KINETIC STUDIES OF THE POLYMERISATION OF VINYL ACETATE IN BENZENE

A summary of the content of the above thesis submitted to Glasgow University in accordance with the regulations governing the award of the degree of Doctor of Philosophy.

Ian Brownlie,
Department of Pure and Applied Chemistry,
University of Strathclyde,
Glasgow, C.1.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

When vinyl acetate is polymerised in the presence of benzene the rate of polymerisation is noticeably lower than that for the bulk reaction even if the concentration of the solvent is as low as 2.5%.

The benzene-vinyl acetate system has been studied using the non-stationary state thermocouple system in an attempt to elucidate the mechanism which causes this reduction in the rate of polymerisation. As a result kinetic chain lifetimes, rates of reaction, overall activation energies, intensity exponents and velocity coefficients of propagation and termination have been determined at arbitrary intervals throughout the photosensitised polymerisation for varying concentrations of benzene.

The purity of the reactants is of great importance in polymerisation studies and both monomer and solvent have been rigourously treated. The removal of impurity from the solvent has been accomplished by the growth of single crystals of benzene. The melt from the single crystal has been subjected to an accurate melting point determination and found to have a melting point of 5.51°C which is in agreement with values from the literature for pure benzene.

The number of benzene units in each polymer chain has been determined quantitatively using benzene prepared from the trimerisation of $^{14}CH\equiv{}^{14}CH$. This solvent was also purified by the growth of a single crystal to remove any acetylinic impurities which have been retained from the original preparation. This has been done to prove if these impurities were responsible for discrepancies in other workers results.

The results from the radio-active tracer work have been combined with those from non-stationary state experiments to determine which is the most probable of a number of postulated mechanisms for the polymerisation reaction.

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INTRODUCTION

When vinyl acetate is polymerised in the presence of benzene the rate of polymerisation is noticeably lower tha that for the bulk polymerisation even if the concentration of the solvent is as low as 0.28 moles litre^{-1}.

Burnett and Loan[1] developed an equation for the rat of polymerisation on the assumption that chain transfer[2] was occurring followed by the solvent radical combining with (a) monomer molecule, (b) another solvent radical, and (c) a chai carrier. However, the value of the activation energy for th addition of the phenyl radical to monomer appeared to be rath large.

This prompted further investigation by Bengough and Ferguson,[3] who measured the activation energies and kinetic chain lifetimes of the system using the non-stationary state thermocouple method of Bengough and Melville.[4] The results indicated that a benzene molecule added to a polymer chain radical to produce a radical which was slow to reinitiate and caused the retardation of the rate of polymerisation.

Stockmayer *et al.*[5] had also studied this particular system and discovered that when they evaluated a chain transf constant for the reaction from the rates of polymerisation it was twenty times larger than the one derived from the molecul weight of the polymers. The reaction was also of the order of 0.5 with respect to the initiator.

They proposed that the benzene copolymerised with th vinyl acetate monomer and substantiated their results using radio-active benzene and determining the number of radio-activ benzene units in each polymer chain.

However Breitenbach et al.[6] prepared polymers with mono and di-chlorobenzene as solvent and found no evidence of copolymerisation from the determinations of chlorine in the polymer. They then attempted to repeat the radiotracer result of Stockmayer et al.[5] using benzene prepared from (I) the trimerisation of acetylene and (II) the dehydrogenation of cyclohexane. The results with the benzene from the latter source indicated no copolymerisation but the results with the benzene from the other source were too high and Breitenbach[7] concluded that this was due to impurities in the benzene.

The work in this thesis has been an attempt to find agreement with one or other of the proposed kinetic schemes. A detailed study has been made of the photosensitised polymeri tion of vinyl acetate in the presence of definite concentratio of benzene using the non-stationary state thermocouple method of Bengough and Melville[4].

Great attention has been paid to the purity of the solvent and a method for obtaining extremely pure benzene by the growth of single crystals has been developed to overcome the difficulty of removing the acetylenic impurities from the radio-active benzene. The radio-active solvent obtaine from the melt of the single crystal has been used to determin whether the discrepancy in the results of Stockmayer and Breitenbach was due to these impurities.

HISTORY OF POLYMERISATION

The first observations of the polymerisation of vin monomers were made as early as 1839 by Simon[8] who reported the conversion of styrene to a gelatinous mass. The term polymerisation was coined by Berthelot[9] in 1866. In 1910 Stobbe and Posnjak[10] postulated that polystyrene was a "colloidal body" but almost immediately Lebedev[11] showed tha polymers had high molecular weights, although his suggested mechanism for the growth process involved intermolecular association.

The first major advance in vinyl polymerisation too place in 1920 when Staudinger[12] published a paper assigning structures of the form

$$-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\underset{C_6H_5}{\underset{|}{CH}}- \quad , \qquad -CH_2-O-CH_2-O-CH_2$$

to polystyrene and paraformaldehyde respectively and suggesti a mechanism for polymerisation in which intermediate structur were regarded as having a free valence at each end. He considered that the activation of the monomer resulted in the opening of the double bond and that the activated molecule reacted with successive monomer units. Thus the acceptance of the macromolecular hypothesis in the 1920's was largely du to the efforts of Staudinger who received the Nobel prize in 1953 for championing this viewpoint. The molecular structure was finally confirmed by Carothers[13] with his work on condensation polymers.

The first complete free radical mechanism for a polymerisation was given by Taylor and Bates[14] in 1930. It wa ultimately accepted when it was shown that polymerisation coul be initiated by substances which were known to decompose to fo free radicals on photo-excitation.

The search for new polymers, which may offer a combination of properties markedly superior for certain purpos by comparison with conventional materials, has provided the incentive for investigations into the fundamental chemical and physical processes by which polymers are formed.

MECHANISM OF VINYL POLYMERISATION

Unsaturated compounds can be made to polymerise by two basic methods (1) ionic or (2) a free radical mechanism

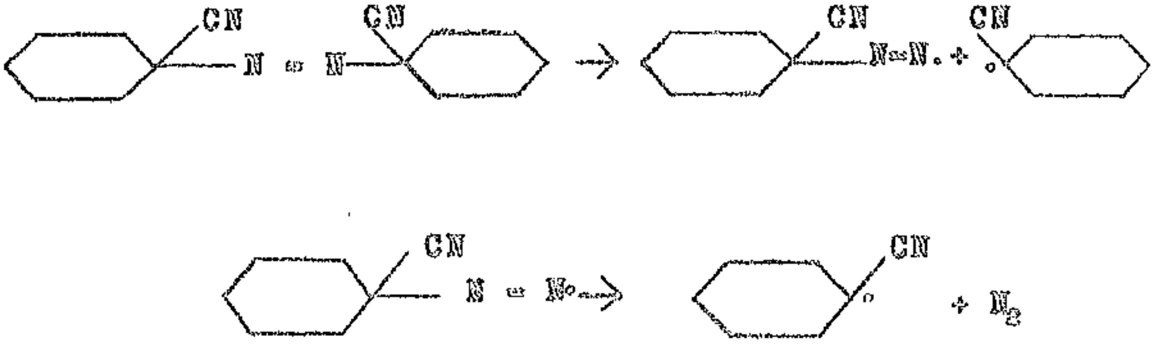
In a free radical mechanism, which is the only one which will be dealt with here, there are three basic steps, which are:-

(1) Initiation.
(2) Propagation.
(3) Termination.

Initiation

The polymerisation of vinyl compounds is normally initiated by free radicals formed from the breakdown of catalys molecules by ultraviolet light or heat.

The initiator used in this work was 1:1-azobiscyclohexane carbonitrile (ABC) which ultraviolet light degrades in the following manner.[15,16]



Not every radical is effective in initiating a polymer chain. Some take part in other reactions e.g.

(a) direct interaction between radicals derived from the initiator,

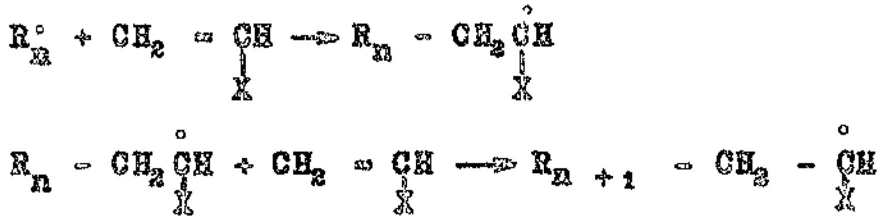
(b) a termination reaction involving a polymer radical and an initiator radical i.e. primary radical termination,

(c) reaction of the radical with another component of the syste

Measurement of the efficiency of initiation has been undertaken by several workers and is generally about 50 to 60%.[17,18,19]

Propagation

The free radical produced then combines with a unit of monomer by opening the vinyl bond and successive units of monomer are rapidly added to the subsequent free radical thus propagating the chain length



$$R_n^{\circ} + CH_2 = \underset{X}{CH} \longrightarrow R_n - CH_2\underset{X}{\overset{\circ}{CH}}$$

$$R_n - CH_2\underset{X}{\overset{\circ}{CH}} + CH_2 = \underset{X}{CH} \longrightarrow R_{n+1} - CH_2 - \underset{X}{\overset{\circ}{CH}}$$

R_n is a free radical consisting of n monomer units and X is generally a polar group e.g. an acetate group in the case of vinyl acetate.

