KINETIC STUDIES ON VINYL POLYMERISATION

by

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James Ferguson

CONTENTS

INTRODUCTION

When vinyl acetate polymerises in the presence of a solvent the normal characteristic features of the bulk polymerisation undergo considerable changes. These can be attributed to the solvent acting as (a) a diluent and (b) a chemically reactive retarder of the reaction. The purpose of this thesis is to examine the effect of aromatic solvents on the polymerisation of vinyl acetate from these two points of view in order to obtain a quantitative picture of the effect of monomer dilution, by various solvents, on the polymerisation and to clear up the anomalies which at present exist concerning the mechanism of the reaction between polymeric radicals and aromatic solvents.

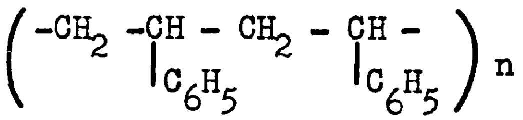
The work previously carried out on vinyl acetate in solution has been done by means of stationary state dilatometric rate measurements. In order to get more detailed information on the polymerisation it is necessary to examine the non-stationary state (i.e. the period during which the radical concentration is building up from zero to a steady value). The thermocouple method has been used to do this. As a result the kinetic chain lifetimes, rates of reaction, velocity coefficients, and energies of initiation, propagation, and termination have been determined at arbitrary intervals throughout each of the polymerisations examined. For the vinyl acetate/benzene systems transfer constants at several temperatures were measured and energies of activation for the transfer reaction were calculated.

Several very interesting facts have emerged. With as little as 5% v/v of benzene the gel effect, which gives an acceleration in rate followed by a decrease as conversion to polymer proceeds in the bulk polymerisation, was almost completely removed, while with a poor solvent, cyclohexane, the resulting coiling of the radical chains more than offset the large dilution effect. The overall energies of activation increased with the amount of benzene present and toluene was found, most unexpectedly, to retard the initial rate of polymerisation by the same amount as benzene.

It will be shown in the discussion that the commonly accepted explanation for the reaction between aromatic solvents and kinetic chain radicals, chain transfer, does not account for the experimental facts, nor can all of the more recent attempts to give a mathematical analysis of solution polymerisation be sustained in the face of experimentally derived results. From these it would appear that with aromatic compounds the retardation is due to an addition reaction, while chain transfer may also be occurring but not causing any retardation. Furthermore, when vinyl acetate is polymerised in the presence of toluene, it seems likely that free radical attack takes place at the ring as well as at the methyl group.

THE HISTORY OF POLYMERISATION

Although it is only within the last 30 years that the structure of high polymers has been determined the substances themselves have been known to chemists for more than a century.[1] The term polymerisation was coined by Berthelot[2] in 1866. No quantitative work was done, however, until Raoult[3-5] developed the cryoscopic method for determining molecular weight. The high molecular weights obtained by this method were explained by regarding high polymers as association compounds, and it was not until 1920 that chain formulae were proposed, by Staudinger[6], for polystyrene and paraformaldehyde as



$$\left(-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\underset{C_6H_5}{\underset{|}{CH}}- \right)_n$$

and

$$(-CH_2-O-CH_2-O-CH_2-O-)_n$$

respectively.

The molecular structure was finally confirmed by Carothers[7] with his work on condensation polymers. Since then progress has been rapid and the work in the last 20 years has been mainly concerned with the reaction kinetics and physical properties of the polymers. The reaction of vinyl monomers to form long chain addition products lends itself easily to investigation. The polymerisation can take place thermally or photochemically and by varying the amount of initiator present the rate of reaction can be altered to suit the particular set of conditions required.

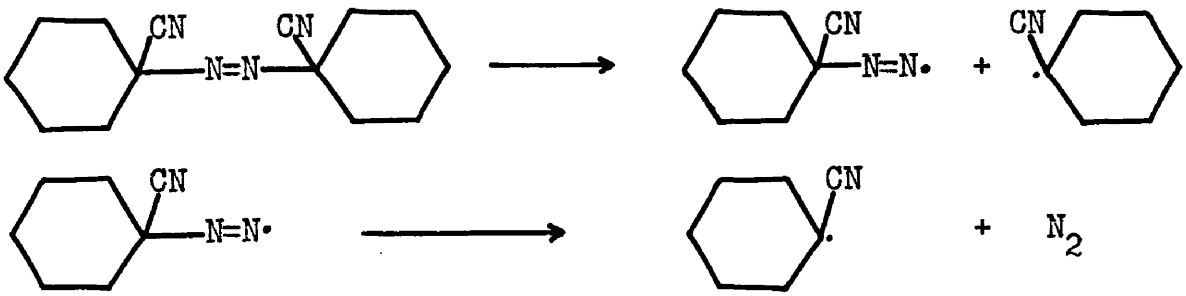
The Mechanism of Addition Polymerisation

Polymerisation of unsaturated compounds can take place either by an ionic or a free radical mechanism. Only the latter will be dealt with in this work. Any chain reaction proceeding by this means can be considered to take place in three basic steps, initiation, propagation, and termination. These, together with chain transfer, are summarized below.

Initiation.

The normal method of initiating a free radical polymerisation is to heat or irradiate with ultra violet light a solution of monomer containing a compound which will break down to produce free radicals. A variety of compounds will act as initiators in this way e.g. peroxides, azo and nitroso compounds. Not all monomers require the presence of an initiator however. Styrene will polymerise thermally alone, but the mechanism of initiation in these cases is complicated and not fully understood.

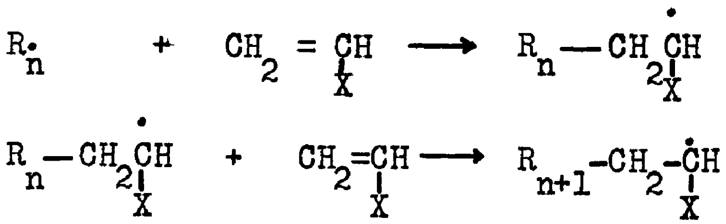
In this work 1:1' azo biscyclohexane carbonitrile (C.H.D.N.) was used as the initiator. The ultra violet light degrades it as follows:[8,9]



Not every radical produced initiates a chain. For azo compounds the efficiency of initiation (the fraction of initiator radicals that are successful in starting a chain) has been shown to lie between 0.5 and 1.0.[10,11,12].

Propagation

The free radicals produced by the decomposition of the C.H.D.N. add to molecules of monomer by opening the double bond of the vinyl group. Successive molecules of monomer then add to the free radicals produced in this way. The propagation reaction first proposed by Taylor and Bates,[13] and Staudinger[14] is



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

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

Where R• is a free radical and X is usually a polar group e.g. an acetate group in the case of vinyl acetate.

Chain Transfer

It is possible for a polymer radical to terminate by the abstraction of a hydrogen atom from a molecule. The free radical produced by the reaction reinitiates another chain. Under certain circumstances this reinitiation may not occur, causing retardation. For the purpose of this thesis the reactions will be termed chain transfer whether reinitiation occurs or not.

$$R\cdot \quad + \quad S \longrightarrow P \quad + \quad S\cdot$$

In bulk polymerisation S would be monomer molecule and in solvent polymerisation either a molecule of monomer or solvent.

Termination

A polymer chain radical can terminate either by combination with another polymer radical or by disproportionation.

Combination

$$\begin{array}{ccc} R_1-(CH_2CHX)_n-CH_{2\bullet}CHX & + & R_2-(CH_2CHX)_m-CH_{2\bullet}CHX \\ (A) & \downarrow & (B) \end{array}$$

$$R_1-(CH_2CHX)_nCH_2CHXCHXCH_2(CH_2CHX)_m-R_2$$

Disproportionation

$$\begin{array}{ccc} (A) & + & (B) \\ & \downarrow & \\ R_1-(CH_2CHX)_nCH{=}CHX & + & R_2-(CH_2CHX)_mCH_2CH_2X \end{array}$$

Kinetically the two reactions are similar, since in each the reactivity of two radicals is destroyed. Radioactive tracer techniques using C^{14} have shown that of the monomers studied, in most combination is the preferred reaction.[10,15].

Previous Work on Vinyl Acetate

The preceding section dealt with the principal free radical reactions involved in addition polymerisation. This scheme was built up over many years during which experimental techniques were gradually improved and developed to cope with the demand for more and more detailed knowledge of the various factors involved in reaction kinetics. Before the detailed analysis of these kinetics is given it would be useful to review the development of work on polymerisation, particularly with regard to vinyl acetate.

The nature of the molecules comprising poly vinyl acetate was recognised by Staudinger in 1927[16] who reported that it was made up of polymeric homologous compounds. The decrease in volume which accompanies the polymerisation was realised as providing a simple method of following the reaction and this enabled the kinetics of the stationary state to be investigated. The polymerisation of vinyl acetate in bulk was reported by Starkweather and Taylor[17] who found consistent unimolecular velocity coefficients while in toluene a progressive fall was observed. Other workers[18] showed that, in the benzoyl peroxide initiated reaction, the rate is proportional to the square root of the initiator concentration.

Much of this early work was characterised by induction periods before polymerisation commenced and oxygen was shown to have an inhibiting effect.[19] It was not at all certain whether this inhibition was a characteristic feature of the reaction or due to impurities. In most of this early work the vinyl acetate was purified by distilling in air then degassing in the dilatometer. The resultant monomer gave unreliable results and it was suggested, among other things, that the reaction might be heterogenious.[20]

In 1937 Flory[21] published an important paper in which he proposed that a chain transfer reaction could take place during polymerisation and showed that it was theoretically possible for occasional formation of branched polymer chains to occur. The chain transfer concept was subsequently developed mathematically by Mayo[22] to enable a "transfer constant" for any monomer/solvent system to be obtained. Later work by Flory[23,24] also showed that a 1.5 mole percentage of 1:2 glycol structures does occur in polyvinyl acetate and that at all temperatures above 0°C the steric factor is of greater importance than the energy term. This is because activation energy for the abnormal reaction is only 1.25 K Cals higher than the normal preferred addition while the steric factor for the abnormal addition is about 1/10th that for the normal addition.

The initiation reaction of thermal polymerisation was investigated by Cuthbertson Gee and Rideal[25] who found that freshly prepared vinyl acetate did not react, although it did so after standing in air, due they suggested, to the hydrolysis of the vinyl acetate to acetaldehyde followed by peroxidisation. In a later paper[26] the thermal polymerisation of vinyl acetate in bulk and in the presence of toluene was reported, a chain transfer reaction being suggested.

The question of the induction period was finally settled when improved experimental techniques resulted in purified vinyl acetate showing no induction period when polymerised thermally with benzoyl peroxide.[27]

An important advance in the work on polymerisation kinetics was the development of non stationary state methods which enabled lifetimes and individual velocity coefficients to be determined in photoinitiated reactions. These have been obtained for bulk vinyl acetate by workers using the dielectric constant[28], the rotating sector[29], the refractometric[30], the thermistor[31] and the thermocouple[32] methods.

Much work has been done on the chain transfer reaction. Nozaki[33], using results by Cuthbertson, Gee and Rideal, has calculated the transfer constant for the vinyl acetate/toluene polymerisation and since then Kapur and Joshi[34], and Palit and Das[35] have reported values for a large number of solvents.

The monomer transfer reaction, between a growing polymeric radical and a molecule of monomer has been shown by Ohsugi[36] and Wheeler, Ernst and Crozier[37] to take place on the methyl group of the vinyl acetate.

Attempts to determine the relationship between rate of reaction and monomer concentration, complicated by the gel effect and reaction between solvent and monomer, have been made by various workers. Conix and Smets[38] have reported a strong retardation of rate in benzene solution, due they say to transfer, and claim that the rate is proportional to $M^{3/2}$. More mathematical treatments of solution polymerisation have been published recently, based on the assumptions that copolymerisation, chain transfer and primary radical reactions are taking place.

Vinyl acetate is a difficult monomer to work with since any impurities present seem to have a lasting effect on the polymerisation instead of, as happens with most monomers, being eliminated in the initial stages of the reaction. Matsumoto and his coworkers[39] have polymerised vinyl acetate in the presence of likely impurities e.g. mono and di vinyl acetylene, and various aldehydes. Retardation was found to occur in most cases.

As will be seen from this summary although bulk vinyl acetate polymerisation has been examined by non stationary state methods and much solution polymerisation has been carried out, mainly to determine transfer constants, no work has been done to examine the solution polymerisation of vinyl acetate by non stationary state measurements over the entire range of conversion and determine the individual velocity coefficients and activation energies.

THE KINETICS OF ADDITION POLYMERISATION[40]

In normal additon polymerisation chain transfer does not occur to any great extent, thus although it will be detailed here it need not be considered in the kinetic analysis.

Let $[M]$ = Concentration of monomer

$[B]$ = Concentration of Initiator

$[R\cdot]$ = Concentration of polymeric radicals

I = Rate of initiation

k_p, k_{tr}, k_t = velocity coefficients of propagation, transfer and termination respectively.

It will be assumed that the reactivity of the terminal group is independent of the size of the molecules[41-43].

The reactions as outlined previously are -

INITIATION $M + B \longrightarrow R_1\cdot$ ....RATE $= I$

PROPAGATION $R_n\cdot + M \longrightarrow R_{n+1}\cdot$ ......RATE $= k_p [R\cdot][M]$

TRANSFER $R_n\cdot + M \longrightarrow P_n + R_1\cdot$ ...RATE $= k_{tr}[R\cdot][M]$

TERMINATION $R_n\cdot + R_m\cdot \longrightarrow P_{n+m}$ .....RATE $= k_t [R\cdot]^2$

When the stationary state has been reached the rate of production of radicals will equal the rate of removal.

$$\therefore \quad \frac{d[R\cdot]}{dt} = I - k_t[R_s\cdot]^2 = 0 \quad \ldots\ldots\ldots\ldots\ldots(1)$$

where $[R_s\cdot]$ = steady state concentration of radicals.

$$\therefore \quad [R_s\cdot] = \left(I/k_t\right)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

During the non stationary state the concentration of radicals is constantly altering,

$$\therefore \quad \frac{d[R\cdot]}{dt} = I - k_t[R\cdot]^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Integrating, $\frac{1}{2}(k_t I)^{-\frac{1}{2}} \quad . \quad \ln\left[\frac{I + (k_t/I)^{\frac{1}{2}}[R\cdot]}{I - (k_t/I)^{\frac{1}{2}}[R\cdot]}\right] = t + C..(4)$

$C = 0$ since $[R\cdot] = 0$ at $t = 0$

$$\therefore \quad \tanh^{-1}\frac{[R\cdot]}{[R_s\cdot]} = (k_t I)^{\frac{1}{2}} = \frac{t}{\tau} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

where τ = the lifetime of the kinetic chain. This will be referred to in future as "the lifetime".

From equation (5) $[R\cdot] = [R_s\cdot] \tanh \frac{t}{\tau} \ldots\ldots\ldots\ldots(6)$

For long chain polymers the rate of polymerisation equals the rate of propagation.

$$\therefore \quad \frac{-d[M]}{dt} = k_p[R\cdot][M] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

$$\text{i.e.} \quad \frac{-d[M]}{dt} = k_p[R_s\cdot][M] \tanh(t/\tau)\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Integrating equation 8 gives:-

$$-\ln\frac{[M]}{[M_o]} = \frac{k_p}{k_t} \quad . \quad \ln\left[\cosh\left(t/\tau\right)\right]\ldots\ldots\ldots\ldots(9)$$

If F is the fraction of monomer converted to polymer

$$\frac{[M]}{[M_o]} = 1 - F \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

FIGURE 1

THEORETICAL PLOT OF FRACTIONAL CONVERSION AGAINST TIME

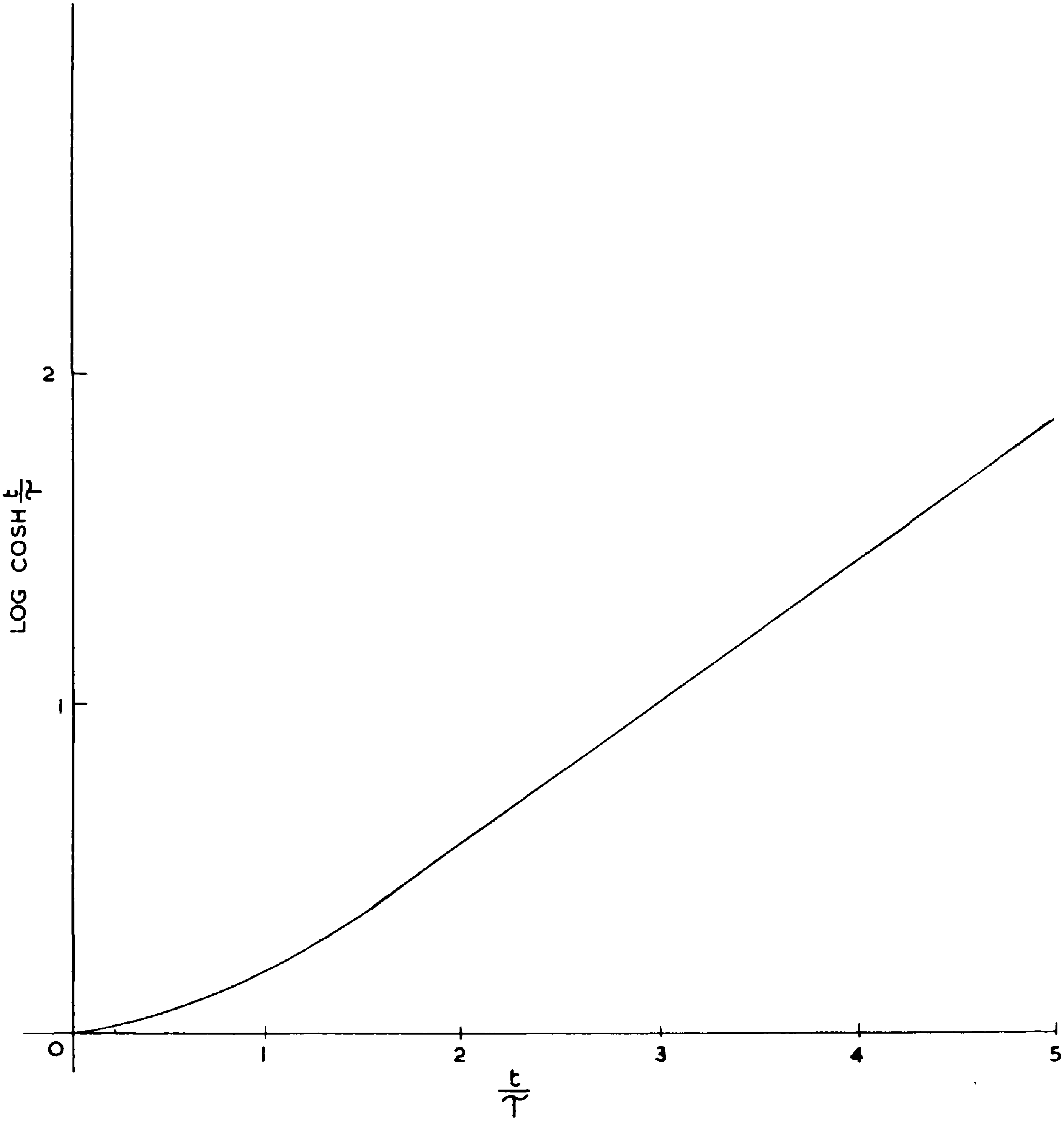
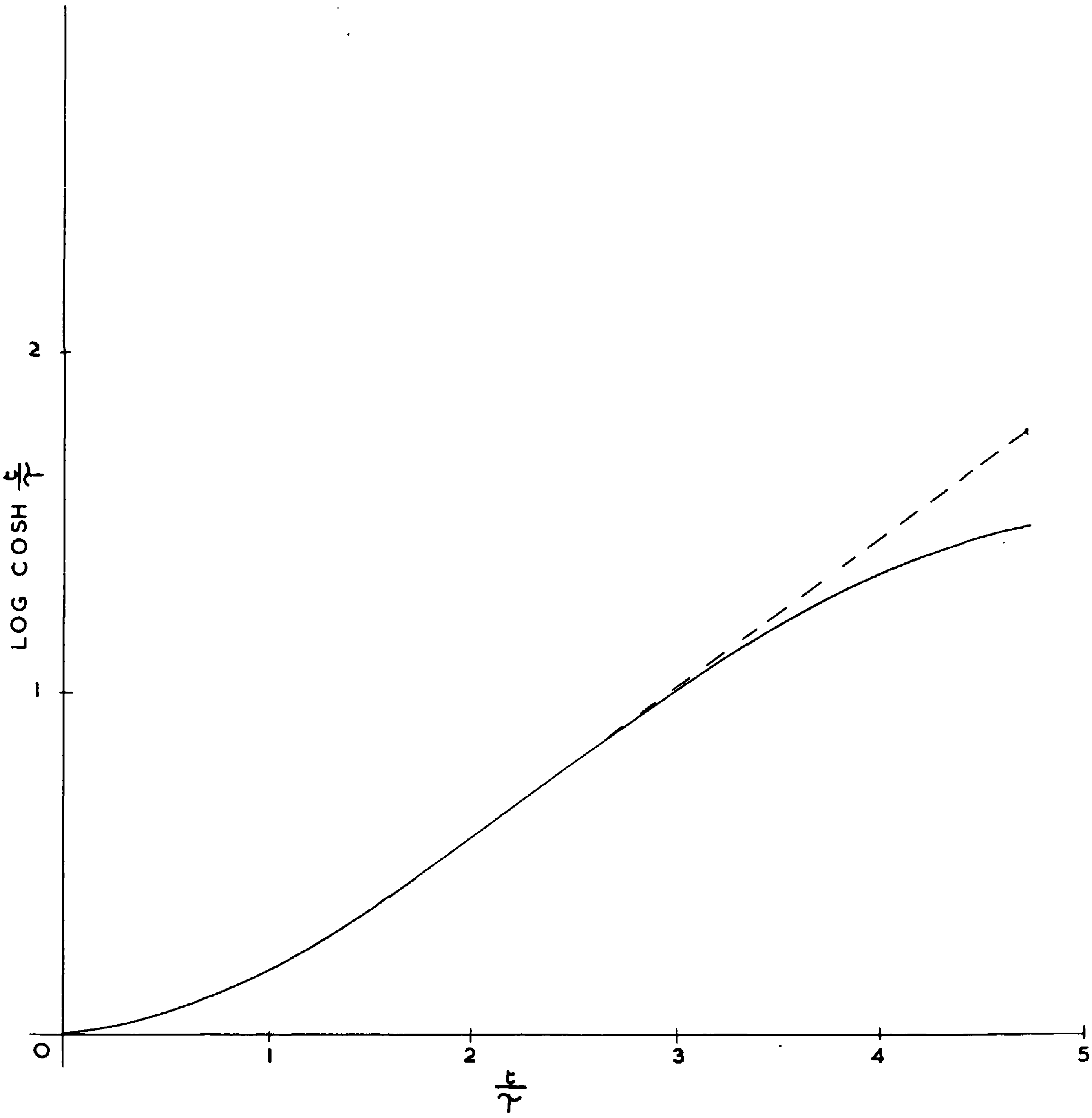


FIGURE 2

THEORETICAL PLOT OF FRACTIONAL CONVERSION AGAINST TIME

EFFECT OF NON ADIABATIC CONDITIONS.



If $F \ll 1$, $- \ln (1 - F) = F \ldots\ldots\ldots\ldots\ldots\ldots(11)$

$$\therefore F = k_p/k_t \left[\ln \left\{ \cosh t/\tau \right\} \right] \ldots\ldots\ldots\ldots\ldots\ldots(12)$$

Also when $t \gg \tau$, i.e. during the stationary state

$$F = k_p/k_t \cdot \left[t/\tau - \ln 2 \right] \ldots\ldots\ldots\ldots(13)$$

Plotting equation 13 gives a straight line of slope $\frac{k_p}{k_t}$ and intercept on the time axis $= \tau \ln 2$.

The lifetime can also be calculated from the decay curve obtained when illumination is stopped. When this happens the production of radicals by initiation ceases and the concentration of the radicals is reduced by termination.

$$\text{i.e.} \quad \frac{d[R\cdot]}{dt} = - k_t [R\cdot]^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

$$\text{Integrating} \quad [R\cdot] = [R\cdot_s] \Big/ \left[t/\tau + 1 \right] \ldots\ldots\ldots\ldots\ldots\ldots(15)$$

$$\therefore \quad F = k_p/k_t \left[\ln \left\{ t/\tau + 1 \right\} \right] \ldots\ldots\ldots\ldots(16)$$

The lifetime is obtained by graphing equation 16.

By stationary state rate measurements it is possible to determine the ratio of the velocity coefficients of propagation and termination. This can be done in two ways.

(1) From equation (2) $\left[R_s^{\cdot}\right] = \left(\frac{I}{k_t}\right)^{\frac{1}{2}}$

$\therefore$ Rate of Reaction = $k_p \left[R\cdot\right]\left[M\right] = k_p/k_t^{\frac{1}{2}} \cdot \left[M\right] I^{\frac{1}{2}}$ ......(17)

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

(11) The intercept on the time axis of the straight line portion of the fractional conversion against time curve is $\Upsilon \ln 2$, therefore if the system has an instrument lag of C secs. the equation for relating rate and measured intercept can be written as

$$\frac{1}{\text{Rate}} = \left(k_t/k_p\right) \cdot \frac{X}{\ln 2} + C \text{ ....(18)}$$

By plotting the reciprocal of the rate against the measured intercept, a straight line is obtained of slope $\frac{k_t}{k_p \ln 2}$ and intercept on the time axis = C.

From equation 5 $\Upsilon = \frac{1}{(k_t I)^{\frac{1}{2}}}$

k_t is obtained for this, and hence the ratio k_p/k_t being known, k_p can be obtained.

This analysis of the kinetics of addition polymerisation is based on the reactions known to take place in the bulk polymerisation i.e. where the pure monomer is being polymerised. In the presence of a retarder it is possible for chain termination to occur by reaction between a polymeric radical and a molecule of retarder giving first order termination. If second order termination is taking place at the same time the result is what is referred to as mixed order termination. This will create errors in the kinetics and the following section deals with the corrections necessary to allow for this.

Kinetic Analysis of Mixed Order Termination.

When a mixed order termination occurs in a polymerisation it has been the custom to assume second order kinetics. The only available method for correcting for the mixed order is that used by Burnett & Wright[44] for the rotating sector. Even this is not entirely satisfactory since it is difficult to apply to the later stages of homogeneous polymerisation or to heterogeneous polymerisation.

The following method devised by Bengough[45] eliminates the errors due to the assumption of second order kinetics by introducing a correction factor.

The kinetic scheme is:

Initiation	$B + h\nu \longrightarrow C$	Rate = I
	$C + M \longrightarrow R\cdot$	
Propagation	$R\cdot + M \longrightarrow R\cdot$	Rate = $k_p[R\cdot][M]$
Mutual Termination	$R\cdot + R\cdot \longrightarrow$ polymer	Rate = $k_t[R\cdot]^2$
Monomer Termination	$R\cdot + M \longrightarrow$ polymer	Rate = $k_m[R\cdot][M]$
Retarder Termination	$R\cdot + Q \longrightarrow$ polymer	Rate = $k_q[R\cdot][Q]$
Occlusion Termination	$R\cdot + ? \longrightarrow$ polymer	Rate = $k_o[R\cdot][?]$

where $R\cdot$ = a growing polymer radical

B = a molecule of initiator

C = a radical from the initiator

M = a molecule of monomer

Q = a molecule of a retarder

The constants k_p, k_t, k_m, k_q, k_o are the reaction velocity coefficients for the various stages in the reaction.

The rate of increase in concentration of growing polymer radicals is given by

$$\frac{d[R\cdot]}{dt} = I - [R\cdot]\left\{k_m[M] + k_q[Q] + k_o[?]\right\} - k_t[R\cdot]^2 \qquad \ldots(19)$$

$$= I - [R\cdot]X - k_t[R\cdot]^2$$

$$\text{where } X = k_m[M] + k_q[Q] + k_o[?] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(20)$$

In the steady state $\frac{d[R\cdot]}{dt} = 0$

$$\therefore [R_s\cdot]^2 + [R_s\cdot]\cdot X - I = 0$$

$$\therefore [R_s\cdot] = -\frac{X}{2k_t} + \left[\left(\frac{X^2 + 4Ik_t)}{4k_t^2}\right]^{\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots\ldots(21)$$

$$= -\beta + \alpha$$

$$\text{where } \alpha = \left[\left(\frac{X^2 + 4I\,k_t)}{4\,k_t^2}\right]^{\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(22)$$

$$\beta = \frac{X}{2\,k_t} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(23)$$

Integrating equation (21) over the period 0 to t, with the radical concentration changing from 0 initially to R at time t gives

$$\alpha^{-1}\tanh^{-1}\left[([R\cdot] + \beta)/\alpha\right] = \alpha^{-1}\tanh^{-1}(\beta/\alpha) + k_t.t \qquad \ldots\ldots(24a)$$

Rearranging

$$R = -\beta + \alpha\tanh\left[\alpha k_t.t + \tanh^{-1}(\beta/\alpha)\right] \qquad \ldots\ldots\ldots\ldots(24b)$$

The Rate of Polymerisation is

$$-\frac{d[M]}{dt} = k_p[R\cdot][M] \quad \ldots\ldots\ldots\ldots\ldots\ldots(25)$$

Substituting for $[R\cdot]$ from equation (24b) in equation (25)

$$-\frac{d[M]}{dt} = k_p[M]\left[-\beta + \alpha\tanh\left\{\alpha k_t t + \tanh^{-1}(\beta/\alpha)\right\}\right]$$

Integrating over the range 0 to t gives

$$\ln\left\{[M_o]/[M]\right\} = k_p\left[-\beta t + k_t^{-1}\ln\left\{\cosh(\alpha k_t.t) + \alpha^{-1}\beta\sinh(\alpha k_t.t)\right\}\right] \ldots(26)$$

where $[M_o]$ is the concentration of monomer initially and

$[M]$ is the concentration of monomer at time t.

For values of $t \gg (\alpha k_t)^{-1}$ we get from equation (26)

$$\ln\left\{[M_o]/[M]\right\} = k_p(\alpha-\beta)t - (k_p/k_t)\ln\left\{2\alpha/(\alpha+\beta)\right\} \quad \ldots\ldots\ldots(27)$$

and Since $\ln\left\{[M_o]/[M]\right\} = -\ln(1-F) \ldots\ldots\ldots\ldots\ldots\ldots(28)$

where F is the fractional conversion of monomer to polymer

When $F \ll 1 \quad -\ln(1-F) \triangleq F \quad \ldots\ldots\ldots\ldots\ldots\ldots(29)$

Equation (27) then becomes

$$F = k_p(\alpha-\beta).t - (k_p/k_t)\ln 2\alpha/(\alpha+\beta) \quad \ldots\ldots\ldots(30)$$

This is a straight line which intercepts the time axis (at F = 0) giving an intercept t_i :-

$$t_i = \ln\left\{2\alpha/(\alpha+\beta)\right\} \Big/ k_{t/(\alpha-\beta)} \quad \ldots\ldots\ldots\ldots(31)$$

A second equation relating α and β with measured quantities is obtained from the intensity exponent.

The intensity exponent (n) is usually determined from the gradient of the curve relating log (rate) against log (intensity)

$$\text{i.e.} \qquad n = \frac{d(\log \text{rate})}{d(\log \text{intensity})}$$

Now the rate is proportional to $[R_s \cdot]$ and the intensity of irradiation to I (the rate of initiation)

$$\therefore \qquad n = \frac{d(\ln [R_s \cdot])}{d [R_s \cdot]} \cdot \frac{d [R_s \cdot]}{d I} \qquad \frac{d\, I}{d(\ln I)}$$

$$\therefore \qquad n = \frac{I}{2[R_s \cdot] \alpha . k_t} = \frac{I}{2k_t \alpha(\alpha - \beta)} \qquad \text{.........(32)}$$

Squaring equation (32) and substituting for α and β from equations (22) and (23) gives

$$X^2 = \frac{(2n-1)^2}{n(1-n)} \cdot I \cdot k_t \qquad \text{.........................(33)}$$

which relates X to k_t in terms of the measurable quantities n and I.

By using the substitution $\alpha = p\beta$ where p is any integar or fraction, equations (31) and (32) can be solved to give

$$X = \frac{(2n-1)}{(1-n)t_i} \qquad \ln({}^1/n) \qquad \text{.........................(34)}$$

This means X is now given in terms of n and t_i which can be obtained experimentally.

Substituting for X in equation (33) and solving for k_t we get

$$k_t = \frac{n\left\{\ln(1/n)\right\}^2}{(1-n)t_i^2\,(I)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(35)$$

Thus both k_t and X can be calculated from experimental measurements.

Once X, I and k_t are known, k_p can be calculated since

$$k_p = \frac{\text{rate}}{[R_s^{\cdot}][M]}$$

$$\therefore \quad k_p = \text{rate}/[M]\left[-\frac{X}{2k_t} + \left\{\frac{(X^2 + 4Ik_t)}{4\,k_t^2}\right\}^{\frac{1}{2}}\right] \ldots\ldots\ldots(36)$$

Solving for k_p in terms of the intensity exponent gives

$$k_p = \frac{\text{rate}}{\left(\frac{I}{k_t}\right)^{\frac{1}{2}}[M]} \cdot \left[\frac{n}{1-n}\right]^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(37)$$

Correction for the 2nd Order Termination Assumption

Let k_t' be the calculated value of the coefficient of termination assuming complete second order termination

$$\text{Thus} \quad k_t' = \frac{(\ln 2)^2}{I.t_i^2}$$

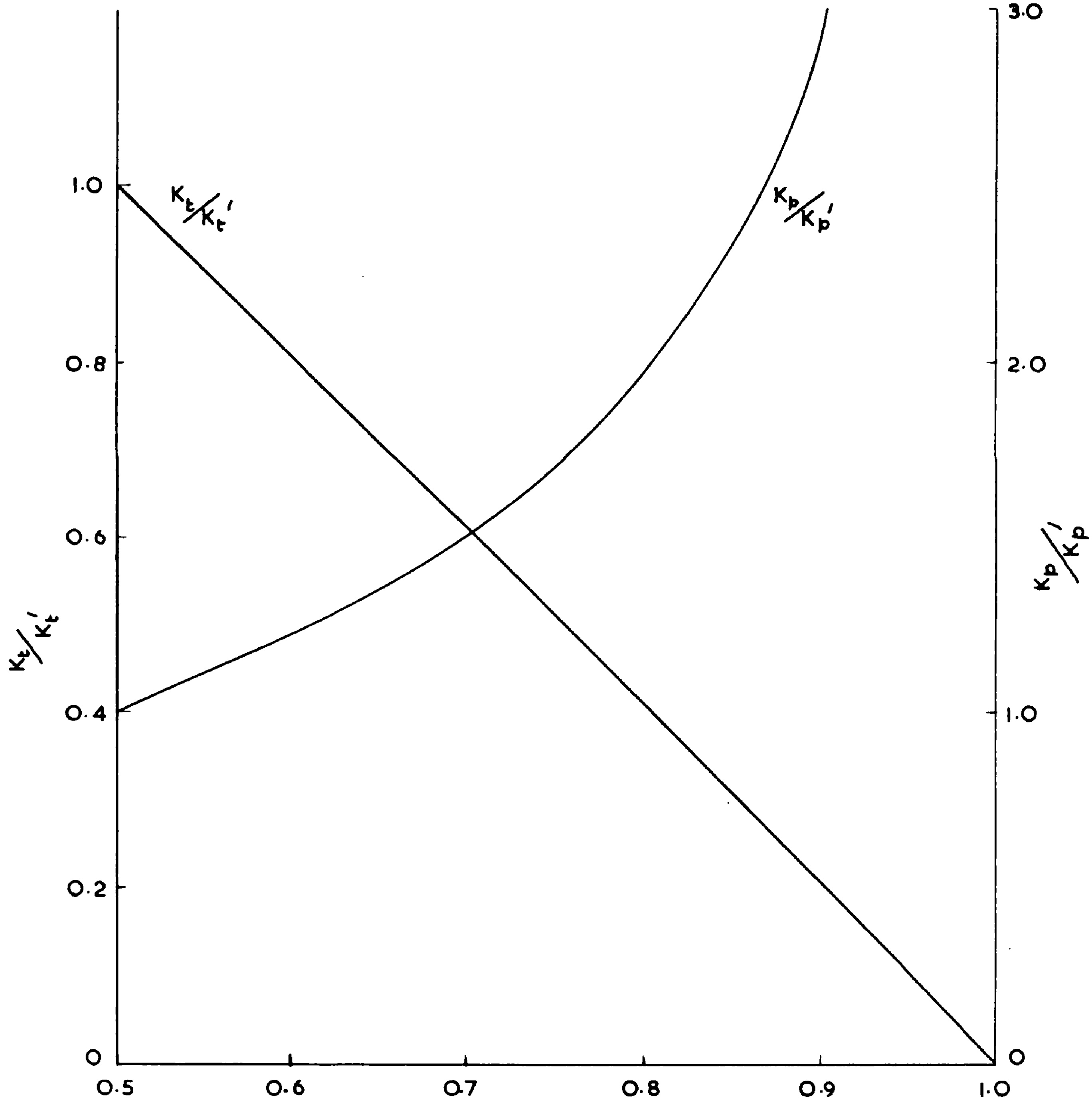
The correct value of k_t was given by equation (35)

The correction factor is, therefore, k_t/k_t'

FIGURE 3.

MIXED ORDER TERMINATION CORRECTION

FACTORS FOR K_p AND K_t



INTENSITY EXPONENT

The correction factor, $k_t/k_t{}'$ $= \dfrac{n\left\{\ln({}^1/n)\right\}^2.(I)t_i{}^2}{(1-n)t_i{}^2.(I).(\ln 2)^2}$

$$= \frac{n\left\{\ln({}^1/n)\right\}^2}{(1-n)(\ln 2)^2} \quad \ldots\ldots\ldots\ldots(38)$$

The correction factor for k_p is given from equation (37) as

$$k_p/k_p{}' = \left[\frac{n}{(1-n)}\right]^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots(39)$$

Thus equations (38) and (39) give a value for the correction factor calculated solely on the basis of the intensity exponent. The correction factors for various values of n are given in figure (3).

Non Stationary State Methods for Measuring the Kinetics of Vinyl Polymerisation.

The non stationary state period in a free radical reaction is not suitable for investigation by normal chemical means since it lasts for only a brief period of time. The physical changes brought about by the reaction must then be used as a basis for determining lifetimes and it is the particular physical properties measured which distinguish between the different methods.

Rotating Sector Method[46,47]

A reaction vessel in a thermostatic tank is subjected to intermittent illumination from a mercury vapour lamp. The periods of light and dark are governed by the size of the remaining segment of a rotating disc situated between the lamp and the reaction vessel, and the speed of rotation of the disc. By measuring the rates of reaction, by contraction measurements during continuous irradiation, over a range of sector speeds it is possible to calculate the lifetimes. During each determination the polymerisation advances an appreciable extent. This can, however, be reduced by using a modification of the technique in which the rate is measured as a function of the initial expansion when the reaction mixture is irradiated under adiabatic conditions.[48]

The rotating sector method is not suitable for use when first order termination of the reaction is occurring since the rate is independent of the flash time under these conditions.

Refractometric Method[30,49].

It was originally intended to measure the change in the refractive index of the reaction mixture as it changes from monomer to polymer. It was found that the variation in refractive index due to heating effects was much greater than was caused by the polymerisation. Since isothermal conditions were virtually impossible to achieve the change due to temperature rise caused by polymerisation under adiabatic conditions was measured instead. A correction was applied to allow for the alteration in refractive index due to polymer formation.

A Hilger interferometer with the interferometer tubes serving as reaction vessels was used, and the movement of fringes with time across an eyepiece noted while irradiation was taking place. By using a photoelectric recording technique a temperature change of 10^{-4} °C in 10^{-2} seconds could be detected.

The method is not suitable for use beyond the gel stage since specially designed tubes are required which are not expendable. The operating difficulties are considerable. The focal plane of the fringes tends to change causing a decrease in the intensity of the fringes. The axis of the fringes begins to rotate and fringe width changes since it is a function of the separation of the virtual sources. The method has the advantage over the rotating sector method that individual determinations can be carried out quickly.

