Kinetic studies on the polymerisation of vinyl acetate in the presence of solvents.

A thesis submitted to the University of Glasgow in accordance with the regulations for the award of the degree of Doctor of Philosophy

by

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SUMMARY

The kinetics of the polymerisation of vinyl acetate in the presence of solvents has been studied. Azobis isobutyronitrile has been used as photoinitiator.

As little as 5% of benzene lowers the rate of polymerisation of vinyl acetate to about one-half its value in the absence of benzene. For the polymerisation of vinyl acetate alone and of various benzene/vinyl acetate mixtures the rates of polymerisation, molecular weights and chain transfer constants over the temperature range 25-60°C have been measured. The intensity exponents were found to be in the region of 0.51-0.54 both with benzene and in its absence.

Labelled benzene, grown as a single crystal, has been used at different temperatures to find out the number of benzene molecules incorporated in each polymer chain, and on an average one molecule of benzene has been found per polymer molecule. A possible mechanism for the polymerisat of vinyl acetate in the presence of benzene has been put forward.

The rate of polymerisation of vinyl acetate in the presence of toluene has been found the same as in the presence of benzene. Greater retardation was observed in

the presence of cyclohexadiene and also the lowering of molecular weight of the polymer formed. Termination was found to be second order with respect to the growing polymer radical concentration.

The effect of other solvents (mainly substituted benzenes) on the polymerisation of vinyl acetate was studied and different rates of reaction have been explained by steric hinderance.

The rate of polymerisation of vinyl acetate was very much retarded by styrene which has been shown to copolymerise with vinyl acetate. Labelled styrene and labelled vinyl acetate were used in turn to evaluate the monomer reactivity ratios.

Velocity coefficients for propagation termination, and kinetic chain lifetime for the polymerisation of vinyl acetate in the presence of small amounts of styrene have been determined using the thermocouple method. The value of k_p was found to decrease with increase in styrene concentration, while that of k_t remained unchanged.

ACKNOWLEDGEMENTS

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CONTENTS

INTRODUCTION

The polymerisation of vinyl acetate in the presence of solvents has been, for sometime, the subject of controversy. The rate of polymerisation is retarded in aromatic solvents[1,2]. Different workers have suggested various mechanisms based on their results but none of the schemes put forward completely satisfies the observed kinetic measurements.

Burnett and Loan[3] suggested that a chain transfer reaction between a growing polymer radical and benzene occurs producing a phenyl radical, which they claimed was more stable than the growing polymer radical. This would lower the rate of polymerisation.

Stockmayer, Peebles and Clarke[4] claimed that copolymerisation occurs and supported this view by using C14-benzene as solvent in the polymerisation of vinyl acetate.

Breitenbach and Faltlhansel[5] subsequently published the results of their work in which they reacted chlorobenzene and m-dichlorobenzene with vinyl acetate. They did not find any copolymerisation and considered that the findings of Stockmayer _et al_[4] might have been due to acetylenic impurities in their radioactive benzene since it was prepared by the trimerisation of acetylene. This was confirmed by Breitenbach, Billek, Faltlhansel and Weber[6] using radioactive benzene prepared; (a) by the dehydrogenation of cyclohexane and (b) by the trimerisation of acetylene. Considerably greater radioactivity was found in the samples prepared from the latter than from the former radioactive benzene.

Bengough, Brownlie and Ferguson[7], attempted to measure the kinetic constants for the propagation and termination reactions in the polymerisation of vinyl acetate containing up to 20% benzene. Their results indicated a lowering of both the propagation rate constant (k_p) and the termination rate constant (k_t) in the presence of benzene. They also made some preliminary measurements with radioactive benzene and this has been extended in the present work.

C14-benzene, grown as a single crystal, has been used in experiments with a very high benzene/vinyl acetate ratio at different temperatures to find out the number of benzene units per polymer chain. For the polymerisation of the monomer alone and the various benzene/vinyl acetate mixtures the reaction rates, molecular weights and chain transfer constants at several temperatures have been measured.

The effect of other solvents (mainly substituted benzenes) on the polymerisation of vinyl acetate has been studied and the difference in the rates of reaction found in the presence and absence of substituted benzene have been explained by steric hindrance.

Since the resonance stabilised radical type (I) which could be formed by the addition of a growing polymer radical to an unsubstituted aromatic ring

(I)

the reactivity of such a radical towards vinyl acetate was further studied. Styrene which could form a radical of similar stability on polymerisation was reacted with different amounts of vinyl acetate. C14-styrene was used with inactive vinyl acetate and C14-vinyl acetate was used with inactive styrene.

Using a little styrene in vinyl acetate, velocity coefficients for propagation, termination and kinetic chain lifetime have been obtained at 25°C by the thermocouple method[9].

Molecular weights were measured by the viscosity method and by the initiator-fragment method.

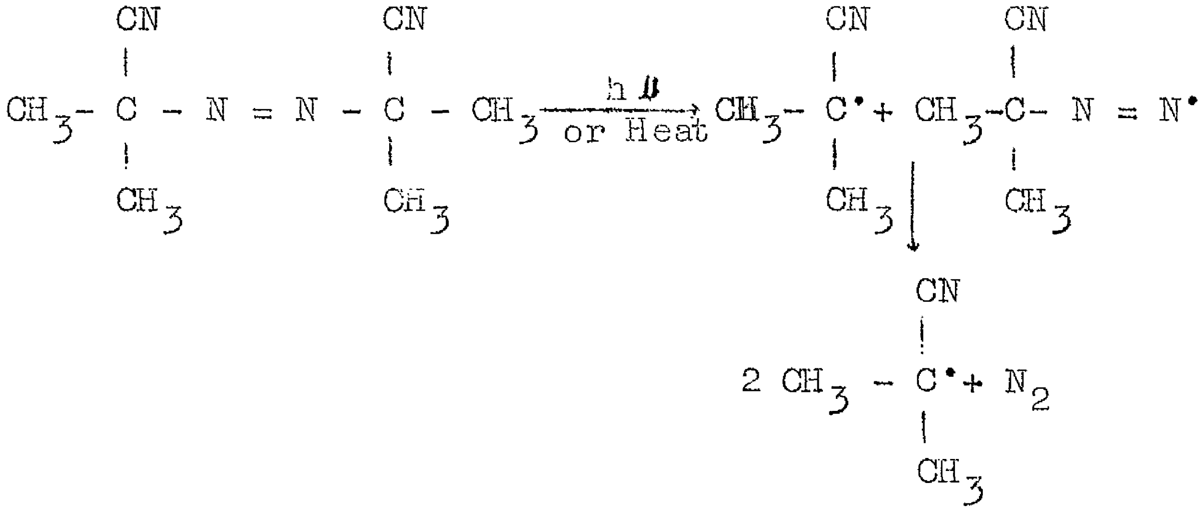
Mechanism of vinyl polymerisation

Free radical polymerisation is the most important and also the commonest method of polymerisation. The free radical chain mechanism involves three basic reactions as given below:

1. Initiation.
2. Propagation.
3. Termination.

1. Initiation. Free radicals are usually obtained by the thermal or photochemical decomposition of compounds such as organic peroxides, azo and diazo compounds.

In this work 1:1 azobisisobutyronitrile (AIBN) has been used as the catalyst. The AIBN has been shown by kinetic studies to decompose by a unimolecular process;



$$CH_3-\underset{CH_3}{\overset{CN}{C}}-N=N-\underset{CH_3}{\overset{CN}{C}}-CH_3 \xrightarrow[\text{or Heat}]{h\nu} CH_3-\underset{CH_3}{\overset{CN}{C^\bullet}} + CH_3-\underset{CH_3}{\overset{CN}{C}}-N=N^\bullet \longrightarrow 2\,CH_3-\underset{CH_3}{\overset{CN}{C^\bullet}} + N_2$$

All the radicals generated do not initiate the polymer chains. Some are consumed in other destructive reactions for example:

(i) Some of the radicals may undergo primary radical termination i.e. between polymer radical and initiator radical.

(ii) Some radicals may react with each other directly.

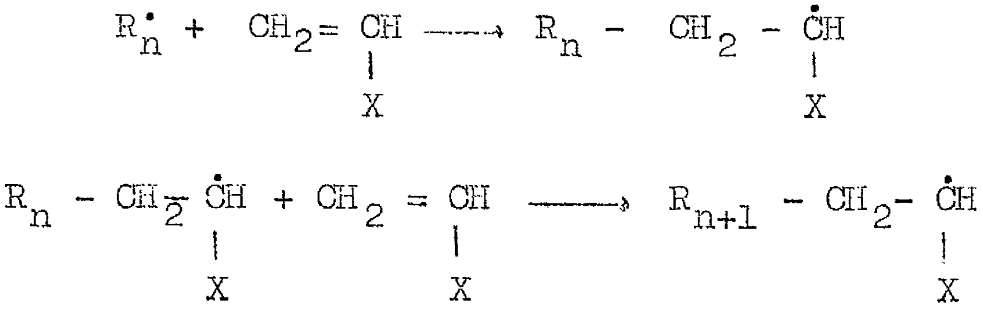
(iii) Some radicals may react with some impurity of the system.

Again the initiator can also partially decompose by a non-radical mechanism to give products which cannot attack the monomer.

Several workers[10-14] have measured the efficiency of AIBN initiation in different monomers and values of 50 to 80% have been reported. The comparatively low efficiencies have also been explained in terms of a "cage effect" in which the solvent or monomer molecules are assumed to form a barrier which hinders the separation of newly formed radicals and so encourages the interaction.[15]

2. Propagation.

The addition of a free radical to the double bond of the monomer generates a larger radical which leads to the formation and propagation of the growing polymer chain. At each addition one electron of the double bond pairs with that of the free radical and second electron of the double bond forms a free radical which repeats the process. Large numbers of monomer units add, one at a time, to the polymer chains at an extremely fast rate.



$$R_n^{\bullet} + CH_2 = \underset{X}{\underset{|}{CH}} \longrightarrow R_n - CH_2 - \underset{X}{\underset{|}{\dot{C}H}}$$

$$R_n - CH_2 - \underset{X}{\underset{|}{\dot{C}H}} + CH_2 = \underset{X}{\underset{|}{CH}} \longrightarrow R_{n+1} - CH_2 - \underset{X}{\underset{|}{\dot{C}H}}$$

$R_n^{\bullet}$ is a free radical containing n monomer units and X a substituent group, in the case of vinyl acetate, the acetate group.

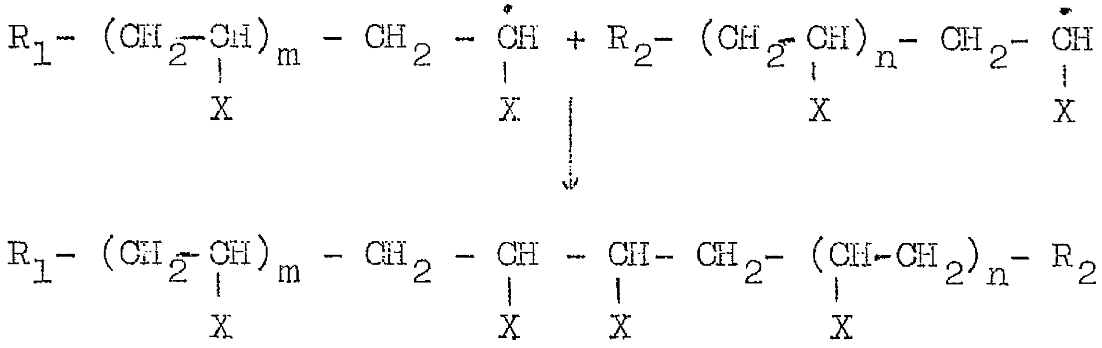
3. <u>Termination.</u>

The growing polymer radicals can be deactivated to give stable polymer molecules. Termination can occur at least by two ways:

a. Combination

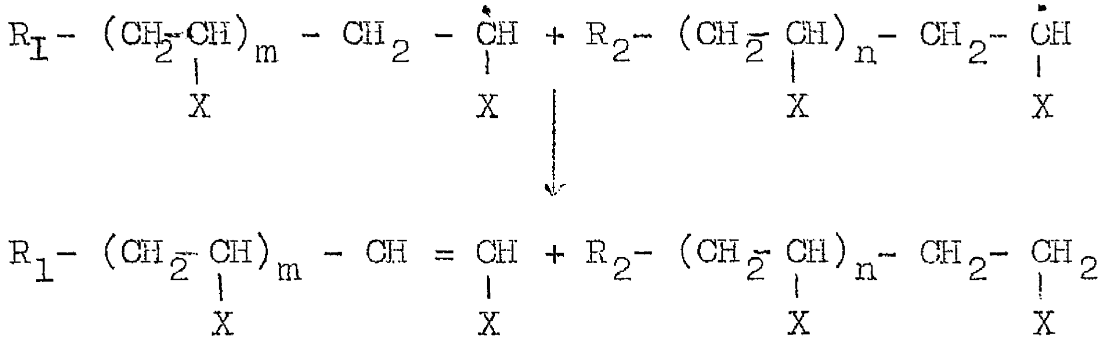
b. Disproportionation

In combination two growing polymer radicals combine by the formation of a covalent bond between the two free radicals. Radioactive tracer techniques using C14 have shown that in most of the monomers studied, combination is the preferred reaction[10,11].



$$R_1-(CH_2-\underset{X}{CH})_m-CH_2-\underset{X}{\dot{C}H}+R_2-(CH_2-\underset{X}{CH})_n-CH_2-\underset{X}{\dot{C}H}\longrightarrow R_1-(CH_2-\underset{X}{CH})_m-CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2-(\underset{X}{CH}-CH_2)_n-R_2$$

Disproportionation involves the transfer of a hydrogen atom from one growing radical to another, the result being that the polymer chain losing the hydrogen atom becomes unsaturated.



$$R_1-(CH_2-\underset{X}{CH})_m-CH_2-\underset{X}{\dot{C}H}+R_2-(CH_2-\underset{X}{CH})_n-CH_2-\underset{X}{\dot{C}H}\longrightarrow R_1-(CH_2-\underset{X}{CH})_m-CH=\underset{X}{CH}+R_2-(CH_2-\underset{X}{CH})_n-CH_2-\underset{X}{CH_2}$$

Chain transfer reaction.

The kinetic chain length ν is described as the number of monomer units per polymer radical, and is related to the degree of polymerisation ($\overline{DP}$). In combination $\overline{DP} = 2\nu$ because two polymer radicals form one large polymer molecule and in disproportionation

$\overline{DP} = \nu$. But in some cases several polymer molecules are formed per kinetic chain length. In such cases the rate of polymerisation remains the same but the $\overline{DP}$ is lowered. Such reactions may be attributed to chain transfer. The activity of a growing polymer radical is satisfied by the abstraction of usually a hydrogen atom from a transfer agent which becomes a free radical. This free radical may be or may not be capable of reacting with monomer to form another chain.

$$R^{\bullet} + S \longrightarrow P + S^{\bullet}$$

S can be a molecule of monomer, polymer or solvent.

In this work chain transfer to polymer and initiator has been assumed to be insignificant.

Previous work on vinyl acetate

The search for new polymers has provided the incentive for investigations into the fundamental chemical processes by which polymers are formed. Kinetic studies of polymerisation and examination of the resulting polymer can lead to a comprehensive understanding of the mechanism of the reactions occurring during polymerisation and factors governing their rates. Before a detailed analysis of the kinetics is given it would be useful to review the development of work on the polymerisation of vinyl acetate.

Staudinger[16] studied the nature of the molecules comprising polyvinyl acetate and reported that it was made up of polymeric homologous compounds. It was also recognised that a simple method of following the stationary state kinetics of polymerisation was to follow the decrease in volume accompanying polymerisation.

Starkweather and Taylor[17] reported on the polymerisation of vinyl acetate in bulk and found first order reaction with respect to monomer, while in toluene solution the rate of reaction was retarded. The retardation of the reaction by toluene was explained on the basis that activated molecules gave up their energy to the toluene molecules before they could combine with other molecules. Other workers[18] found that in the reaction initiated by benzoyl peroxide the rate is proportional to the square root of the initiator concentration.

In most of this early work the vinyl acetate was purified by distillation in air and then degassing the monomer in the dilatometer on the vacuum line. Therefore all of this work was characterised by induction periods before polymerisation commenced and oxygen was shown to have an inhibiting effect.[19] It was not quite certain whether this inhibition was a characteristic feature of the reaction or due to the impurities. Various suggestions were put forward to explain the unreliable results obtained in the previous work and it was even suggested that the reaction might be heterogeneous.[20]

In 1937 Flory[21] published a paper proposing that a chain transfer reaction could take place during the polymerisation. The chain transfer concept was subsequently developed by Mayo[22] who developed a method of obtaining the chain transfer constant for any monomer solvent system.

Cuthbertson, Gee and Rideal[23] investigated the initiation reaction of the thermal polymerisation and found that freshly prepared vinyl acetate did not react but did so after standing in air. To explain this they suggested that the hydrolysis of vinyl acetate to acetaldehyde occurs and was followed by the formation of peroxides. In a later paper[24] the thermal polymerisation of vinyl acetate in bulk and in toluene was studied and chain transfer with toluene was suggested.

However, the highly purified vinyl acetate when polymerised thermally with benzoyl peroxide gave no induction periods.

The introduction of non-stationary state methods which made it possible to determine the individual velocity coefficients and kinetic chain lifetime in photoinitiated reactions was an important development in the work on polymerisation kinetics. The non-stationary state period of the bulk polymerisation of vinyl acetate has been studied by workers using the dielectric constant[26], the rotating sector[27], the refractrometer[28], the thermistor[29], and the thermocouple methods[9].

Chain transfer reactions have also been the subject of much study. The chain transfer constant for vinyl acetate polymerisation in toluene has been calculated by Nozaki[30] using the results of Cuthbertson Gee and Rideal[24]. Kapur and Joshi[31], Palit and Das[32], Clark, Howard and Stockmayer[33], have reported values for a large number of solvents including saturated, unsaturated, halogen substituted and nitrated hydrocarbons, alcohols, esters, ethers, amides, sulphides and a series of substituted benzaldehydes.

However, controversy has arisen regarding the polymerisation of vinyl acetate in benzene. The marked retardation of the polymerisation of vinyl acetate in benzene solution has been attributed to a chain transfer reaction by Conix and Smets[34] who claimed that the rate is proportional to $M^{3/2}$. Simultaneously Stockmayer and Peebles[35] claimed that the reduction in rate is not due to chain transfer but to copolymerisation.

A third paper was put forward by Allen, Merret and Scanlan[36] who noted a marked retardation when vinyl acetate was polymerised in the presence of the isoprenic substances dihydromyrcene and isopropylbenzene but no retardation when methylmethacrylate was the monomer. Since dihydromyrcene and isopropylbenzene behave as simple chain transfer agents with other monomers a probable explanation for their retarding effect on the polymerisation of vinyl acetate is that a "degradative chain transfer" reaction is taking place. By "degradative chain transfer" is meant a chain transfer reaction in which the radicals produced from the chain transfer agent are resonance stabilised and slow to reinitiate the polymerisation; they are thus frequently removed by a termination reaction with the growing polymer radicals. Their kinetic scheme yielded a value for the chain transfer constant for isopropylbenzene 100 times greater than that found for benzene by Stockmayer and Peebles[35] from molecular weight determinations. They said if copolymerisation was the important retarding mechanism in isopropylbenzene the values for the two compounds would be of comparable magnitude.

Burnett and Loan[3] assumed that radicals produced by the chain transfer step reinitiate the polymerisation and that the rate of initiation is equal to the rate of the chain transfer reaction. They derived an equation for the rate of polymerisation which demonstrated that the order of reaction with respect to the monomer concentration was dependent on the monomer concentration in the solvent.

However, Jenkins[37], stated that Burnett and Loan's kinetic scheme was applicable only if the retardation was weak. He put forward a kinetic scheme on the basis of chain transfer reaction with solvent occurring and derived an equation for the rate in terms of the various rate constants involved within his kinetic scheme. He used the geometric mean assumption i.e. the velocity coefficient of termination between two dissimilar radicals is the geometric mean of those for the reaction between like radicals. However, the value of their chain transfer constant derived from kinetic data was greater than determined by Palit and Das from the molecular weight determinations.

Similar results were obtained by Clarke, Peebles and Stockmayer[4] who put forward the view that copolymerisation was occuring and supported this by carrying out the reaction with C14-benzene.

Breitenbach and Falthansel[5] reported their work in which they had obtained polymers containing chlorine from the polymerisation of vinyl acetate in chlorobenzene and in m-dichlorobenzene, while styrene polymerised in the same solvents and under similar conditions gave chlorine free polymers. They explained these results by assuming that the reactive growing polyvinyl acetate radicals undergo a chain transfer reaction with chlorobenzene but the relatively stable polystyryl radical does not.

The fact that these observations disagreed with the Stockmayer theory led Breitenbach et al[6] to repeat Stockmayer's radioactive tracer experiments which had indicated copolymerisation. The polymerisation of vinyl acetate was carried out in the presence of benzene prepared by two methods;

(a) trimerisation of C14-acetylene

(b) and dehydrogenation of C14-cyclohexane.

The results obtained from the two samples of radioactive benzene showed marked differences. The polymer prepared in the presence of benzene made from C14-acetylene had a very high radioactive content but all other tests on the polymers e.g. I.R., U.V. and carbon hydrogen determinations showed an almost pure polyvinyl acetate indicating no incorporation of benzene in the polymer. The polymer obtained in the presence of benzene prepared from the dehydrogenation of C14-cyclohexane had an extremely low radioactive count, an average content of 0.9 molecules of benzene for an average chain length of 100 units being found. Since this latter value was in agreement with the value obtained from the chlorinated polymers, they concluded that there is no evidence of copolymerisation with the aromatic system and that the high radioactivity was due to the acelylenic impurities of high specific activity having copolymerised with the vinyl acetate.

Mortimer and Arnold[38] have rejected the idea of copolymerisation occurring with ethylene in the presence of deuterated benzene and said on the basis of their results that the benzene units incorporated in the polymer find their way there through a chain transfer reaction.

Hass and Huseck[39] concluded that diphenyl behaves chiefly as a chain transfer agent in the vinyl acetate/diphenyl system, the observed retardation in rate probably being due to "degradative chain transfer".

Bengough and Ferguson[7] using a non-stationary state thermocouple system studied the polymerisation of vinyl acetate in the presence of benzene. They measured the overall activation energies, activation energies of propagation, termination and chain transfer together with the rates and corresponding kinetic chain lifetimes. From their results it appeared more probable that the benzene molecule added to a polymer chain to produce a radical which was slow to reinitiate and so caused the reduction in the rate of polymerisation.

Bengough and Brownlie[8] continued this work in an attempt to determine quantitatively the number of benzene units incorporated in the chain in conjunction with the non-stationary state results. Their results, using radioactive benzene, indicated that not more than two benzene molecules were incorporated per polymer molecule. They also obtained considerable kinetic measurements which substantiated the findings of Bengough and Ferguson.

In this work further studies have been made on the effect of benzene, substituted benzenes and other solvents on the polymerisation of vinyl acetate, with a view to support or contradict the above results. For similar reasons the polymerisation of vinyl acetate in the presence of styrene has been carried out (using stationary and non-stationary methods to determine the kinetic constants) since the styrene radical is thought to act as a retarder by virtue of the formation of an unreactive styryl radical which delays the growth of the chain[40,41].

The kinetics of addition polymerisation

The basic reactions in vinyl polymerisation can be represented by the following kinetic scheme:-

Catalyst	C	$\longrightarrow R^{\bullet}_{c}$	Rate
Initiation	$R^{\bullet}_{c}+M$	$\longrightarrow R^{\bullet}_{1}$	
Propagation	$R^{\bullet}_{n}+M$	$\longrightarrow R^{\bullet}_{n+1}$	$k_p\,[R^{\bullet}][M]$
Chain transfer	$R^{\bullet}_{n}+M$	$\longrightarrow P_n+R^{\bullet}_{1}$	$k_{tr}[R^{\bullet}][M]$
Termination	$R^{\bullet}_{n}+R^{\bullet}_{m}$	$\longrightarrow P_{n+m}$ or P_n+P_m	$k_t\,[R^{\bullet}]^2$

where

$R^{\bullet}_{c}$ is the radical derived from the initiator,

$[M]$ is the concentration of the monomer,

$R^{\bullet}$ is the growing polymer radical,

P_n is the dead polymer molecule,

and k_p, k_{tr} and k_t are the velocity coefficients for the propagation, the chain transfer, and the termination reactions respectively.

It is assumed that the reactivity of the growing polymer radical is independent of its size.

The only reactions which involve the consumption of free radicals are the initiation and termination steps, and therefore the rate of change of radical concentration can be expressed:

$$d[R^{\bullet}]/dt = I - k_t\,[R^{\bullet}]^2 \qquad \ldots\ldots(1)$$

and when a stationary state has been attained, the rate of production of radicals will equal their rate of removal

$$d[R^{\bullet}]/dt = I - k_t[R_s^{\bullet}]^2 = 0 \qquad \ldots\ldots(2)$$

where $[R_s^{\bullet}]$ represents the steady concentration of radicals under stationary state condition

$$[R_s^{\bullet}] = (I/k_t)^{\frac{1}{2}} \qquad \ldots\ldots(3)$$

Under stationary state conditions the rate of polymerisation can be expressed in terms of the rate of removal of monomer, thus

$$-d[M]/dt = k_p[R_s^{\bullet}][M] + k_{tr}[R_s^{\bullet}][M] \qquad \ldots\ldots(4)$$

Assuming that high polymer is formed during the reaction i.e. $k_p \gg k_{tr}$ and the second term becomes negligible then

$$\text{rate} = k_p[R_s^{\bullet}][M] \qquad \ldots\ldots(5)$$

$$= k_p\ (I/k_t)^{\frac{1}{2}}[M] \qquad \ldots\ldots(6)$$

This is the basic equation governing all the free radical polymerisation reactions. The rate of polymerisation is thus a composite function of the velocity coefficients of the steps in the overall reaction.

Chain transfer reaction to monomer and solvent.

The ratio of the velocity coefficient for chain transfer to the velocity coefficient for propagation is called the chain transfer constant (C_m) i.e. $C_m = k_{trm}/k_p$ the chain transfer reaction with monomer can be represented by

$$R_n^{\bullet} + M \longrightarrow P_n + R^{\bullet}$$

and the rate of this reaction by $k_{trm}[R^{\bullet}][M]$

The degree of polymerisation ($\overline{DP}$) is equal to the ratio of the number of monomer units reacted to the number of polymer molecules formed.

$$\text{i.e.} \quad \overline{DP} = \frac{\text{Rate of polymerisation}}{\text{Rate of formation of polymer molecules}}$$

In the absence of solvent in the system ($\overline{DP} = \overline{DP}_o$) we have

$$\overline{DP}_o = \frac{k_p [R_s^{\bullet}][M]}{k_t [R_s^{\bullet}]^2 + k_{trm}[R_s^{\bullet}][M]} \qquad \text{......(7)}$$

(other symbols have been defined already).

From equation (5)

$$[R_s^{\circ}] = \frac{\text{Rate}}{k_p [M]} \qquad \text{......(8)}$$

and (7) becomes

$$1/\overline{DP}_o = \frac{k_t \text{ Rate}}{k_p^2 [M]^2} + \frac{k_{trm}}{k_p} \qquad \text{......(9)}$$

Thus if $1/\overline{DP}_o$ is plotted against rate of polymerisation the intercept will be given as C_m.

The effect of a solvent as a chain transfer agent is reflected in the $\overline{DP}$ of the polymer formed, and the following method of deriving a relationship between the $\overline{DP}$ and the kinetic quantities involved was developed by Mayo[22]. In the presence of solvent (S) the equation (7) can be written as

$$\overline{DP} = \frac{k_p [R_s^\bullet][M]}{k_t [R_s^\bullet]^2 + k_{trm}[R_s^\bullet][M] + k_{trs}[R_s^\bullet][S]} \quad ..(10)$$

where k_{trs} = velocity coefficient for chain transfer to solvent

From equation (10) we get

$$1/\overline{DP} = \frac{k_t^{\frac{1}{2}} I^{\frac{1}{2}}}{k_p [M]} + \frac{k_{trm}}{k_p} + \frac{k_{trs}[S]}{k_p [M]} \quad .....(11)$$

In the absence of solvent equation (11) becomes equivalent to equation (9a)

i.e.

$$1/\overline{DP}_o = \frac{k_t^{\frac{1}{2}} I^{\frac{1}{2}}}{k_p [M]} + \frac{k_{trm}}{k_p} \quad .....(9a)$$

Substituting $1/\overline{DP}_o$ in equation (11) gives

$$1/\overline{DP} = 1/\overline{DP}_o + C_s[S]/[M] \quad .....(12)$$

where $C_s = k_{trs}/k_p$ is the chain transfer constant to the solvent.

The plot of $1/\overline{DP}$ against $[S]/[M]$ should give a straight line of slope C_s and the intercept as $1/\overline{DP}_o$ if $I^{\frac{1}{2}}/[M]$ is kept constant for all values of $[S]/[M]$.

Theory of copolymerisation

The propagation reactions in the copolymerisation of two monomers A and B may be described as follows:-

$$A^\bullet + A \xrightarrow{k_{pAA}} A^\bullet$$

$$A^\bullet + B \xrightarrow{k_{pAB}} B^\bullet$$

$$B^\bullet + A \xrightarrow{k_{pBA}} A^\bullet$$

$$B^\bullet + B \xrightarrow{k_{pBB}} B^\bullet$$

where $A^\bullet$ and $B^\bullet$ are growing polymer radicals having either terminal A or terminal B group respectively. We assume that the reactivity of the radical is independent of the chain length and is determined by the terminal monomer unit. Moreover, the monomer is consumed only in the propagation step and the rate of removal of each monomer is given by:

$$-d[A]/dt = k_{pAA}[A^\bullet][A] + k_{pBA}[B^\bullet][A] \quad \ldots(13)$$

$$-d[B]/dt = k_{pAB}[A^\bullet][B] + k_{pBB}[B^\bullet][B] \quad \ldots(14)$$

Thus the ratio of the number of moles of the two monomer entering the polymer initially is given by

$$\frac{d[A]}{d[B]} = \frac{[A]}{[B]} \; \frac{k_{pAA}[A^\bullet] + k_{pBA}[B^\bullet]}{k_{pAB}[A^\bullet] + k_{pBB}[B^\bullet]} \quad \ldots\ldots(15)$$

Assuming steady state concentrations for polymer radical $\dot{A}$

$$k_{pAB}[A^{\bullet}][B] = k_{pBA}[B^{\bullet}][A] \qquad \text{......(16)}$$

from which

$$\frac{[B^{\bullet}]}{[A^{\bullet}]} = \frac{k_{pBA}[B]}{k_{pBA}[A]} \qquad \text{......(17)}$$

substituting (17) into (15)

$$\frac{d[A]}{d[B]} = \frac{[A]}{[B]} \; \frac{r_1[A]+[B]}{r_2[B]+[A]} \qquad \text{......(18)}$$

where $k_{pAA}/k_{pAB} = r_1$, $k_{pBB}/k_{pBA} = r_2$ and are called monomer reactivity ratios.

This equation is called as the "copolymer composition equation" and was derived in 1944 by several workers[42-44] independently.

Equation (18) can be rewritten as

$$f = F\,\frac{r_1 \; F + 1}{r_2 \; + F} \qquad \text{......(19)}$$

where $[A]/[B] = F$ and $d[A]/d[B] = f$

Fineman and Ross[45] rearranged equation (19) to the linear form

$$\frac{F}{f}\,(f-1) = r_1 \; \frac{F^2}{f} - r_2 \qquad \text{......(20)}$$

A plot of $F(f-1)/f$ against F^2/f would give a straight line whose slope is r_1 and intercept is minus r_2.

Determination of individual rate constants.

The three quantities which can be readily obtained experimentally in a polymerisation reaction are; the reaction rate, the degree of polymerisation and the kinetic chain length. With this information it is not possible to evaluate the individual velocity coefficients k_p and k_t separately since they only occur as ratios in the overall rate equation (6).