Termination

The termination reaction involves the deactivation of the growing polymer radicals and two mechanisms are possible

(1) Combination

(2) Disproportionation

In combination the growing polymer radicals combine to give a larger polymer molecule each radical contributing one electron to form a covalent bond.

$$\begin{array}{c} R_1 - (CH_2CHX)_n - CH_2\overset{\circ}{C}HX + R_2 - (CH_2CHX)_m - CH_2\overset{\circ}{C}HX \\ \downarrow \\ R_1 - (CH_2CHX)_n - CH_2CHX \quad CHXCH_2 - (CH_2CHX)_m - R_2 \end{array}$$

The result of disproportionation is that one polymer molecule has an unsaturated end group while the other has a saturated end group.

$$\begin{array}{c} R_1 - (CH_2CHX)_n \; CH_2\overset{\circ}{C}HX + R_2 - (CH_2CHX)_m - CH_2\overset{\circ}{C}HX \\ \downarrow \\ R_1 - (CH_2CHX)_n \; CH{=}CHX + R_2 - (CH_2CHX)_m CH_2CH_2X \end{array}$$

Though these are the three main reactions in any polymerisation additional effects can occur when another substance is added to a polymerising vinyl monomer. In addition to acting as a diluent the substance may alter the rate of polymerisation by,

(1) increasing the rate of initiation resulting in an increase in the rate of polymerisation,

(2) inhibiting the polymerisation and suppressing it completely and

(3) retarding the rate of polymerisation.

These all result in a change in the degree of polymerisation i.e. in the average number of monomer units consumed per polymer molecule.

A further class of additives has no specific effect on the rate of polymerisation but reduces the degree of polymerisation. These are called chain transfer agents and the polymer radical is terminated by the abstraction of a hydrogen atom, while the free radical produced by the reaction then reinitiates a further chain.

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

In bulk polymerisation S could either be a monomer molecule or impurity and in solvent polymerisation these two o a solvent molecule. This reaction is generally known as Chain Transfer.

THE KINETICS OF ADDITION POLYMERISATION

The complete kinetics for a polymerisation reactio are very complex and it is normal to make the following assumptions:

(a) The reactivity of the growing chain is independent of the chain length. Thus one velocity coefficient can be used to describe all termination steps or to characterise a chain transfer reactions between growing polymer radicals and any other species. Similarly only one velocity coefficient is necessary to define all the propagation reactions which occur.

(b) The major portion of the monomer is removed in the propagation step. The rate of polymerisation is then taken to equal the rate of removal of monomer in this step. With high polymers, where the number of radicals formed by chain transfer is small compared with the number formed by the breakdown of the initiator, this is justifiable.

(c) A stationary concentration of radicals is rapidly attained. Making use of these assumptions and including a chain transfer step, the simplest kinetic scheme based on the reactions previously outlined is,

		Rate
	$C \longrightarrow R^{\circ}_{c}$	
Initiation	$R^{\circ}_{c} + M \longrightarrow R^{\circ}_{1}$	I
Propagation	$R^{\circ}_{n} + M \longrightarrow R^{\circ}_{n+1}$	$k_p[R^{\circ}][M]$
Chain Transfer	$R^{\circ}_{n} + M \longrightarrow P_n + R^{\circ}_{1}$	$k_{tr}[R^{\circ}][M]$
Termination	$R^{\circ}_{n} + R^{\circ}_{m} \longrightarrow P_{n+m}$	$k_t[R^{\circ}]^2$

where $[c]$ is the concentration of initiator,

$[M]$ is the concentration of monomer,

R°_{c} is a radical derived from the initiator,

R° is a growing polymer radical,

the subscripts referring to the number of units in the chain and k_p, k_{tr} and k_t are the velocity coefficients for the propagation, chain transfer and termination reactions respectively.

When the stationary state has been attained then the rate of production of radicals will equal their rate of removal.

$$\therefore \quad \frac{d[R^{\circ}]}{dt} = I - k_t\,[R^{\circ}]_s^2 = 0 \qquad \dots\dots\dots\dots(1$$

where $[R^{\circ}]_s$ = the steady state concentration of radicals

$$\therefore \quad [R^{\circ}]_s = (I/k_t)^{1/2} \qquad \dots\dots\dots\dots(2$$

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

$$\therefore \quad \frac{d[R^{\circ}]}{dt} = I - k_t\,[R^{\circ}]^2 \qquad \dots\dots\dots\dots(3$$

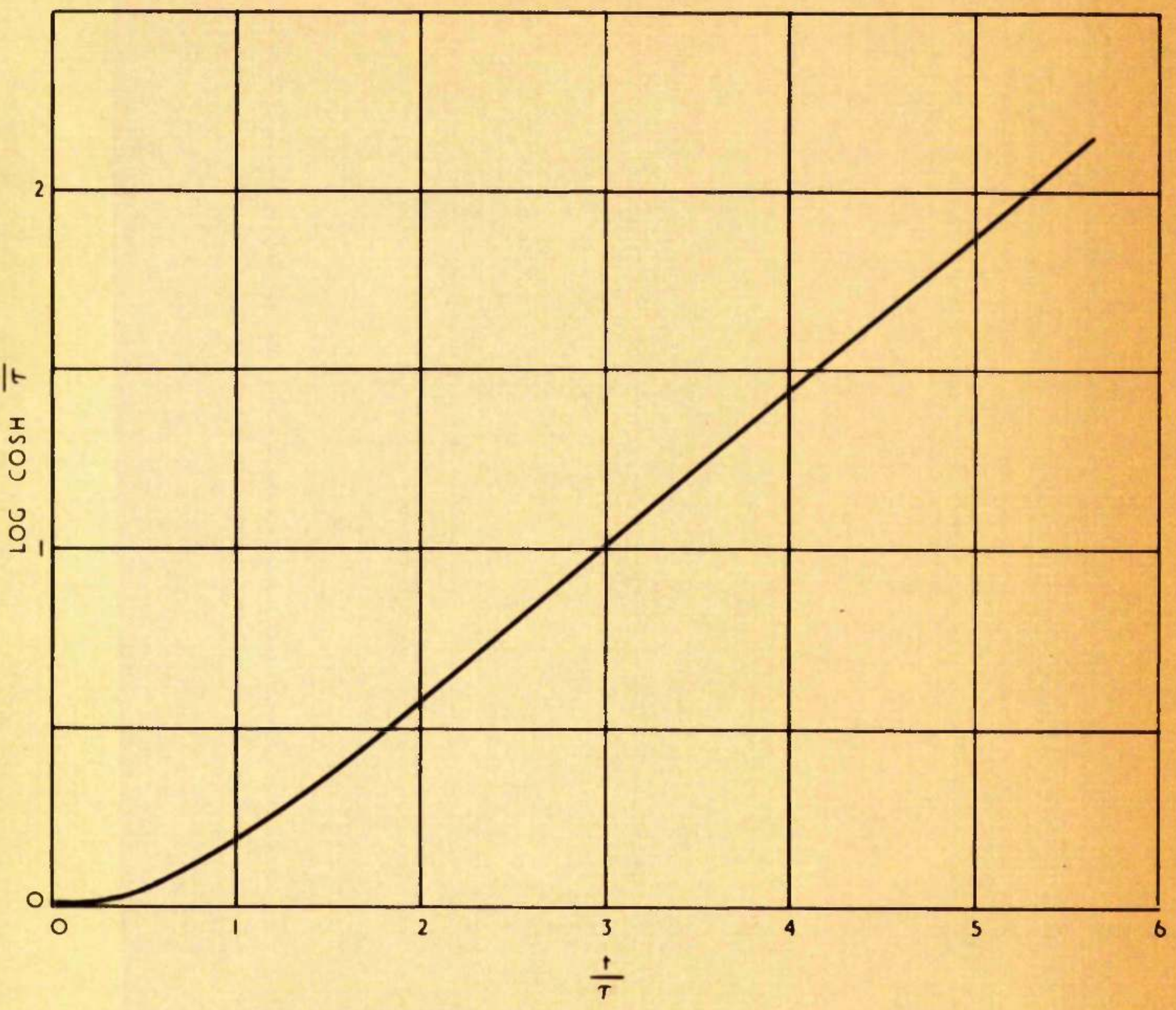


FIG. I THEORETICAL PLOT OF FRACTIONAL CONVERSION AGAINST TIME

Integrating,

$$\tfrac{1}{2}(k_t I)^{-1/2} . \ln \left[\frac{1 + (k_t/I)^{1/2}[R^\circ]}{1 - (k_t/I)^{1/2}[R^\circ]}\right] = t + C \qquad \ldots\ldots\ldots\ldots\ldots(4)$$

