitted with an efficient stirrer run by an electric
motor. The bath was heated by means of a 150 watt light
bulb and a mercury-toluene thermoregulator with a hot
wire vacuum relay switch was used to control the temp-
erature to $\pm$ 0.1^{O}C. Reactions were carried out in amber-
coloured glass ampoules of 10 and 20 ml. capacity.

(g) For viscosity determinations U-tube micro viscometers
sizes M_1 and M_2 BS/U/M as specified by British standards
specifications, BS 188: 1957 were used (178). These
measurements were carried out by suspending the viscometer
in a water-filled glass thermostat in which a constant
temperature of 25°C $\pm$ 0.1 was maintained by a mercury-
toulene termo-regulator operating a vacuum relay switch.
The viscometers, when not in use, were filled with
benzene, sealed against dust and suspended in the bath.
They were supplied by Townson and Mercer Limited.

All the specific viscosities and viscosity ratios
were determined by using the same viscometer and the
kinetic energy and end effect corrections were not applied
in view of the low rate of flow.

II.2.   Materials.

Styrene or phenylethylene, $C_6H_5 \cdot CH = CH_2$. This
monomer was the B.D.H. product stabilised with ten to
fifteen parts per million of tertiary butylcatechol as
an inhibitor. Before using the monomer the inhibitor
was removed by treating 250 ml. of commercial styrene
with three 100 ml. portions of 10°/o caustic soda or
caustic potash solution in a separatory funnel. The
alkali contamination was removed by successive washings
with distilled water. The styrene was then dried over
anhydrous sodium sulphate or calcium chloride in the
dark under vacuum for 24 hours. The monomer, after
filtration, was distilled at reduced pressure in an
atmosphere of dry oxygen-free nitrogen gas and the middle
fraction, distilling at $32°C$ (10 mm. Hg), was collected,
the first and the last 20°/o being discarded. The monomer,
which had a refractive index $n_D^{20} = 1.5462$, was stored
in vacuum at $0°C$ and used within 24 hours.

Boundy and Boyer (15) have suggested argon in place
of nitrogen in the distillation of styrene. In their
opinion nitrogen gas does react with styrene at high
temperature. However, nitrogen was used throughout this
work as it did not seem to affect the viscosity of the
monomer up to $50°C$.

Methyl meth acrylate (MMA). B.D.H. product was
used. The commercial monomer stabilised with ten to
twenty parts per million of Quinol was washed successively
with aqueous solution of sodium nitrite, sodium bisulfite
and caustic soda. After three washings with distilled
water, it was dried over sodium sulfate or calcium
chloride. The monomer was filtered and distilled at
100 mm. under dry nitrogen. The middle fraction boiling
at $46^{\circ}C$ was collected.

$$n_{30}^{25}D = 1.4120, \quad d_4^{30} = 0.9311$$

Tetrachloroethylene, commonly known as perchloroethylene,
$ccl_2=ccl_2$. B.D.H. solvent was used throughout. The
purification was done by using a tall fractionating column
packed with raschig rings and distilling the commercial
product at 30 mm. Hg $(33^{\circ}C)$ in an atmosphere of nitrogen.
The middle $60^{\circ}/o$ fraction was collected and stored in
vacuum at $0^{\circ}C$.

AZO-bis-iso-butyro nitrile (AIBN or simply azo),
$(CH_3)_2-C(CN).N=N.C(CN)-(CH_3)2$. The Eastman Kodak chemical
was purified by fractionally crystallising from a saturated
solution in chloroform. The crystalline product was
filtered, dried and stored in an amber coloured bottle
over fused calcium chloride at $0^{\circ}C$. M.P.$106^{\circ}C$.

Benzoyl peroxide (ϕ.CO.O.O.CO.ϕ)

The wet paste supplied by B.D.H. was dried in vacuo and its saturated solution in chloroform was prepared. Cold methanol was added to the solution and the initiator was obtained as a crystalline solid. This was filtered off and dried under vacuum. It was kept in the dark in a vacuum desiccator.

Toluene.

The Analar material supplied by B.D.H. was used without further purification.

Benzene.

Two grades were used. M and B "Benzene, Pure, crystallisable" was employed as a diluent. For molecular weight determinations, a special Analar quality benzene was used, which was supplied by B.D.H.

Methanol.

The I.C.I. solvent was used as received, after filtration

1:2 epoxy Propane or propylene oxide.

The diluent supplied by Hopkins and Williams was used as received.

Chloroform.

Analar quality supplied by B.D.H. was used.

Di-tertiary Butyl peroxide and Tertiary Butyl Perbenzoate were used as such.

Boron Trifluoride diethyl etherate was also used as supplied.

II.3.   Procedure

(a) Preparation of reaction mixtures.

A standard flask of 10 or 25 ml. capacity was generally employed for the preparation of solutions of desired [S]/[M]and [c]/[M]. After thorough mixing of the reagents, the reactants were placed into the inverted stoppered reaction tube previously filled with a small amount of mercury and subsequently flushed with nitrogen. The tube was then re-inverted and after a check to ensure the absence of any air bubble was floated on mercury in the steel bucket previously warmed to 60°C. The same procedure was followed when P.T.F.E. tube was used, except that no mercury was necessary in that case.

(b) Technique of Polymerisation.

After checking the temperature in the pressure vessel, the thermometer was removed. The steel bucket containing the reaction tube was placed in the high pressure vessel, with valve A open and B closed, and the time was noted. A hard rubber bung (Poulter packing) was inserted into the bore of the vessel by means of a special tool kept in the bath at 60°C. The steel screw plug, also kept in the bath, was turned down until hand-tight, and the pump return valve, C, was closed. Pumping was started at a noted time and a pressure of approximately 900

atmospheres was developed. The valve A was now closed
and valve B opened, and the intensifier was brought into
operation. Pumping was then continued until the desired
pressure was obtained. The time was recorded. Care
was taken during pressurisation that the gauge pressure
did not exceed the required value. Due to leakage at
valve A intermittent pumping was necessary and this was
done by the partially-open valve B. At the highest
pressures it was observed that the pressure at first
tended to fall repidly from the desired value, which was
probably due to the combined effects of the delayed
compression of packings and the increased viscosity of
the oil in the pressure lines.

From experience the length of the reaction times
was adjusted so that the yield of polymer was between 5 and 10%

After the desired reaction time, valve B was closed
and the pump return valve was opened. The time was noted
and the valve opened slowly, releasing the pressure at
a controlled rate until the intensifier pistons were
restored to their original position. The valve B was
now closed and the remaining pressure in the line was
released by opening the valve A. The time was recorded.
The steel plug was removed and with a few gentle strokes
of the pump, the rubber bung was ejected. The bucket

was taken out and the reaction tube removed. The time
taken for these operations was approximately 2 minutes
altogether and the time taken in releasing the pressure
was generally 30 seconds. The total time of a run was
found by adding the time during which the materials were
at the desired pressure to half the time taken in generating
and releasing the pressure.

The contents of the clean and wiped reaction tube
were separated from mercury and poured into a weighed
stoppered Erlenmeyer flask which was reweighed after
cooling to room temperature.

For atmospheric runs, sealed amber-coloured glass
ampoules of 10 and 20 ml. capacity were employed. The
reaction mixture was introduced by means of a pipette
and the air displaced by flushing out with nitrogen.
The oil bath was shielded from bright light during the
polymerisation and maintained at $60^{o}C \pm 0.1^{o}C$.

(c) Precipitation and separation of Polymers.

The polymer solution in the flask was diluted
with about 20 ml. of epoxy propane and transferred to
a dropping funnel. The flask was rinsed with another
5 ml. solvent and the washings added to the funnel. The
polymer was precipitated by dropwise addition of the
solution into a 400 ml. beaker containing 150 ml. of cold

methanol, with constant stirring. The beaker was placed
in hot water at about 60°C and the contents vigorously
stirred until the polymer precipitate coagulated. The
precipitate was allowed to stand for a few hours in the
ice-chest, after adding a little quinol, and then filtered
through a weighed sintered-glass crucible of porosity
4 at room temperature. The filtrations were carried
out under vacuum. The precipitate was thoroughly washed
with methanol, dried in a desiccator for about 10 hours
at atmospheric pressure and subsequently in vacuum at
30°C for 10 - 15 hours. The crucible was cooled in a
desiccator and reweighed.

(d) <u>Percentage conversion</u>.

The percentage yield of the high polymer was
calculated by using the following relationship:-

$$\text{conversion} = \frac{W}{m} \times \frac{p}{S} \times 100$$

where W is the total weight of the reaction mixture,
m is the weight of styrene in the mixture and p is the
weight of polymer obtained from sample of weight S.

(e) <u>Molecular weight determination</u>.

Most of the polymers obtained had molecular weights
in the range of 8 X 10^3 ------ 6 X 10^5. All determinations
of molecular weights were done by the viscometry method

and benzene solutions were used throughout, at 25°C. The solutions were generally in the range of 0.1 to 0.5 gm. of polymer/100 ml.

Since the literature on solution viscosities is full of confusing terminology, it is best if the old symbols and the new ones are explained in the light of the I.U.P.A.C. recommendations (179). The old symbols and names which are sometimes used are given in brackets. To avoid confusion, old terminology will be retained while discussing the published work.

η represents the viscosity of a dilute polymer solution and η_0 is the viscosity of the pure solvent at the same temperature. The relative increase of viscosity (specific viscosity η_{sp}) is given by

$$\frac{\eta - \eta_0}{\eta_0}$$

and is equal to $\frac{\eta}{\eta_0} - 1$, where $\frac{\eta}{\eta_0}$ is the viscosity ratio

(relative viscosity). The relative increase in viscosity divided by the concentration, c, gives the viscosity number, η_c

$$\eta_c = \frac{\eta - \eta_0}{\eta_0 c} \quad (= 100\ \eta_{sp}/c)$$

where c is the concentration of the polymer solution in

gm./ml. (gm./decilitre).

The logarithmic viscosity number is the logarithm of the viscosity ratio divided by the concentration of the polymer solution in gm./ml.

The limiting viscosity number, $[\eta]$, (intrinsic viscosity) is the limiting value of the viscosity number when the concentration approaches zero,

$$[\eta] = \lim_{c \to o} \left(\frac{\eta - \eta_0}{\eta_0 c} \right)$$

$$= \lim_{c \to o} \left[\frac{\ell n(\eta/\eta_0)}{c} \right]$$

The dimensions of viscosity number, logarithmic viscosity number and limiting viscosity number are $[M^{-1}L^3]$ and are expressed in mililitres per gramme.

The limiting viscosity number, $[\eta]$, was determined by plotting the viscosity number against c and extra-polating it to zero. A similar set of extrapolated values was obtained by substituting logarithmic viscosity number for viscosity number and the mean value of the two was taken as the limiting viscosity number (intrinsic viscosity).

<u>The molecular weight-limiting viscosity correlation.</u>

Staudinger was among the first to recognise the large size of polymer molecules and to utilise the

dependence on molecular weight of a physical property
such as dilute solution viscosity (180). He proposed
the first empirical relationship between molecular
weight and limiting viscosity number (abbreviated to
L.V.N.) for flexible chain molecules (181);

$$[\eta] = k.M$$

where k is a constant dependant on the particular polymer-
solvent system. Subsequent work showed that this equation
was not of general applicability. The Mark-Houwink
equation (182-185) was found to be generally satis-
factory and has been found to give best correlationship
for a large number of polymer-solvent systems over wide
ranges of molecular weight. The equation is written
as

$$[\eta] = KM^{\alpha}$$

K and α being constants, for a given polymer, solvent
and temperature, and found by determining the number
average molecular weight by such methods as osmometry,
cryoscopy or end-groups analysis. The constants, K and
α, are different for different solvents and are independent
of the molecular weight over a wide range. These values
have been reported by a number of workers and are given
below, using benzene as a solvent:-

Reference	$K \times 10^4$	α
111	1.74	0.714
47	1.54	0.73
186	0.953	0.744
187	1.13	0.73

The molecular weight calculations in this work were based on the equation of Bawn et al (187), with $K = 1.13 \times 10^{-4}$ and $\alpha = 0.73$ as the results were in agreement to those reported in the literature for benzene. Although Alfrey and co-workers (73) have reported that 'K' and 'α' vary with temperature of polymerisation, their claim was not supported by later workers (111,187).