To determine the velocity coefficients it is therefore necessary to find other relationships between the constants. These can be found by measuring the reaction rate using a non-stationary state method. In order to apply such a method and obtain reliable results the following conditions should be satisfied:

(a) the time of the start of the reaction must be known accurately,

(b) an accurate method of measuring the rate of reaction must be used, and

(c) all the reactants must be pure to prevent any initial inhibition period.

Non-stationary state methods used to evaluate the velocity coefficients k_p and k_t include direct measurement of the temperature rise in the reaction vessel using either a thermistor[29] or a thermocouple[9].

The above methods are based on the assumption that the conditions remain approximately adiabatic within the reaction vessel during the first 20 seconds of the reaction.

Theory of non-stationary state method.

The theory of Burnett[46] can be applied to the reaction scheme given in page (16) of this thesis.

During non-stationary state the concentration of the radicals is changing continuously

i.e. $$d[R^\bullet]/dt = I - k_t[R^\bullet]^2 \qquad \ldots\ldots(21)$$

Integrating equation (21) we get

$$\tfrac{1}{2}(k_tI)^{\frac{1}{2}} \ln \frac{1 + (k_t/I)^{\frac{1}{2}}[R^\bullet]}{1 + (k_t/I)^{\frac{1}{2}}[R^\bullet]} = t + C \qquad \ldots\ldots(22)$$

Now from equation (3) $[R_s^\bullet] = (I/k_t)^{\frac{1}{2}}$

and the kinetic chain lifetime τ is defined as

$$\tau = \frac{\text{Radical concentration}}{\text{Rate of removal of radicals}}$$

$$\frac{[R_s^\bullet]}{k_t[R_s^\bullet]} = \frac{I}{k_t[R_s^\bullet]}$$

$$\tau = (k_tI)^{-\frac{1}{2}} \qquad \ldots\ldots(23)$$

Substituting τ and $[R_s^\bullet]$ in equation (22) we have

$$\tfrac{1}{2}\tau \ln \frac{1 + [R^\bullet]/[R_s^\bullet]}{1 - [R^\bullet]/[R_s^\bullet]} = t + c \qquad \ldots\ldots(24)$$

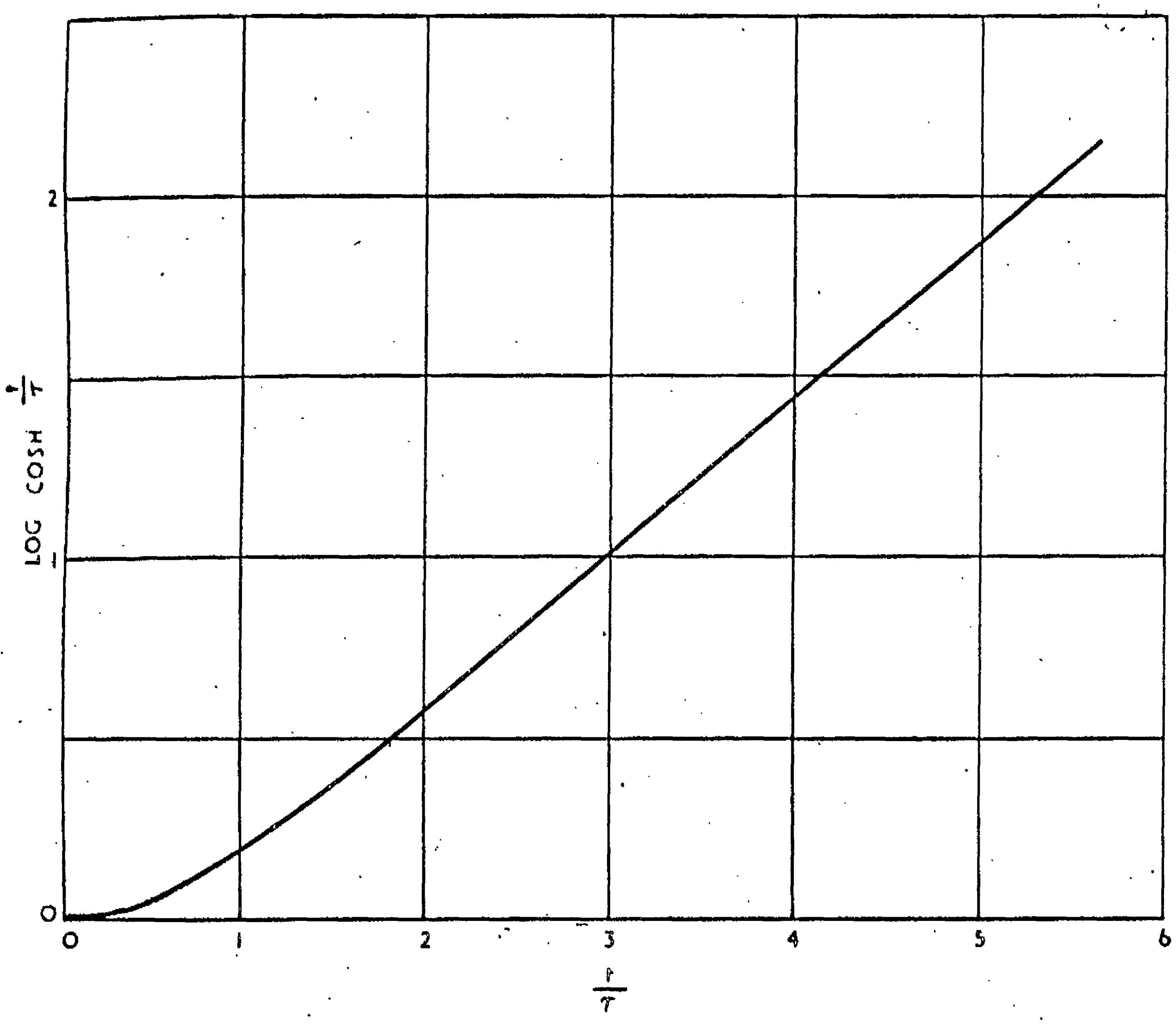


FIG. 1 THEORETICAL PLOT OF FRACTIONAL CONVERSION AGAINST TIME

and $c = 0$ since $[R^{\bullet}] = 0$ at $t = 0$

Rearranging equation (24) gives

$$\tanh^{-1} [R^{\bullet}]/[R^{\bullet}_{s}] = t/\tau$$

$$\text{i.e. } [R^{\bullet}] = [R^{\bullet}_{s}] \tanh (t/\tau) \qquad \text{......(25)}$$

Now the rate of polymerisation is given as

$$-d[M]/dt = k_{p}[R][M] \quad \text{(equation 5)}$$

$$\text{i.e. } -d[M]/dt = k_{p}[R^{\bullet}_{s}][M] \tanh (t/\tau) \qquad \text{......(26)}$$

Integrating equations (26) between time $t = 0$ and $t = t$

$$- \ln [M]/[M_{o}] = k_{p}/k_{t} \ln \cosh(t/\tau) \qquad \text{..(27)}$$

where $[M_{o}]$ is the initial monomer concentration and $[M]$ is the monomer concentration at any time t.

If F is the fraction of monomer converted into polymer, then

$$[M]/[M_{o}] = (1-F) \qquad \text{......(28)}$$

$$\text{i.e. } -\ln(1-F) = k_{p}/k_{t} \ln \cdot \cosh(t/\tau) \qquad \text{......(29)}$$

$$\text{Now if } F \ll 1, \text{ then } - \ln (1-F) = F \qquad \text{......(30)}$$

$$F = k_{p}/k_{t} \ln \cdot \cosh(t/\tau) \qquad \text{......(31)}$$

also when $t \gg \tau$ i.e. during the stationary state period

$$F = k_{p}/k_{t} (t/\tau - \ln 2) \qquad \text{......(32)}$$

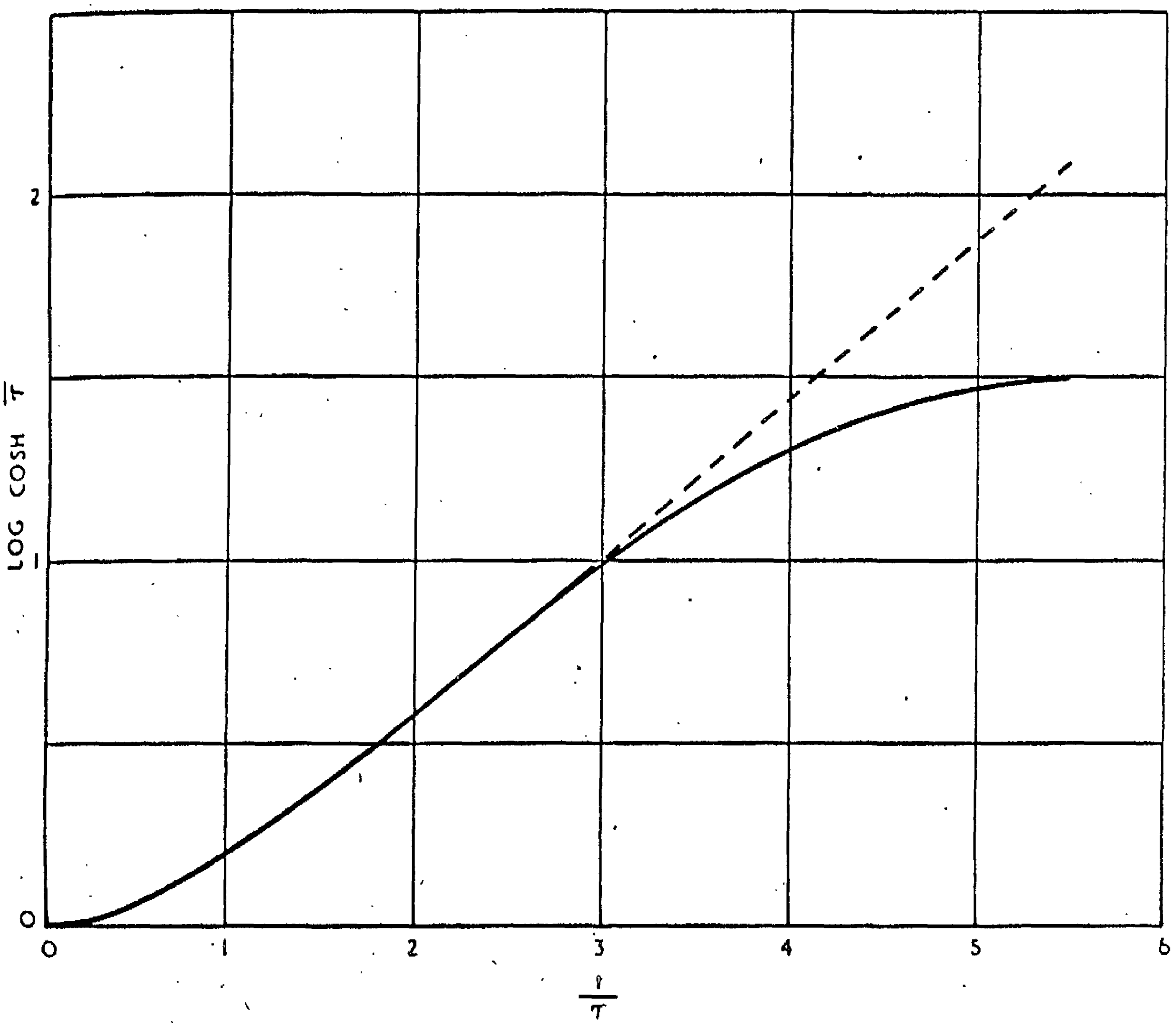


FIG. 2 THEORETICAL PLOT OF FRACTIONAL CONVERSION AGAINST TIME — EFFECT OF NON ADIABATIC CONDITIONS

A plot of F against t gives a straight line of slope k_p/k_t and an intercept on the time axis equal to τ ln2.

The lifetime can also be obtained from the decay curve produced when illumination is stopped. When this happens the production of radicals is reduced by termination in the absence of initiation

i.e. $$d[R^\bullet]/dt = -k_t[R^\bullet]^2 \qquad \text{......(33)}$$

Integrating between time limits t = 0 and t = t we get

$$[R^\bullet] = [R_s^\bullet]/(t/\tau + 1) \qquad \text{......(34)}$$

$$F = k_p/k_t \ \ln(t/\tau + 1) \qquad \text{......(35)}$$

The kinetic chain lifetime is obtained by plotting equation (35). By stationary state rate measurements it is possible to determine ratios of the velocity coefficients in two ways.

(1) From the overall rate equation (6)

$$\text{Rate of reaction} = k_p[M]I^{\frac{1}{2}}/k_t^{\frac{1}{2}}$$

If the rates of reaction, initiation and the monomer concentration are known $k_p/k_t^{\frac{1}{2}}$ can be calculated.

(2) The intercept on the time axis of the straight line portion of the fractional conversion curve is τ ln2. If the system has an instrument lag of c

seconds the equation relating the rate and the measured intercept, x, can be written as,

$$1/\text{Rate} = k_t/k_p \quad x/\ln 2 \; + c \qquad \ldots\ldots(36)$$

By plotting the reciprocal reaction rate against the measured intercept, a straight line of slope $k_p/k_t \ln 2$ and intercept c on the time axis is obtained.

From equation (23)

$\tau = 1/(k_t I)^{\frac{1}{2}}$ and k_t can be obtained provided the rate of initiation I is known, both k_p and k_t can be evaluated separately.

EXPERIMENTAL

APPARATUS.

Dilatometers. These vessels were made of vacuum tested Pyrex glass tubes. The size of the bulb and bore of the Veridia tubing were chosen according to the reaction rate expected. The size ranged from 5 ml. to 45 ml.

The Cathetometer used had a 53 cm scale and could be read to 0.001 cm.

Thermostat water bath.

The bath was a 25 litre cylindrical Pyrex glass tank lagged with a one inch thick layer of fibrous glass surrounded by an aluminium jacket. The aluminium jacket had one window for observation and one for irradiation. A ring type large 2 KW booster heater controlled by a Variac was used to raise the temperature of the bath when required, and to supply the background heat to keep it at a particular temperature. It was normally adjusted to maintain a temperature of approximately 1°C below the required temperature. The additional heat necessary to maintain the temperature at the required value was supplied by a 60W Robertson lamp heater actuated by a mercury-toluene regulator and relay made in the laboratory. The water was stirred vigorously by a propellor type stirrer, and the temperature was controlled to ± 0.02°C.

Source of irradiation.

A 125W Osira mercury arc lamp was used as a source of ultraviolet light. The lamp was connected to a capacitor or condenser to improve the power factor of the circuit and to a choke to limit the current through the lamp to a safe value. The light was passed through a Chance OX1 filter to remove U.V. light of wavelengths other than 3650Å. The lamp was housed in an asbestos box which was fixed in position so as to keep the distance between source and reaction vessel constant.

High vacuum system.

The high vacuum line was made of a series of traps and taps of Pyrex Glass connected via a mercury diffusion pump to an Edward's rotary high vacuum pump. Cold traps were placed just before and after the mercury diffusion pump, and an acetone/Drikold (solid carbon dioxide) mixture was used as a coolant. All taps and joints were greased with Apiezon high vacuum grease.

Vacuum line for styrene work.

A diagram of the vacuum line made for the work with styrene is given in Fig.(3). Due to the low volatility of the styrene (bp. = 145.2°C at 760 mm.) the distillation was conducted at 50°C. To avoid condensation the connecting line was heated.

The heating unit consisted of a nichrome wire windings (resistance 3.4 ohms per yard) which was connected to mains via a variable transformer. The operating potential was 12 volts. This part of the line contained no Quickfit ground glass joints to avoid the possibility of any air leakage through the heated greased joints. The unavoidable lubricated joints elsewhere in the line were greased with a little silicone grease.

Monomer distillation column.

This consisted of a 6 ft. vacuum-jacketted column (Fig.4) containing wire gauze rings. It was attached to a five-litre round bottom flask A. Purified nitrogen was passed into the flask via the condenser C. At the top of the column there were five cold fingers D to condense the vapours. These could be rotated so that any one of the fingers could be brought over a distillate outlet E which allowed

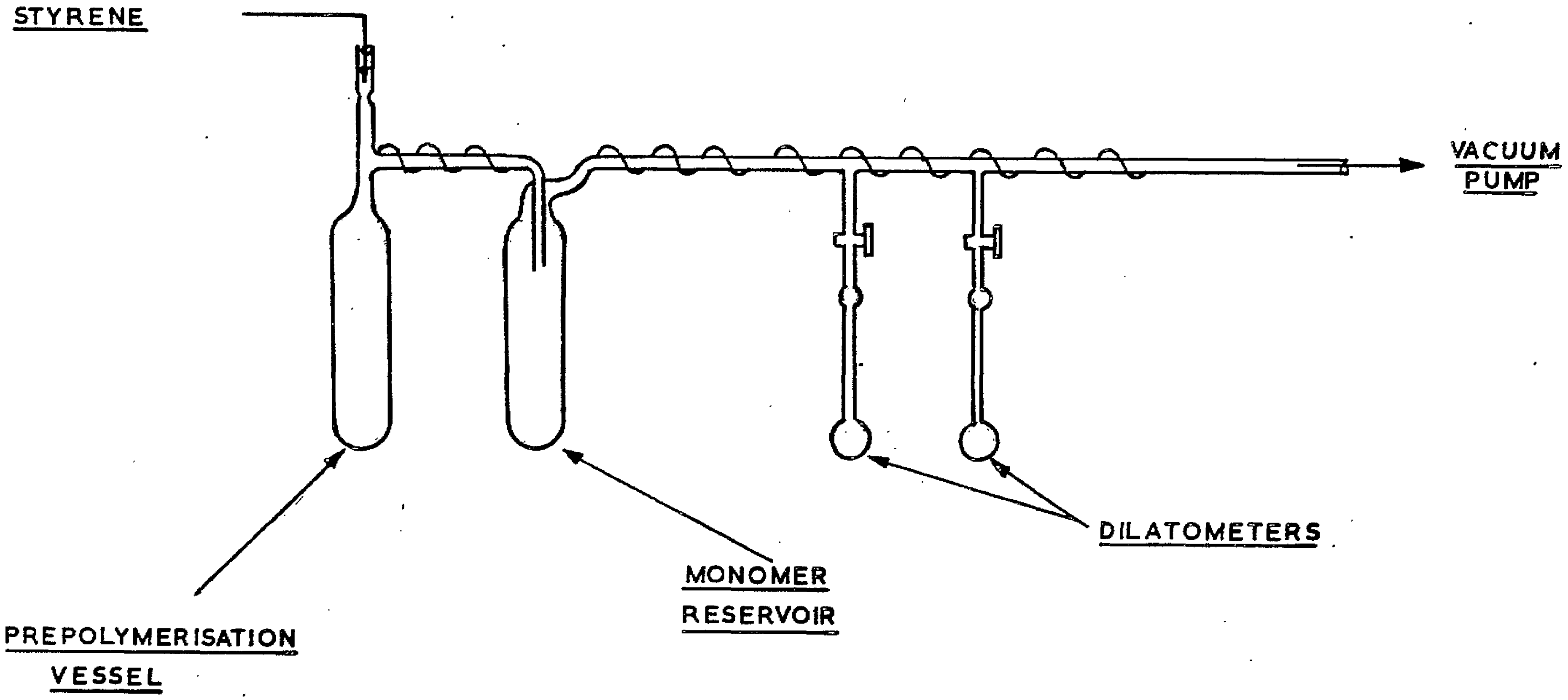


FIG.3. VACUUM LINE FOR STYRENE WORK

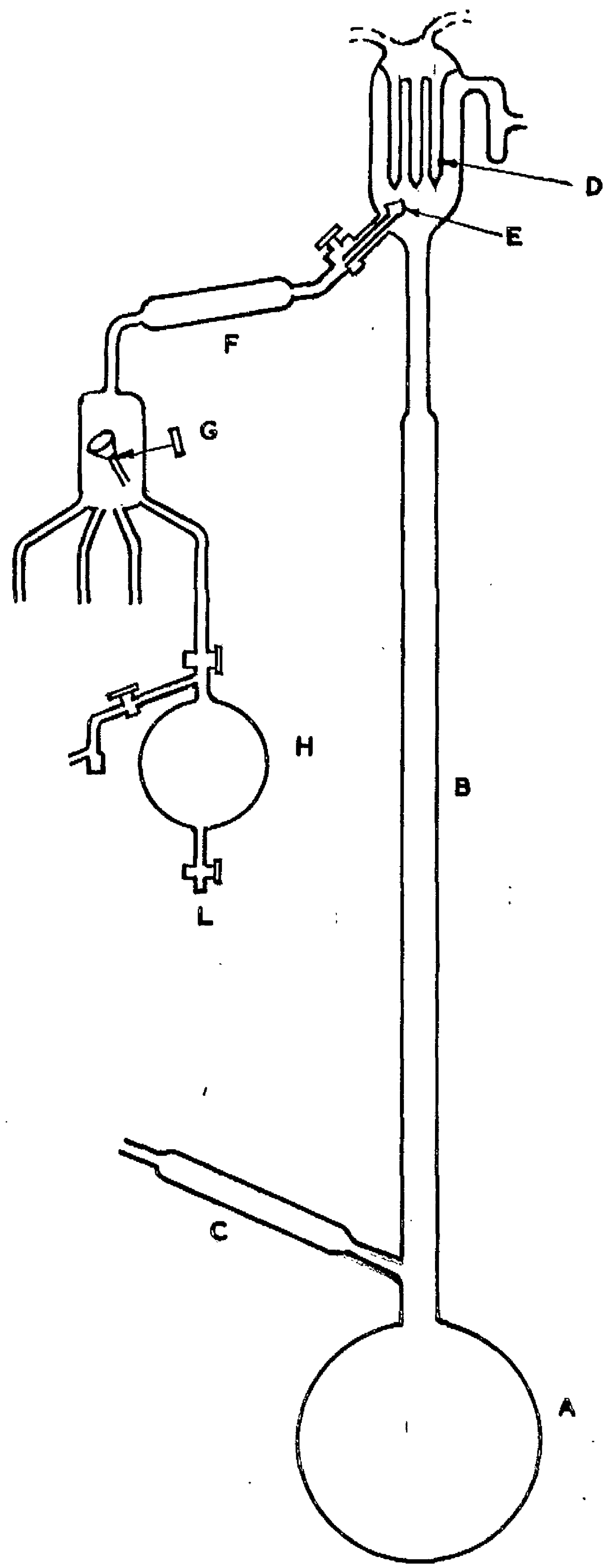


FIG.4. MONOMER DISTILLATION APPARATUS.

the distillate to pass through the condenser F. The reflux ratio could then be adjusted. The end of this condenser had a movable distributor G which could be directed into any of the four 500 ml. receiving flasks H. Mercury seal traps were fitted in all outlets of the column to prevent oxygen entering the system. Two of the four receiving flasks had taps L at their base through which could be removed a sample of the distillate for spectra measurements.

Modified Ubbelohde suspended level viscometer.

This viscometer was made to measure the flow time of the dilute polymer solutions. It enables one to dilute the polymer solution *in situ*.

Crystallization apparatus (Fig.5)

This was made of a vertical 2.5 inch diameter Pyrex glass tube A. A temperature gradient was established along this tube which was sealed through the base of a two litre copper tank B. The temperature of this tank, filled with water with a surface layer of paraffin oil to prevent evaporation, was maintained by a 60W light bulb which was controlled by a mercury toluene regulator.

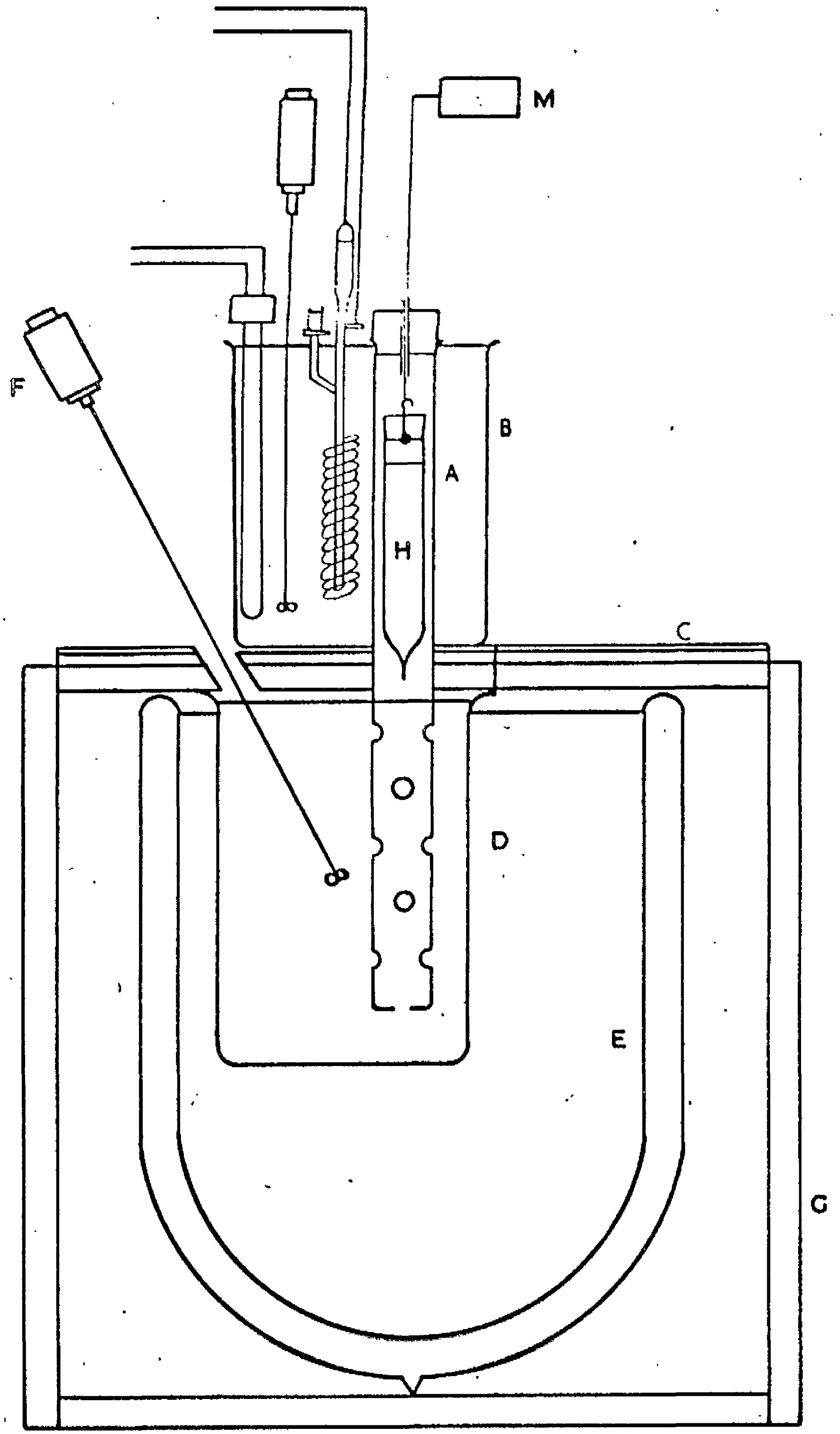


FIG. 5 CRYSTALLISING APPARATUS

This enabled one to keep the temperature in the upper part of tube A above the melting point of benzene.

The lower part of the tube A had holes at regular intervals and passed through into the Pyrex glass beaker D which was filled with acetone and attached to the underside of C. The acetone was maintained below 5°C by means of an acetone/Drikold slurry contained in a 15 litre Dewar flask D. This flask was held in a wooden box G and its contents stirred by means of stirrer F. The single crystal growing tube H was attached to a slow moving Sangamo motor M located vertically above tube A.

Scintillation counting.

In scintillation counting use is made of the photons created when a suitable luminescent material is excited by nuclear radiation. These photons are collected at the cathode of the photomultiplier tube which converts them into electrons. Multiplication of these electrons in the photomultiplier tube gives rise to electrical pulses which can be recorded on the normal scaler and timing unit. Each isotope produces a typical pulse dependent on its energy output and a discriminator is introduced into the circuit to differentiate between spurious pulses and those due to the presence of the isotope.

Scintillation counting equipment.

The circuit diagram for the scintillation counting equipment is given in Fig (6).

EHT and stabilized power unit NE 5302.

This unit was supplied by Nuclear Enterprises (NE) G.B. Ltd. It gives a stable supply free from an extraneous pulses. The unit is operated from the mains supply and produces a stabilized voltage which could be varied from 500 to 1400 volts at intervals of 100 volts with a coarse switch and from 0 to 100 volts at intervals of 0.1 volt with a fine switch.

Scaler type No. 1009F.

This was supplied by Dynatron Electronics. The unit is used to count impulses the amplitude of which are greater than a predetermined value. This value may be between 5 and 50 volts amplitude. The electrical pulses are fed to the input circuit, and then are applied to the discriminator which may be set at any predetermined value. Any electrical pulses below this value will not be counted. In the

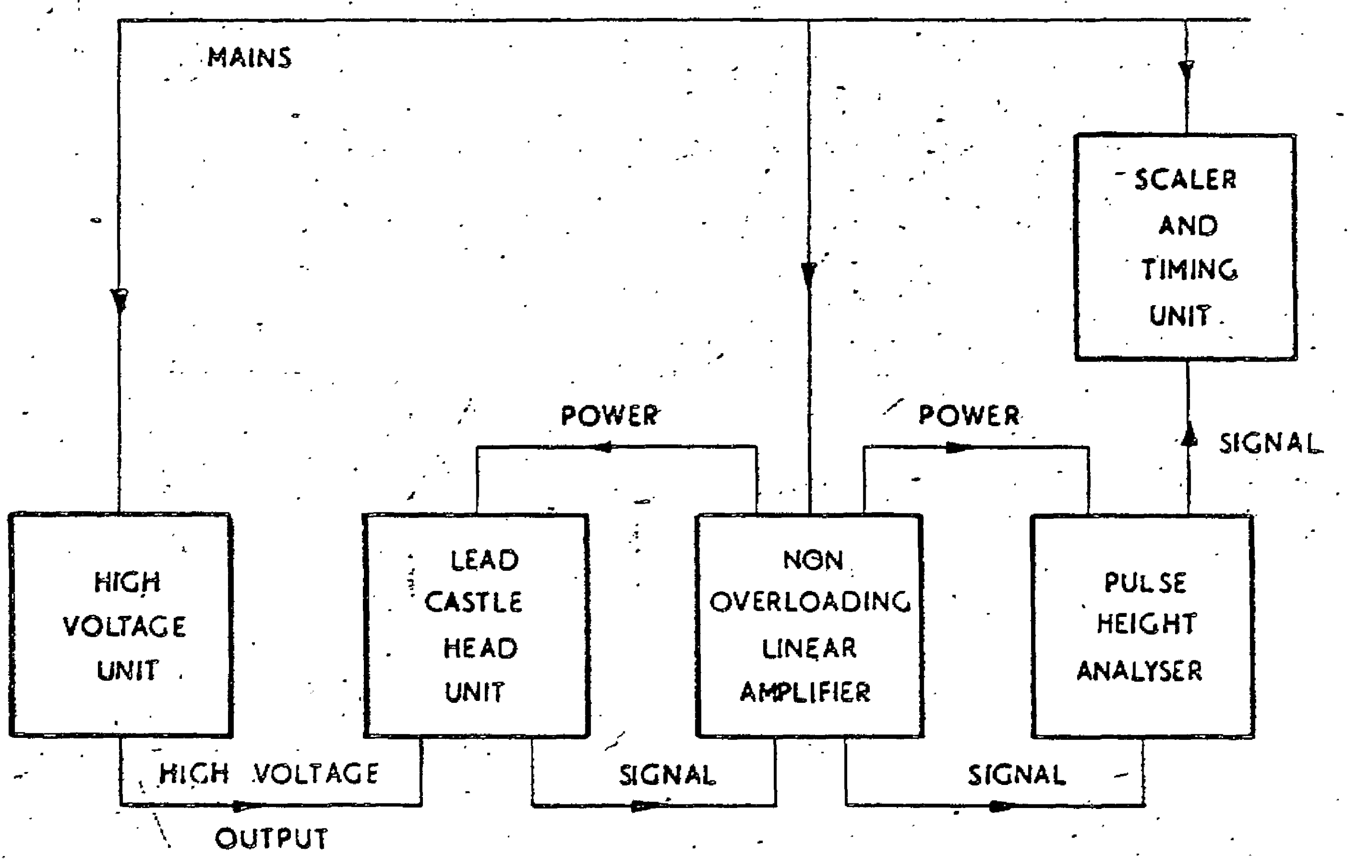


FIG.6 CIRCUIT DIAGRAM FOR THE SCINTILLATION COUNTING EQUIPMENT.

case of this work +5 was the setting used on discriminator bias.