$C = 0$ since $[R^\circ] = 0$ at $t = 0$

$$\therefore \tanh^{-1} \frac{[R^\circ]}{[R^\circ]_s} = t(k_t I)^{1/2} = \frac{t}{\tau} \qquad \ldots\ldots\ldots\ldots\ldots(5)$$

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

From equations (5) $[R^\circ] = [R^\circ]_s \tanh \frac{t}{\tau}$ $\ldots\ldots\ldots\ldots(6)$

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

$$\therefore \frac{-d[M]}{dt} = k_p \; [R^\circ] \; [M] \qquad \ldots\ldots\ldots\ldots(7)$$

$$\text{i.e.} \quad \frac{-d[M]}{dt} = k_p \; [R^\circ]_s \; [M] \tanh \; (t/\tau) \qquad \ldots\ldots\ldots\ldots(8)$$

Integrating equation (8) gives:-

$$\therefore -\ln \frac{[M]}{[M_0]} = \frac{k_p}{k_t} \ln \; [\cosh(t/\tau)] \qquad \ldots\ldots\ldots\ldots(9)$$

If F is the fraction of monomer converted

$$\frac{[M]}{[M_0]} = 1 - F \qquad \ldots\ldots\ldots\ldots(10)$$

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

$$\therefore F = {}^{k_p}/_{k_t} . \ln \cosh \; (t/\tau) \qquad \ldots\ldots\ldots\ldots(12$$

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

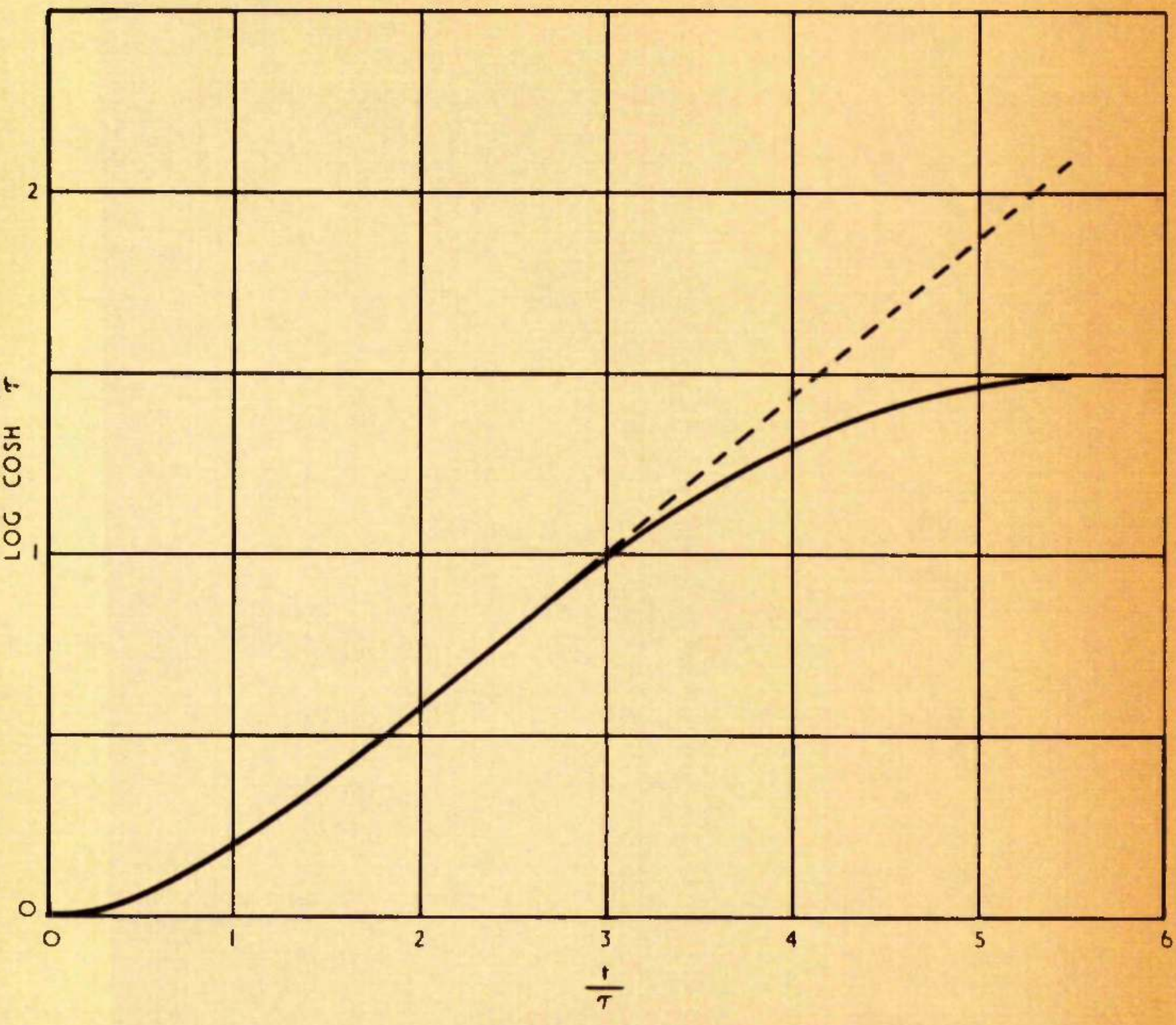


FIG. 2 THEORETICAL PLOT OF FRACTIONAL CONVERSION AGAINST TIME — EFFECT OF NON ADIABATIC CONDITIONS

$$F = \frac{k_p}{k_t}\left(t/\tau - \ln 2\right)$$ ....(1

Plotting equations (13) gives a straight line of slope k_p/k_t and intercept on the time axis equal to $\tau \ln 2$.

The kinetic chain lifetime can also be calculated from the decay curve obtained when illumination has ceased. When this happens the production of radicals is reduced by termination.

i.e. $$\frac{d[R^\circ]}{dt} = -k_t \; [R^\circ]^2$$ ....(14

Integrating $$[R^\circ] = [R^\circ]_s \;\left(t/\tau + 1\right)$$ ....(15

$$\therefore \; F = \frac{k_p}{k_t} \; \ln \left(t/\tau + 1\right)]$$ ....(16

The kinetic chain lifetime is obtained by plotting equation (16). By stationary state rate measurement it is possible to determine the ratio of $k_p/k_t^{1/2}$

from equation (2) $[R^\circ]_s = (I/k_t)^{1/2}$

$\therefore$ the rate of reaction $= k_p \, [R^\circ]_s \, [M] = \frac{k_p}{k_t^{1/2}} \cdot [M] I^{1/2}$ ....(1

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

From non-stationary state kinetics the intercept on the time axis of the straight line portion of the fractional conversion against time curve is $\tau \ln 2$.

If the system has an instrument lag of θ secs. the equation relating rate and measured intercept can be written as,

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

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) $\tau = 1/(k_t I)^{1/2}$ k_t is obtained from this, and hence the ratio k_p/k_t being known, k_p can be obtained.

PREVIOUS WORK ON VINYL ACETATE

The previous section dealt with the principal free radical reactions involved in addition polymerisation and after a detailed analysis of the kinetics is given it would be useful to review the development of work on the polymerisation of vinyl acetate.

The decrease in volume which accompanies polymerisation provided a simple method of following the reaction and was used to study the kinetics of the stationary state. The polymerisation of vinyl acetate in bulk was reported by Starkweather and Taylor[30] who found consistent unimolecular velocity coefficients while in toluene a progressive fall was observed. Other workers[31] found 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 due to the presence of oxygen, the prevalent method of purification being distillation in air and then degassing the monomer in the dilatometer. The resultant monomer gave unreliable results and it was even suggested that the reaction might be heterogeneous.[32]

In 1937 Flory[8] published an important paper in which he proposed that a chain transfer reaction could take place during polymerisation and showed that it was possible for the occasional formation of branched polymer chains to occur.

The chain transfer concept was subsequently developed by Mayo[23] to enable a 'transfer constant' for any monomer solvent system to be obtained.