Dielectric Constant Method[28]

As with the previous method it was intended to measure the change in a physical property, dielectric constant, as polymer was formed from monomer, and it was then found more convenient to measure the temperature rise under adiabatic conditions in terms of the variation in dielectric constant. Quartz reaction vessels are used with the result that the method is unsuitable for use with solidified reaction mixtures. The recording instrument is either a voltmeter or an oscilloscope giving a resolution of 10^{-5} ^{0}C in 10^{-4} seconds.

The applications are limited by the fact that the rate of reaction must be more than 0.4%/hr: the lifetime must not be more than a few seconds, and the quantum efficiency "has to be reasonably high, not less than 0.2 for chain lengths of 1000."

When the reaction is irradiated the measured change in dielectric constant is made up of a decrease due to heat of irradiation; a decrease due to heat of polymerisation during irradiation; a permanent increase due to polymer formed during irradiation; and a permanent increase due to "dark rate" polymerisation. Since only one of these gives the correct rate of reaction a large number of corrections must be applied.

Thermistor Method[50]

The thermistor method represents a variation of the thermocouple method used in this work. It was found necessary in the two previous methods to measure, indirectly, temperature rise as a function of rate of reaction. It is obviously better, and as it happens, simpler, to measure the temperature rise directly. The measuring device is a glass coated thermistor which records the adiabatic temperature rise at the centre of the reaction mixture when polymerisation takes place. A greater temperature sensitivity is claimed than that obtained using the thermocouple but this is offset by the greater difficulty in calibration.

The Thermocouple Method[51]

The principle on which the method is based has already been explained for the thermistor method. A thermocouple of negligible size and heat capacity is situated at the centre of a reaction vessel in which the rate can be measured dilatometrically if required. When the reaction takes place the temperature rise at the junction of the two dissimilar metals of the thermocouple results in an electromotive force being set up. The relationships between electromotive force and temperature are available in the literature and, providing the signal can be amplified sufficiently to enable it to be measured, the rate of reaction is easily obtained.

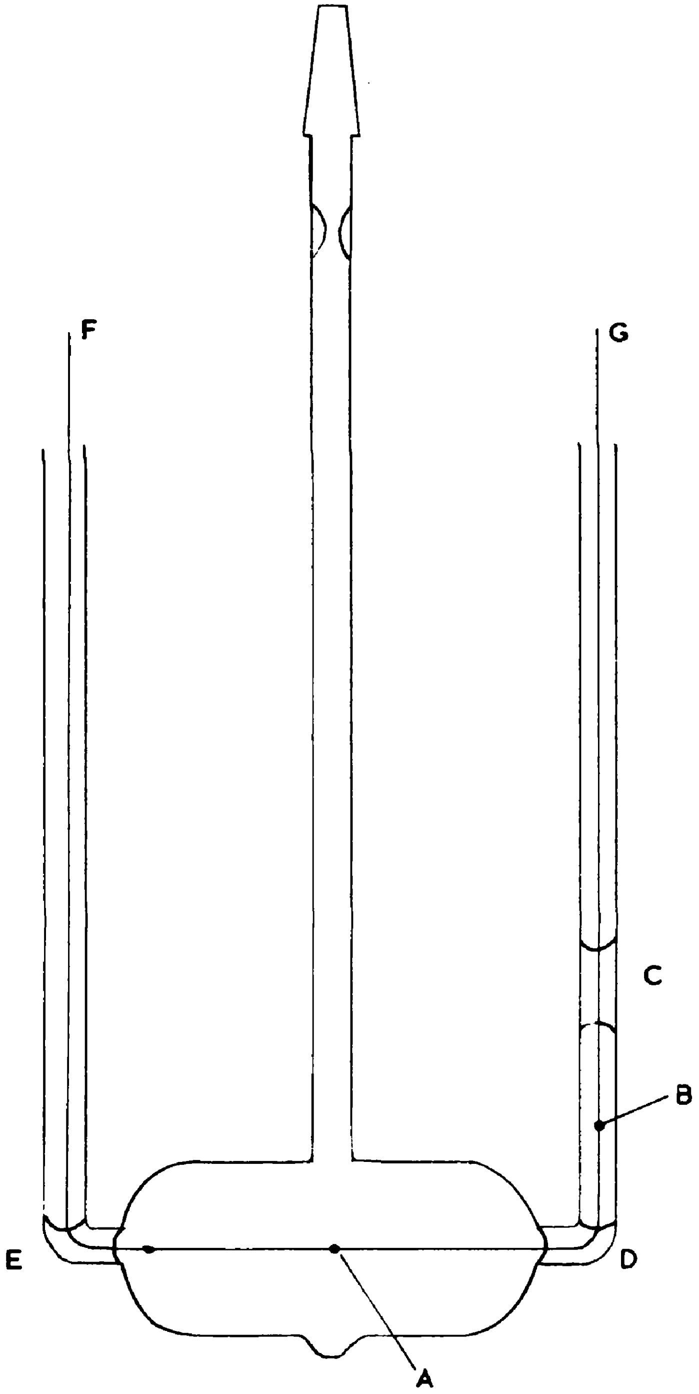
The reaction vessels are easily made and are expendable so that the method is very suitable for investigating the gel effect. During this period in the polymerisation the centre of the reaction vessel stays adiabatic for longer periods than it does initially, due to convection cooling being reduced, so that correspondingly longer lifetimes can be measured with accuracy. The fact that it is the temperature at the centre of the reaction which is being measured gives the thermocouple an advantage over the refractometric, dielectric constant and modified rotating sector methods. Although it is assumed in those that adiabatic conditions exist throughout the mixture there must obviously be considerable surface cooling effects making the apparent temperature rise less than it actually is. Unless the reaction vessels are vacuum jacketted these methods will contain this inherent error.

A simple dilatometric method[52,53] has been devised which uses the decay curve obtained in the period immediately following the end of irradiation. The cooling effects are allowed for and it provides a useful method of investigating the initial stages of polymerisation.

FIGURE 4

THERMOCOUPLE METHOD

DILATOMETER



EXPERIMENTAL

APPARATUS

The apparatus consisted of a reaction vessel with built in thermocouples, a constant temperature bath, an amplifier and a recording voltmeter. A mercury vapour lamp supplied ultra violet radiation.

The reaction vessel was a soda glass dilatometer with two side arms in addition to the normal stem (fig.4).

The thermocouple system which consisted of one situated at the centre of the dilatometer and a second cold junction thermocouple in the side arm, was made by brazing together copper and constantan wires with silver solder to give point contact. It was necessary to seal the copper wire into the glass at E and C to give vacuum tight joints and in order to achieve this, borated copper clad iron wire had to be brazed to the 2 m.m. copper wire used to make the thermocouple at A. The thermocouple B was made by brazing the borated copper clad iron wire directly to the 2 m.m. constantan wire.

In preparing the dilatometer for filling, the wire FG was threaded through the dilatometer and with the thermocouples in the correct position the constrictions at E and C were collapsed to give a vacuum-tight seal. It was then attached to the high vacuum system through a cone and socket joint and evacuated. The constriction at D was collapsed about the constantan wire. The dilatometer was now ready for calibration and was kept under vacuum until required since the seal D, although liquid tight, was not airtight.

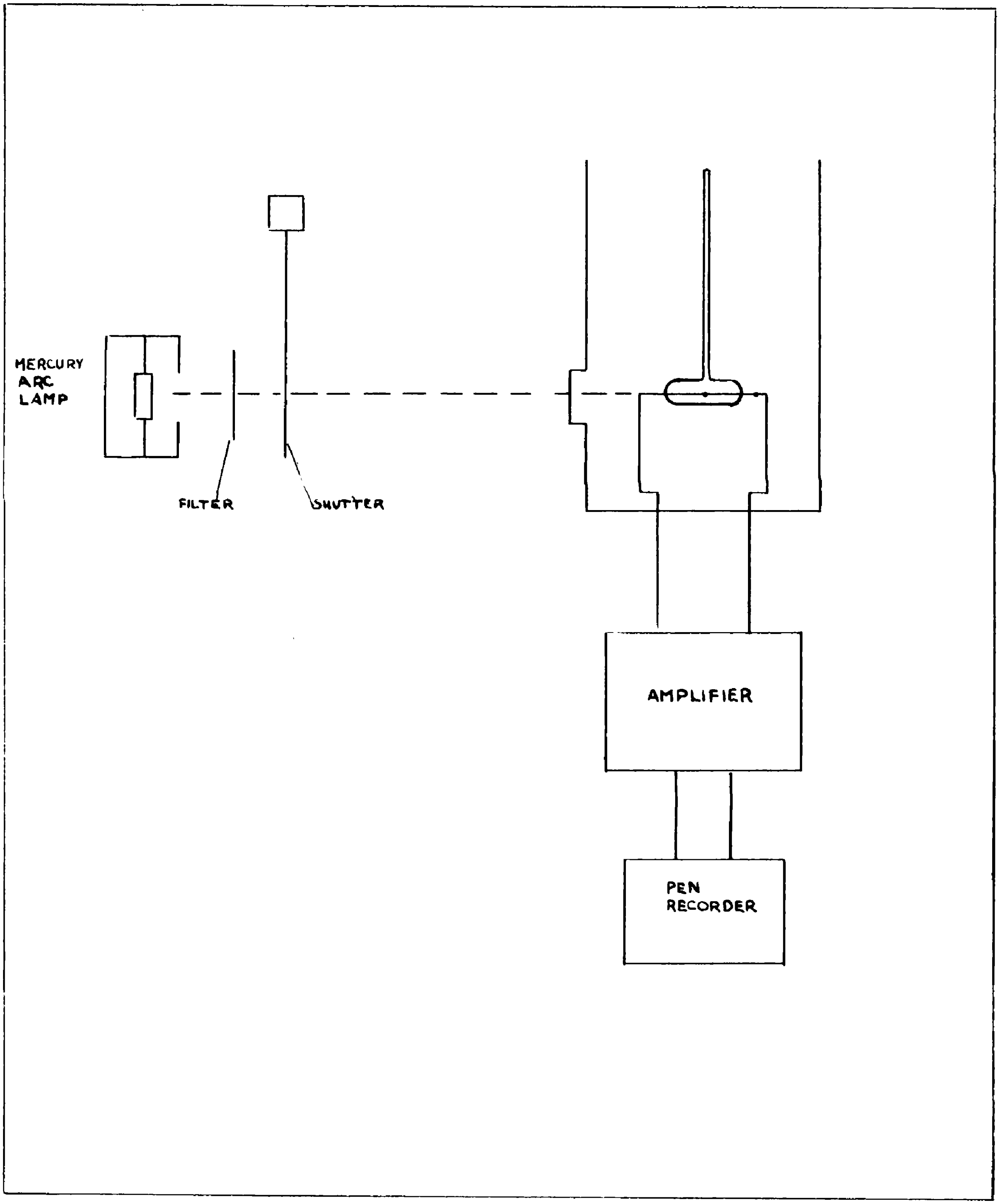
The water bath was made of pyrex and lagged with an expanded ebonite base and lid, and fibre glass round the sides. A mercury/toluene regulator operated a low power heater to give temperature control of about 0.005°C, even temperature distribution being ensured by vigorous stirring. A larger 2 KW heater was used to raise the bath temperature when required.

The amplifier was the 5132 Tinsley D C type designed for an input impedance of less than 10 ohms. It was particularly suitable for this work since it gave a voltage amplification of more than 10^6. E m fs of up to 400μvolts in the input circuit could be balanced out by coarse and fine balance controls. This meant that temperatures of up to 10°C could be measured, enabling the continuous polymerisation to be followed.

The temperature rise was calibrated by means of a test signal varying from 0.01μvolts to 100μ volts as required. The output circuit, designed for a 500 ohm load, gave a current of up to 10 m.amps.

FIGURE 5

DIAGRAM OF THERMOCOUPLE CIRCUIT



A 125 watt Osira mercury arc lamp, stabilised with a constant voltage transformer, provided the source of the ultra violet light for the photochemical reaction. Thermal radiation effects on the thermocouple, and radiations outwith the range 3000 - 4000A°, were cut out by a Chance OXI filter.

A quick moving shutter operated by an electromagnet was placed between the lamp and the reaction vessel.

An Elliot pen recording D.C. voltmeter gave a chart trace of the output signal from the amplifier. A clutch mechanism enabled the chart speed to be quickly altered from 12 inches per minute to 12 inches per hour.

An all glass high vacuum system was constructed with an Edwards oil pump backed by a Speedivac mercury diffusion pump. A vacuum of 10^{-5} mm. of mercury could be obtained.

EXPERIMENTAL PROCEDURE

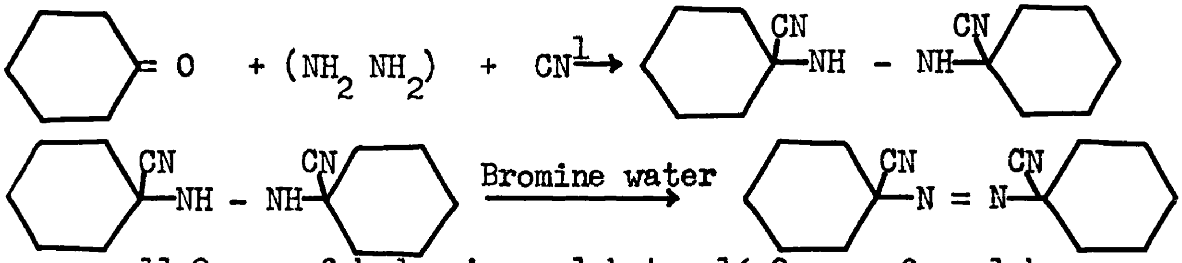
Purification of Monomer

Vinyl Acetate supplied by the Shawinigan Chemical Corporation was distilled in a 6 ft. vacuum jacketted column, packed with wire gauze rings, and giving a high reflux ratio. Distillate was taken over a very narrow boiling range (72.2 - 72.3°C) and washed with 5% sodium carbonate several times, then with water, and finally dried overnight by standing over calcium chloride. It was then filtered through a column of calcium chloride and distilled under high vacuum into a flask containing initiator. The distillation process served to degas the vinyl acetate which was polymerised to about 5% conversion by ultra violet light, distilled into a second flask and once more polymerised to about 5% conversion. It was kept at a temperature of -75°C under vacuum until required.

This rather elaborate procedure was necessary to remove all traces of impurity from the vinyl acetate.

The more normal purification procedure used for most monomers consists of distillation followed by one prepolymerisation. Preliminary experiments on vinyl acetate purified in this way showed a considerable degree of mixed order termination even when there was no apparent retardation of the polymerisation. On examining the purity of the vinyl acetate after distillation by vapour phase chromatography small traces of acetic acid were found. The sodium carbonate wash was intended to remove this. 5% sodium hydroxide was used to wash the monomer initially. The polymerisation was strongly retarded in this case, due presumably to hydrolysis of the vinyl acetate. The double prepolymerisation was simply an added precaution against impurities.

Preparation of 1:1' azo bis cyclohexane carbonitrile[54] (C.H.D.N.).



11.9 gm. of hydrazine sulphate, 16.2 gm. of cyclohexanone and 12 gm. of potassium cyanide were mixed in aqueous solution for two days. The disubstituted hydrazine separated out as a yellow solid and was filtered off and mixed with 25 ml ethanol and 50 ml dilute hydrochloric acid. The mixture was cooled in melting ice, bromine water being slowly added with vigorous stirring.[55] The product which separated out as a white solid was recrystallised from 95% ethanol to a constant M Pt. of 115°C.

Impure C.H.D.N., under the trade name Genitron C.H.D.N., was kindly supplied by Whiffen and Sons, and purified by recrystallisation.

Initiator Solutions

Preliminary experiments using normal stationary state dilatometric measurements indicated that an initiator concentration of 4×10^{-3} moles/litre would be required to give an initial rate of reaction of about 10%/hr. for bulk vinyl acetate. The solution made up in freshly distilled chloroform was kept in the dark when not required. In spite of this precaution some decomposition still took place, and fresh solutions were made up every few weeks.

Filling the Dilatometer

When the dilatometer was required for use the construction at D (fig.4) was collapsed under high vacuum isolating the thermocouple B. The dilatometer was then calibrated by determining its volume using spectroscopically pure benzene. The benzene was removed and the calculated quantity of initiator introduced in a solution of chloroform which was then pumped off under vacuum. It was necessary to complete these operations quickly in case air should leak past the seal D.

In most experiments it was necessary to introduce solvent into the dilatometer. This was done using a micro pipette or a micrometer syringe for very small quantities. The solvent was then degassed by repeated freezing, evacuating

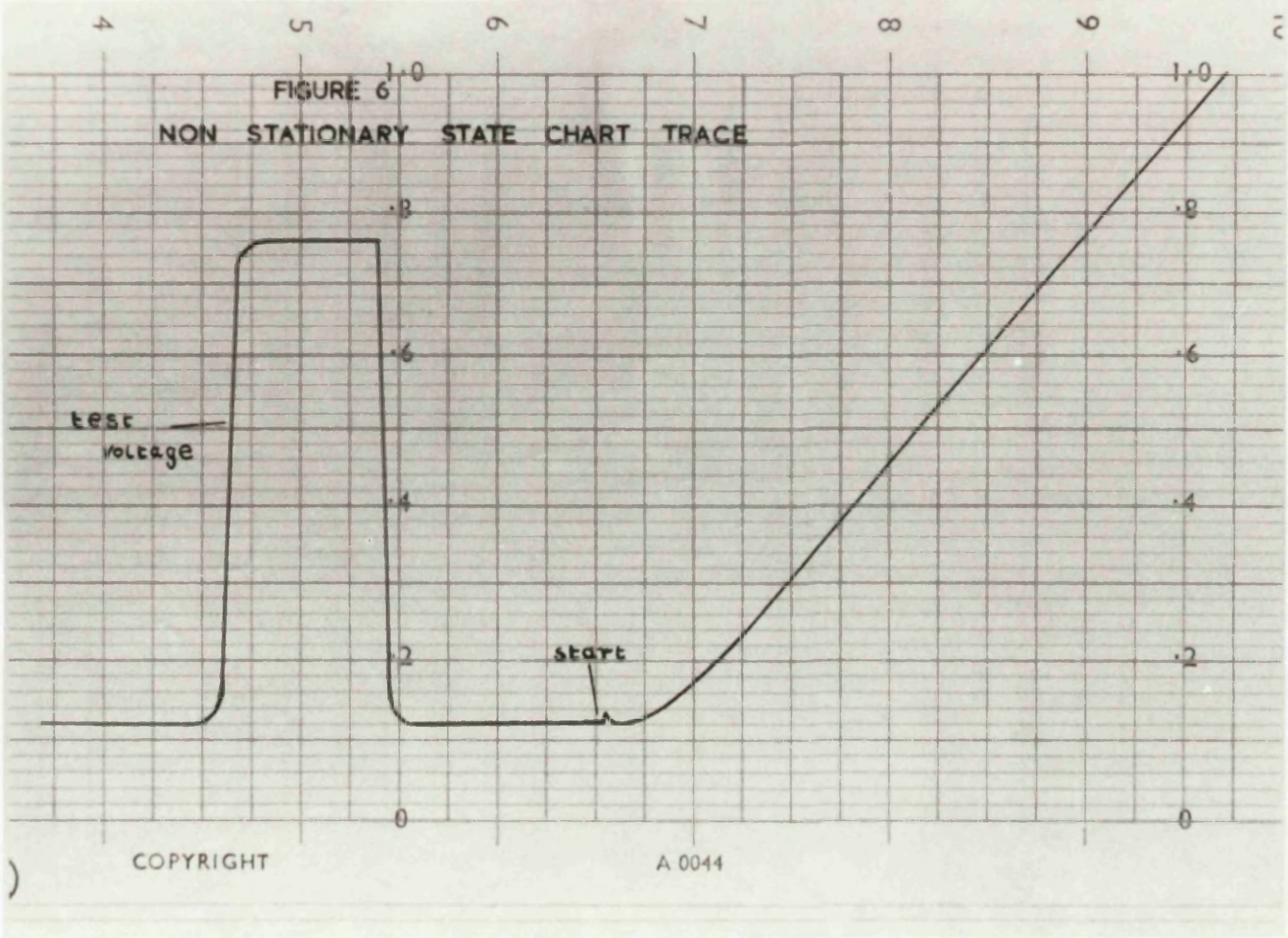


FIGURE 6

NON STATIONARY STATE CHART TRACE

and heating to room temperature.

Purified monomer, stored on the line, was distilled into the reaction vessel to a predetermined level and the dilatometer sealed off.

Non Stationary State Experimental Technique

Narrow rubber tubes were slipped over the side arms to prevent water entering, the leads F and G were soldered to screened leads from the amplifier input and the dilatometer was immersed in the water bath. The mercury arc lamp and the amplifier were switched on and left for 30 minutes to warm up, by which time the reaction mixture had reached thermal equilibrium.

With a chart speed of 12 inches/minute a known test voltage was put through the circuit for 5 seconds to calibrate the system at the desired amplification. The water bath stirrer was switched off and the reaction started immediately by actuating the electromagnet to pull the shutter aside. The rise in temperature of the reaction mixture was observed on the pen recorder and when a steady rate of increase was reached the shutter was replaced, stopping the reaction.

From the chart trace the rate of reaction and lifetime of the kinetic chain radical were obtained at one temperature and light intensity. The procedure was repeated for different light intensities and temperatures, each determination being repeated at least once.

It was found that to do a complete investigation of a polymerisation took several weeks. In order to cut down the dark rate the dilatometer was kept in an acetone/drikold mixture over the weekend, and overnight where a set of experiments had not been completed at a given conversion.

NOTE

Gel Effect

In most polymerisations the rate of reaction increases up to about 50% conversion. This autoacceleration, or gel effect, varies greatly with the monomer and the experimental conditions. Methyl methacrylate shows a pronounced increase in rate, while in vinyl acetate the effect is comparatively slight. The explanation for the gel effect, first suggested by Norrish and Smith[56] and developed by Trommsdorff. et al.[57] and Schulz[58] is that the rate of termination is progressively reduced during the initial stages of the reaction. Since the rate of propagation remains constant, the rate of reaction increases.

More recent work has shown that the autoacceleration stops at some stage in the reaction and the rate starts to fall. This is due to a reduction in the rate of propagation caused by monomer diffusion becoming controlled. Although originally the gel effect was only regarded as the autoacceleration, for the purposes of this thesis it will be expanded to include the reduction in rate which takes place in the later stages of the reaction.

EXPERIMENTAL

RESULTS

I. The Polymerisation of Vinyl Acetate.

The extent conversion was followed dilatometrically until gelling distorted the meniscus. Thereafter it was calculated from the measured rate of reaction and the known dark rate. The accuracy of the final estimated conversion was checked by weighing a thin slice of the polymer, pumping off the residual monomer overnight and reweighing. This showed that the error in estimating the final extent conversion was no more than 5%.

The initiator concentration was 4×10^{-3} mole.1^{-1}.

Table 1. Variation of rate and lifetime with extent conversion at 25°C and full light intensity (Instrument lag = 1.3 sec.)

Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
5	9.4	1.6	0.5
10	9.7	1.8	0.6
20	11.0	1.85	0.8
30	13.5	1.9	0.9
40	15.8	2.0	1.0
50	18.5	2.9	2.3
60	16.5	4.0	3.8
70	15.0	4.5	4.5
80	8.5	8.7	10.6

Table 1 shows that the rate of reaction increases to a maximum at about 50% conversion then falls off rapidly due to the expected gel effect. This also accounts for the rise in the lifetimes with extent conversion.

Table 2. Variation of rate and lifetimes with extent conversion at 25°C and at a reduced light intensity.

Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
5	5.0	2.0	1.0
10	5.2	2.1	1.2
20	5.8	2.2	1.3
30	7.2	2.3	1.5
40	8.4	2.6	1.9
50	9.8	3.8	3.6
60	8.3	6.1	6.9
70	6.7	6.5	7.5
80	2.8	13.3	17.3

Table 2 shows that the variations of rate and lifetime are parallel to those at the higher light intensity. The decrease in the rate of reaction and increase in the lifetimes agree with the derived kinetics of the reaction.

Table 3. Variation of rate and lifetime with extent conversion at 35°C and full light intensity.

Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
5	12.3	1.8	0.7
10	12.8	1.85	0.8
20	13.3	1.85	0.8
30	16.7	1.85	0.8
40	19.3	1.85	0.8
50	21.4	2.2	1.3
60	21.3	3.45	3.1
70	17.2	3.5	3.2
80	10.1	6.8	7.9

The variation of the rate and lifetimes is seen from Table 3 to be not so pronounced at the higher temperature as it was at 25°C.

Table 4. Variation of rate and lifetime with extent conversion at 45°C and full light intensity.

Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
5	17.4	1.6	0.4
10	17.6	1.65	0.5
20	17.8	1.75	0.7
30	19.7	1.8	0.8
40	20.5	1.8	0.8
50	24.0	2.1	1.2
60	22.5	2.8	2.1
70	21.8	3.3	2.9
80	11.6	5.1	5.5

It is seen from Table 4 that the decrease in the gel effect with temperature is continued at 45°C. Since the increasing temperature decreases the viscosity of the solution it is obvious that the gel effect is, as its name implies, a viscosity effect.

The lifetimes noted in Table 4 are noticeably lower, particularly at greater conversions, than the corresponding ones at 25°C (Table 1).

Determination of the Intensity Exponent

It is important to know the nature of the termination reaction in a polymerisation in order to apply the correct kinetic analysis. In a system containing free radicals termination can occur by a first or second order reaction with respect to the radicals.

The relation between rate of reaction and light intensity can be expressed in the form

$$\frac{m_1}{m_2} = \frac{L_1}{L_2}^{n} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(40)$$

where m_1 is the rate at light intensity L_1 and m_2 is the rate at light intensity L_2. The intensity exponent = n.
For first order termination, since the rate is proportional to the rate of initiation, $n = 1$.
For second order termination the rate is proportional to the square root of the initiator concentration, therefore $n = \frac{1}{2}$
It is possible for the termination to be a combination of first and second order reactions. In this case the value of the intensity exponent will lie between $\frac{1}{2}$ and 1.0
The intensity exponent was determined from the slope of the straight line obtained by graphing log rate against log light intensity.

Determination of the Transmission of the Screens

This was done using a Unicam spectrophotometer. By measuring the intensity of the light of wavelength 3650°A falling on a photoelectric cell before and after the screen was inserted a direct reading of the transmission was obtained.

Table 5. Intensity Exponents at 25°C. $L_2 = 0.307\ L_1$

Extent Conversion %	Rate of Reaction Full Intensity	Reduced Intensity	Intensity Exponent.
5	9.4	5.0	0.53
10	9.7	5.2	0.53
20	11.0	5.8	0.54
30	13.5	7.2	0.53
40	15.8	8.4	0.53
50	18.5	9.8	0.53
60	16.5	8.3	0.58
70	15.0	6.7	0.68
80	8.5	2.8	0.92

It would appear, from Table 5, that from 60% conversion the intensity exponent increases rapidly. This is, in fact, not a completely real effect, being due in part to the rapid falling off in the rate during the later stages in the polymerisation. The termination reaction is almost exclusively second order.

Determination of the Velocity Coefficients of Propagation and Termination.

The ratio of the velocity coefficients was determined by plotting the reciprocal of the rate of reaction against the measured intercept. The slope was a measure of k_{t/k_p} . As has been pointed out in the introduction, before the individual values of k_p and k_t can be obtained, the rate of initiation must be known. The value for this was taken from the literature.[32] The rate given was 5.2 . 10^{-8} mole.l^{-1} sec.$^{-1}$ giving a rate of reaction of 7.0%/hr.

The diphenyl picryl hydrazyl (D.P.P.H.) used in determining the above value was reported as having been recrystallised from a benzene solution. It has since been reported that the compound obtained has one molecule of crystallisation of benzene per D.P.P.H. molecule. Correcting for this, and assuming an initiator efficiency of 0.5 gives a rate of initiation of 2.17 . 10^{-8} moles, l^{-1} sec.$^{-1}$ at 7.0% polymerisation per hour.

Since the rate of initiation is proportional to the rate of reaction, a rate of 9.2%/hr. at zero conversion gives a value of 2.85 mole.l^{-1}.sec.$^{-1}$ for the rate of initiation. The values of k_p and k_t calculated using this value are shown in Table 6.

Table 6. Variation of velocity coefficients with extent conversion at 25°C and full light intensity.

Extent Conversion %	Lifetime sec.	$k_p/k_t \times 10^6$	k_p l.mole^{-1} sec.$^{-1}$	$k_t \times 10^{-7}$ l.mole^{-1} sec.$^{-1}$
5	0.5	7.45	1090	14.6
10	0.6	7.45	730	9.8
20	0.8	8.8	500	5.6
30	0.9	12.2	570	4.6
40	1.0	28.2	1100	3.9
50	2.3	36.4	240	0.66
60	3.8	64.0	170	0.24
70	4.5	46.8	80	0.17
80	10.6	36.0	11	0.031

Table 6 shows that k_t decreases throughout the polymerisation. The values for k_p fluctuate more although there is a significant overall decrease over the polymerisation range.

Determination of Energies of Activation

The relationship between the velocity coefficient and activation energy is expressed by an equation of the form

$$k = A\ e^{-E/RT} \quad \text{.....................(41)}$$

using the usual symbols.

With the above equation it is possible to determine the overall energy of activation (E_o) from the slope of the straight line obtained by graphing log (rate) against the reciprocal of the absolute temperature. The slope of log $\frac{1}{\ }$ against the reciprocal of the absolute temperature is a measure of the activation energy of termination (E_t). The activation energy of propagation (E_p) is then obtained from the equation

$$E_o = E_p - \tfrac{1}{2} E_t \quad \text{....................(42)}$$

Table 7. Variation of activation energies with extent conversion over the range 25°C to 45°C.

Extent Conversion %	E_o Kcal	E_p Kcal	E_t Kcal
5	5.8	6.2	0.8
10	5.6	6.2	1.1
20	4.7	5.4	1.3
30	3.6	4.2	1.1
40	2.4	3.1	1.4
50	2.6	5.1	4.9
60	3.0	6.3	6.5
70	3.6	6.9	6.5
80	3.3	9.3	12.0

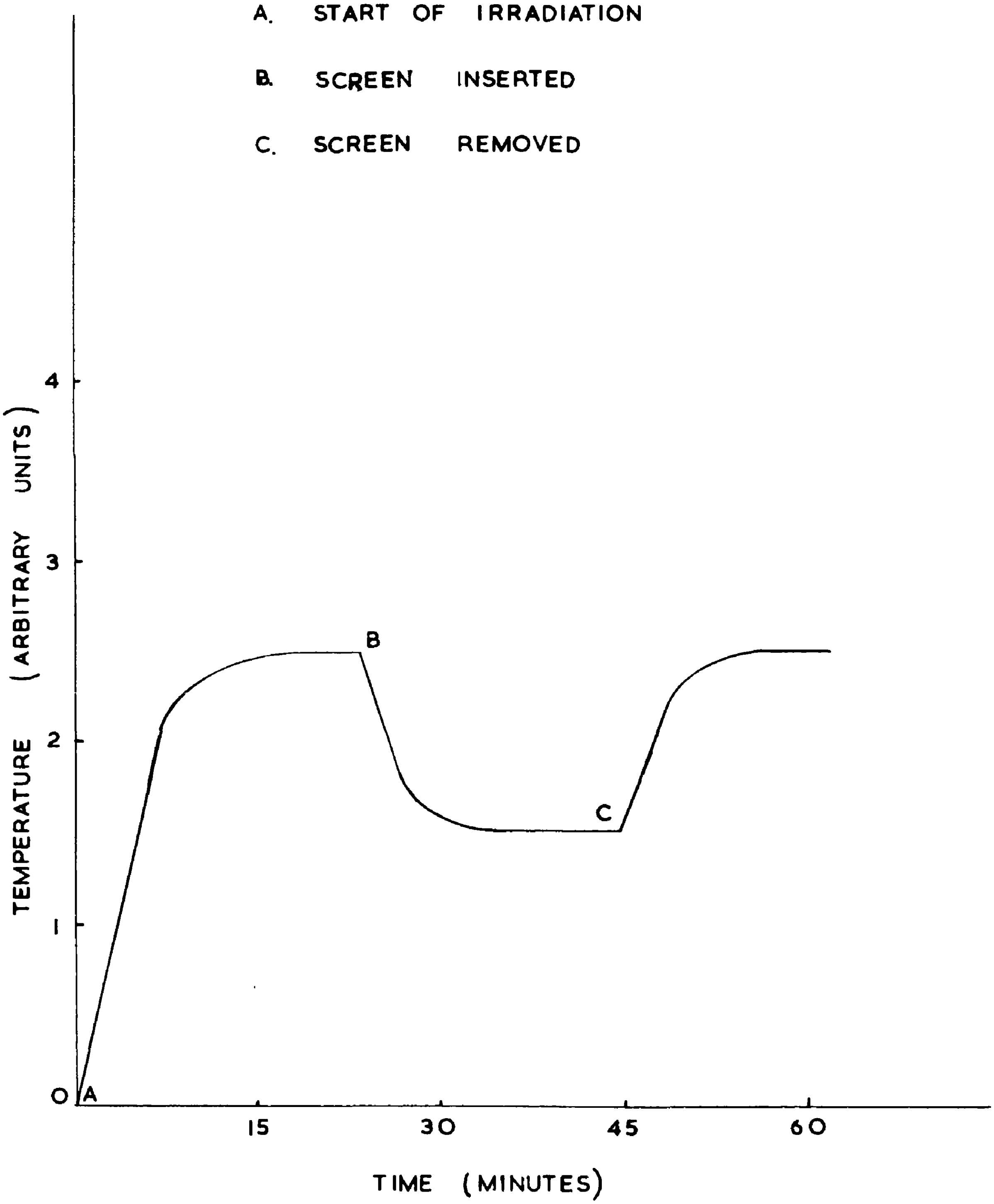
Owing to the short lifetimes in the initial stages it is not possible to obtain E_t with an accuracy greater than 1 Kcal.

The values for E_o shown in Table 7 are more accurate, however.

FIGURE 7.

VARIATION OF REACTION TEMPERATURE

DURING CONTINUOUS IRRADIATION



Continuous Irradiation

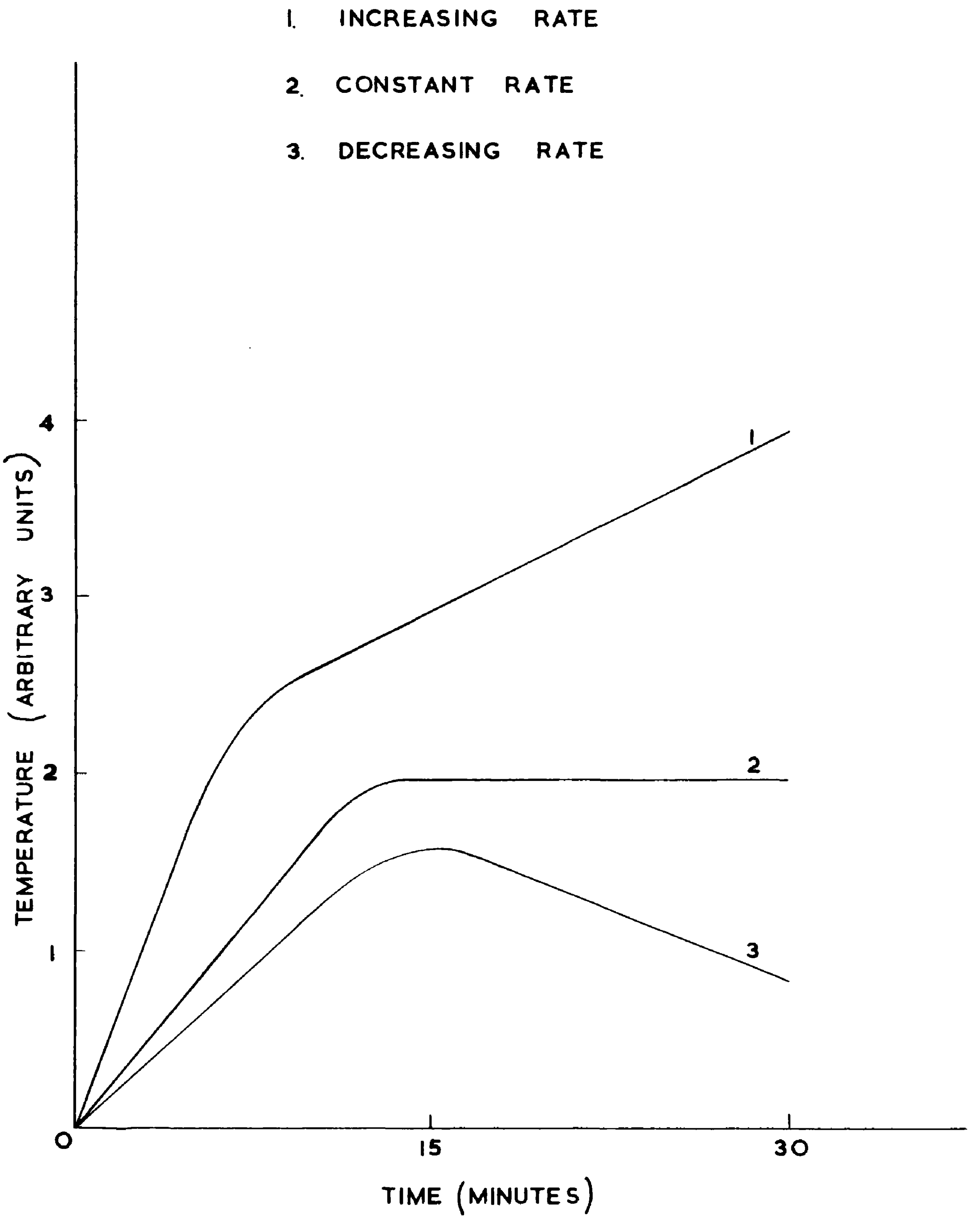
When the necessary measurements had been completed at any particular extent conversion the vinyl acetate was polymerised by continuous irradiation until the required extent conversion at which the next set of measurements were to be made was reached. By reducing the amplification it was possible to follow this continuous polymerisation on a quantitative basis.

Consider a reaction mixture being continuously irradiated. The temperature will rise since the polymerisation is exothermic. Since the rate at which heat is lost from a body is proportional to the temperature difference between the body and its surroundings, a stage will be reached at which the heat lost will equal the heat being produced in the reaction. The temperature will then remain constant. This temperature rise in the reaction mixture is proportional to the rate of reaction, provided of course that the thermal conductivity does not change during the irradiation.

It is possible, thus, to tell at a glance the condition of the reaction during continuous irradiation. Also, by inserting screens of known transmission during this period the intensity exponent can be checked. Figure (7) shows the type

FIGURE 8.

VARIATION OF REACTION TEMPERATURE DURING CONTINUOUS IRRADIATION.



of chart trace obtained.

In most polymerisations and particularly with bulk vinyl acetate, the rate of reaction alters continuously (fig.8). This merely meant that the average height of the pen, at the full intensity, before insertion and after removal of the screens, was taken as corresponding to the height when the screen was present. The intensity exponents found by this method agreed with those shown in Table 5.

Discussion of the bulk polymerisation of Vinyl Acetate

For convenience the polymerisation will be considered to take place in three parts comprising the initial, intermediate and final stages of the reaction.

Initial Stage 0% - 20% conversion.

The initial readings were taken at 5% conversion as an added safeguard against the presence of small quantities of impurities.