Timing unit No. N.108A.

This unit was also obtained from Dynatron Electronics, and had 999,999 counts or 99,999 seconds store scales. When a number of counts or seconds preset on the Auto-stop-selector had been recorded this unit stopped the scaler automatically.

Scintillation head unit or castle.

This was also supplied by Nuclear Enterprises G.B. Ltd. It has a two inch lead shielding to exclude any radiation from entering or leaving the measuring compartment, and a special rotary light locking device so that cells can be put in, and taken out, without exposing the photomultiplier tube housed in the castle. Moreover the sample can be changed by means of a special device without switching off the voltage. The castle was cooled by a continuous flow of tap water through it which maintained the temperature low and fairly constant.

Above the photomultiplier (PM) tube is a well which is filled with 20 cs grade silicone oil through a hole on the side of the castle. The PM tube was connected to a N.E. (G.B) 5202 Amplifier with gain settings of from 0.4 to 200. The amplifier was connected to a single channel pulse height analyser NE (G.B) 5102 type. This was employed to optimise the signal to background ratio for a particular problem.

For C14 isotope counting best settings were found to be:

Stabilised high voltage	0.740 K.volts
Amplification	50 x 1
Pulse height	30
Gate width	30

Silicone oil.

The 20 cs grade silicone oil was also supplied by N.E. (G.B) Ltd. This oil acts as an optical contact between the cathode of the PM tube and the bottom of the scintillation bottle. The shallow well was always left filled with this oil.

Scintillation bottle.

These bottles of 18 ml. capacity were also obtained from N.E. (G.B) Ltd. They were made of Silica which is useful in reducing the effects produced by K40 beta particles in the glass walls of the ordinary cells. Silica also gives good light transmission. These cells were aluminised from outside and were coated with an epoxy resin.

Liquid scintillator obtained from N.E. (G.B) Ltd. consisted of a toluene solution containing 3 g. per litre 2,5 diphenyloxazole and 0.1 g. per litre diphenyloxazolylbenzene.

Non-stationary state apparatus.

The apparatus consisted of a dilatometer with built in thermocouple, a thermostat water bath, an amplifier, recording voltmeter, and the mercury vapour lamp for the source of ultravoilet light.

The water bath and the mercury lamp were the same as described before except that a quick moving shutter operated by an electromagnet was placed between the lamp and the reaction vessel.

Reaction vessel. The reaction vessel consisted of a soda glass dilatometer Fig.(7) with two additional side arms. The thermocouple system consisted of two thermojunctions, one situated at the centre of the dilatometer A, and a second junction B in a side arm. Wires CA and AB were of copper and constantin respectively, while connecting wires

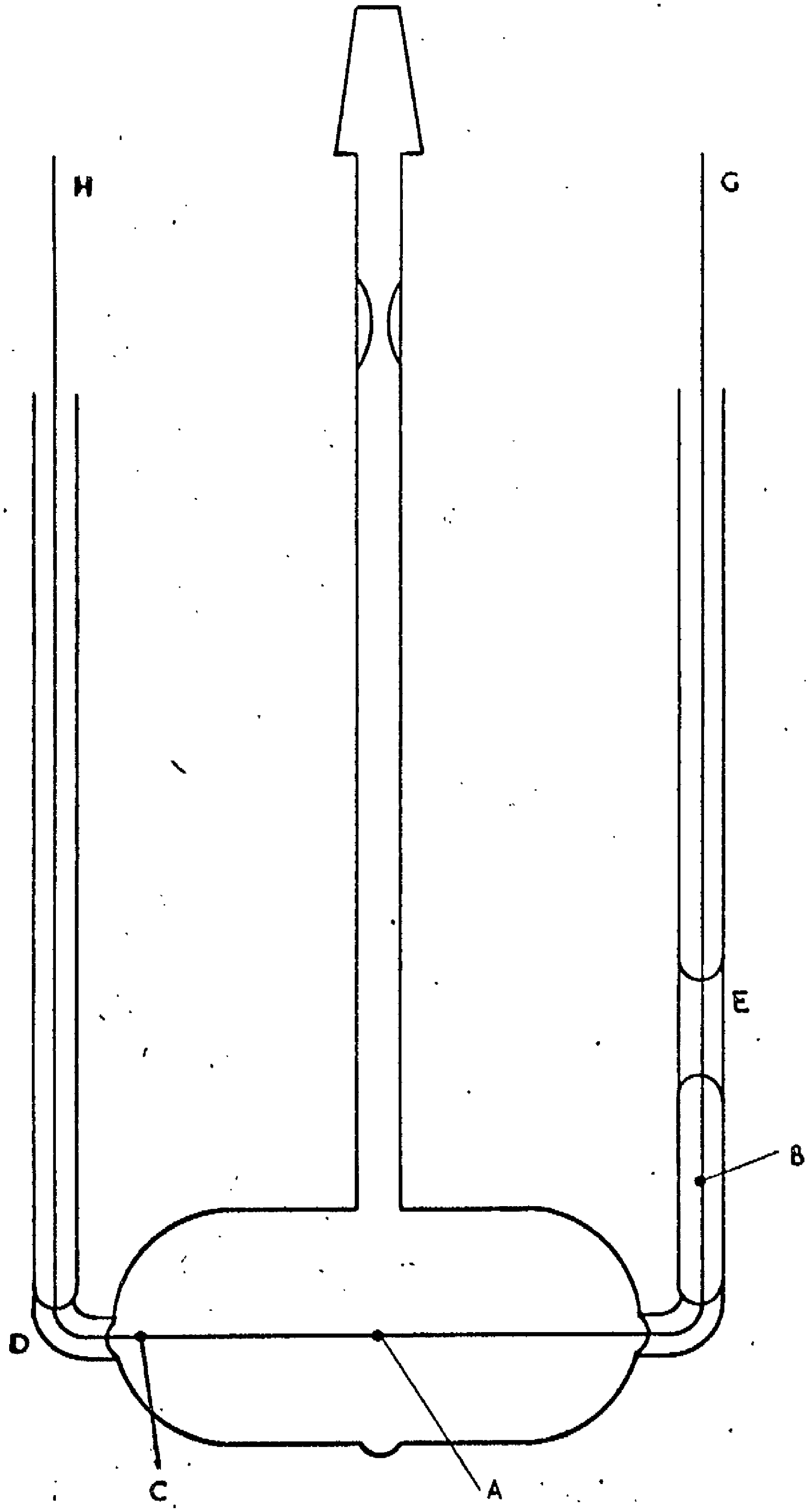


FIG. 7 THE THERMOCOUPLE VESSEL

EG and GH were made of borated copper clad iron which is necessary to get vacuum tight seals with the soda glass.

The thermocouple system was made by brazing the required lengths of wire at A, B and C. The junctions were smoothed with a very fine file and were thoroughly cleaned by rinsing in chloroform and hot water.

The wire GH was threaded through the dilatometer placing the thermojunctions in their correct positions. The constrictions at F and D were collapsed and arm DH was bent parallel to the stem. It was then attached to the vacuum line for evacuation. The constriction at F was collapsed about the constantin. The dilatometer was then ready for calibration and was exposed to air for the minimum length of time since the joint F, although liquid tight, was not absolutely airtight.

Amplifier.

The amplifier was the Tinsley D.C. type No. 5132 which is designed for an input impedence of less than 10 ohms. It was particularly suitable for this work as it was capable of giving a voltage amplification of more than 10^6. One could balance out e.m.f. of up to 400 microvolts (μV) in the input circuit by coarse and fine balance controls.

The temperature rise could be calibrated by means of a test voltage signal varying from 0.1 to 10 μV as required, and the output circuit gave a current of up to 10 milliamps.

The amplifier was very sensitive to 'pick up' and all the other electrical equipment was kept as far away as possible. The motor of the stirrer in the water bath was also kept well above the 'pick up' area.

Recorder.

An Elliot pen recorder voltmeter gave a chart trace of the output signal from the amplifier. During the reaction the chart was operated at a speed of 12 inches per minute but this speed could quickly be reduced to 12 inches per hour by a clutch mechanism.

MATERIALS

Vinyl acetate. Vinyl acetate was supplied by Shawinigan Chemical Co. (Canada). Three litres of monomer was put in the five litre flask which was attached to the distillation column as shown in Fig. (2).

The column was flushed overnight with purified nitrogen. The pressure required to break the mercury seal at the head of the column was adjusted so as to be greater than required to break the four mercury seals in the receiving flasks. The nitrogen escaped through these four mercury seals.

The distillation was carried out at a high reflux ratio. From previous experience, it was found that the monomer distilling in the early stages contained retarding impurities, and that 'pure' monomer usually appeared during the filling of the third flask. Samples were therefore not normally taken at this stage,

A sample of the distillate was taken from time to time and its U.V. spectrum measured. The monomer was collected in the fourth flask when its spectrum started showing a rapid change in absorption in the range 2650-2750A°. The type of change occuring is shown in Fig. (8). According to Matheson et al[47] this is the

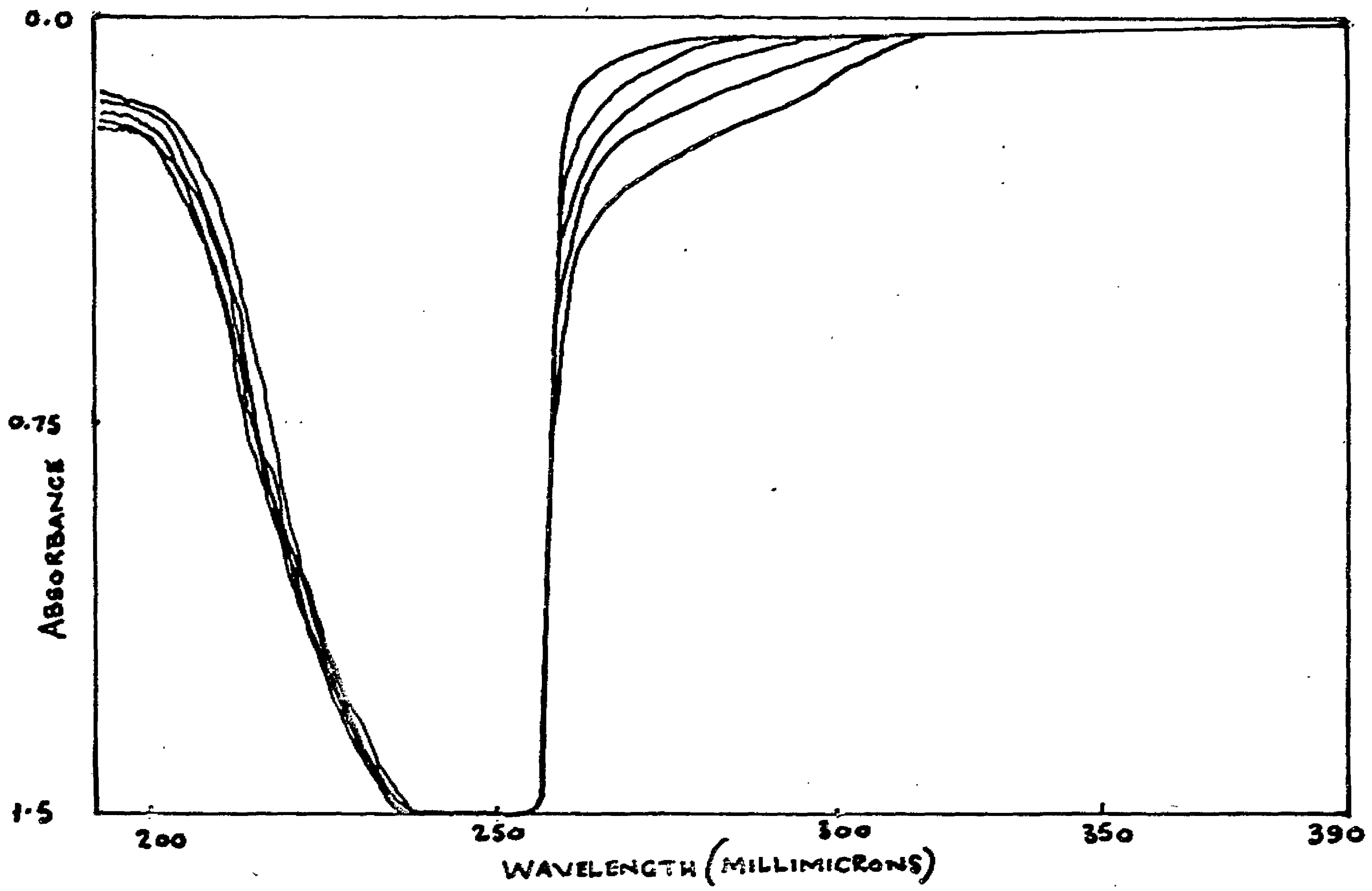


FIG 8. U.V. SPECTRA OF VINYL ACETATE DURING DISTILLATION

range where the main light absorbing impurities are present.

The monomer was then transferred to the vacuum line and thoroughly degassed by distilling it at room temperature from one vessel to another using acetone/Drikold as coolant. It was finally collected at the end of the vacuum line in a rather large vessel (attached by a moveable arm) containing a small glass encased magnet and a little benzoyl peroxide. The monomer was prepolymerised to about 10% by irradiating it with a mercury U.V. lamp. The temperature of the prepolymerisation vessel was kept at about room temperature by surrounding it with a beaker of water. The glass encased magnet and the moveable arm were used to break the skin of the polymer on the surface. After prepolymerisation the unreacted monomer was distilled at room temperature into the central vessel of the line and stored there at-78°C.

During the latter stage of this work two samples of vinyl acetate inhibited and uninhibited, were received from I.C.I. Ltd. It was unnecessary to use the distillation column to purify the inhibited vinyl acetate. It was purified by distilling and prepolymerising on the vacuum line, whereas uninhibited and Shawinigan vinyl acetate needed the elaborate purification as described above.

Benzene.

In this work benzene was purified by growing it as a single crystal in a crystallisation apparatus constructed by Brownlie[8], and described earlier.

Analar grade benzene was obtained from British Drug Houses (B.D.H) Ltd. A little benzene was put in the benzene growing tube capillary and air was removed from the end with the fine capillary by careful alternately heating and cooling it. More benzene was added, and the tube was stoppered with a rubber bung with a hook to attach the thread, the other end of which was attached to the Sangamo electric motor M (Fig.5). Care was taken to ensure that the tube was held completely vertical. Tube H was allowed to stand for two hours to reach temperature equilibrium. Then the motor was switched on.

As the tip of the capillary of tube H was lowered, its temperature fell below the freezing point of the benzene, nucleation occurred, and growth of the single crystal started. It took about three days to grow a single crystal from about 15 ml. of benzene. The clear single crystals grown were stored in deep freeze immediately after taking off the motor M. The liquid benzene above the single crystal froze forming multicrystals and these were separated from the single crystal by cutting the tube H just below the interface between the single and multicrystalline material. The impurities were contained in the multicrystals.

Styrene.

Styrene (B.D.H.) grade was freed from inhibitor by distilling it under vacuum. The middle fraction was collected, and transferred to the flask on the vacuum line (Fig.1). The degassing, and prepolymerisation operations were carried out as described for vinyl acetate.

1:1 Azobisisobutyronitrile (AIBN).

Eastman Kodak grade of AIBN was purified by two recrystallisations from ethanol below 28°C. The solution was not heated above this temperature to avoid decomposition. This material had a melting point of 102°C. The AIBN was put into the dilatometer in the form of solution in freshly distilled anaesthetic grade chloroform. Since AIBN decomposes when left in solution at room temperature fresh solutions were made immediately before using them.

C14 labelled AIBN.

This was avialable in the laboratory having been prepared by Henderson[48] using the method of Overberger and coworkers[49] from C14 labelled acetone.

Dimethyl formamide (DMF).

This solvent was obtained from May and Baker Ltd. It was shaken up for one hour with phosphorus pentoxide. This process was repeated four times, and the solvent then distilled at reduced pressure, the middle fraction being collected.

Halogenated substituted aromatic solvents.

Monochloro-, o-dichloro-, m-dichloro-, p-dichloro-, monofluoro-, m-difluoro, monobromo-, m-dibromo-, monoiodo- and hexachloro-benzene, were obtained from B.D.H. Ltd. 1,2,4-trichloro- and 1,2,3,4-tetrachloro-benzene were supplied by Koch-Light laboratories. With the exception of p-dichloro- and hexachloro-benzene which were supplied in fine crystalline form, all the others were distilled under reduced pressure, and the middle fraction was used in the polymerisation studies.

Tetrachloro-benzene was recrystallised from ether.

The purity of the liquid solvents was confirmed by vapour phase chromatography (VPC).

Aromatic carboxylic acids.

Analar grade benzoic acid and phthalic acid were obtained from B.H.D. Ltd. in fine crystalline form and were used without further purification.

1,2,3-hemimellitic acid, and mellitic acid were supplied by Koch-Light laboratories, and the Aldrich Chemical Co. respectively. The former was recrystallised from ether, and the latter from ethanol.

Other Solvents.

Tetrachlorotetrahydronaphthalene was purchased from Eastman Organic Chemicals, and was recrystallised from ether.

Hexaethylbenzene and benzene hexol were obtained from Kodak Ltd., and diphenyl from Hopkin and Williams (fine Chemicals) in fine crystalline form and were used without recrystallisation.

Cyclohexadiene was obtained from Koch-Light Laboratories. It was distilled on the vacuum line immediately after opening the bottle as it tends to oxidize readily. The clear colourless middle fraction was taken for the polymerisation reactions. The purity was confirmed by VPC.

EXPERIMENTAL PROCEDURE

Calibration and filling of dilatometer.

The dilatometers were calibrated by introducing Analar acetone from a burette. Then the initiator was introduced through a long fine capillary, in standard chloroform solution. The dilatometer was connected to the vacuum line, and the chloroform was distilled off carefully, so that no initiator was carried up in fine powder form with the chloroform vapours. The solvents were introduced into the dilatometers at atmospheric pressure, and then degassed completely by repeatedly freezing, evacuating, and thawing on the vacuum line. The required amount of monomer was distilled in from a precalibrated vessel. The dilatometer was sealed in a flame, and if not required immediately, was stored in acetone/Drikold.

Then the sealed dilatometers were immersed in the water bath at the required temperature. About 10 to 15 minutes were allowed for thermal equilibrium to be attained before commencing the irradiation. The movement of the meniscus in the dilatometer was followed with the cathetometer, and rate of reaction was determined in terms of contraction per unit volume.

Radioisotope experimental procedure.

0.5 millicuries of benzene, prepared from the trimerisation of $H\overset{14}{C} \equiv \overset{14}{C}H$, was obtained from the Radio-chemical centre, Amersham, in a breakseal ampoule. The ampoule was attached to the vacuum line, the seal then broken and 10 ml. of inactive benzene was distilled into the ampoule using liquid N_2 as coolant. When thoroughly mixed, 0.1 ml. sample was taken, made up to 50 ml. in inactive benzene, and grown as single crystal. This benzene was used for polymerisation experiments and is referred to as stock benzene. More dilute solutions of known concentration were prepared using this stock benzene, and were used to construct a calibration curve.

C14-styrene.

0.1 millicuries C14-styrene containing inhibitor was supplied by New England Nuclear Corporation (U.S.A) in a sealed ampoule with a constriction at one end. The styrene in the main bulb was frozen in acetone/ Drikold, and was cut gently at the constriction. The radioactive styrene was then transferred to a vessel with a B10 cone by washing out the ampoule with 10 ml. of pure inactive styrene. The contents of the vessel were degassed on the vacuum line, and 1 ml. of active styrene was distilled into the neighbouring vessel containing 100 ml. inactive styrene. This 100 ml. of active styrene (referred to in future as stock styrene) was transferred to the special vacuum line for styrene, degassed and polymerised as described before. This stock styrene was used for polymerisation reactions and further dilutions were made in benzene to calibrate the activity of the styrene.

C14-vinyl acetate.

0.5 millicuries C14-vinyl acetate stabilized by inhibitor was also obtained from New England Nuclear Corporation (U.S.A.) in a breakseal ampoule. The breakseal was broken and 10 ml. of pure vinyl acetate was distilled into the ampoule after following the same procedure as adopted in the case of styrene. 0.2 ml. of this active solution was then distilled into 80 ml. of purified vinyl acetate stored already on the line. This stock vinyl acetate was used for polymerisation experiments; for the calibration curve further dilutions were made in benzene.

Very dilute calibration solutions of active styrene and vinyl acetate were made in benzene to reduce quenching.

Scintillation counting procedure.

The power for the voltage stabilizer, the amplifier, the scaler and timing unit was switched on at least 24 hours before any measurements were made. The E.H.T. was switched on and allowed to stabilize overnight.

To determine the activity of a radioactive solution 5 ml. of liquid scintillator and 5 ml. of radioactive solution were placed in the counting bottle. When assaying the activity of the polymer, the solution used contained 20 milligrams of the polymers dissolved in inactive benzene. The bottle was placed in the castle, and after checking that ample oil is present, it was left for 20 minutes to minimise the residual phosphorescence, and to settle down to the temperature of the castle.

The well was "topped up" with silicone oil in subdued light after 8 or 10 samples had been counted.

Precipitation of polymers.

In the case of bulk polymerisation, the contents of the dilatometers were poured into so much acetone that when put in the well stirred n-hexane dropwise the polymer was precipitated as a sticky fibrous material. Usually about 5 ml. acetone was added to

10 ml. dilatometer contents.

After filtration the polymer was dried at room temperature for several hours in a vacuum dessicator containing phosphorus pentoxide. The polymer was then dissolved in 40 ml. of benzene (Analar grade) in one litre round bottom flask. The solution was frozen by rotating the flask in a basin containing acetone/Drikold mixture and attached to the vacuum line quickly. The benzene sublimed and was trapped in the neighbouring vessel cooled in liquid nitrogen. After 4 hours the flask was removed from the vacuum line, and the polymer was in a white fluffy form free from any solvent.

In the presence of solvents the contents of the dilatometer were poured into the flask and freeze-dried, the process being repeated until the polymer was free of unreacted solvent.

In lower [S]/[M] ratios the polymer was precipitated to remove any catalyst but it was found that this did not make any difference to the value obtained for intrinsic viscosity.

<u>Low styrene/vinyl acetate ratio.</u>

The contents of the dilatometer were added dropwise to 500 ml. vigorously stirred water. The polymer was precipitated in a fine suspension and filtered through a sintered funnel. The polymer was then dissolved in 10 ml. of acetone and reprecipitated in water, this step being carried out several times until all the unreacted radioactive additives had been removed from the polymer. Then polymer was freeze-dried on the vacuum line.

High styrene/vinyl acetate ratio and pure styrene.

For this system the solvent and non-solvent used were methyl ethyl ketone and methanol respectively, otherwise the reprecipitation process was the same as for low styrene/vinyl acetate ratios.

Non-stationary state experimental procedure.

The calibration of the dilatometer, and the introduction of the catalyst and the monomer was done the same way as described for the stationary state dilatometer.

The leads from the input circuit of the amplifier were passed through two rubber tubes. Then the connecting leads G and H from the arms of the dilatometer were soldered to the leads from the amplifier, and the rubber tubes were slipped over the ends of the side arms of the dilatometer.

The reaction vessel was placed in the water bath in a fixed position, care being taken to ensure that no water entered through the top of the rubber tubes. Then the amplifier, and the mercury lamp were switched on, and left for 30 minutes to reach the stable operating conditions. Meanwhile, the reaction mixture had reached thermal equilibrium.

With a chart speed of 12 inches per minute a known voltage was put through the circuit for 5 seconds, and the gain adjusted to the desired amplification. The chart was let to run at this speed for about 10 seconds more to ensure a steady temperature before starting the reaction.

The reaction was started by actuating the electromagnet to pull aside the shutter in front of the lamp. A record of the start of the reaction time was given on the chart by an induced signal.

The rise in temperature of the reaction mixture was observed on the pen recorder, and after 30 seconds the shutter was replaced to stop the reaction.

From the chart trace, the rate of the reaction in microvolts per second, and the intercept in seconds on the time axis, were found. The rate of reaction was varied by putting gauze screens of known light transmission in front of the light beam, and repeating the above process.

EXPERIMENTAL RESULTS

Except in the non-stationary state experiments the rate of reaction was measured dilatometrically. Data of Starkweather and Taylor[17] and interpolation of the data of Matheson *et al*[47] were used to calculate the densities of vinyl acetate monomer, and polymer, and from this the conversion factor was calculated.

The AIBN concentration used except where otherwise stated was 5×10^{-4} molar. The polymerisation was not taken further than about 7% conversion.

Determination of the intensity exponent.

It is necessary to establish the nature of the termination reaction in a free radical polymerisation so that the correct kinetic analysis may be applied to the system. In a free radical system termination can occur by a first, or a second order reaction, with respect to the growing polymer radical concentration. The rate of the reaction, and the light intensity are related in the following form:

$$X_1/X_2 = \left[L_1/L_2\right]^n \qquad \text{......(37)}$$

where X_1 is the rate of reaction at light intensity L_1, X_2 is the rate of reaction at light intensity L_2 and n is the intensity exponent.

If termination occurs between two growing polymer radicals then the rate is proportional to the square root of the light intensity i.e. $n = \frac{1}{2}$. If termination occurs between a radical and a non-radical species, then the reaction is first order with respect to the radical concentration, and the rate of the reaction is proportional to the light intensity i.e. $n = 1$.

It is also possible for the termination to involve both first and second order reactions; then the value of n will lie between $\frac{1}{2}$ and 1.0.

The slope of the straight line obtained by plotting log (rate) against log (light intensity) gave an intensity exponent (Fig.9) of 0.51 at 25°C; this shows that termination is second order with respect to the growing polymer radical concentration.

Molecular weight determinations. The molecular weight of the polymers was determined by the viscosity method. Although it is not an absolute method of characterization of polymers it is still a very useful method.

Dilute solution viscosities were measured with a capillary Ubbelohde type viscometer as described earlier. Measurements were made at 25°C ± 0.02°C,

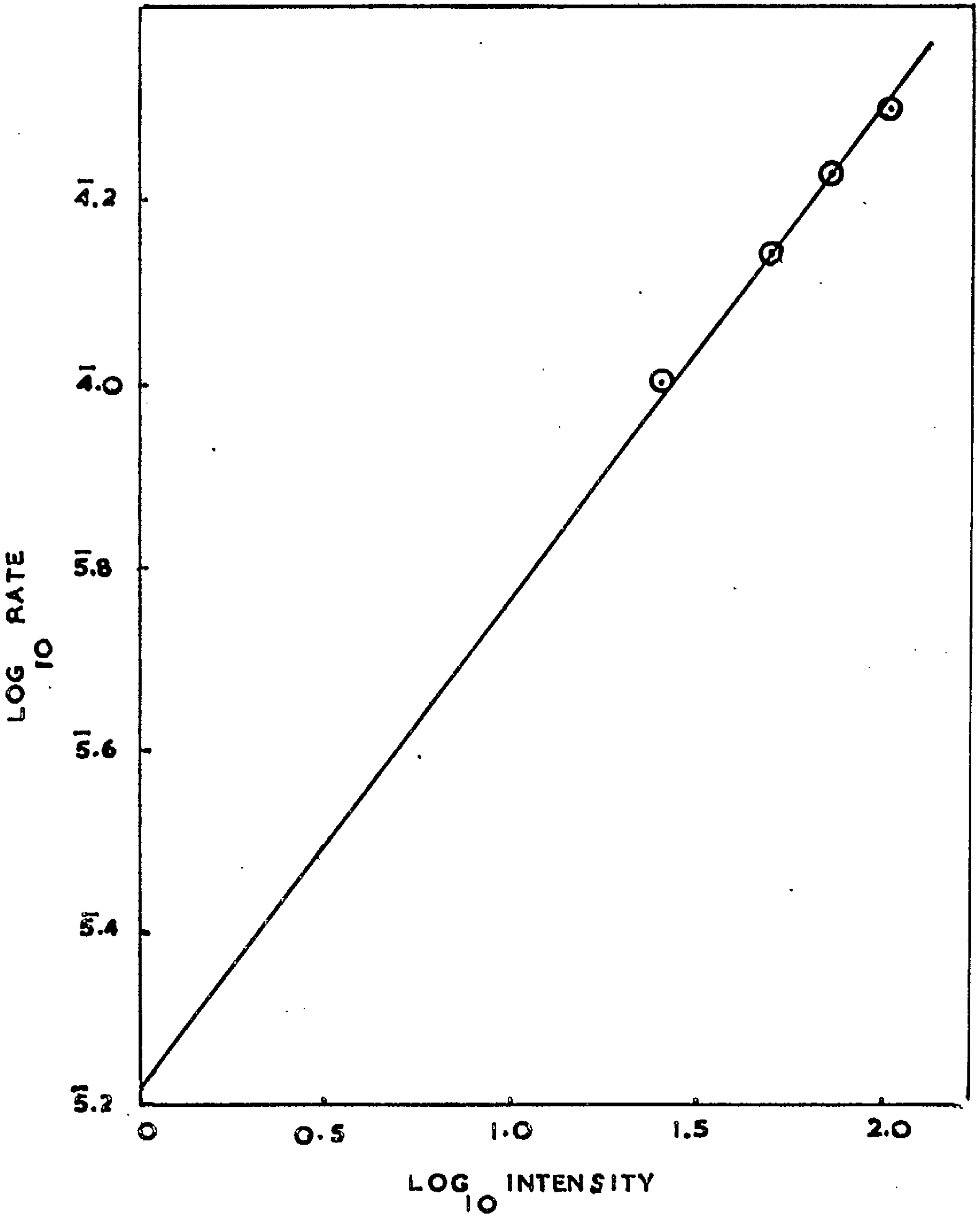


FIG. 9 PLOT FOR THE DETERMINATION OF INTENSITY EXPONENT IN BULK VINYL ACETATE POLYMERISATION.

using a stopwatch. The viscosity was calculated from an equation of the form

$$\eta = Adt - Bd/t \qquad \text{......(38)}$$

where d is the density of the liquid, t is the flow time of the liquid in seconds, A and B are constants for the viscometer. Bd/t is a small correction for the kinetic energy of the liquid. The sizes of the capillary, and of the top bulb of the viscometer were chosen so that the flow time was at least 100 seconds, in order that kinetic energy corrections might be small.

In the system studied in this work, namely polyvinyl acetate in acetone at 25°C

$$A = 0.00287$$

$$\text{and} \quad B = 3.064$$

The flow time for solvent was 142.2 seconds and its density 0.785

$$\eta_o = 0.303$$

If η_o is the viscosity of the solvent, and η that of the solution, then the specific viscosity(η_{sp}) of the solution is $(\eta - \eta_o)/\eta_o$. The ratio η_{sp}/c (where c is the concentration g./100 ml) was plotted against c, and extrapolated to a zero concentration to give the intrinsic viscosity $[\eta]$

$$\text{i.e } [\eta] = \lim_{c \to 0} (\eta_{sp}/c)$$

The $[\eta]$ value is related to the molecular weight of the polymer by the modified Staudinger equation

$$[\eta] = K\ M^{a} \qquad \ldots\ldots(39)$$

where K and a are constants for a particular polymer-solvent system at a given temperature.

In the polyvinyl acetate - acetone system at 25°C, where the polymer is of low conversion Stockmayer et al[4] obtained the following equation

$$\log \bar{M}_v = 5.44 + 1.40 \log [\eta] \qquad \ldots\ldots(40)$$

where $\bar{M}_v$ is the viscosity average molecular weight. Also they found

$$\bar{M}_v/\bar{M}_n = 1.85 \qquad \ldots\ldots(41)$$

where $\bar{M}_n$ is the number average molecular weight. From equations (31) and (32) they derived the relationship

$$\log \overline{DP} = 3.24 + 1.40 \log [\eta] \qquad \ldots\ldots(42)$$

In this work $\overline{DP}$ was obtained from this relationship.