Later work by Flory[24,25] 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 in determining the structure of the polymer. This is because the activation energy for the abnormal reaction is only 1.25 k cals. higher than for the normal preferred addition while the steric factor for the abnormal addition is about 1/10th of that for the normal addition.

The initiation reaction of thermal polymerisation was investigated by Cuthbertson, Gee and Rideal[26] who found that freshly prepared vinyl acetate did not react although it did so after standing in air. They suggested that this resulted from the hydrolysis of vinyl acetate to acetaldehyde followed by peroxidisation. However the question of the induction period was finally settled when improved techniques resulted in purified vinyl acetate showing no induction period when polymerised thermally with benzoyl peroxide.[24]

An important advance in the work on the kinetics of polymerisation was the introduction of non-stationary state methods which enabled lifetimes and individual velocity coefficients of photo-initiated reactions to be determined. These have been obtained for bulk vinyl acetate by workers using the dielectric constant,[28] the rotating sector,[29,30] the refractometric,[31] the thermistor,[32] and the thermocouple[4] methods.

Much work has been done on the chain transfer reaction. Nosaki,[33] using results of Cuthbertson, Gee and Rideal[26] has calculated the transfer constant for the vinyl acetate polymerisation in toluene while Rapur and Joshi,[34] Palit and Das,[35] and Clarke, Howard, and Stockmayer[36] have reported values for a large number of solvents including saturated, unsaturated, halogen substituted and nitrated hydrocarbons and for alcohols, esters, ethers, amides, sulphides and a series of substituted benzaldehydes.

However, controversy has arisen concerning the polymerisation of vinyl acetate in benzene. Conix and Smets[37] reported a strong retardation of rate in benzene solution which they attributed to chain transfer and claimed that the rate was proportional to $M^{3/2}$. At the same time Stockmayer and Peebles[38] issued a note in which they claimed that the reduction in rate was not due to chain transfer, but that the reaction was copolymerisation.

Allen, Merrett and Scanlan[39] also noted a strong retardation of the rate of polymerisation when vinyl acetate was polymerised in the presence of the isoprenic substance dihydromyrcene and isopropyl benzene but no retardation of the rate when the monomer was methyl methacrylate. Their explanation for the retarding effect on the polymerisation of vinyl acetate was degradative chain transfer i.e. chain transfer in which the radicals produced from the transfer agent are resonance stabilised such that they are slow to re-initiate with the rather unreactive monomer and are frequently lost by termination. On deriving a kinetic scheme, which took monomer transfer into account, they obtained a transfer constant for isopropylbenzene which was 100 times greater than that found by Stockmayer and Peebles.[38] Since the transfer constants for isopropylbenzene and benzene should be of comparable magnitude they considered it more probable that degradative chain transfer and not copolymerisation was occurring.

Burnett and Loan[1] derived an equation for the rate of polymerisation which demonstrated that the order of reaction with respect to the monomer concentration was dependant on the monomer concentration in the solvent. They assumed that it was possible for radicals produced by the transfer step to terminate the propagating chain radical as well as to re-initiate the polymerisation process. Although their analysis gave the correct shape of curves for the thermal polymerisation of vinyl acetate in benzene they obtained an activation energy of 24 K.cals for the addition of the phenyl radical to monomer which is a high value.

However Jenkins[40] indicated that Burnett and Loan's[4] kinetic scheme could only be applied if the retardation was comparatively weak. He derived a kinetic scheme on the basis of chain transfer and used the hypothesis 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. However the transfer constant which he derived from other workers results was greater than that derived by Palet and Das[36] from conventional molecular weight determinations.

Peebles, Clarke and Stockmayer[5] then published results which indicated that, although the velocity constants which they obtained and the reduction in rate could be attributed to a chain transfer step, the molecular weights of the polymer could not. They also substantiated their results by polymerising vinyl acetate in the presence of radio-active benzene and converting the subsequent polymer to CO_2 for gas counting in a Geiger-tube.

Breitenbach and Falthansl[8] had obtained chlorinated polymer from the polymerisation of vinyl acetate in chlorobenzene and meta dichlorobenzene while the polymerisation of styrene in the same solvents and under similar conditions produced only chlorine free polymer. They explained this difference by assuming that the radicals of the growing polyvinyl acetate chain react quickly enough in a transfer reaction to form a measurable end group while this is not therefore possible in the case of the relatively weakly reactive polystyrene radical.

This assumption was in opposition to Stockmayer's theory and so Breitenbach and his co-workers[9] proceeded to duplicate the radio-active tracer experiments which had been used to substantiate the evidence for copolymerisation.

For the first series of experiments benzene prepared from the trimerisation of $^{14}CH \equiv {}^{14}CH$ was used which was freed from non volatile radioactive impurities by distillation.

After nine reprecipitations the polymer obtained from the polymerisation of this benzene with vinyl acetate had a very high radio-active content but all other tests on the polymer e.g. I.R.; U.V. carbon-hydrogen determination indicated an almost pure polyvinyl acetate showing no relationship between radio-activity and benzene content. This, they suggested was due to the benzene containing a volatile compound of high specific activity as impurity which was copolymerisable with vinyl acetate. For a second series of experiments the labelled benzene was obtained from the dehydrogenation of cyclohexane-1-C^{14} from which source a greater freedom from impurity was expected. The polymer obtained by polymerising this benzene with vinyl acetate in a ratio of 10:1 for 54 hr. at 60°C with initiator concentration of 0.02 moles litre^{-1} to a conversion of 36.8% had an extremely low radio-active count, an average content of 0.9 molecules of benzene for an average chain length of 100 units being determined, which was of the same order as the values obtained from the chlorinated polymers and they have indicated that they find no evidence of copolymerisation with the aromatic system.

These results have been obtained using stationary state dilatometers and elucidating data from rates of polymerisation and molecular weights etc. Bengough and Ferguson[8] however used a non-stationary state thermocouple system. They found that when they attempted to correlate the overall activation energies, the activation energies of propagation, termination and transfer, together with the kinetic lifetimes which they obtained it appeared more probable that a benzene unit added to a polymer chain radical producing a radical which was slow to re-initiate and so caused the retardation of vinyl acetate polymerisation in benzene. However although this solution seemed quite satisfactory they did not attempt to determine the number of benzene units quantitatively in conjunction with the non-stationary state results.

In this work, polymers containing radio-active benzene have been prepared using stationary and non-stationary state dilatometers and in the latter case, the activation energies and kinetic lifetimes found have been related to the analysis of the radio-active polymer.

Recently Mortimer and Arnold[42] have studied the reactio of ethylene with deuterated benzene. On the basis of the isotopi effect which they obtained they have refuted the idea of copolymerisation occurring and maintain that the inclusion of benzene units in the polymer is by chain transfer. Hass and Husock[42] have polymerised vinyl acetate in the presence of diphenyl and have determined a chain transfer constant from the conventional kinetic analysis and molecular weight data. They found their value of 6.4×10^{-4} to be in reasonable agreement with one obtained by estimating the combined diphenyl units present in the corresponding polyvinyl alcohols by ultraviolet spectroscopy. They concluded that diphenyl behaves chiefly as a transfer agent in the system while the retardation in rate is probably due to the addition of diphenyl to a vinyl chain radical to form a radical which is slow to reinitiate. However it must be observed that their kinetic evidence for this is rather small.

PURITY OF REACTANTS

The most difficult problem associated with this work has been obtaining a sufficient degree of purity of the reactants especially the vinyl acetate monomer.

Early work was characterised by induction periods but even after improved degassing techniques were used to remove all traces of oxygen it was found that the termination reaction of the bulk polymerisation was not second-order with respect to the radical concentration i.e. the intensity exponent was not 0.5 which indicated that there were traces of chemical impurities present.

The most obvious suggestions were either acetic acid or acetaldehyde and these were located using ultraviolet spectroscopy.

The advent of the gas chromatograph meant that substances could be identified, where they were present in sufficient quantity, by their retention time and both gas chromatography[43] and ultraviolet spectroscopy[44,45] have been used to identify further substances e.g. acetone, divinyl acetylene and benzene which are present in the commercial product.

Bartlett and Swain[29] attempted the purification of their monomer using various types of distillation columns and prepolymerising the product to different conversions. The criterion for determining the best method was the monomer which under specific catalyst and temperature conditions gave the greatest rate of polymerisation with a negligible induction period. They found that their best sample polymerised at a rate of 8.5 moles litre^{-1} sec.$^{-1}$ at 25°C when the concentration of the initiator, benzoyl peroxide, was 0.105 moles litre^{-1}.

Matheson *et al*[46] used this rate to test their final distillate. They also compared the monomer with that of other workers[47,48] by determining its ultraviolet spectrum against n-hexane and plotting the extinction coefficient against the wavelength of the incident light. They indicated that the main light absorbing impurities were present in the range 2650-2750 Å.