It must be pointed out that the molecular weights calculated on the basis of limiting viscosity number (intrinsic viscosity) are not generally exactly the number average $\bar{M}_n$. The viscosity method is not an absolute one and requires prior determination of the constants K and α. These constants can be obtained by determining the molecular weights of a number of fractions of the polymer by such methods as light scattering and osmotic pressure and their intrinsic viscosities are then determined in the appropriate solvent. However it is assumed that the fractions are sufficiently homogeneous so that $\bar{M}_n \simeq \bar{M}_v \simeq M_\omega$. (73).

The viscosity molecular weight of any polymer molecule is generally considered to be independent of the temperature at which the measurements are made or the solvents employed. But recent investigations have provided considerable evidence that the viscosity molecular weight of a polymer species depends upon the nature of the solvents employed in viscosity measurements. It has also been observed that the molecular weight of some polymers are higher in a non-polar solvent than a polar solvent (188-189).

(f) <u>Experimental determination of viscosities.</u>

The viscosity ratios were generally determined by means of an M2 viscometer but a few measurements were done with the M1 type (178). Molecular weight grade Benzene was used throughout as a solvent and all measurements were done at 25°C over a range of concentration. A representative sample of the thoroughly dried polymer was weighed in a 10 ml. calibrated flask and benzene was added to within a few mm. of the graduation and the flask was immersed in the constant temperature bath for about 30 minutes. When the sample completely dissolved, the solution was made up to the mark.

The viscometer was well washed and was almost filled with benzene filtered through a coarse porosity sintered

glass filter and suspended vertically in the bath for
about 20 minutes to make allowance for expansion.
All possible precaution was taken to exclude the
presence of any foreign body during the filling operation.
The level was brought to the filling mark by removing
the excess liquid by means of a long capillary tube.
By the application of pressure to the wide arm the
liquid was filled in the upper bulb and was raised about
1 cm. above the upper graduation mark. The liquid
was allowed to flow freely and the time was determined
for the meniscus to pass from the upper to the lower
mark. This was repeated at least three times. The
solvent was poured from the viscometer which was then
dried.

The homogenised polymer solution was filtered
into the viscometer which was suspended in the bath.
The volume was adjusted and the flow times were measured
according to the procedure described above.

When not in use, the viscometer was filled with
benzene, (after flushing it four or five times), and
was sealed and kept in the thermostatic bath (184,190).

(g) Composition of Polymers.

For elemental analysis of the polymers, the samples
were sent for analysis to the organic Micro-analytical

Laboratory of the Department of Chemistry. The analysis
was generally carried out with 10 mg. samples. Quite
often the $^\circ$/o of chlorine was reported by difference
because of the low chlorine content of the polymers.
In one instance polymers prepared at atmospheric pressure
were reported to contain 8 - 15°/o of chlorine which
could not be explained by any interpretation. The runs
were repeated and the purified samples resubmitted for
analyses. It was then found that the analyses previously
reported were erroneous and the second set of polymers
were quite low in their chlorine content. It was also
found that the reported carbon percentages were low
by 0.3°/o and hence corrections were made in calculating
the composition of the polymers.

(h) Experiments with MMA/TCE system.

Methylmethacrylate was polymerised in Tetrachloro-
ethylene using AIBN as an initiator at 60°C at atmospheric
and high pressures. The apparatus and technique were
exactly similar to that described for the styrene -
tetrachloroethylene system. The polymers were purified
and dried. The elemental analyses were also done by the
Micro-analytical Laboratory of the College.

(i) <u>Attempted experiments on the polymerisation of</u>
<u>T.C.E. at high pressures.</u>

A number of runs were performed to study the effect
of pressure on tetrachloroethylene in toluene at different
temperatures (up to $100^{\circ}C$), and pressures (≈ 7000 atmospheres)
using Benzoyl peroxide, di-tertiary butyl peroxide and
tertiary butyl perbenzoate as initiatives. The apparatus
and the technique have been described in II.1 (e) above.

Some runs were conducted at atmospheric pressure
using BoronTrifluoride diethyletherate, at lower
temperatures.

Section III: Results and Discussion

III.1 Experimental Results

Throughout the course of this work styrene was used as a monomer (unless otherwise specified) and tetrachloroethylene as a solvent. The experiments were carried out at 60°C, using azobisisobutyronitrile as an initiator. The runs were conducted at 1 atmosphere, 1030, 1510, 1980 and 2680 atmospheres.

All experiments (with few exceptions) were done by keeping the $[C]/[M]$ ratio constant, instead of $[C]^{\frac{1}{2}}/[M]$, for reasons explained in Section I.

The units of the various quantities listed in the following tables are:

Pressure:	atmosphere
Concentration:	moles/litre (uncorrected for volume changes due to pressure)
Overall rate:	moles/litre/second
Intrinsic viscosity: $[\eta]$	decilitres/gm.

Benzene was used as a solvent for all viscometric measurements and Bawn's equation (187) was employed for all the determinations of molecular weights and $1/\overline{DP}$, at a temperature of 25°C.

Table IX

The Overall Rate of Polymerisation of Styrene in
Tetrachloroethylene with AIBN at 60°C and at
Atmospheric Pressure

Run No.	[M] moles per litre	$[C] \times 10^3$ moles per litre	Time (hours)	% Polymer	conversion % per hour	$V \times 10^5$ moles /litre/ second
1	4.18	1.31	16.0	12.3	0.766	0.89
2	4.18	2.65	6.0	6.89	1.15	1.33
3	4.18	3.96	7.0	9.48	1.35	1.57
4	4.18	5.36	6.0	9.48	1.58	1.83
5	4.18	7.95	6.0	11.5	1.91	2.22
6	1.57	6.09	7.0	7.89	1.13	0.48
7	1.87	6.09	6.0	7.12	1.19	0.61
8	2.35	6.09	5.0	7.53	1.51	1.08
9	3.05	6.09	5.0	7.66	1.53	1.28
10	4.18	6.09	4.0	7.09	1.77	2.02
11	8.70[*]	6.09	3.0	7.22	2.41	5.74

[*] Bulk polymerisation

Table X

Dependence of Overall Rate of Polymerisation on Pressure

$[C]/[M] = 0.64 \times 10^{-3}$ Temperature: $60^{\circ}C$

Solvent: Tetrachloroethylene   Initiator: AIBN

Run No.	Pressure (atm)	Time (hour)	% Polymer	conversion % per hour	$V \times 10^5$ moles/litre-second
[M] = 1.57 moles/l			[C] = 1.00 $\times 10^{-3}$ moles/l		
12	1	22.5	9.88	0.44	0.19
13	1030	8.0	7.05	0.88	0.38
14	1510	6.5	9.91	1.52	0.66
15	1980	5.0	8.91	1.64	0.71
16	2680	3.0	6.20	2.07	0.91
[M] = 1.87 moles/l			[C] = 1.19 $\times 10^{-3}$ moles/l		
17	1	24.0	12.4	0.52	0.27
18	1030	8.0	9.79	1.22	0.52
19	1510	5.5	7.40	1.35	0.70
20	1980	4.0	7.75	1.94	1.01
21	2680	4.6	11.97	2.59	1.71

Table X (continued)

Run No.	Pressure (atm)	Time (hour)	% Polymer	conversion % per hour	V x 10^5 moles/litre-second
[M] = 2.35 moles/l			[C] = 1.49 x 10^{-3} moles/l		
22	1	8.0	5.55	0.69	0.36
23	1030	5.5	8.53	1.55	1.00
24	1510	4.5	9.09	2.02	1.32
25	1980	4.0	10.6	2.65	1.66
26	2680	3.0	9.32	3.11	2.14
[M] = 3.05 moles/litre			[C] = 1.93 x 10^{-3} moles/litre		
27	1	8.0	7.13	0.89	0.75
23	1030	8.0	14.2	1.78	1.50
29	1510	4.0	10.8	2.70	2.29
30	1980	3.0	10.4	3.46	2.93
31	2680	3.0	12.9	4.30	3.56
[M] = 4.18 moles/l			[C] = 2.65 x 10^{-3} moles/l		
32	1	6.0	6.89	1.15	1.33
33	1030	4.0	9.60	2.40	2.80
34	1510	4.0	13.5	3.38	3.92
35	1980	3.0	12.8	4.26	4.94
36	2680	2.0	13.4	6.70	7.55

Table X (continued)

Run No.	Pressure (atm)	Time (hour)	% Polymer	conversion % per hour	$V \times 10^5$
[M] = 5.92 moles/l			[C] = 3.75 x 10^{-3} moles/l		
37	1	6.0	9.33	1.55	2.55
38	1030	2.0	6.0	3.00	4.93
39	1510	3.0	12.1	4.03	7.45
40	1980	2.0	11.9	5.95	9.79
41	2270	1.5	9.87	6.58	10.8
42	2630	1.0	8.44	8.44	13.5
[M] = 8.70 moles/l			[C] = 5.54 x 10^{-3} moles/l		
43	1	6.0	12.0	2.00	5.34
44	1030	1.0	5.10	5.10	12.3
45	1120	1.0	5.36	5.36	12.9
46	2270	1.0	10.8	10.8	25.4

Table XI

Measurements of Molecular Weight of Polystyrenes for Chain
Transfer Studies at Atmospheric Pressure

Solvent: Tetrachloroethylene   Initiator: AIBN

Temperature: 60°C $[C]/[M]$: 0.64 x 10^{-3}

Run No.	$[S]/[M]$	% Polymer	$[\eta]$ (dl/gm)	(x 10^{-3}) Molec.wt.	$1/\overline{DP}$x10^4
47	Bulk	6.50	0.811	192	5.43
48	0.53	9.33	0.302	49.6	21.2
49	1.21	6.89	0.186	25.5	40.9
50	2.08	7.14	0.136	15.8	66.0
51	3.04	5.55	0.105	11.6	89.5
52	4.10	12.4	0.103	11.4	91.7
53	5.12	9.88	0.079	7.89	132

Table XII

Measurements of Molecular Weight of Polystyrenes for Chain
Transfer Studies at High Pressures.

Solvent: Tetrachloroethylene   Initiator: AIBN

Temperature: $60^{o}C$ $[C]/[M] = 0.64 \times 10^{-3}$

Runs 54 - 65: 1030 atmospheres

Runs 66 - 72: 1510 atmospheres

Runs 73 - 78: 1980 atmospheres

Runs 79 - 84: 2680 atmospheres

Run No.	[S]/[M]	% Polymer	$[\eta]$ (dl/gm)	$\times 10^{-3}$ Molec.wt.	$1/\overline{DP} \times 10^4$
54	Bulk	5.08	1.81	573	1.82
55	0.111	8.32	0.93	231	4.5
56	0.198	7.73	0.777	180	5.78
57	0.317	6.95	0.562	116	8.98
58	0.416	6.36	0.505	100	10.4
59	0.529	5.99	0.432	81.0	12.9
60	0.749	5.16	0.369	65.2	16.0
61	1.21	9.60	0.250	38.2	27.3
62	2.08	14.2	0.170	22.5	46.2

Table XII (continued)

Run No.	[S]/[M]	%/o Polymer	$[\eta]$ (dl/gm)	x 10^{-3} Molec.wt.	1/DPx10^4
63	3.04	8.53	0.120	14.0	74.6
64	4.10	9.73	0.104	11.4	91.2
65	5.12	7.05	0.093	9.82	106
66	0.111	8.48	0.797	187	5.56
67	0.529	12.2	0.352	70	17.1
68	1.21	13.5	0.205	29.2	35.6
69	2.08	10.1	0.152	19.4	53.8
70	3.04	9.09	0.146	18.2	57.1
71	4.10	7.40	0.105	11.5	90.3
72	5.12	9.91	0.097	10.5	94.6
73	0.529	11.9	0.362	63.7	16.33
74	1.21	12.8	0.206	28.0	35.5
75	2.08	10.4	0.135	16.4	63.7
76	3.04	10.6	0.110	12.4	83.9
77	4.10	7.45	0.109	12.3	84.9
78	5.12	8.19	0.092	9.77	107

Table XII (continued)

Run No.	[S]/[M]	% Polymer	$[\eta]$ (dl/gm)	x 10^{-3} Molec.wt.	$1/DP \times 10^4$
79	0.529	11.4	0.386	69.7	14.9
80	1.21	13.4	0.192	31.1	33.5
81	2.08	12.9	0.139	17.1	60.9
82	3.04	9.32	0.105	11.6	90.1
83	4.10	12.0	0.093	9.84 ~~9.93~~	106
84	5.12	6.5	0.092	9.77	107