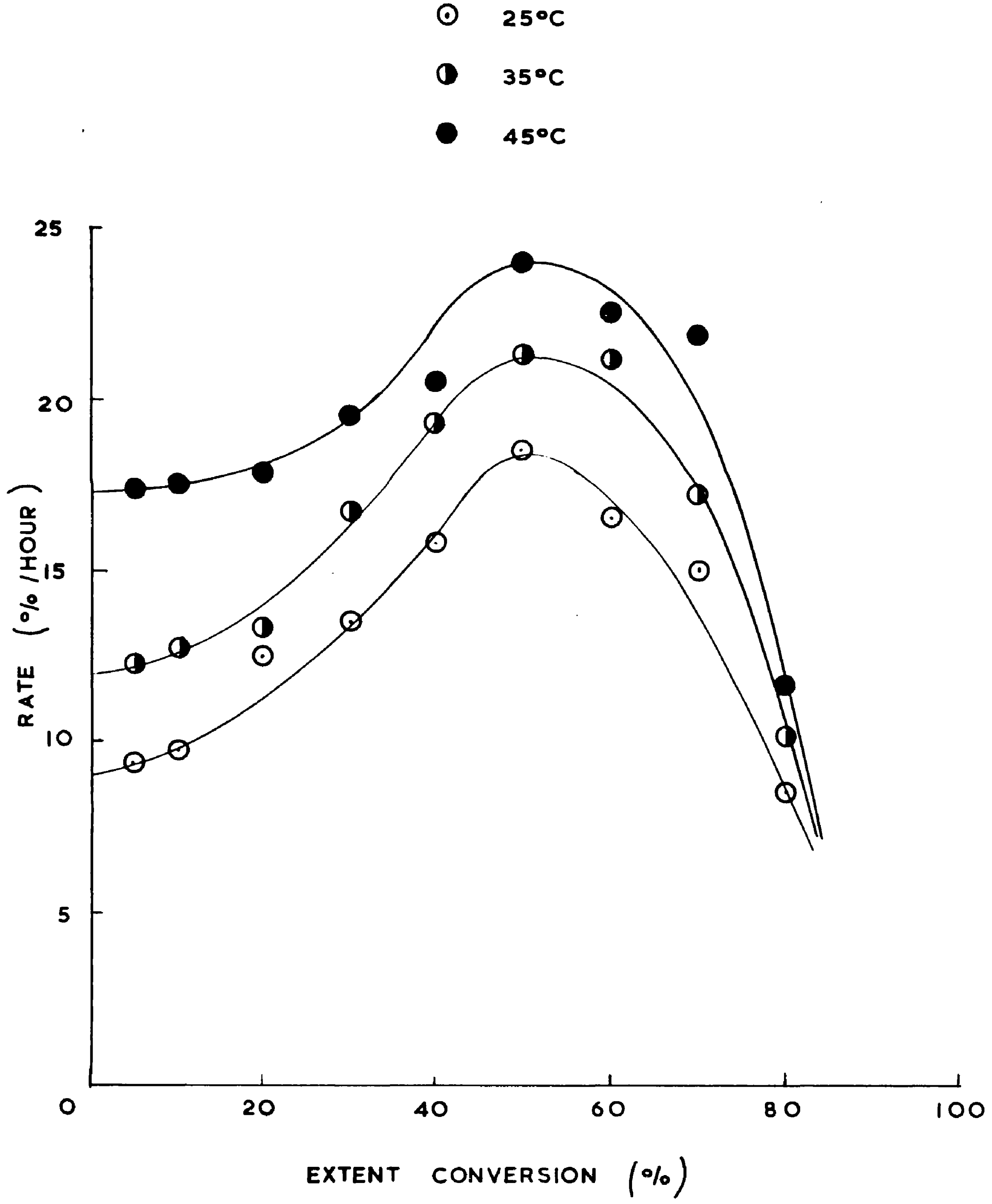
In the initial stage the gel effect is seen from Table 1 to be comparatively small causing only a slight acceleration in rate and an increase in the lifetime by less than a factor of two. This is sufficient, however, to cause k_t to decrease due to the increasing viscosity of the system making it more difficult for the polymer radicals to diffuse together to terminate. It is doubtful if the apparent decrease in k_p is a real effect since it is extremely unlikely that monomer diffusion would be affected at this stage. Furthermore other workers[32] have found k_p to increase slightly during this period.

Examination of the activation energies confirm the slight gel effect. The reduction in E_o is due to termination becoming more difficult and as a result E_t increasing.

FIGURE 9

BULK VINYL ACETATE POLYMERISATION

VARIATION OF RATE WITH CONVERSION



Intermediate Stage 20% - 50% conversion.

It was found that the gel effect was becoming greater as the polymerisation proceeded with the rate of reaction increasing over this range by a factor of about 1.7 at 25°C, 1.6 at 35°C and 1.35 at 45°C. This effect over the entire polymerisation is shown in Figure (9). This supports the view that the gel effect is due to viscosity, which varies inversely as the temperature, with the result that the gel effect is less at higher temperatures.

The expected increase in k_p is seen in Table 6, although the value at 50% conversion does show a drop. The fall in the value of k_t, discussed in the initial stage is continued.

With increasing viscosity causing termination to become more and more difficult E_t increases and since the monomer diffusion is still not affected E_o decreases.

Final Stage 50% - 80% conversion.

From 50% conversion the rate of polymerisation drops off. This is accompanied by a rapid rise in the lifetimes. Two effects can be considered to cause the drop in the rate of reaction. The first is the fall in the monomer concentration as conversion to polymer proceeds and the second is the high

FIGURE 10.

TYPICAL GRAPH FOR THE DETERMINATION OF INSTRUMENT LAG AND K_p/K_t.

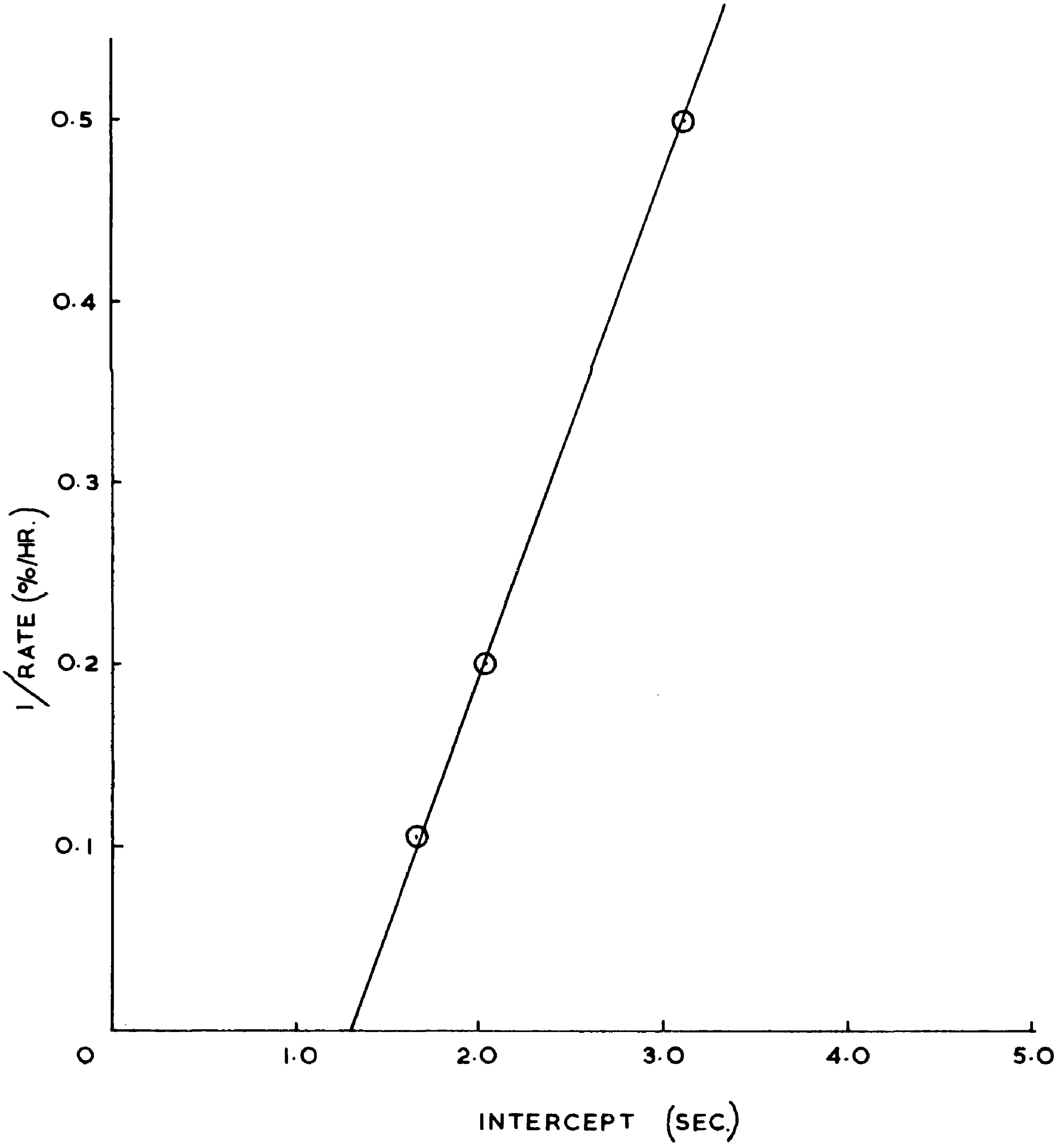


FIGURE 11.

TYPICAL GRAPH FOR THE DETERMINATION OF E_t

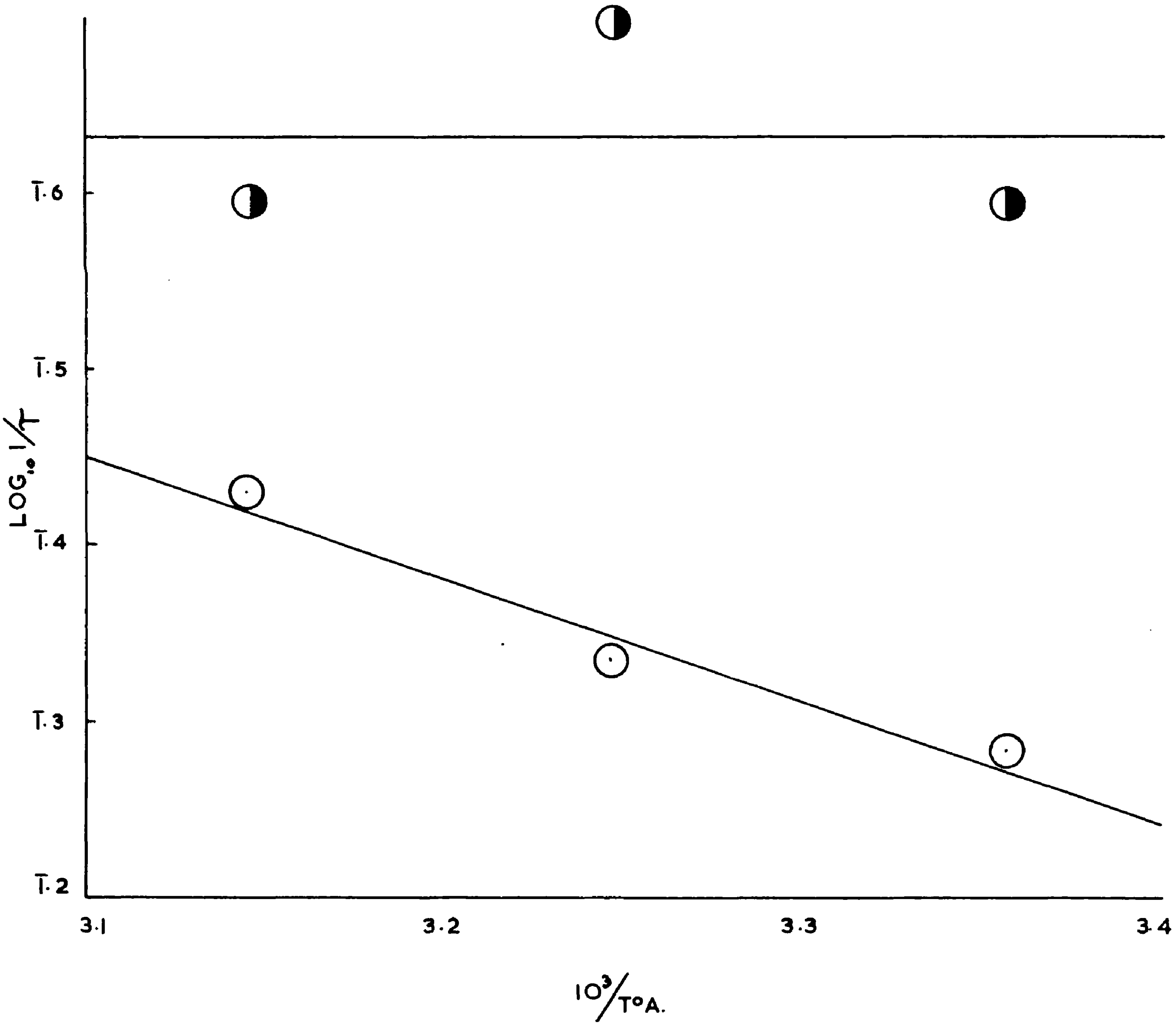
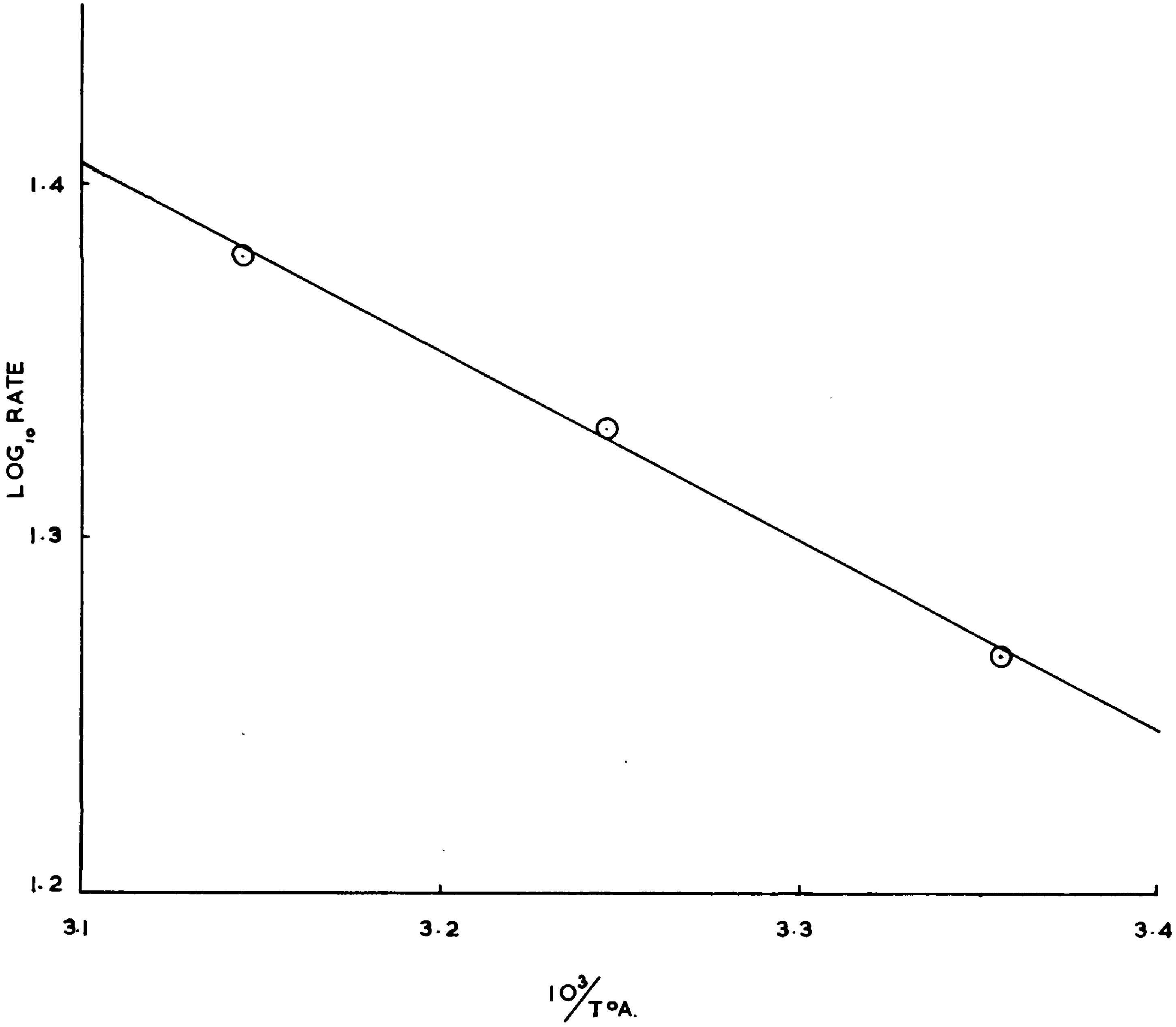


FIGURE 12.

TYPICAL GRAPH FOR THE DETERMINATION OF E_o



viscosity of the reaction mixture at this stage.

The variation in the monomer concentration makes it difficult to compare rates of reaction at various stages in the polymerisation, especially in the later stages when the reaction mixture solidifies. Regardless of the apparent monomer concentration, unless the monomer molecules can come in contact with a radical, in effect monomer concentration will be zero. Thus monomer diffusion becomes all important and it is this being retarded in the final stage of the polymerisation which causes the rate to drop and the lifetimes to rise. This is supported by the variation in k_p and k_t over this range. Table 6 shows that k_p reaches a maximum at about 40% conversion. As the rate falls k_p and k_t decrease.

E_o also shows a tendency to increase over the last 50% conversion due to E_p increasing faster than $\frac{1}{2}E_t$.

Table 5 shows that from 50% conversion the intensity exponent apparently increases. This is due in part, as has been explained previously, to the drop in rate, and in part to the non adiabacity of the system at large lifetimes.

The picture of the polymerisation of vinyl acetate which now appears is of a reaction mixture through which initially monomer molecules and polymer radicals can diffuse freely with the result that their reactivities are governed by purely chemical factors. As the polymerisation proceeds the viscosity of the mixture increases, first of all retarding radical diffusion causing an acceleration in the rate of reaction. As the mixture becomes more viscous a second effect takes place. Monomer diffusion becomes controlled, the rate of propagation decreases and the rate of reaction falls.

Comparison of Results with Literature values.

The values for k_p and k_t agree fairly well with published literature results. The following table shows a comparison with those obtained by Bengough and Melville[32] using a similar thermocouple method.

Table 8. Velocity Coefficients for propagation and termination for photoinitiated bulk vinyl acetate polymerisation at 25°C.

Reference	k_p $\text{l.mole}^{-1}\ \text{sec}^{-1}$	k_t $\text{l.mole}^{-1}\ \text{sec}^{-1} \times 10^{-7}$
This Work	1090	14.6
Bengough and Melville	895	2.4

The apparent large discrepancy in k_t quickly disappears as the polymerisation proceeds.

The energy of termination also agrees well with the literature values although E_o is rather higher than previously reported (Table 9).

Table 9. Energies of activation for the initial stages of vinyl acetate polymerisation.

Reference	E_o Kcal	E_t Kcal
This work	5.8	0.8
Bengough and Melville[32]	4.2	1
Burnett and Melville[59]	4.4	0
Dixon-Lewis[60]	3.2	0
Matheson et al[61].	4.7	5.2

II. The Polymerisation of Vinyl Acetate in the presence of Benzene.

In the following section the polymerisation of vinyl acetate in the presence of different quantities of benzene will be examined in order to find the solvent and retarder effects of benzene on the polymerisation. The quantities of solvent added were governed by the latter effect due to the fact that in order to obtain accurate rate measurements it was advisable to have a rate of reaction which did not fall much below 1.0%/hr. Below this rate, temperature fluctuations, particularly at the higher temperatures, became appreciable.

The Polymerisation of Vinyl Acetate with 2.5% v/v Benzene (0.281 mole.l^{-1}).

"Spectro grade" benzene was used throughout, being added by pipette, or in the case of very small quantities by syringe and then degassed in the reaction vessel.

The presence of a substance with a different specific heat from that of the monomer meant that a correction had to be made to the rate of reaction. It was assumed that the specific heat of the mixture varied linearly with the amount of benzene present. With 2.5% benzene the correction was very small but it became increasingly important as more solvent was added.

The initiator concentration was 4×10^{-3} mole l^{-1}.

Table 10. Variation of rate and lifetime with extent conversions at 25°C and full light intensity (Instrument lag = 1.15 sec.)

Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
0	5.12	2.0	1.2
10	6.09	2.0	1.2
20	6.14	2.2	1.5
30	6.30	1.85	1.0
40	6.25	2.1	1.4
50	5.59	2.2	1.5
60	5.43	3.2	2.9
70	5.16	4.5	4.8
80	4.00	8.0	9.9

It will be seen from Table 10 that there is a marked retardation in the initial rate of reaction. The lifetimes are significantly longer than in the bulk polymerisation

Table 11. Variation of rate and lifetime with extent conversion at 25°C and reduced light intensity. $L_2 = 0.307\ L_1$.

Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
0	2.34	2.2	1.5
10	2.80	2.1	1.4
20	2.68	2.3	1.6
30	2.93	2.1	1.4
40	3.00	2.1	1.3
50	2.64	2.7	2.2
60	2.47	3.9	3.9
70	2.59	5.8	6.7
80	1.62	11.1	14.4

Table 11 shows the expected drop in rate and increase in lifetime due to therate of initiation being reduced. The general characteristics of the polymerisation parallel those at the higher light intensity.

In Table 12 following, the results at 35°C and 45°C are shown. It will be seen that the gel effect decreases progressively with temperature, and at 45°C the rate of reaction shows no acceleration, although it falls off in the later stages. The lifetimes seem to decrease with temperature rise, and also increase in the later stages at both temperatures.

Table 12. Variation of rate and lifetime with extent conversion at 35°C and 45°C with full light intensity.

Temperature °C	Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
35	0	7.77	1.8	0.9
	10	7.83	1.8	0.9
	20	7.90	1.8	0.9
	30	8.55	1.6	0.8
	40	8.36	1.8	0.9
	50	8.38	1.9	1.0
	60	7.52	2.8	2.3
	70	7.15	3.5	3.3
	80	5.46	6.1	7.1
45	0.	11.4	1.6	0.6
	10	10.1	1.6	0.6
	20	10.4	1.6	0.6
	30	10.4	1.6	0.6
	40	10.4	1.6	0.6
	50	10.9	1.8	0.9
	60	9.73	2.0	1.2
	70	9.25	3.0	2.7
	80	7.83	4.3	4.6

Table 13. Intensity Exponents at 25°C for the polymerisation of vinyl acetate with 2.5% benzene. $L_2 = 0.307\ L_1$

Extent Conversion %	Rate of Reaction %/hr L_1	Rate of Reaction %/hr L_2	Intensity Exponent.
0	5.12	2.34	0.67
10	6.09	2.80	0.67
20	6.14	2.68	0.71
30	6.30	2.93	0.66
40	6.25	3.00	0.63
50	5.59	2.64	0.65
60	5.43	2.47	0.68
70	5.16	2.59	0.59
80	4.00	1.62	0.78

The intensity exponents shown in Table 13 indicate that mixed order termination is occurring, since the value of the intensity exponent lies between 0.5 and 1.0. In order to take this into account it will be necessary to correct, by using Bengough's analysis shown on page 20 , the values for the velocity coefficients derived on the assumption that termination is taking place by a second order mechanism. The derived and corrected values for the velocity coefficients are shown in Tables 14 and 15.

Table 14. Variation of velocity coefficients with extent conversion at 25°C and full illumination.

Extent Conversion %	Lifetime sec.	$k_p/k_t \times 10^6$	k_p l. mole.$^{-1}$ sec.$^{-1}$	$k_t \times 10^{-7}$ l. mole.$^{-1}$ sec.$^{-1}$
0	1.2	2.28	56	2.4
10	1.2	2.38	58	2.4
20	1.5	3.45	54	1.6
30	1.0	3.90	140	3.5
40	1.4	4.54	81	1.8
50	1.5	5.40	84	1.6
60	2.9	9.74	41	0.42
70	4.8	1.84	2.2	0.15
80	9.9	2.05	0.74	0.036

Table 15. Variation of corrected velocity coefficients with extent conversion at 25°C and full illumination.

Extent Conversion %	Intensity Exponent	$k_p/k_t \times 10^6$	k_p l. mole.$^{-1}$ sec.$^{-1}$	$k_t \times 10^{-7}$ l. mole.$^{-1}$ sec.$^{-1}$
0	0.67	4.85	79	1.63
10	0.67	5.04	82	1.63
20	0.71	8.94	84	0.94
30	0.66	7.50	180	2.4
40	0.63	8.46	110	1.3
50	0.65	10.9	120	1.1
60	0.68	21.9	59	0.27
70	0.59	2.58	3.4	0.13
80	0.78	8.74	1.4	0.016

A comparison of the values of the velocity coefficients in Tables 14 and 15 shows that the error involved in assuming second order termination, when in fact mixed order termination is taking place, is comparatively small. The greatest difference is shown in the values of k_p/k_t since the correction increases k_p and decreases k_t.

It would be possible now, knowing the correct value for k_t, to calculate the value for the corresponding lifetime. Compared with the experimental error in measuring this, the correction is small and can be ignored.

The values for k_p and k_t shown in Table 15 are considerably lower than those for the bulk polymerisation (Table 6). The value for k_p is, moreover, affected more by the presence of the benzene than k_t, with the result that k_p/k_t is smaller throughout than the corresponding values for the bulk polymerisation.

Effect of mixed order termination on activation energies.

The equation relating energies of activation which is derived for second order termination, $E_o = E_p - \frac{1}{2} E_t$, can not be used in a polymerisation in which mixed order kinetics apply. The same argument applies to the equation for exclusive first order termination. In view of the complicated termination reactions taking place, therefore, the value calculated for E_t by taking the slope of the straight line obtained by graphing log $\frac{1}{\quad}$ against $\frac{1}{T^{o}A}$ has no real meaning. Nevertheless the slope of this line, which gives $\frac{1}{2} E_t$ can be regarded as a measure of the temperature coefficient of $\frac{1}{\quad}$, and as such it will be quoted here. The value for E_o, is of course still valid regardless of the termination mechanism.

Table 16. Activation energies at full illumination over the range 25°C to 45°C.

Extent Conversion	0	10	20	30	40	50	60	70	80
E_o Kcal.	4.7	4.8	5.4	5.5	5.5	6.1	5.0	4.8	5.9
$\frac{1}{2} E_t$	3.0	3.0	4.2	2.6	4.2	2.3	3.3	2.9	3.2

It will be seen from Table 16 that E_o is fairly constant and appears to have an average value of 5.3 Kcal.

The Polymerisation of Vinyl Acetate with 5% v/v Benzene (0.562 mole. 1^{-1})

In order to find the effect of benzene concentration on the rate and on the gel effect the concentration was increased to 5% benzene. As with the 2.5% benzene the apparent rate of reaction was corrected to allow for the presence of a substance with a different specific heat. The following results were obtained and tabulated. The initiator concentration was 4×10^{-3} mole.1^{-1}.

Table 17. Variation of rate and lifetime with extent conversion at 25°C and full light intensity. (Instrument lag = 0.8 sec.).

Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
5	3.41	1.7	1.3
10	3.48	2.0	1.7
20	3.55	2.0	1.7
30	3.35	2.0	1.7
40	4.24	2.0	1.7
50	4.22	2.5	2.5
60	3.78	3.0	3.2
70	3.74	3.5	3.9
80	3.80	3.8	4.3
90	3.42	4.5	5.3

From the variation of rate with conversion shown in Table 17 it would appear that the gel effect is almost completely removed. This smoothing out effect does not occur to the same extent in the lifetimes which start increasing between 40% and 50% conversion.

Table 18. Variation of rate and lifetime with extent conversion at 25°C and reduced light intensity.

Extent Conversion %	Rate of Reaction %/hr	Intercept sec.	Lifetime sec.
5	1.88	2.3	2.1
10	2.02	2.3	2.1
20	1.57	2.3	2.1
30	2.00	2.4	2.3
40	2.24	2.8	2.9
50	2.08	3.0	3.2
60	2.21	4.3	5.0
70	1.94	4.3	5.0
80	1.99	6.0	7.5
90	1.44	7.2	9.3

As would be expected the results in Table 18 show that the rate varies very little with conversion and the lifetimes are constant in the initial stages of the reaction.

The following results, in Table 19, support the view that the rate at 25°C remains constant because of two opposing effects, namely a tendency for the rate to fall and a tendency of the gel effect to increase it. At the higher temperatures the rate falls during the later stages due to the lessening of the gel effect.

The lifetimes decrease with temperature, and the variation with conversion alters with the temperature; 25°C $>$ 35°C $>$ 45°C.

Table 19. Variation of rate and lifetime with extent conversion at 35°C and 45°C with full light intensity.

Temperature °C	Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
35	5	5.23	1.65	1.2
	10	5.21	1.65	1.2
	20	5.45	1.65	1.2
	30	5.90	1.65	1.2
	40	6.37	1.65	1.2
	50	6.55	1.7	1.3
	60	6.46	2.1	1.8
	70	6.23	2.8	2.8
	80	5.49	2.3	3.5
	90	5.15	3.8	4.3
45	5	8.00	1.3	0.7
	10	8.20	1.3	0.7
	20	7.46	1.3	0.7
	30	9.30	1.3	0.7
	40	8.60	1.4	0.8
	50	8.60	1.4	0.8
	60	8.50	1.5	1.0
	70	8.10	1.8	1.4
	80	7.80	2.3	2.1
	90	7.20	2.8	2.9

Table 20. Intensity Exponents for the polymerisation of vinyl acetate with 5.0% benzene at 25°C.

$L_2 = 0.307 L_1$.

Extent Conversion %	Rate of Reaction %/hr L_1	Rate of Reaction %/hr L_2	Intensity Exponent.
5	3.41	1.88	0.50
10	3.48	2.02	0.46
20	3.55	1.57	0.69
30	3.35	2.00	0.43
40	4.24	2.24	0.53
50	4.22	2.08	0.60
60	3.78	2.21	0.46
70	3.74	1.94	0.55
80	3.80	1.99	0.55
90	3.42	1.44	0.73

It would appear that this reaction has approximately a second order termination, from the intensity exponents in Table 20. In view of the intensity exponents for the 2.5% benzene reaction, Table 13, and for the 20% benzene reaction, Table 29, this seems unlikely.

Table 21. Variation of velocity coefficients with extent conversion at 25°C and full illumination.

Extent Conversion %	Lifetime sec.	$k_p/k_t \times 10^6$	k_p mole.l.$^{-1}$ sec.$^{-1}$	$k_t \times 10^{-7}$ mole.l.$^{-1}$ sec.$^{-1}$
5	1.3	4.4	92	2.1
10	1.7	2.3	27	1.2
20	1.7	1.9	22	1.2
30	1.7	5.4	63	1.2
40	1.7	7.3	85	1.2
50	2.5	3.9	23	0.59
60	3.2	12.7	45	0.35
70	3.9	5.8	14	0.23
80	4.3	18.0	35	0.19
90	5.3	13.0	16	0.12

Table 22. Variation of corrected velocity coefficients with extent conversion at 25°C and full illumination.

Extent Conversion %	Intensity Exponent	k_p/k_t x 10^6	k_p mole.l.$^{-1}$ sec.$^{-1}$	k_t x 10^{-7} mole.l.$^{-1}$sec.$^{-1}$
5	0.5	4.4	92	2.1
10	0.46	2.3	27	1.2
20	0.69	4.3	33	0.76
30	0.43	5.4	63	1.2
40	0.53	8.0	90	1.1
50	0.6	5.8	28	0.48
60	0.46	12.7	45	0.35
70	0.55	7.6	16	0.21
80	0.55	23.0	39	0.17
90	0.73	34.0	24	0.07

Table 22. shows that the tendency of the velocity coefficients to vary less with conversion, as more benzene is added, is continued.

Table 23. Activation energies at full illumination over the range 25°C to 45°C.

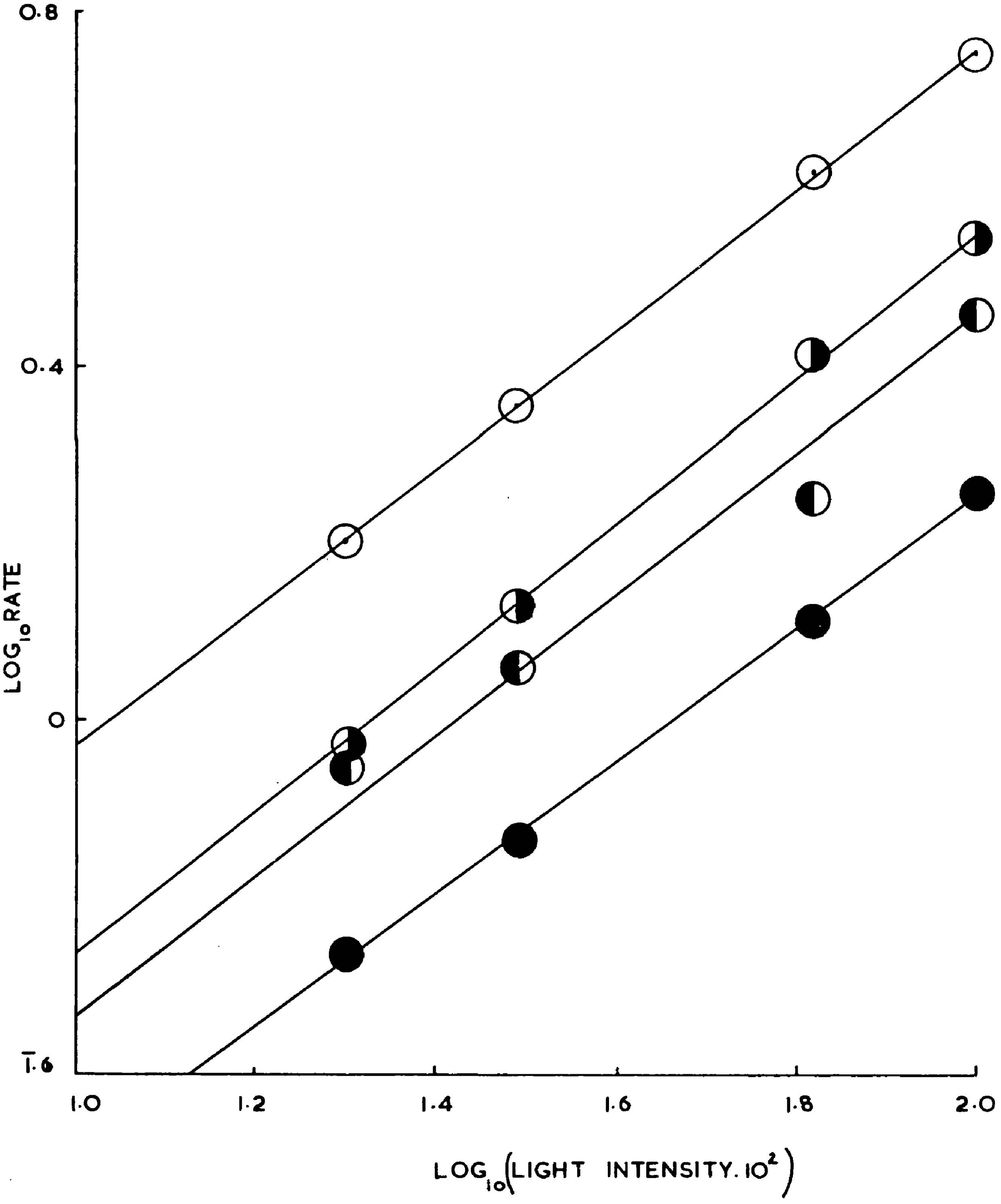
Extent Conversion %	5	10	20	30	40	50	60	70	80	90
E_o Kcal.	8.5	6.6	7.0	9.6	7.5	7.8	7.8	7.8	6.9	7.0
$\frac{1}{2}$ E_t	2.8	4.4	4.2	4.2	3.6	5.1	5.3	4.8	3.5	2.8

The values of E_o in Table 23 seem to be fairly constant averaging 7.7 Kcals. This is higher than the average value for 2.5% benzene (Table 16).

FIGURE 13.

EFFECT OF LIGHT INTENSITY ON RATE

AT DIFFERENT INITIATOR CONCENTRATIONS



Variation of Rate of Reaction with Initiator Concentration for the Polymerisation of Vinyl Acetate with 5% Benzene.

In order to determine the relation between rate of reaction and initiator concentration, vinyl acetate containing 5% benzene was polymerised in the presence of different amounts of C.H.D.N. The rates of reaction were determined in each case at full and at several reduced light intensities. The results are shown in Table 24.

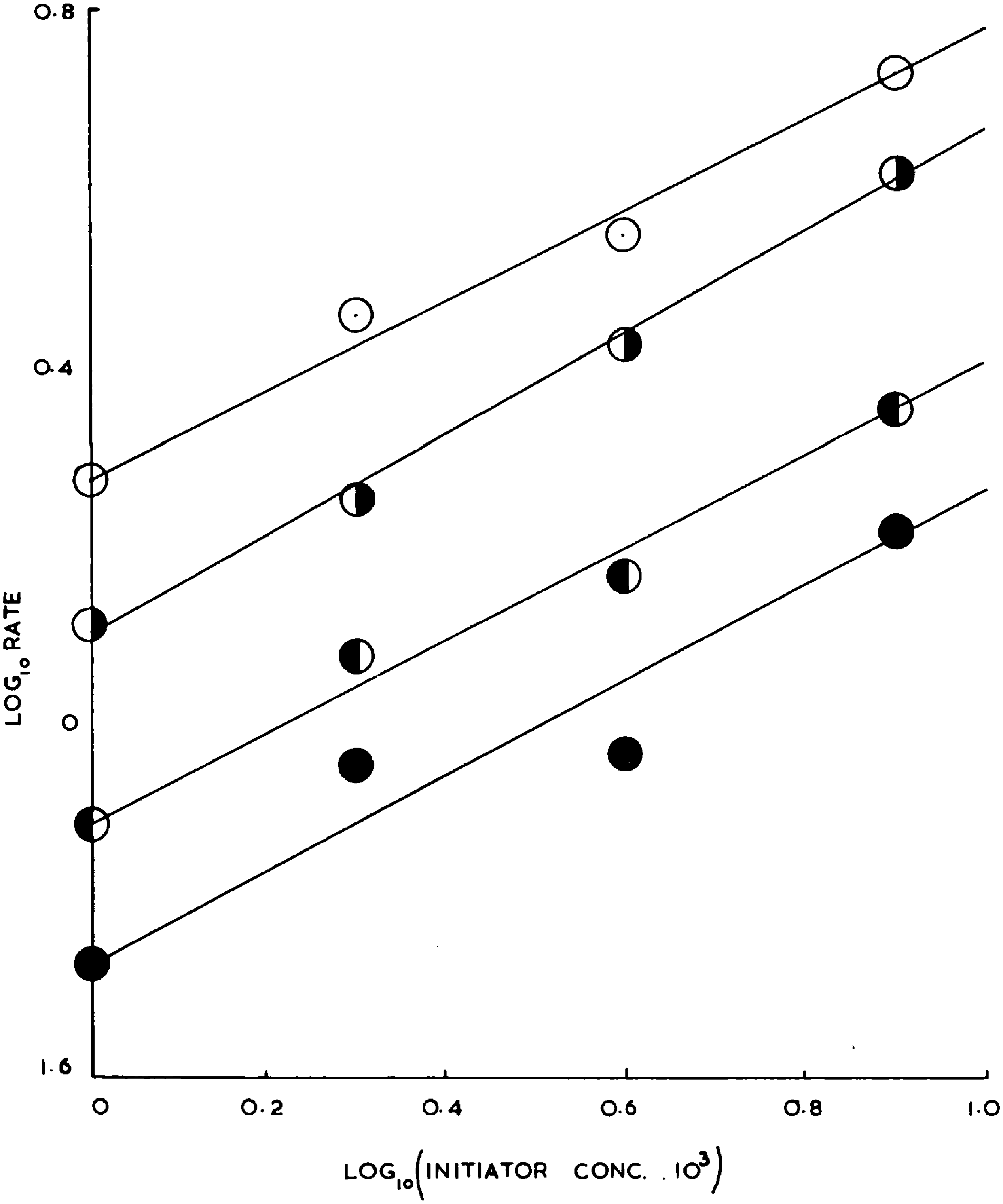
Table 24. Rates of reaction at different light intensities for various initiator concentrations.

Light Intensity %	Rate (%/hr.) at initiator conc. of:-			
	10^{-3} mole.1^{-1}	2×10^{-3} mole.1^{-1}	4×10^{-3} mole.1^{-1}	8×10^{-3} mole.1^{-1}
100.0	1.83	2.94	3.52	5.61
66.0	1.30	1.78	2.61	4.16
30.7	0.77	1.13	1.36	2.27
20.0	0.54	0.89	0.93	1.63

The rates of reaction were obtained by the thermocouple method. The intensity exponent at each initiator concentration was obtained from the slope of the line obtained by plotting log (light intensity) against log rate (fig.13). The values obtained are shown in Table 25.

FIGURE 14.

EFFECT OF INITIATOR CONCENTRATION ON RATE AT DIFFERENT LIGHT INTENSITIES



The Polymerisation of Vinyl Acetate with 20% v/v Benzene (2.25 mole.$l.^{-1}$

In the previous polymerisations only small quantities of benzene were present with the result that the dilution effect was negligible. In order to find the effect of a large quantity of solvent and at the same time have a measureable rate of reaction, the vinyl acetate was polymerised in the presence of 20% v/v benzene with an initiator concentration of 4×10^{-3} mole.$l.^{-1}$.