Both these criteria have been used to study the condition of the monomer during the various stages of preparation A sample of the monomer was taken at regular intervals during the distillation and its spectrum obtained. The monomer was collected when two successive spectra were identical. Spectra were used as criteria since they could be obtained more rapidly than the rate of polymerisation of the monomer. After two prepolymerisations the final distillate was polymerised according to the specified conditions of Bartlett and Swain[29] before use in non-stationary state vessels.

Benzene Purification

The radio-chemical benzene prepared by the trimerisati of $C^{14}H\equiv C^{14}H$[49] (Radiochemical Centre, Amersham, England) has 3% chemical impurity present according to gas liquid chromatograph The problem was to remove all the impurities present, since, according to Brietenbach et al,[7] these were responsible for the excess radioactivity in the polymer. This was difficult because of the small volume of benzene which had to be used in the radio tracer experiments.

This was overcome by using the method of Hood and Sherwood[50] for the growth of single crystals of low melting point solids.

The single crystals of benzene were grown in a specially constructed crystallisation apparatus where the liquid is confined in a growth tube which is slowly lowered through a temperature gradient according to the moving vessel technique of Bridgman.[51]

The benzene used for growing the crystals was supplied by British Drug Houses for molecular weight determination and although it was claimed that the freezing point was not less than 5.4°C this frequently fell to 3.5°C on standing due, perhaps, to absorption of water. After growth in the crystallisation apparatus the melting point rose to 5.5°C which corresponds to the value given in the literature[5a] for the pure material.

The melting points were determined using a calibrated thermister and Wheatstone bridge arrangement and from the plot of resistance against time the melting point and mole percentage impurity present were calculated [Appendix I].

The growth of single crystals overcame the difficulty that Breitenbach experienced in purifying his radio-active benzene and all the benzene used throughout this work was purified by this technique.

EXPERIMENTAL

Apparatus

The non-stationary state system consisted of a reaction vessel with built in thermocouples, a constant temperature bath, an amplifier and a recording voltmeter. A mercury vapour lamp supplied the ultraviolet radiation.

Dilatometers

The reaction vessel was a soda glass dilatometer with two side arms in addition to the normal stem (fig.5).

The thermocouple system, which consisted of one junction 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 a silver-borax flux to give point contact at A. Borated copper clad iron wire was brazed to each end of the copper and constantan wires so that a seal could be made at E and C. The join of the constantan to the iron wire served as the cold junction thermocouple B.

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 a high vacuum system and evacuated for 30 mins. The constriction at D was then slowly collapsed about the

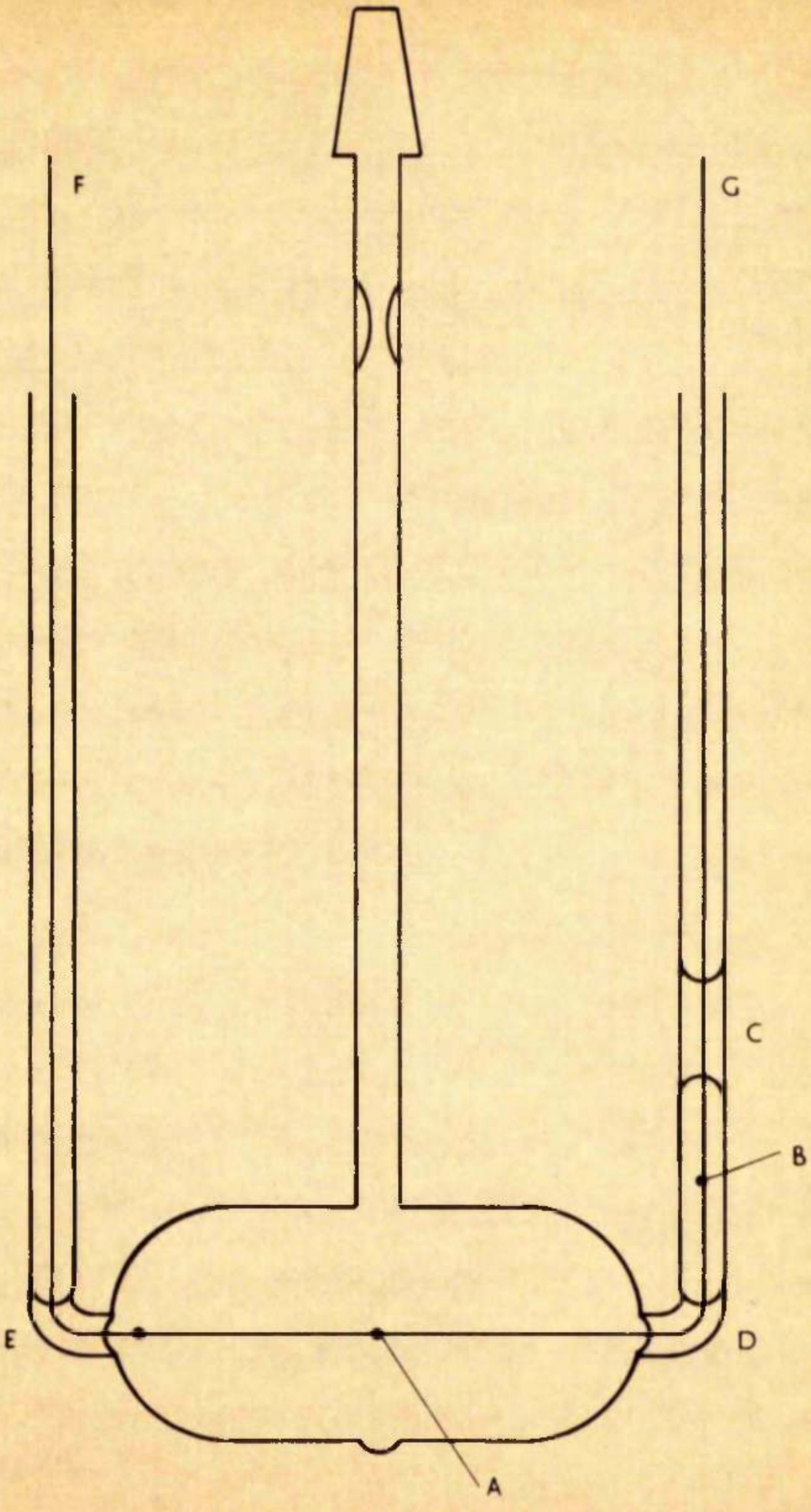


FIG. 3 THE THERMOCOUPLE VESSEL

constantan wire using a light blue air-gas flame. It was inspected to ensure that there were no air pockets or bubbles along the wire since the seal, although liquid-tight, was not air tight.

The dilatometer was now ready for calibration and was kept under vacuum until required.

Thermostatical Controlled Water Bath

The water bath was made of Pyrex glass and lagged with an expanded ebonite base and fibre glass around the sides. A large 2KW Heater controlled by a Variac was used to raise the temperature when required and to supply the bulk of heat to maintain any particular water temperature, the discrepancy being provided by a low powered lamp which was operated by a mercury toluene regulator giving temperature control of about ± 0.02°C.

Amplifier

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 as it gave a voltage amplification of more than 10^8. E.M.F.'s of up to 400 μ volts in the input circuit could be balanced out by coarse and fine balance controls.

The temperature rise was calibrated by means of a test signal varying from 0.01 μ volts to 100 μ volts as required.

The output circuit, designed for a 500 ohm load, gave a current of up to 10 m. amps.

The amplifier was extremely sensitive to 'pick up' and it was found advisable to keep all electrical apparatus e.g. rela condensers, capacitors etc. as distant as possible from the instrument. The stirrer rod was made much longer than normal so that the magnetic field of the motor driving the paddle was located well above the 'pick up' area and a guide was used to prevent the 3 ft. rod from vibrating in the tank. This meant that the bath could be stirred during the reaction period when the amplifier was receiving the thermocouple voltage.

Irradiation

A 125 watt Osira mercury arc lamp provided the source of the ultraviolet light for the photochemical reaction. To smooth out variations in the applied current, the lamp was connected to a capacitator and choke. The emitted light was filtered through a CHANCE OXI filter such that 3650 Å. was the predominant wavelength of light.

A quick moving shutter operated by an electromagnet was placed between the lamp and the reaction vessel. The field of the magnet was picked up by the amplifier and the consequent blip on the recording chart served to mark the beginning of the reaction period.