Determination of the chain transfer constant with monomer

The rates of polymerisation were varied by changing the intensity of the incident light.

Fig (10) shows the plots of $1/\bar{DP}$ against rate (according to the equation 9) at 25, 35, 45, and 60°C. The plots are linear, and $1/\bar{DP}$ does not extrapolate to zero at zero rate. This indicates a chain transfer reaction independent of the rate, and the intercepts were noted as chain transfer constants. Rates, molecular weights, and chain transfer constants at various temperatures are given in Table 1.

TABLE 1 Chain transfer constant to monomer at 25, 35, 45 and 60°C obtained from rate and $\overline{DP}$ measurements for the polymerisation of vinyl acetate, photosensitized with 5 x 10^{-4} molar AIBN.

Temperature °C		$10^4/\overline{DP}$	Rate x 10^4 (mole $l.^{-1}$ sec.$^{-1}$)	C_m x 10^4
25	2.875	1.315	0.974	1.40
	2.850	1.328	1.38	
	2.80	1.361	1.62	
	2.825	1.345	2.00	
35	2.260	1.838	1.552	1.74
	2.212	1.893	2.167	
	2.177	1.943	2.592	
	2.150	1.971	3.047	
45	2.017	2.140	2.382	1.91
	1.940	2.275	3.077	
	1.880	2.345	3.775	
	1.845	2.441	4.325	
60	1.860	2.415	4.601	2.15
	1.815	2.498	6.285	
	1.775	2.577	7.250	
	1.735	2.661	9.263	

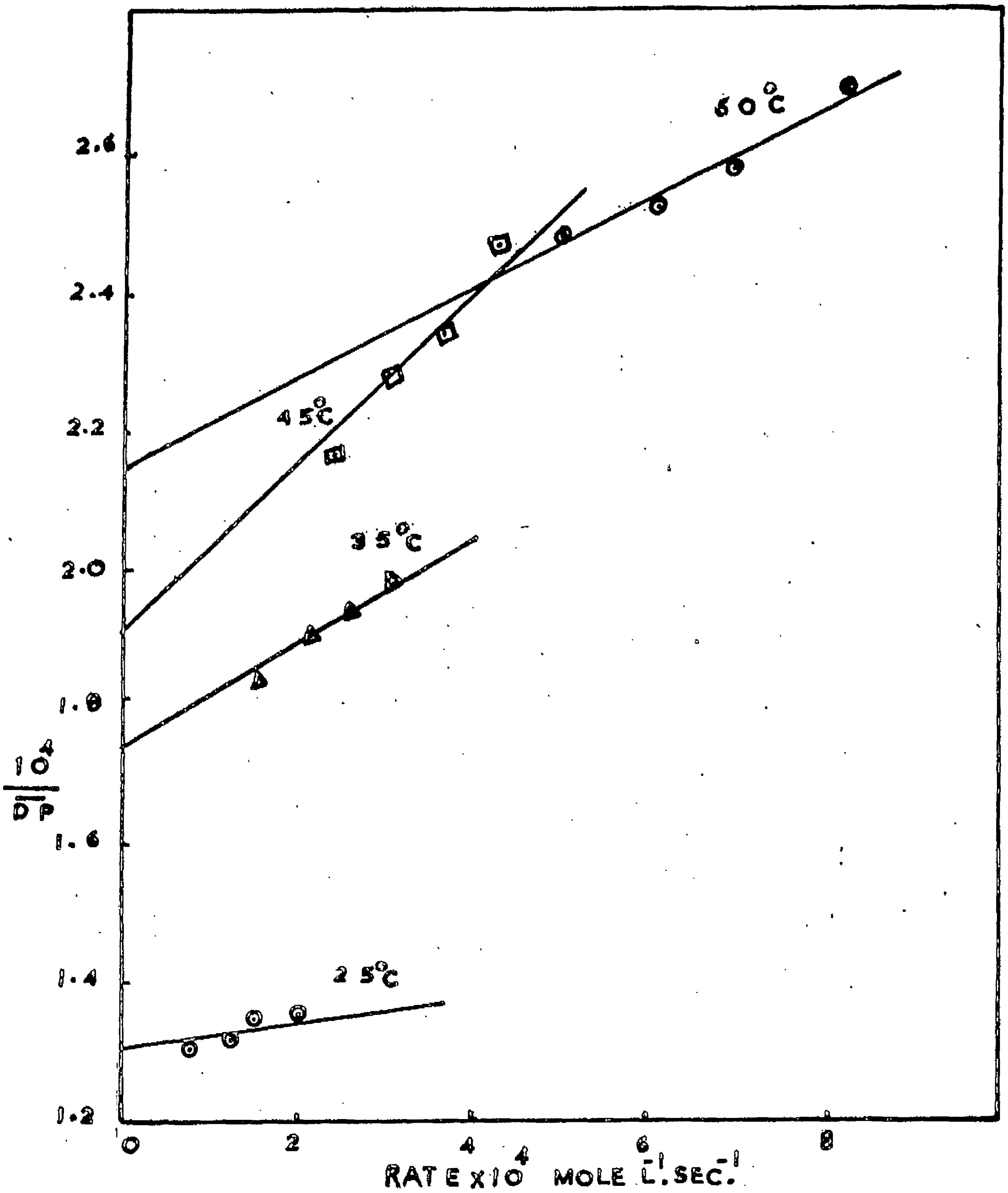


FIG. 10 RECIPROCAL OF $\overline{DP}$ AGAINST RATE OF POLYMERISATION OF VINYL ACETATE AT DIFFERENT TEMPERATURES

From Table 1 it can be seen that $1/\overline{DP}$ increases with the increase in temperature. The value of C_m at 60°C is about 50% greater than the value at 25°C.

TABLE 2 Dark rate at various temperatures for the polymerisation of vinyl acetate with 5×10^{-4} molar AIBN.

Temperature °C	Dark rate x 10^4 (mole $l.^{-1}$ sec.$^{-1}$)
60	4.5
45	0.9
35	0.3
25	0.12

Table 2 shows the very large increase in the dark rate with increase in temperature. This is to be expected because of the substantial increase in the rate of the thermal decomposition of the initiator with increase in temperature.

Determination of energies of activation.

The effect of temperature on a chemical reaction is expressed by the usual Arrhenius equation

$$K = A . e^{-E/RT} \qquad \ldots\ldots(43)$$

where K is the velocity constant of the reaction, A is the frequency factor i.e. the total frequency of encounters between the reacting species, E is the activation energy for the reaction, T is the temperature of the reaction in degrees absolute, and R is the molar gas constant.

Using the above equation the overall activation energy (E_o) was determined from the plot of the logarithm of the reaction rate against the reciprocal of the absolute temperature (1/T) for the temperature range 25°C to 60°C (Table 1). Figs.(11-12) show the plots.

Now from the kinetic scheme on page (16) and equation (43) we have

$$E_o = E_p + \tfrac{1}{2} E_i - \tfrac{1}{2} E_t \qquad \ldots\ldots(44)$$

where E_p, E_i and E_t are the activation energies for the propagation, the initiation and the termination reactions respectively.

In the photo-initiated system studied E_i is zero, and thus equation (44) becomes

$$E_o = E_p - \tfrac{1}{2} E_t \qquad \ldots\ldots(45)$$

From Fig. (11)

$$\begin{aligned} \text{slope} &= E_o/2.303R \\ &= 1.05 \\ E_o &= 4.8 \text{ k.cal.mole}^{-1} \end{aligned}$$

Using the literature value[8] of 4.8 k.cal.mole^{-1} for

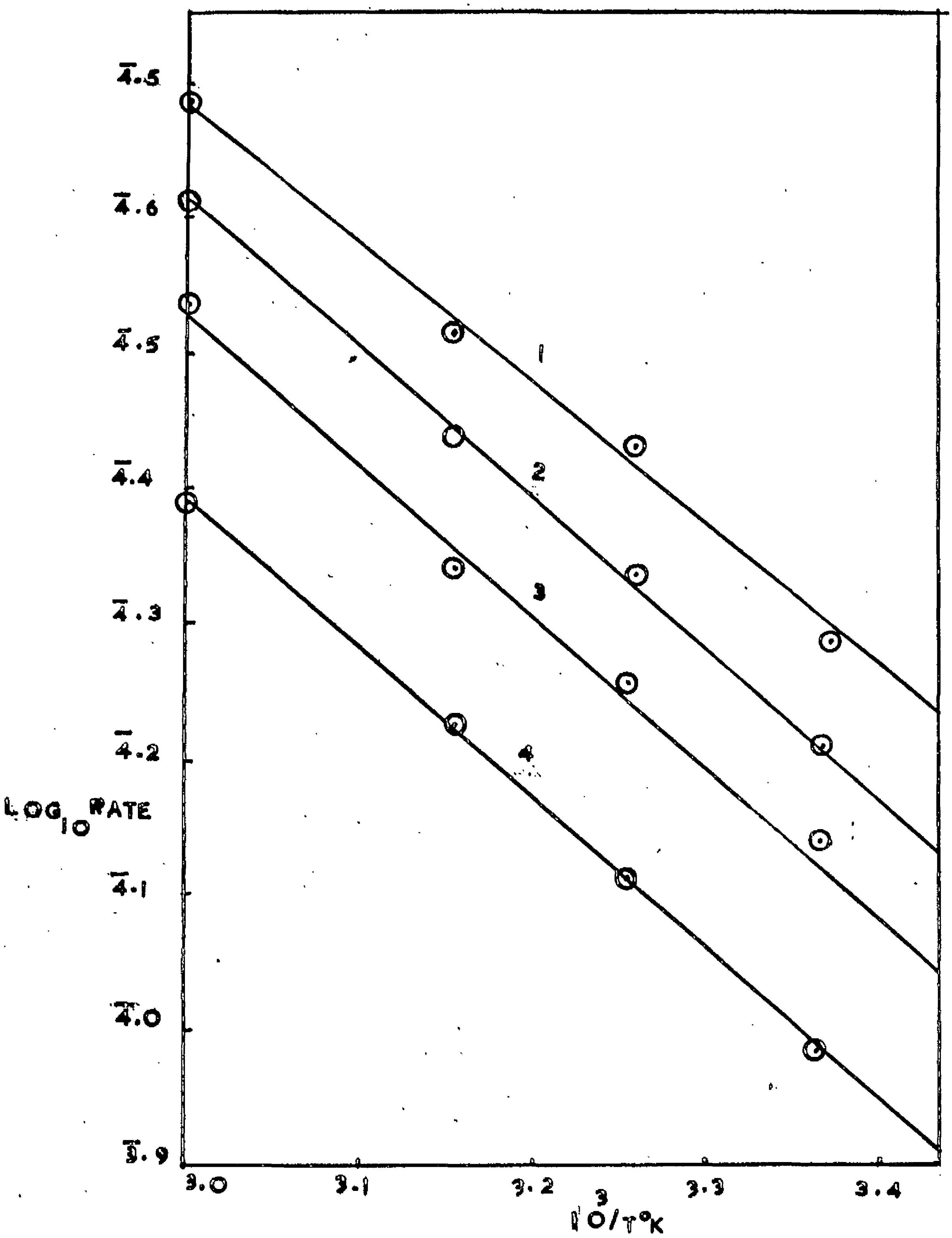


FIG. 11 ARRHENIUS PLOT FOR R_0 FOR THE PHOTO-INITIATED POLYMERISATION OF VINYL ACETATE AT DIFFERENT LIGHT INTENSITIES (1) 100%, (2) 63%, (3) 48.5% AND (4) 24%

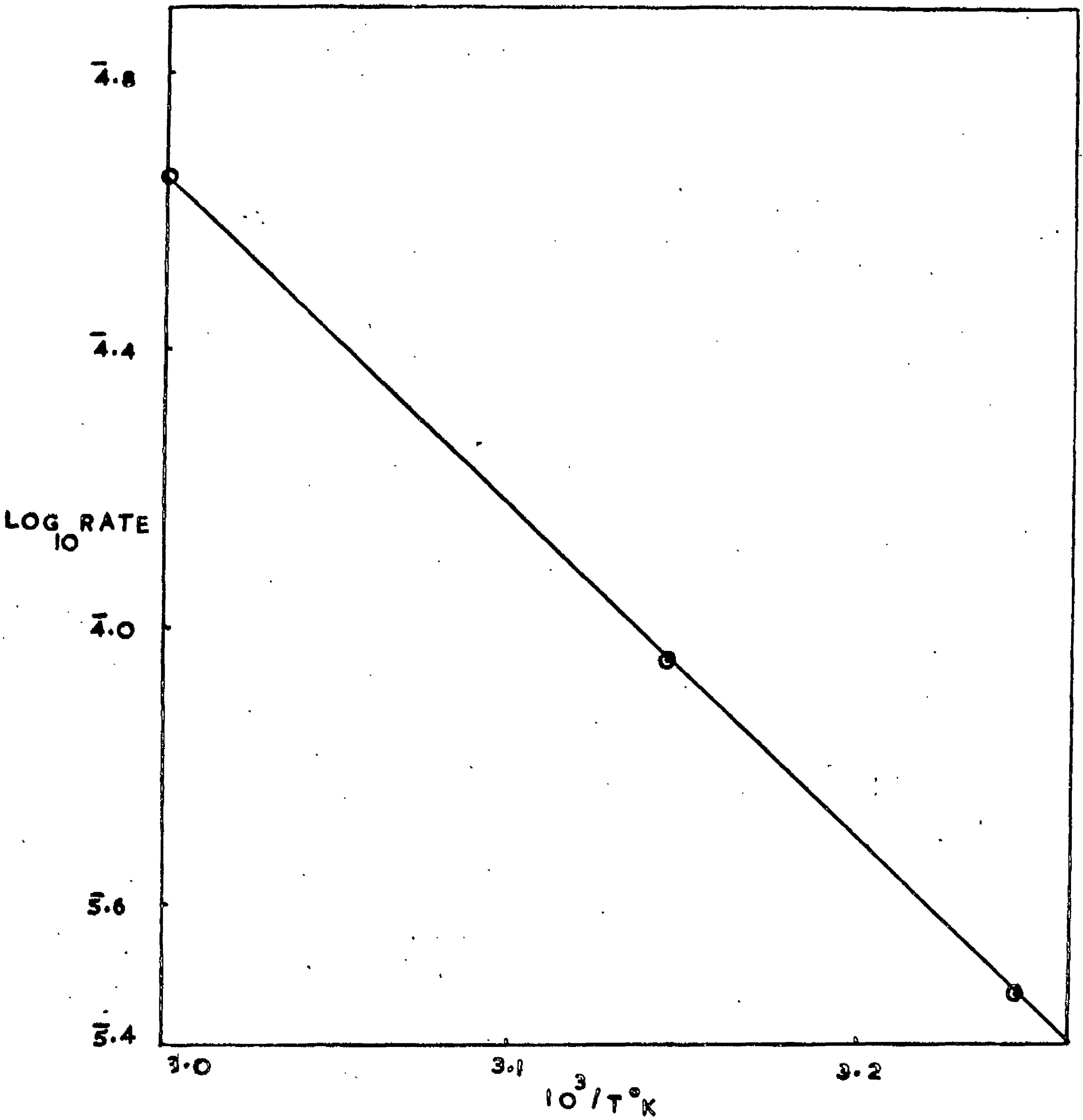


FIG. 12 LOG DARK RATE AGAINST RECIPROCAL OF ABSOLUTE TEMPERATURE

E_p we have $E_t = 0.1$ k.cal.mole^{-1}, i.e. zero to within experimental error.

In the absence of photoinitiation from Fig.(12) $E_o = 20.8$ k.cal.mole^{-1}. Using the above values for E_p and E_t we get $E_i = 31.9$ K.cal.mole^{-1}

Activation energy for the chain transfer reaction with monomer.

From the relationship (43) the equation

$$\log k_{trm}/k_p = (E_p - E_{trm})/2.303RT + \text{constant}. \quad (46)$$

can be derived, where $k_{trm}/k_p = C_m$ is the chain transfer constant to the monomer and E_{trm} is the activation energy for this reaction.

From the plot of Log (C_m) against 1/T (Fig.13) we have

$$E_p - E_{trm} = -2.1 \text{ K.cal.mole}^{-1}$$

which gives $E_{trm} = 6.9$ K.cal.mole^{-1}

Discussion and comparison of results with literature values.

The intensity exponent 0.51 shows that the termination is second order with respect to the growing polymer radical concentration (Fig.9). The graph is linear and gives an intercept of 1.26×10^{-5} mole l.$^{-1}$ sec.$^{-1}$ as a dark rate which agrees with the

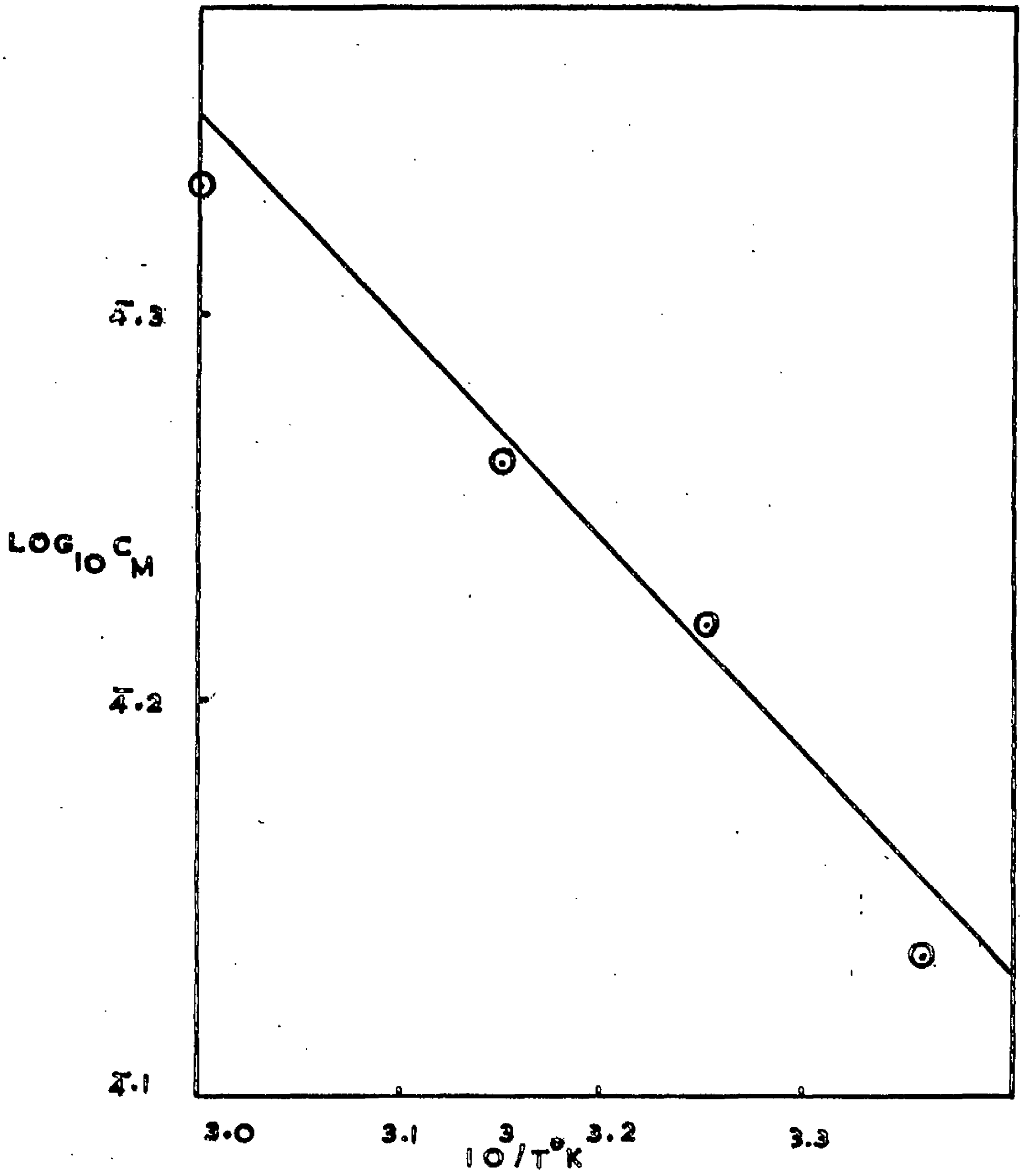


FIG. 13 PLOT OF LOG C_M AGAINST RECIPROCAL OF ABSOLUTE TEMPERATURE

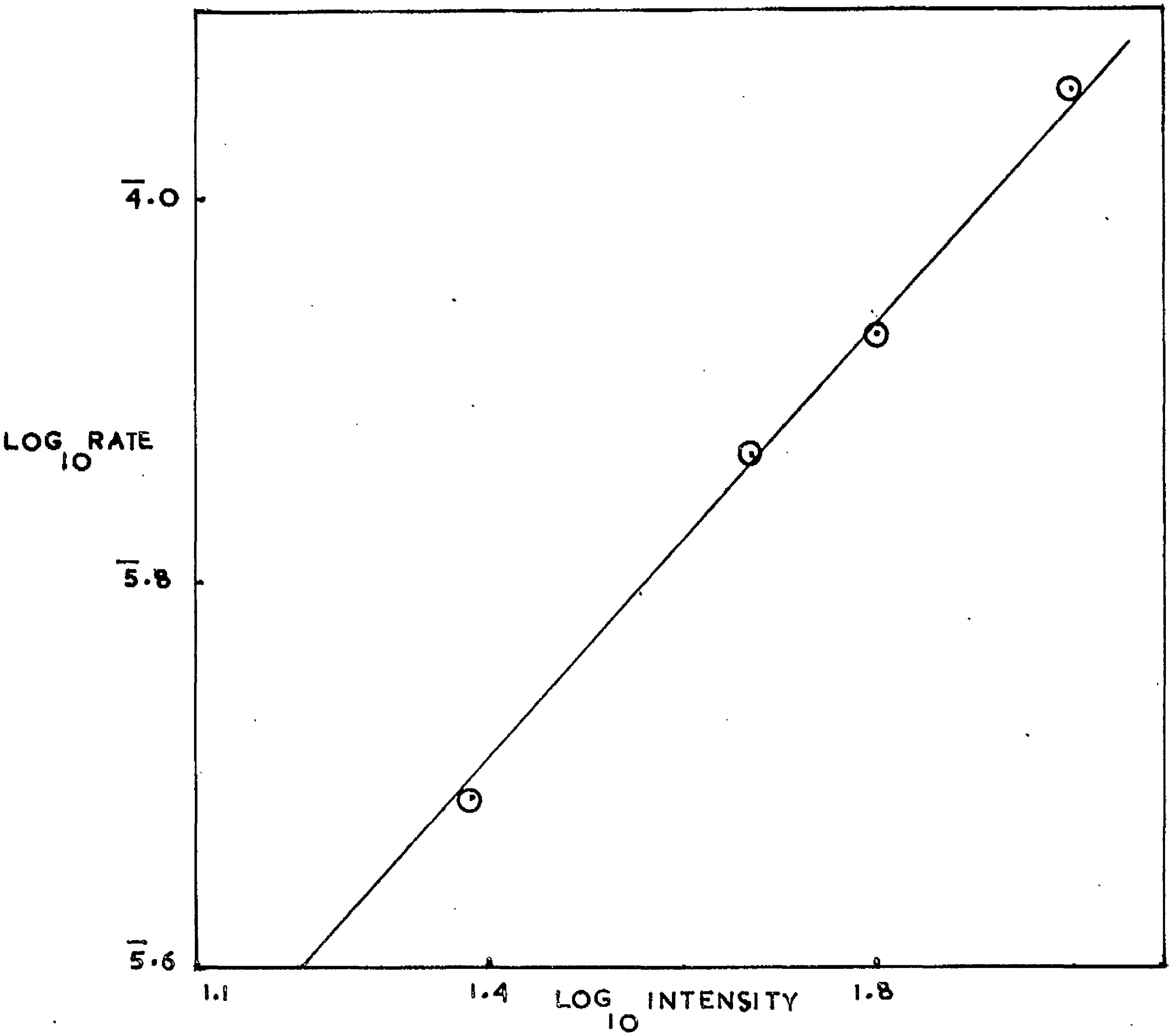


FIG. 14 PLOT FOR THE DETERMINATION OF INTENSITY EXPONENT FOR THE POLYMERISATION OF VINYL ACETATE IN 5% BENZENE.

observed value of dark rate 1.2 x 10^{-5} mole $l.^{-1}sec.^{-1}$ measured independently at 25°C (See Table 2).
The plot in Fig. (10) and values in Table 1 show that there is chain transfer to the monomer and this increases with increasing temperature. This is also reflected in the positive value of 6.9 $K.cal.mole^{-1}$ for E_{trm} obtained from Fig. (13). Table 3 gives a list of C_m values at various temperatures obtained in this work and by other workers.

Table 3 C_m for the polymerisation of vinyl acetate at various temperatures

Reference	Temperature °C	$C_m \times 10^4$
This work	25	1.4
Dixon-Lewis[50]	"	1.45
Kwart & Workers[51]	"	1.3
This work	35	1.74
"	45	1.91
"	60	2.15
Clark and Stockmayer[4]	"	2.5
Palit & Das[32]	"	2.08

The values obtained at various temperatures are in agreement with those obtained by other workers.

The values of E_o and E_i namely 20.7 and 31.9 K.cal.mole^{-1} under dark conditions agree with those obtained by Van Hook and Tobolsky[52] namely 20.0 and 30.8 K.cal.mole^{-1}.

In the photoinitiated polymerisation of vinyl acetate E_o is also in good agreement with the published values as shown in Table 4.

TABLE 4 The comparison of E_o with the literature values for the polymerisation of vinyl acetate

Reference	E_o k.cal.mole^{-1}
This work	4.77
Bengough & Brownlie[8]	4.8
Bengough & Ferguson[53]	5.8
Bengough & Melville[9]	4.2
Burnett & Melville[54]	4.2
Dixon-Lewis[50]	3.2

The activation energy of chain transfer to monomer (namely 6.9 K.cal.mole^{-1}) is also in reasonable agreement with the value of 6.1 K.cal.mole^{-1} reported by Dixon-Lewis[50].

Polymerisation of vinyl acetate in benzene.

The rates of polymerisation and corresponding degrees of polymerisation have been measured in the presence of benzene at 25, 35, 45 and 60°C at full light intensity. The AIBN concentration was 5×10^{-4} molar.

$1/\overline{DP}$ had been plotted against $[S]/[M]$ at various temperatures (Fig.15). The slope of this plot gives the value of C_s (see equation 12). The experimental results and the C_s values obtained are given in Table 5 and it can be seen that the rate for the bulk polymerisation falls nearly to half with 5% benzene (v/v) at all temperatures. With higher concentrations of benzene there is a similar effect but the retardation is not quite so great.

The degree of polymerisation of the polymer produced in the presence of benzene decreases with increase in the benzene concentration.

In Fig. (15) the best straight lines have been drawn through the points corresponding to the three lowest solvent concentrations since the ratio $\sqrt{I}/[M]$ (equation 11) would not be expected to vary appreciably as I is constant and $[M]$ changes only up to 25%. Thus the values of C_s while not necessarily very accurate do give an indication of chain transfer with benzene.

TABLE 5 Rate, $\overline{DP}$ and C_s values obtained at various temperatures for the polymerisation of vinyl acetate in benzene initiated with 5×10^{-4} molar AIBN.

Temperature °C	Benzene %	$10^4/\overline{DP}$	$[S]/[M]$	Rate x 10^4 (mole $l.^{-1}$ $sec.^{-1}$)	C_s x 10^4
25	0	1.345	0	2.05	8.9
	5	1.784	0.051	1.14	
	15	3.203	0.185	0.57	
	25	4.554	0.35	0.27	
	35	6.276	0.571	0.159	
35	0	1.98	0	3.02	10.5
	5	2.26	0.055	1.38	
	15	3.55	0.185	0.71	
	25	5.86	0.349	0.42	
	35	7.86	0.56	0.256	
45	0	2.44	0	4.32	12.0
	5	2.98	0.055	2.29	
	15	4.12	0.184	1.05	
	25	6.27	0.349	0.75	
	35	8.45	0.56	0.47	
60	0	2.60	0	9.26	13.5
	5	3.31	0.055	4.75	
	15	4.80	0.184	2.32	
	25	7.30	0.349	1.82	
	35	9.75	0.564	1.01	

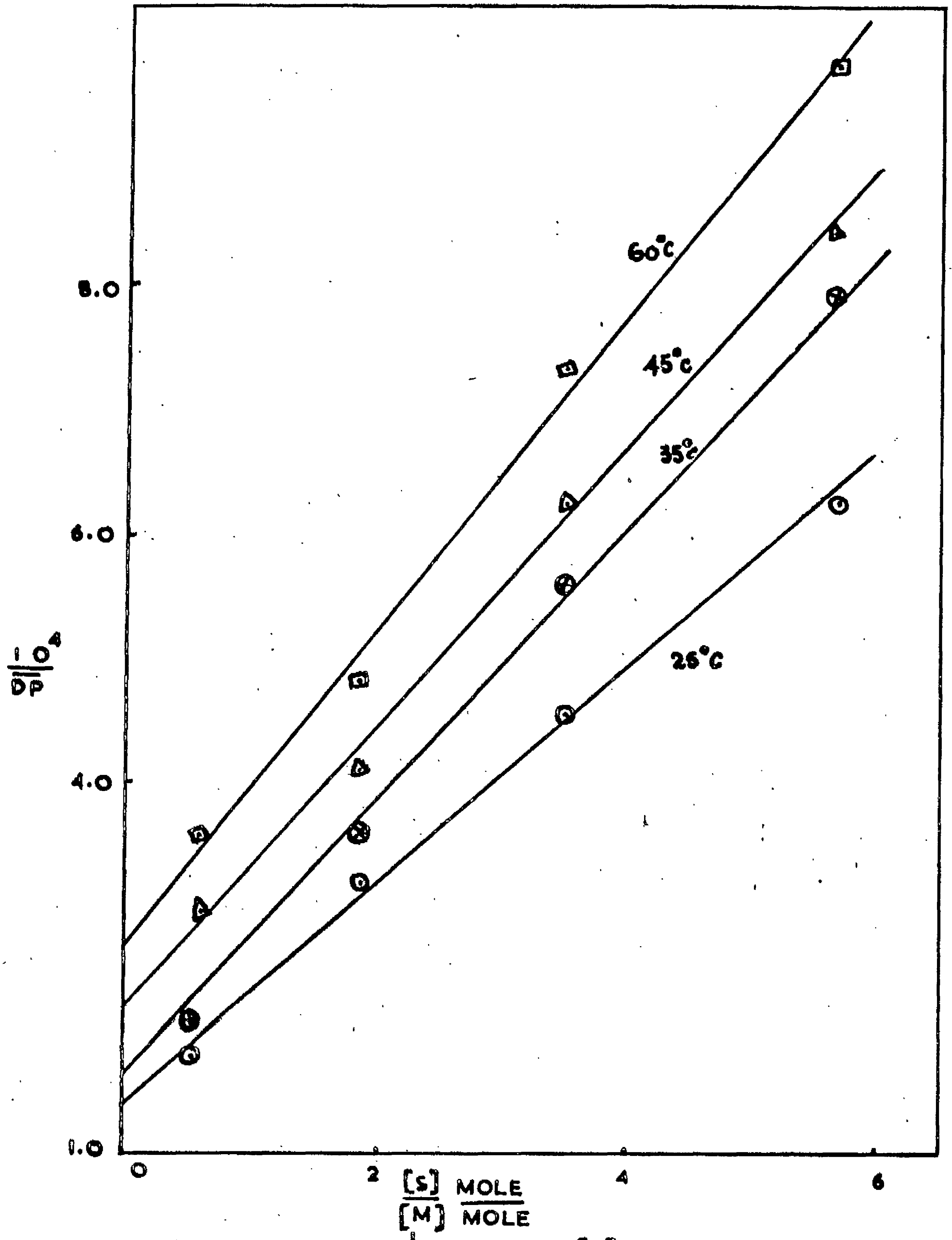


FIG.15 PLOT OF $\frac{1}{DP}$ AGAINST $\frac{[S]}{[M]}$ FOR THE POLYMERISATION OF VINYL ACETATE IN BENZENE SOLUTION AT VARIOUS TEMPERATURES.