Table XIII

Effect of Pressure on Chain Transfer to Solvent in the
Polymerisation of Styrene with AIBN at 60°C.

solvent: Tetrachloroethylene

Pressure (atm.)	[S]/[M]	$1/\overline{DP} \times 10^4$	$c_S \times 10^4$
1	Bulk	5.43	29.0
	0.530	21.2	
	1.21	40.9	
	2.08	66.0	
	3.04	89.5	
	4.10	91.7	
	5.12	132	
1030	Bulk	1.82	21.1
	0.53	12.9	
	1.21	27.3	
	2.08	46.2	
	3.04	74.6	
	4.10	91.2	
	5.12	106	

Table XIII (continued)

Pressure (atm.)	[S]/[M]	$1/\overline{DP} \times 10^4$	$c_S \times 10^4$
1510	0.53	17.1	24.8
	1.21	35.6	
	2.08	53.8	
	3.04	57.1	
	4.10	90.3	
	5.12	94.6	
1980	0.53	16.3	26.8
	1.21	35.5	
	2.08	63.7	
	3.04	83.9	
	4.10	84.9	
	5.12	107	
2680	0.53	14.9	27.4
	1.21	33.53	
	2.08	60.9	
	3.04	90.1	
	4.10	106	
	5.12	107	

Table XIV

Determination of Solvent Transfer Constant by

Breitenbach – Schindler Method

Runs 85 – 91 : 1 atmosphere

Runs 92 – 97 : 1510 atmospheres

Runs 98 – 103: 2680 atmospheres

Run No.	$(1/\overline{DP}-C_m)10^5$	$[S]/[M]/V \times 10^{-5}$	$\dfrac{[M]^2}{V}(1/\overline{DP}-C_m)10^{-2}$	$\times 10^5$ C_m	$\times 10^4$ C_s	$C_s/2$
85	48.3	0	6.85			
86	206	7.25	28.3			
87	403	15.9	52.8			
88	654	25.6	80.5	6	29.0	685
89	831	46.4	127			
90	911	53.5	119			
91	1315	65.6	168			
92	50.6	0.56	2.55			
93	166	2.49	7.79			
94	331	5.39	14.7	5	24.8	115
95	533	8.44	21.6			
96	561	12.7	23.5			
97	898	20.5	44.9			

Table XIV (continued)

Run No.	$(1/\overline{DP}-C_m)10^5$	$[S]/[M]/V \times 10^{-5}$	$\frac{[M]^2}{V}(1/\overline{DP}-C_m)10^{-2}$	$\begin{array}{c}\times 10^5 \\ C_m\end{array}$	$\begin{array}{c}\times 10^4 \\ C_s\end{array}$	$\mathcal{G}^2/2$
98	146	1.37	3.79			
99	331	2.80	7.65			
100	605	5.42	15.8	4	25.6	3
101	897	7.87	23.2			
102	1053	8.37	21.5			
103	1061	13.8	28.6			

Table XV

Effect of Pressure on Transfer Constants of Styrene to
Tetrachloroethylene and Carbon Tetrachloride

Pressure (atm.)	$C_s \times 10^4$		Reference
	Tetrachloroethylene	carbontetrachloride	

(Styrene-AIBN System)

Pressure (atm.)	Tetrachloroethylene	carbontetrachloride	Reference
1	29.0	–	
1030	21.1	–	
1510	24.8	–	
1980	26.8	–	
2680	27.4	–	This work

(Styrene-Benzoylperoxide System)

Pressure (atm.)	Tetrachloroethylene	carbontetrachloride	Reference
1	–	98	(112)
2000	–	90	(112)
3950	–	84	(112)
3950	–	67[*]	(112)
6000	–	59[*]	(112)

(Styrene-AIBN System)

Pressure (atm.)	Tetrachloroethylene	carbontetrachloride	Reference
1		148(corrected)	(88)

[*]Figures obtained at higher [S]/[M] ratios (0.5-1.85)

Table XVI

The Overall Rate Constants in the Polymerisation
of Styrene in Tetrachloroethylene at 60°C at 1 Atmosphere.

$[M]$ = 4.18 moles per litre   Initiator: AIBN

Run No.	$[C] \times 10^3$ moles per litre	$V \times 10^5$ moles per litre per second	$V/[M]^{1.5}[C]^{0.5} \times 10^5$ litre/mole-second
1	1.31	0.89	2.88
2	2.65	1.33	3.03
3	3.96	1.57	2.93
4	5.36	1.83	2.93
5	7.95	2.22	2.92

Table XVII

Polymerisation of Styrene in Tetrachloroethylene
at 60°C and at one Atmosphere

$[C]/[M] = 1.90 \times 10^{-3}$ Initiator: AIBN

Run	$[S]/[M]$	$[C] \times 10^3$ moles per litre	$[M]$ moles per litre	% conversion (hours)	Time (hours)	$V \times 10^5$ moles/ℓ/sec
104	1.21	7.95	4.18	11.4	6	2.22
105	2.08	5.79	3.04	8.9	6	1.25
106	3.04	4.47	2.35	7.0	6	0.76
107	4.10	3.56	1.87	5.6	6	0.46
108	5.12	2.97	1.57	4.7	6	0.34

Table XVIII

Composition of Polymers Prepared by Polymerising Styrene in T.C.E. Using A.I.B.N. at 60°C and at 1 atmosphere.

M = Styrene

C = A.I.B.N.

Run No.	M mole % in feed	[C] mole %	Composition of Polymer			Mol.wt x10^{-3}
			wt.% C	wt.% H	wt.% Cℓ	
37	65.3	0.042	91.79	7.31	0.5	49.6
32	45.0	0.028	91.05	7.38	1.57	25.5
27	32.3	0.021	89.15	7.43	3.42	15.8
22	24.6	0.016	89.48	7.44	2.38[*]	11.6
17	19.5	0.012	89.45	7.18	2.90[*]	11.4
12	16.2	0.010	88.92	7.32	3.76	7.9

[*] Found gravimetrically, others by difference.

Table XIX

Composition of Polymers Prepared by Polymerising Styrene in T.C.E. using A.I.B.N. at 60°C at High Pressures.

M = Styrene

C = A.I.B.N.

Run No.	M mole % in feed	[C] mole %	Composition of Polymer			Mol.wt x10^{-3}
			wt.% C	wt.% H	wt.% Cl	
(60°C, 1030 atmospheres)						
109	89.99	0.057	91.09	7.84	1.05[x]	236.6
110	45.0	0.028	91.52	7.85	1.37[x]	38.2
111	32.3	0.021	90.31	7.50	2.19	22.5
112	24.6	0.016	90.51	7.87	2.25[x]	14.0
113	19.5	0.012	88.98	7.43	3.59	11.4
(60°C, 1510 atmospheres)						
114	32.3	0.021	90.53	7.43	3.33[x]	19.4
115	24.6	0.016	87.18	7.62	2.14[x]	18.2
116	16.2	0.010	88.67	7.45	3.2[x]	9.8

Table XIX (continued)

Run No.	M mole % in feed	[C] mole %	Composition of Polymer			Mol.wt x10^{-3}
			wt.% C	wt.% H	wt.% Cℓ	
(60°C, 1980 atmospheres)						
117	65.3	0.042	90.63	7.33	0.95[x]	63.7
118	45.0	0.028	90.69	7.43	1.5[x]	28.0
119	24.6	0.016	88.47	7.39	2.89[x]	12.4
(60°C, 2680 atmospheres)						
120	45.0	0.028	91.11	7.72	1.38	31.1
121	32.3	0.021	90.78	7.60	1.8	17.1
122	24.6	0.016	89.43	7.46	2.68	11.6
123	19.5	0.012	88.51	8.37	2.26[x]	9.84
124	16.2	0.010	88.61	7.55	4.41	9.77
(80°C, 3110 atmospheres)						
125	32.3	0.021	89.73	7.75	3.52	–
126	19.5	0.012	88.0	6.99	3.87	–

Table XIX (continued)

Run No.	M mole % in feed	[C] mole %	Composition of Polymer			Mol.wt x10^{-3}
			wt.% C	wt.% H	wt.% Cℓ	
			(80°C, 3350 atmospheres)			
127	8.99	0.0057	82.28	7.07	5.88	–
			(80°C, 3540 atmospheres)			
128	16.2	0.010	86.34	7.23	6.37	–

≭ Found gravimetrically, others by difference.

Table XX

Average Molar Composition of Polymers Obtained

at $60^{\circ}C.$

Run No.	Styrene mole % in feed	Styrene mole % in polymer	Mean numbers of styrene units (n_1) and T.C.E. units (n_2) per polymer molecule	
			$\{CH_2-CH\phi\}_{n_1}$	$\{CCl_2-CCl_2\}_{n_2}$

(1 atmosphere)
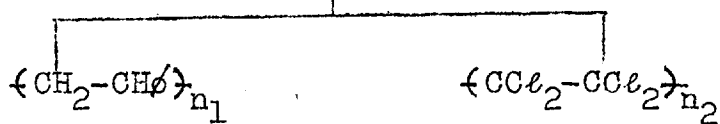
Run No.	Styrene mole % in feed	Styrene mole % in polymer	n_1	n_2
32	45.0	98.86	255	3
22	24.6	97.72	112	2
17	19.5	97.86	90	2

(1030 atmospheres)

Run No.	Styrene mole % in feed	Styrene mole % in polymer	n_1	n_2
110	45.0	98.99	392	4
111	32.3	98.38	244	4
112	24.6	98.33	148	4
113	19.5	97.32	104	3

(1500 atmospheres)

Run No.	Styrene mole % in feed	Styrene mole % in polymer	n_1	n_2
115	24.6	98.42	186	3
116	16.2	97.63	82	2

Table XX (continued)
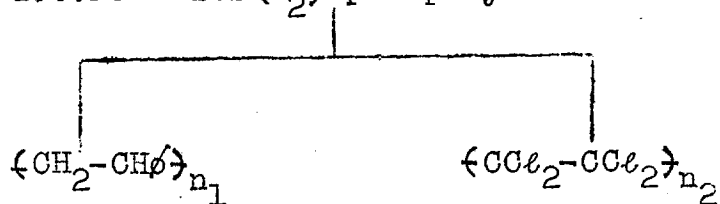
Run No.	Styrene mole % in feed	Styrene mole % in Polymer	Mean numbers of styrene units (n_1) and T.C.E. units (n_2) per polymer molecule	
			$\{CH_2\text{-}CH\phi\}_{n_1}$	$\{CCl_2\text{-}CCl_2\}_{n_2}$
			(1980 atmospheres)	
118	45.0	98.91	267	3
119	24.6	97.85	138	3

Table XXI

Composition of Polymers Prepared by Polymerising

Methyl methacrylate in tetrachloroethylene at 60°C

using A.I.B.N. at 1 Atmosphere and 2675 Atmospheres.

Run No.	Pressure	MMA mole % in feed	MMA mole % in polymer	$[C]$ mole %	Composition of Polymer			
					wt. %/o C	wt. %/o H	wt. %/o Cℓ	wt. %/o O
129	1	46.9	99.17	.0061	59.58	7.96	0.46	32
130	2675	46.9	99.79	.00262	59.64	8.05	0.34	32
131	2675	29.76	99.79	.00152	58.65	7.84	1.51	32
132	2675	19.52	98.86	.00097	58.02	8.17	1.62*	32

* By gravimetric estimation, others

  by difference.