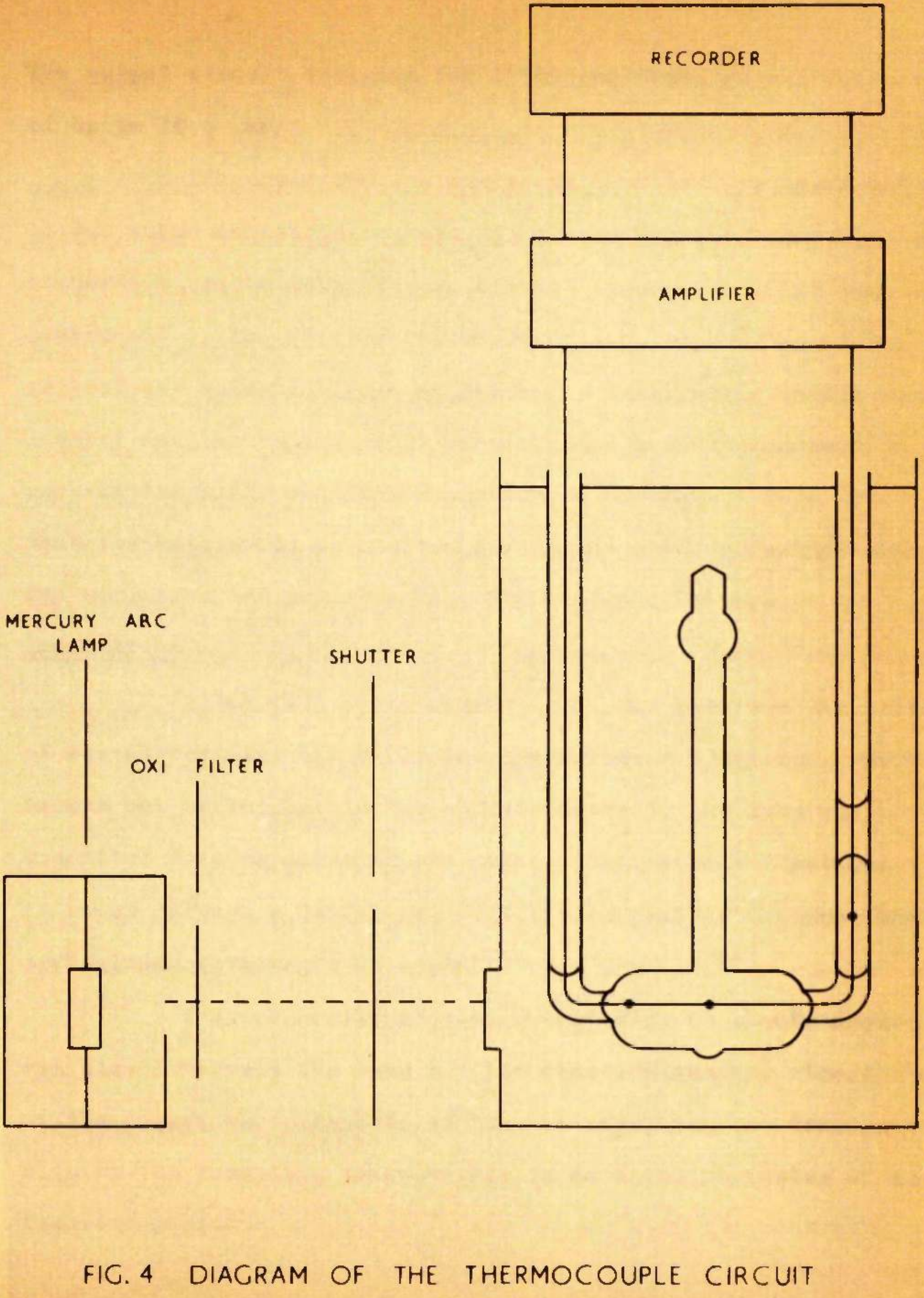


FIG. 4 DIAGRAM OF THE THERMOCOUPLE CIRCUIT

Recorder

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. (fig. 4).

High Vacuum System

This consisted of a series of traps and vacuum tested taps in Pyrex glass connected via a mercury diffusion pump to an Edwards rotary high vacuum pump.

Cold traps were placed immediately before and after the mercury diffusion pumps, and a Dricold-Acetone mixture was used as coolant in both traps. All taps and joints were greased with Apiezon high vacuum greases.

A pressure of about 10^{-4} mm. of mercury was attained.

Crystallising Apparatus

The need for purity of the solvent has been stressed and the most convenient method to attain this is the growth of single crystals of the material.

The crystallising apparatus (fig. 5) consists of a central Pyrex glass tube A, 2½ inches in diameter along which the necessary temperature gradient is established. The upper part of the tube was sealed by Araldite into the bottom of a two litre copper tank B which was lagged with asbestos cord

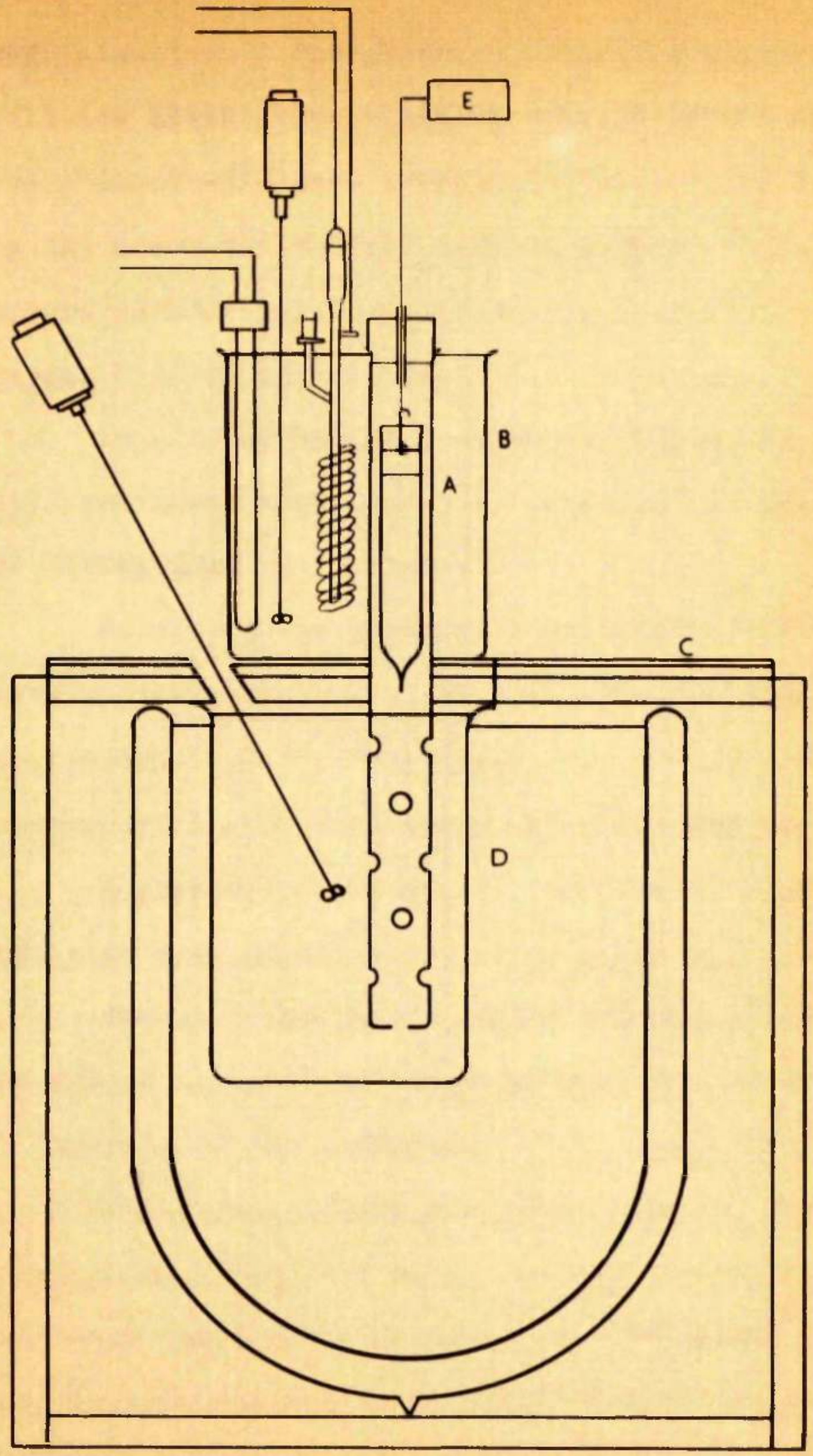


FIG. 5 CRYSTALLISING APPARATUS

1 inch in diameter. The paraffin oil-water mixture was stirred by a variable speed stirrer and was heated by a 60 watt light bulb while the temperature of the tank was controlled by a mercury-toluene regulator to within ± 0.02°C. In this way, the temperature in A above the wooden board C could be maintained at a temperature above the melting point of benzene.