Table 26. Variation of rate and lifetime with extent conversion at 25°C and full light intensity (Instrument lag = 0.8sec.).

Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
0	2.66	1.3	0.7
20	1.63	2.0	1.7
40	1.07	2.0	1.7
60	0.75	3.0	3.2

The trend of previous polymerisations is reversed in the results shown in Table 26. The decrease in the rate of reaction with conversion is in marked contrast to the autoacceleration of the bulk reaction. Above 60% conversion the rate of reaction became too small for accurate measurement and the experiment was terminated.

Table 27. Variation of rate and lifetime with extent conversion at 25°C and at reduced light intensity.

Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
0	1.16	2.2	2.0
20	0.69	2.1	1.8
40	0.52	3.3	3.6
60	0.30	4.0	4.6

Table 27 shows the same trends in rates and lifetimes with conversion as those in Table 26. The rates of reaction are very low and consequently the radical lifetimes are not accurate and should only be taken as a general indication of the actual values.

Table 28. Variation of rate and lifetime with extent conversion at 35°C and 45°C with full light intensity.

Temperature °C	Extent Conversion %	Rate of Reaction %/hr	Intercept sec.	Lifetime sec.
35	0	3.42	1.4	0.9
	20	2.54	1.6	1.1
	40	2.00	1.8	1.4
	60	1.39	1.5	1.0
45	0	4.70	1.2	0.6
	20	4.08	1.7	1.3
	40	3.10	1.5	1.0
	60	2.57	2.5	2.5

It will be seen in Table 28 that the rates also decrease with conversion at the higher temperatures, and the lifetimes show a tendency to increase as the reaction proceeds. Since the rate of initiation is probably a constant and there is no gel effect this must be due to chemical reactions involving benzene as opposed to purely environmental factors.

Table 29. Intensity Exponents at 25°C for the polymerisation of vinyl acetate in 20% benzene. $L_2 = 0.307\ L_1$.

Extent Conversion %	Rate of Reaction %/hr L_1	Rate of Reaction %/hr L_2	Intensity Exponent.
0	2.66	1.16	0.70
20	1.63	0.69	0.73
40	1.07	0.52	0.61
60	0.75	0.30	0.77

Table 29 shows that mixed order termination is taking place as expected. It is likely that intensity exponents in the region of 0.75 would have been obtained even with bulk vinyl acetate polymerisation at these rates of reaction. Bengough and Melville[32] have pointed out that termination tends to first order with the pure monomer if the rate of reaction falls much below 3%/hr.

Table 30. Variation of velocity coefficients with extent conversion at 25°C and full light intensity.

Extent Conversion %	Lifetime sec	$k_p/k_t \times 10^6$	k_p l.mole.$^{-1}$ sec.$^{-1}$	$k_t \times 10^{-7}$ l.mole.$^{-1}$sec.$^{-1}$
0	0.7	1.8	120	6.8
20	1.7	0.9	11	1.2
40	1.7	3.7	45	1.2
60	3.2	2.3	8	0.35

The values for k_p and k_t in Table 30 corrected to allow for mixed order termination are shown below.

Table 31. Variation of corrected velocity coefficients with extent conversion at 25°C and full illumination light intensity.

Extent Conversion %	Intensity Exponent.	$k_p/k_t \times 10^6$	k_p l.mole.$^{-1}$ sec.$^{-1}$	$k_t \times 10^{-7}$ l.mole.$^{-1}$ sec.$^{-1}$
0	0.7	4.8	184	3.8
20	0.73	2.7	18	0.66
40	0.61	5.9	56	0.95
60	0.77	8.9	15	0.17

The ratio of k_p/k_t is seen in Table 31 to be fairly constant, varying by no more than a factor of two. The variations in the individual rate constants are also fairly slight.

Table 32. Activation energies at full light intensity over the range 25°C to 45°C.

Extent Conversion %	E_o Kcal.	$\frac{1}{2}$ E_t Kcal.
0	6.1	1.0
20	8.5	1.4
40	9.0	2.1
60	9.5	1.0

Table 32 shows an increase in E_o with conversion, the average value being 8.3 Kcal. From the value for $\frac{1}{2}$ E_t it would seem that the lifetime varies only very slightly with temperature.

Measurement of the Transfer Constant and the Activation Energy of the Transfer Reaction between Vinyl Acetate and Benzene.

The transfer constant is defined as the ratio of the velocity coefficient of transfer to the velocity coefficient of propagation. Thus if the transfer reaction is

$$R\cdot + S \rightarrow P + S\cdot \quad \text{.........Rate} = k_{tr}[R\cdot][S]$$

$$\text{the transfer constant } (C_s) = k_{tr}/k_p \quad \text{................(43)}$$

In order to find the effect of temperature on C_s and hence to obtain a value for the activation energy of the transfer reaction, the polymerisation of vinyl acetate in the presence of different quantities of benzene was carried out at different temperatures.

The following method of deriving an equation for C_s was developed by Mayo[22] :-

By definition, the degree of polymerisation ($\overline{DP}$) is the ratio of the rate of chain growth to the rate of chain termination.

$$\therefore \overline{DP} = \frac{k_p[R_s\cdot][M]}{k_t[R_s\cdot]^2 + k_{tr}[R_s\cdot][S] + k_{tr'}[R_s\cdot][M]} \quad \text{......(44)}$$

using the usual symbols (see appendix) with $k_{tr'}$ = velocity coefficient of monomer transfer.

From equation (1) $[R_s^{\cdot}] = \left\{ \frac{k_i [B] [M]}{k_t} \right\}^{\frac{1}{2}}$

$$\therefore \quad \frac{1}{\overline{DP}} = \frac{k_t [R_s^{\cdot}]}{k_p [M]} + \frac{k_{tr} [S]}{k_p [M]} + \frac{k_{tr'}}{k_p} \quad \ldots\ldots\ldots\ldots (45)$$

$$= \frac{(k_t \; k_i)^{\frac{1}{2}} \; [B]^{\frac{1}{2}}}{k_p \; [M]^{\frac{1}{2}}} + \frac{k_{tr} \; [S]}{k_p \; [M]} + \frac{k_{tr'}}{k_p} \quad \ldots\ldots (46)$$

Let $\overline{DP}_o$ = The degree of polymerisation when $[S] = 0$

$$\therefore \quad \frac{1}{\overline{DP}_o} = \frac{(k_t k_i)^{\frac{1}{2}}}{k_p} \; \frac{[B]^{\frac{1}{2}}}{[M]^{\frac{1}{2}}} + \frac{k_{tr'}}{k_p} \quad \ldots\ldots\ldots\ldots\ldots\ldots (47)$$

Substituting $\frac{1}{\overline{DP}_o}$ in equation (46) gives

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_o} + \frac{C_s [S]}{[M]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (48)$$

Thus if $\frac{1}{\overline{DP}}$ is plotted against $\frac{[S]}{[M]}$ a line of slope C_s will be obtained.

The value for C_s is obtained on the assumption that the reduction in molecular weight occurring in the presence of solvents is due solely to a transfer reaction. Where strong inhibition is occurring the molecular weight will also be reduced, and C_s will include this reaction in its final value.

Before C_s could be determined it was necessary to know the molecular weight of the polymer formed. The following section describes how this was done.

Determination of Molecular Weight by Viscosity Measurements.

The viscosity of a polymer solution can be expressed in terms of the time taken by the solution to flow through a narrow capillary. The ratio of the time of flow of the solution to the time of flow of the solvent $_o$ gives the relative viscosity

$$\text{i.e.} \quad \eta_r = \frac{\eta}{\eta_o} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(49)$$

$$\text{By definition the specific viscosity } (\eta_{sp}) = \frac{\eta - \eta_o}{\eta_o} = \eta_r - 1 \ldots(50)$$

The ratio of the specific viscosity to the concentration of the polymer, usually expressed in gm/100 ml., is a measure of the specific capacity of the polymer to the intrinsic viscosity (η_i)

$$\therefore \quad \eta_i = \left(\frac{\eta_{sp}}{C}\right)_{c \rightarrow o} = \left(\frac{\eta_r - 1}{C}\right)_{c \rightarrow o} \ldots\ldots\ldots\ldots\ldots (51)$$

Graphing $\frac{\eta_{sp}}{C}$ against C gives η_i where C = 0.

The general relationship between molecular weight and viscosity can now be expressed in terms of the modified Staudinger equation as

$$\eta_i = K\,M^{\alpha} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (52)$$

where M = molecular weight; and K and are constants.

The relationship used in this work was derived by Chinai, Scherer and Levi [62] from light scattering measurements as

$$\eta_i = 8.6 \times 10^{-5}\,Mw^{0.74} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (53)$$

where Mw = weight average molecular weight.

This can be converted to number average molecular weight and hence $\overline{DP}$ since Mn:Mw = 1:2 for the most probable molecular weight distribution.[63]

Experimental determination of transfer constants.

Vinyl acetate was distilled into a 30 ml. dilatometer containing initiator and a measured amount of degassed "spectro grade" benzene. The reaction vessel was sealed under high vacuum and polymerised to between 5% and 10% conversion. The contents were then dissolved in 150 ml. of analar benzene in a 1 litre round bottomed flask. The solution was frozen by rotating the flask in an acetone-drikold mixture so that the solid solution coated the walls of the flask in a thin layer.

The flask was put under high vacuum and the benzene sublimed, taking with it the residual monomeric vinyl acetate. After about 6 hours, during which time the cooling induced by the sublimation kept the mixture frozen, the flask was removed from the high vacuum line. There was no benzene left in the flask and the polymer was in an easily handled and very soluble form.

In order to free the polymer from initiator and residual monomer the polymer was originally precipitated from a benzene solution before being freeze dried. It was found that this made no difference to the intrinsic viscosity, since the concentration of initiator (4 x 10^{-3} mole.$l.^{-1}$) was very small.

Viscosity Measurements

A weighed amount of the polymer, about 1 gm., was dissolved in 100 ml. of acetone and the viscosity of the solution, to infinite dilution, was measured in a modified Ubbelohde viscometer at 30°C. This type of viscometer enabled dilution to be carried out in situ.

The following table shows the results obtained.

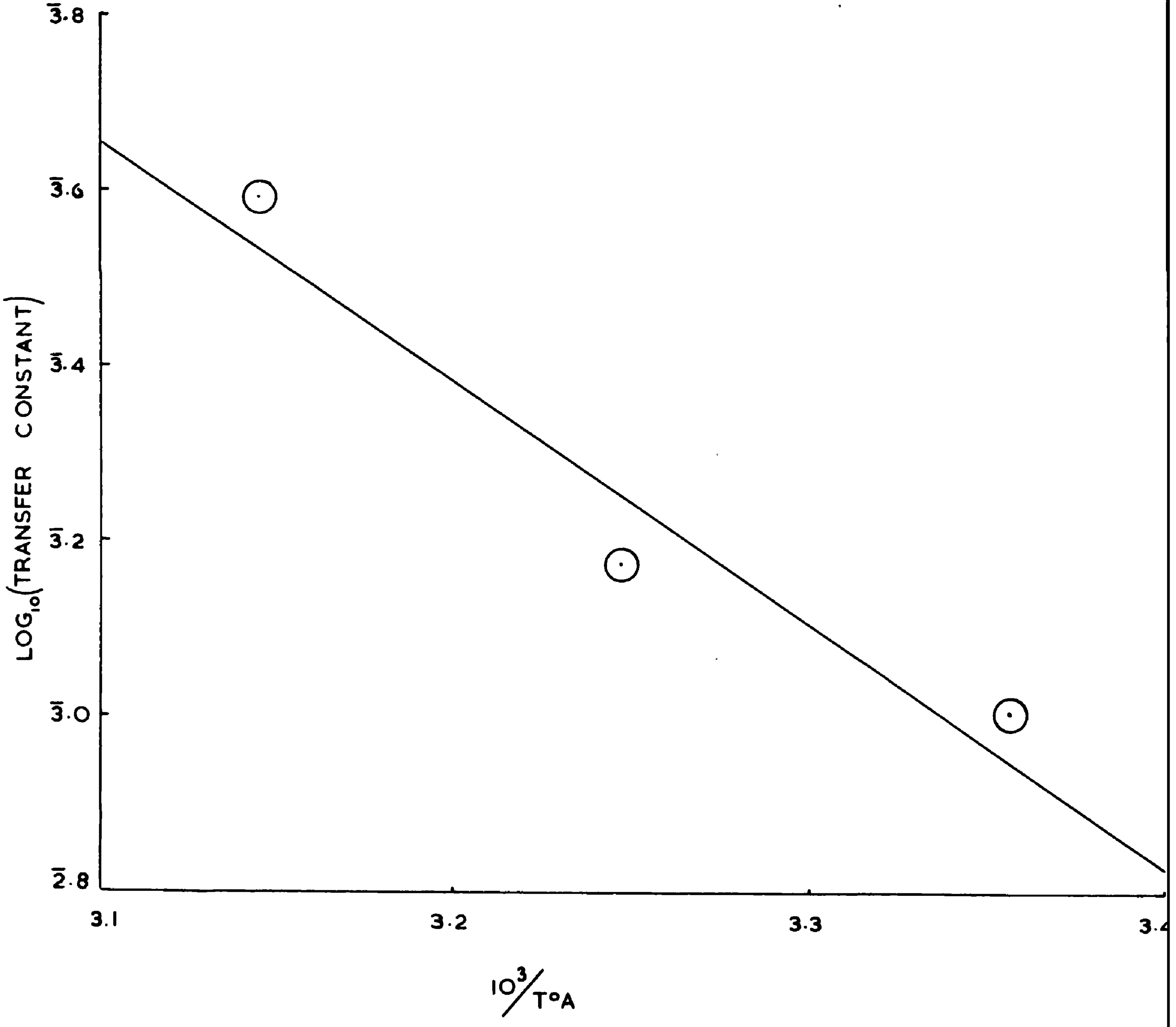
Table 33. Transfer constants, for the benzene/vinyl acetate polymerisation, at different temperatures.

Temperature °C	Intrinsic Viscosity	Molecular Weight $M_w \times 10^{-5}$	$\frac{[S]}{[M]}$ %	$C_s \times 10^3$
25	1.495	5.383	0	2.3
	1.228	4.111	5.56	
	0.900	2.710	11.4	
	0.825	2.400	17.0	
35	1.130	3.635	5.56	3.0
	0.984	3.011	11.4	
	0.813	2.328	17.0	
45	0.885	2.610	5.56	4.6
	0.730	2.013	11.4	
	0.680	1.829	17.0	

From Table 33 it will be seen that C_s increases with temperature showing that the transfer reaction has a positive energy of activation.

FIGURE 15.

DETERMINATION OF E_{tr}



Calculation of the activation energy for the transfer reaction.

From equation (41) it is possible to develop the equation

$$\log_{10} \frac{k_{tr}}{k_p} = \frac{1}{2.303\ RT} (E_p - E_{tr}) + \text{Constant.....}(54)$$

where E_{tr} is the activation energy of the transfer reaction.

$\therefore$ if $\log_{10} C_s$ is plotted against $\frac{1}{T^oA}$ a straight line is obtained which is a measure of $(E_p - E_{tr})$.

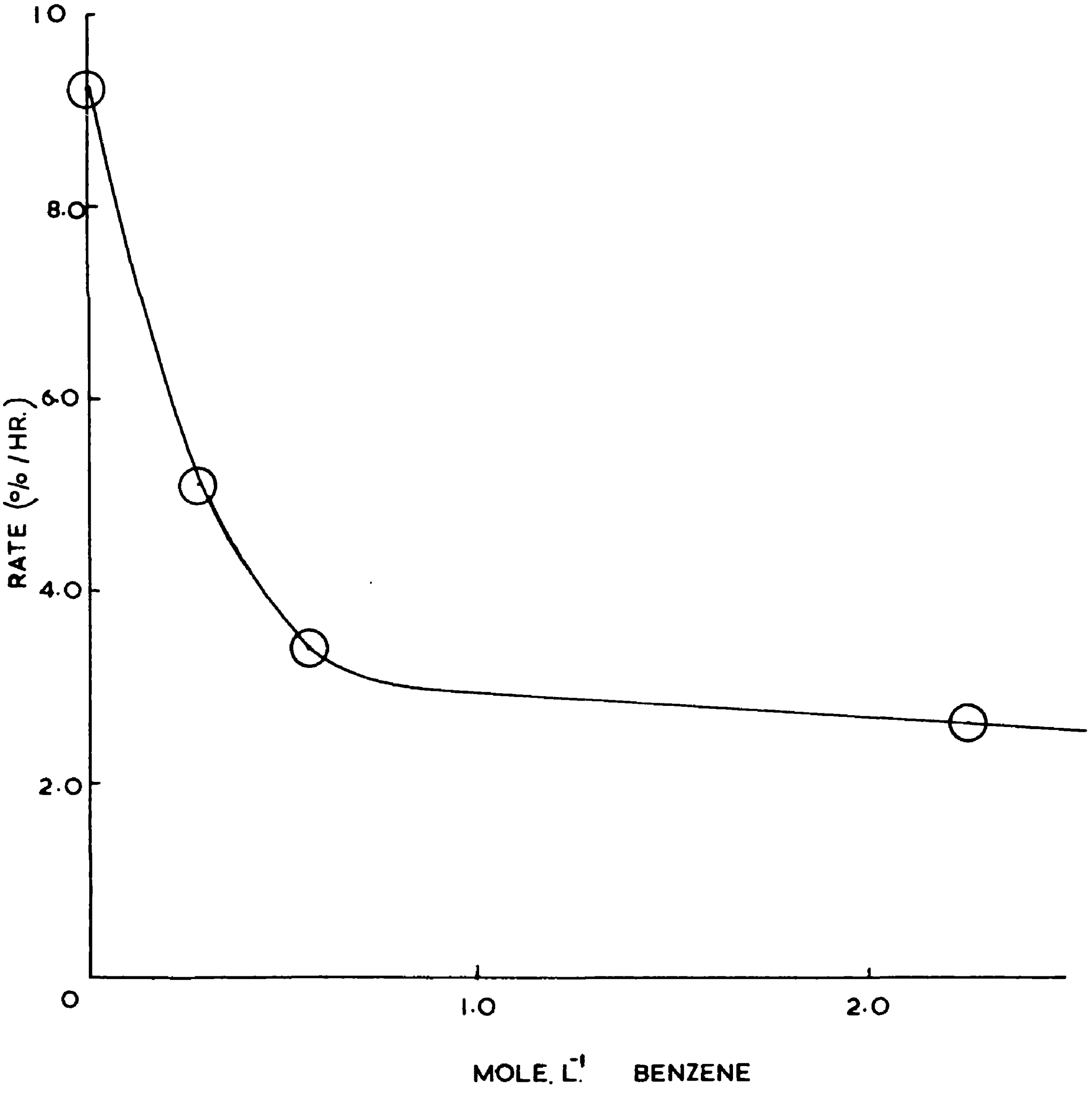
This gives $(E_p - E_{tr}) = -4.8$ Kcal.

From the bulk polymerisation $E_p = 6.2$ Kcal.

$$\therefore \underline{\underline{E_{tr} = 11.0 \text{ Kcal.}}}$$

FIGURE 16

VARIATION OF RATE OF REACTION WITH BENZENE CONCENTRATION



The Polymerisation in the Presence of Benzene.

Discussion

Two main effects are to be seen in these reactions. Firstly the rate of reaction is retarded by an amount dependent on the benzene concentration (Figure 16) and secondly the solvent properties of the benzene are such that the gel effect becomes greatly reduced and finally removed completely as more solvent is added.

The variation in the rate with benzene concentration shown in Figure 7 makes it obvious that the rate dependence on monomer concentration varies with the particular range of monomer/solvent ratios employed. This explains the disagreement among previous workers about the relationship between rate and monomer concentration. The mechanism of the retardation reaction will be discussed later and it is sufficient to say at the moment that the rate is not linear with respect to benzene concentration.

Before comparing the results in the final discussion, each polymerisation will be reviewed briefly.

Polymerisation of vinyl acetate with 2.5% benzene.

The presence of 2.5% benzene was found to exert a surprisingly large effect on the polymerisation. Since the gel effect appeared to be almost completely removed, particularly at the higher temperatures, the reaction can be considered to have only two stages, a combined initial and intermediate stage (0% - 40% conversion) and a final stage (40% - 80% conversion).

Table 10 shows that the rate shows only a small acceleration over the first stage and an almost equally slight fall in the final stage. This levelling off is also apparent in k_p and k_t the latter, like the lifetimes, being virtually constant, while k_p only increases slightly over the first 40% conversion. From 40% conversion onwards, however, both k_p and k_t fall suggesting that radical diffusion and to a small extent monomer diffusion are being retarded.

It has been pointed out already that E_o is fairly constant.

Polymerisation of vinyl acetate with 5% benzene.

The trends shown in the previous polymerisation are contimued with 5% benzene. The rate of reaction shows a further reduction, to slightly more than a third of the initial rate in the bulk reaction, and a very small acceleration over the initial stages at 25°C. Similarly the lifetimes are constant to 40% conversion. It would appear then, at first sight, that the viscosity increase is not sufficient to cause a gel effect. However in the later stages of the reaction, while the rate drops only to its initial value, the lifetimes do show an increase indicating that the termination reaction is being reduced. Unlike the polymerisation with 2.5% benzene, k_p is constant in the later stages and it would seem from this that at no time does monomer diffusion become retarded.

The values for E_o are once again constant, at about 7.7 Kcals., throughout the polymerisation, while $\frac{1}{2}E_t$ appears to fall slightly in the later stages. This could be due to an increase in a termination reaction with a low activation energy.

The generally accepted explanation for the gel effect is that radical diffusion is reduced in the initial stages of the reaction causing an autoacceleration in rate which only ceases when monomer diffusion becomes retarded. It has, however, been shown that in this polymerisation monomer diffusion remains unrestricted. An acceleration would then be expected. The reason why this does not happen is that as polymerisation advances and monomer is consumed, the ratio of benzene to vinyl acetate in the solution increases, the retardation reaction will occur more frequently and the rate will tend to fall.

The decreasing monomer concentration will also tend to slow down the propagation reaction. These two effects then, the tendency for acceleration due to gel effect and a reduction in rate due to falling monomer concentration and increasing retardation, balance each other out. This theory is supported by the fall in $\frac{1}{2}E_t$ that has been pointed out already as occurring in the later stages of the reaction.

It will be seen in the following reaction that this effect also explains the course of the polymerisation of vinyl acetate with 20% benzene.

Polymerisation of vinyl acetate with 20% benzene.

In the previous reactions that have been examined the gel effect, although decreasing as the amount of benzene increased, was always present. With 20% solvent, for the first time, the rate of polymerisation showed no tendency to increase and indeed fell throughout the reaction (Table 26). Similarly the lifetimes increased steadily throughout in a quite dissimilar way from those in the bulk, 2.5% and 5% benzene reactions. The quantity of solvent was sufficient to make the increase of viscosity with conversion sufficiently small not to affect the polymerisation. The result of this absence of gel effect was that the variations of rates, lifetimes velocity coefficients and activation energies were caused solely by chemical factors. The environment although it appeared externally to become more viscous with polymerisation, was constant on the molecular scale.

Under these circumstances it is interesting to examine closely what happened in the reaction. The rate, as has been stated, fell with conversion due to the falling monomer concentration and the increase in the retardation reaction between the benzene and polymer radicals. At the same time the lifetime increased. This would seem unlikely as the lifetime would tend to be reduced by retardation. It suggests that some secondary effect, such as reinitiation of the products of the retardation reaction may be taking place. The exact significance of this will be discussed later.

Both k_p and k_t showed only a slight fall over the 60% conversion range measured, while E_o seemed to increase.

These variations support the view that the retardation reaction increases with conversion. Moreover the increase in E_o can be related to the increase in E_o which occurs when the quantity of benzene in a reaction is increased.

III. The Polymerisation of Vinyl Acetate in the Presence of Toluene.

In the previous experiments with benzene the reaction between it and the kinetic chain radical whether it be transfer, as has been assumed up till now, or addition followed by some secondary effect, can only have occurred at the aromatic ring. In order to find if this effect would continue in a molecule with an alternative point of attack, vinyl acetate was polymerised in the presence of toluene under exactly the same conditions that had been employed during the polymerisation with benzene. Toluene was chosen because it has a much higher transfer constant than benzene and the benzyl radical, which is normally considered to be the product of the transfer reaction, is claimed to be very stable. The retardation under these circumstances would be much greater in toluene than in benzene.

The Polymerisation of Vinyl Acetate with 2.5% v/v Toluene (0.235 mole.$l.^{-1}$).

The initiator concentration (4×10^{-3} mole.$l.^{-1}$) was the same as was used previously. The toluene, prepared from sulphonic acid, was of high purity and was redistilled before use.

Table 34. Variation of rate and lifetime with extent conversion at 25°C and full light intensity (Instrument lag = 1.10 sec.).

Extent Conversion %	Rate of Reaction %/hr	Intercept sec.	Lifetime sec.
0	5.55	1.3	0.2
10	5.19	1.5	0.6
20	4.33	1.4	0.4
40	4.01	1.4	0.4

The drop in rate with conversion shown in Table 34 is in contrast to the reaction involving the corresponding amount of benzene. The lifetimes above seem to be fairly constant.

Table 35. Variation of rate and lifetime under different experimental conditions.

Extent Conversion	25°C Reduced Light Intensity		35°C Full Light Intensity		45°C Full Light Intensity	
%	Rate	Lifetime	Rate	Lifetime	Rate	Lifetime
10	2.13	1.0	6.8	0.4	8.8	0.4
20	1.95	1.3	5.5	0.3	7.7	0.4

The fall in rate with conversion is also shown in Table 35 over the narrow range of conversion examined. The lifetimes do not appear to vary with temperature.

Table 36. Velocity coefficients at 25°C and full illumination.

Extent Conversion %	Lifetime sec.	$k_p/k_t \times 10^6$	k_p l.mole.$^{-1}$sec.$^{-1}$	$k_t \times 10^{-7}$ l.mole.$^{-1}$sec.$^{-1}$
10	0.6	1.9	210	11
20	0.4	0.44	120	27

As would be expected Table 36 shows that k_p and k_t are very much smaller than the corresponding bulk polymerisation values. Since, as will be seen in Table 37, the termination is once more taking place by a mixed order reaction, the values in Table 36 must be corrected.

Table 37. Corrected velocity coefficients at 25°C and full illumination.

Extent Conversion %	Intensity Exponent	$k_p/k_t \times 10^6$	k_p l.mole.$^{-1}$sec.$^{-1}$	$k_t \times 10^{-7}$ l.mole.$^{-1}$sec.$^{-1}$
10	0.74	6.1	350	5.7
20	0.67	0.94	170	18

Since the value of at 10% conversion (Table 34) was rather high it is likely that the corresponding value of k_t is low. The value at 20% conversion represents a more realistic figure.

Due to the fact that mixed order termination occurs in this reaction it is impossible to apply the usual formulae relating activation energies used in either first or second order reactions. As in the case of benzene, $\frac{1}{2} E_t$ will be taken as a measure of the temperature coefficient of τ .

Table 38. Activation energies at full light intensity over the range 25°C to 45°C.

Extent Conversion %	E_o Kcal.	$\frac{1}{2} E_t$ Kcal.
10	5.7	0
20	5.9	0

Table 38 shows that unlike the previous reactions $\frac{1}{2} E_t$ is zero. The value of E_o seems slightly higher than the corresponding bulk vinyl acetate polymerisation values.

The Polymerisation of Vinyl Acetate with 5% v/v Toluene 0.47 mole.l.$^{-1}$

The previous experiment indicated an initial retardation effect by toluene on the polymerisation of vinyl acetate, very similar to that of benzene. In order to determine whether this effect would continue, the polymerisation was carried out in the presence of 5% toluene. It was examined more fully than the 2.5% toluene reaction in order to get a clearer overall picture of the variation of the reaction characteristics with conversion.

As before the initiator concentration was 4×10^{-3} mole.l.$^{-1}$

Table 39. Variation of rate and lifetime with extent conversion at 25°C and full light intensity.

Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
0	4.04	1.7	0.8
10	3.80	1.7	0.8
20	3.55	1.6	0.7
40	2.88	1.7	0.8
60	1.57	2.9	2.5

It will be seen from Table 39 that once again the retardation is approximately the same as for 5% benzene (Table 17). The rate does, however, drop throughout the reaction, showing no sign of any gel effect.

Table 40. Variation of rate and lifetime with extent conversion at 25°C and reduced light intensity.

Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
0	1.82	2.0	1.3
10	1.80	2.1	1.4
20	1.76	2.1	1.4
40	1.36	2.15	1.5
60	0.75	3.6	3.5

Table 40 shows that the rate drops in the same way as at full intensity. At 60% conversion the rate had reached a very low value and the experiment was terminated.

Table 41. Variation of rate and lifetime with extent conversion at 35°C and 45°C.

Temperature °C	Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
35	0	5.50	1.5	0.6
	10	5.00	1.7	0.9
	20	4.90	1.6	0.7
	40	3.90	1.7	0.9
	60	2.40	2.7	2.2
45	0	7.80	1.65	0.8
	10	7.60	1.6	0.7
	20	7.30	1.8	1.0
	40	6.02	1.7	0.9
	60	3.90	2.6	2.1

It will be seen from Table 41 that while the rates increase with temperature the lifetimes seem to be unaffected. The rates appear to fall off less rapidly with conversion at the higher temperatures, indicating that E_o will increase with conversion.

Table 42. Intensity Exponents at 25°C. $L_2 = 0.307\ L_1$

Extent Conversion %	Rate of Reaction L_1 %/hr	Rate of Reaction L_2 %/hr	Intensity Exponent.
0	4.04	1.82	0.67
10	3.80	1.80	0.63
20	3.55	1.76	0.59
40	2.88	1.36	0.63
60	1.57	0.75	0.62

As would be expected from previous results the intensity exponents in Table 42 show that mixed order termination is occurring.

Table 43. Variation of velocity coefficients with extent conversion at 25°C and full illumination.

Extent Conversion %	Rate of Reaction %/hr.	$k_p/k_t \times 10^6$	k_p l.mole^{-1}sec^{-1}	$k_t \times 10^{-7}$ l.mole^{-1}sec^{-1}
0	4.04	2.20	130	5.7
10	3.80	2.50	140	5.7
20	3.55	3.20	210	6.8
40	2.88	2.4	140	5.7
60	1.57	1.9	11	0.55

Due to the mixed order termination the velocity coefficients must be corrected.

Table 44. Variation of corrected velocity coefficients with conversion at 25°C and full light intensity.

Extent Conversion %	Lifetime sec.	$k_p/k_t \times 10^6$	k_p $\mathrm{l.mole.^{-1}sec.^{-1}}$	$k_t \times 10^{-7}$ $\mathrm{l.mole.^{-1}sec.^{-1}}$
0	0.8	4.9	190	3.8
10	0.8	4.3	180	4.3
20	0.7	4.5	250	5.7
40	0.8	4.3	180	4.3
60	2.5	3.3	14	0.43

The velocity coefficients in Table 44 show no definite change in value until 60% conversion when the increasing lifetimes indicate a gel effect which is not shown in the rate of reaction.

Table 45. Activation energies at full light intensity over the range 25°C to 45°C.

Extent Conversion %	E_o Kcal	$\frac{1}{2} E_t$ Kcal
0	6.7	0
10	6.5	0
20	6.9	0
40	7.3	0
60	7.1	1

The values for E_o in Table 45 are larger than the corresponding ones for 2.5% toluene, Table 38, indicating the same trend noted in the previous polymerisations in the presence of benzene.

The Polymerisation in the Presence of Toluene.

Discussion

Two main effects appear when the polymerisation of vinyl acetate in the presence of toluene is examined. The first is that the retardation effect of toluene is very similar to that of benzene and the second is that the rate of reaction drops throughout the polymerisation.

The fact that toluene retards the polymerisation by the same amount as benzene is, at first sight, rather surprising. As has been pointed out at the beginning of this section the normal product of the transfer reaction with toluene, the benzyl radical, is considered to be fairly stable. If the retardation was a result of the presence of this radical then it would be expected that toluene, since it transfers more readily, would be much more effective in reducing the rate of reaction than benzene. The fact that it is not suggests that the retardation takes place by some other means. If the radical produced by this step was even more stable than the benzyl radical then this other reaction would represent the rate controlling step. The exact mechanism of this reaction will be considered in the final discussion.

The second effect, the fall in rate of reaction as the polymerisation advances, can be explained by an increase in the retardation reaction. As in the case of the benzene experiments there are two main influences acting in different ways on the rate of reaction. The increasing solution viscosity tends to increase it and the decreasing monomer concentration and increasing solvent to monomer ratio tend to decrease it. The latter effect is caused by monomer being removed by polymerisation. The concentration of solvent is virtually constant with the result that retardation reaction occurs more frequently.

It has been pointed out that with 2.5% benzene the gel effect was still sufficiently large to cause a slight acceleration in rate. With 2.5% toluene, however, it is not large enough to overcome the fall in rate due to the increasing termination reaction and the rate falls. The same thing happens with 5% toluene as would be expected since the dilution effect of the solvent has increased.

The picture of increasing retardation is supported by the velocity coefficients. Comparison of Table 44 with Table shows that both k_p and k_t are smaller than in the bulk polymerisation. However k_p is more affected with the result that k_p/k_t is smaller with toluene than in the bulk reaction.

The effect, noted in the polymerisations of vinyl acetate in the presence of benzene, that E_o increases with solvent concentration is also evident in toluene. At 10% conversion E_o = 5.7 and 6.7 with 2.5% and 5.0% toluene respectively. It seems likely that this is related to the retardation reaction in some way, possibly through the activation energy of the chain reinitiation step involving the stable radicals formed during the retardation reaction.

IV. The Polymerisation of Vinyl Acetate in the Presence of Cyclohexane.

Where an unsaturated compound is used as a retarder in free radical polymerisation there is the possibility that the reaction between the retarder and the chain radical will be by a chain transfer or an addition mechanism. In order to remove any chance of the addition reaction taking place and at the same time to find the effect of a bad solvent for the polymer on the reaction, vinyl acetate was polymerised in the presence of cyclohexane. The usual concentration of initiator, 4×10^{-3} mole.$l.^{-1}$, was present in both reactions investigated.

The Polymerisation of Vinyl Acetate with 5% v/v Cyclohexane (0.46 mole.$l.^{-1}$)

Spectroscopically pure cyclohexane was used, being degassed in the usual way in the dilatometer.

Table 46. Variation of rate and lifetime with extent conversion at 25°C and full light intensity.(Instrument lag = 1.05 sec.)

Extent Conversion %	Rate of Reaction %/hr	Intercept sec.	Lifetime sec.
0	6.78	1.9	1.2
10	7.26	1.9	1.2
20	7.87	1.8	1.1
40	9.17	2.2	1.7
60	6.12	3.2	3.1

Table 46 shows that there is a much smaller retardation with cyclohexane than with benzene, Table . The rate of reaction shows a slight acceleration.

Table 47. Variation of rate and lifetime under different reaction conditions.

Extent Conversion %	25°C Reduced Intensity		35°C Full Intensity		45°C Full Intensity	
	Rate	Lifetime	Rate	Lifetime	Rate	Lifetime
0	3.14	1.6	9.1	1.2	12.4	1.2
10	3.7	1.4	10.2	1.3	13.4	1.0

It will be seen from Table 47 that, as in Table 46, the rates increase with conversion. The lifetimes appear to be unaffected by temperature.

Table 48. Velocity coefficients at 25°C and full light intensity.

Extent Conversion %	Rate of Reaction %/hr	$k_p/k_t \times 10^6$	k_p $\text{l.mole}^{-1}\text{sec}^{-1}$	$k_t \times 10^{-7}$ $\text{l.mole}^{-1}\text{sec}^{-1}$
0	6.78	3.4	82	2.4
10	7.26	1.7	49	2.9

It will be seen in the following table that the intensity exponents indicate a degree of mixed order termination and the results in Table 48 must be corrected to allow for this.

Table 49. Corrected velocity coefficients at 25°C and full illumination.

Extent Conversion %	Intensity Exponent	$k_p/k_t \times 10^6$	k_p l.mole.$^{-1}$sec.$^{-1}$	$k_t \times 10^{-7}$ l.mole.$^{-1}$sec.$^{-1}$
0	0.65	6.5	110	1.7
10	0.54	1.96	53	2.7

The values of k_p in Table 49 are considerably lower than in the bulk reaction as would be expected since the rate is reduced.

Table 50. Activation energies at full light intensity over the range 25°C to 45°C.

Extent Conversion %	E_o Kcal	$\frac{1}{2}$ E_t Kcal
0	4.9	0
10	5.8	0

The values of E_o seem fairly similar to those in the bulk polymerisation. Although the intensity exponent at zero conversion indicates mixed order termination, the value at 10% conversion is very close to the complete second order value of 0.5. In view of the later results it is likely that termination is second order and E_p can, in this case, be quoted as 4.9 Kcal and 5.8 Kcal. at 0% and 10% conversion respectively.

The Polymerisation of Vinyl Acetate with 20% Cyclohexane (2.24 mole 1^{-1})

The previous experiment has shown that cyclohexane inhibits the polymerisation of vinyl acetate much less than benzene and it was also seen, in table 46, that the rate accelerated over the range of conversion investigated. Since it has already been noted that 20% benzene completely removes any gel effect it is interesting to compare the effect of an equivalent amount of cyclohexane. Precipitation of polymer could be expected to take place during the later stages of the reaction because the polymer is insoluble in cyclohexane. A similar effect has been noted for the polymerisation of vinyl acetate in n- hexane solution.

Table 51. Variation of rate and lifetime with extent conversion at 25°C and full light intensity. (Instrument lag = 1.05sec.)

Extent Conversion %	Rate of Reaction %/hr.	Intercept sec.	Lifetime sec.
0	5.3	1.4	0.5
20	6.4	1.5	0.7
40	6.8	1.5	0.7
60	7.1	2.2	1.6
80	7.6	3.2	3.0
85	6.4	4.7	5.2

Table 51 shows that the rate increased with conversion to 80%. The poly vinyl acetate precipitated from solution immediately before the determination of the rate at a reduced light intensity at 25°C and 80% conversion. This caused the apparent reduction in rate at 85% conversion.

Table 52. Variation of rate and lifetime with extent conversion at 25°C and reduced light intensity.

Extent Conversion %	Rate of Reaction %/hr	Intercept sec.	Lifetime sec.
0	2.8	2.1	1.5
20	3.3	2.0	1.4
40	3.8	2.1	1.5
60	3.8	3.0	2.8
80	3.2	4.7	5.3
85	3.0	6.8	8.1

The rate in Table 52 appears to fall at 80% conversion but this is due, as has been pointed out, to precipitation. In the following Table, 53, the same effect is evident in the rates at 80% and 85% conversion. When precipitation occurred the solution became opaque to U.V. light, with the result that the rate of initiation was reduced, resulting in a fall in the rate of reaction.

Table 53. Variation of rate and lifetime with extent conversion at 35°C and 45°C with full light intensity.

Temperature °C	Extent Conversion %	Rate of Reaction %/hr	Intercept sec.	Lifetime. sec.
35	0	7.3	1.5	0.7
	20	7.6	1.5	0.7
	40	8.5	1.5	0.7
	60	8.2	2.0	1.4
	80	7.8	3.1	3.0
	85	7.4	4.1	4.3
45	0	8.1	1.45	0.6
	20	10.1	1.5	0.7
	40	11.2	1.5	0.7
	60	10.3	1.95	1.3
	80	8.8	1.65	2.3
	85	9.8	3.6	3.7

Unlike the results at 25°C, Table 53 shows that at the higher temperatures the rate started to drop at 60% conversion, before precipitation occurred.

Table 54. Intensity Exponents at 25°C. $L_2 = 0.307\ L_1$

Extent Conversion %	Rate of Reaction %/hr L_1	Rate of Reaction %/hr L_2	Intensity Exponent.
0	5.3	2.8	0.54
20	6.4	3.3	0.56
40	6.8	3.8	0.49
60	7.1	3.8	0.53
80	7.6	3.2	0.73
85	6.4	3.0	0.64

The intensity exponent, Table 54, at 80% conversion is high due to the fact that precipitation of polymer occurred between the determination of the rate at the reduced light intensity. This value should, therefore, be ignored. The intensity exponents in the above table indicate that the reaction has, substantially, a second order termination reaction.