From Table 5 it is clear that chain transfer constant with benzene increases with rise in temperature.

Activation energy for chain transfer to benzene.

The equation (43) can be rewritten as

$$\log k_{trs}/k_p = (E_p-E_{trs})/2.303RT + \text{constant}..(47)$$

where $k_{trs}/k_p = C_s$ and E_{trs} is the activation energy for the chain transfer reaction with solvent.

The plot of log C_s against $1/T$ has a slope equal to $(E_p-E_{trs})/2.303R$

From Fig (16)

$$E_p - E_{trs} = - 2.05 \text{ K.cal.mole}^{-1}$$

$$E_{trs} = 4.8 + 2.05$$

$$= 6.85 \text{ K.cal.mole}^{-1}$$

Bengough *et al*[8] found

$$E_p - E_{tr} = 0$$

$$\text{i.e. } E_p = E_{trs}$$

$$= 4.8 \text{ K.cal.mole}^{-1}$$

The intensity exponent in the presence of 5% benzene at 25°C was found to 0.54 (Fig.14), while in bulk polymerisation it was 0.51 (Fig.9). This change is not really significant, since at very low rates the intensity exponent in bulk polymerisation tends to

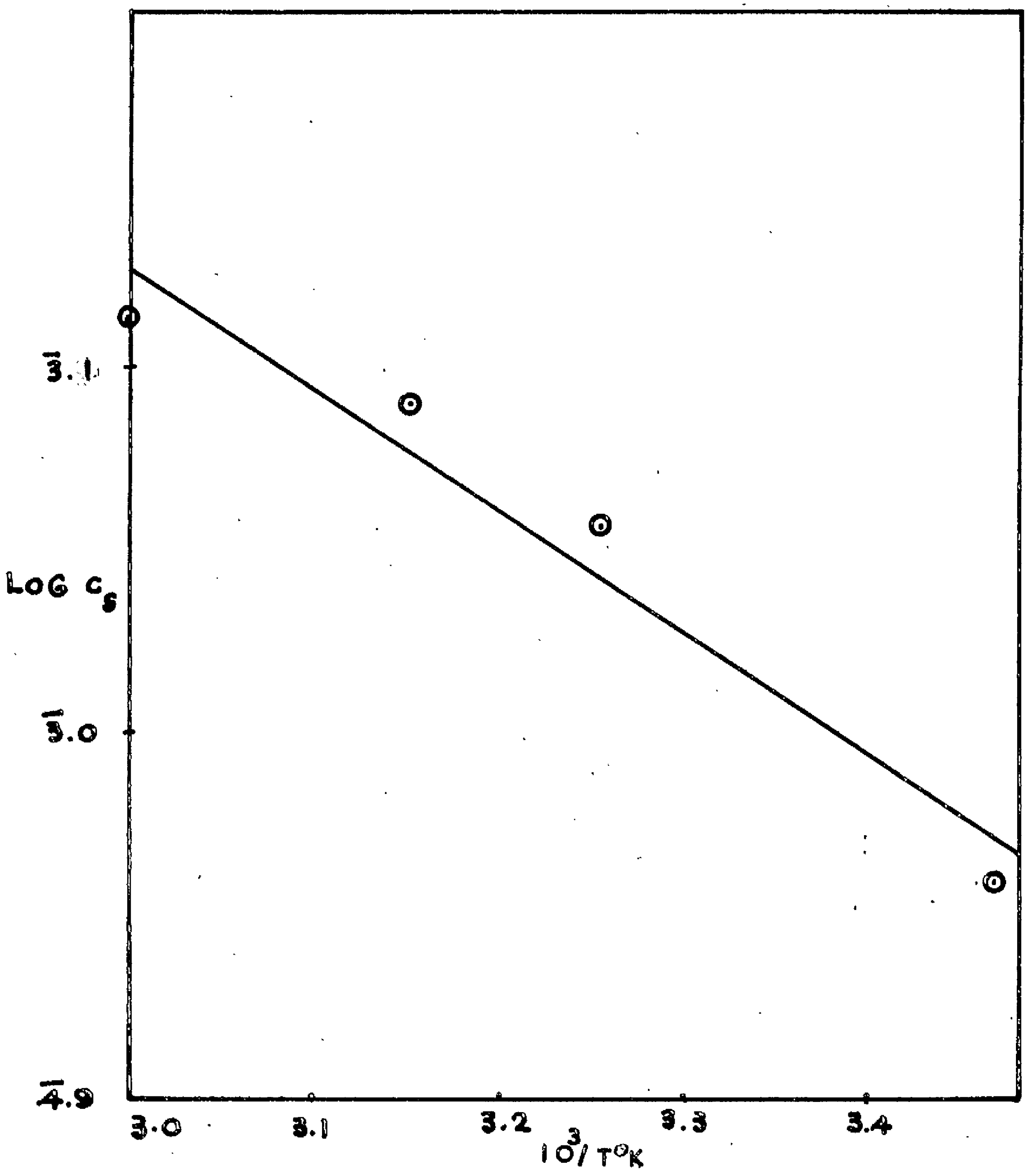


FIG.16 PLOT FOR THE DETERMINATION OF $E_p - E_{TRM}$ FOR THE POLYMERISATION OF VINYL ACETATE IN BENZENE SOLUTION.

increase[55]. It would appear that the termination reaction is mainly second order with respect to polymer radical concentration.

Polymerisation of vinyl acetate in the presence of C14 Labelled benzene

In this section vinyl acetate was polymerised in the presence of C14 labelled benzene in an attempt to clarify the position regarding the possibility of copolymerisation due to contradicting results of recent workers[4,5].

Using this method the number of benzene molecules incorporated in each polymer chain, if any, can be determined quantitatively. The radioactive benzene was purified by the single crystal growth technique as described earlier.

The polymer from each reaction was freeze-dried about fifteen times to remove the unreacted radioactive benzene.

Table 7 shows the effect of the number of freeze-drying operations on the activity of the polymer recovered from an exceptional experiment No.1 at 60°C to give greatest possibility of incorporation of benzene. Other conditions were the same as in the previous experiments.

TABLE 7 The effect of sequence of freeze-drying operations on the activity of the polymer of experiment No.1.

No. of freeze-drying operation	ml. inactive benzene used for freeze-drying operation.	c.p.s. (20mg. polymer)	c.p.s Distilled benzene (5ml.)
1	-	2.36	6.296 *
2	40	1.98	6.80
3	"	1.71	2.47
4	"	1.56	2.04
5	"	1.44	1.90
6	"	1.37	1.25
7	"	1.30	1.02
8	"	1.29	0.89
9	"	1.10	0.67
10	"	0.90	0.50
11	"	0.80	0.46
12	"	0.69	0.455
13	"	0.685	0.450
14	"	0.679	0.405
15	"	0.690	0.404

* This activity is for 1 ml. distilled unreacted mixture (V.A. + benzene).

Experiment No. 1:

Volume of monomer	= 5 ml.
Volume of benzene	= 40 ml.
Conversion	= 40%
Weight of the polymer	= 1.9 g.
Background counts with 5 ml. inactive benzene	= 0.404 c.p.s.

Except for the first freeze-drying operation all subsequent freeze-drying operations were done by dissolving the polymer in 40 ml. of inactive Analar grade benzene.

It can be seen from the Table 7 that the activity of the polymer is decreasing slowly and it comes to a constant value at the 14th freeze-drying operation. The activity of the distilled benzene also levels off at the 14th freeze-drying operation.

Evaluation of the number of benzene units per polymer chain from the results obtained in experiment No.1.

Background with inactive benzene = 0.404 c.p.s.

From the calibration curve (Fig.17) the specific activity of the benzene used $= \frac{7000}{0.87}$

$= 8045$ c.p.s.

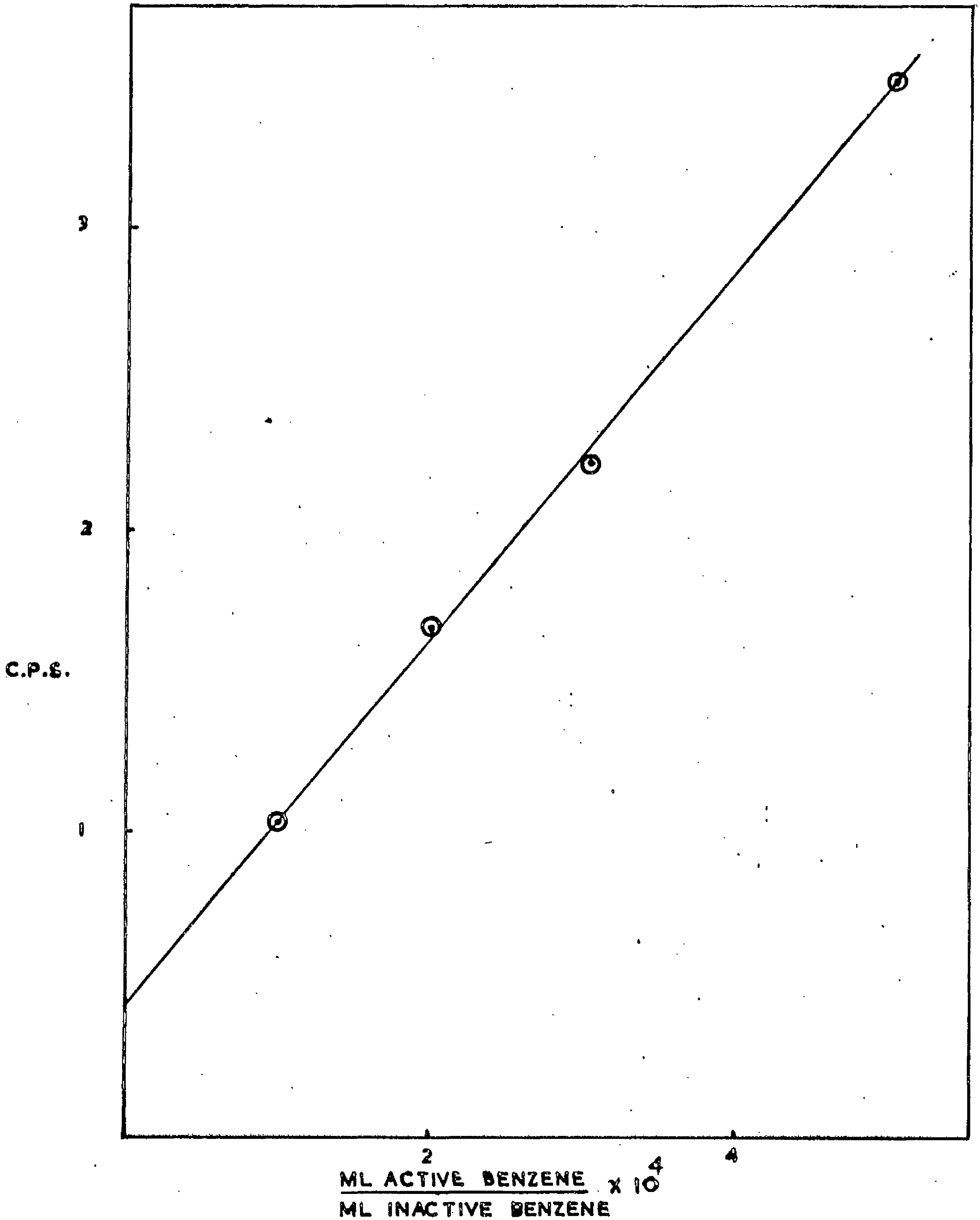


FIG.17 CALIBRATION CURVE FOR THE ACTIVITY OF BENZENE BY SCINTILLATION COUNTING.

Activity of the 0.02 g. polymer = 0.68 - 0.404

= 0.276 c.p.s.

Specific activity of the polymer = 0.276 x 50

= 13.8 c.p.s.

The weight fraction of benzene in the polymer

$$= \frac{13.8}{8045}$$

Now the $\overline{\mathrm{DP}}$ of the polymer = 500 (viscosity method)

Molecular weight of monomer = 86

Molecular weight of benzene = 78

Number of benzene molecules per polymer molecule

$$= \frac{13.8}{8045} \times \frac{86 \times 500}{78}$$

$$= 0.95$$

On considering the results in Table 7 it is feasible that some active benzene remains absorbed on the polymer molecules and this is removed by successive freeze-drying operations. Alternatively, the polymer may be breaking down and giving rise to the incorporated labelled benzene. To clarify these two points, experiment No.1 was repeated. After four freeze-drying operations 0.1 g. of polymer was used to make 1% solution in toluene, and the viscometric flow time was measured as 163.4 seconds.

The rest of the polymer was dissolved and refluxed in 40 ml. of toluene for one hour. Then toluene was distilled and its activity was assayed. The polymer was again dissolved in 40 ml. inactive benzene and freeze-dried. The results are given in Table 8.

Table 8 The effect of sequence of freeze-drying operations and toluene on the activity of the polymer obtained by the repetition of experiment No.1.

No. of freeze-drying operation	ml. benzene used for freeze-drying	c.p.s. (20mg. polymer)	c.p.s. Distilled benzene (5ml.)
1	–	2.48	6295 *
2	40	2.01	6.57
3	"	1.82	2.50
4	"	1.64	2.21 9.72 (5ml. toluene)
5	"	0.80	0.49
6	"	0.71	0.46
7	"	0.69	0.420
8	"	0.68	0.403
9	"	0.68	0.403

* This activity is for 1 ml. distilled unreacted mixture (V A. + benzene).

Table 8 shows that after refluxing the polymer with toluene, its specific activity falls to half the value before refluxing. The loss in the activity of the polymer was balanced by the gain in activity of the toluene. However, not all of the benzene was removed by this treatment. Four further freeze-drying operations were required to remove the remainder of the unreacted active benzene from the polymer.

When the activity in the polymer became constant (i.e. after 9th freeze-drying operation, see Table 8) it was again treated with toluene, freeze-dried and its activity measured. The activity of the polymer still remained constant and was assumed to be due to chemically incorporated radioactive benzene.

Again a 1% solution of the polymer was made in toluene and the flow time was recorded viscometrically to be 163.5 sec. Both flow times are identical within experimental error, showing there is no breakdown of the polymer chains during freeze-drying or treatment with toluene.

In order to determine whether any radioactive benzene is permanently absorbed by the polymer a further experiment was carried out using inactive benzene and the polymer was recovered by freeze-drying.

This inactive polymer was dissolved in 25 ml. of radioactive stock benzene and freeze-dried. The results of subsequent freeze-dryings are shown in Table 9.

Table 9 Mass balance of active benzene used for first freeze-drying operation (0.5 g. polymer).

No. of freeze-drying operation	ml. benzene used for freeze-drying	c.p.s. (20mg. polymer)	c.p.s. Distilled benzene (5 ml.)
1	25 ml.(active)	2.04	698.3 *
2	40 ml.(inactive)	1.64	1.83
3	"	1.28	1.56
4	"	0.93	1.47
5	"	0.62	1.28
6	"	0.41	0.95
7	"	0.406	0.42
8	"	0.403	0.404

* 1 ml. distilled active benzene.

The polymer has absorbed some active benzene but this is removed in eight freeze-drying operations. However, in the polymerisation in radioactive benzene it required 15 freez-drying operations to remove all the unreacted labelled benzene.

Further experiments were carried out at 60°C and 25°C with varying amounts of radioactive benzene. The number of benzene molecules were evaluated and the results are given in Table 10.

Table 10 The effect of benzene on the rate, the $\overline{DP}$, and the number of benzene units per polymer chain in the polymerisation of vinyl acetate initiated with 5×10^{-4} molar AIBN.

Expt. No.	Temp.	Benzene (moles)	V.A (moles)	$\overline{DP}$ ($\times 10^{-2}$)	Rate $\times 10^4$ (mole l^{-1} sec.$^{-1}$)	No. of Benzene molecules per chain
1	60°C	0.450	0.048	5.0	0.55	0.95
2	"	0.370	0.49	6.3	0.63	1.00
3	"	0.55	0.099	10.0	1.01	0.95
4	"	0.024	0.130	20.32	2.32	0.98
5	"	0.0089	0.153	30.20	4.75	0.90
6	25°C	0.39	0.050	12.10	0.08	1.03

It is clear from the Table 10 that on an average there is one molecule of benzene incorporated in each polymer molecule. At lower concentrations of benzene Brownlie[8], using the gas counting technique also found one molecule of benzene per polymer molecule. Using the scintillation counting method he found from 1 to 1.72 molecules of benzene per polymer molecule.

This higher value may be due to the presence of absorbed radioactive benzene in the polymer since he used only four freeze-drying operations in the latter work.

The polymerisation of vinyl acetate in the presence of toluene.

Vinyl acetate was polymerised in toluene because it has a higher chain transfer constant than benzene. In the chain transfer reaction with toluene the benzyl radical is considered to be produced, and it is claimed to be very stable; hence retardation in toluene would be expected to be greater than in benzene.

Reactions were carried out in the presence of 2.5% and 5% (v/v) toluene at 60°C and the rates obtained are given in Table 11.

Table 11 A comparison of the rates of polymerisation of vinyl acetate in the presence of benzene and toluene initiated with 5×10^{-4} molar AIBN.

Solvent	%	Rate $\times 10^4$ (mole $l.^{-1}$ $sec.^{-1}$)	$C_s \times 10^3$
Benzene	2.5	5.53	1.3
	5	4.77	
Toluene	2.5	5.4	3.4[33]
	5	4.66	
No solvent	0	9.26	

From the Table 11, it appears that the rate of polymerisation in toluene is practically the same as in the presence of benzene. As mentioned earlier the rate of reaction was expected to be far lower than in benzene since the benzyl radical might be expected to be unreactive and increase the rate of termination. A possible mechanism will be put forward in the discussion.

Polymerisation of vinyl acetate in the presence of substituted benzene.

The experiments in the previous sections showed that the polymerisation of vinyl acetate is strongly retarded by benzene and toluene, and that only one molecule of benzene is incorporated in each polymer molecule. This benzene molecule is included in the polymer molecule either by chain transfer reaction, or by an addition reaction followed by a chain transfer step. It the latter type of reaction occurs one might expect that if a completely substituted benzene with large substituent groups was used instead of benzene, steric effects might prevent the reaction from occurring.

Vinyl acetate was therefore polymerised in the presence of halogeno-, carboxy-, and hydroxy-benzenes. These reactions were performed at 60°C, and all other conditions were the same as for the previous experiments. The results are shown in Table 12.

Table 12 Rates of polymerisation of vinyl acetate in the presence of different halogenated substituted benzenes at 60°C.

AIBN concentration = 5×10^{-4} molar

Rate in pure vinyl acetate = 9.26×10^{-4} mole $l.^{-1}$ $sec.^{-1}$

Solvent = 2.5% (V/V)

Vinyl acetate = 97.5% (V/V)

Solvent	Rate x 10^4 (mole $l.^{-1}$ $sec.^{-1}$)
Benzene	5.53
Monochlorobenzene	4.80
O-Dichlorobenzene	4.50
m-Dichlorobenzene	4.53
p-Dichlorobenzene	4.55
1,2,4-Trichlorobenzene	4.21
Monofluorobenzene	5.00
m-Difluorobenzene	5.10
Monobromobenzene	4.72
m-Dibromobenzene	4.50
Iodobenzene	1.30

Since p-dichlorobenzene is a solid it was added (V/W) to the dilatometer in chloroform solution, the solvent being pumped off under vacuum.

The chain transfer constant was also determined for the reaction of monochlorobenzene, and vinyl acetate at 60°C in the presence of varying amounts of solvent. The plot $1/\overline{DP}$ against $[S]/[M]$ is given in figure (18), and the results are shown in Table 13, along with rates and C_s to benzene for comparison.

Table 13 Chain transfer constant with monochlorobenzene at 60°C.

Rate for vinyl acetate = 9.26 mole $l.^{-1}$ $sec.^{-1}$

% Solvent (V/V)	Rate x 10^4 (mole $l.^{-1}$ $sec.^{-1}$)	C_s x 10^3
Benzene		
2.5	5.53	
5	4.75	1.3
15	2.32	
25	1.82	
Chlorobenzene		
2.5	4.8	
5	3.84	4.0
15	1.99	
25	1.31	

It can be seen from the Table 12 and 13 that the rate of polymerisation decreases as number of substituted chlorine atoms increases. The rates in mono- and difluorobenzene are practically the same, but the rate is lower in m-dibromobenzene compared

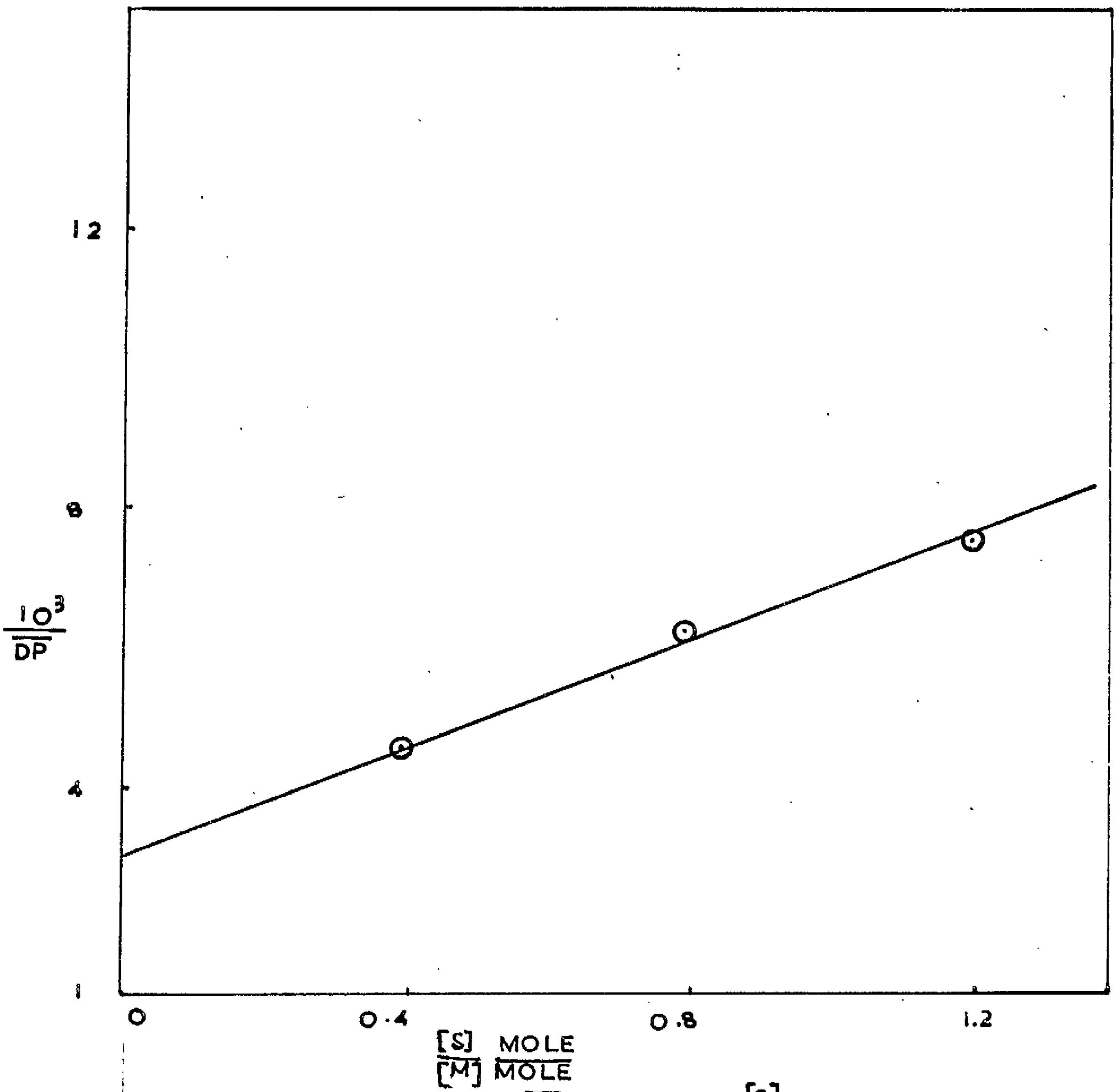


FIG.18 RECIPROCAL $\overline{DP}$ AGAINST $\frac{[S]}{[M]}$ FOR THE POLYMERISATION OF VINYL ACETATE IN MONOCHLOROBENZENE

with bromobenzene. In general, there is a progressive fall in rate in the order, benzene, fluorobenzene, chlorobenzene, bromobenzene and iodobenzene, i.e. as the electronegativity of the substituent groups decreases there is greater retardation.

The value of the chain transfer constant with chlorobenzene is about three times that with benzene. The rate of polymerisation in the former is however only slightly lower than the rate in benzene.

The polymerisation of vinyl acetate in the presence of hexachlorobenzene.

Since hexachlorobenzene is a solid and is insoluble in vinyl acetate, chloroform was used as a solvent to study its effect on vinyl acetate polymerisation.

Initially the reaction was studied in the presence of 50% (V/V) chloroform and effect on the rate of reaction was noted. Then the effect of 2.5% (V/W) hexachlorobenzene in 50% chloroform (V/V) was studied. The polymer was recovered by freeze-drying the dilatometer contents and pumping off the chloroform, vinyl acetate and benzene. After first freeze-drying the polymer was dissolved in 20 ml. of benzene. The hexachlorobenzene being insoluble in benzene was filtered off from the solution which was again freeze-dried. As mentioned earlier (Page 57) the catalyst concentration was so small that it did not make much difference to the intrinsic viscosity.

Vinyl acetate was also polymerised in the presence of 25% and 35% (V/V) chloroform for the evaluation of chain transfer constant. The plot of $1/\bar{DP}$ against $[S]/[M]$ is shown in Fig. (19). The rates of reaction, and chain transfer constant values are recorded in Table 14.

Table 14 The rates of polymerisation of vinyl acetate in the presence of chloroform hexachlorobenzene, and the chain transfer constant in chloroform at 60°C. AIBN concentration = 5×10^{-4} molar.

Solvent		Rate $\times 10^{4}$ (mole $l.^{-1}$ $sec.^{-1}$)	C_s
Chloroform	25%	4.64	0.02
	35%	3.50	
	50%	2.52	
2.5% (V/W) C_6 CL_6 + 50% Chloroform		2.57	
2.5% (V/V) Benzene + 50% Chloroform		1.87	

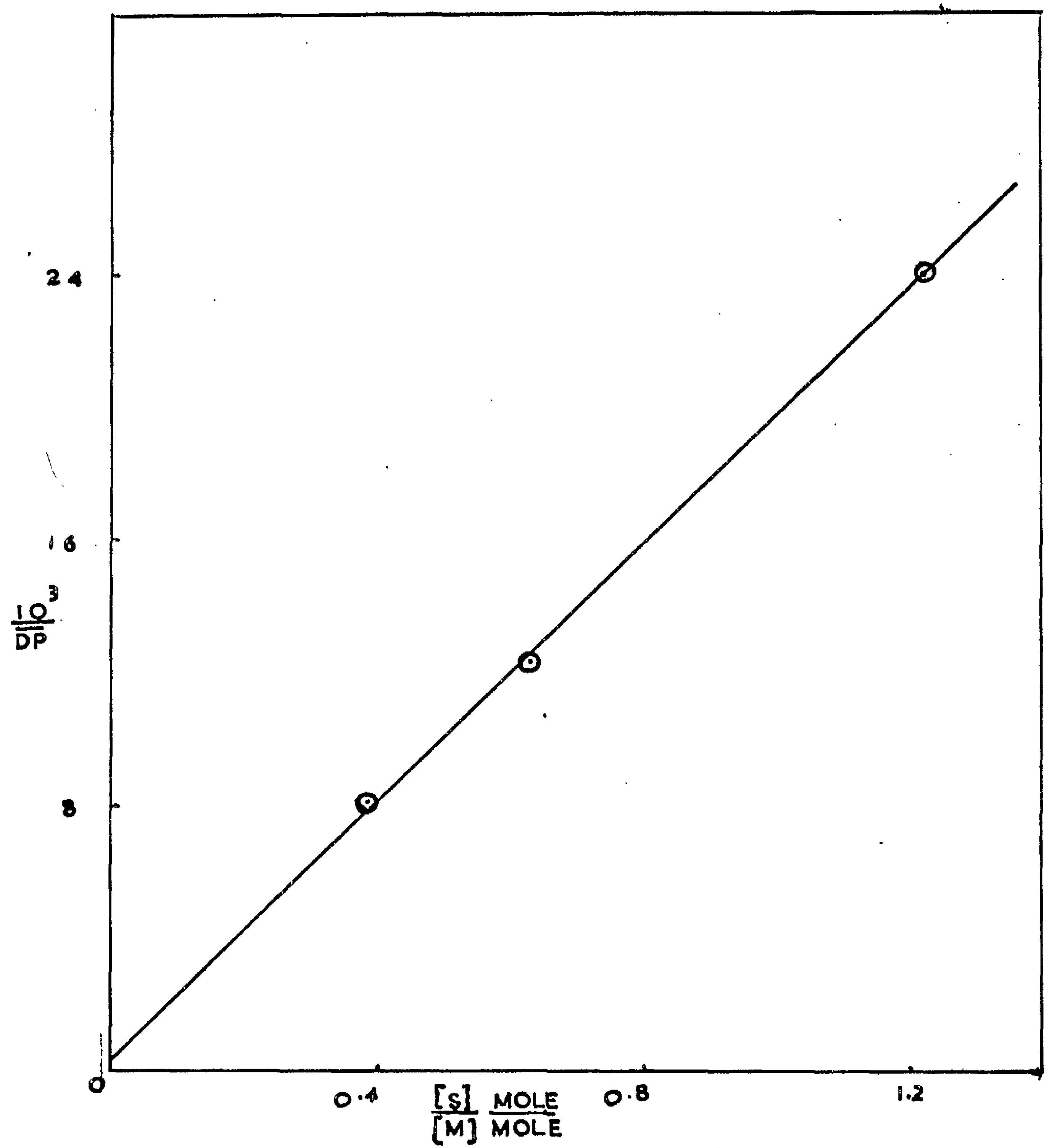


FIG. 19 RECIPROCAL $\overline{DP}$ AGAINST $\frac{[S]}{[M]}$ FOR THE POLYMERISATION OF VINYL ACETATE IN CHLOROFORM.

Table 14 indicates that the rate of reaction in the presence of 50% chloroform is not affected by the addition of 2.5% hexachlorobenzene, whereas addition of 2.5% benzene causes marked retardation. The value of 0.015 for the chain transfer constant reported by Clark *et al*[33] is not very different from the value of 0.02 measured in this work.

The polymerisation of vinyl acetate in the presence of carboxy substituted benzenes.

Since all the benzene carboxylic acids are solids, and insoluble in vinyl acetate, dimethyl formamide (DMF) was used as a cosolvent. Initially the effect of 25% DMF alone on vinyl acetate was studied, and then runs were carried out using 25% DMF, 75% vinyl acetate and 5% (V/W) acid. The rates of polymerisation in the presence of different acids are listed in Table 15.

Table 15 The rates of polymerisation of a DMF solution of vinyl acetate (DMF: V A :: 1:3) in the presence of aromatic carboylic acids at 60°C, with 5×10^{-4} molar AIBN as initiator.

Solvent 5%	Rate $\times 10^4$ (mole $l.^{-1}$ $sec.^{-1}$)
Benzene (V/V)	3.6
Benzoic Acid (V/W)	1.62
Phthalic Acid (V/W)	1.37
Hemimellitic Acid (V/W)	1.09
2.5% (V/W) Mellitic Acid	no rate

From the above results it can be seen that as the number of carboxyl group increases in the benzene ring the rate of polymerisation decreases and complete inhibition with mellitic acid is noted. This suggests that the effect is not due to nucleus but to the carboxyl substituents.

Effect of benzene hexole on the polymerisation of vinyl acetate at 60°C with 5 x 10^{-4} molar AIBN as initiator.

Vinyl acetate was polymerised in the presence of 5% (V/W) benzene hexole in 25% DMF. Complete inhibition was observed. This effect may be attributed to the hydrogen atom of the hydroxyl group which can be abstracted easily by the growing chain radical.

Effect of various other compounds on the polymerisation of vinyl acetate.