A piece of expanded polystyrene was glued to the underside of C and the temperature gradient was established across this region.

The lower end of A which was pierced at regular intervals protruded into a long 2 litre beaker D which was filled with acetone and fixed to the underside of C by a retaining plate. The acetone in the beaker which was stirred to maintain constant circulation in the central tube was cooled by an acetone-driccold slush contained in a 15 litre Dewar flask. This flask was surrounded by cotton wool packing and housed in a wooden box which also served to support board C.

The benzene growth vessel was attached by a piece of fine thread to a Sangamo electric motor E which lowered the vessel at approximately 1 mm/hr. The thread passed through a piece of glass capillary tubing in the middle of the rubber bung which sealed off the top end of the central tube A. The capillary acted as a guide for the growing vessel and also ensured that the plane of the crystal face was horizontal during its passage through the temperature gradient.

Sherwood and Thomson[83] have stated that a steep temperature gradient is essential for the growth of good crystals. The temperature of the paraffin oil-water was therefore maintained at 40°C while the bottom beaker was kept at -78°C by the acetone-dricold slush and the crystals obtained using this temperature difference were of good quality and optically clear.

Melting Point Apparatus

A freezing point curve was required to obtain the melting point of the benzene crystals and to deduce the mole fraction impurity according to the formulae of Guggenheim and Prue[84] [Appendix I]. A melting point apparatus was constructed to obtain this curve [Fig. 6].

A double walled glass vessel A, 12 inches in length and 2.5 inches in diameter was evacuated to a pressure of 10^{-3} mm. of Hg and was sealed at its open end by means of a B.49 socket and stopper. A piece of crystal was placed in a $\frac{1}{4}$ inch diameter glass tube B, which was supported by a cork in the middle of the vacuum vessel and at a distance of 2 inches from the foot of it. A copper rod C, bent at one end into a series of $\frac{3}{8}$ inch diameter rings passed through a central downcomer tube in the B.49 stopper into the benzene solution. The rod was

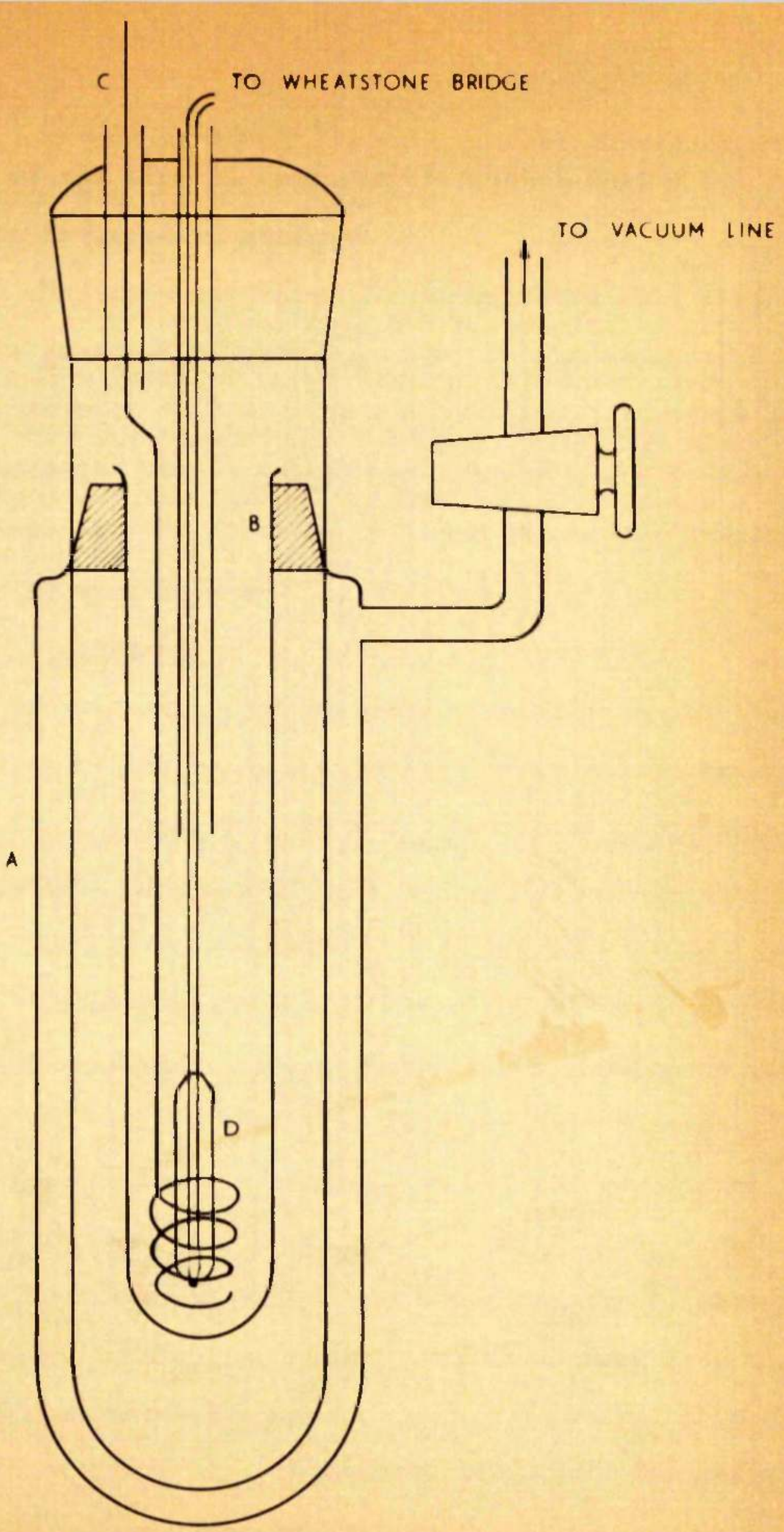


FIG. 6 MELTING POINT DETERMINATION APPARATUS

raised and lowered by gearing attached to an electric motor and the motion of the rings thoroughly mixed the solution while the experiment took place. The connecting wires attached to the standardised thermistor D, which was placed in the middle of the rings, also passed through another downcomer tube.

The thermistor was connected into a standard Wheatston bridge system and the circuit balanced using a variable resistance decade box and spot galvanometer.

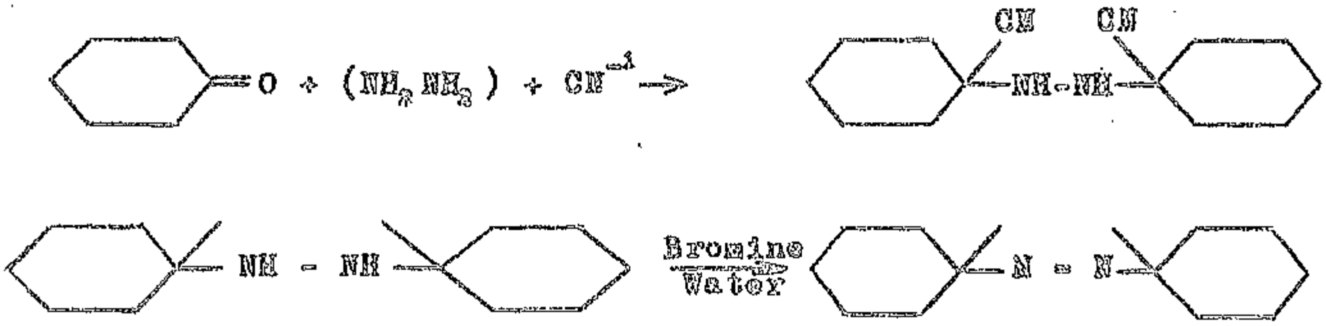
EXPERIMENTAL PROCEDURE

Vinyl acetate, obtained initially from Shawingain Chemical Co. and latterly from Distillers Company Ltd. was distilled in an atmosphere of prepurified nitrogen in a 6 ft. vacuum jacketted column containing stainless steel Lessing 'Hy Contact' rings.

At the top of the column the condensate from one of five water cooled fingers was taken off down another condenser which also condensed any further vapours which were carried over the stream of nitrogen. The condensate then passed into another subdivider by which it could be directed into any of four 500 ml. flasks. Each flask had a mercury seal and the whole apparatus was flushed out overnight with prepurified nitrogen to prevent any possible oxidation process of vinyl acetate in the vapour state. At the foot of the 3rd and 4th flasks a tap enabled a sample of the distillate to be taken and an ultraviolet spectrum of the sample could be taken to study the purity of the distillat at these stages. Generally after 2 litres had been discarded 200 ml. of the monomer were collected under nitrogen the distillation having been conducted for 12 to 13 hours.