Table 55. Variation of velocity coefficients with extent conversion at 25°C and full light intensity.

Extent Conversion %	Rate of Reaction %/hr	$k_p/k_t \times 10^6$	k_p l.mole.$^{-1}$sec.$^{-1}$	$k_t \times 10^{-7}$ l.mole.$^{-1}$sec.$^{-1}$
0	5.3	6.0	930	13.5
20	6.4	8.0	660	8.3
40	6.8	13.0	1080	8.3
60	7.1	17.0	240	1.4
80	7.6	24.0	94	0.39
85	6.4	31.0	40 45$^+$	0.13 0.15$^+$

$^+$These represent the values for k_p and k_t corrected to allow for the reduction in the rate of initiation in Table 55.

Table 56. Variation of corrected velocity coefficients at 25°C and full light intensity.

Extent Conversion %	Intensity Exponent	k_p/k_t	k_p l.mole.$^{-1}$sec.$^{-1}$	k_t l.mole.$^{-1}$sec.$^{-1}$
0	0.54	8.1	1010	12.5
20	0.56	10	750	7.4
40	0.49	13	1080	8.3
60	0.53	19	254	1.3
80	0.73	43	125	0.29
85	0.64	60	60	0.11

As will be seen comparing the values for k_p and k_t in Tables 55 and 56, the correction factor is very small, being much less than the experimental error, and could consequently be ignored. In order to correct k_p and k_t at 80% conversion the average value of the other intensity exponents was used.

As has been pointed out the intensity exponents are very close to 0.5. Since second order termination is occurring it is possible to obtain a value for E_t, unlike the previous experiments with benzene and toluene. Table 57, therefore, gives values for both E_t and E_p.

Table 57. Variation of activation energies with extent conversion over the range 25°C to 45°C.

Extent Conversion %	E_o Kcal.	E_p Kcal.	E_t Kcal.
0	3.6	3.6	0
20	4.1	4.1	0
40	4.1	4.1	0
60	3.5	4.4	2.0
80	1.5	2.8	2.5
85	3.6	5.2	3.2

Once more the effect of precipitation is evident in the apparently low value of E_o at 80% conversion. The values of E_o are lower than in the bulk polymerisation.

The Polymerisation in the Presence of Cyclohexane.

Discussion

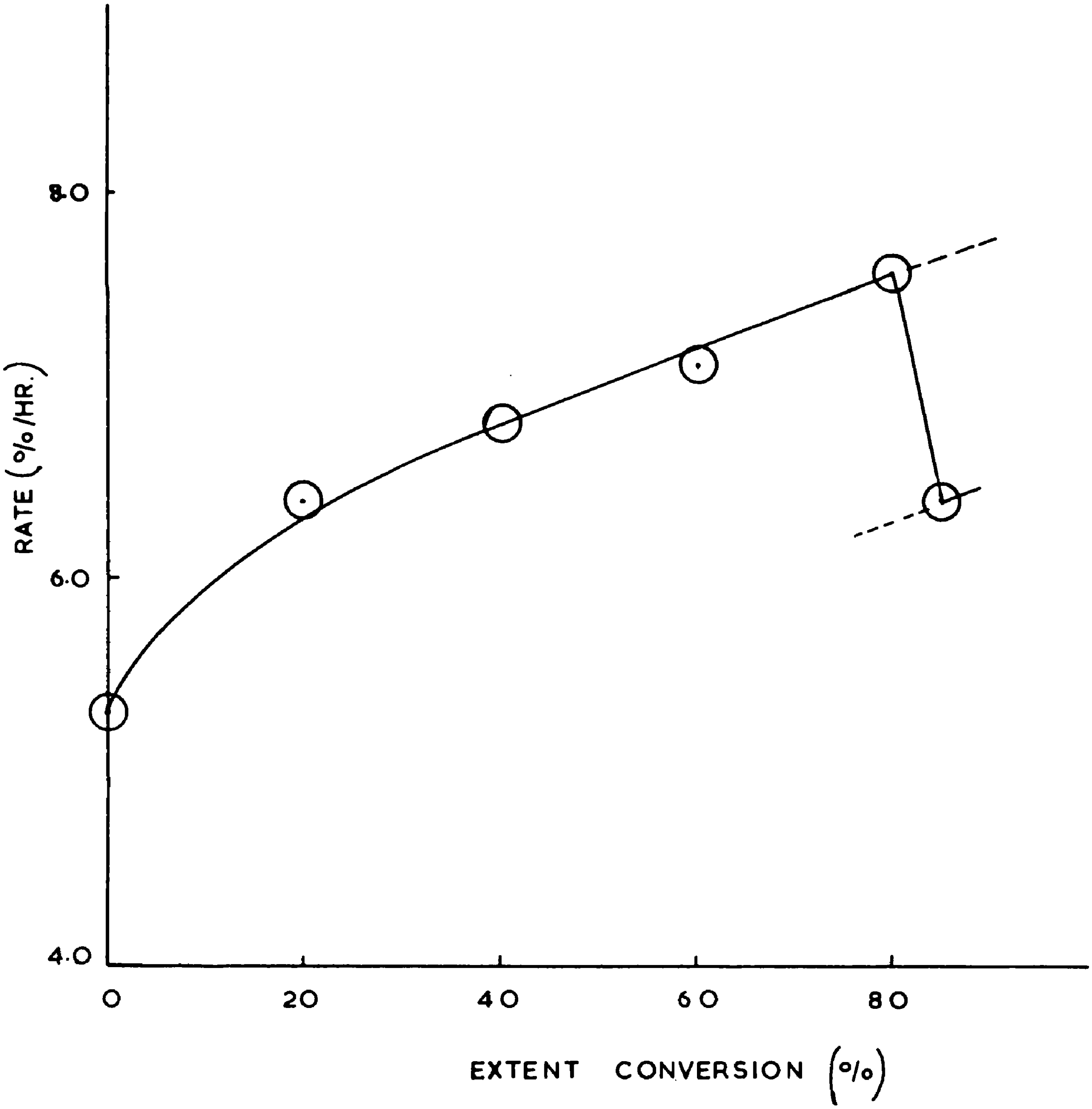
There is a close parallel between these results and those obtained in the bulk polymerisation. Apart from the variation of rate with conversion the results are precisely what would be expected from a polymerisation in the presence of an inert diluent. The intensity exponent shows almost exclusive second order termination taking place up to 80% conversion, the values of k_p and k_t are very similar initially to those in the bulk polymerisation and also E_t is zero in the initial stages of the reaction. It has been found, however, that cyclohexane has a transfer constant with vinyl acetate very similar to that of benzene.[34] Since the only reaction which can take place between a chain radical and cyclohexane is transfer, the cyclohexyl radical formed must presumably be able to reinitiate another chain readily.

The precipitation which occurred at 80% conversion gives this reaction the distinction of being homogeneous and heterogeneous at different stages. There was no sudden change in any of the measured or derived quantities, however,

FIGURE 17

VINYL ACETATE WITH 20 % CYCLOHEXANE.

VARIATION OF RATE WITH CONVERSION



except in the rate of reaction. In a bad solvent the polymer tends to coil more than it does when in a good solvent. Thus as the ratio of cyclohexane to monomer increased, the solubility of the polymer in the solution decreased, with the result that the chains became progressively more coiled until precipitation finally occurred. Had precipitation not taken place the rate could be expected to have increased as shown in Figure (17).

The gel effect in these reactions is caused by a coiling of the radical chains with the result that the active centre of the polymer becomes inaccessible to the corresponding active centre of another chain. The rate of termination thus being reduced, the rate of reaction accelerates. This is rather different from the bulk polymerisation of vinyl acetate. In this case the autoacceleration is caused by an increase in solution viscosity rather than by the configuration of individual radical chains.

The coiling of the radical chains also accounts for the unusually low value of E_o. Since the solubility of the polymer in the solution increases with temperature, the chain radicals tend to straighten out as the temperature rises. This enables termination to take place more readily at the higher temperatures, with the result that the rate of reaction will be less than it would have been had the radical chain remained coiled. The result is a low value of E_0. The same effect has been reported by Burnett and Melville[59] who found a negative value of E_0 for the polymerisation of vinyl acetate in *n*-hexane.

V. The Polymerisation of Vinyl Acetate in the Presence of Strong Retarders.

While benzene and toluene have been shown to have a fairly strong retarding effect on the polymerisation of vinyl acetate, there are many compounds which retard the polymerisation much more efficiently. The following section gives the results obtained in such reactions. In most the rate was too low to be measureable and in order to get a high rate it would have been necessary to use retarder concentrations of the same order as the initiator concentration.

The Polymerisation of Vinyl Acetate in the Presence of 0.153 mole.$l.^{-1}$ Diphenyl.

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

This compound was of interest due to its similarity to benzene.

The initiator concentration was 4×10^{-3} mole.$l.^{-1}$

Table 58. Variation of rate and lifetime with extent conversion at 25°C and full light intensity. (Instrument lag = 1.3 sec.)

Extent Conversion %	Rate of Reaction %/hr	Intercept sec.	Lifetime sec.
0	2.50	1.5	0.3
10	1.80	1.5	0.3
20	1.42	1.5	0.3
30	1.10	1.6	0.5

The fall in rate with conversion shown in Table 58 is similar to the effect noted in toluene. Since diphenyl is a solid a pronounced gel effect might have been expected, but the lifetimes as well as rates show no sign of this.

Table 59. Variation of rate and lifetime under different reaction conditions.

Extent Conversion	25°C Reduced Intensity		35°C Full Intensity		45°C Full Intensity.	
%	Rate %/hr	Lifetime sec.	Rate %/hr	Lifetime sec.	Rate %/hr	Lifetime sec.
0	1.1	0.6	3.2	0.3	3.7	0.1
10	0.78	0.6	2.5	0.3	3.1	0.3
20	0.50	-	2.0	-	2.5	-

Table 59 shows that the fall in rate with conversion is maintained under the above conditions. The lifetimes are not accurate since they are very short and the rate is low. The general indication is however that they do not vary with temperature.

Table 60. Velocity coefficients at 25°C and full light intensity.

Extent Conversion %	Rate of Reaction %/hr	$k_p/k_t \times 10^7$	k_p l.mole.$^{-1}$sec.$^{-1}$	$k_t \times 10^{-8}$ l.mole.$^{-1}$ sec.$^{-1}$
0	2.50	9.7	400	4.2
10	1.80	6.4	270	4.2

As will be seen in the next table, mixed order termination is occurring. The values for k_p and k_t in Table 60 must be corrected, as usual, to allow for this.

Table 61. Corrected velocity coefficients at 25°C and full light intensity.

Extent Conversion %	Intensity Exponent	$k_p/k_t \times 10^6$	k_p $l.mole^{-1}sec^{-1}$	$k_t \times 10^{-8}$ $l.mole^{-1}sec^{-1}$
0	0.69	2.26	600	2.7
10	0.71	1.68	420	2.5

The values for k_t in Table 61 are fairly high, as would be expected in the presence of a strong retarder; k_p also seems high.

Table 62. Activation energies over the range 25°C to 45°C.

Extent Conversion %	E_o Kcal.	$\frac{1}{2}$ E_t Kcal.
0	2.6	0
10	3.2	0
20	4.2	-

Once again a value for the energy of termination cannot be given due to the mixed order termination reaction. The value of E_o is very low in Table 62, but seems to increase with conversion.

The Polymerisation of Vinyl Acetate in the Presence of 5% v/v Benzyl Bromide (0.42 mole.l^{-1})

The benzyl bromide was purified by washing with dilute sodium carbonate solution, then water, drying and distilling under vacuum.

The rate of polymerisation, with an initiator concentration of 4×10^{-3} mole.l^{-1}, was too small to be measured by the thermocouple method, and with the reaction taking place in the thermocouple dilatometer the rate was found dilatometrically to be 2.8×10^{-2} %/hr. It was noticed that the polymer formed was green and this colouration was not removed by repeated precipitation.

The Polymerisation of Vinyl Acetate in the Presence of 5% v/v Cyclohexene

The initiator concentration was the same as before. Strong inhibition was once more experienced, the rate being found by contraction measurements to be 0.36%/hr.

The Polymerisation of Vinyl Acetate in the Presence of (a) 5% v/v Tetralin (0.58 mole.l^{-1}) and (b) 5% by weight of Naphthalene (0.39 mole.l^{-1})

The tetralin was purified by washing with dilute potassium permanganate then water, drying overnight, and refluxing over sodium in a nitrogen atmosphere to remove peroxides.

The naphthalene was a sample from the National Coal Board laboratories and had been purified by chromatography.

In both reactions the initiator concentration was 4×10^{-3} mole.l^{-1}.

Complete inhibition was found in each case.

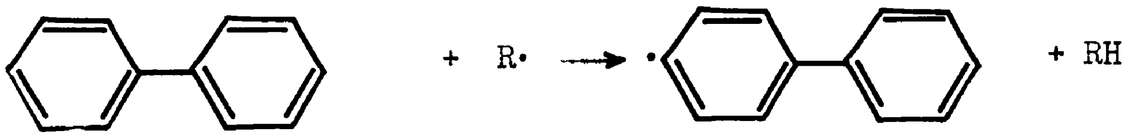
The Polymerisation in the Presence of Strong Retarders.

Discussion

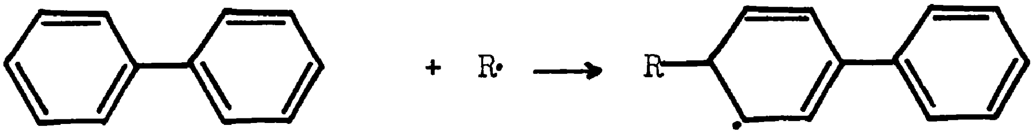
During the polymerisation of vinyl acetate the rate, as has been pointed out, fell with conversion. This can be related to the retardation reaction. Where there is a strong retarder present a small increase in the ratio of retarder to monomer will result in a large fall in the rate of reaction. Under these circumstances the tendency for the rate to fall is much greater than the normal autoacceleration. In the previous polymerisations in which the rate fell with conversion i.e. with 20% benzene and the toluene experiments, the gel effect was fully or partly removed by the dilution action of the solvent. Diphenyl, however, would tend to increase the initial viscosity since it is a solid.

The strong retardation of the polymerisation of vinyl acetate by diphenyl is not surprising in view of the highly conjugated aromatic radical that would be formed by reaction between a chain radical and diphenyl.

I. Chain Transfer



II. Addition



The radical, whether formed by chain transfer or addition, would have a high resonance energy and hence would be very stable. Under these circumstances reinitiation could not easily occur. The same argument applies to the reaction between chain radicals and cyclohexene, tetralin and naphthalene.

The retardation of the polymerisation by benzyl bromide presents rather a special case. It was noticed that the polymer formed was coloured green and after standing for several days it turned a dark colour. This was found to be due to the presence of copper in the polymer. It would appear that the benzyl bromide reacted with the copper thermocouple wire to give copper bromide which further reacted with a chain radical:

$$R\cdot + Cu \longrightarrow Cu\,R.$$

DISCUSSION
AND
CONCLUSIONS

DISCUSSION AND CONCLUSIONS

Limitations of the Thermocouple Method.

The thermocouple method for making non stationary state measurements is one of the most convenient and accurate of those available. There are, nevertheless, certain difficulties and limits on its use, as there must be in all such systems. It is in the knowledge of the possible shortcomings that the results obtained by it must be considered. The following is a review of the limits of the thermocouple method.

Temperature Measurement.

The temperature was recorded by the thermocouple at the centre of a reaction mixture in a soft glass vessel. It has been assumed that the temperature of the water bath in which the reaction was immersed was constant. In fact the signal obtained by the pen recorder voltmeter was due to opposing electromotive forces from two thermocouples, namely the one mentioned above and a "cold junction" in an evacuated space in the side arm. The distance separating these was approximately 4 cm. and this was sufficient, while the bath was being stirred vigorously, to result in an apparent temperature fluctuation of 0.005°C. When the stirrer was switched off it was found that the temperature apparently remained completely steady for a period of about 2 minutes. This was ample time in which to obtain a chart trace on initiating the reaction. It was thus possible to obtain greater accuracy than would seem at first possible.

The noise level in the Tinseley D.C. amplifier corresponded to a temperature fluctuation of 0.00014°C and this represents the ultimate limit of temperature measurement.

The electromotive force - temperature relationship for the copper constantan thermocouples was obtained from the literature[64] and was quoted for 25°C. The rates of reaction using the thermocouple method were found to agree well with dilatometric measurments, and previous workers[51] have obtained close agreement with rates measured using platinum - platinum/rhodium thermocouples.

Taking all the various factors into consideration the final limit of temperature measurement is 0.001°C.

Adiabatic Conditions.

In bulk polymerisation the period during which the reaction is adiabatic in the region of the thermocouple increases as the mixture gels. In the presence of large quantities of solvent this gelling does not occur so that it is impossible to measure accurately such large lifetimes. Fortunately it was found that there was no necessity to do so, since as gelling was reduced so radical lifetimes deviated less from their initial low values.

Under adiabatic conditions if fractional conversion is plotted against time a steadily increasing curve will be obtained which at time equal to three times the lifetime (τ) becomes a straight line showing a constant rate of increase in temperature (fig.1). This will continue to be the case until the reaction becomes non adiabatic (fig.2). If the period for which the reaction is adiabatic is less than 3 a straight line will never be attained, the initial upward curve going through a point of inflection to a downward curve. The resulting temperature, as has already been stated, reaches a maximum depending on the rate of reaction. These factors, then, determine the upper limit of the radical lifetimes. Since the values found in this work were never greater than 17 seconds it was not found necessary to employ any special techniques. In many polymerisations lifetimes of 50 seconds and upwards do occur and vacuum jacketted dilatometers[65] have been used, with some success, to increase the adiabatic period.

Errors in Measuring the Lifetime of the Kinetic Chain Radical

There is always the possibility of inaccuracies in the extrapolation of the stationary state time-temperature curve. The start of the reaction is signalled by a pip on the recorder chart. This could move the pen from its original path, creating an error. Since this is a constant for each reaction it would almost certainly be included in the instrument lag and consequently be allowed for.

It is the variation of the instrument lag from run to run which results in the greatest errors. The response times of the amplifier, 0.04 sec., and the thermocouple, due to its very small heat capacity, are a constant. The lag of the pen recorder is very much larger, about 1.0 seconds, and varies with the amount of ink in the pen reservoir. To obtain accurate values the radical lifetime should be about 3 seconds. They were, in fact, mostly shorter than this when a solvent was present and it required several determinations at each stage to get a reliable figure.

Polymerisation in the Presence of Compounds Reactive with Metals.

The inhibition obtained during the polymerisation in the presence of benzyl bromide shows yet another limitation of the use of the thermocouple method. When there is a compound present which will react with the metals of the thermocouple the method fails. In general this does not affect the investigation of the vast majority of organic reactions, although halogen compounds must be avoided. It is in this respect that the thermistor method has the advantage, since the temperature detector is glass coated and therefore immune to attack.

The Influence of Aromatic Compounds on Vinyl Acetate Polymerisation.

As stated in the introduction the action of solvents on the polymerisation of vinyl acetate is due to a dilution and a retardation effect. The energies of activation, velocity coefficients, magnitude and variation of the rate of reaction with conversion, and the lifetimes are all different from their corresponding bulk polymerisation values. Some of the properties are more influenced by retardation than by the dilution and vice versa; for example the magnitude of the lifetimes and rates of reaction are governed by the former, while the variation in the rate with conversion is almost exclusively, at high monomer concentration, a function of the hydrocarbons solvent properties. Thus it is possible to discuss the two influences separately, even although many of the effects overlap.

Action of Solvents on the Polymerisation of Vinyl Acetate.

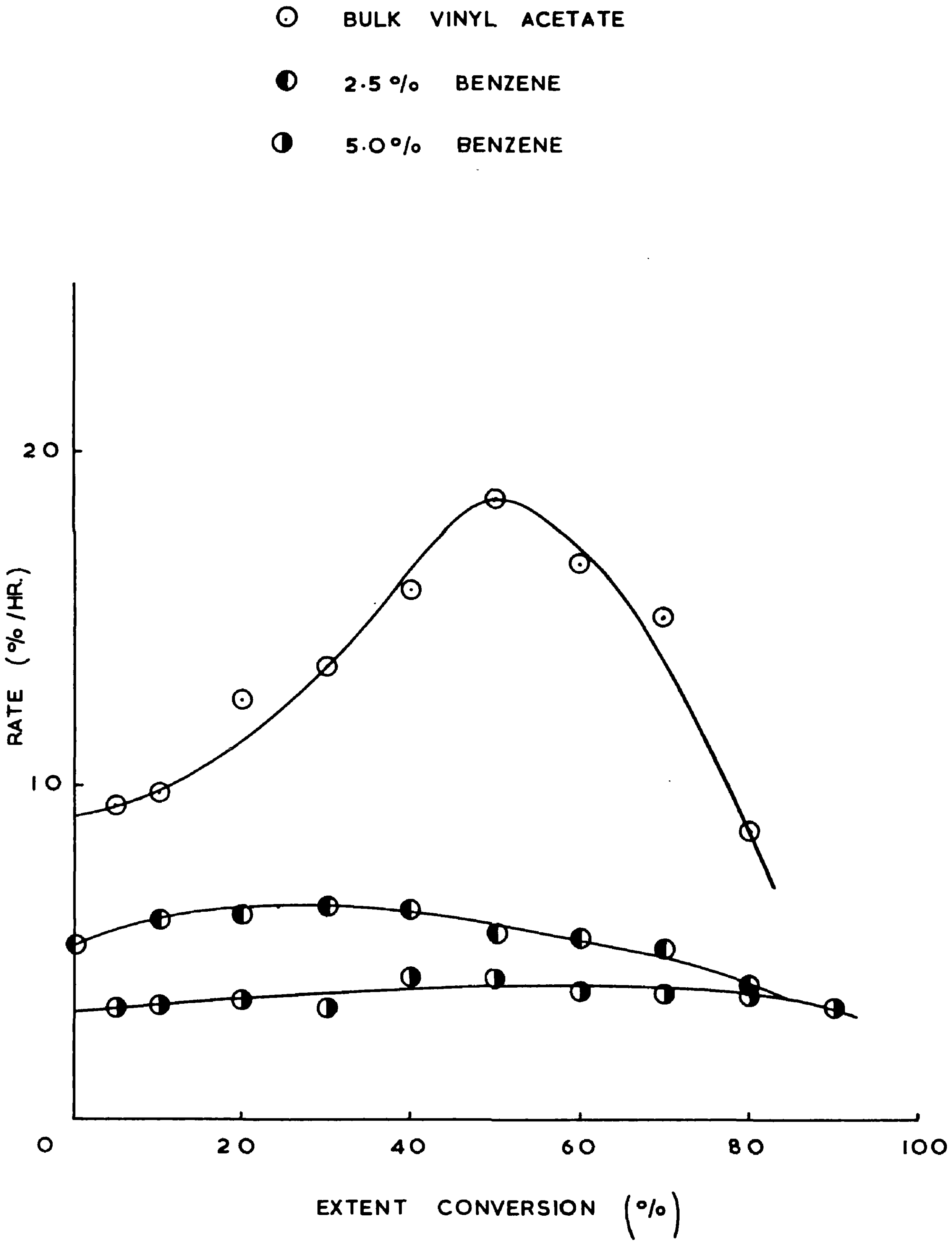
Every homogeneous liquid phase bulk polymerisation can be regarded as taking place in solution in all but the final stages of the reaction, with the monomer as solvent. When an inert liquid is added the tendency is for the rate of reaction to fall due to the reduction in the concentration of the monomer. If the reaction products were of low molecular weight this effect would be fairly easy to show. As it is, the structure of a high polymer in solution is influenced by its environment. If the growing polymers are surrounded by a solvent which is unfavourable they will be more attracted to themselves than to the solvent. The result of this is that the solvent will tend to be removed from contact with the polymers which will become coiled and in the most unfavourable circumstances will be precipitated from solution. In contrast a good solvent will be attracted to the polymer chain which will assume an extended configuration. Thus, in the work reported in this thesis, since every diluent was a poorer solvent for the polymer than monomeric vinyl acetate, the polymer was always more coiled in solution than in the initial stages of the bulk polymerisation. The direct result of this coiling is that the rate of termination is reduced and the rate of polymerisation becomes greater than would be expected from the theoretical rate - monomer concentration equation (page 16. As was pointed out in the introduction, various attempts have been made to obtain a strict relationship between monomer concentration and the rate of polymerisation in dilute solution. The most frequently quoted relationship is expressed by the equation reported by Conix and Smets[38].

$$\text{Rate} = K.[B]^{\frac{1}{2}}[M]^{3/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(55)$$

using the usual symbols with K as a constant.

FIGURE 18.

VARIATION OF RATE WITH CONVERSION



The rate of reaction of a vinyl polymerisation in which the growing chain contains a large number of monomer units should, of course, be proportional to the monomer and free radical concentrations since the rate of consumption of monomer is the same as that in the propagation reaction. The departure from the expected relationship has been suggested by Bamford, Jenkins and Johnstone[66] to be due to termination of the reaction by the primary radicals produced from the initiator, particularly at low monomer concentration. This does not apply to the work done in this thesis since monomer concentration was always high.

When reaction takes place between the chain radicals and solvent resulting in retardation equation (55) does not apply. In order to find the effect of solvent it is more profitable to examine the variation of rate with conversion at different solvent concentrations. The fall in rate which occurs from about 50% conversion in bulk vinyl acetate polymerisation is normally considered to be due to monomer diffusion becoming restricted causing a reduction in the rate of propagation. In the presence of a diluent, since the viscosity of the solution is reduced, this effect would be expected to be less important. This is confirmed by figure (18) which shows that in the presence

FIGURE 12

VARIATION OF LIFETIME WITH CONVERSION

☉ BULK VINYL ACETATE

◐ 2.5 % BENZENE

◑ 5.0 % BENZENE

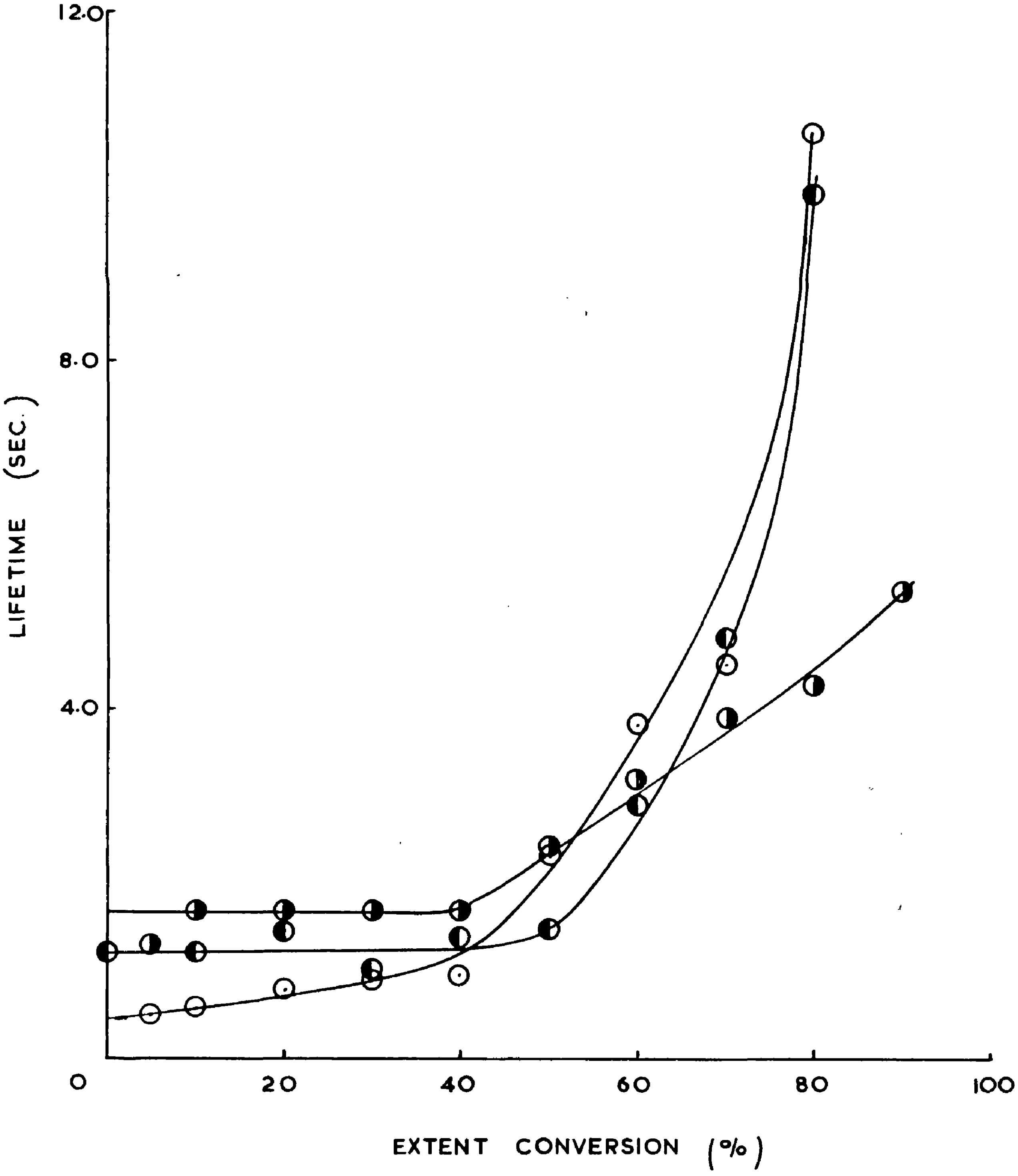
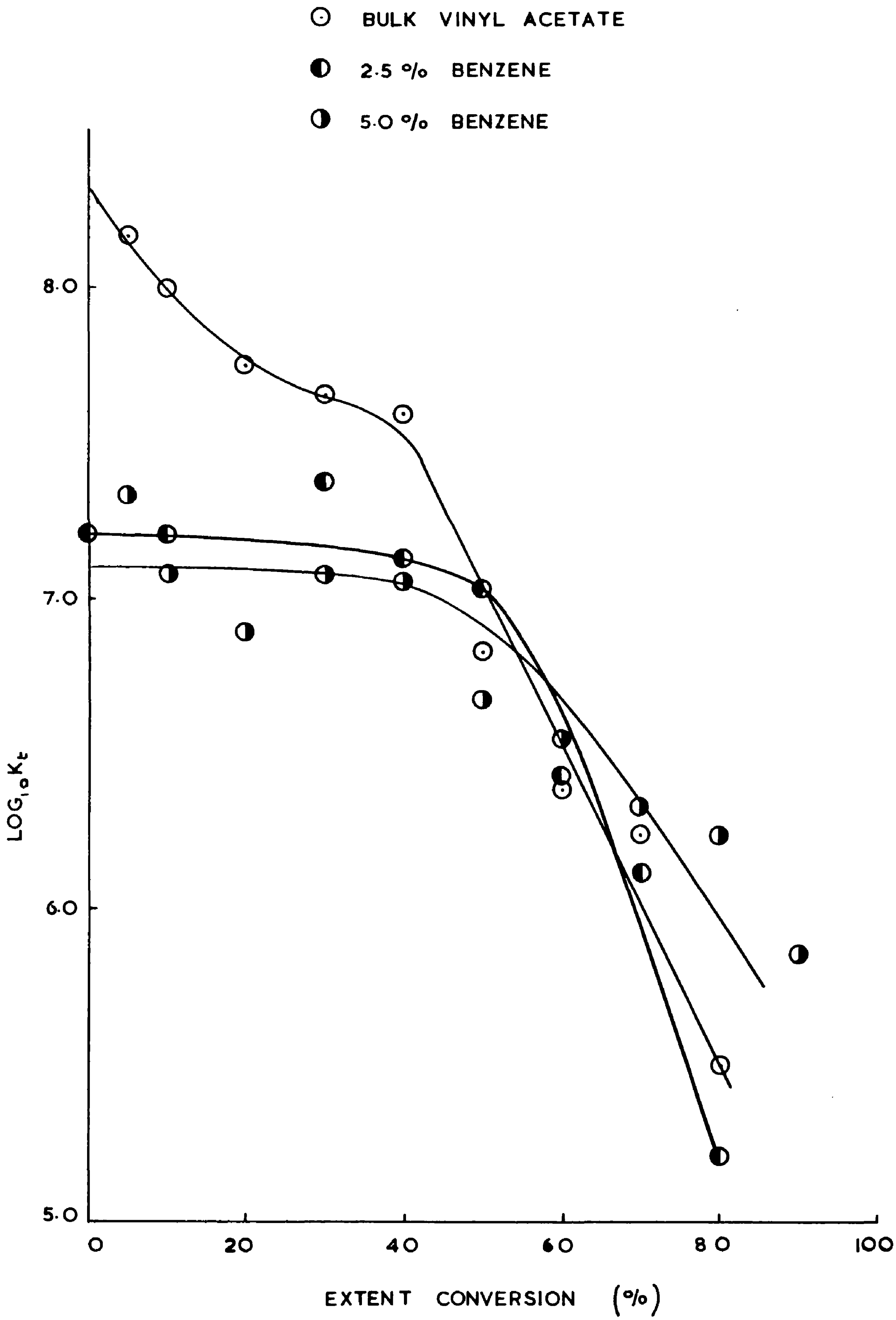


FIGURE 20.

VARIATION OF K_t WITH CONVERSION



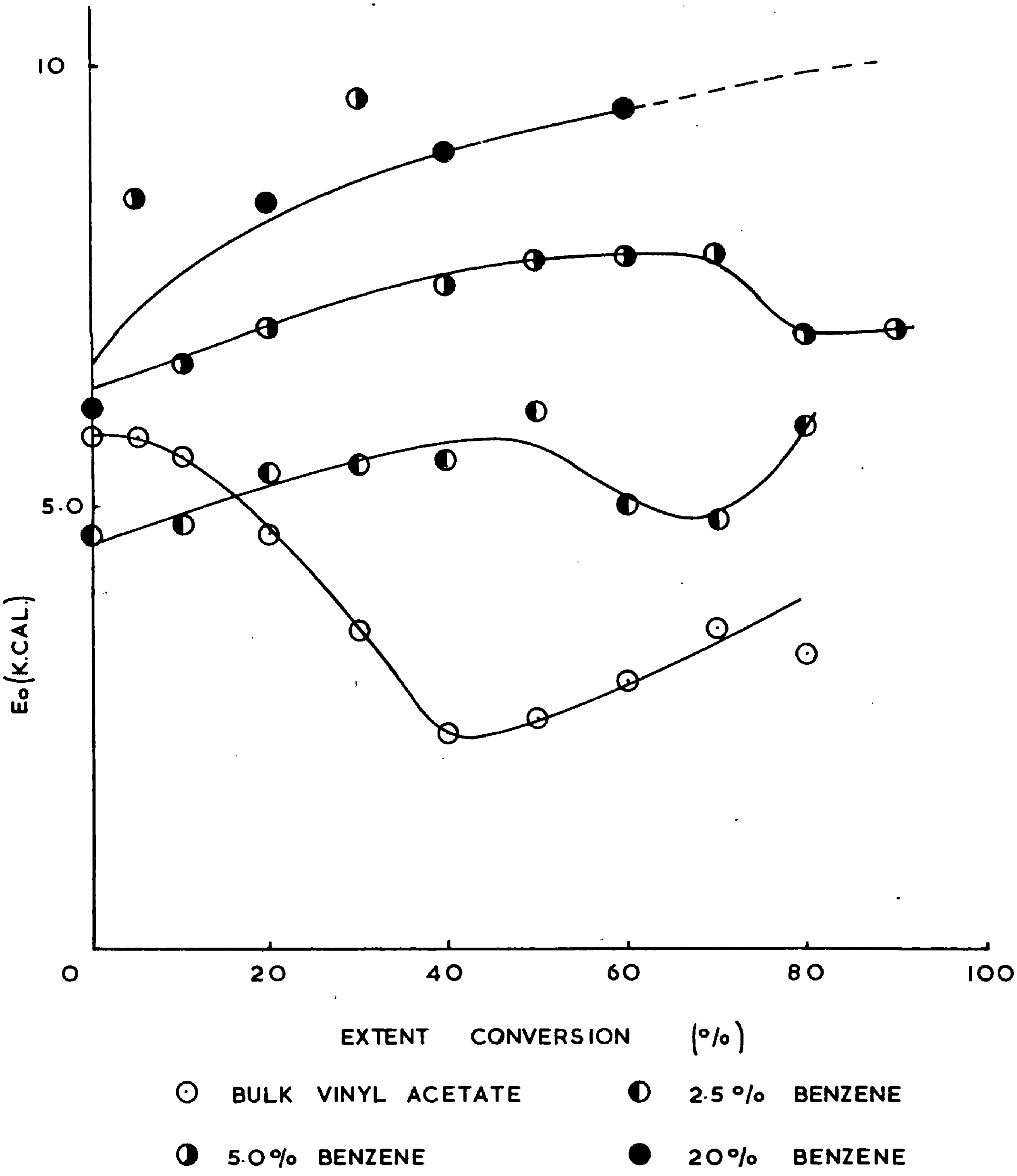
of benzene the drop in rate of reaction during the later stages of the polymerisation is reduced.

In each of the three cases shown in figure (18) there is an initial acceleration in rate, even though with 5% benzene it is almost negligible. It must be assumed, therefore, that the increase in viscosity with conversion is still sufficient to restrict the diffusion of polymer radicals. An examination of the corresponding variation in lifetimes (figure 19) bears this out. In the bulk polymerisation the lifetimes start increasing immediately while in benzene they remain constant to about 40% conversion, whereupon they start to increase at a reduced rate.

Benzene has been shown to cause the rate-conversion curve to flatten and consequently k_p also tends to a steady value. Similarly, in the case of k_t, the dilution effect means that termination does not become hindered to the extent it does in the bulk polymerisation. In the bulk reaction radical diffusion is increasingly hindered from the start of the polymerisation so that k_t must start decreasing immediately. Figure (20), however, shows that this does not occur with 2.5% and 5.0% benzene. In these cases k_t is almost constant for the first 40% conversion, with the result that the rate of

FIGURE 21.

VARIATION OF E_o WITH CONVERSION



reaction accelerates only slightly. In the later stages of the two solution polymerisations, after 40% to 50% conversion, as well as in the bulk reaction, k_t does fall, the effect being most marked in the latter reaction and smallest with 5% benzene. This emphasizes once again that the presence of solvent reduces the purely physical factors which control the polymerisation. The limit, as has been pointed out previously, is reached with 20% benzene when the dilution is such that purely chemical factors influence the course of the reaction.

The Effect of Dilution on Energies of Activation.

As with rates and velocity coefficients, the effect of benzene on the energies of activation is to reduce the variation with conversion. From figure (21) it is seen that in bulk vinyl acetate E_o decreases over the first 40% conversion due to E_t increasing rapidly. From 40% to 50% when monomer diffusion begins to be affected, E_p increases faster, causing E_o to increase also. With solvent, however, E_o increases slightly and it is not until 50% conversion in the case of 2.5% benzene and 70% in the case of 5% benzene, that E_o falls in value. This shows that polymer radical diffusion is relatively unhindered compared to the bulk vinyl acetate over these ranges. When radical diffusion control does tend to increase the benzene reduces its effect. This agrees very well with the picture

FIGURE 22.