All the experiments were done at 60°C, and with other conditions the same as used before.

Tetrachlorotetrahydronaphthalene. Since this compound is solid and insoluble in vinyl acetate, 1% of it was dissolved in 25% benzene and reacted with the monomer. No rate of polymerisation was observed.

Diphenyl. Since diphenyl is a solid it was added to the dilatometer in chloroform solution, the solvent being pumped off.

A very low rate of polymerisation 0.9 x 10^{-4} mole $l.^{-1}$ sec.$^{-1}$ was observed. This effect was expected due to the similarity of this compound to the benzene.

The polymerisation of vinyl acetate in the presence of 1,3 cyclohexadiene (CHD)

To produce a free radical similar to the one produced by the addition of a growing polymer radical to the benzene ring, vinyl acetate was polymerised in the presence of cyclohexadiene. It was expected that on abstraction of a methylene hydrogen the resultant radical i.e. cyclohexadienyl radical, can not readily add to the monomer, hence decreasing the rate of polymerisation.

This would be in marked contrast to the hydrogen abstraction from a benzene molecule giving rise to a phenyl radical which is quite efficient in chain initiation[56].

Preliminary experiments showed that CHD is a strong retarder, but it was possible to observe the rate when CHD : V A :: 1: 10^2 ratio was used. Due to the minute quantities required for each reaction CHD was diluted in pure vinyl acetate in air by means of a micrometer syringe, and the required amount was introduced into the dilatometer by using the syringe. The dilatometer was then connected to the vacuum line and degassed quickly, because CHD tends to oxidize in the presence of air. It was also found that the small amount of vinyl acetate added to the dilatometer in air does not give any inhibition. Using the above mentioned ratio two experiments were carried out at 25°C and 60°C. The $\overline{DP}$ was measured viscometrically and results are given in Table 16.

Table 16 The rates for the polymerisation of vinyl acetate $\overline{DP}$ in the presence of cyclohexadiene with 5×10^{-4} molar AIBN.

CHD : VA	Temp. °C	$\overline{DP} \times 10^{-3}$	Rate $\times 10^{4}$ (mole $l.^{-1}$ sec.$^{-1}$)
1 : 100	60	0.64	0.19
1 : 100	25	0.91	0.05
No solvent	60	3.8	9.26
No solvent	25	7.44	2.05

The results in Table 16 indicate that the rate of polymerisation is retarded very much by very small amount of cyclohexadiene. $\overline{DP}$ is also very low, showing that some chain transfer or chain termination process is occuring. This effect is not surprising in view of the diene structure present. A possible mechanism will be attempted in discussion.

Polymerisation of vinyl acetate and styrene.

In the preceding sections, the results have indicated that retardation in the rate of polymerisation of vinyl acetate is mainly due to the attack of the chain radical on the aromatic ring. It was therefore of interest to polymerise vinyl acetate in the presence of a vinyl monomer which would readily form resonance stabilized growing polymer radical of similar stability to the one produced by the addition of a radical to benzene. Styrene was chosen because of the stability of the styryl radical. Since styrene is a very reactive monomer a large number of such radicals can readily be produced.

For systems containing small amounts of styrene the monomer reactivity ratios r_1 and r_2 were determined by finding the composition of the initial copolymer for different mixtures of styrene and inactive vinyl acetate using C14-styrene. According to equation (18) r_1 represents the ratio of the rate constants for the reaction of the styryl radical with styrene monomer and vinyl acetate monomers respectively, and ratio r_2 similarly expresses the relative reactivity of vinyl acetate and styrene towards the vinyl acetate radical.

For systems with excess styrene, C14-vinyl acetate and inactive styrene were used.

The AIBN concentration was 5×10^{-3} molar and all experiments were carried out at 60°C thermally. The conversions were taken to 2.0% in all reactions.

Evaluation of monomer reactivity ratios from the composition of initial copolymers of radioactive styrene (S) and inactive vinyl acetate (VA).

20 mg. of the polymers in benzene solution were used for radioactive assay. The background count was = 0.4 c.p.s.

Typical calculation of results for 1 : 1000 :: S:VA.

Activity of 20 mg. of polymer = 10.5 c.p.s. From the calibration curve (Fig. 20) for the stock radioactive styrene solution 10.1 c.p.s. are given by 0.0005 ml. styrene. The density of styrene is 0.9 at 20°C.

The weight of vinyl acetate in 20 mg. of polymer = 0.02 - 0.00045

= 0.01955 g.

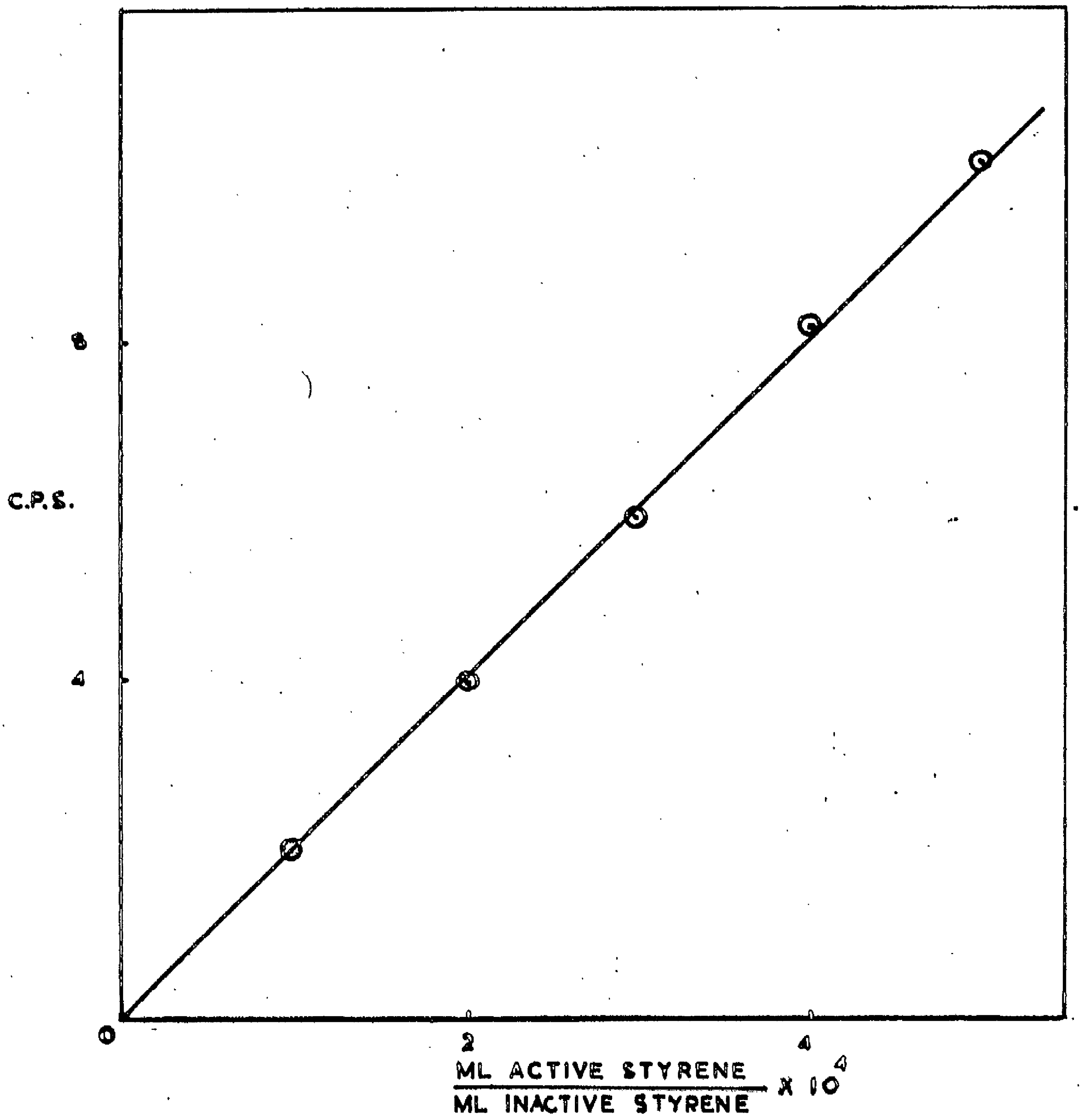


FIG. 20 CALIBRATION CURVE FOR THE ACTIVITY OF STYRENE BY SCINTILLATION COUNTING IN BENZENE.

The mol. wt. of styrene = 104

The mol. wt. of vinyl acetate = 86

$$f = \frac{\text{styrene (moles)}}{\text{vinyl acetate (moles)}}$$

$$= \frac{\frac{0.00045}{104}}{\frac{0{\cdot}01955}{86}}$$

$$= 0.019$$

The polymer composition was calculated for all the monomer feeds and is recorded in Table 17 along with other results required for the determination of r_1 and r_2.

Table 17 Results for the determination of monomer reactivity ratios at 60°C.

S: VA	c.p.s. (20mg) polymer	$F (x10^3)$	f	$F(f-1)/f$ $(x\ 10^2)$	F^2/f $(x\ 10^4)$
1: 1000	10.5	0.82	0.019	-4.2	0.39
1: 500	20.5	1.57	0.038	-3.80	0.61
1: 100	110.5	8.38	0.254	-2.72	2.60

From the results given in Table 17 $F(f-1)/f$ was plotted against F^2/f (Fig.21) according to the Fineman and Ross[45] equation (20), and the values for r_1 and r_2

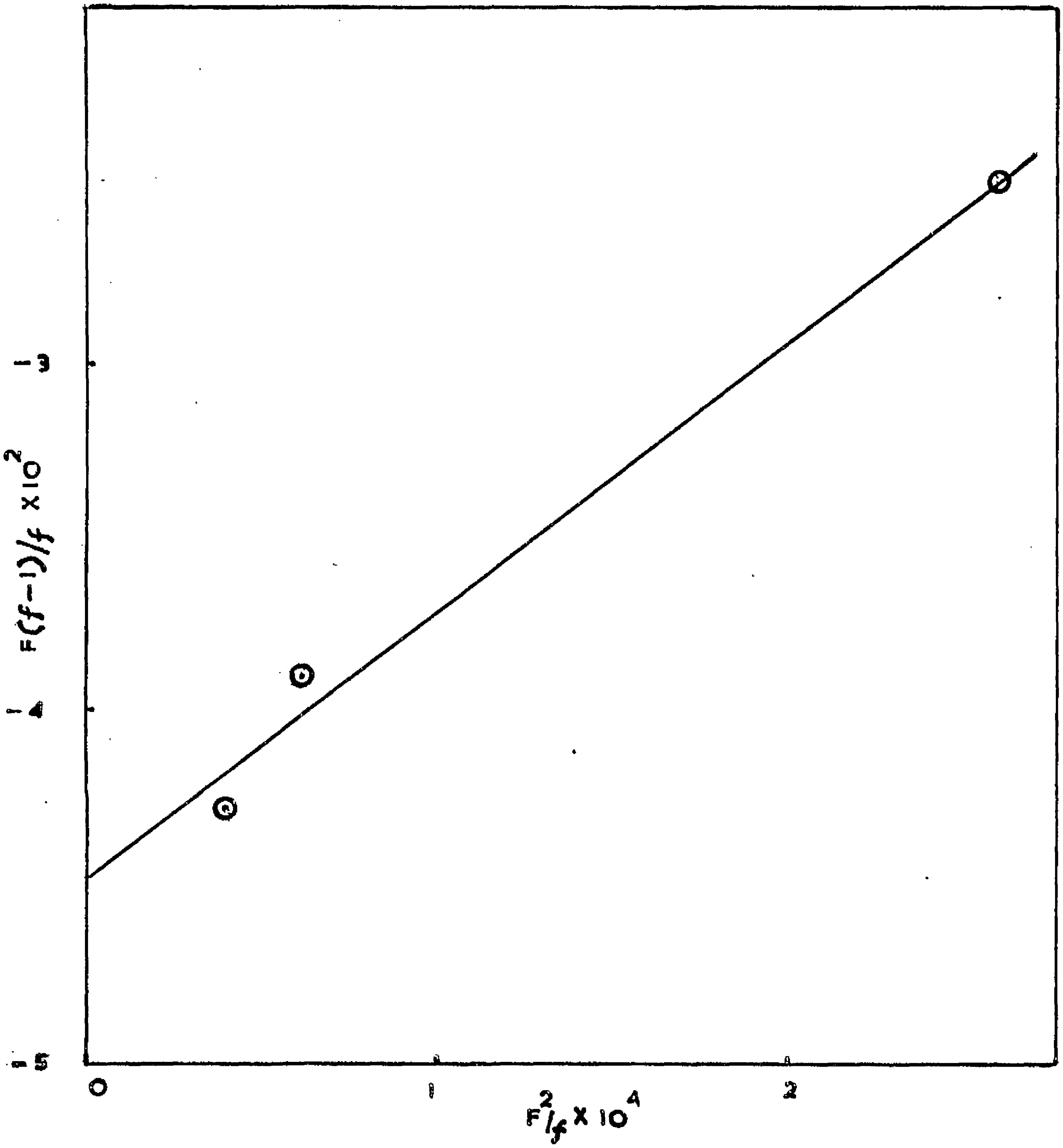


FIG. 21 FINEMAN AND ROSS PLOT FOR COPOLYMERISATION OF VINYL ACETATE AND C-14 STYRENE AT 60°C

obtained from the slope and intercept respectively are as follows:

$$r_1 = \frac{k_{pS.S}}{k_{pS.VA}}$$

$$= 65$$

$$r_2 = \frac{k_{pVA.VA}}{k_{pVA.S}}$$

$$= 0.045$$

The values of monomer reactivity ratios show that styrene is 65 times more reactive towards itself than towards vinyl acetate.

It should be emphasised that the values for monomer feed ratios (F) given in Table 17 are derived directly from the initial concentrations of styrene and vinyl acetate, i.e. at zero per cent conversion.

These values might be expected to change during the course of polymerisation due to the very high reactivity of styrene although conversions were held to a very low value. Calculations have therefore been carried out to estimate the effect of this change. Thus e.g. for 1:100 (S:VA) ratio at the outset the polymer produced at 2% conversion contains

$$\frac{0.0047 \times 2}{0.02} = 0.47\% \text{ styrene.}$$

Original styrene in the feed = 1%.

$$\therefore \text{ average styrene content} = \frac{1 + 0.53}{2}$$

$$= 0.77\%.$$

$$\text{Average vinyl acetate content} = \frac{100 + 98}{2}$$

$$= 99\%.$$

$$\therefore \text{ average value of F} = \frac{0.77}{99}$$

$$= 0.0077$$

Values for F were calculated in this way for other two ratios, and are given in Table 18.

Table 18 Results for the determination of monomer reactivity ratios at 60°C using mean values for the monomer composition during the copolymerisation

S: VA	Wt. of styrene (gm) in 0.02 g. of polymer	$F \times 10^3$	f	$F(f-1)/f \times 10^2$	$F^2/f \times 10^4$
1:1000	0.00045	0.74	0.019	-3.83	0.28
1:500	0.0009	1.46	0.038	-3.60	0.57
1:100	0.0047	7.7	0.252	-2.22	2.30

The values of 75 and 0.04 were obtained for r_1 and r_2 respectively from the slope and intercept by plotting $F(f-1)/f$ against F^2/f in Fig. 21(a). The value for r_1 is higher than the one obtained using

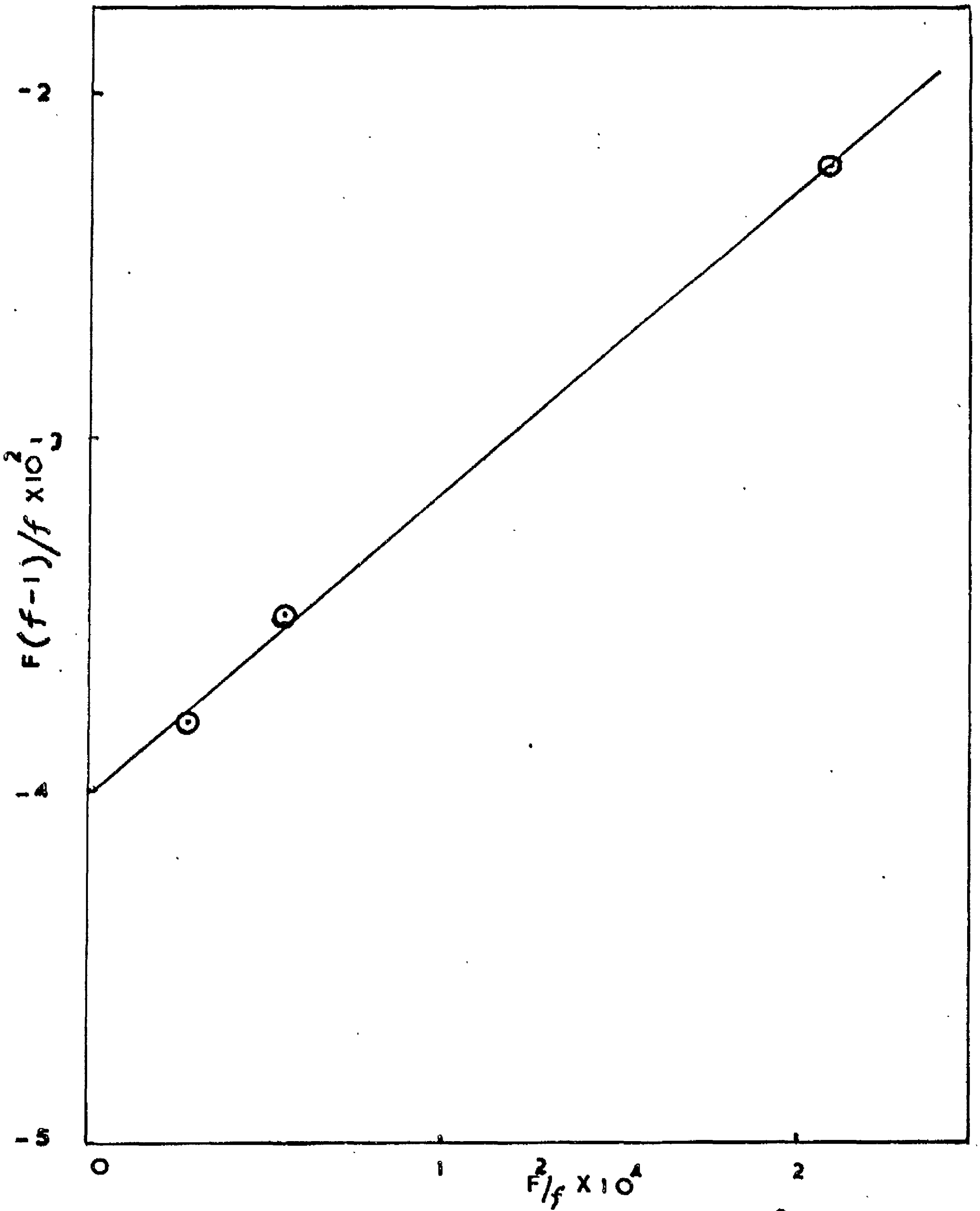


FIG. 21(a).PLOT OF F(1-f)/f AGAINST F²/f (CORRECTED) USING THE METHOD OF FINEMAN AND ROSS FOR THE COPOLYMERISATION OF VINYL ACETATE C14-STYRENE AT 60°C.

the monomer feed ratios at zero per cent conversion. Those values along with the values obtained on page (92) will be compared with the literature values in the discussion.

Determination of molecular weight by the initiator-fragment method.

The molecular weight of a vinyl polymer may be calculated from the number of initiator fragments occurring in the polymer. The method pre-supposes that both mechanisms of initiation and termination are known, and that chain transfer reactions are not significant.

In this work molecular weight of the copolymer was determined from the number of C14 labelled AIBN fragments incorporated in the chain. The initiator concentration, S:VA ratio, temperature, and per cent conversion were the same as for the determination of the monomer reactivity ratios. The copolymer was precipitated five times to get rid of the unreacted AIBN. 20 mg. of the copolymers in benzene solution were counted for activity assay.

Typical calculation of molecular weight for 1:1000 (S:VA) ratio.

From the calibration curve (Fig.22) 3.28×10^{-5}g. radioactive AIBN give 7.8 c.p.s.

i.e. $136/164 \times 3.28 \times 10^{-5}$g. of the isopropyl initiator groups in AIBN give 7.8 c.p.s.

20 mg. of polymer give 13 c.p.s.

Specific activity of the copolymer/g.

$$= 13 \times 50$$
$$= 650 \text{ c.p.s.}$$

1 g. of polymer contains $2.72 \times 10^{-5} \times \frac{650}{7.8}$ g. of isopropyl initiator groups.

Now assuming combination is the mode of termination, one molecule of the copolymer will contain two isopropyl fragments and therefore the molecular weight of one molecule of copolymer $\bar{M}_n$ = $(2 \times 68 + n \times 104 + 86 \times m)$ where n and m are the number of styrene and vinyl acetate units respectively.

$$136/\bar{M}_n = \frac{2.72 \times 10^{-5} \times 650}{7.8}$$

$$\bar{M}_n = 60{,}000$$

$$\therefore (2 \times 68 + n \times 104 + 86 \times m) = 60000$$

From Table 17 for 1: 1000 (S: VA) ratio

$$\frac{\text{moles of styrene in copolymer}}{\text{moles of vinyl acetate in copolymer}} = 0.019$$

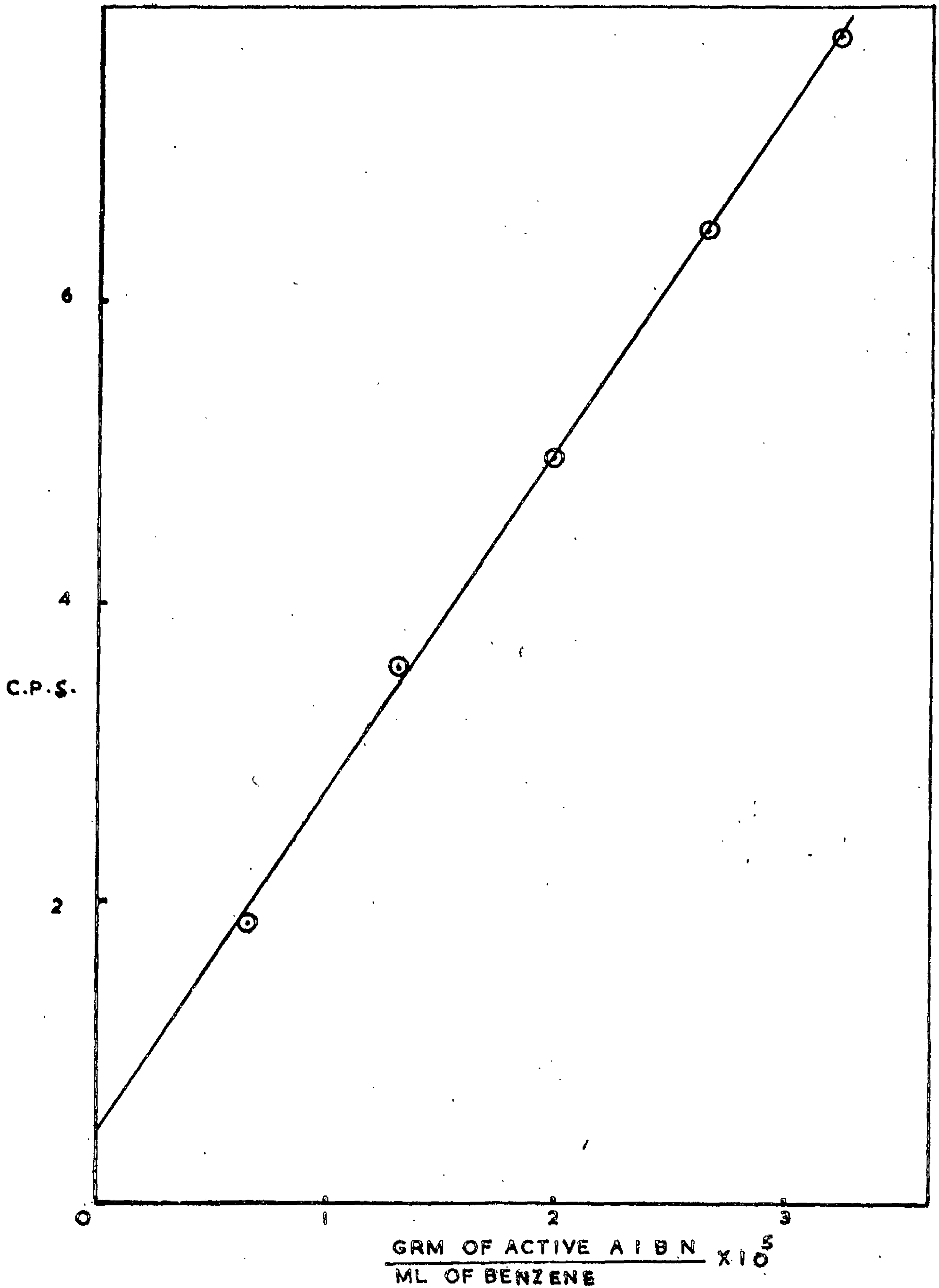


FIG. 22 CALIBRATION CURVE FOR THE ACTIVITY OF AIBN IN BENZENE SOLUTION

$$n/m = 0.019$$

$$\text{hence } n = 0.019m$$

$$\text{and } m = \frac{n}{0.019}$$

$$\text{Therefore } 136 + (104 \times 0.019m) + 86m = 60000$$

$$m = 682.52$$

$$\text{and } 136 + (104n) + 86 \times \frac{n}{0.019} = 60000$$

$$n = 12.92$$

Styrene units per copolymer molecule = 12.92 and vinyl acetate units per copolymer molecule = 582.52.

Molecular weights and number of units for each monomer per copolymer molecule were calculated for other S: VA ratios. Molecular weights were also measured viscometrically by the use of equation (33). This equation has been used on the assumption that copolymer chains predominantly consist of vinyl acetate units. The results obtained have been recorded in Table 19.

Table 19 Molecular weights by initiator-fragment and viscosity method of the copolymers prepared with different S: VA ratios at 60°C with 5×10^{-3} molar of AIBN.

S:VA	c.p.s. (20mg.) polymer	Molecular weight		Rate x 10^5 (mole $l.^{-1}$ $sec.^{-1}$)	No.of monomer units per chain	
		AIBN fragment	viscosity method		S	VA
1:1000	13	60,000	72,6000	3.0	12.92	682.52
1:500	25	31,000	43,000	1.58	13.038	343.12
1:100	113	6,830	9,200	0.63	15.12	59.54

The results given in Table 19 indicate that as the ratio of styrene to vinyl acetate decreases the molecular weight also decreases progressively. This shows that the chains are being prevented from growing as styrene concentration increases. The number of monomer units per copolymer molecule increase as styrene in the feed mixture is decreased, suggesting that styrene is responsible for the lower molecular weights observed.

The molecular weights obtained by viscosity method are higher than the molecular weights obtained by the initiator-fragment method. This may be due to the viscosity relationship used as this might not give the true molecular weight of the copolymer.

The rates of polymerisation were calculated dilatometrically. As the conversion factor for deriving the rates of reaction depends on the composition of the copolymer formed, the copolymerisation was taken to 2%; it was assumed that the polymer produced had a constant composition.

From the copolymer composition in Table 19 it is clear that the copolymer is predominantly polymerised vinyl acetate, therefore, the conversion factor for vinyl acetate was used. It was also observed that as the styrene concentration in the monomer feed was increased the rate of reaction decreased.

Evaluation of the monomer reactivity ratios from the initial composition of the copolymer of inactive styrene (S) and radioactive vinyl acetate (VA).

20 mg. of the polymers in benzene solution were used to assay the activity.

From the calibration curve (Fig.23) for the activity of the stock vinyl acetate the composition of the copolymer (f) can be calculated as described in the previous section. The results for the determination of monomer reactivity ratios are given in Table 20 along with the c.p.s. for 20 mg. of polymer.

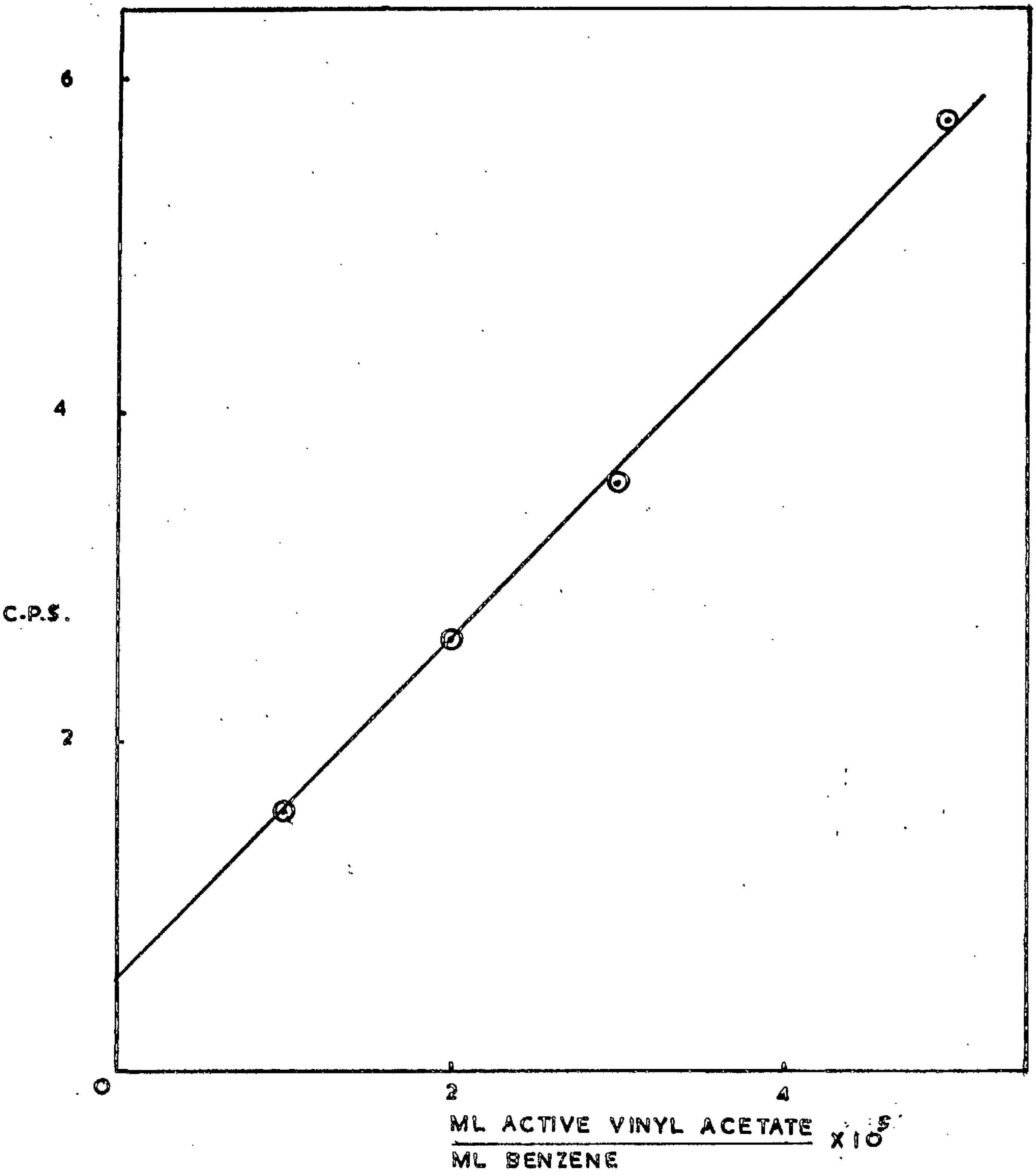


FIG. 23 CALIBRATION CURVE FOR THE ACTIVITY OF VINYL ACETATE IN BENZENE

Table 20 Results for the determination of monomer reactivity ratios at 60°C for the copolymerisation of vinyl acetate and styrene initiated with 5 x 10^{-3} molar AIBN.