FIGURE 6: ORDER OF REACTION WITH RESPECT TO INITIATOR CONCENTRATION
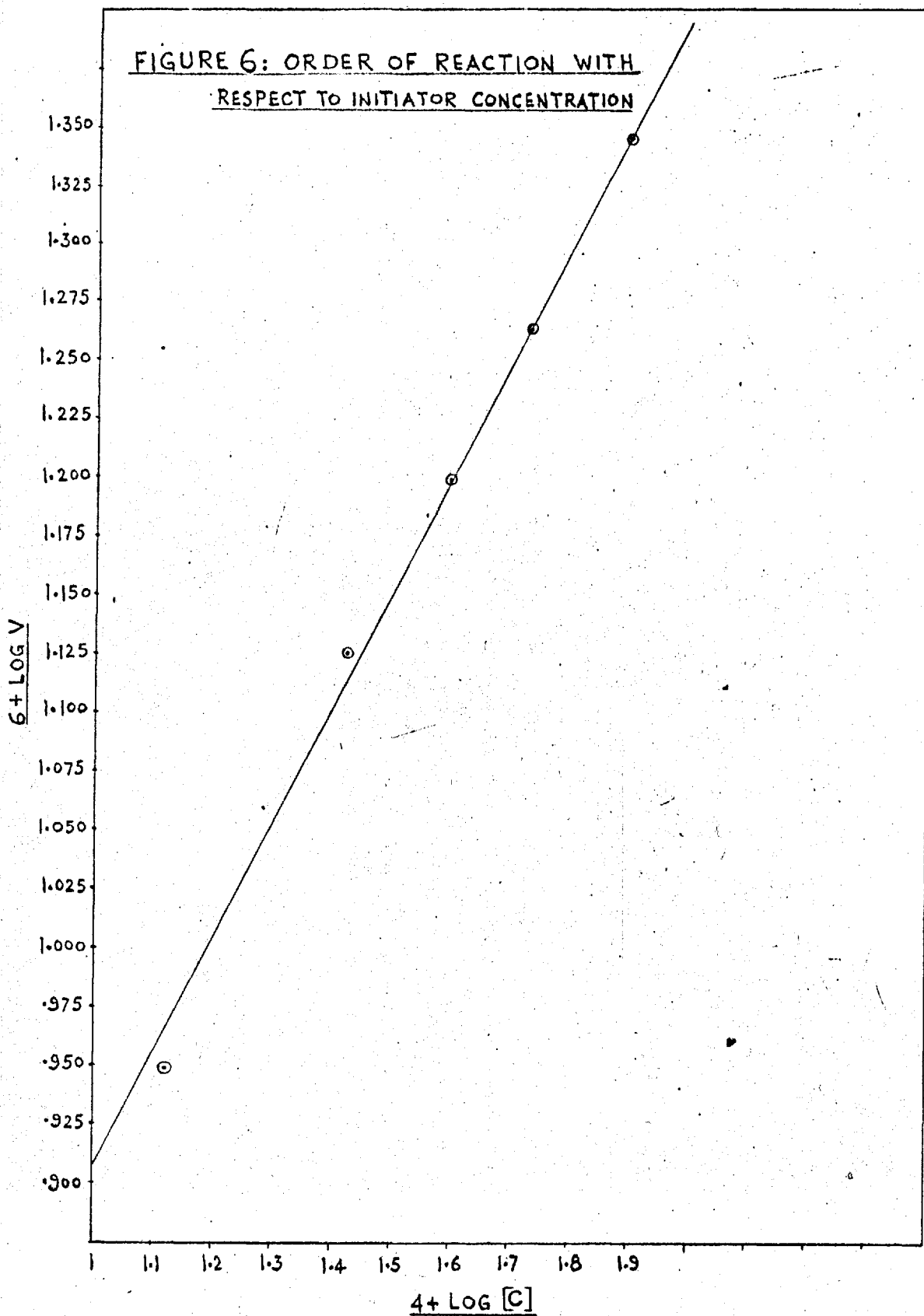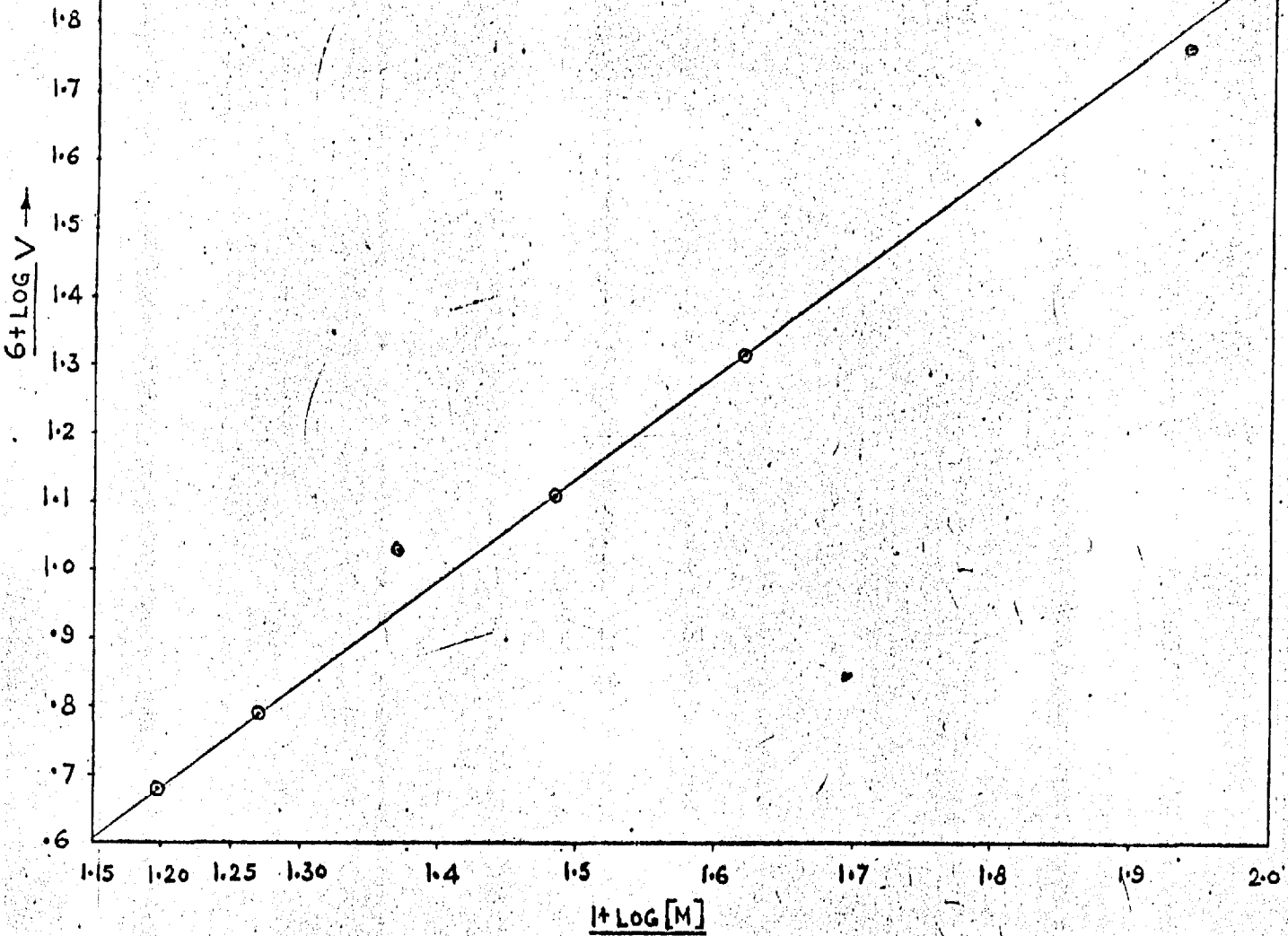
FIGURE 7: ORDER OF REACTION WITH RESPECT TO MONOMER CONCENTRATION