VARIATION OF RATE WITH CONVERSION

1. 5% CYCLOHEXANE

2. 5% BENZENE

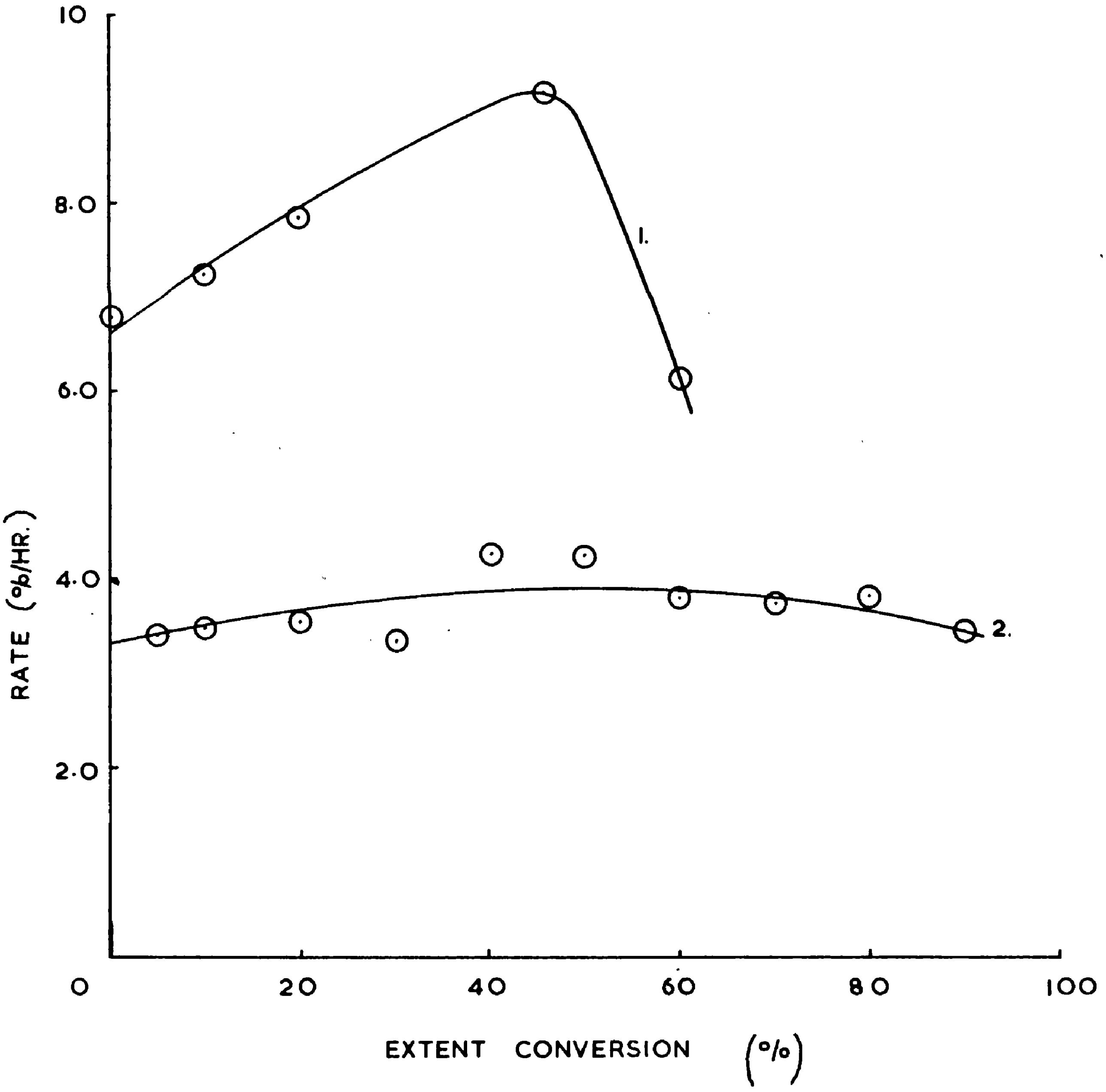
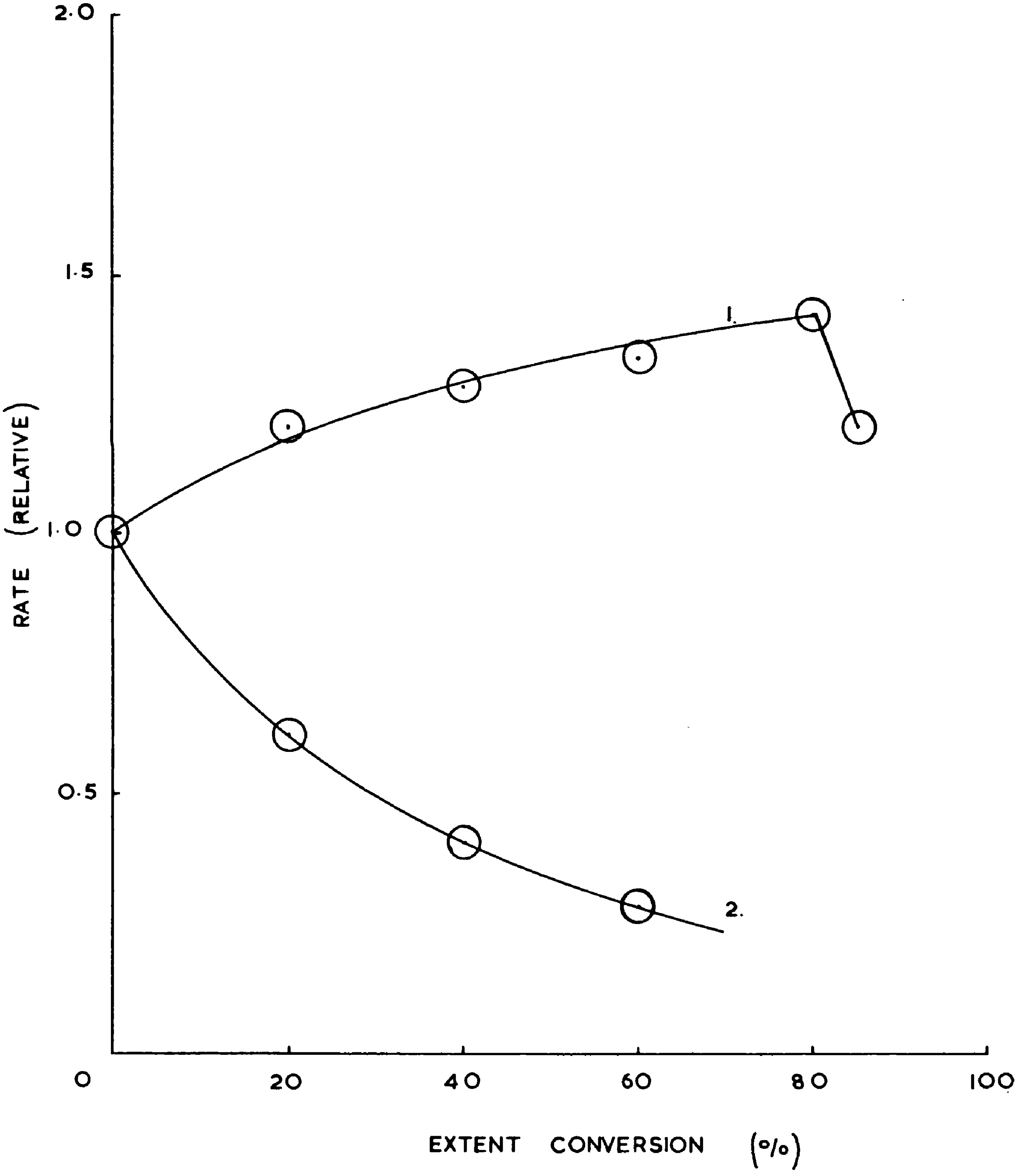


FIGURE 23

VARIATION OF RATE WITH CONVERSION

1. 20 % CYCLOHEXANE

2. 20 % BENZENE



shown by the rates and velocity coefficients. The same applies to the results for 20% benzene. It has already been shown that there is no gel effect of any sort in this case. While readings were only taken to 60% conversion it can be anticipated that E_o will continue to increase as shown in the extrapolated curve.

Relative Solvent Effects of Benzene and Cyclohexane.

The differences in the rate of reaction in these two solvents is due to their reactivity with vinyl acetate and to their solubility for the polymer. Poly vinyl acetate is insoluble in cyclohexane, therefore, as has been pointed out already, precipitation of the polymer formed during the reaction must occur at some time during the polymerisation. With 5% cyclohexane this would not happen until about 95% of the monomer had reacted, while with 20% cyclohexane, as has been seen, precipitation occurred as early as 80% conversion. The cause of this precipitation is that the cyclohexane is a non solvent for poly vinyl acetate, and the effect that the subsequent coiling has on the rates, compared to a good solvent, benzene, is shown in figures (22) and (23). In both experiments the volumes of the solvents, as well as their concentrations in mole.$l.^{-1}$, were

FIGURE 24.

VARIATION OF LIFETIMES WITH CONVERSION

1. 5 % CYCLOHEXANE

2. 5 % BENZENE

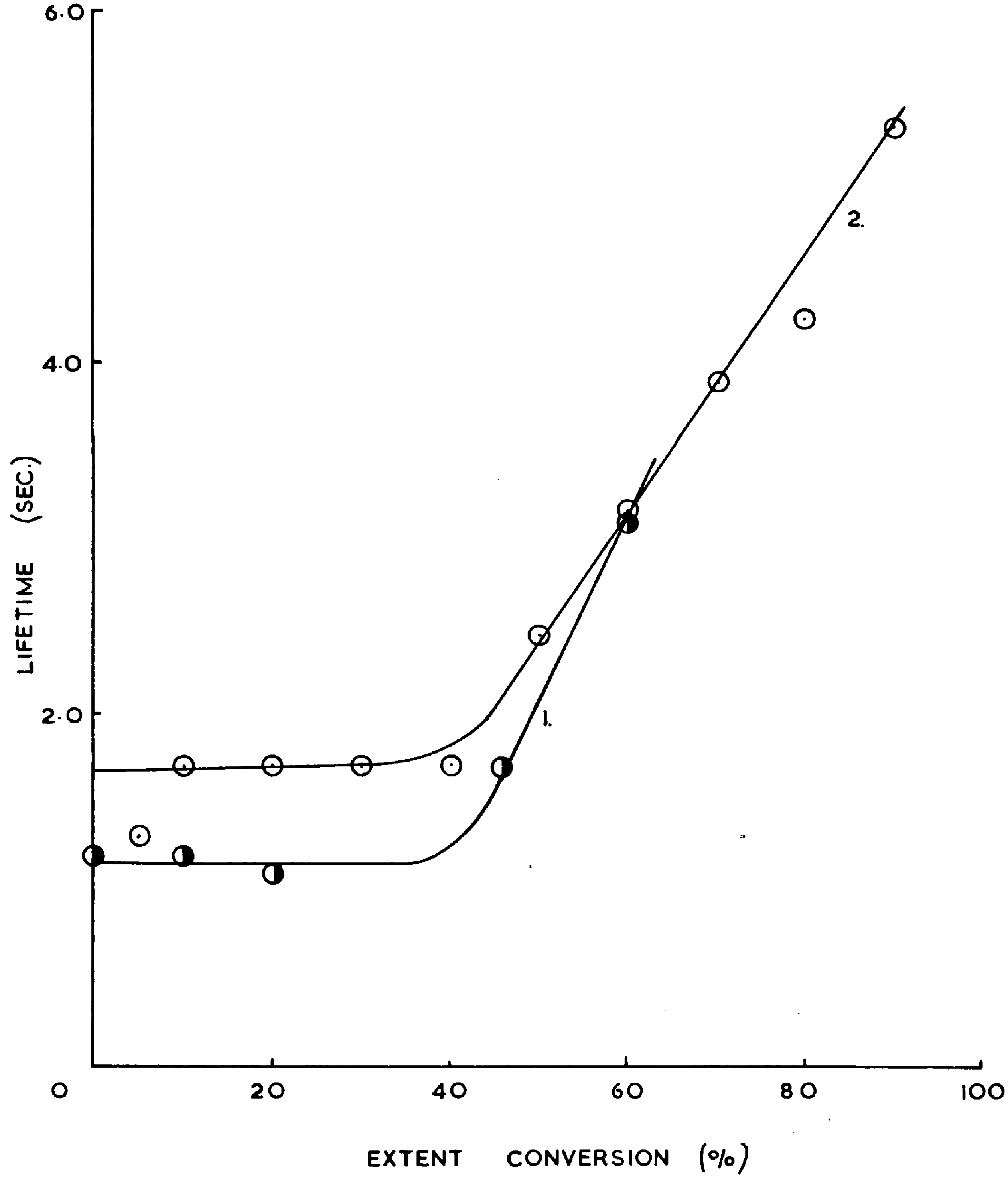
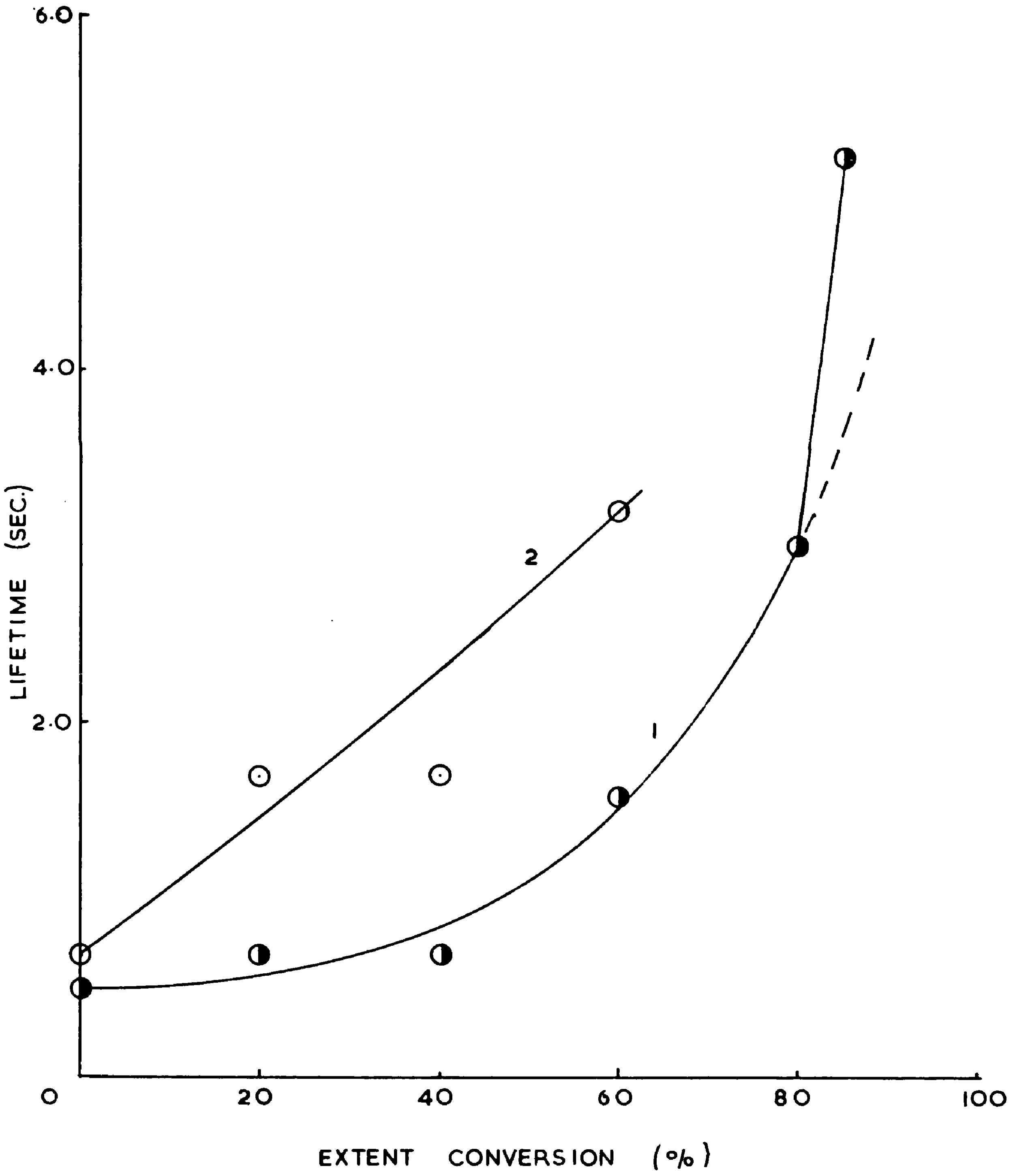


FIGURE 25.

VARIATION OF LIFETIMES WITH CONVERSION

1. 20% CYCLOHEXANE

2. 20 % BENZENE

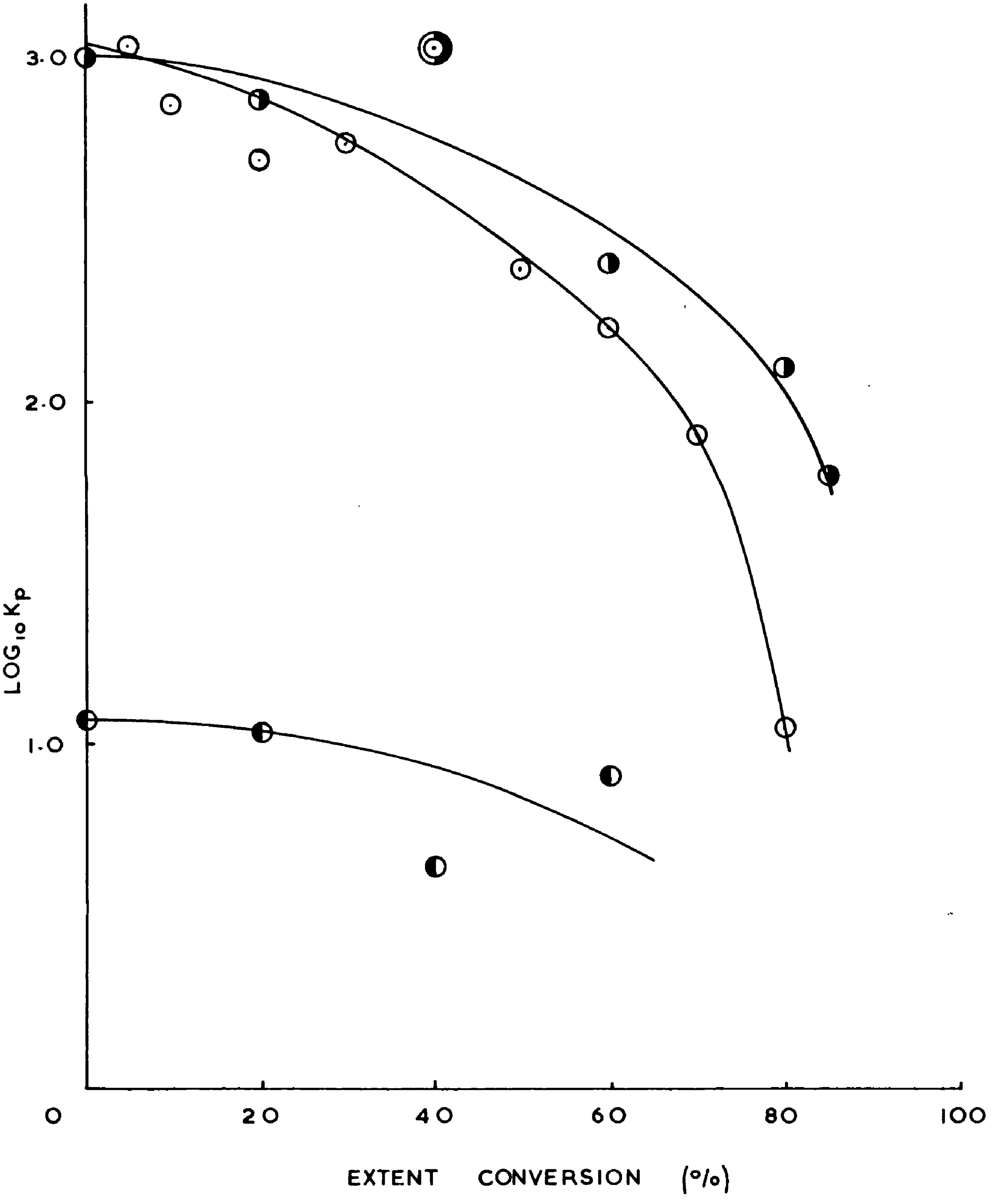


the same, yet the variation in rate with conversion is vastly different. In the presence of a solvent the viscosity of the solution at any particular conversion is less than in the bulk polymerisation at the same conversion, yet with cyclohexane the coiling of the chain, tending to increase the rate of reaction, acts in an opposite direction from the dilution. The same effect is shown by the lifetimes, although to a lesser extent, in figure (24). The dilution effect is sufficient to keep these at a steady value to 40% conversion. When the lifetime does start to rise it does so at a faster rate than the lifetimes in the benzene reaction.

The results for 20% solvent emphasize the importance of the coiling effect (figure 23). While the increasing concentration of benzene relative to monomer causes the rate to fall with conversion, with cyclohexane the effect is quite different. Since any chain transfer which occurs does not cause an appreciable retardation the main factor governing the rate is the solubility of the polymer in the monomer/cyclohexane mixture. This steadily decreases as the monomer is used up, the polymer chains become more coiled, and the rate of reaction increases in spite of the falling monomer concentration. As the rate increases so does the lifetime. The dotted line in figure (25) shows the expected increase in the lifetime had precipitation

FIGURE 26.

VARIATION OF K_p WITH CONVERSION



⊙ BULK VINYL ACETATE. ◑ 20 % CYCLOHEXANE.

◐ 20% BENZENE.

not occurred. The increase in the lifetimes for benzene, on the other hand, are due not so much to a viscosity effect as to the increasing frequency with which the retardation reaction occurs. This only applies, of course, where gelling does not take place. The exact mechanism of the reaction will be discussed later.

Figure (26) compares k_p for pure vinyl acetate, 20% cyclohexane and 20% benzene. The fall in the value of k_p with conversion is greatest in the bulk polymerisation and least with 20% benzene, with the cyclohexane between the two.

The similar initial values of k_p for the bulk and cyclohexane reactions are to be expected since the cyclohexane, in spite of the fact that some chain transfer will occur with polymer radicals, acts essentially as an inert diluent. Furthermore, in the initial stages there is a high ratio of monomer to solvent and the polymer chains will be comparatively uncoiled. The environment in which the initial stage of the polymerisation is taking place, and the chemical reactions involved, are thus approximately the same as in the bulk reaction. This situation will not prevail for long since the bulk reaction will quickly become viscous and the solution polymerisation will tend towards a heterogeneous stage. A comparison of k_t at different conversions

FIGURE 27.

VARIATION OF K_t WITH CONVERSION

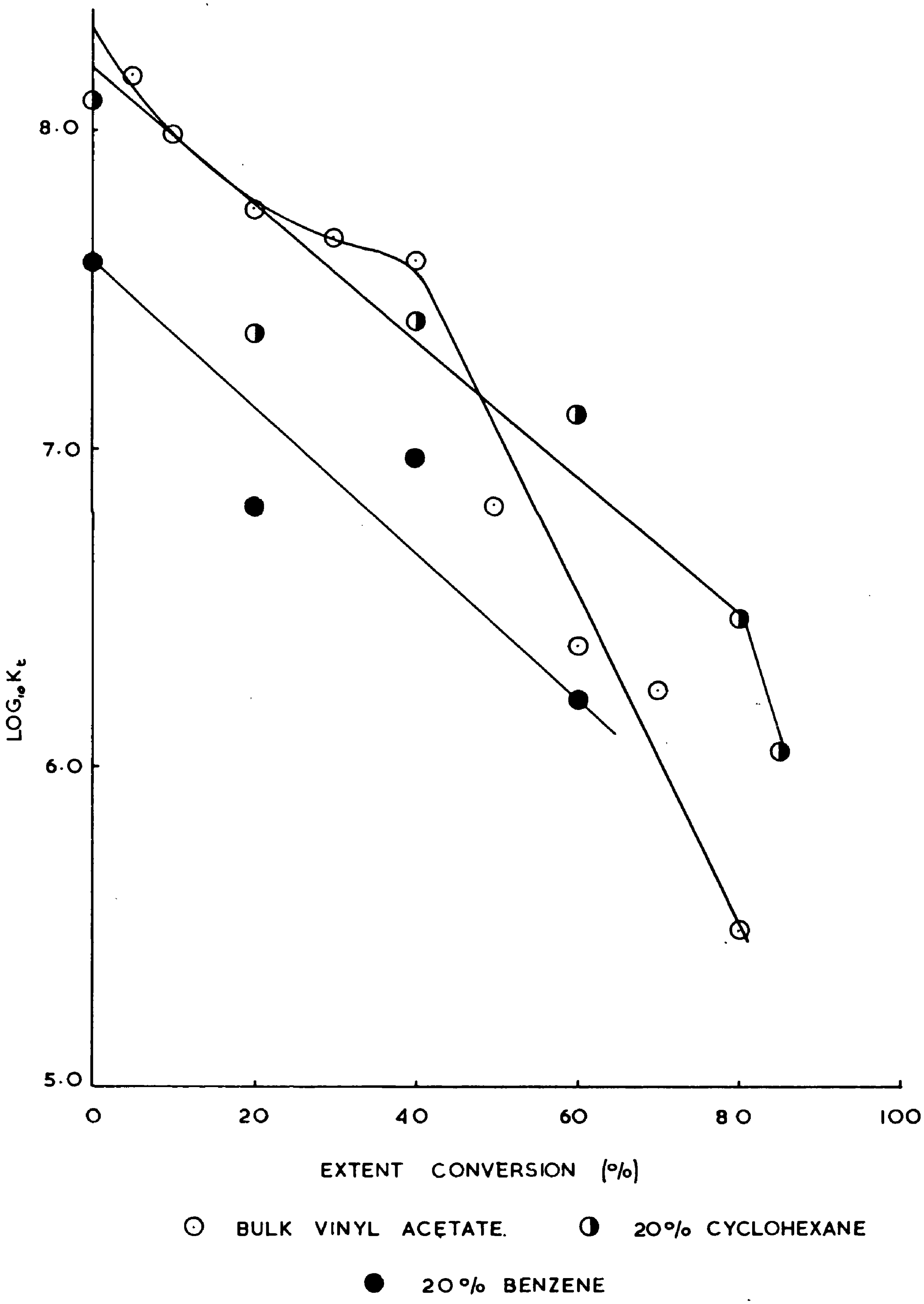


FIGURE 28.

VARIATION OF E_o WITH CONVERSION

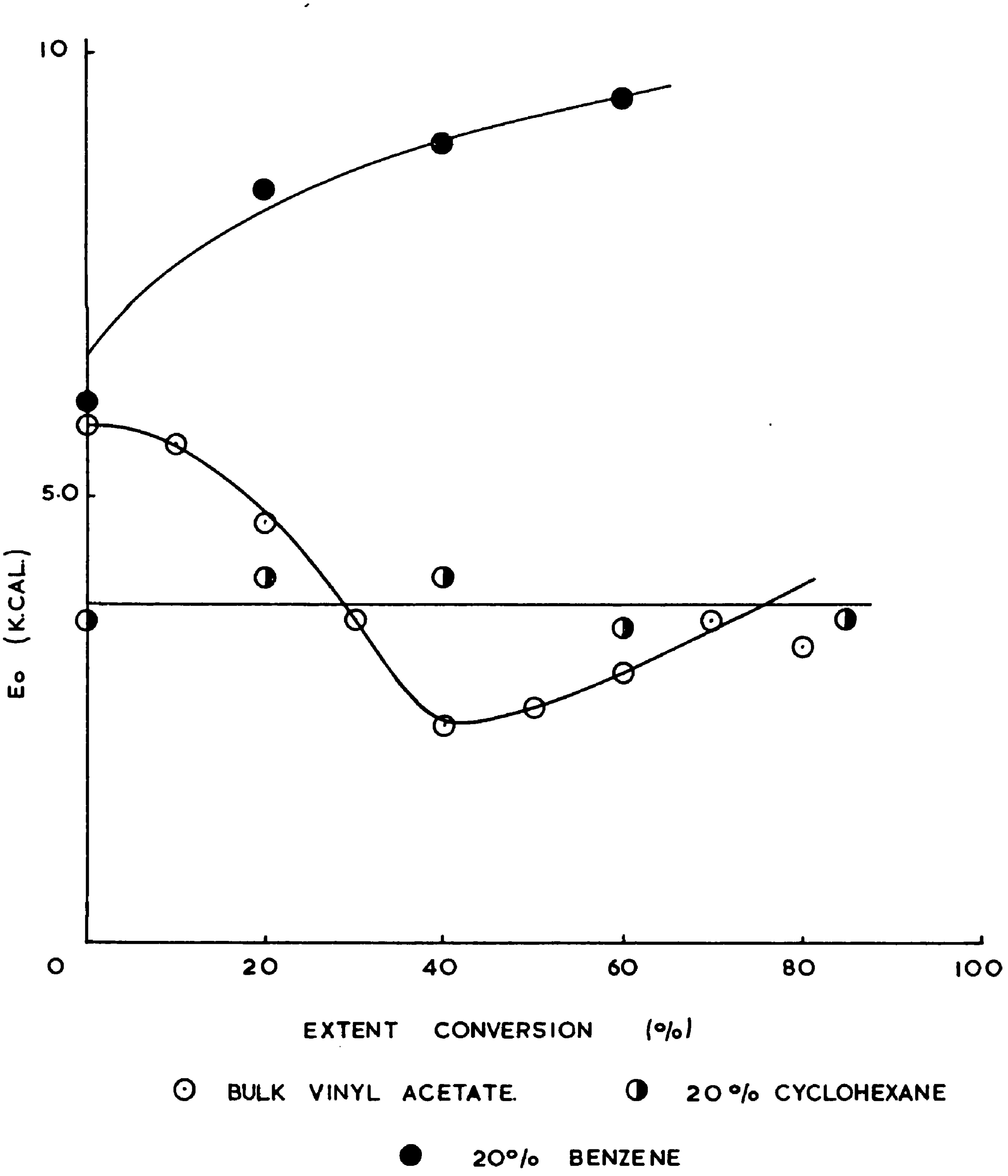


figure (27), bears this out. The initial values for bulk and 20% cyclohexane are similar but the latter does not show the rapid fall in k_t experienced by the bulk reaction after 40% conversion. The values of log k_t seem to vary almost linearly with conversion until 80% when it suddenly drops due to polymer precipitating out. This linear variation is very similar to the corresponding fall in k_t for the benzene reaction. The result is that k_p/k_t increases in both reactions but the rate drops in benzene as the retardation reaction occurs more frequently, while in cyclohexane the rate increases as termination is reduced.

A comparison of the energies of activation for the three reactions, figure (28) is more useful from the retarder than from the diluent viewpoint. E_o has already been discussed for the benzene reaction and increases throughout the polymerisation. The value for 20% cyclohexane stays constant since E_p is a constant initially and E_t zero, then in the later stages when coiling results in E_t getting larger, E_p also increases.

The Retarder Action of Solvents on Vinyl Acetate Polymerisation

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

The polymerisations studied were initiated by the action of ultra violet light on azo bis cyclohexane carbonitrile. This produced free radicals which, in the bulk polymerisation, could react either with another of the same kind or with a molecule of monomer to initiate a chain. The situation is more complicated in the presence of solvent. In this case it is possible for the following reactions to take place.

$$\begin{array}{lll}
C\cdot + M & \longrightarrow & R_1^{\cdot} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{I} \\
C\cdot + S & \longrightarrow & S\cdot \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{II} \\
C\cdot + C\cdot & \xrightarrow[\text{Combination}]{\text{Disproportionation}} & \text{Unreactive products} \quad \ldots\ldots \text{III}
\end{array}$$

where C• is an initiator fragment.

Since reaction II does not arise in bulk polymerisation there is the possibility that the efficiency of initiation will be reduced in the presence of solvent. Bevington[11] has, however, shown that this remains fairly constant over a wide range of solvent concentration and the rate of initiation has been assumed to be constant in this work.

The radical chain produced by I can react as follows:

$$R\cdot_n + M \longrightarrow R\cdot_{n+1} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{IV}$$

$$R\cdot_n + M \longrightarrow P + R\cdot_1 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{V}$$

$$R\cdot_n + S \longrightarrow S\cdot \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{VI}$$

Reaction VI can take place by various mechanisms which will be discussed later.

The chain radical can, of course, terminate by combination and disproportionation as outlined previously.

If we now consider the solvent radical, this can react in several different ways.

$$S\cdot + M \longrightarrow R\cdot \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{VII}$$

$$S\cdot + R\cdot \longrightarrow \text{Polymer} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{VIII}$$

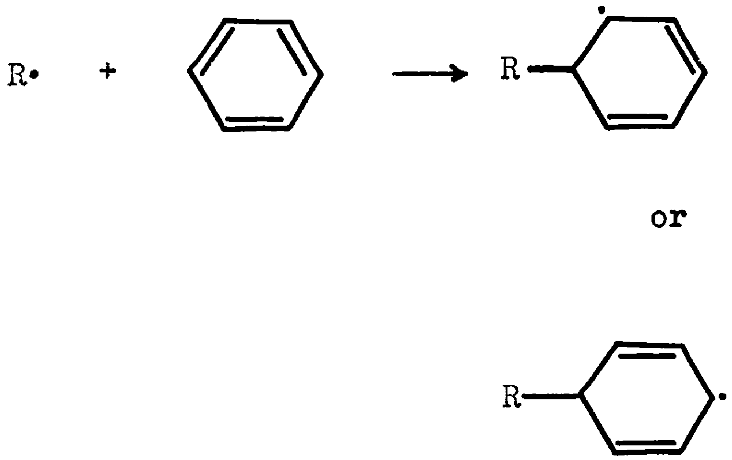
$$S\cdot + S\cdot \longrightarrow \text{Stable Products} \;\ldots\ldots\ldots\ldots\ldots\ldots \text{IX}$$

The radical S· can be formed by addition of a chain radical to a solvent molecule or by a chain transfer reaction between them, and the products of these reactions will reinitiate chains if reaction VII takes place. Allen, Merrett and Scanlan[67] have treated the retardation of vinyl acetate polymerisation by dihydromyrcene from this point of view. An equation relating rate and retarder concentration has also been developed by Kice[68,69] taking into consideration both the termination and reinitiation reactions of radicals produced by chain transfer.

In the polymerisations in which benzene was the solvent the transfer and addition reactions would be

VI (a)

VI (b)



respectively.

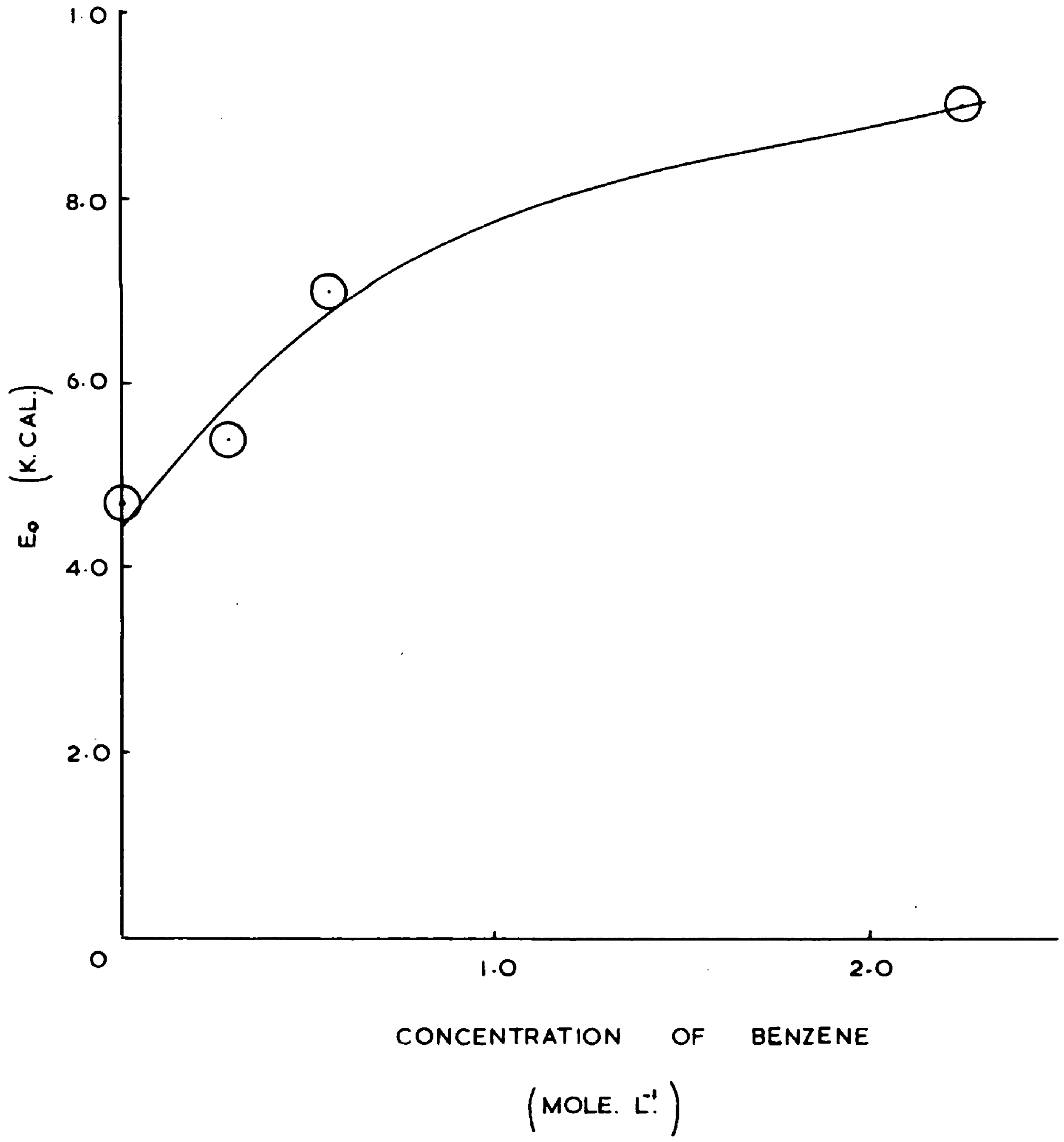
Since a high polymer is formed, reaction VI can only take place occasionally. Thus it will only affect the rate of reaction when VII is very much slower than the normal propagation reaction IV. One fast addition among several thousand slower ones would have no effect on the rate.

There is no doubt that reaction VI takes place. The difficulty is to determine its exact nature. Flory's chain transfer theory has been accepted as the main reaction between

FIGURE 29.

VARIATION OF E_o WITH BENZENE CONCENTRATION.

20% CONVERSION



solvent molecules and chain radicals since it was proposed. While chain transfer may occur it is doubtful, in benzene solution, if it is the cause of retardation. The transfer reaction, VI (a), produces a phenyl radical. To account for the strong retardation experienced in benzene the phenyl radical would require to be unreactive. There is strong evidence to suggest that this assumption is unjustified. Barson et al.,[70] using C^{14} labelled benzoyl peroxide as an initiator of vinyl acetate polymerisation, have found that the phenyl radical is an efficient chain initiator. Other evidence also tends to suggest that the theory of chain transfer is incorrect. It has been pointed out that E_o increases with the amount of benzene present during the polymerisation of vinyl acetate. Figure 29 shows this. Also during the polymerisation in the presence of 20% benzene, with no gel effect, E_o increases as the ratio of benzene to residual monomer increases. At the same time the rate of reaction falls due to the retardation reaction occurring more frequently. If the retardation reaction was due to chain transfer, E_o in the presence of benzene would be less than E_o in the bulk reaction and E_o would decrease throughout the polymerisation of vinyl acetate in the presence of 20% benzene. This is because $E_{tr} > E_t$ and would be a negative term in the equation relating E_o to E_p, E_t and E_{tr} .

Various attempts have been made to give a kinetic analysis on the basis of chain transfer. Jenkins has done this on the basis of the geometric mean assumption, i.e. that the velocity coefficient of termination between two dissimilar radicals is the geometric mean of those for the reactions between like radicals. In view of the evidence from copolymerisation studies that termination may occur preferentially between unlike radicals [72] this is doubtful. Therefore on the assumption that cross termination is much more important than reaction between two solvent radicals, the following equation for the velocity coefficient of transfer with a solvent is developed.

$$k_{tr} = \frac{(I\,k_t)^{\frac{1}{2}}}{2[S]} \cdot \left(\frac{1}{\lambda} - \lambda\right) \qquad \ldots\ldots\ldots\ldots\ldots(56)$$

using the usual symbols with

$$\lambda = \frac{m \cdot [M_o]}{m_o \cdot [M]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(57)$$

where m and m_o are the rates of polymerisation in the presence and absence, respectively, of benzene.