VA: S	c.p.s. (20mg)	F	f	F(f-1)/f	F^2/f
1: 5	10.51	4.20	198	4.18	0.091
1: 10	5.92	8.07	352	8.05	0.185
1: 20	3.35	16.20	688	16.16	0.380
1: 40	1.93	33.00	1370	32.99	0.802

A Fineman and Ross plot has been drawn in Fig.(24) and the values of r_1 and r_2 obtained are as follows:

$$r_1 = \frac{k_{pS.S}}{k_{pS.VA}} = 45$$

$$r_2 = \frac{k_{pVA.VA}}{k_{pVA.S}} = 0.05$$

The molecular weights have been determined by initiator-fragment and viscosity method. Number average molecular weight was obtained using the expression[32]

$$\bar{M}_n = 184000 [\eta]^{1.4}$$

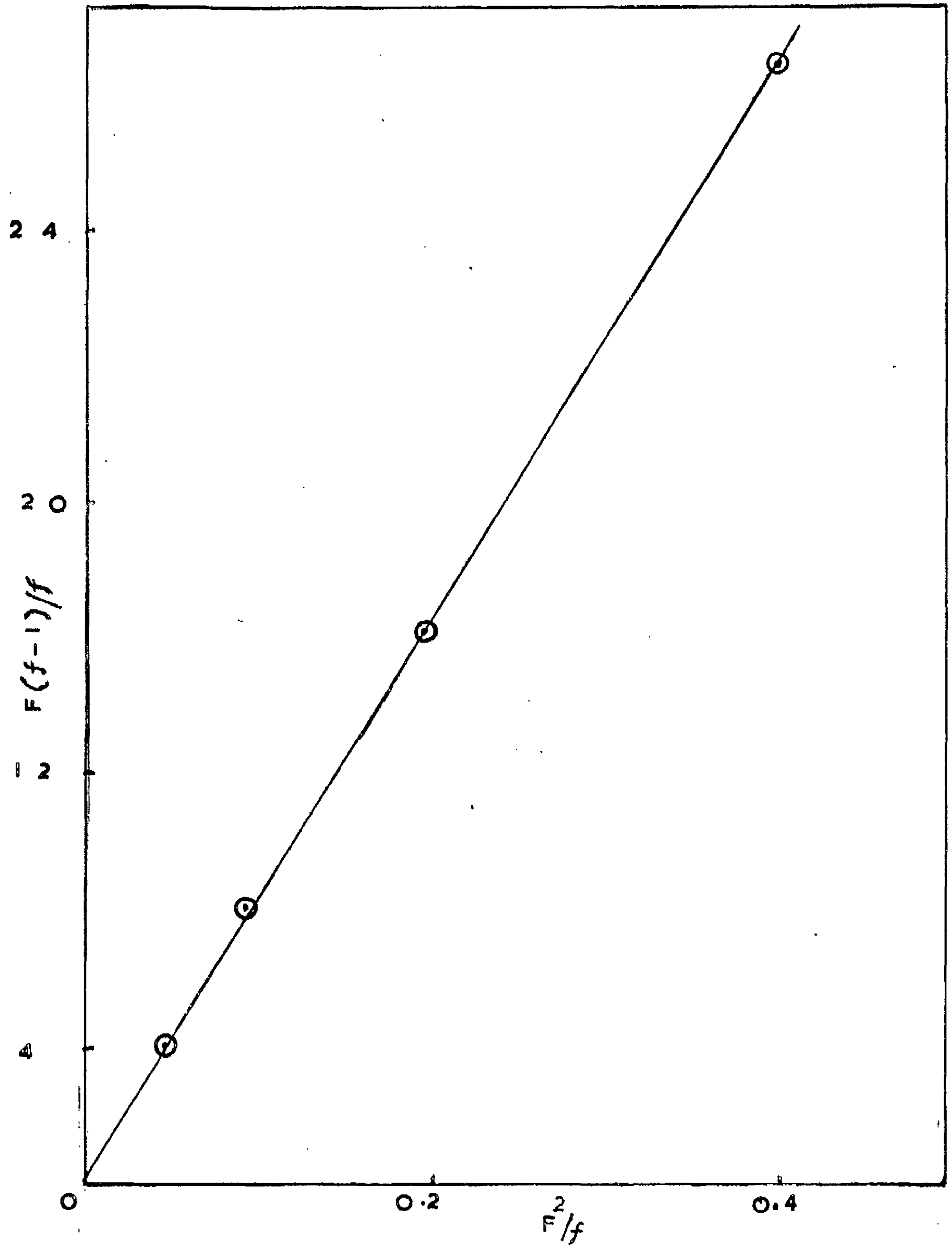


FIG. 24 FINEMAN AND ROSS PLOT FOR THE COPOLYMERISATION OF STYRENE AND C 14— VINYL ACETATE

assuming that polymer mainly consists of styrene. The flow times were measured in benzene at 30°C. The values obtained by both methods are shown in Table 21.

Table 21 Molecular weights determined by initiator-fragment and viscosity method of the copolymers prepared with different VA: S ratios at 60°C with 5×10^{-3} molar AIBN as initiator.

VA: S	c.p.s. (20mg) polymer	Molecular weight by initiator-fragment method	Molecular weight by viscosity method
1: 5	10.20	77,000	76,700
1: 10	13.00	66,000	76,300
1: 20	12.40	65,000	73,200
1: 40	15.23	53,800	55,800

Table 21 again indicates that the molecular weight of the copolymer decreases as the styrene concentration of the monomer feed is increased. The molecular weights by both methods are in good agreement.

Determination of velocity coefficients in the copolymerisation of styrene and vinyl acetate by non-stationary state method[35].

In the last section the effect of styrene on the polymerisation of vinyl acetate was studied at 60°C by the stationary state method. The styrene was found to copolymerise, and the rate of reaction was very low as compared to the vinyl acetate alone. It was felt that it would be worthwhile to examine the individual values of the kinetic constants in the polymerisation of vinyl acetate in the presence of small amounts of styrene.

All runs were carried out with 10^{-3} molar AIBN at 25°C to avoid the complications which would arise at higher temperature due to thermal catalysed polymerisation. The rates were varied by inserting the screens of different light transmission in front of the U.V. lamp.

The rate of polymerisation of vinyl acetate can be determined from the trace on the recorder chart in the following manner.

From a typical chart trace in Fig. (25) a slope of 3.4×10^{-1} divisions per second was obtained. The

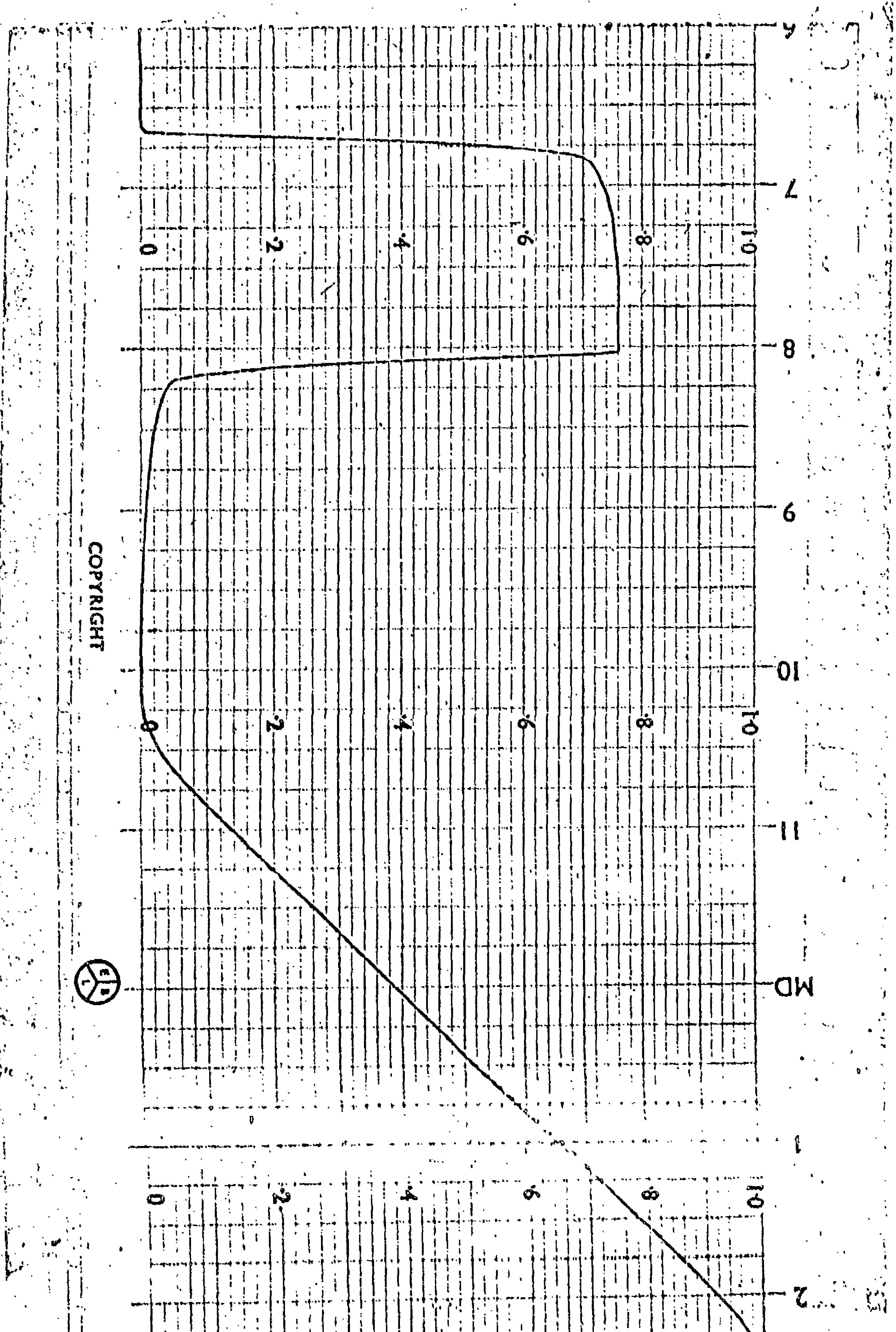


FIG.25 TYPICAL NON-STATIONTIONARY STATE TRACE CHART

calibration curve showed that at the amplication used, 10μ volts were equivalent to 7.2 chart divisions, and since 40μv $\equiv$ 1°C, the rate of temperature rise of polymerising mixture $= \dfrac{3.4 \times 10^{-1}}{0.72 \times 40}$

$= 11.8 \times 10^{-3}$ °C sec.$^{-1}$

From the literature values [36];

heat of polymerisation of vinyl acetate

$= 21.3$ K.cal.mole^{-1}

specific heat of monomeric vinyl acetate

$= 0.47$ cal.g.$^{-1}$

molecular weight of vinyl acetate

$= 86$

heat required to raise the temperature of one mole

through 1°C $= 86 \times 0.47$

$= 40.4$ cal.

Fractional rate of polymerisation

$$= \frac{11.8 \times 10^{-3} \times 40.4}{21.3 \times 10^{3}}$$

$$= 2.22 \times 10^{-5} \text{ sec}^{-1}$$

Evaluation of k_p and k_t

Fig. (26) shows a plot of intercept against the reciprocal of the rate. The instrument lag was obtained

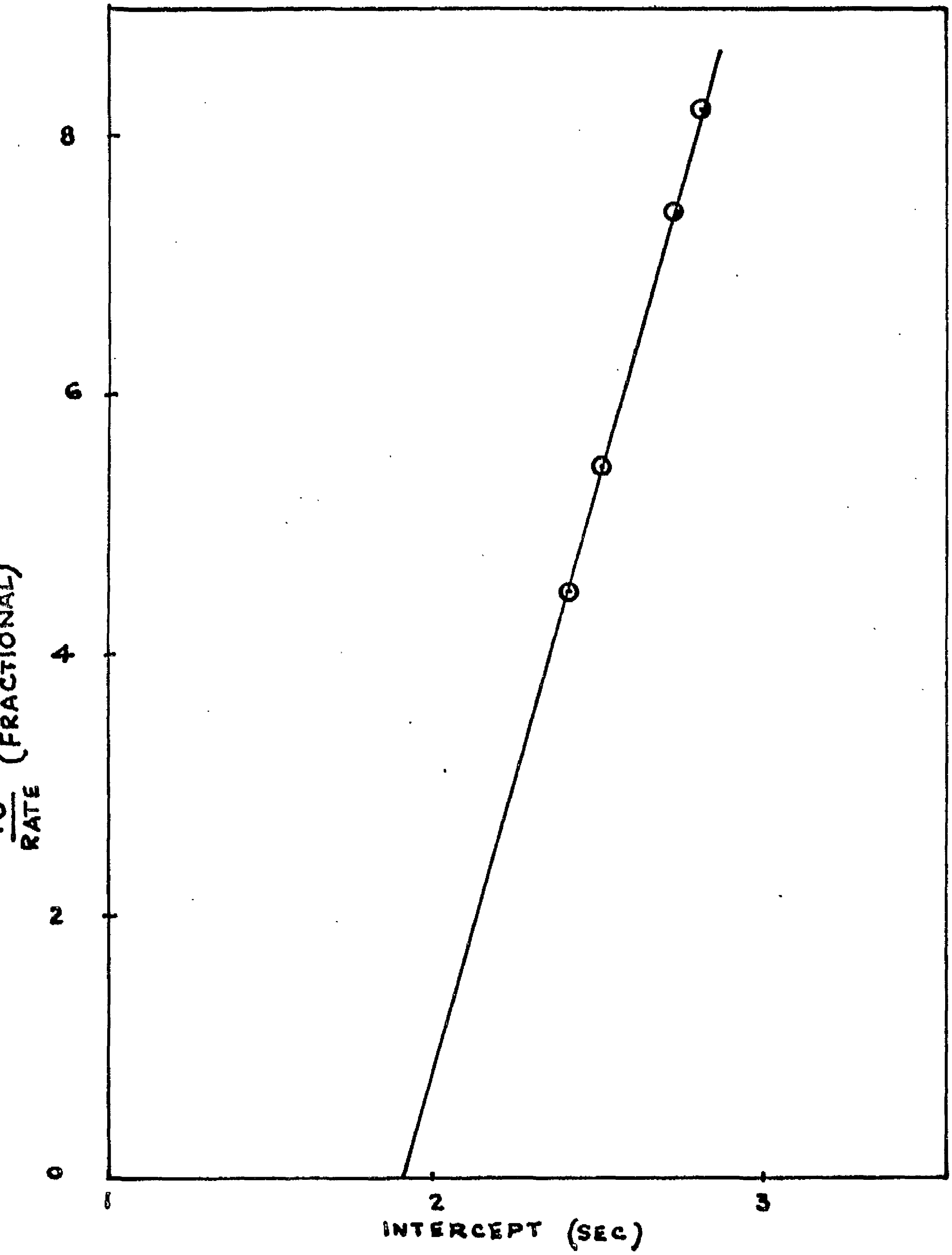


FIG. 26 PLOT OF FRACTIONAL RATE AGAINST INTERCEPT IN VINYL ACETATE POLYMERISATION AT 25°C

from the intersection of the plot with the horizontal co-ordinate axis. The plot is linear and gives 1.9 seconds as lag of the instrument.

Now slope of line fig.(26) $= \dfrac{k_t}{k_p . \ln 2}$

$$= 1 \times 10^5$$

$$k_t/k_p = 0.693 \times 1 \times 10^5$$

$$k_p/k_t = 1.48 \times 10^{-5}$$

The kinetic chain lifetime was then calculated from the equation :

$$\tau \times \text{fractional rate} = k_p/k_t$$

$$\text{i.e. } \tau = \frac{1.48 \times 10^{-5}}{2.22 \times 10^{-5}}$$

$$\tau = 0.7 \text{ sec.}$$

The rate of initiation was taken from literature[8] and was given as 2.17×10^{-8} mole $l.^{-1}$ $sec.^{-1}$ at 7.0% per hour polymerisation of vinyl acetate alone.

Since the square root of the rate of initiation is proportional to the rate of reaction, the observed rate of 8% per hour at zero conversion for vinyl acetate polymerisation gives a value of 2.9×10^{-8} mole $l.^{-1}sec.^{-1}$ for the rate of initiation.

$$\text{From equation (23)} \quad = \quad 1/(k_tI)^{\frac{1}{2}}$$

$$k_t = 1/\tau^2 \times 1/I$$

$$= 1/(0.7)^2 \times 1/2.9 \times 10^{-8}$$

$$= 7.0 \times 10^7 \text{ l.mole}^{-1}\text{sec.}^{-1}$$

$$\text{and } k_p/k_t = 1.48 \times 10^{-5}$$

$$k_p = 1.48 \times 10^{-5} \times 7.0 \times 10^7$$

$$= 10.36 \times 10^2 \text{ l.mole}^{-1}\text{sec.}^{-1}$$

Plots in Fig (27) and (28) show 1/Rate against intercept for 1:6000 and 1:3000 styrene : vinyl acetate ratios at 25°C and these are fairly linear.

The values of k_p, k_t and kinetic chain lifetime obtained in given in table 22.

<u>Table 22 The velocity coefficients in the polymerisation of vinyl acetate alone and in the presence of styrene at 25°C with 1 x 10^{-3} molar AIBN</u>

System	k_p/k_t (x 10^6)	k_p (l.mole^{-1} sec.$^{-1}$)	k_t x 10^{-7} (l.mole^{-1} sec.$^{-1}$)	τ sec.	Rate x 10^4 (mole l.$^{-1}$ sec.$^{-1}$)
VA (Bulk)	14.8	1036	7.0	0.70	2.5
S:VA (1:6000)	2.90	215	7.4	0.70	0.5
S:VA (1:3000)	1.47	91	6.2	0.73	0.2

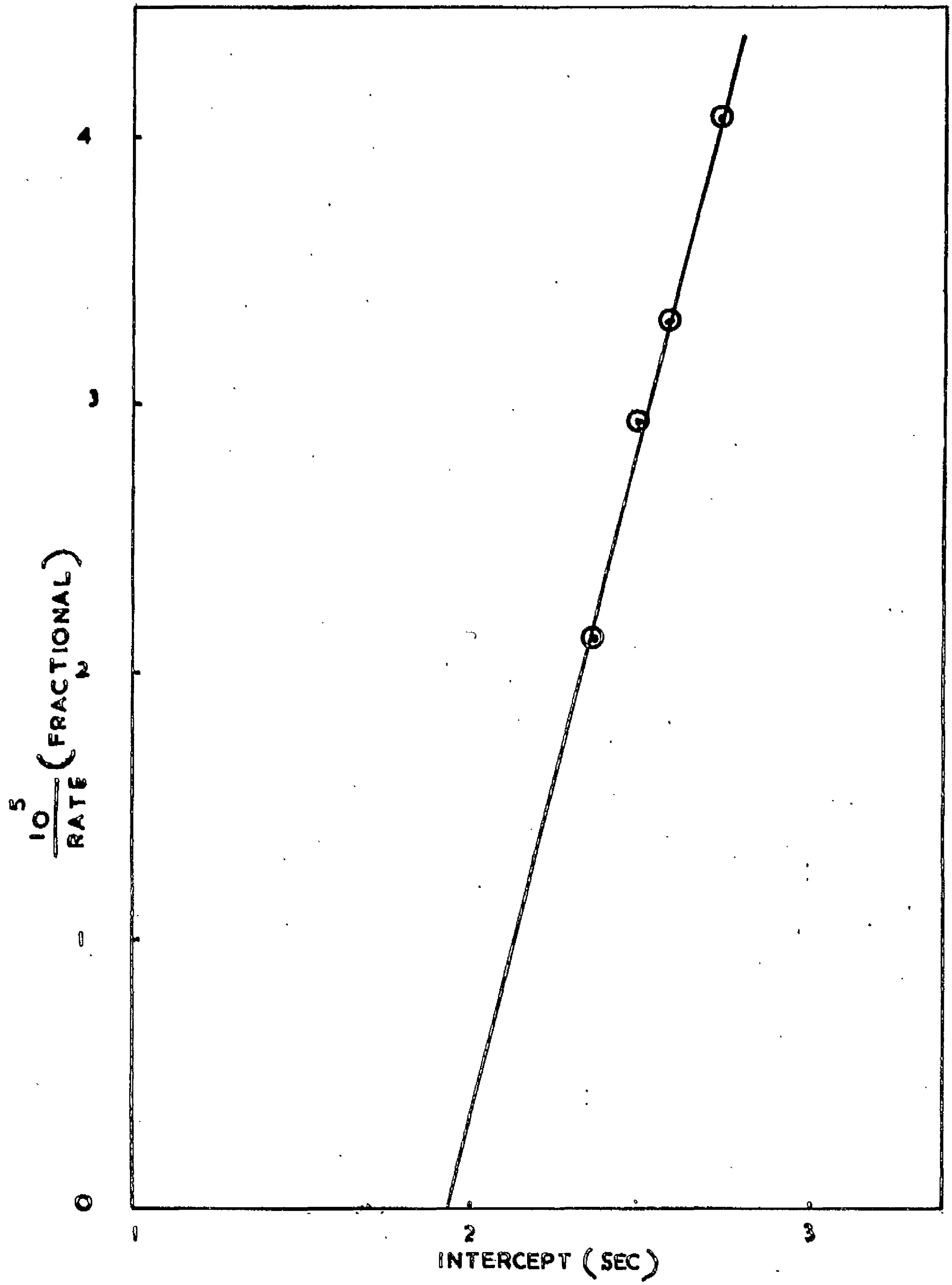


FIG. 27 PLOT OF FRACTIONAL RATE AGAINST INTERCEPT IN THE COPOLYMERISATION OF VINYL ACETATE AND STYRENE $[S] = 1.44 \times 10^{-5}$ MOLES $[VA] = 0.11$ MOLES

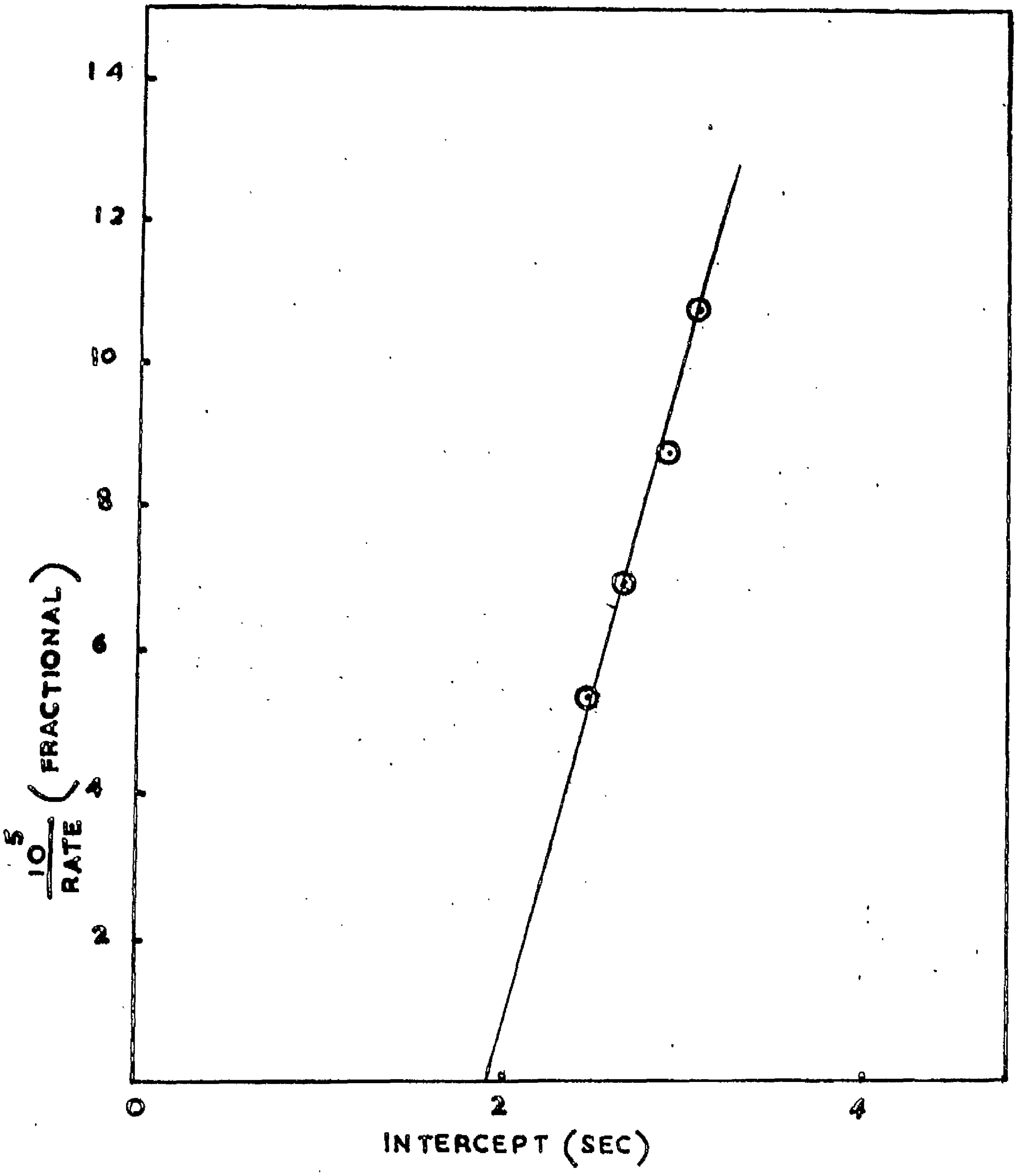


FIG. 28 PLOT OF FRACTIONAL RATE AGAINST INTERCEPT IN THE COPOLYMERISATION OF VINYL ACETATE AND STYRENE[S] = 2.9×10^{-5} MOLES [VA] = 0.11 MOLES

Table 21 indicates that the value of k_p decreases as the styrene concentration is increased, but there is no appreciable change in the value of k_t. The kinetic chain lifetime is practically constant. It is also observed that even very small amount of styrene retards the rate of vinyl acetate polymerisation strongly. The possible mechanism will be given in the discussion.

DISCUSSION

It is important to realise the experimental errors and practical limitations which may have been associated with the methods used and the results obtained.

Errors in the radioactive work

It was found during assaying the activity of the solutions that abnormalities in the room temperature did affect the counting rate in spite of the fact that the head unit was kept cold with running tap water. The results are liable to errors especially when the activity of the samples is low. Therefore, room temperature was kept reasonably constant at 21 ± 1°C by avoiding draughts. The results were thus reproducible to within 5%.

The silicone oil in the head unit was also found to be a serious source of trouble since the amount of oil diminished more quickly than was expected due to leakage past the rubber seal. Replacement of the rubber seal did not completely prevent the leakage. This error was therefore eliminated by checking that the oil contact had been maintained at the end of each counting operation.

Limitations of the non-stationary state method

Of the methods which are available for evaluating kinetic constants, the thermocouple method is probably the most useful method, but, there are certain limitations which should be mentioned.

Temperature measurement

The temperature was recorded by the thermocouple at the centre of the reaction vessel. It has been assumed that the temperature of the bath remained constant but this was not found true in practice. The signal obtained by the pen recorder was due to the opposing electromotive forces (e.m.f.) from the thermojunction. Any random fluctuations in the bath would be reflected in the trace but to a lesser degree because of the lag in response. With the arrangement mentioned in experimental section the fluctuation of temperature in the bath over long periods was in the region of 0.01°C. However, during the 30 seconds required to carry out a non-stationary state run, the fluctuation in temperature was normally not greater than 0.001°C.

The noise level of the amplifier corresponded to a temperature fluctuation of 1.4×10^{-4} °C and this represents the ultimate limit of temperature measurement.

The e.m.f. temperature relationship was obtained from the literature. Bengough and Melville[9] reported that rates obtained with copper-constantin thermocouple are in agreement with those obtained used platinum-platinum rhodium thermocouple, and with rates measured dilatometrically, thus showing that e.m.f. temperature relationship is quite reliable.

Measurement of the kinetic chain lifetime.

There is always the possibility of inaccuracy in the extrapolation of the stationary state-time curve. The start of the reaction was indicated by a pip on the recorder chart. If the amplificationapplied to the system was large then the pip increased in size and the pen did not always return to the original base line. This tended to increase the value obtained for the kinetic chain lifetime. This error did not affect the bulk vinyl acetate polymerisation but was significant in the presence of styrene where the amplification was about one microvolt equal to 5 to 6 chart divisions.

The variation of the instrument lag from run to run also causes about 10% error. The response of the amplifier is 0.04 second, and the response time of the thermocouple due to its small heat capacity will also be very short. The lag of the pen recorder is very much greater, about one second. The combined lag in this work was 1.9 seconds.

To obtain a reasonably accurate value, the lifetime of kinetic chain should be 2 to 3 seconds. But the lifetimes measured were shorter than this and it was necessary to repeat each determination several times to get a reliable value. The points which are plotted in the 1/Rate against intercept graphs (Fig.26-28) are the average of at least three separate determinations. In Fig.26 the intercept on the time axis corresponding to the instrument lag is 1.9 seconds. It is seen that although this could vary by about ± 0.3 sec. the slope of the graph would alter only slightly i.e. about 4%.

Effects of solvents on vinyl acetate polymerisation.

Benzene.

Two main effects are observed in the polymerisation of vinyl acetate in benzene. Firstly the rate of reaction is retarded to an extent dependent on the benzene concentration. Secondly, the $\overline{\overline{DP}}$ decreases with increasing amounts of benzene. The values of rates and $\overline{\overline{DP}}$ are given in Table 23 to eliminate reference to previous section.

Table 23 The rates of reaction and $\overline{DP}$ of the polymer formed in the polymerisation of vinyl acetate in the presence of benzene at various temperatures with 5×10^{-4} molar AIBN as initiator.

Temp. °C	Benzene % (by volume)	Rate $\times 10^{4}$ (mole $l.^{-1}$ $sec.^{-1}$)	$\overline{DP} \times 10^{-3}$
25	0	2.05	7.44
	5	1.14	5.62
	15	0.57	3.13
	25	0.27	2.20
	35	0.159	1.59
35	0	3.02	5.05
	5	1.38	4.43
	15	0.71	2.82
	25	0.42	1.71
	35	0.25	1.27
45	0	4.32	4.10
	5	2.29	3.36
	15	1.05	2.43
	25	0.75	1.96
	35	0.47	1.18
60	0	9.26	3.85
	5	4.75	3.03
	15	2.32	2.82
	25	1.82	1.37
	35	1.01	1.025

From Fig.(29) it can be seen that the decrease in rate is very sharp up to 15% benzene but with higher concentrations it shows a tendency to level off indicating that the rate is not directly proportional to benzene concentration.

The values for chain transfer constant obtained in this work do not agree with the literature values as shown in Table 24.

Table 24 Comparison of values of C_s with literature values in the polymerisation of the vinyl acetate benzene system.