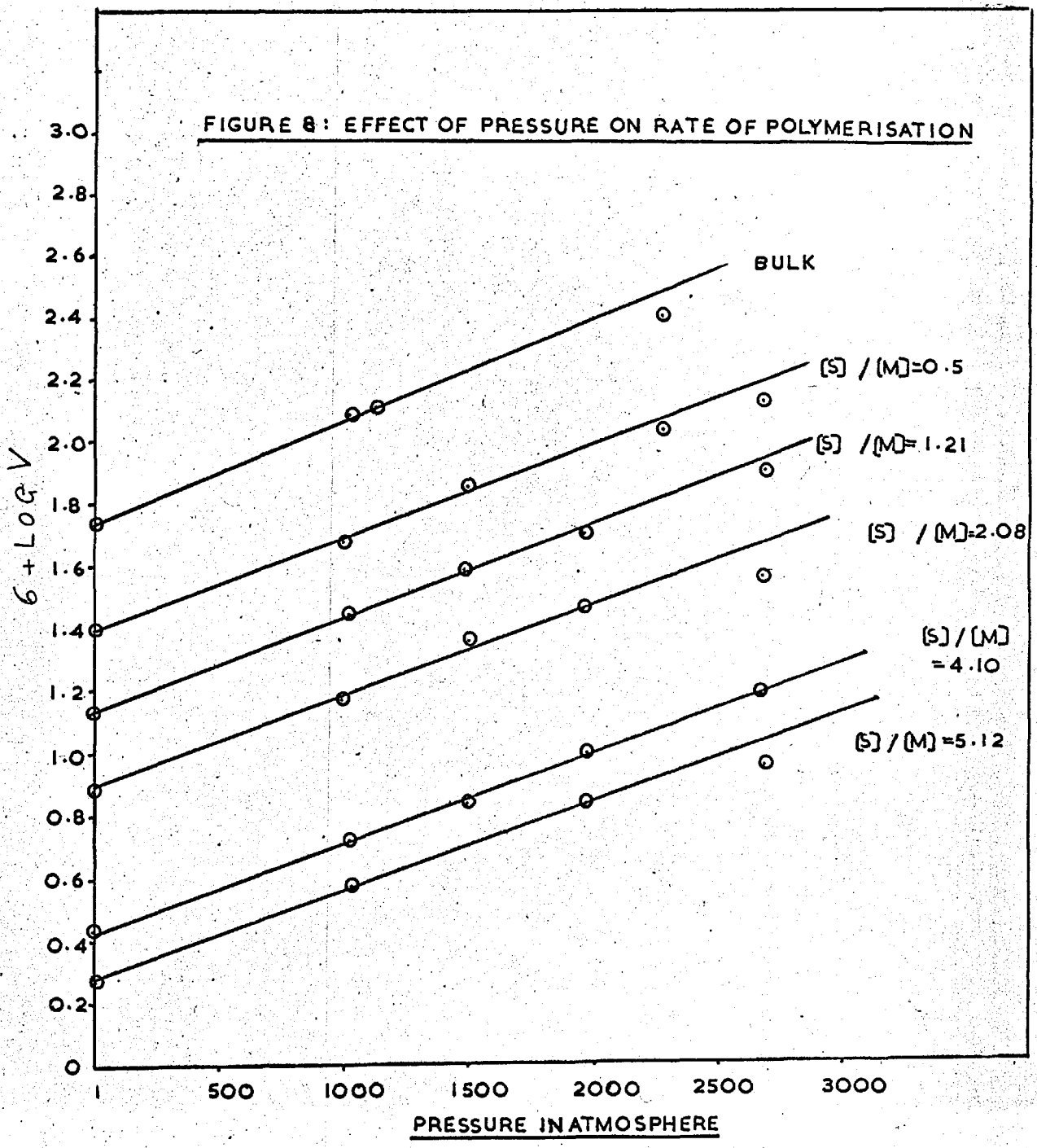FIGURE 8: EFFECT OF PRESSURE ON RATE OF POLYMERISATION

FIGURE 9: EFFECT OF PRESSURE ON MOLECULAR WEIGHT
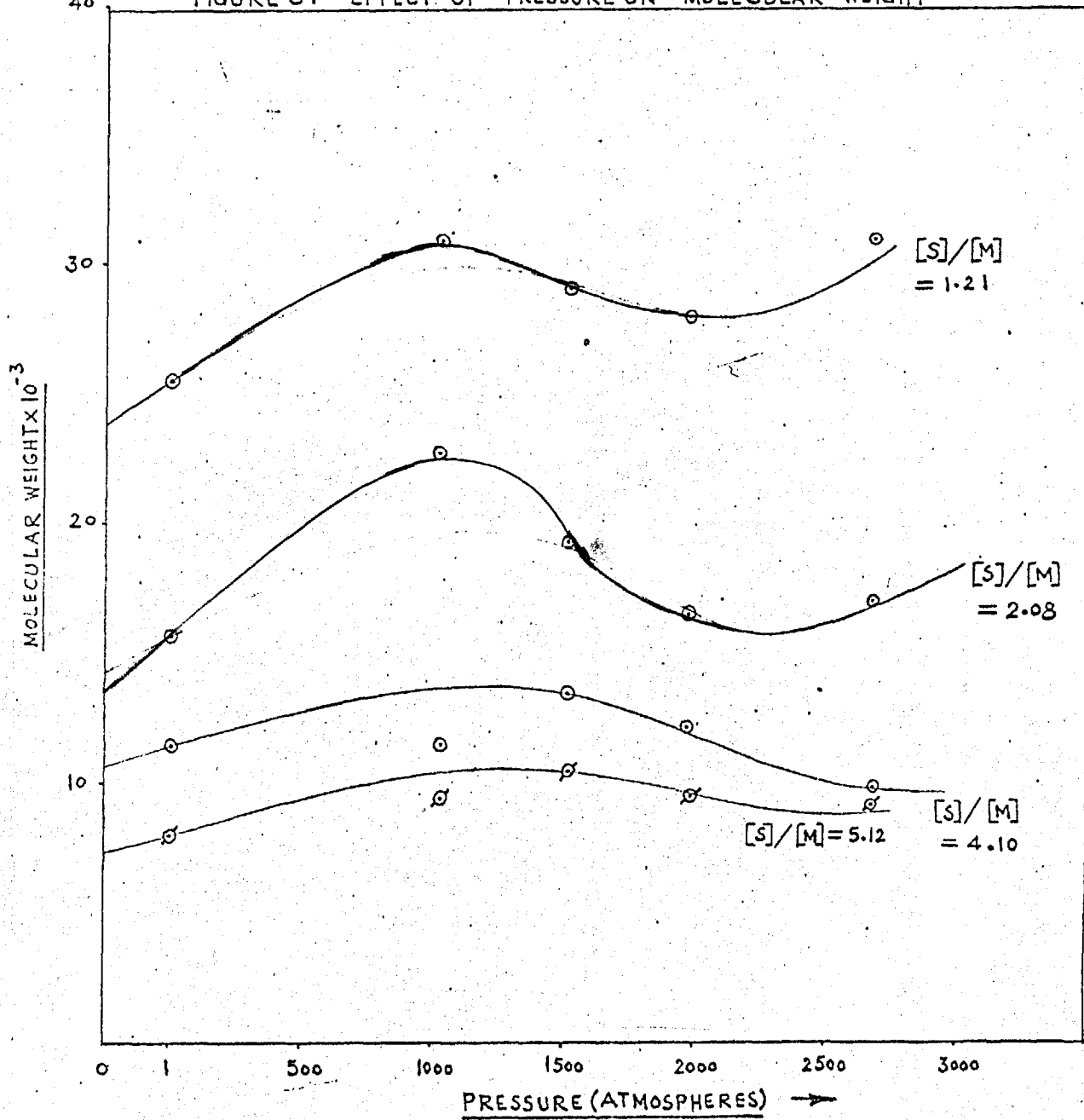
FIGURE 10:

EFFECT OF PRESSURE ON C_s

(STYRENE-T.C.E. SYSTEM)
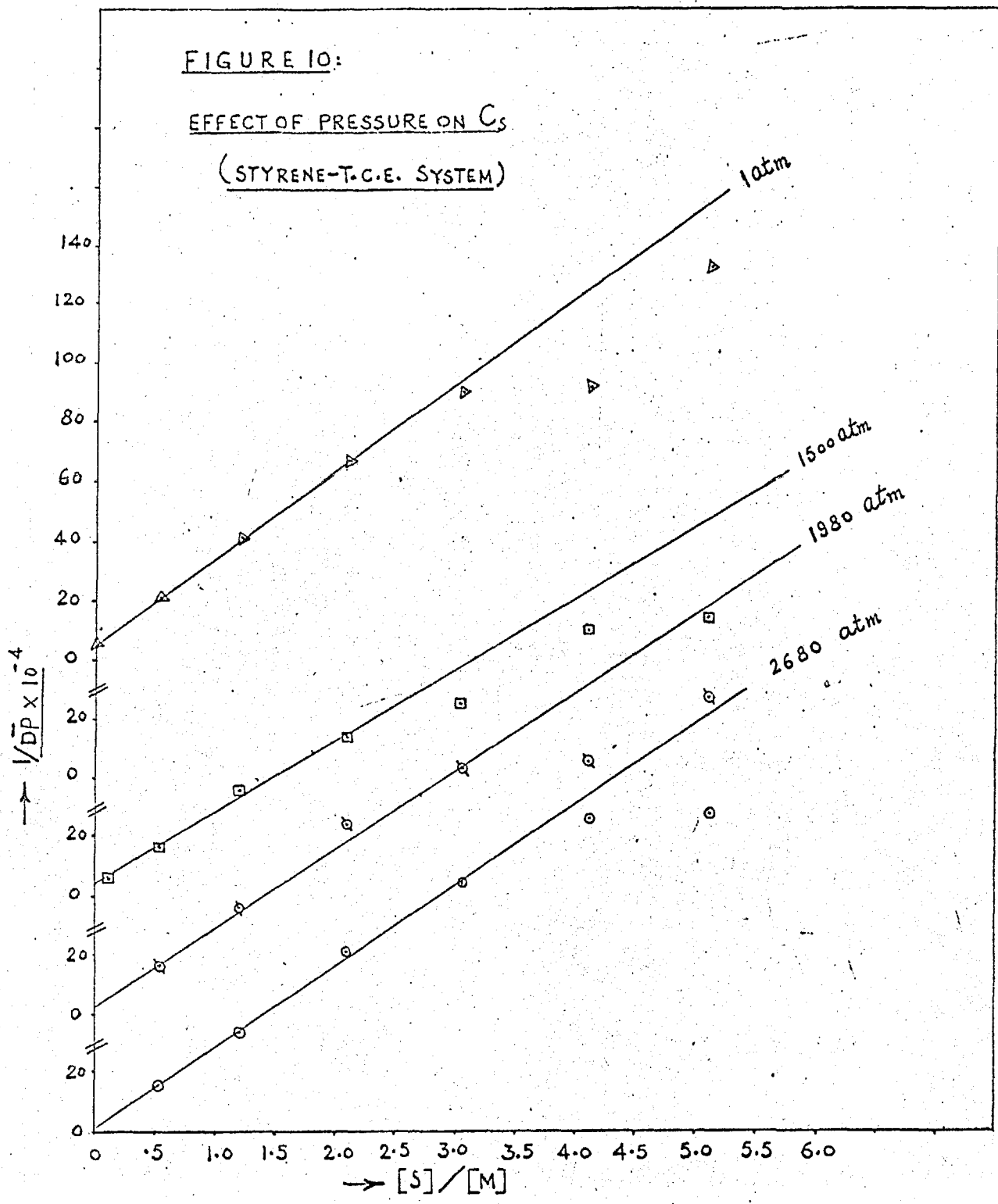
FIGURE 11   Breitenbach_Schindler Plots for C_s values.   161
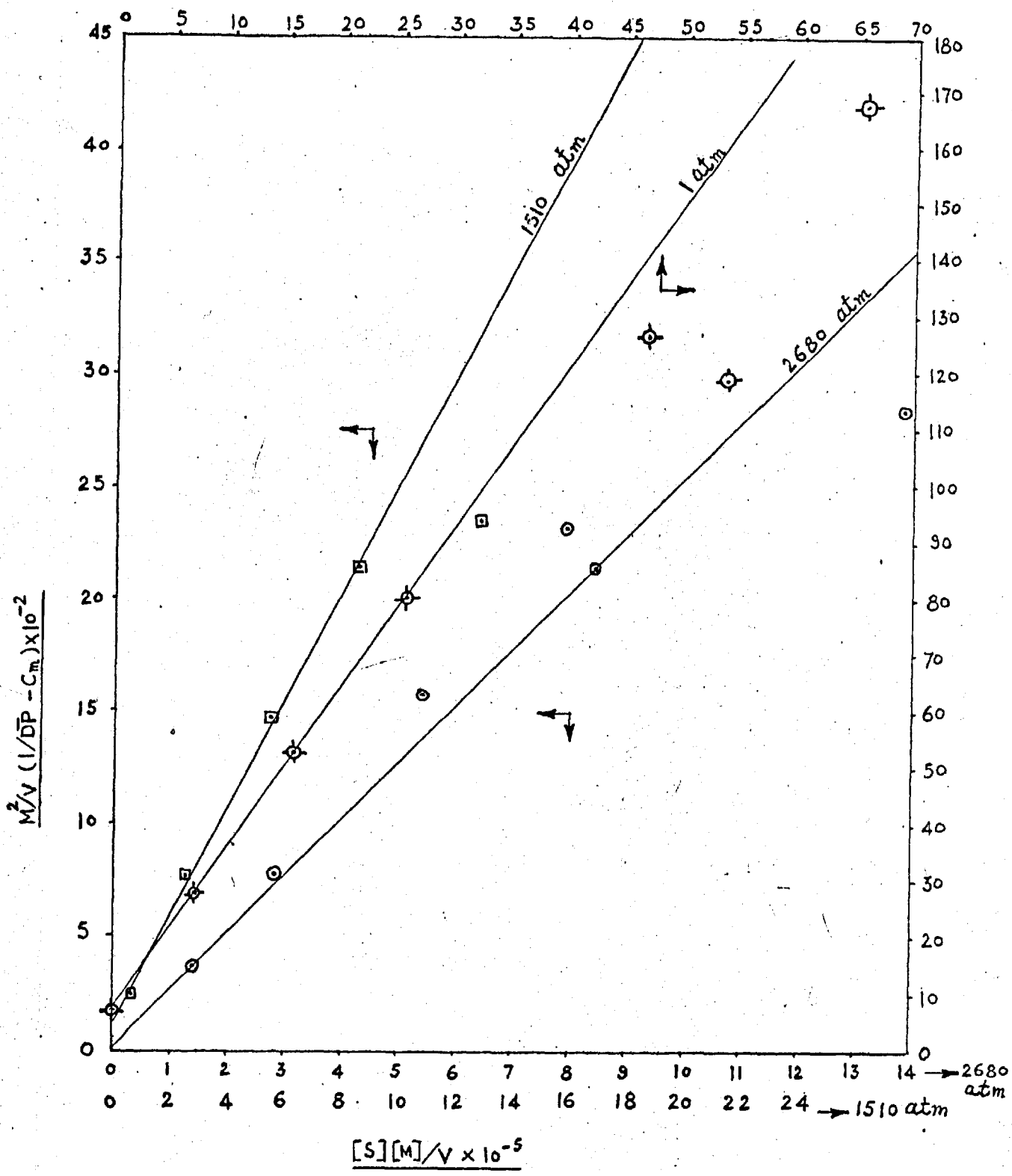
III.2.   Results and Discussion

(i)   Order of Reaction with Respect to Initiator

Concentration.

A series of experiments with constant monomer con-
centration, [M] = 4.18 moles per litre were carried out
(Runs 1-5) and the results are given in Table IX. On
plotting log V (overall rate) versus log initiator
concentration, the exponent obtained from the slope of
the straight line is 0.49 (Figure 6). This indicates
that two chains are involved in the termination reaction,
that is, the process is bimolecular and the process of
transfer is not degradative.

That the rate of radical polymerisation is usually
proportional to the square root of the initiator con-
centration had been known for more than three decades
and the data of figure 6 are in accord with the usual
kinetic scheme, according to which the rate of the homo-
geneous polymerisation of styrene is given by equation (10):

$$V = \delta^{-1}(2fk_d)^{\frac{1}{2}} [M][C]^{\frac{1}{2}}$$

where δ (or d) = $k_t^{1/2}/k_p$.

This can be shortened to:

$$V = k_p[M](I/k_t)^{1/2} \quad \ldots\ldots\ldots \quad (45)$$

These imply that polymerisation rates should be proportional to the square root of the rate of initiation, I, even when other initiation processes are involved.

Similar results for the dependence of the rate of polymerisation of styrene on the initiator concentration in other solvents at 1 atmosphere have been reported (64, 106, 191, 192).

The results for polymerisation of styrene in tetra-chloroethylene at 1 atmosphere are thus in keeping with the idea of the generality of bimolecular termination process in free radical polymerisation. The deviations reported by some workers under special conditions, which have been discussed in Section I.$\measuredangle$(vi), were not observed in the conditions used in this work.

(ii) Order with Respect to Monomer Concentration.

A series of experiments (Runs 6-11) with a constant initiator concentration, [C] = 6.09 moles per litre, were carried out and the results are listed in Table IX. By plotting log V versus log [M], an order of 3/2 is

obtained with respect to the monomer concentration
(Figure 7).