$[M_o]$ = Concentration of undiluted monomer

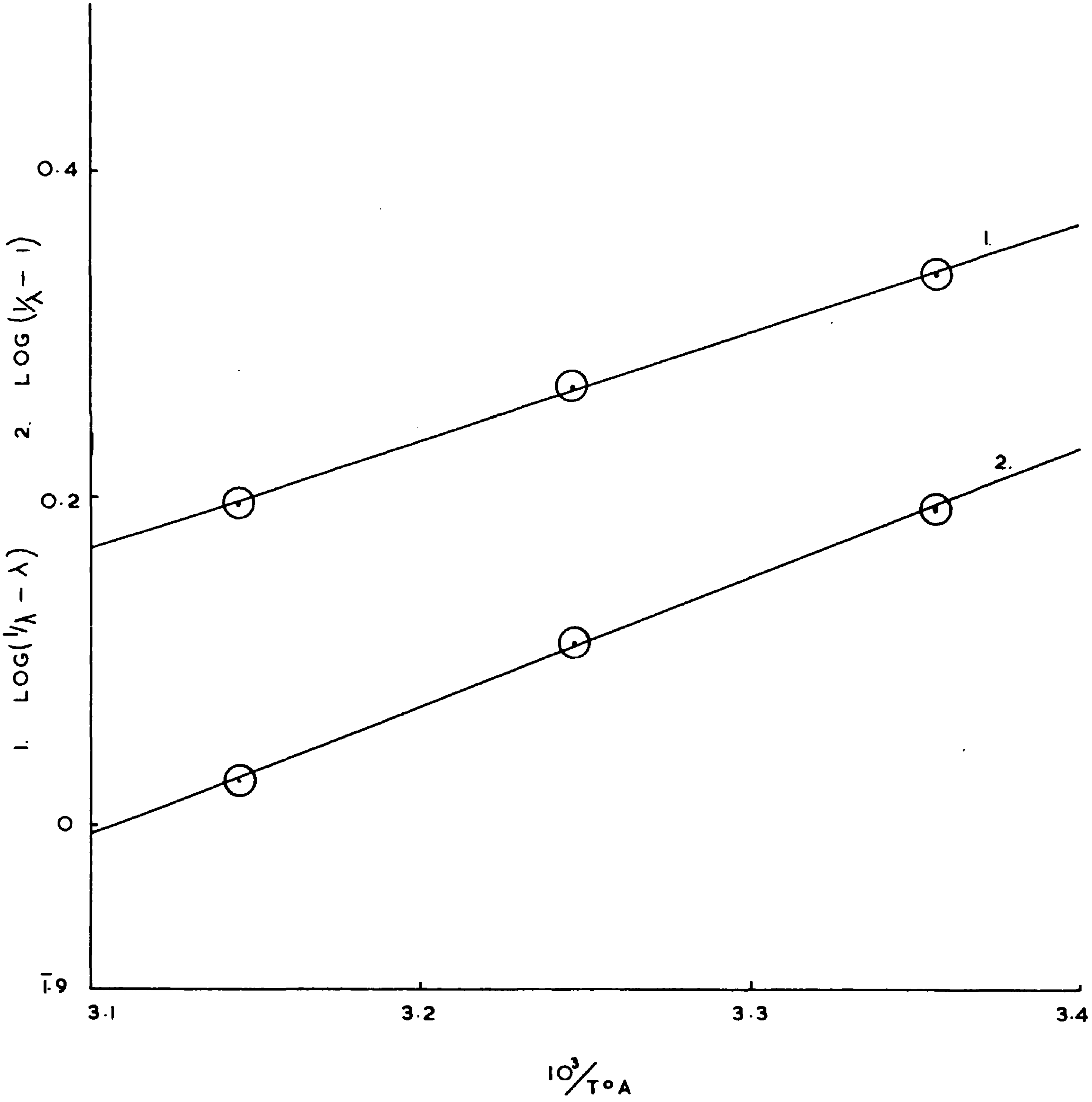
$[M]$ = Concentration of monomer with solvent present.

Equation can be rewritten

$$k_{tr} = K\left(\frac{1}{\lambda} - \lambda\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(58)$$

FIGURE 30.

THEORETICAL DETERMINATION OF E_{tr} BASED ON JENKINS' CHAIN TRANSFER ANALYSIS.



where K is a constant for any given polymerisation at any particular extent conversion. Equation (58) seems at first sight to provide a reasonable method of calculating k_{tr} . Closer examination, however, shows that the equation cannot be correct. It is possible to express k_{tr} in the form

$$k_{tr} = A\, e^{-E_{tr}/RT}$$

Thus plotting log $\left(\frac{1}{\lambda} - \lambda\right)$ against the reciprocal of the absolute temperature should give a value for E_{tr}. Figure **30** shows this plot for the polymerisation of vinyl acetate in the presence of 5% benzene. The slope of this line indicates that E_{tr} is negative. A similar result is obtained using the geometric mean assumption which gives

$$k_{tr} = K'\left(\frac{1}{\lambda} - 1\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(59)$$

where K' only differs from K (equation 58) by a factor of 2.

For the transfer reaction to have a negative energy of activation the amount of transfer would have to decrease as temperature increased. In fact it does the reverse, E_{tr} having been shown to have a positive value of 11.0 Kcal (page 88)

In view of this evidence it must now be assumed that the transfer theory of retardation is incorrect. Before discussing the alternative explanations for the reactions taking place when vinyl acetate polymerises in benzene it would be interesting to review the other attempts that have been made to give a kinetic analysis.

A copolymerisation between vinyl acetate and benzene has been reported by Peebles and Hockmeyer [73] who found evidence, in this case by using labelled benzene, that the solvent was incorporated in the polymer chain. The first attempt to give an analysis of this type of reaction was made by Mayo and Walling[74] who derived an equation for the rate which is rather unsatisfactory. On the assumption that chain transfer occurs followed by reaction of the solvent radical with (a) a monomer molecule to reinitiate the chain (b) another of its own kind and (c) a chain carrier, Burnett and Loan [75] have also developed an equation for the rate. This is only applicable where the solvent does not produce any gel effect. In the thermal polymerisation of vinyl acetate in benzene they find, assuming chain transfer, an activation energy of 24 Kcal. for the addition of the phenyl radical to monomer. This is an extremely high value and suggests, once more, that the assumption of chain transfer is unjustified. It is, therefore, not certain what quantitative significance can be attached to their analysis. Nevertheless it gives the correct shape of curves for the polymerisation of methyl methacrylate, methyl acrylate and vinyl acetate in benzene.

It has now been shown that chain transfer does not cause retardation of the polymerisation of vinyl acetate in benzene. The question of which reaction does cause the retardation remains to be answered. There are several possible explanations.

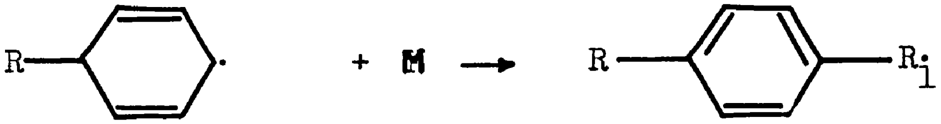
The following table shows the ratio of the rates of reaction in bulk and in 5% benzene at different temperatures.

Table 63

Temperature °C	25	35	45
Bulk: Rate (m_1) %/hr.	9.4	12.3	17.4
5% Benzene Rate (m_2) %/hr.	3.41	5.23	8.0
m_1/m_2	2.75	2.35	2.18
Molecular wts. of polymer Mw x 10^{-5} (5% benzene reaction)	4.11	3.64	2.61

As would be expected, since E_{tr} is positive, the molecular weight falls with increasing temperature. The ratio m_1/m_2 also falls, however, showing that there is relatively less retardation at the higher temperatures. If transfer alone was taking place it would seem likely that there would be relatively more retardation, especially since E_{tr} is larger than E_p .

One possible explanation is that reaction IV (b) is taking place followed by reinitiation. The radical formed by addition would be more stable than the phenyl radical and consequently the energy of reinitiation would be high.



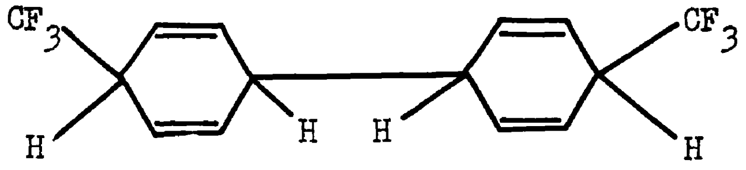
.....VIIa

The reinitiation concept is attractive. Reaction **VIIa** would undoubtedly have a high activation energy. Consequently it would occur more readily at higher temperatures giving a smaller retardation. It could also be used to explain the fact that the lifetimes in solution are greater than in the bulk polymerisation during the initial stage of the reaction. A slow addition step would tend to increase the lifetime. Moreover if it was sufficiently slow the addition reaction would represent a termination step and thus account for the mixed order termination.

It is possible for hydrogen abstraction to occur between a chain radical and a radical formed by VI b

.....X

Mayo[22] has suggested that the above reaction takes place during the polymerisation of styrene in benzene. A similar reaction has been suggested for the reaction of methyl radicals with aromatic compounds.[76] A recent paper by Charles and Whittle[77] also proposes it for the photolytic reaction of trifluoromethyl radicals with aromatic hydrocarbons. With benzene they found that a substituted cyclohexadienyl radical was formed giving compounds of the type



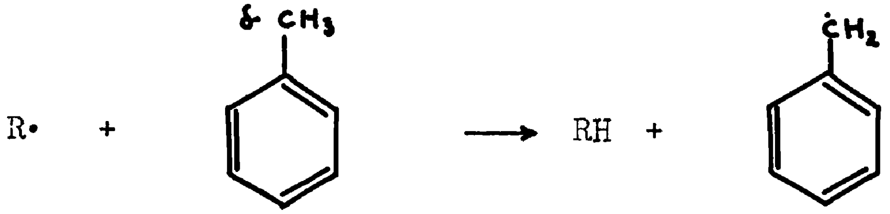
They suggest that if hydrogen abstraction occurs it is by X rather than by direct transfer between a radical and the benzene molecule. The case for the chain transfer reaction occurring after addition rather than directly can be justified on energy grounds. For the normal transfer reaction a C_6H_5– H bond must be broken. This requires an energy of 101 Kcal. In reaction X however the aromatic character of the ring is being restored. The energy required to break the C – H bond in this case is 100 Kcal. and the resonance energy of the restored aromatic ring is 36 Kcal.[78] The total energy is then only 64 Kcal. making it easier for addition to take place.

Kooyman and Farenhorst[79] have also found that trichloro methyl radicals add to naphthalene rather than abstract a hydrogen.

In conclusion the above evidence, coupled with the evidence mentioned earlier, that benzene copolymerises with vinyl acetate, seems 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. It also seems likely that transfer can also take place although it is not so important in causing retardation as the addition step.

The Reaction between Vinyl Acetate and Toluene.

Toluene has been shown to have the same retarding effect as benzene on the polymerisation of vinyl acetate. This is rather surprising in view of the expected mode of attack by a free radical on the toluene involving chain transfer with a hydrogen atom on the methyl group. The electron withdrawing effect of the aromatic ring leaves the methyl group electron deficient and therefore prone to attack of this kind.

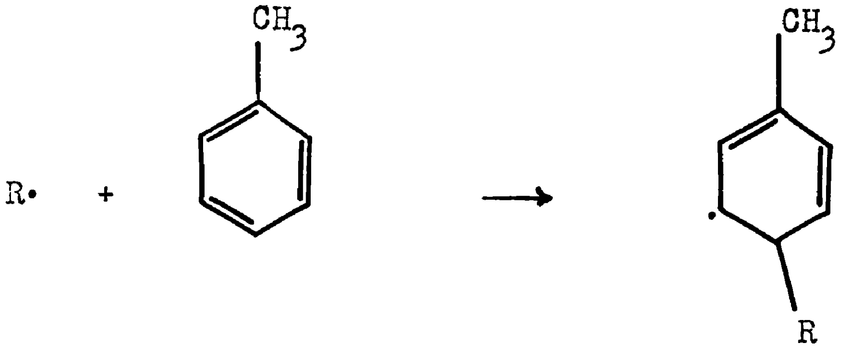


.....XI

The benzyl radical would be expected to be fairly stable and not as liable to reinitiate polymerisation as the radical formed by transfer with benzene.

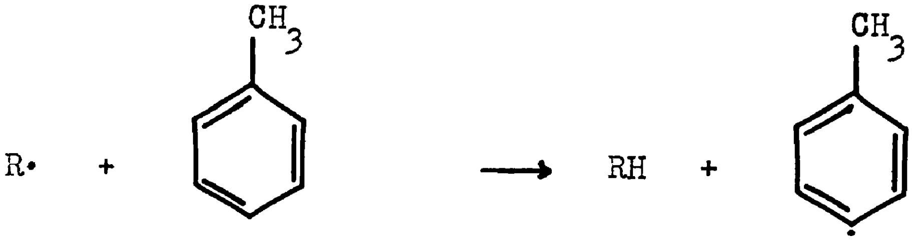
It is possible for transfer and addition reactions to take place at the aromatic ring of the toluene.

Addition



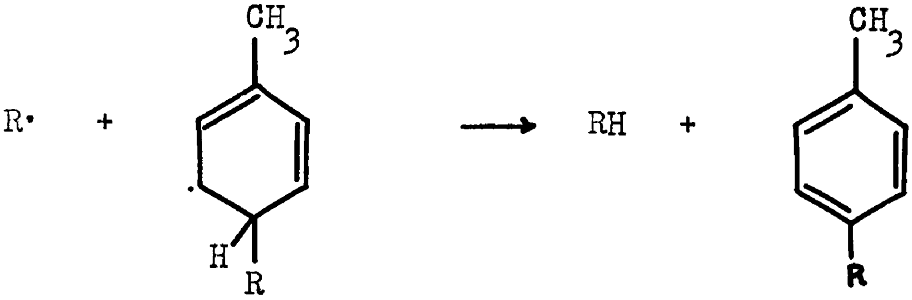
....XII

Transfer



....XIII

Hydrogen abstraction



....XIV

There is an increasing amount of evidence to support the theory that free radical attack takes place at the ring. In a recent paper Wilen and Eliel[80] showed, using ring deuterated toluene, that ring abstraction of hydrogen by methyl radicals occurs. Charles and Whittle[77] have suggested that the main reaction of trifluoromethyl radicals with toluene and O-Xylene, as well as with benzene, is addition to the ring with the expected hydrogen abstraction occurring only to a limited extent.

It would seem however that chain transfer does occur at the methyl group in solution polymerisation. Palit and Das[81] have quoted transfer constants for toluene and benzene in vinyl acetate polymerised at 60°C. They find the ratio of the transfer constants for toluene and benzene to be 7:1. The greater ease with which the toluene transfers is almost certainly due to the presence of the methyl group. Under these circumstances if the retardation of vinyl acetate polymerisation by toluene was due to the radical produced by reaction XI, toluene would be a much more efficient retarder than benzene and the rate of polymerisation in toluene would be much less than in benzene. The addition reaction to the ring would occur to the same extent in both solvents and in view of the fact that the retardations are the same it would seem that this is the rate retarding reaction in toluene.

The Retarder Action of Polycyclic Aromatic Compounds.

The retarder efficiency of the aromatics used in this work increased in the order benzene $<$ diphenyl $<$ naphthalene, the retarder efficiency being defined as the ratio of the rate of polymerisation in the presence of retarder to the rate in the absence of retarder. Measurement of the efficiency of a retarder of polymerisation reactions is complicated by the gel effect acting to different degrees in each polymerisation depending on the solubility of the polymer in the reaction mixture and whether the retarder is liquid, solid, etc. Moreover, the naphthalene, as has been pointed out in the results, retarded so strongly that to obtain measureable rates would have required a concentration of naphthalene of the same order as the initiator concentration.

The relationship between the structure of polycyclic aromatics and their reactivity with free radicals has been interpreted in terms of the free valence numbers of each molecule.[79] This can be defined as a measure of the unused bonding power of given atoms. Using this method for the reactivity of the $CCl_3\cdot$ radical with an aromatic relative to its reactivity with n-hexane, Kooyman and Farenhorst have found the ratio of the retarder efficiency of diphenyl relative to bezene to be 2.8 : 1. The corresponding value calculated in terms of the rate of polymerisation in benzene relative to the rate in diphenyl at a retarder concentration of 0.153 mole.$1.^{-1}$ is 3.38 : 1, which is fairly similar to the theoretical value, taking reaction conditions into consideration. This tends to suggest that the retarder action of higher aromatics on the polymerisation of vinyl acetate is similar to that of benzene, namely an addition reaction.

Suggestions for further work.

The theory that the retardation of the polymerisation of vinyl acetate in the presence of benzene is due to addition poses interesting problems concerning the polymerisation of vinyl monomers containing aromatic rings, e.g. styrene and vinyl benzoate. It has been suggested that polystyrene contains a certain number of weak links due to addition of the vinyl chain radical to the aromatic ring. It is also possible that the low rate of reaction encountered in the copolymerisation of vinyl acetate and styrene is due to the ring addition and not altogether to the stability of the styryl radical.

Another line of work which suggests itself is the photochemical and thermal polymerisation of vinyl acetate in the presence of very small quantities of polycyclics, where it is possible that certain light sensitive compounds, such as anthracene, may actually initiate photochemical polymerisations.

Investigations of these aspects would follow as a natural extension of this work and provide information not only on particular polymerisations but on free radical reactivity in general.

APPENDIX

I. Determination of the rate of polymerisation of vinyl acetate from the experimental chart trace.

From a typical chart trace a slope of 3.53×10^{-1} divisions/sec. was obtained. The calibration curve showed that at the amplification used 10 μ volts was equivalent to 9.45 chart divisions, and since 40 μ v. = 1°C.,[64]

$$\text{rate of temperature rise of polymerising mixture} = \frac{3.53 \times 10^{-1}}{0.945 \times 40} \ {}^{\circ}\text{C/sec.}$$

$$= 9.33 \times 10^{-3} \ {}^{\circ}\text{C/sec.}$$

From the literature values:[82]

Heat of polymerisation of vinyl acetate = 21.3 Kcal./mole

Specific heat of monomeric vinyl acetate = 0.47 cal./gm.

Molecular weight of vinyl acetate = 86

$\therefore$ Heat required to raise the temperature of 1 mole. 1°C = 86 x 0.47 cal.

= 40.4 cal.

$\therefore$ 100%/hr. reaction would raise the temperature $\dfrac{21.3 \times 10^{3}}{40.4 \times 3600}$ °C/sec.

= 1.47×10^{-1} °C/sec.

$\therefore$

$$\therefore \quad \text{Rate of Polymerisation} = \frac{9.33 \times 10^{-3}}{1.46 \times 10^{-3}} \ \%/\text{hr.}$$

$$= 6.36\ \%/\text{hr.}$$

The temperature rise could be converted directly into rate of reaction by the relationship

$$1\%/\text{hr.} = 5.86 \times 10^{-2} \mu\ \text{v/sec.}$$

This relationship was corrected as conversion proceeded to allow for the difference in specific heat of the monomer and polymer.

APPENDIX

II. GLOSSARY OF PRINCIPAL SYMBOLS

A	Frequency factor.
°A	Temperature in degrees absolute. Ångstrom unit (10^{-8}cm) in the case of wavelength.
B [B]	Initiator and its concentration.
C	Concentration of polymer in gm./100ml. for viscosity measurements.
C· [C·]	Initiator fragment and its concentration.
°C	Temperature in degrees centigrade.
C_s	Chain transfer constant for solvent.
$\overline{DP}$	Degree of polymerisation.
e	Base of natural logarithms.
E_o, E_p etc.	Activation energies for the overall reaction, propagation etc.
F	Fraction of monomer converted to polymer.
$h\nu$	A quantum of light.
I	Rate of initiation.
k_i, k_p, k_{tr}, k_t, etc.	Velocity coefficients for initiation, propagation, transfer termination, etc.
k_t/k_t', k_p/k_p'	Mixed order termination correction factors for the velocity coefficients of termination and propagation.

K	Constant factor used in various contexts.
L	Light intensity.
m_1, m_2	Rates of reaction.
M, $[M]$	Monomer and its concentration.
M_w, M_n	Weight average and number average molecular weights.
n	Intensity exponent. Where used in formulae it denotes an indefinite large number.
P	Polymer.
Q, $[Q]$	Retarder molecule and its concentration.
$R\cdot$, $[R\cdot]$	Chain radical and its concentration
R_s	Stationary state radical concentration.
S, $[S]$	Solvent molecule and its concentration.
$S\cdot$, $[S\cdot]$	Solvent radical and its concentration
T	Temperature (degrees centigrade unless otherwise specified)
t_i	Intercept on the time axis of the fractional conversion against time curve.

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82. Tong and Kenyon, J.A.C.S., 69, 2245 (1947)

See p.464

University of Glasgow

Session 1960-61

HIGHER DEGREES AND SPECIAL STUDY AND RESEARCH

SUMMARY OF FEES

Fees for Higher Degrees, payable in most cases on submission of a thesis :

	Fee
B.Litt.	(See footnote[1])
D.Litt.	£20
D.Mus.	£20
LL.D.	£20
M.D.	£25
Ch.M.	£25
M.D.S.	£25
D.V.M.	£25
M.V.S.	£25
M.Sc.	£20[2]
D.Sc.	£20
Ph.D.	£20

Research fees, payable by registered research students :

Research fee,	without laboratory facilities	£20 per annum
	with laboratory facilities	£35 per annum

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[1] The annual fee for B.Litt. is £20, plus £4 4s. Matriculation Fee

[2] M.Sc. candidates pay in addition the annual Matriculation Fee of £4 4s. and the annual Research fee (with Laboratory facilities) of £35.

GENERAL INFORMATION

Higher Degrees

The University awards the following higher degrees :

In the Faculty of Arts :	Bachelor of Letters (B.Litt.) ; Doctor of Letters (D. Litt.) ; Doctor of Music (D. Mus.) ;
In the Faculty of Law :	Doctor of Laws (LL.D.) ;
In the Faculty of Medicine :	Doctor of Medicine (M.D.) ; Master of Surgery (Ch.M.) ; Master of Dental Surgery (M.D.S.) ; Doctor of Veterinary Medicine (D.V.M.) ; Master of Veterinary Surgery (M.V.S.) ;
In the Faculties of Science and Engineering	Master of Science (M.Sc.); Doctor of Science (D.Sc.);
In the Faculty of Science:	Doctor of Science in Public Health (D.Sc.) ;
In all Faculties :	Doctor of Philosophy (Ph.D.).

The regulations governing these degrees are printed below (pp. 447–465). Candidates for any higher degree are required to submit a thesis[1] embodying original work ; candidates for the degrees of Doctor of Music, Doctor of Medicine, Master of Surgery and Doctor of Science in Public Health are required also to submit to examination, and candidates for other higher degrees may be required to do so.

The degree of Bachelor of Letters is open to graduates in Arts with first or second class honours of this University; and to applicants from other Universities who hold qualifications recognised as equivalent by the Senatus of this University. All candidates must pursue studies at this University for a prescribed period. The degrees of Doctor of Letters and Doctor of Laws are open to graduates of this University, of whom no further residence is required, and to graduates of any University who have held approved office in this University for a prescribed continuous period. The Degree of Doctor of Music is open both to Bachelors of Music with Honours of this University, of whom no further residence is required, and to Bachelors of Music of other Universities who have spent a prescribed period as Research Students[2] in this University. For the degrees of Doctor of Medicine and Master of Surgery only Bachelors of Medicine of this University, and for the degree of Doctor of Science in Public Health only Bachelors of Science in Public Health of this University may be candidates, and no residence is required for these degrees. The degree of Master of Dental Surgery is open to Bachelors of Dental Surgery of this University, and to Bachelors of Medicine or Bachelors of Science of this University who hold a registrable dental qualification. The degrees of Doctor of Veterinary Medicine and Master of Veterinary Surgery are open to Bachelors of

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[1] Thesis may be optional for B.Litt.

[2] The conditions under which candidates are admitted to the status of Research Students are printed below, (pp. 465–467). Enquiries should be addressed to the Clerk of Senate.

Veterinary Medicine and Surgery of this University, of whom no further residence is required, and to teaching Officers of this University who are graduates of this University and who have been on the register of the Royal College of Veterinary Surgeons for a prescribed period. The degree of Master of Science is open to graduates of this University and to applicants from other Universities or Institutions whose qualifications are approved for this purpose by the Senatus of this University. All candidates must pursue full-time study or research at this University or at a college affiliated thereto, for a prescribed period. The Degree of Doctor of Science is open both to graduates in Arts or Pure Science or Engineering with Honours of this University, of whom no further residence is required, and to other graduates of this University, or graduates of other Universities, who have spent a prescribed period as Research Students in this University. The degree of Doctor of Philosophy is open to graduates of this University or of other Universities; all candidates are required to spend a prescribed period as Research Students in this University.

Diplomas and Certificates for Post-graduate Study

Graduates and other advanced students may be candidates for the Diploma and the Certificate of Proficiency awarded for special study in the Faculty of Arts. The Diploma is intended for Honours graduates who have pursued advanced study of a special subject under the direction of a Professor or Lecturer, the Certificate for others who have attended one of the regular advanced courses provided in the Faculty. The minimum period of study required either for the Diploma or for the Certificate is one year ; in addition to the normal matriculation fee, candidates are required to pay an annual fee of £35 to cover tuition and entry to the appropriate examinations. The regulations are printed in the syllabus of the Faculty of Arts.

The Regulations for the Diploma in Public Health are printed in the syllabus of the Faculty of Medicine.

ORDINANCES AND REGULATIONS FOR HIGHER DEGREES

I. DEGREE OF BACHELOR OF LETTERS

The degree of Bachelor of Letters is governed by Ordinance CCLXXXI (Glasgow No. 72), which came into force in October 1952. The relevant provisions of this Ordinance are as follows :

I. A degree of Bachelor of Letters (B.Litt.) may be conferred by the University of Glasgow in such departments of study in the Faculty of Arts as the Senatus Academicus with the approval of the University Court may determine.

II. Every candidate for the degree of Bachelor of Letters, before being admitted to a course of study qualifying therefor (*a*) must have obtained a degree in Arts with first or second class honours in the University of Glasgow or in another University recognised for this purpose by the University Court on the recommendation of the Senatus Academicus, provided that the University Court may, on the same recommendation, recognise another qualification obtained in a University other than a British University as equivalent to such a degree, and (*b*) must have satisfied the Senatus Academicus of his fitness to undertake advanced study.

III. Every candidate for the degree of Bachelor of Letters shall pursue full-time study in the University of Glasgow for two academic years, provided that the Senatus Academicus shall have power (*a*) for special reasons to permit a candidate to pursue study elsewhere for part of the prescribed period, and (*b*) in the case of graduates of the University of Glasgow, ***either*** to reduce the period of full-time study to one year ***or*** to accept a period of at least two academic years of study which is not full-time.

IV. The Senatus Academicus shall designate a Professor or Lecturer in the University to supervise the study of each candidate. Each candidate will be required to satisfy his supervisor as to his progress and a candidate may be required to attend such instruction as the Senatus Academicus may prescribe.

V. On the conclusion of his period of study each candidate for the degree shall ***either*** submit a dissertation on a subject falling within his special study *or* present himself for written or other examination in a branch of advanced study *or* both submit such a dissertation and present himself for such examination, as may be prescribed by the Senatus Academicus by regulation in the several departments of study. A candidate who submits a dissertation may be required also to undergo oral or other examination on the subject-matter of it.

VI. The examiners for the degree of Bachelor of Letters shall be such Professors and Lecturers in the University as the Senatus Academicus shall designate and such additional examiners as the University Court, on the recommendation of the Senatus Academicus, shall appoint.

VII. The degree of Bachelor of Letters shall in no case be conferred on persons who have not satisfied the conditions hereinbefore set forth and shall not be conferred *honoris causa tantum* except in the condition contained in University Court Ordinance No. CIX (Glasgow No. 28) (Regulations as to Principal Lecturers, Membership of Faculties, etc.), Section III.

DEPARTMENTS OF STUDY

The Departments of Study recognised by the Senatus under Section I of the Ordinance are as follows :

- Classics
- English Language and Literature
- French
- German
- Italian
- Hispanic Studies
- Slavonic Languages
- Semitic Languages
- Celtic Languages
- Philosophy
- Political Economy
- Political Science
- History
- Mathematics
- Psychology
- Geography
- Music
- History of Fine Art

REGULATIONS

Admission

Admission to study will be granted only from the beginning of the academic year.

Examination

Application for admission to examination must be made by 31st March in any year. If a dissertation is prescribed two typed copies of it must be submitted : one copy will remain in the possession of the University. A candidate who submits a dissertation will normally be orally examined.

2. DEGREE OF DOCTOR OF LETTERS

The Degree of Doctor of Letters is awarded under The Scottish Universities Ordinance No. 6, which came into force in October 1959. The following are the relevant provisions of that Ordinance.

I. The Degree of Doctor of Letters (D.Litt.) may be conferred in each of the Scottish Universities.

II. A graduate of any of the Scottish Universities may offer himself for the Degree of D.Litt. in that University after the expiry of seven years from the date of his first graduation therein.

III. Any person who holds such office or offices in each of the said Universities as the Senatus may approve who is not already a graduate of the University in which he holds such post or appointment may offer himself for the Degree of Doctor of Letters in the University in which he holds office, after the expiry of four years' continuous tenure of one or more of these offices, posts or appointments, provided always that not less than seven years shall have elapsed from the date of his first graduation in any University.

IV. A candidate for the Degree of D.Litt. shall present a published work or works accompanied by a signed declaration that he is the author thereof.

V. The Senatus shall appoint such Professors, Readers or Lecturers in the University as it may think suitable to examine the work or works submitted by a candidate for the Degree and the University Court shall, after consultation with the Senatus Academicus, appoint an additional examiner or examiners to act along with them. Such additional examiner or examiners shall be of recognised eminence in the subject of the work or works presented by the candidate. The candidate shall be awarded the Degree only if in the opinion of the Senatus, on the recommendation of these examiners, the body of work shall be held to constitute an original and substantial contribution to humane learning.

VI. The fee to be paid for examination for the Degree shall be such sum as may from time to time be determined by the University Courts of the four Universities. . . . Candidates for examination or graduation shall not be required to pay a matriculation fee.

VII. The Senatus of each University shall have power to make such additional regulations governing the conferment of the Degree as may be approved by the University Court.

VIII. The Degree of D.Litt. shall not be conferred upon a person who has not satisfied the conditions hereinbefore set forth, provided always that the Senatus of any of the four Universities may, at its discretion, permit a candidate to offer himself for the Degree under the regulations previously in force during a period not exceeding five years from the date on which this Ordinance shall come into operation; and provided always that it shall be in the power of the Senatus of any of the four Universities to confer the Degree of D.Litt. *honoris causa* under such regulations as may be made by the Senatus with the approval of the University Court.

SUPPLEMENTARY REGULATION

A candidate must submit two copies of each of the published works which he presents.

3. DEGREE OF DOCTOR OF MUSIC

The Degree of Doctor of Music was instituted by Ordinance CLXXIII (Glasgow No. 42); the following are the sections of that Ordinance which govern the award of the Degree.

XI. (1) Bachelors of Music of the University of Glasgow, who have taken Honours either before or after graduation, may offer themselves for the degree of Doctor of Music (D.Mus.), after the expiry of five years from the date of their graduation.

(2) Bachelors of Music of other Universities recognised for the purpose by the University Court after consultation with the Senatus may offer themselves for the degree of Doctor of Music, after the expiry of five years from the date of their graduation, provided they have spent not less than three years as Research Students in the University of Glasgow, under Ordinance No. 61 (General, No. 23), and produce to the Senatus evidence of satisfactory progress in the special study undertaken by them during that period.

XII. The Degree shall be given in three Departments, and candidates may present themselves in one or more of these Departments.

The Departments shall be those of:

(*a*) Composers;
(*b*) Executants;
(*c*) Theorists or Historians.

Composers

XIII. (1) Candidates for the Degree of Doctor of Music as Composers shall submit a prescribed number of original works in accordance with regulations to be prescribed by the Senatus.

Compositions must be accompanied by a declaration signed by the candidate that they are his own unaided work, and that no portion has been submitted previously to any University.

(2) Candidates in this department shall also be examined in the following subjects:

(*a*) Eight-part Harmony and Counterpoint;

(*b*) Canon and Double Counterpoint in four parts, and Fugue in five parts;
(*c*) Scoring for full Orchestra;
(*d*) Historical Knowledge.

Executants

XIV. (1) Candidates for the Degree of Doctor of Music as Executants shall be required to pass a test of a wide repertoire of concert works in accordance with regulations to be prescribed by the Senatus.

(2) Candidates in this department must also qualify for the optional subject set forth in VI (8) p. 194 (Degree of Bachelor of Music), and may also be required to pass an examination in any or all of the subjects prescribed for candidates for the Degree of Doctor of Music as Composers in accordance with regulations to be prescribed by the Senatus.

Theorists or Historians

XV. (1) Candidates for the Degree of Doctor of Music as Theorists or Historians shall present, in accordance with regulations to be prescribed by the Senatus, one or more treatise on Theoretical or Historical subjects. Such treatises must be the result of original thought and research, not merely abstracts or compilations of existing works.

Each treatise must be accompanied by a declaration signed by the candidate that it is his own unaided work and that it has not been submitted to any other University.

(2) Candidates in this department may also be required to pass an examination in any or all of the subjects prescribed for candidates for the Degree of Doctor of Music as Composers, in accordance with regulations to be prescribed by the Senatus.

SUPPLEMENTARY REGULATIONS

1. **Executants, Theorists and Historians.** All candidates in these categories will be examined in the following four subjects:

(*a*) Harmony and counterpoint in not more than eight parts.
(*b*) Canon and Double and Triple counterpoint in not more than three parts, and Fugue in not more than five parts.
(*c*) Scoring for full orchestra.
(*d*) The History of music from 1500 A.D. to the present day.

2. **Executants.** Each candidate must submit, not later than six weeks before the examination, an extensive list of works which he professes; if the list is approved, he will be informed, a month before the examination, of not more than four works which he will be required to perform. Violinists and violoncellists must include one or more of the unaccompanied sonatas or suites of J. S. Bach; candidates who profess instruments other than pianoforte, violin, violoncello or organ must include concertos and chamber works; vocalists must include rôles in opera and oratorio.

3. **Theorists and Historians.** Before submitting a treatise, candidates must submit a précis indicating its scope and general character; a treatise may not be submitted until the précis has been approved.

4. DEGREE OF DOCTOR OF LAWS

The Degree of Doctor of Laws is awarded under The Scottish Universities Ordinance No. 1, which came into force in October 1957. The following are the relevant provisions of that Ordinance.

I. (1) Graduates who have taken a degree in a Scottish University may offer themselves for the degree of Doctor of Laws (LL.D.) in that University after the expiry of seven years from the date of such graduation.

(2) It shall be open to the Senatus Academicus of each University with the approval of the University Court, to exempt from the requirement in the foregoing sub-section respecting previous graduation in that University any person who for a continous period of not less than four academic years has held such office or offices in that University as the Senatus Academicus may approve, provided that not less than seven years shall have elapsed from the date of his first graduation in any University.

II. All candidates for the degree of Doctor of Laws shall present written work not previously submitted for any degree of any University which shall be approved for the award of the degree only if the Senatus Academicus deems the work to be of sufficient merit as constituting an original and substantial contribution to the study of Law. The work shall be accompanied by a declaration signed by the candidate that it has been composed by himself. If the work has not been published in full, then, before being submitted, it shall have been published so far and in such manner as the Senatus Academicus accepts as reasonable in the circumstances. Two copies of the work, if approved for the degree, shall be deposited by the candidate in the University Library.

III. The Senatus Academicus of each University shall appoint such Professors, Readers or Lecturers as it may think suitable to examine the work submitted by candidates who may offer themselves for the Degree of Doctor of Laws and the University Court shall, after consultation with the Senatus Academicus, appoint one or more additional examiners to act along with them in adjudicating on the merits of the work submitted by the candidates. Every such additional examiner shall be a person of recognised eminence in the subject of the work presented by the candidate.

IV. The fee to be paid by a candidate for the degree of Doctor of Laws shall be fixed from time to time by the University Courts of the four Universities. The said fee shall be payable on each occasion on which the candidate offers himself for the Degree.

V. The Degree of Doctor of Laws shall not in any case be conferred upon any person who has not satisfied the conditions hereinbefore set forth, provided that nothing in this Ordinance shall be held to restrict or govern the conferment of that degree *honoris causa* according to the terms of Ordinances by which the conferment of the Degree of Doctor of Laws *honoris causa* is now or may hereafter be regulated.

VI. The Senatus Academicus of each University shall have power to make such additional regulations governing the conferment of the Degree as may be approved by the University Court.

SUPPLEMENTARY REGULATIONS

1. Application for the degree shall be made by letter addressed to the Clerk of Senate, which shall be accompanied by two copies of each item of the written work submitted in support of the application and of any connective statement required under Regulation (2) hereof, and also by a declaration signed by the applicant certifying that all the written work submitted has been composed by himself, that it has not been previously submitted either successfully or unsuccessfully for the award of any degree of any University, and stating, in the case where the applicant is submitting work not completely published, the extent to which it has been published and what efforts have been made to have the work published in full. The applicant must furnish any further information on these matters which may be requested by the Senatus Academicus.

2. The written work submitted in support of an application may have been published in full, or be partly published and partly unpublished. It should preferably take the form of one or more books or other substantial and independent pieces of writing. Papers published in periodicals of recognised standing under various titles may be submitted, either alone or in conjunction with other work, published or unpublished, only if all the papers and other items of work which are not by themselves substantial and independent pieces of writing form parts of a larger unity or unities, and are accompanied by a separate statement extending to about 500–1000 words composed by the applicant showing the connection between the various writings, their relation to the theme of the whole work, and the results and conclusions of the whole body or bodies of writings on which the application is based.

3. The Senatus Academicus shall consider the application and declaration and shall remit the works submitted in support thereof to the Committee of Examiners provided for in Section III of the Ordinance only if satisfied in all respects with the candidate's declaration and, in particular, that publication has been made so far and in such manner as is reasonable in the circumstances. If the Senatus Academicus rejects the application on the ground that in any respect it has not been satisfied by the candidate's declaration, the works shall be returned to the applicant without prejudice to their resubmission at a later date in changed circumstances. If the Senatus Academicus accepts the application, admits the applicant to candidature for the degree, and remits the works to the Examiner, both copies of all the works submitted shall become the property of the University, whether they are ultimately approved for the award of the degree or not, and the candidate shall be then liable to pay the fee fixed for the degree.

5. DEGREE OF DOCTOR OF MEDICINE

The following regulations for the award of the degree of Doctor of Medicine are contained in Ordinance XXXI (Glasgow No. 9).

XXII. (1) Subject to the conditions hereinafter specified, the Degree of Doctor of Medicine may be conferred on any candidate who has obtained the Degrees of Bachelor of Medicine and Bachelor of Surgery of the University of Glasgow, and is of the age of twenty-four years or upwards, and has produced a certificate showing that, after having received the degrees of Bachelor of Medicine and Bachelor of Surgery, he has been engaged for at least one year in attending the Medical Wards of a Hospital or in scientific work bearing directly on his profession, such as is conducted in the Research Laboratories of the University, or in the Naval, Military, Colonial, or Public Health Medical Services, or has been engaged for at least two years in Practice other than Practice restricted to Surgery.

(2) Each candidate for the degree of Doctor of Medicine shall be required to pass an examination in Clinical Medicine or in such special department of Medical Science or Practice professed by the candidate as the Senatus, on the recommendation of the Faculty of Medicine, may approve ; and he may be admitted to the examination at such time, not sooner than one year after he has received the degrees of Bachelor of Medicine and Bachelor of Surgery, as the Senatus may appoint for the purpose.

(3) Each candidate for the degree of Doctor of Medicine shall submit for the approval of the Faculty of Medicine a thesis on any branch of knowledge, comprised in the several divisions of the Examination for the degrees of Bachelor of Medicine and Bachelor of Surgery, which he may have made a subject of special study, excepting a subject that is exclusively surgical ; and the thesis, accompanied by a declaration signed by the candidate that the work has been done and the thesis composed by himself, shall be lodged with the Dean of the Faculty of Medicine on or before a date to be fixed by the Senatus. The Faculty may, if it sees fit, before approving the thesis, require the candidate to present himself for oral or other examination on the subject-matter thereof. If the thesis is, in the judgment of the Faculty, of special merit, the Senatus may, on the recommendation of the Faculty, exempt the candidate from the whole or part of the examination prescribed in sub-section 2 of this Section.

(4) A Bachelor of Medicine and Bachelor of Surgery, who produces to the Senatus satisfactory evidence of his intention of entering within twelve months after obtaining such degrees on the practice of his profession in a British Possession or Colony, or in a Foreign Country, may, under such conditions as the Senatus may from time to time prescribe, be admitted to the examination in Clinical Medicine or in a special department of Medical Science or Practice prescribed in sub-section 2 of this Section at such time after he has received such degrees as the Senatus may appoint for the purpose : provided always that in special circumstances the Senatus may, if it sees fit, on the recommendation of the Faculty of Medicine, exempt him from the whole or part of the Examination ; but the degree of Doctor of Medicine shall not be conferred on him unless he shall produce a certificate showing that, after having received the degrees of Bachelor of Medicine and Bachelor of Surgery, he has been engaged for at least one year in attending the Medical Wards of a Hospital or in scientific work bearing directly on his profession, such as is conducted in the Research Laboratories of the University, or in

the Naval, Military, Colonial or Public Health Medical Services, or for at least two years in Practice other than Practice restricted to Surgery, and unless his thesis, in the judgment of the Faculty of Medicine, is of special merit.