Reference	Temp. °C	$C_s \times 10^4$
This work	25	8.9
	35	10.5
	45	12.0
	60	13.5
Clark and Stockmayer[4]	60	1.2
Palit and Das[32]	60	2.96

Although Stockmayer also obtained a straight line without keeping $I^{\frac{1}{2}}/[M]$ constant at different ratios of $[S]/[M]$, his value for C_s is about ten times less than the value obtained in this work. The value obtained by Palit and Das should be more reliable since they kept

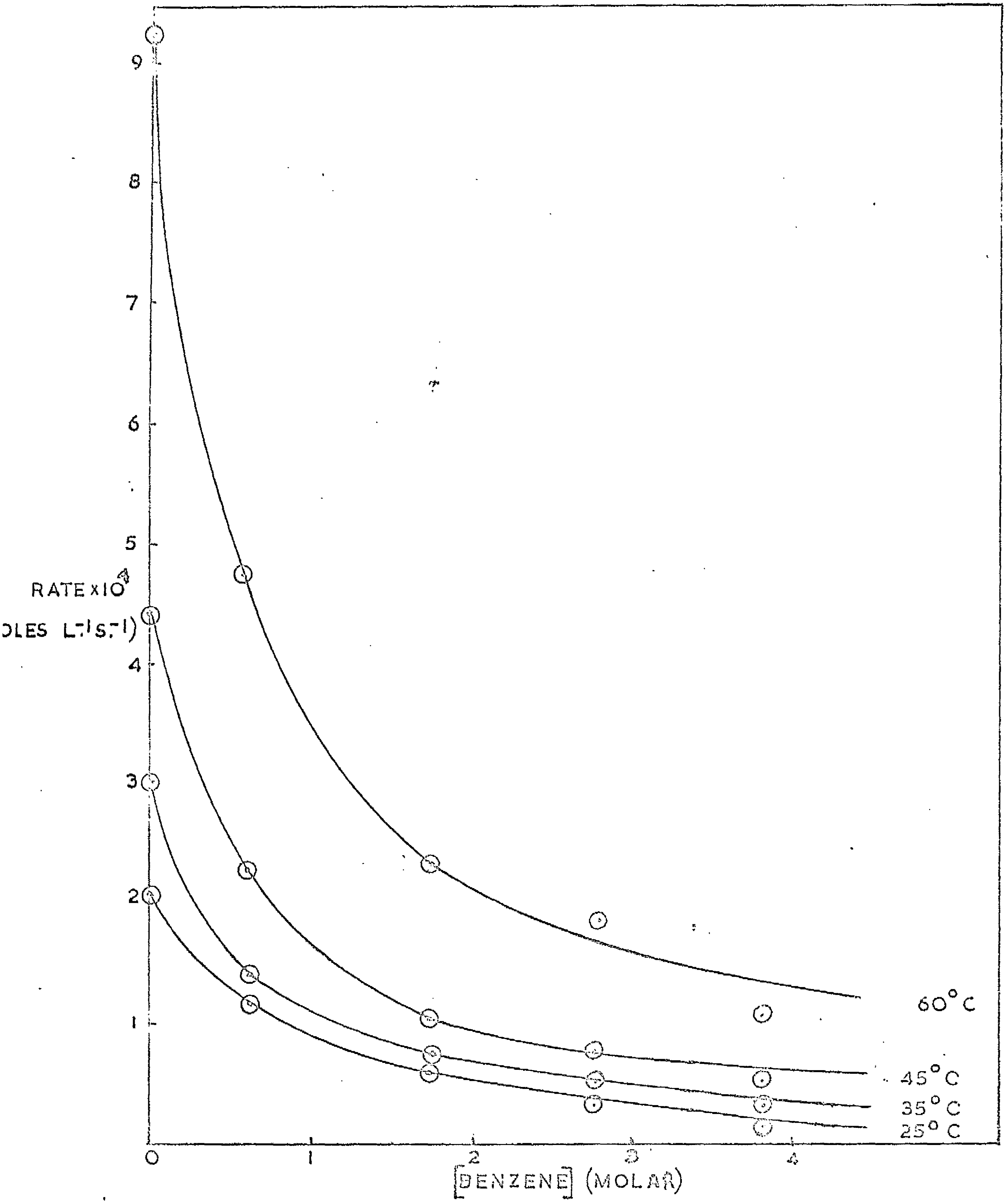


FIG. 29 VARIATION OF RATE OF POLYMERISATION OF VINYL ACETATE WITH BENZENE CONCENTRATION AT DIFFERENT TEMPERATURES.

$I^{\frac{1}{2}}/[M]$ constant. However, it is difficult to understand why the difference in values is so great, particularly as the same method of measuring the molecular weight of the polymer was used.

The results of vinyl acetate polymerisation in benzene show a number of features which are summarized below. Any mechanism for the reaction between solvent and the growing polymer radical must account for these features.

(i) Addition of solvent causes a decrease in the rate of polymerisation.

(ii) The molecular weights of the polymers prepared in the presence of benzene are lower than those of polymers prepared in bulk.

(iii) The intensity exponent with respect to the growing polymer radical concentration in the presence of benzene is around 0.54.

(iv) Only one molecule of benzene is incorporated in each polymer chain.

The retarder effect of solvent on vinyl acetate polymerisation.

Kinetic analysis of the polymerisation of vinyl acetate in the presence of solvent are complicated by the number of different reactions that can take place.

The overall rate of polymerisation is governed essentially by the rate constants for the initiation, propagation and termination steps of the chain reaction. Decrease in the first two or increase in the last would give rise to a decrease in the rate of polymerisation in the presence of solvent.

The polymerisations were initiated by the photolysis of AIBN. This produces free radicals which, in bulk polymerisation, can react with another of the same kind, or with a molecule of monomer to initiate a chain. In the presence of solvent the situation is more complicated, and it is possible for the following reactions to take place:

$$R_c^{\bullet} + M \longrightarrow R_1^{\bullet} \qquad \text{......(I)}$$

$$R_c^{\bullet} + S \longrightarrow S^{\bullet} \qquad \text{......(II)}$$

$$R_c^{\bullet} + R_c^{\bullet} \xrightarrow[\text{or combination}]{\text{disproportionation}} \text{unreacted products..(III)}$$

where $R_c^{\bullet}$ is a primary initiator radical.

Since reaction (II) does not take place in bulk polymerisation it is possible that the rate of chain initiation might be reduced in the presence of solvent, either by decrease in the rate of initiator decomposition, or in the initiation efficiency.

However, it is well established that the initiator decomposition is not affected by solvents, and Bevington[13] has shown that the initiation efficiency remains fairly constant over a wide range of solvent concentration. Therefore reaction (II) appears to be unimportant, and so the rate of initiation has been assumed to be constant in this work.

The radical chain produced by reaction (I) can react as follows:

rate

$R_n^{\bullet} + M \longrightarrow R_{n+1}$ $k_p [R^{\bullet}][M]$ ......(IV)

$R_n^{\bullet} + M \longrightarrow P + R_n^{\bullet}$ $k_{tr} [R^{\bullet}][M]$ ......(V)

$R_n^{\bullet} + S \longrightarrow S^{\bullet}$ $k_{trs} [R^{\bullet}][S]$ ......(VI)

where S is the molecule of solvent and $S^{\bullet}$ is the solvent radical.

Reaction (VI) may take place by various mechanisms which will be discussed later.

The growing polymer radical can terminate by combination or disproportionation as outlined on page (6). The solvent radical can react in several different ways:

rate

$S^{\bullet} + M \longrightarrow R^{\bullet}$ $k_{ri} [S^{\bullet}][M]$ ....(VII)

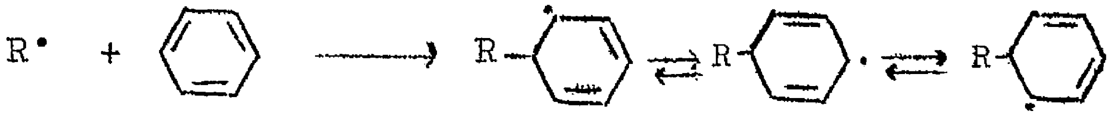
$S^{\bullet} + R^{\bullet} \longrightarrow$ polymer $k_t [S^{\bullet}][R^{\bullet}]$ ....(VIII)

$S^{\bullet} + S^{\bullet} \longrightarrow$ stable products $k_t [S^{\bullet}]^2$ .... (IX)

The radical S• in reaction (VI) can be formed (a) by a chain transfer reaction between a growing polymer radical and a solvent molecule or (b) by the addition of a growing polymer radical to a solvent molecule.

In the polymerisation of vinyl acetate where benzene was the solvent, the chain transfer and addition reactions might be as follows:

.....(VIa)



(VIb)

Reaction (VI) may take place occasionally. Reaction (VI) will affect the rate of polymerisation when (VII) is very much slower than the normal propagation reaction (IV).

Bengough <u>et al</u>[7] found that the value of kinetic chain lifetime increases in the presence of benzene. This result indicates a decrease in the value of the rate constant for termination, although an increase in the rate constant of termination would account for the observed retardation. In their work they found a decrease in the value of rate constant for propagation, and termination which was accompanied by an increase in activation energies. This increase in the activation energies is probably due to the existance of radicals of greater stability than the growing polymer radicals when polymerisation is studied in the presence of benzene, e.g. the radicals formed in reaction (VIb).

The normal chain transfer reaction by hydrogen abstraction (VIa) produces a phenyl radical. To account for the strong retardation observed in benzene, the phenyl radical would have to be unreactive. Barson, Bevington and Eaves[56], using C14 benzoyl peroxide as an initiator of vinyl acetate polymerisation, found that the phenyl radicals are quite efficient in initating polymerisation. Thus reaction (VI a) cannot explain the observed retardation.

Burnett and Loan[2] developed an equation for the rate of polymerisation on the assumption that a chain transfer reaction occurs and is followed by reactions of the radical with (a) a monomer molecule to reinitiate the polymer chain (b) another its kind or (c) the growing polymer chain radical. But their assumption that

$$k_{trs}[R^{\cdot}][S] = k_{ri}[S^{\cdot}][M] \qquad \ldots\ldots(48)$$

can not explain the strong retardation observed.

Their kinetic scheme yielded theoretical curves for the rate of polymerisation in benzene which were similar to the observed one, but they obtained an extremely high value (24 K.cal.mole^{-1}) for the activation energy for the addition of a phenyl radical to vinyl acetate. This is again contrary to the results of Bevington thus indicating that reaction (VIa) as the source of $S^{\bullet}$ radicals is not correct.

Jenkins[37] stated that their equation represents the condition that a negligible proportion of the solvent radicals participated in the termination reaction. If nearly all the transfer radicals were to undergo reinitiation then no retardation would occur. He concluded that this approximation can only be applied if the retardation is comparatively weak.

Jenkins in his own kinetic treatment of effects of solvents on polymerisation made the "geometric mean" assumption regarding the termination reaction i.e. the velocity constant for termination between dissimilar radicals is the geometric mean of those for reactions between like radicals. This assumption is doubtful in view of the evidence from copolymerisation studies[57] that termination may occur preferentially between unlike radicals.

It would appear that reaction (VIII) probably occurs more easily than (IX) and therefore equal number of R$^\bullet$ and S$^\bullet$ radicals are removed when S$^\bullet$ radicals are terminated by this reaction.

Now if we assume that reaction (VI) takes place quickly and reaction (VII) is slow then a large concentration of S$^\bullet$ radicals will accumulate in the system since termination involves the removal of another R$^\bullet$ radical, the concentration of S$^\bullet$ radicals would quickly increase while that of the R$^\bullet$ radicals would decrease. Moreover, as only R$^\bullet$ radicals are active in propagation the rate of reaction will fall as their concentration decreases.

In his treatment Jenkins derived an equation which related the velocity coefficient of chain transfer with solvent (K_{trs}) to the degree of retardation. This equation is simplified, when cross-termination coefficient ϕ is unity, and $k_{ri} = 0$ i.e. when no reinitiation takes place and becomes

$$k_{trs} = (IK_t)^{\frac{1}{2}}/[S]\ (1/\lambda - 1) \qquad \ldots\ldots(49)$$

using the usual symbols with $\lambda = m[M_0]/m_0[M]$ where m and m_0 denote the rates of polymerisation in the presence and absence of solvent respectively.

Jenkins calculated values of k_{trs} from Burnett and Loan's results, and showed that the values obtained varied least with benzene concentration. This led him to the conclusion that reinitiation did not take place in the vinyl acetate-benzene system. His conclusions, however, suggest that the initiator exponent, and the intensity exponent should be between 0.5 and 1.0, which is in conflict with the experiments of Burnett and Loan[2] and Bengough, Brownlie and Ferguson.

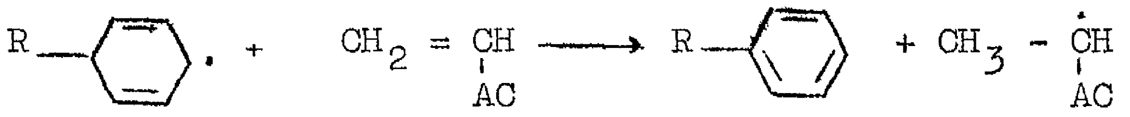
Bengough <u>et</u> <u>al</u>[9] applied the equation (49) to determine the value of k_{trs} from their results, and found zero activation energy for the chain transfer reaction. This is not acceptible since that activation energy for chain transfer with benzene had been found[8] to be equal to that of the propagation reaction. This also supports to some extent the idea of an addition reaction between the growing polymer radical and benzene.

Since in this work the rates of initiation at various temperatures have not been measured, it is not possible to use this relationship to calculate k_{trs} from rate measurements.

It has now been shown that chain transfer by a hydrogen abstraction reaction cannot account for the observed retardation of the polymerisation of vinyl acetate in benzene. The S˙ radical is therefore probably produced by the addition of a benzene molecule to the growing polymer radical.

One possible explanation for the retardation in the rate of polymerisation is that reaction (VIb) takes place and is followed by reinitiation (VII). The radical formed by addition of the growing polymer radical and benzene would be more stable than a phenyl radical, and consequently the activation energy for the reinitiation reaction (VII a or b) would be high.


... (VIIa)


··(VIIb)

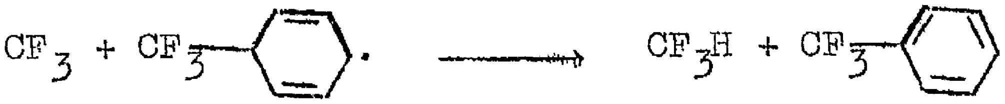
The question whether the reinitiation step takes place by copolymerisation (VIIa), or by chain transfer (VIIb) has still to be answered.

Stockmayer et al[4] explained the high activity of the polyvinyl acetate obtained by polymerising the monomer in the presence of radioactive benzene at 60°C as being due to the copolymerisation of vinyl acetate with benzene.

However, in the present work it had been found that there is only one molecule of benzene incorporated per polymer molecule. Therefore it seems possible that the benzene adds to the growing polymer radical by reaction (VIb) and that reinitation occurs by reaction (VIIa).

Similar work by Breitenbach et al[6] also led them to conclude that no copolymerisation between vinyl acetate and benzene was taking place.

Addition reactions between free radicals and benzene have also been proposed by other workers, for example, Charles and Whittle[58] have suggested that the main reaction of trifluoromethyl radicals with benzene is addition to the ring followed by hydrogen abstraction.



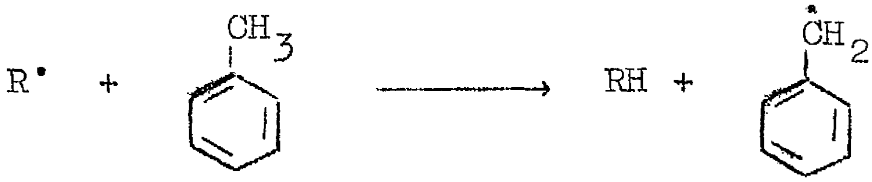
..(X)

They justified their postulation on thermochemical grounds saying that direct hydrogen abstraction requires more energy than the hydrogen abstraction after addition step.

In conclusion the above evidence together with the evidence mentioned earlier tends to suggest that addition of a chain radical to benzene producing a radical which is slow to reinitiate is the cause of the retardation of vinyl acetate polymerisation in benzene.

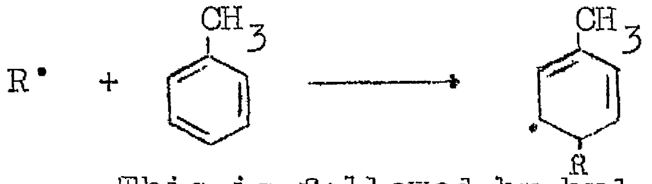
The retardation of the polymerisation of vinyl acetate in the presence of toluene.

The effect of toluene on the rate of vinyl acetate polymerisation has been observed to be practically the same as that of benzene. It was thought that the growing polymer radical would attack the methyl group of toluene producing a benzyl radical of the following type:



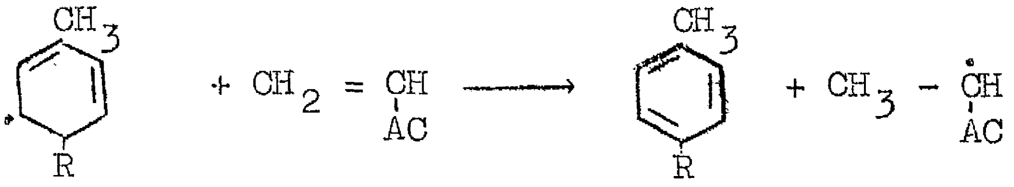
......(XI)

This radical would be quite stable and would not be as efficient in reinitiating polymerisation as the radical produced by addition to benzene. Hence greater retardation would be expected to occur than for benzene. But this is not the case, and the rate is about the same in both solvents. It is possible that an addition reaction similar to (VIb) at the aromatic ring of toluene takes place for example



......(XII)

This is followed by hydrogen elimination to the monomer as follows



.. (XIII)

The chain transfer constant for toluene in vinyl acetate polymerisation has been reported[33] to be about seven times greater than for benzene at 60°C. The increase in the rate of the transfer reaction is surely due to the presence of methyl group. This reaction would produce radicals similar to those shown by reaction (XI) and toluene might be expected to give greater retardation than benzene. The same rate of polymerisation of vinyl acetate would only be given if the addition of the growing polymer radicals to the aromatic ring takes place to the same frequency in both solvents, and provided the benzyl radicals formed by chain transfer with the methyl group of toluene reinitiate polymerisation effectively. This latter suggestion is difficult to accept and the precise nature of the effect of toluene on the polymerisation of vinyl acetate must still remain unanswered.

The effect of substituted benzenes on the polymerisation of vinyl acetate.

It has been shown in the experimental results that the rate of polymerisation of vinyl acetate is further retarded by halogenated-benzenes as the number of halogen atoms on the ring increases to three but that there is no change in rate in the presence of hexachlorobenzene. These results would definitely support the view of addition of the growing polymer radical to the aromatic nucleus by the reaction (VIb) already proposed.

If hydrogen abstraction were the main factor causing retardation it would be expected to be greater in the presence of benzene than in the substituted benzenes simply on the basis of number of sites available for abstraction reactions, and to decrease with the progressive substitution of the benzene ring. However, the substituents used have an activating effect on the nucleus since they donate electrons. As the electron density on the nucleus increases in the order of substituents $F < cl < Br < I$ the activation of the latter increases, and hence the ring becomes more prone to attack by the growing polymer radicals. Thus a greater number of $S^{\bullet}$ radicals are formed and greater retardation occurs.

In the hexachlorobenzene-vinyl acetate system there is no chance of attack on the polymer radical due to the fully blocked benzene ring. This can be explained by the steric effect. The chlorine atoms themselves are bulky and hence prevent close approach to the growing polymer radical.

In the case of vinyl acetate polymerisation in the presence of iodobenzene free iodine may be liberated and it can act as a radical scavanger to give marked retardation in the rate of polymerisation.

The value of the chain transfer constant for monochlorobenzene at 60°C is about three times than for benzene, but the rate of polymerisation of vinyl acetate in the presence of monochlorobenzene is not very much different than in the presence of benzene. For this system there may be some additional chain transfer reaction by hydrogen, or chlorine abstraction which would lower the $\overline{DP}$ of the polymer formed but not affect the extent of the retardation of the polymerisation.

Breitenbach et al[6] obtained chlorinated polymers from the polymerisation of vinyl acetate in the presence of chlorobenzene. The chlorine could have come in the polymer only by addition of the growing polymer radical to the aromatic nucleus but may also have been incorporated by normal chain transfer abstraction reactions. In case of chlorine abstraction the resultant phenyl radical would be quite efficient chain initiator.

The effect of aromatic carboxylic acids and other solvents on the polymerisation of vinyl acetate.

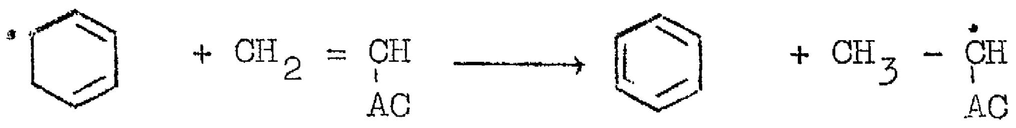
Retardation in the rate of polymerisation of vinyl acetate has been shown to occur in the presence of aromatic carboxylic acids, the retardation increases with increase in the number of substituent - COOH groups in the benzene ring. Complete inhibition in the presence of mellitic acid, and benzene hexole would suggest that the effect is not to do with the nucleus but with the substituent groups.

The hydrogen atom of the carboxyl group is acidic and is possible that the acidic groups are responsible for the retardation of vinyl acetate polymerisation. The actual cause of retardation cannot be explained in the light of the results obtained in this work.

In the case of benzene hexole the growing polymer radical may remove the hydrogen of the hydroxyl group by a chain transfer reaction to create a phenoxy radical which can act as a retarder.

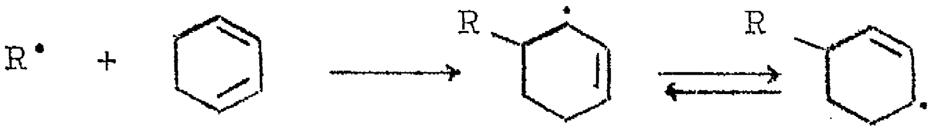
The retardation of the polymerisation of vinyl acetate in the presence of cyclohexadiene can be explained by a rapid hydrogen abstraction reaction by the growing polymer radical followed by the addition of the resultant cyclohexadienyl radical to the monomer viz.

....(XIV)



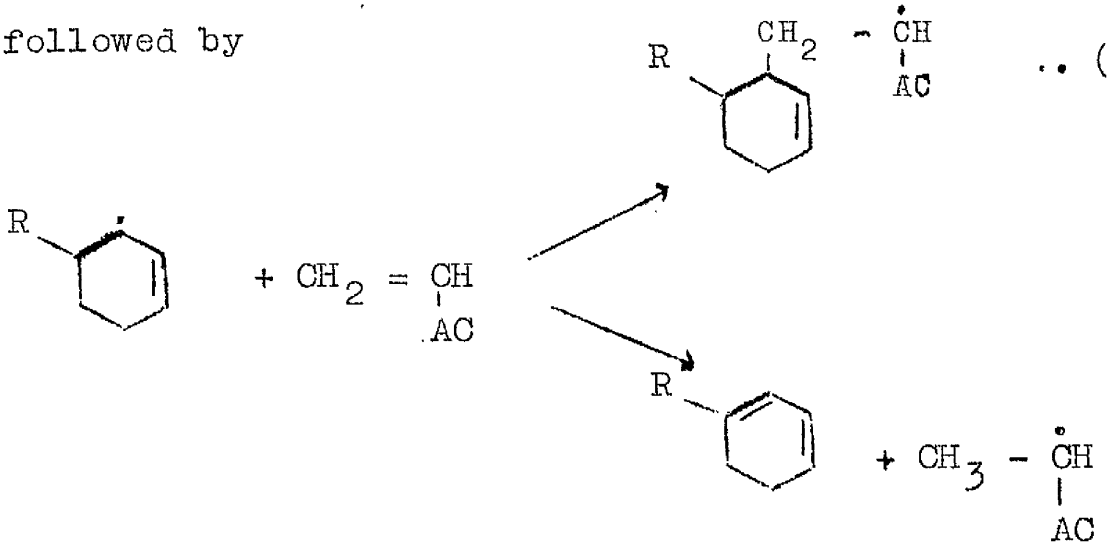
.. (XV)

It is also possible that



.. (XVI)

followed by



.. (XVII)

(XVIIb)

The radical formed by reaction(XIV) is of the same type as obtained in reaction (VIb) by the addition of a growing polymer radical to the benzene ring. The reaction(XIV) and (XV) being rapid cause a reduction in molecular weight as observed while the resonance stabilized radicals produced are slow to reinitiate the polymerisation, thereby causing great retardation. Termination was found to be second order with respect to the polymer radical concentration as was found for the benzene vinyl acetate system.

This, once again, supports the already postulated theory that retardation of the polymerisation of vinyl acetate in the presence of benzene occurs only through slow reinitiation following the addition of the growing polymer radical to the benzene ring.

The effect of styrene on the polymerisation of vinyl acetate.

Styrene has been found to be copolymerised with vinyl acetate and it is worthwhile to compare the values of monomer reactivity ratios obtained in this work by using C14-styrene and C14-vinyl acetate in turn, with those reported by other workers.

Table 25 Comparison of the values of r_1 and r_2 in the copolymerisation of styrene and vinyl acetate.

Reference	System	r_1	r_2
This work	C14-S:VA	65	0.045
	C14-S:VA (corrected)	75	0.040
	C14-VA:S	45	0.050
Mayo & Lewis[22]	S:VA	55	0.010

It can be seen that the value of r_1 obtained by using C14-styrene is higher than the value obtained by using C14-vinyl acetate. The higher value is likely to be less accurate as error in the measurement of C14-styrene in the feed mixture may be greater due to the small amounts of styrene used. The correction applied to allow for the change in composition during polymerisation does nothing to bring the r_1 values into closer agreement. They are still subject to errors in the measurement of the initial volumes of radioactive styrene used.

The value of r_1 obtained by Mayo and Lewis[22] is also liable to errors as the carbon analysis method is not as accurate as the radiotracer technique.

Taking the experimental errors into account the values are in fairly good agreement and it can be said that values of 45 and 0.05 for r_1 and r_2 respectively are probably the more accurate ones.

The other feature of this work is that the rate of vinyl acetate polymerisation is retarded in the presence of small amounts of styrene. For the purpose of comparison the velocity coefficients for the polymerisation of styrene, vinyl acetate and styrene-vinyl acetate system, are given in Table 26.

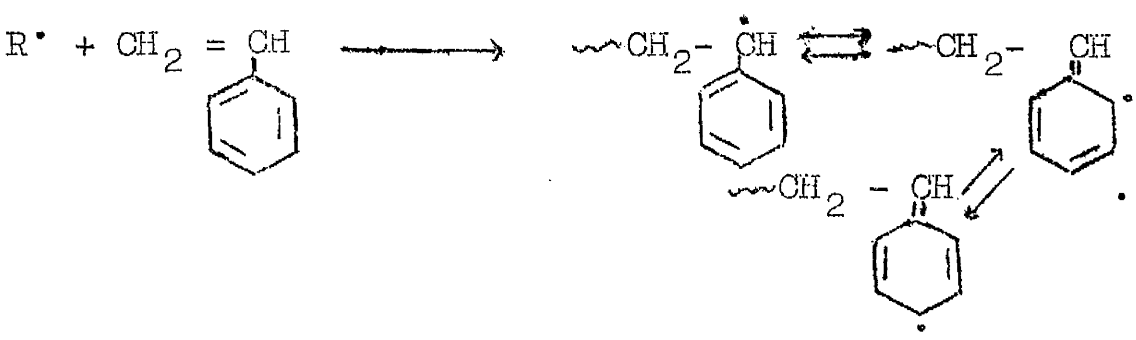
Table 26 The velocity coefficients for the polymerisation of styrene, vinyl acetate (bulk) and styrene-vinyl acetate system at 25°C.

Reference	System	k_p ($l.mole^{-1}$ $sec.^{-1}$)	$k_t x 10^{-7}$ ($l.mole^{-1}$ $sec.^{-1}$)
This work	VA	1036	7.0
Bengough Brownlie[7]	"	860	6.0
Bengough Melville[9]	"	895	2.4
Matheson et al[47]	S	44	4.75
Burnett[46]	"	19.7	6.30
This work	S:VA(1:6000)	215	7.4
"	S:VA(1:3000)	91.74	6.2
Bengough Brownlie[7]	2.5% benzene + VA (V/V)	280	2.3

Table 26 indicates that vinyl acetate has the higher value of k_p. The radical formed from this monomer is very reactive mainly because it lacks strong resonance stabilization, while the styryl radical on the other hand, is strongly stabilized by resonance and much less reactive.

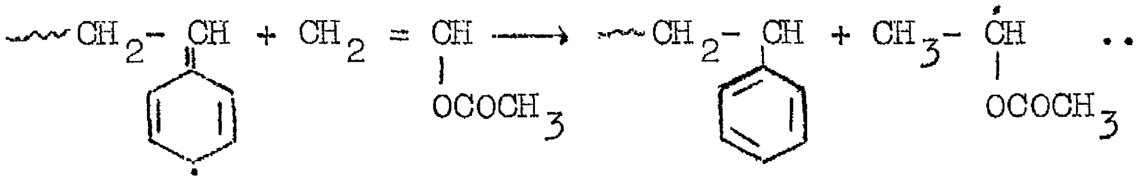
Moreover, it can be seen that the k_p value for vinyl acetate polymerisation decreases in the presence of styrene, and benzene appreciably. The values for k_t obtained in this work in the presence of styrene do not vary but they vary in the work reported by Bengough et al[7] in the presence of benzene. As the k_t value obtained by Matheson et al[47] for the bulk polymerisation of styrene is in agreement with the value obtained for the styrene-vinyl acetate system, and for vinyl acetate bulk polymerisation, normal termination can be assumed to be taking place.

It may be concluded that the value of k_p for the polymerisation of vinyl acetate in the presence of styrene decreases due to the formation of radicals of similar stability to those produced in the presence of benzene by the reaction (VIb). Such radicals are slow to reinitiate, and hence retard the rate of polymerisation of vinyl acetate. A resonance stabilized radical comparable to that postulated in reaction VI(b) can be formed in the presence of styrene as follows:



..(XVIII)

This can propagate by addition of styrene or undergo chain transfer with vinyl acetate as shown below:



..(XIX)

The decrease in molecular weight (see Table 21) with increasing amount of styrene in the polymerisation of vinyl acetate can be explained by chain transfer to vinyl acetate taking place after the addition step (XVIII). Addition of increasing amounts of styrene would result in the formation of more $S^{\bullet}$ radicals and hence more chance of chain transfer to vinyl acetate, although this step is slow.

Alternatively since the concentration of styrene is very low, propagation by addition of styrene to the styryl radical will be a slow process compared with the propagation reaction in vinyl acetate polymerisation. Now as the rate of termination is not affected by the presence of the styrene, the overall rate of polymerisation will clearly be slower when this monomer is present in the system.

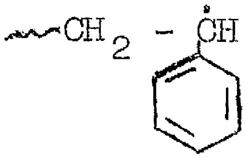
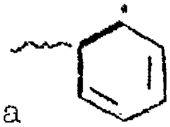
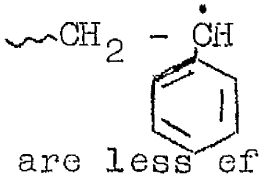
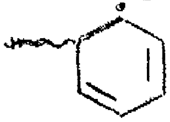
From the foregoing discussion and earlier evidence it is suggested that the rate of polymerisation of vinyl acetate in the presence of benzene is due to the addition of the growing polymer radical to the aromatic ring resulting in a relatively stable radical, which slowly reinitiates the polymerisation by chain transfer with vinyl acetate.

Comparison of effectiveness of retarders for vinyl acetate polymerisation.

In order to compare the relative retardation brought about by the addition of the various solvents used in the course of this work, a table has been drawn up showing the estimated amount of solvent required to cause 50% reduction in the rate of bulk vinyl acetate polymerisation.

Table 27 The various additives arranged in the order of their increasing effectiveness as retarders for the polymerisation of vinyl acetate.

Added material	Estimated volume % required to reduce rate to half its value in absence of additives
Benzene	5.1
Toluene	5.0
Fluorobenzene	2.8
Chlorobenzene	2.7
Bromobenzene	2.6
m-Difluorobenzene	2.6
o,m,p-Dichlorobenzenes	2.5
m-Dibromobenzene	2.5
1,2,4-Trichlorobenzene	2.0
Benzoic Acid	2.0
Phthalic Acid	1.7
Iodobenzene	1.4
Diphenyl	1.3
Hemimellitic acid	1.2
Cyclohexadiene	0.05
Styrene	0.01

From the Table 27 it would appear that the amount of styrene required to reduce the rate of 50% was the least compared with other solvents. From the previous results it has been shown that the  radical can copolymerise with vinyl acetate, but the  radical from benzene cannot. Because it is a vinyl monomer styrene would be expected to appear much higher in Table 27, but its position is due to the resonance stability of the styryl radical formed (reaction XVIII). It appears that the frequency of formation of styryl radicals, and consequently their concentration, will be much higher than for any other retarder due to the presence of the vinyl double bond. Presumably the benzyl radical formed by chain transfer with toluene can also add to vinyl acetate. The very marked retardation with styrene is therefore due to the very large concentration of  (styryl) radicals although in themselves they are less effective than the  type radical.

In conclusion the effectiveness of an additive as a retarding agent for vinyl acetate polymerisation can be explained in terms of the readiness with which a radical derived from the retarder can be formed, and its ability to reinitiate polymerisation.

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