The interpretation of the order of reaction with
respect to the monomer concentration is not as clear
cut as that for the initiator concentration. The simple
kinetic scheme (Equation 45) predicts first order dependence
on the monomer concentration and for the styrene/Benzene/
benzoylperoxide system the reaction is close to the first
order with respect to the monomer (47).

However, as stated in Section I.3.(vi), orders higher
than unity have been reported in the literature and
generally the values lie between 1 and 1.50 (47, 63-67,
70, 79, 80).

Horikx and Hermans (67) investigated the system
styrene/toluene/benzoyl peroxide with great precision
and obtained orders with respect to the monomer concen-
tration greater than one, increasing from 1.18 at
[M] = 1.8 moles per litre to 1.36 at [M] = 0.4.

While discussing the solvent-cage theory in Section
I.3 (vi). (b) it was shown that the application of the
stationary state procedure yields the following rate
equation:

$$ - \frac{d[M]}{dt} = \delta^{-1} k_d^{1/2} [M][c]^{1/2}[\frac{k_D + k'_p[M]}{k_R + k_D + k'_p[M]}]^{1/2} $$

and that the exact form of this equation will be determined
by processes 3 and 4 of the 8-step scheme explained,
that is, by the relative magnitudes of k_D and $k'_p[M]$.

The order of reaction with respect to monomer is
unity if k_D is much greater than $k'_p[M]$, and if k_D is
much smaller than $k'_p[M]$, the rate becomes proportional
to

$$ [M][\frac{k'_p[M]}{k_R + k'_p[M]}]^{1/2} $$

which means that the order of reaction will vary from
1.0 to 1.5 with respect to monomer.

There is no general agreement regarding the under-
lying causes of the observed behaviour nor has any
quantitative account been given of the variation. It
appears from the available data of the different workers
that it may be due to many factors, amongst which the
following are important:

(a) variation in k_d and efficiency (f) with medium.

(b) casual impurities present in solvents may cause
retardation.

(c) reaction between growing polymer chains and the
solvents, the solvent having a great influence on
the order of polymerisation.   Retardation may occur
if the growing polymer chain is more reactive than
the resulting radicals.

Various theories have been advanced to account for this
behaviour and have been discussed in the first section
of this work.   Jenkins (95) has thoroughly analysed this
matter and has shown that neither the monomer-initiator
complex theory, the cage hypothesis, nor the solvent
transfer theory is able to explain fully the various
kinetic data.   The complex theory is particularly difficult
to sustain in view of the findings of Josefowitz and
Mark (162),   Matheson (69) and Mayo, Gregg and Matheson
(47).   The primary radical termination theory has also
been shown lacking in certain respects by Bamford,
Jenkins and Johnston in a separate paper (84).

(iii)   The Pressure Effect on the Rate and Molecular
        Weight in Bulk Polymerisation of Styrene.

Bulk polymerisation of pure styrene, $[M]$ = 8.70
moles/litre, initiated by azobisisobutyronitrile was
carried out at 60°C and at four different pressures and

the results are summarised in Table X, runs 43-46. The
initiator concentration was 5.5×10^{-3} moles per litre.
Figure 8 shows the effect of pressure on the overall
rate of reaction. The rate increases from 5.34×10^{-3}
at 1 atmosphere to 25.4×10^{-3} moles/litre-second at
2270 atmospheres, an increase of 4.7 fold. The rate
at 1 atmosphere is fairly close to that reported by
Saha, Nandi and Palit (121) as would appear from the
following:-

[AIBN]/[styrene] $\times 10^4$	$V \times 10^5$ moles/litre-second	$1/\overline{DP} \times 10^5$	δ	Reference
6.41	5.6	71.77	~29	(121)
6.40	5.34	54.3	~36	This work

The value for the degree of polymerisation obtained
by Saha et al is lower than that obtained in this work
and consequently the value of δ is also lower. Saha
et al have not furnished the details of the method
employed by them for the determination of molecular
weights.

The polymers prepared at 1 atmosphere and 1000
atmospheres (Runs 47 and 54) with [C] = 5.54×10^{-3} moles/litre,

at 60°C, showed a 2.9 fold increase in the molecular weight from 1 atm. to 1000 atmospheres.

It is appropriate to mention that the values of rates throughout this work are uncorrected for increases in monomer, solvent and initiator concentrations due to compressibility at high pressures.

III.3 (a) Polymerisation in Solution at Atmospheric Pressure.

The results of the atmospheric pressure runs for styrene in tetrachloroethylene, using azobisisobutyronitrile, at 60°C, are shown in Table X (Runs 12, 17, 22, 27, 32 and 37). The values are uncorrected for increases in monomer and solvent concentrations due to compressibility. The monomer concentration was varied from 1.57 to 5.92 moles per litre, but the [C]/[M] ratio, 0.64×10^{-3}, was kept constant in order to maintain a constant rate of initiation. The conversions were not allowed to exceed $10°/o$. The rate increases from 0.19×10^{-5} moles/litre/ second with [M] = 1.57 moles per litre to 2.55×10^{-5} as the monomer concentration increases to 5.92 moles per litre.

For runs 1-5 in which the monomer concentration was kept constant, [M] = 4.18 moles per litre in tetrachloro- ethylene as solvent, but the initiator concentration, [C] was varied, the overall rate constants, $V/[M]^{3/2}[C]^{1/2}$ were calculated and are given in Table XVI.

The results, except that for run 2, for the overall rate constant are concordant within the limits of the experimental error. This confirms that the system under

observation obeys the simple half-order law for initiator concentration as postulated in Section I.3. The results of another set of experiments on the polymerisation of styrene in T.C.E. with [C]/[M] ratio equal to 1.9×10^{-3} are classified in Table XVII.

(b) <u>Polymerisation in Solution at High Pressures.</u>

The dependence of the overall rate of polymerisation on pressure was studied over a range of [S]/[M] ratios up to a pressure of 2700 atmospheres, keeping the relation-ship [C]/[M] constant throughout. The results along with the rates calculated in moles per litre per second have been classified in Table X. Comparing the rates obtained at one atmosphere with those at higher pressures, it is seen that pressure has an accelerating effect. There is a 5 to 6-fold increase in the rate from 1 atmosphere to 2680 atmospheres over a range of molar ratios, [S]/[M], between 0.529 and 5.12.

(c) <u>Molecular Weights.</u>

Inspection of Table XI shows that the molecular weight of styrene polymerised in bulk, using azobisiso-butyronitrile at $60^{\circ}C$ increases from 192×10^{3} at 1 atmos-phere to 573×10^{3} at 1030 atmospheres. Pressure increases k_{p} relative to $k_{t}^{1/2}$ and k_{s}.

The molecular weights of polymers obtained from the styrene-tetrachloroethylene-A.I.B.N. system show additional features of interest. It is apparent from Table XI and Figure 9 that the intrinsic viscosity, and consequently the molecular weight, increases with increase in pressure up to about 1030 atmospheres for solvent-monomer molar ratio up to 3.04. With increasing dilution of the monomer, the change in molecular weight is less pronounced and with solvent-monomer molar ratios, [S]/[M] > 3.04, the molecular weight remains almost constant. As tetrachloroethylene is active in transfer with the growing polystyrene chains, the average molecular weights of the polymer are markedly reduced in the reactions at high dilutions.

Figure 9 also shows a trend to increased molecular weights at about 3000 atmospheres and higher pressures. Although the present work is mostly confined to studies up to 2680 atmospheres, Lamb and Weale (197) have studied the same system at 60°C between 3000 and 6000 atmospheres and report that the molecular weight increases much more rapidly in this range, probably because of the phase separation of solid tetrachloroethylene at these pressures.

III.4 (a) Determination of Chain Transfer Constant
at 1 Atmosphere.

For the determination of the numerical value of C_S, the dilution method was employed, which has been discussed in Section I.4 (ii) (a). Styrene was polymerised in tetrachloroethylene at $60^{\circ}C$, using azo-bis-isobutyronitrile. For reasons stated in the concluding paragraph of Section I.4 (iii), the molar ratio, $[C]/[M] = 0.64 \times 10^{-3}$ was maintained constant. An $[S]/[M]$ range varying between 0.53 and 5.12 was employed for conducting atmospheric pressure runs (Runs 47-53). The viscosity measurements were done in benzene solutions at $25^{\circ}C$ and the intrinsic viscosity was obtained by extrapolating the graph of η_{sp}/C against C to zero concentration.

The degree of polymerisation, $\overline{DP}$, was determined from the relationship of Mark and Houwink (182-185):

$$[\eta] = K.M^{\alpha}$$

The molecular weight calculations were based on the equations of Bawn et al (187) which cover both benzene and toluene and give fairly concordant results with published work. As stated above toluene was not employed as a solvent for the polymer.

Table XI summarises the data on [S]/[M], percentage conversions of the polymer, intrinsic viscosities, molecular weights and $1/\overline{DP}$.

For the determination of C_S, Mayo's equation was used:

$$1/\overline{DP} = 1/\overline{DP}_0 + C_S \left[\frac{S}{M}\right]$$

in which $\overline{DP}_0$ is the value of $\overline{DP}$ in the absence of the solvent. It may be pointed out that in the system under study, the initiator transfer and the monomer transfer terms are negligible. The solvent transfer constant, C_S, was found by plotting the values of $1/\overline{DP}$ against the range of molar ratios, [S]/[M], the slope of the straight line being equal to the transfer constant (Figure 10). It has already been pointed out that in view of the various types of solvent reactivity, the relationships of reaction rate and molecular weight of product with concentration are not simple, nor the same from one monomer to another. The rate of polymerisation is normally reduced with greater dilution of monomer and dilution, apart from non-solvent effects, also reduces the polymer average molecular weight. Inspection of Table XI shows that the molecular

weight decreases from 49.61×10^3 at $[S]/[M] = 0.53$ to 7.89×10^3 at $[S]/[M] = 5.12$. This marked decrease in the value of $\overline{DP}$ is mainly due to the activity of the tetrachloroethylene as a chain transfer solvent. The numerical value of C_S obtained graphically is 29×10^{-4}.

Schulz, Dinglinger and Husemann (193), and Suess and Springer (41) have studied the polymerisation of styrene in several chlorinated solvents and compared the rates and degrees of polymerisation of the polymers obtained. Gregg and Mayo (109) have determined the transfer constants of halides with polystyrene radicals at $60^{\circ}C$ and the numerical values are given in Table III, page 60. Breitenbach and Schindler (122) investigated the polymerisation of styrene in chlorinated aliphatic and aromatic hydrocarbons and reported some interesting results which will be discussed below. Carbon tetrachloride possesses a very high transfer constant, and benzal chloride and benzotrichloride are also fairly reactive.

(b) (i) Chain Transfer at High Pressures.

Styrene initiated with azobisisobutyronitrile was polymerised at $60^{\circ}C$ in tetrachloroethylene over a range of solvent/monomer concentration ratios. $[S]/[M]$ ratios

above 5.12 were not employed in view of the observations
of Walling and Pellon (112) and George and Onyon (88)
on the styrene/carbon tetrachloride system, as discussed
below. The ratio of the initiator to monomer concentration
was kept constant, following the procedure of Toohey
and Weale (106) and Basu et al (100). The polymerisation
was carried out at four different pressures and the high
polymers isolated according to the procedure explained
in Section II.3 (c). The degrees of polymerisation, $\overline{DP}$,
were determined by the viscometry method, the details
of which are given in Section II.3 (e). The results are
summarised in Table XII. The solvent transfer constant
at each pressure was determined graphically by plotting
the values of $1/\overline{DP}$ versus $[S]/[M]$, the slope of the
straight line being equal to C_S (Figure 10). As in the
case of chain transfer studies at 1 atmosphere, the values
of C_I for styrene/A.I.B.N. system were taken as zero.
The values of C_M were also ignored as these affect only
the fifth place of the figures for C_S. The plot of $1/\overline{DP}$
against the molar ratios of the solvent to the monomer
was linear up to $[S]/[M] = 3.04$, although for 1500 atmos-
pheres, the experimental points began to fall below the

line at dilution of styrene beyond an [S]/[M] ratio of

2.08. As mentioned above similar trends have been

observed in the case of carbon tetrachloride. Walling

and Pellon (112) observed during their investigations of

the styrene/carbon tetrachloride/benzoyl peroxide system

that at higher dilutions of styrene, [S]/[M] > 0.4, the

experimental points fell below the line. Gregg and Mayo

(111) observed a similar trend, and their values of $1/\overline{DP}$,

(uncorrected for loss of low-molecular-weight materials)

vary linearly with [S]/[M] up to [S]/[M] ratios of approxi-

mately 0.6 beyond which a curvature is observed both at

$60^{\circ}C$ and $100^{\circ}C$. They attributed it to the loss of low

molecular weight polymers during isolation. Accordingly

Walling and Pellon estimated C_S only from those points

which were obtained for [S]/[M] ratios ranging from 0.1

to 0.4. George and Onyon (88) investigated the thermal

polymerisation of styrene in carbon tetrachloride at

$60^{\circ}C$ at 1 atmosphere. They found that the use of incorrect

$\overline{DP}$ values as a result of the loss of low molecular weight

polymer during isolation produces a serious source of

error, and that the corrected results lie on a straight

line. By varying the [S]/[M] ratios from 0.244 to 6.026,

they obtain a straight line up to [S]/[M] = 2.452 but the

experimental point for [S]/[M] = 6.026 falls below the line. George and Onyon did not study 1/D̄P as a function of [S]/[M] between 2.452 and 6.026 and hence it is difficult to decide at what value the [S]/[M] ratio ceases to vary linearly with the reciprocal degree of polymerisation and the pronounced curvature begins.