SUPPLEMENTARY REGULATIONS

1. To comply with the conditions prescribed in sub-sections 2 and 3 above, a candidate, after submitting a thesis, may be required to present himself before the examiners for interview or for further examination on the subject-matter of his thesis and related subjects. When a candidate is required to undergo further examination, this examination may be a written, or oral, or practical test, or any combination of these, as the examiners think fit.

2. One copy only of a thesis is required. It must be typewritten on paper of crown quarto size (10 inches by 7½ inches), bound in cloth with stiff boards, and have its title and the name of the author printed in block letters on the outside binding. The thesis should be lodged with the Dean of the Faculty of Medicine not later than 15th September, or 15th December, or 15th March, for adjudication during the Martinmas, Candlemas, and Whitsun terms respectively.

3. A thesis will not be approved unless it gives evidence of original observation, or, if it deals with the researches of others, gives a full statement of the literature of its subject with accurate references and critical investigation of the views or facts cited : mere compilations will in no case be accepted.

4. A thesis submitted for the degree must be a dissertation written for the purpose, provided that the results of original observations already published in medical or scientific journals or in the transactions of learned societies or otherwise may be accepted in place of such a dissertation.

5. Two grades of distinction may be awarded for the excellence of theses submitted for the degree—Commendation and Honours.

6. The copies of theses submitted by candidates, whether the theses are approved for the degree or not, shall become the property of the University.

6. DEGREE OF MASTER OF SURGERY

The following regulations for the award of the degree of Master of Surgery are contained in Ordinance XXXI (Glasgow No. 9).

XXIII. (1) Subject to the conditions hereinafter specified the degree of Master of Surgery may be conferred on any candidate who has obtained the degrees of Bachelor of Medicine and Bachelor of Surgery of the University of Glasgow, and is of the age of twenty-four years or upwards, and has produced a certificate showing that, after having received the degrees of a Bachelor of Medicine and Bachelor of Surgery, he has been engaged for at least one year in attending the Surgical Wards of a Hospital or in scientific work bearing directly on his profession, such as is conducted in the Research Laboratories of the

University, or in the Naval, Military, or Colonial Medical Services, or has been engaged for at least two years in Practice other than Practice restricted to Medicine.

(2) Each candidate for the degree of Master of Surgery shall be required to pass an examination in the following subjects: Surgical Anatomy, Operations upon the dead body, and Clinical Surgery or such special department of Surgery professed by the candidate as the Senatus, on the recommendation of the Faculty of Medicine, may approve ; and he may be admitted to the examination at such time, not sooner than one year after he has received the degrees of Bachelor of Medicine and Bachelor of Surgery, as the Senatus may appoint for the purpose.

(3) Each candidate for the degree of Master of Surgery shall submit for the approval of the Faculty of Medicine a thesis on any branch of knowledge, comprised in the several divisions of the Examination for the degrees of Bachelor of Medicine and Bachelor of Surgery, which he may have made a subject of special study, excepting a subject that is exclusively medical ; and the thesis, accompanied by a declaration signed by the candidate that the work has been done and the thesis composed by himself, shall be lodged with the Dean of the Faculty of Medicine on or before a date to be fixed by the Senatus. The Faculty may, if it sees fit, before approving the thesis, require the candidate to present himself for oral or other examination on the subject-matter thereof. If the thesis is, in the judgment of the Faculty, of special merit, the Senatus may, on the recommendation of the Faculty, exempt the candidate from the whole or part of the examination prescribed in sub-section 2 of this Section.

(4) A Bachelor of Medicine and Bachelor of Surgery who produces to the Senatus satisfactory evidence of his intention of entering within twelve months after obtaining such degrees on the practice of his profession in a British Possession or Colony, or in a Foreign Country, may, under such conditions as the Senatus may from time to time prescribe, be admitted to the examination in the subjects specified in sub-section 2 of this Section, at such time after he has received such degrees as the Senatus may appoint for the purpose : provided always that in special circumstances the Senatus may, if it sees fit, on the recommendation of the Faculty of Medicine, exempt him from the whole or part of the examination ; but the degree of Master of Surgery shall not be conferred on him unless he shall produce a certificate showing that, after having received the degrees of Bachelor of Medicine and Bachelor of Surgery, he has been engaged for at least one year in attending the Surgical Wards of a Hospital or in scientific work bearing directly on his profession, such as is conducted in the Research Laboratories of the University, or in the Naval, Military, or Colonial Medical Services, or for at least two years in Practice other than Practice restricted to Medicine, and unless his thesis in the judgment of the Faculty of Medicine is of special merit.

SUPPLEMENTARY REGULATIONS

1. To comply with the conditions prescribed in sub-sections 2 and 3 above, a candidate, after submitting a thesis, may be required to present himself before the examiners for interview or for further examination on the subject-matter of his thesis and related subjects. When a

candidate is required to undergo further examination, this examination may be a written, or oral, or practical test, or any combination of these, as the examiners think fit.

2. One copy only of a thesis is required. It must be typewritten on paper of crown quarto size (10 inches by 7½ inches), bound in cloth with stiff boards, and have its title and the name of the author printed in block letters on the outside binding. The thesis should be lodged with the Dean of the Faculty of Medicine not later than 15th September, or 15th December, or 15th March, for adjudication during the Martinmas, Candlemas, and Whitsun Terms respectively.

3. A thesis will not be approved unless it gives evidence of original observation, or, if it deals with the researches of others, gives a full statement of the literature of its subject with accurate references and critical investigation of the views or facts cited : mere compilations will in no case be accepted.

4. A thesis submitted for the degree must be a dissertation written for the purpose, provided that the results of original observations already published in medical or scientific journals or in the transactions of learned societies or otherwise may be accepted in place of such a dissertation.

5. Two grades of distinction may be awarded for the excellence of theses submitted for the degree—Commendation and Honours.

6. The copies of theses submitted by candidates, whether the theses are approved for the degree or not, shall become the property of the University.

7. DEGREE OF MASTER OF DENTAL SURGERY

The following regulations for the award of the degree of Master of Dental Surgery (M.D.S.) are contained in Ordinance CCXLI (Glasgow No. 56) which was approved by His Majesty in Council on 26th January, 1948.

XXII. Subject to the conditions hereinafter specified, the Degree of Master of Dental Surgery may be conferred on any candidate who has obtained the Degree of Bachelor of Dental Surgery of the University of Glasgow ; or, having obtained the Degrees of Bachelor of Medicine and Bachelor of Surgery, or the Degree of Bachelor of Science, of the University of Glasgow, holds in addition a Registrable Dental Qualification. The candidate must have produced certificates showing that, after having received his Registrable Dental Qualification, he has been engaged for at least one year in attending a Dental Hospital or the Dental Department of a General Hospital approved by the University Court, after consultation with the Senatus, or in the Naval, Military, or Public Health Services, or in practice in Dental Surgery.

XXIII. Each candidate for the Degree of Master of Dental Surgery shall be required to pass a clinical examination in Dental Surgery, and he may be admitted to that examination at such time, not sooner than one calendar year after he has received his Registrable Dental Qualification as the Senatus may appoint for the purpose : provided always that in special circumstances the Senatus may, if they see fit, on the recommendation of the Board of Studies in Dentistry and the Faculty of Medicine, exempt a candidate from the whole or part of such examination.

XXIV. Each candidate for the Degree of Master of Dental Surgery shall submit for the approval of the Faculty of Medicine a Thesis on any branch of knowledge in the Second, Third, or Fourth divisions of the examination for the Degree of Bachelor of Dental Surgery, which he may have made a subject of study, excepting those subjects which are exclusively medical or surgical; and the Thesis, accompanied by a declaration signed by the candidate that the work has been done and the Thesis composed by himself, shall be lodged with the Dean of the Faculty of Medicine on or before a date to be fixed by the Senatus. The Faculty may, if it sees fit, before approving the Thesis, require the candidate to present himself for oral or other examination on the subject-matter thereof.

8. DEGREE OF DOCTOR OF VETERINARY MEDICINE

The award of the Degree of Doctor of Veterinary Medicine is provided for in Ordinance CCLXI (Glasgow No. 66), which was approved by His Majesty in Council on 26th June, 1950. The following are the Regulations governing the award:

(1) Subject to the conditions hereinafter specified, the Degree of Doctor of Veterinary Medicine may be conferred on any candidate who, not less than two years previously, has obtained the Degree of Bachelor of Veterinary Medicine and Surgery of the University of Glasgow, or, in the case of a teaching officer of the University, who holds a degree of the University and who has been on the Register of the Royal College of Veterinary Surgeons for a period of not less than two years.

(2) Each candidate for the degree of Doctor of Veterinary Medicine shall submit for the approval of the Faculty of Medicine a thesis on any branch of knowledge comprised in the several divisions of the Examination for the degree of Bachelor of Veterinary Medicine and Surgery, which he may have made a subject of special study, excepting a subject that is exclusively surgical; and the thesis, accompanied by a declaration signed by the candidate that the work has been done and the thesis composed by himself, shall be lodged with the Dean of the Faculty of Medicine on or before a date to be fixed by the Senatus.

(3) The Faculty may, if it sees fit, before approving the thesis, require the candidate to present himself for interview or for further examination of the subject-matter thereof. When a candidate is required to undergo further examination, this examination may be a written, or oral, or clinical, or practical test, or any combination of these, as the examiners think fit.

(4) Two copies of a thesis are required, and must be typewritten on paper of crown quarto size (10 inches by 7½ inches) bound in cloth with stiff boards, and have the title and the names of the author printed in block letters on the outside binding. The thesis should be

lodged with the Dean of the Faculty of Medicine not later than 15th September, or 15th December, or 15th March, for adjudication during the Martinmas, Candlemas, and Whitsun terms respectively.

(5) A thesis will not be approved unless it gives evidence of original observation, or, if it deals with the researches of others, gives a full statement of the literature of its subject with accurate references and critical investigation of the views of facts cited ; mere compilations will in no case be accepted.

(6) A thesis submitted for the degree must be a dissertation written for the purpose, but the results of original observations already published in medical or scientific journals or in the transactions of learned societies or otherwise may be incorporated in such a dissertation.

(7) The merit of a thesis approved for the degree shall be assessed in three grades : Sufficient, Commendation, and Honours.

(8) The copies of a thesis submitted by a candidate, whether approved for the degree or not, shall become the property of the University.

9. DEGREE OF MASTER OF VETERINARY SURGERY

The award of the Degree of Master of Veterinary Surgery is provided for in Ordinance CCLXI (Glasgow No. 66), which was approved by His Majesty in Council on 26th June, 1950. The following are the Regulations governing the award :

(1) Subject to the conditions hereinafter specified, the degree of Master of Veterinary Surgery may be conferred on any candidate who, not less than two years previously, has obtained the degree of Bachelor of Veterinary Medicine and Surgery of the University of Glasgow, or, in the case of a teaching officer of the University, who holds a degree of the University and who has been on the Register of the Royal College of Veterinary Surgeons for a period of not less than two years.

(2) Each candidate for the degree of Master of Veterinary Surgery shall submit for the approval of the Faculty of Medicine a thesis on any branch of knowledge comprised in the several divisions of the Examination for the degree of Bachelor of Veterinary Medicine and Surgery, which he may have made a subject of special study, excepting a subject that is exclusively medical ; and the thesis, accompanied by a declaration signed by the candidate that the work has been done and the thesis composed by himself, shall be lodged with the Dean of the Faculty of Medicine on or before a date to be fixed by the Senatus.

(3) Each candidate for the degree of Master of Veterinary Surgery may be required to pass an examination in all or any of the following subjects : Surgical Veterinary Anatomy, Clinical Surgery or such special department of Veterinary Surgery professed by the candidate as the Senatus, on the recommendation of the Faculty of Medicine, may approve. If the thesis is, in the judgment of the Faculty, of special merit, the Senatus may, on the recommendation of the Faculty, exempt the candidate from the whole or part of the examination prescribed in the sub-section.

(4) Two copies of a thesis are required, and must be typewritten on paper of crown quarto size (10 inches by 7½ inches) bound in cloth with stiff boards, and have the title and the name of the author printed in block letters on the outside binding. The thesis should be lodged with the Dean of the Faculty of Medicine not later than 15th September, or 15th December, or 15th March, for adjudication during the Martinmas, Candlemas and Whitsun terms respectively.

(5) A thesis will not be approved unless it gives evidence of original observation, or, if it deals with the researches of others, gives a full statement of the literature of its subject with references and critical investigation of the views or facts cited : mere compilations will in no case be accepted.

(6) A thesis submitted for the degree must be a dissertation written for the purpose, but the results of original observations already published in medical or scientific journals or in the transactions of learned societies or otherwise may be incorporated in such a dissertation.

(7) The merit of a thesis approved for the degree shall be assessed in three grades : Sufficient, Commendation, and Honours.

(8) The copies of a thesis submitted by a candidate, whether approved for the degree or not, shall become the property of the University.

10. DEGREE OF MASTER OF SCIENCE

The Degree of Master of Science (M.Sc.) is awarded under Ordinance CCCXXXIV (Glasgow No. 97), which was approved by Her Majesty in Council on 21st October 1959. The following are the provisions of that Ordinance:

I. A Degree of Master of Science (M.Sc.) may be conferred by the University of Glasgow in such departments of study in the Faculties of Science and Engineering as the Senatus Academicus may from time to time determine.

II. Every candidate for the Degree of Master of Science before being admitted to a course of special study or research leading to the Degree (*a*) must have obtained a degree in any Scottish University or in another University or Institution specially recognised for this purpose by the University Court on the recommendation of the Senatus Academicus or, in exceptional circumstances, other qualifications approved by the University Court on the recommendation of the Senatus Academicus, and (*b*) must have satisfied the Senatus Academicus that the course of study or research proposed is suitable and that he is qualified to pursue it.

III. Every candidate for the Degree of Master of Science shall pursue a full-time course of special study or research during a period of two academical years, each consisting of three terms, in the University of Glasgow, or in a College affiliated thereto; provided always that the Senatus Academicus may reduce the period to twelve months in the case of graduates of any recognised University with Honours of the First or Second Class in an appropriate department of study and that the Senatus Academicus may, in special circumstances, permit graduates of the University of Glasgow to prosecute part of their studies elsewhere; but in no case shall the period of full-time residence and study in the University of Glasgow or in a College affiliated thereto be less than twelve months.

IV. Every candidate for the degree shall be required to matriculate each year of his prescribed period of special study or research and to pay the appropriate fees.

V. The Senatus Academicus shall designate, for each candidate, a supervisor who shall report at least once a year to the Senatus Academicus on the progress of the candidate.

VI. On the completion of the prescribed period of study or research each candidate shall present a thesis embodying the result of his work which may be either a record of original research or a critical review of existing knowledge. Except by special permission of the Senatus Academicus a thesis may not be presented after the lapse of four years from the date of the candidate's admission.

VII. A Committee of Examiners shall be appointed to examine the thesis of each candidate. The Committee shall consist of one or more members appointed by the Senatus Academicus together with one or more Additional Examiners appointed by the University Court on the recommendation of the Senatus Academicus. The Examiners shall conduct such oral and written examinations as they may desire or as the Senatus Academicus may prescribe in each case.

VIII. The fee payable on submission of the thesis for the degree shall be prescribed by the University Court.

IX. The Senatus Academicus shall have power to make from time to time Regulations (1) in respect of the course of study or research to be pursued by candidates for the degree, and (2) otherwise to carry out the provisions of this Ordinance.[1]

X. The Degree of Master of Science (M.Sc.) may be conferred *honoris causa* (*a*) upon persons who have done work deserving of such recognition in any department of science, and (*b*) upon any person holding office in the University who is not already a graduate of the University.

II. DEGREE OF DOCTOR OF SCIENCE

The degree of Doctor of Science is awarded under Ordinance XXVI (Glasgow No. 7), which came into force in September, 1908. The following are the relevant provisions of that Ordinance, with the amendments made in subsequent Ordinances.

I. Graduates who have obtained any degree in the University of Glasgow, and who have either before or after graduation passed the Examination in an Honours Group for the degree in Arts, or the Final Science Examination for the degree in Pure Science or in Engineering with Honours, may offer themselves for the degree of Doctor of Science (D.Sc.) after the expiry of five years from the date of their graduation.

II. Research Students within the meaning of Ordinance No. 61 (General No. 23—Regulations for the Encouragement of Special Study

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[1] Regulations now being made, will it is expected be in force in Session 1960–1961.

and Research and for the Appointment of Research Fellows), who have prosecuted in the University of Glasgow (or in a College affiliated thereto) some special study or research under that Ordinance, may offer themselves for the degree of Doctor of Science : provided :

(1) That they have obtained a degree in any Scottish University, or a degree in another University specially recognised by the University Court for the purpose of this section which the Senatus shall deem to be equivalent to the corresponding degree in the University of Glasgow ; and provided that candidates who have obtained any such degree in a University outside the United Kingdom so recognised may be required, if the Senatus think fit, before beginning their course as Research Students with a view to the degree of Doctor of Science, to pass an examination equivalent to an Honours or to a Final Science Examination in a group of subjects cognate to their line of work as Research Students.

(2) That they have spent not less than two terms in each of two academical years, or an equivalent period, as Research Students in the University of Glasgow (or in a College affiliated thereto), and that they produce to the Senatus evidence of satisfactory progress in the special study or research undertaken by them during that period.

(3) That a period of not less than five years shall have elapsed from the date of the graduation required in subsection (1) of this section.

III. All candidates for the degree of Doctor of Science shall present a thesis or a published memoir or work, to be approved by the Senatus on the recommendation of the Faculty of Science ; provided that, if required by the Senatus, the candidate shall also be bound to pass such an examination conducted orally or practically, or by written papers, or by all of these methods, on the subjects of his special study or of his thesis, memoir, or work, as may from time to time be determined. The thesis shall be a record of original research in relation to science undertaken by the candidate, or of some important engineering work designed by the candidate and actually carried out, and shall be accompanied by a declaration signed by him that the work has been done and the thesis composed by himself. If the thesis has not already been published, it shall be published by the candidate in such manner as the Senatus shall approve, and a copy thereof shall be deposited by the candidate in the University Library.

X. Notwithstanding, and in supplement of the provisions of Ordinance No. 13 (General, No. 8—Regulations as to Examinations), Sections XIV and XV, the Senatus shall appoint such Professors or Lecturers in the University as it may think suitable to examine the theses and to conduct the examination of candidates who may offer themselves under the provisions of Ordinance No. 12 (General, No. 7—Regulations for Degrees in Science) or of Ordinance No. 23 Glasgow, No. 2—Regulations for Degrees in Engineering Science, or of this Ordinance, for the degree of Doctor of Science . . . ; and the University Court shall, after consultation with the Senatus, appoint one or more additional Examiners to act along with them in adjudicating on the merits of the candidates. Every such additional Examiner shall be a person of recognised eminence in the subject of the thesis or memoir or work which is to be submitted for approval, and may be a Professor or Lecturer in any Scottish University other than the University of Glasgow. The result of the examination and adjudication shall be reported to the appropriate Faculty or Special Committee of Senatus, who shall if they think fit make a recommendation thereon to the Senatus ; and no candidate shall be approved for the degree unless the Senatus is satisfied that his work is of distinction as a record of original research undertaken by himself, or of important engineering work designed by himself and actually carried out, or as an original contribution to learning.

SUPPLEMENTARY REGULATIONS

1. Candidates who have been awarded a Certificate of Proficiency in the subjects of an Honours Group will be regarded as having " passed the Examination in an Honours Group " for the purpose of proceeding to the degree of D.Sc.

2. Each candidate must submit two copies of his thesis : both copies, whether the thesis is approved for the degree or not, shall become the property of the University.

3. In addition to making the declaration required under Section III of the Ordinance a candidate must, if the whole or any part of the subject-matter of the thesis submitted by him has been included in a thesis already approved for a degree in this or another University, make a declaration to that effect, and must lodge together with his thesis either a copy of such previously approved thesis or a precise statement of its scope.

4. Before acceptance for adjudication, a thesis, or an important part of it, shall have been published either as a book or in periodicals of recognised standing. The thesis may be presented in the form of a single memoir or writing containing a connected account of the candidate's research or work. Published papers under various headings may be submitted in lieu of a single thesis provided that they are accompanied by a statement showing the relationship between the various studies and placing the whole work critically into perspective with the general state of knowledge in the field of investigation to which the candidate's researches are related. The thesis should also be accompanied by two copies of a separate summary (500–1000 words) which must be an adequate and informative abstract of the work, suitable for publication by the University.

12. DEGREE OF DOCTOR OF SCIENCE IN PUBLIC HEALTH

The regulations for the award of the degree of Doctor of Science in Public Health are contained in Ordinance VI (Glasgow No. 2), which came into force in May, 1903. The relevant provisions of the Ordinance are :

X. Graduates who have held the degree of Bachelor of Science in Public Health from the University of Glasgow for a term of five years, may offer themselves for the degree of Doctor of Science in Public Health in the said University.

XI. Each candidate for the degree of Doctor of Science in Public Health shall present a thesis or a published memoir or work to be approved by the Senatus, on the recommendation of the Faculty of Science, and shall also be required to pass an examination in Public Health, and in such of its special departments as the Senatus, with the approval of the University Court, by regulations framed from time to time, shall determine.

The thesis, or published memoir or work, shall be a record of original research undertaken by the candidate, and shall be accompanied by a declaration, signed by him, that the work has been done, and the thesis or memoir composed, by himself.

XII. The Senatus Academicus shall appoint such Professors or Lecturers as it may think suitable to conduct the examination of candidates who may offer themselves under the provisions of this Ordinance for the degree of Doctor of Science, and the University Court shall, after consultation with the Senatus Academicus, appoint such additional Examiners as they deem necessary to act along with them. Such additional Examiners shall be persons of recognised eminence in the subject of the thesis, or memoir, or work which is to be submitted for approval, and may be Professors or Lecturers in any Scottish University other than the University of Glasgow.

XIII. The thesis, memoir, or work submitted by a candidate for the degrees of Doctor of Science shall in each case be examined by the additional Examiner to be appointed by the University Court, as well as by the Examiners to be appointed by the Senatus under the provisions of Section XII of this Ordinance.

XIV. The result of the examination of the thesis, memoir, or work submitted by a candidate, as well as the result of the Examination prescribed under Section XI of this Ordinance, shall be reported to the Faculty of Science.

13. DEGREE OF DOCTOR OF PHILOSOPHY

The degree of Doctor of Philosophy was instituted by Ordinance LXXIV (Glasgow No. 21), which came into force in October, 1919. The relevant provisions of the Ordinance are as follows :

II. Research Students within the meaning of Ordinance No. 61 (General No. 23), who have prosecuted in the University of Glasgow, or in a College affiliated thereto, a course of special study or research in accordance with the provisions of that Ordinance, may offer themselves for the degree of Doctor of Philosophy, under the following conditions, namely—

(1) That they have obtained a degree in any Scottish University, or in another University or College specially recognised for the purpose of this Section by the University Court on the recommendation of the Senatus : provided always that a diploma or certificate recognised in like manner as equivalent to a degree may be accepted in place of a degree.

(2) That they have prosecuted a course of special study or research during a period of three academical years as Research Students in the

University of Glasgow, or in a College affiliated thereto, and that they produce to the Senatus evidence of satisfactory progress in the special study or research undertaken by them during that period : provided always that the Senatus shall have power, in exceptional cases, to reduce the period to two academical years, and to permit a Research Student during part of the period to prosecute elsewhere his special study or research.

III. All candidates for the degree of Doctor of Philosophy shall present a thesis to be approved by the Senatus on the recommendation of a Special Committee appointed by the Senatus. The thesis shall embody the results of the candidate's special study or research, and shall be accompanied by a declaration signed by the candidate that it has been composed by himself. The Special Committee shall always include the Professor or other Head of a Department who has been appointed by the Senatus to supervise the candidate's work as a Research Student.

The University Court may, on the recommendation of the Senatus, appoint one or more additional Examiners to act along with the Special Committee in adjudicating on the merits of the thesis. The Senatus may, on the recommendation of the Special Committee, require the candidate to present himself for oral or other examination on the subject-matter of his thesis. A copy of the thesis, if approved, shall be deposited by the candidate in the University Library.

SUPPLEMENTARY REGULATIONS

1. Except in the case of members of the teaching staff of the University, the Senatus will not recognise Research Students as candidates for the degree of Ph.D. in the Faculties of Arts, Medicine, Science and Engineering unless they are able to devote the major part of the day during term-time to the object of their research.

2. In submitting a thesis a candidate must state, generally in the preface and specifically in the notes, the sources from which his information is derived, the extent to which he has availed himself of the work of others, and the portions of the thesis which he claims as original.

3. A candidate must submit two copies of the thesis and in addition two copies of a separate summary of the thesis. The separate summary (250–750 words) must be an adequate and informative abstract of the work, suitable for publication by the University. Both copies of the thesis, whether approved for the degree or not, become the property of the University.

RESEARCH STUDENTS

The following are the provisions of Ordinance No. 61 (General No. 23), by which the admission of Research Students is controlled :

I. It shall be in the power of the Senatus Academicus in each University, with the approval of the University Court, to make regulations under which graduates of Scottish Universities or of other Universities recognised by the University Court for the purposes of this Ordinance, or other persons who have given satisfactory proof of general education and of fitness to engage in some special study or research, may be admitted to prosecute such study or research in the University [or in a College affiliated thereto [1]].

II. It shall be the duty of the Senatus Academicus in each University :

(1) To receive and decide upon all applications for admission to prosecute special study or research ;

(2) To prepare a list of all persons so admitted (hereinafter referred to as Research Students) ;

(3) To make regulations for the supervision of their work

(4) To satisfy themselves from time to time that the Research Students are carrying on their work in the University in a satisfactory manner ;

(5) To suspend or exclude from any course any student whose conduct or progress is unsatisfactory.

III. Every applicant for admission must send in to the Senatus Academicus a written application stating any degree or other distinction which he has already obtained, the line of study or research which he wishes to prosecute, and the probable period of its duration, together with evidence as to his character, capacity, and general qualifications.

IV. Any application for admission shall be in the first instance referred by the Senatus Academicus to the appropriate Faculty, or to a Committee appointed by the Senatus ; one member of the Committee shall always be a Professor or Lecturer within whose department the proposed line of study or research falls. No applicant shall be recommended by the Faculty or the Committee who has not satisfied them by examination or otherwise that he is qualified to prosecute the proposed line of study or research, and further :

(*a*) That his proposed line of study or research is a fit and proper one ;

(*b*) That he possesses a good general education ;

(*c*) That he is of good character ;

(*d*) That he proposes to prosecute his studies or research during a period to be approved by the Senatus Academicus.

The Faculty or the Committee shall make a report to the Senatus Academicus upon each application. It shall also be their duty, subject to the regulations of the Senatus Academicus, to provide for the supervision of the Research Student's work, and to report at least once a year to the Senatus as to his progress and conduct. The Senatus shall then determine whether he shall remain a Research Student.

V. Every Research Student shall be required to matriculate each year, paying the ordinary fee.

VI. Research Students shall have access to and the use of the University Laboratories and Museums, under such conditions as to payment and otherwise as the University Court, after consultation with the Senatus Academicus, may determine.

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[1] Added by Ordinance XXXIX (Glasgow No. 12).

VII. The title of Research Fellow may be conferred by the Senatus Academicus, with the approval of the University Court, on Research Students who have shown special distinction. Such title shall not of itself confer any right to stipend, but it shall be in the power of the University Court to provide a stipend of such amount and for such period as it may think fit to any Research Fellow, under the powers of Section XI, sub-section 8, of Ordinances numbered 25 and 27, Section X, sub-section 8, of Ordinance numbered 26, and Section IV, sub-section 2, of Ordinance numbered 46.

VIII. (1) The Research Fellows shall be appointed as aforesaid after consideration of the report or reports submitted in terms of Section IV hereof.

(2) The title of Research Fellow may be conferred either at the commencement of the Research Student's course of study or research, or at any time during its progress, as the Senatus Academicus may determine.

(3) Research Fellows shall retain their title and stipend, if any, for the period during which they are engaged in special study or research in the University, and no longer.

(4) Research Students who have been appointed Research Fellows shall continue to be subject to the conditions above prescribed as to the supervision of their work, and the reports to be made thereon.

IX. Nothing herein contained shall prejudice the right of Research Students to such Fellowships, Scholarships, or prizes as may be open to them by Ordinance or Deed of Foundation.

X. The University Court may, subject to the provisions of Section XI, sub-section 8, of Ordinances numbered 25 and 27, Section X, sub-section 8, of Ordinance numbered 26, and Section IV, sub-section 2, of Ordinance numbered 46, provide such sums as it may think fit in aid of the expenses of special study or Research.

SUPPLEMENTARY REGULATIONS

1. Application for admission to the status of Research Student must be made to the Clerk of Senate on the prescribed form.

2. A Research Student may be required at the discretion of the Head of the Department to report his attendance to the supervisor of his research, or to the Clerk of Senate, at least once a week in term-time, except during periods when, with the permission of the Senatus, he is prosecuting his special study or research elsewhere than in the University or in a College affiliated thereto.

3. A Research Student may, with the sanction of his supervisor, attend classes in the University as a Private Student but he shall not be eligible for prizes in classes so attended and his attendance shall not qualify for graduation.

4. All papers arising out of work done in a department shall be submitted before publication to the Professor in charge of the department, and in all such papers, when they are published, a due recognition of the department shall be inserted.

Note: For Fees see page 445.

CARNEGIE TRUST FOR THE UNIVERSITIES OF SCOTLAND

ENDOWMENT OF POST-GRADUATE STUDY AND RESEARCH

The regulations governing the award by the Trust of Scholarships, Fellowships and Grants in aid of research, are printed below. Nominations for Scholarships or Fellowships must be lodged not later than 15th March with the Secretary of the Carnegie Trust, Merchants' Hall, Hanover Street, Edinburgh, from whom forms may be obtained. All Scholarships and Fellowships awarded in any year will normally date from 1st October.

A student who has not graduated but expects to take a degree at the summer or autumn graduation may be nominated for a Scholarship or apply for a Research Grant in the preceding March, but will not be eligible to receive either until he has graduated.

I. SCHOLARSHIPS

I. The Executive Committee are prepared to consider annually applications for Carnegie Scholarships for post-graduate study and research in Science and Medicine and in History, Economics, English Literature and Modern Languages.

II. Applicants for Scholarships must be graduates of a Scottish University, or students who expect to graduate at a Scottish University within a short time of making their application.

The standard required for applicants in the Faculties of Arts and Science is First Class Honours.

III. Applicants for Scholarships must be nominated by a Professor, Reader or Lecturer in a Scottish University, or by a teacher of similar status in a College affiliated to a Scottish University.

Nominators must note that the number of Scholarships for annual award is limited and that the strictest standards of selection will be enforced. In assessing the suitability of applicants for nomination, they will be expected to have regard to the awards obtainable for research from such bodies as the Department of Scientific and Industrial Research, the Agricultural Research Council, and the Medical Research Council.

IV. Applicants for Scholarships in Science must report whether they are eligible to apply to the Department of Scientific and Industrial Research for a post-graduate award, whether they have made such an application, and, if they have not, their reasons for not doing so.

Particularly if their proposed subject for research is in Physics or Chemistry, they are advised that the Executive Committee reserves the right to give preferential consideration to applicants who are not eligible for Department of Scientific and Industrial Research awards.

V. The maximum annual value of a Scholarship will be £450, payable if the Scholar matriculates at the Universities of Oxford, Cambridge or London, or if he necessarily requires to spend the greater part of the year abroad in full-time research. For Scholars who matriculate at a University in the town of their permanent residence, the maximum award will be £350. The maximum for Scholars living away from home and matriculating at either a Scottish or an English provincial University will be £400.

VI. Scholarships will be tenable for one year in the first instance, and will normally be renewed for a second year, subject to satisfactory progress by the Scholar. In exceptional circumstances, they may be extended to a third year. The Scholar will be expected to devote his whole time to the purpose for which the Scholarship is awarded.

VII. The Executive Committee may, at their discretion, supplement bursaries, scholarships or fellowships awarded to their graduates by the Scottish Universities, provided that application has been made as prescribed in these Regulations, and that the application is in every way compatible with these Regulations, and that supplementation is not available from the Scottish Education Department.

Applicants for supplementation must furnish a certificate from the Secretary or Registrar of their University showing the title, value and length of tenure of the Bursary, Scholarship or Fellowship gained, and will be required to conform in every respect to the regulations governing Carnegie Scholars.

(This Regulation is provisional, and subject to alteration in the event of changes of policy by the Scottish Education Department.)

VIII. Scholars are under an obligation to report without delay any awards received after the date of their application.

IX. Scholars will be required to work under a supervisor ; quarterly reports on their work must be made by both Supervisors and Scholars. Payments of the Scholarships will be made at the beginning of October, January, April and July, each instalment after the first being dependent on the receipt of satisfactory reports.

X. Nomination forms, to be signed by the nominator and the applicant, may be obtained from the Secretary to the Carnegie Trust for the Universities of Scotland, The Merchants' Hall, 22 Hanover Street, Edinburgh and must be returned not later than 15th March in each year. The awards will be announced as soon as possible thereafter, probably about the middle of June.

2. SENIOR SCHOLARSHIPS

I. The Executive Committee are prepared to consider annually applications for a restricted number of Senior Scholarships in Science and Medicine, and in History, Economics, English Literature and Modern Languages.

II. The Senior Scholarships will be of the annual value of £500 together with a sum not exceeding £100 for fees, books and any necessary travelling expenses. They will be tenable for one year in the first instance but may be renewed for a second and, in exceptional circumstances, a third year. Payment will be made in quarterly instalments.

III. Applicants must be graduates of a Scottish University and be able to adduce proof of successful research for a period of at least three years prior to the application. Applications are not confined to those who have previously held Carnegie Scholarships.

IV. Applicants must be nominated by a Professor, Reader or Lecturer in a Scottish University, and must submit the names of two authorities, other than the nominator, to whom reference may be made if deemed necessary. Successful applicants will work under the general direction of a supervisor from whom, twice annually, a certificate will be required attesting satisfactory progress. The Senior Scholar will himself furnish reports twice annually on the progress of his work. He will be required to give his full time to the purpose for which the Senior Scholarship is awarded.

3. FELLOWSHIPS

I. The Executive Committee are prepared to consider applications for Carnegie Fellowships in Science and Medicine and in History, Economics, English Literature and Modern Languages.

II. The applicant must be a graduate of a Scottish University or a member of the staff of one of the Universities or Colleges in Scotland receiving grants from the Trust.

III. The number of Fellowships will be limited. Their annual value will not, normally, exceed £800 per annum together with a sum not exceeding £50 for expenses in instances in which such grant is considered necessary. The period of tenure will, normally, be one year but special periods may be arranged.

IV. Nominations of persons holding posts in one or other of the Scottish Universities will be made by the appropriate University Authority ; nominations of graduates not so employed will be made by a Professor, Reader or Lecturer in a Scottish University. Arrangements will be made where necessary to maintain the employer's contribution to the Federated Superannuation System for Universities or similar scheme.

V. The Carnegie Fellows will undertake to give full time to the programme of research in respect of which the applications are made, but may, at the discretion of the Committee, engage in a limited amount of higher teaching or instruction associated with the special nature of their research work. They will come under an obligation to furnish a report once in each year on the progress of their work.

4. SPECIAL AWARDS

The Executive Committee are prepared to consider applications for special awards to be made for the execution of particular research projects which may not fall within the scope of the foregoing Regulations.

5. GRANTS IN AID OF RESEARCH

I. An applicant for a Research Grant must be a Scottish University Graduate resident in Scotland, or an actual member of the staff of one of the Universities or Colleges in Scotland receiving Grants from the Trust.

II. Applications must be made on a form which can be had from the Secretary of the Trust.

III. Applicants proposing to engage on research must furnish information on the following points at the time of making a first application.

(1) Their experience in research, with copies of or references to any published papers ; or, if they have no papers to offer, with references to two or more authorities who are acquainted with their qualifications for research.

(2) The nature of the research in which they desire to engage, and the results expected to follow therefrom.

(3) A statement of special requirements for the proposed research, with a detailed estimate of the cost.

(4) Whether they have received, or are receiving, any grant from any other source for the same object ; and if so, what results have already ensued from their investigations.

NOTE.—*Second or subsequent applications need not be accompanied by copies of published papers.*

IV. By accepting a Grant applicants come under an obligation to pursue the programme of research which has been approved, and to send to the Executive Committee a report containing (*a*) a brief statement (not necessarily for publication) showing the results arrived at, or the stage which the inquiry has reached ; (*b*) a statement of the expenditure incurred ; and (*c*) copies of or references to any papers in which results of the research have been printed.

The Executive Committee expect that in every case the results of the research will be published in some form. Copies of the published records of all work carried out with the aid of a Grant must be forwarded to the Offices of the Trust without delay.

V. A Research Grant is not intended (1) to provide such permanent equipment as it is normally the responsibility of the University Courts to provide, or (2) to provide minor apparatus or research materials or instruments which should form part of the equipment of a Laboratory appropriate to the investigation, or (3) to relieve periodicals of the normal charges involved in publishing the results of researches.

VI. Grants are not applicable to the payment of salaries, wages, or honoraria, except in so far as they may be assigned for a specific purpose, as, for example, the cost of preparing necessary illustrations as specified in the application and approved by the Executive Committee. Such illustrations may include drawings, photographs, or maps.

VII. Applicants for subventions towards the cost of the publication of books must, at the time of application, submit such MSS. as will enable the Trust's advisers to arrive at a recommendation in regard to the application.

VIII. Grants in aid of illustration to an amount not exceeding three-fourths of the estimated cost may be applied towards the preparation of process blocks or other means of reproduction, and of the actual printing of the illustration, including any special paper necessary for the purpose. Grants are not applicable to the cost of printing and publishing the letterpress of the publication unless, in exceptional cases, special tabular matter is required. Applicants for such grants in aid must, at the time of application, submit either an off-print of the publication or such MSS. as will enable the Trust's advisers to arrive at a recommendation in regard to the application.

Note :—Certain grants in aid of the publication of papers on the *Transactions*, *Proceedings* or *Journals* of learned societies in Scotland are now paid direct to the society and not to the individual contributor.

IX. Applications for Grants in aid of Laboratory research, or of the adequate publication of its results, must be made by the individual workers concerned, and Grants made for specific purposes to one worker cannot be utilised by another (whether in the same Laboratory or not) without the express consent of the Executive Committee.

X. An application for a Grant to be used by two or more collaborators in the same research must be signed by each ; but they shall appoint one of their number who shall be responsible for furnishing the report, for receiving and disbursing the money, and in general, for the conduct of the research.

6. TRAVEL AND MAINTENANCE ABROAD ON RESEARCH

The Executive Committee invite applications from members of the staff of a Scottish University who wish to pursue research abroad for a limited period.

Applicants must be at least thirty years of age, and preference will be given to advanced investigators (not Professors) in Science and Medicine and in History, Economics, English Literature and Modern Languages who have lacked adequate opportunities to pursue their particular research work abroad. Normally applicants must intend to spend at least three months, but not more than twelve months, abroad.

The amount of the award will be such as may be found requisite having regard to the expense to be incurred in travel and additional maintenance, but shall, in no case, exceed £600.

The number of awards to be made in any one Academic Year will not, normally, exceed 10.

Applicants must be nominated by the Principal of their University. Full details of the proposed investigation together with the estimated cost thereof must be forwarded with the nomination.

Successful applicants will be responsible for making all arrangements for travel and for residence abroad. The Trust will supply what information is required to enable the applicants' bankers to make the necessary representations to the Bank of England but cannot undertake to arrange details of the journey and residence.

Upon their return applicants will be required to furnish a report to the Trust giving, *inter alia,* such details as will be useful to the Executive Committee in their future consideration of this scheme as a whole.

Special forms of application can be had on request from the Secretary and Treasurer, Carnegie Trust for the Universities of Scotland, Merchants' Hall, 22 Hanover Street, Edinburgh, and must be returned to him not later than 1st February in each Academic Year.