It appears from Table XII that with increase in [S]/[M] ratios, the decrease in molecular weights is very marked up to an [S]/[M] value of 3.04 (2.08 at 1510 atm), beyond which the molecular weight decreases only slowly. (The values of the reciprocal degree of polymerisation given in the present work are uncorrected for loss of low-molecular-weight polymers). The same trend is apparent from Table XI which shows the effect of solvent on the degree of polymerisation at 1 atmosphere. Obviously tetrachloroethylene is reactive in chain transfer and has a profound effect on the molecular weight of the polymer. Similar effects occur in the case of carbon tetrachloride which has a higher solvent transfer constant. The results of George and Onyon show that the decrease in molecular weights is very rapid and marked as the [S]/[M] ratio increases from 0.244 (DP = 326.9) to 2.452 (DP = 31.75),

beyond which the decrease in $\overline{DP}$ is quite slowly falling to 15.79 at an [S]/[M] ratio of 6.026.

The above method of determining $\overline{DP}$ is believed to yield the relative values of C_S at various pressures with good accuracy although the absolute values of C_S may be affected by various contributing factors. For example, a slight error in the numerical values of K and α in the Mark-Houwink equation will considerably increase or decrease the molecular weight.

A useful method of calculating C_S from the values of the degree of polymerisation and the overall rate of polymerisation was suggested by Breitenbach and Schindler (122) who proposed the following modification of the general transfer equation:

$$\frac{[M]^2}{V} \cdot \left[\frac{1}{\overline{DP}} - C_m - C_I \frac{[C]}{[M]}\right] = \frac{\delta^2}{2} + C_S \frac{[S][M]}{V}$$

The only limitation of this method is that the value of C_S will be dependent on $C_m + C_I \cdot \frac{[C]}{[M]}$ when $1/\overline{DP}$ becomes very small. Fortunately, in the system under study C_I may be regarded as zero, so that by plotting the values of $[M]^2/V(1/\overline{DP} - C_m)$ against $[S][M]/V$, the value of C_S is obtained from the slope of the straight line. One

of the advantages of this method is that in the preparation
of reaction mixtures a high degree of precision is not
needed, as the overall rate of polymerisation is not
essentially required in the calculations.

The solvent-transfer constants have been determined
by the Breitenbach-Schindler method at 1 atmosphere, and
at 1510 and 2680 atmospheres. The results are given in
Table XIV (Figure 11). These results compare well with
those obtained by the application of Mayo's equation
which are shown in Table XIII. The figures for C_S at
atmospheric pressure and at a pressure of 1510 atmospheres
are identical (29×10^{-4} and 24.8×10^{-4} respectively) in
both the methods. At 2680 atmospheres a figure of 26.8×10^{-4}
is obtained by the usual method, which is fairly close to
25.6×10^{-4} obtained by Breitenbach-Schindler method.

Lamb (177) during the course of his work on Copolymer-
isation made an approximate determination of C_S in *the*
styrene/tetrachloroethylene system at 1 atmosphere and
reported a figure of $\sim 60 \times 10^{-4}$.

The high reactivity of tetrachloroethylene among the
halides will be apparent from Table III, Section I.3.
(vii)(c). With the exception of carbon tetrachloride which
is unusually reactive, tetrachloroethylene comes next

in reactivity to benzal chloride ($C_S = 50 \times 10^{-4}$) and benzotrichloride ($C_S = 57.5$)

(ii) <u>Effect of Pressure on Solvent-Transfer Constant.</u>

Inspection of Table XIII shows that the value of $C_S = 29.0 \times 10^{-4}$ at 1 atmosphere falls to about 21×10^{-4} at 1030 atmospheres and then rises to 24.8, 26.8 and 27.4×10^{-4} at pressure of 1510, 1980 and 2680 atmospheres respectively, the transfer constant again having almost its atmospheric pressure value. The total fall at the highest pressure is not more than $6^{\circ}/o$. The obvious conclusion is that the solvent-transfer constant is almost independent of pressure. This further indicates that the processes of radical growth and radical termination by chain transfer are almost equally accelerated by pressure.

The above findings are supported by the work of Walling and Pellon (112) in their high pressure studies of styrene-carbon tetrachloride system. They conclude that in their system, the transfer constant is almost independent of pressure, decreasing by about $15^{\circ}/o$ at 3950 Kg/cm^2 ($\doteq 3823$ atm). The solvent transfer constant ($= 98 \times 10^{-4}$) at 1 atmosphere falls to 90 at 2000 Kg/cm^2, with a fall of about $8^{\circ}/o$. For tetrachloroethylene it

falls from 29.0×10^{-4} at 1 atmosphere to 26.8×10^{-4} at 1980 atmospheres, a decrease of about $7.6^{o}/o$. That the acceleration of radical displacement reactions by pressure is quite general was further shown by Walling and Pellon in their studies of the benzoyl peroxide initiated polymerisation of allyl acetate at $80^{\circ}C$ and at pressures up to 8500 Kg/cm^2. They concluded that pressure has little effect on competition between polymer chain growth and transfer with allylic hydrogen and that both reactions are strongly accelerated.

In addition to the evidence of Walling and Pellon that the solvent-transfer constant, C_S, in the styrene-carbon tetrachloride system is independent of pressure, further support comes from the observations of Romani (130) who studied the acenaphthylene-tetrachloroethylene and acenaphthylene-carbon tetrachloride systems at $60^{\circ}C$. The former system was studied at 1 atmosphere and 2880 atmospheres and the values of $C_S \times 10^{4}$ were 29.0 and 29.7 respectively. In carbon tetrachloride the C_S values were 7.8×10^{-4} and 6.0×10^{-4} at 1 atmosphere and 1400 atmospheres respectively.

(c) Chemical Reactivity and Structure.

The highly reactive nature of carbon tetrachloride as a chain transfer agent is rather unexpected. Walling (11) has tried to explain this unusual behaviour. According to the following accepted scheme:-

$$\sim \overset{\text{H}}{\underset{\phi}{\text{C}}}\text{.} + \text{C}l - \text{CC}l_3 \longrightarrow \sim \overset{\text{H}}{\underset{\phi}{\text{C}}} - \text{C}l + \text{.CC}l_3$$

$$\text{M.} + \text{S} \xrightarrow{\text{k}_{tr}} \text{S.}$$

$$\text{.CC}l_3 + \text{CH}_2 = \text{CH.}\phi \longrightarrow \text{C}l_3\text{.C} - \text{CH}_2 - \overset{\text{H}}{\underset{\phi}{\text{C.}}}$$

$$\text{S.} + \text{M} \xrightarrow{\text{k}_a} \text{M.}$$
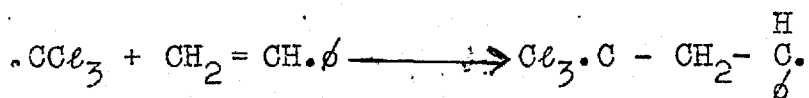
The various factors contributing to high solvent-transfer value are the presence of the generally weaker carbon-chlorine bond (dissociation energy = 66k cal/g.mole) as compared to carbon-hydrogen bond (dissociation energy = 87-94 k cal/g.mole), and the resonance stabilisation of the .CCl_3 radical produced in the transfer process (12 k cal/mole from bond dissociation data). These factors will reduce the activation energy required for transfer. Walling has also suggested that there may be a contribution

from a polar effect in which polyhalomethanes (and thiols)
become electron acceptors and the styrene molecule a
donor. Attack by donor radicals is then facilitated by
the formation of a polar transition state:

$$\sim \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle \phi}{|}}{C}} \cdot Cl \qquad CCl_3 \longleftrightarrow \sim \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle \phi}{|}}{C^{+}}} \ldots\ldots Cl \ldots \bar{C}Cl_3$$
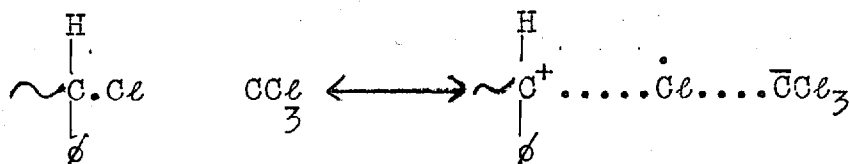
Romani (130) has criticised the above explanation
as it does not account for the low transfer value of
chloroform which according to Walling's hypothesis should
also possess a high transfer constant. Romani has produced
further evidence against the polar transition state
interpretation.

The reactivity of tetrachloroethylene in liquid
phase polymerisations has not been extensively studied
before. Doak (194) made a comparison of the reactivities
of all the chlorinated ethylenes with each of two or
more other radicals, determining the monomer reactivity
ratios graphically. Since he did not find tetrachloroethylene
to homopolymerise under the experimental conditions, he
calculated the reactivity ratios for the styrene-tetra-
chloroethylene system (using 0.1 mole ^{o}/o benzoyl peroxide),

by assuming the reactivity ratio of the T.C.E. radical
to be zero. He based his results on only two experiments
in which the conversions were higher than 80°/o and found
the value of r_2 to be 185. The same reaction was studied
by Lamb (177) at 2000 atmospheres and he reports the
value of r_2 as 236. Breitenbach, Schindler and Pflug
(195) investigated the polymerisation of styrene in tetra-
chloroethylene at 50°C and 90°C and their results along
with those of Doak are given below (196):-

r_1	M_1	M_2	r_2	$T°C$	Reference
0	Tetra chloro- ethylene	Styrene	165	50	Breitenbach-Schindler-Pflug
0		"	208	50	"
0	"	"	185	60	Doak
0	"	"	66.4	90	Breitenbach et al
0	"	"	129	90	"
0	"	"	187	90	"

Doak obtained two polymers, one with a solvent-
monomer ratio, [S]/[M] = 0.99 containing 0.88°/o chlorine
and the other with an [S]/[M] = 1.96 having 2.12°/o
chlorine. The nearest corresponding molar ratios in this
work are 1.21 and 2.08 with a chlorine content of

1.57°/o and 3.42°/o respectively. The results are not very far from each other when it is considered that the chlorine content reported in the present work is mostly found by difference and even the gravimetric estimations are probably on the high side. In the present work the above reactions were allowed to proceed for 6 and 8 hours with °/o conversion not exceeding 7 in either case, whereas Doak carried out his reactions for 25 and 168 hours respectively. It may be mentioned that on repeating Doak's experiments under exactly the same conditions, the chlorine contents of the resulting polymers were almost 1.5 time higher than those reported by Doak.

Lamb and Weale (197) studied the styrene-tetra-chloroethylene system up to 8500 atmospheres using benzoyl peroxide, at 60°C. They found tetrachloroethylene to freeze at about 3100 atmospheres. The polymers obtained were found to contain approximately one tetrachloroethylene unit per molecule. Breitenbach and Schindler (122) investigated the polymerisation of styrene with chlorinated aliphatic and aromatic hydrocarbons at 70°C with azobis-isobutyronitrile and benzoyl peroxide and found that in the case of tetrachloroethane a chlorine-containing polymer was obtained.

In view of the above findings it is clear that tetrachloroethylene does not copolymerise with styrene. The steric hindrance caused by the presence of 1:1, 2:2 chlorine atoms in the molecule would account for this behaviour, making the double bond unreactive.

Tables XVIII, XIX and XX will indicate that the actual mean numbers of the tetrachloroethylene units are very low and independent of mean molecular weight, although these mean numbers are subject to uncertainty as they have been calculated from the chlorine content of the polymer.

Even at pressures beyond 2680 atmospheres (3110, 3350 and 3540 atmospheres) and at a higher temperature (80°C), the °/o of chlorine in the polymer was only about 6, although the molar ratio of solvent to monomer was as high as 10.12 (Table XIX).

Gonikberg and his collaborators (198) claim that tetrachloroethylene does copolymerise with vinyl acetate at atmospheric and high pressure. Their results are given below:-

Vinyl acetate mole % in feed	A.I.B.N. wt.%	Pressure	Polymer yield wt.%	chlorine content of polymer wt.%	Average molecular weight.
49.8	0.5	1	5.6	21.50	610
		4000	6.7	21.80	1100
49.8	0.5	1	15.6	20.80	780
		4000	15.9	22.01	970
35.4	0.5	1	11.7	27.89	500
		4000	17.9	31.68	750
35.4	0.5	1	22.1	30.87	560
		4000	24.0	33.70	640

It will be seen that the amount of data is limited
and generalisation on the basis of these results is very
doubtful. The polymers of high chlorine content prepared
by Gonikberg et al are of very low molecular weight and
it is not possible to make any inferences as to the effect
of structure on reactivity on the basis of these experiments.
It also appears that none of the polymers formed in the
styrene-tetrachloroethylene system can be regarded as
copolymers in the normal sense.

III.5:   Experiments on the Polymerisability of
          Tetrachloroethylene.

Attempts were made to homopolymerise tetrachloro-
ethylene in bulk and in toluene solution at pressures
up to 7000 atmospheres and at temperatures from $60^{\circ}C$
to $100^{\circ}C$, with azobisisobutyronitrile, benzoyl peroxide,
di-tertiary butyl peroxide and tertiary butyl perbenzoate.
There was little indication of any polymeric substance
being formed. The $C = C$ bond in tetrachloroethylene
seems to be unreactive because of steric hindrance, which
is not overcome by pressure.

With borontrifluoride diethyl etherate, however,
tetrachloroethylene seemed to form polymeric substances
between $0^{\circ}C$ and $-20^{\circ}C$ at atmospheric pressure but the
reactions were not further investigated.

III.6: Polymerisation of Methylmethacrylate in Tetrachloroethylene.

Methyl methacrylate was polymerised with tetrachloroethylene at $60^{\circ}C$ at 1 atmosphere and at 2680 atmospheres, using azobisisobutyronitrile. The results are classified in Table XXI, along with the composition of the polymers. With a monomer concentration varying from 4.51 moles per litre to $[M] = 1.69$ moles per litre, the polymers prepared in the above pressure range contained 0.4 to $1.6^{\circ}/o$ of chlorine. Such a low chlorine content is an obvious proof that no copolymerisation is taking place.

SECTION IV

GENERAL DISCUSSION AND CONCLUSIONS

GENERAL DISCUSSION

IV.1: Solution Polymerisation at Atmospheric Pressure.

The polymerisation of styrene in tetrachloroethylene with azobisisobutyronitrile as initiator proceeds according to the modified kinetic scheme discussed on page 46 (equation 18). The rate of polymerisation is half order with respect to initiator concentration and 3/2 with respect to monomer concentration. Values higher than 1.0 in the case of the monomer have been reported in the literature. The half order kinetics with respect to initiator is an indication of the fact that the termination step involves two chains and the reaction is bimolecular, and further that the process of transfer is not degradative. The results of Merrett and Norrish (141), Walling and Pellon (112), Nandi, Saha and Palit (121), and others have already been discussed in Sections I and III. (Table IX, and Figures 6 and 7).

The solvent-transfer constant determined graphically

by the use of Mayo's equation is 29.0×10^{-4} which is not unexpectedly high. Lamb and Weale (197), Gonikberg et al (198), Doak (194) and Breitenbach, Schindler and Pflug (195) have found tetrachloroethylene to be an active chain transfer agent (Table XI, and Figure 10).

The overall rate constants for the solution poly-merisation of styrene are shown in Table XVI, and the figures are fairly concordant.

IV.2: Solution Polymerisation at High Pressures.

(a) The Effect of Pressure on the Overall Rate.

Figure 8 shows the effect of pressure on the rate of polymerisation, and is based on the results classified in Table X.

The overall rate of polymerisation in bulk is accelerated approximately five-fold at 2270 atmospheres. This is attributable to the acceleration of the propagation reaction by pressure and a simultaneous retardation of the mutual chain radical termination process as suggested by Norrish and coworkers (141-142).

In solution polymerisation, the overall rate was found to increase between five- and six-fold from 1 atmosphere to 2680 atmospheres.

(b) The Effect of Pressure on the Degree of Polymerisation.

It is apparent from Tables XI and XII that pressure exerts its maximum influence on the increase in molecular weights up to about 1000 atmospheres. With a solvent-monomer molar ratio of 1.21, the molecular weight increases from 25.5×10^3 at 1 atmosphere to 38.2×10^3 at 1030 atmospheres. At 1510, 1980 and 2680 atmospheres,

the figures are 29.2×10^3, 28.0×10^3 and 31.1×10^3. This clearly shows that there is little variation in the molecular weight beyond 1000 atmospheres. The solvent, tetrachloroethylene, has a profound effect on the degree of polymerisation by acting as a chain transfer agent.

The results of Tables XI and XII have been plotted in Figure 9. As pointed out in Section III.3(c), Figure 9 reveals a tendency of the molecular weight to rise again beyond about 3000 atmospheres, and this has been confirmed by Lamb and Weale (197) in their studies of the styrene-tetrachloroethylene system at 60^oC at atmospheric and high pressure. They found a rapid increase in the molecular weights in the range 3000 to 6000 atmospheres which is probably due to phase separation of tetrachloroethylene as the pure solvent freezes at about 3100 atmospheres at 60^oC.

(c)   The Effect of Pressure on the Solvent Transfer Constant.

The solvent transfer constant for tetrachloro-ethylene with styrene at 60^oC is 29.0×10^{-4} at atmospheric pressure and falls to 27.4×10^{-4} at 2680 atmospheres, the highest pressure used in these studies. It can be

inferred that pressure equally accelerates both the processes of radical growth and chain termination by chain transfer so that the solvent transfer constant is almost independent of pressure. The effect of pressure in accelerating the abstraction of a chlorine atom as much as the radical addition is rather suprising.

These results are in agreement with the findings of Walling and Pellon (112) in their studies of the styrene-carbon tetrachloride system in which C_S is almost pressure-independent. The same authors confirm that the chain transfer with the monomer is not pressure-dependent in their studies of the allyl acetate polymerisation. The data produced by Romani (130) on the acenaphthylene-carbon tetrachloride and acenaphthylene-tetrachloroethylene systems is also in accord with the findings of the present work.

Toohey and Weale (106) in their studies of the styrene-triethylamine and styrene-toluene systems observed that in the former case C_S decreased from 6.7×10^{-4} to 1.4×10^{-4} between 1 atmosphere and 4400 atmospheres and in the latter case also a significant decrease in C_S was found with increase of pressure. Similar behaviour was found with ethyl benzene and tertiary butyl benzene.

Romani has also studied the acenaphthylene-toluene system and reported that C_S decreased with increasing pressure to the extent of about $50^o/o$ in the pressure range 1 to 1500 atmospheres. Probably in this system also, pressure has a greater accelerating effect on the propagation step than on the transfer reaction.

(d) Composition of Polymers.

Doak's investigation on the solution polymerisation of styrene in tetrachloroethylene at 1 atmosphere are based only on two experiments and his assumption that tetrachloroethylene copolymerises with styrene is very doubtful. The results classified in Table XX do not support Doak's view as the mean values of the number of tetrachloroethylene units per molecule of the polymer are very low. On the contrary they appear to show that tetrachloroethylene does not copolymerise with styrene and that, presumably because of steric hindrance, the double bond is unreactive.

Gonikberg's claim that tetrachloroethylene copolymerises with vinyl acetate at atmospheric and high pressure is based on polymers of very high chlorine content and very low molecular weight. Further knowledge of the

structures is necessary before it can be decided whether
they may be termed copolymers.

Experiments performed with methyl methacrylate in
tetrachloroethylene at 1 atmosphere and at 2680 atmospheres
confirm the unreactivity of tetrachloroethylene in co-
polymerisation. In the pressure range 1 to 2680 atmospheres,
with a monomer concentration varying from 4.51 moles
per litre to 1.69 moles per litre, the polymer produced
contains almost 99 mole $^o/_o$ or more of methyl methacrylate
and an insignificant content of chlorine (0.3-1.6$^o/o$).
Obviously no copolymers are formed. The results of these
experiments are classified in Table XXI.

IV.3: CONCLUSIONS.

The conclusions drawn from the foregoing results and observations may be summarised as follows:-

(i)   The kinetic equation for the polymerisation of styrene in tetrachloroethylene is of half order with respect to the initiator, azobisisobutyronitrile, at one atmosphere.

(ii) The termination step is bimolecular, that is two chains are involved in the termination reaction and the process of transfer is not degradative.

(iii) The order of reaction with respect to monomer (styrene) is 3/2 at 1 atmosphere. This is not surprising as orders higher than 1.0 have often been reported in the literature.

(iv) The rate of free radical polymerisation of styrene in tetrachloroethylene at $60^{\circ}C$ is accelerated several fold (5 to 6 times) by pressure up to 2680 atmospheres. This is similar to the effect on the rate of the bulk polymerisation.

(v)   The molecular weight of polystyrene prepared in tetrachloroethylene increases with pressure up to about 1030 atmospheres, the increase being about

1.5 fold. Beyond this the change is slight and the
molecular weight remains almost constant. At high
dilutions, with molar ratios $[S]/[M] > 3.04$, there
is no appreciable change in the molecular weight at
different pressures.

(vi) The solvent transfer constant of tetrachloroethylene
with styrene is fairly high; $C_S = 29.0 \times 10^{-4}$ at 1
atmosphere and is almost independent of pressure.
The activity of tetrachloroethylene in chain transfer
is supported by earlier work, and the small effect
of pressure on C_S when the atom transferred is chlorine
has been observed with styrene.

(vii) Tetrachloroethylene does not copolymerise with styrene
at atmospheric pressure. Doak's assumption that the
products are copolymers is difficult to reconcile
with the very low chlorine content, and he does not
report the molecular weights or the mean numbers of
tetrachloroethylene units in the polymers prepared
by him. The failure to copolymerise is probably
attributed to steric hindrance caused by the bulk of
chlorine atoms in the symmetrical molecule of tetra-
chloroethylene, which is not overcome by the

pressures used in this work. Indirect support
for this view comes from Romani's study of the
acenaphthylene-tetrachloroethylene system at high
pressures.

The claim by Gonikberg and his collaborators
that tetrachloroethylene copolymerises with vinyl
acetate both at 1 atmosphere and at 4400 atmospheres
is doubtful as the molecular weights of their polymers
lie in the range from 500 to 1100. The structure
of these very low-molecular-weight polymers is not
reported and it is likely that high chlorine contents
would not be found in polymers of higher molecular
weight.

(viii) Tetrachloroethylene was found not to homopolymerise
in the presence of azobisisobutyronitrile, benzoyl
peroxide, di-tertiary butyl peroxide or tertiary butyl
perbenzoate, both in bulk and in solution, at
different temperatures and pressures up to 7000
atmospheres. This is also probably attributed to
steric hindrance.

(ix) Tetrachloroethylene seems to produce small yields
of homopolymers with boron trifluoride diethyl etherate

as a catalyst at temperature in the range from 0°C
to -20°C.

(x) Polymers have been prepared from methyl methacrylate
in tetrachloroethylene at 60°C, using azobisiso-
butyronitrile, at 1 atmosphere and 2680 atmospheres.
The chlorine content of these did not exceed 1.6°/o
and it is concluded that no copolymerisation takes
place between the two substances.

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