The monomer was transferred to the vacuum line where it was thoroughly degassed and distilled into a flask containing a few crystals of initiator. It was slowly polymerise to approximately 10% conversion. A rotating arm was used to elevate the flask to break the skin which normally forms on top of the monomer. This prepolymerisation was repeated and the fina distillate was kept at -75°C under vacuum until required.

Preparation of 1:1'-azobiscyclohexane carbonitrile[18]



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

Growth of Benzene Crystals.

The benzene crystal was grown in a pyrex glass tube which was 6 inches long, $^3/_8$ inch in diameter and drawn to a fine capillary 3 cm. long. The capillary was filled by boiling a little of the solvent in the foot of the tube and further benzene added till the tube was three quarters full.

The growing vessel was then hung on the upper half of the central tube A just above the position of the temperature gradient until the solvent had reached temperature equilibrium with its surroundings.

The tube was then lowered at approximately 1/mm hr. and as the tip of the tube passed the melting point isothermal nucleation occurred at the tip of the capillary. The single crystal proceeded to grow as the tube passed through the temperature gradient.

After 4-5 days the growing tube was withdrawn and placed in an acetone-dricold mixture at the same temperature as th acetone in flask D. This prevented the crystal cracking due to thermal strain when placed in the deep freeze. The liquid benzene above the single crystal froze forming polycrystals and these were cut off as they contained the impurities of the system.

Melting Point Determination

A part of the single crystal was placed in the central tube and when it had melted the stirrer was started. After conditions had stabilised the circuit was balanced using the decade resistance box.

An acetone-dricold mixture was placed round the lower half of the vacuum vessel and as the benzene slowly cooled the varying resistance of the thermistor was balanced using the decade box in the opposite arm in conjunction with the spot galvanometer. Resistance readings were taken every minute and a freezing point curve of resistance against time plotted. From this the melting point of the benzene and the mole percentage impurity were calculated. [Appendix I].

Filling the Dilatometer.

When the dilatometer was required for use the constriction at D (fig. 3) was carefully collapsed under vacuum. The dilatometer was then calibrated using A.R. grade acetone. The acetone was then removed and the required quantity of initiator introduced in a solution of freshly distilled chloroform (anaesthetic grade) and pumped off under vacuum. During these operations the dilatometer was tilted to cover the constriction at D with solution and minimise the possible entry of air into the side arm.

In most experiments it was necessary to introduce solvent into the dilatometer. This was done using a 1 ml. burette or a micrometer syringe for very small quantities. The solvent was then degassed by repeated freezing, evacuating and heating to room temperature.

Purified monomer, stored on the vacuum line was distilled into the reaction vessel to a predetermined level. The dilatometer was then cooled with an acetone-dricold mixture and sealed off.

Non-Stationary State Experimental Technique.

The leads F and G were soldered to screened leads from the amplifier input and narrow rubber tubes were slipped over the side arms to prevent water entering them.

The dilatometer was then immersed in a fixed position in the water bath and the reaction mixture allowed to attain thermal equilibrium. The amplifier and mercury arc lamp were then switched on an left for 30 minutes to stabilise.

With a chart speed of 12 inches/min. a known test voltage was put through the circuit for 5 secs. to calibrate the system at the desired amplification.

The reaction was started by actuating the electromagnet to pull the shutter aside.

The rise in temperature of the reaction mixture was observed on the pen recorder and after 30-35 secs. the shutter was replaced, stopping the reaction.

From the chart trace the rate of reaction and the lifetime of the kinetic chain radical were obtained at one temperature and light intensity. The procedure was repeated for

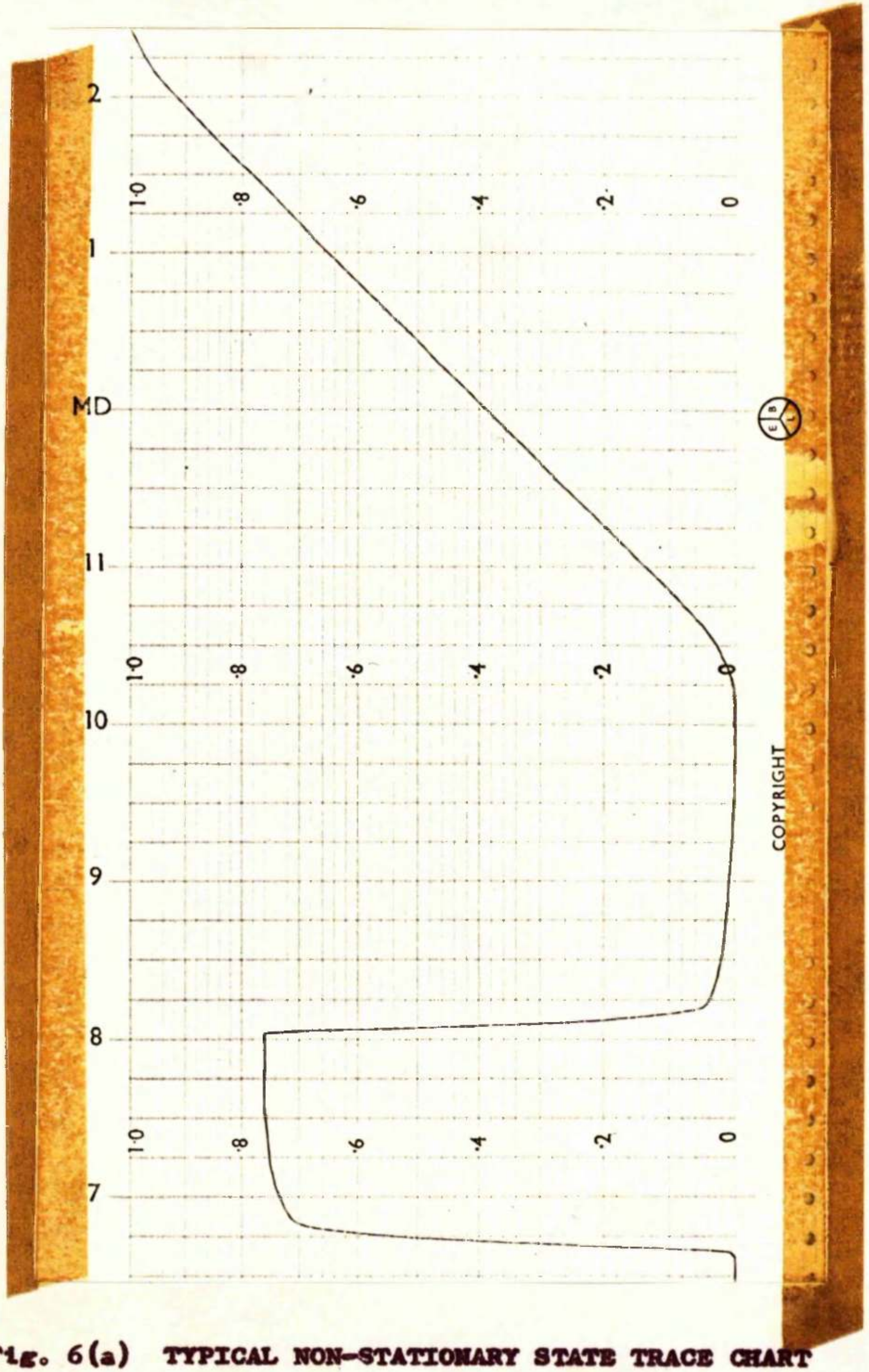


Fig. 6(a) TYPICAL NON-STATIONARY STATE TRACE CHART different light intensities and temperatures, each determination being repeated at least once.

To complete the polymerisation took several weeks and to prevent any dark rate the dilatometer was kept in an acetone-dricold mixture overnight and during weekends.

EXPERIMENTAL

RESULTS

BBulk Polymerisation of Vinyl Acetate

Initially the extent of conversion of the reaction was followed dilatometrically until the meniscus in the calibrated central arm became distorted. Subsequently the conversion 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 polymer, pumping off the residual monomer overnight and reweighing.

The catalyst concentration for the non-stationary state experiments was 4×10^{-3} moles litre^{-1}.

Table 1 Variation of rate and kinetic chain lifetime with extent conversion at 25°C and full light intensity.

Extent Conversion %	Rate of Reaction $\times 10^{4}$ moles l^{-1} s^{-1}	Intercept s	Kinetic Chain Lifetime s
5	3.95	2.3(5)	0.4(3)
10	4.04	2.3(0)	0.3(6)
20	4.11	2.3(0)	0.3(6)
30	4.42	2.4(3)	0.5(4)
40	5.50	2.4(5)	0.5(8)
50	5.39	2.6(0)	0.8(0)
60	5.12	2.9(8)	1.3(3)

A plot of intercept against the reciprocal of the rate was drawn and the lag of the instrument was obtained from the

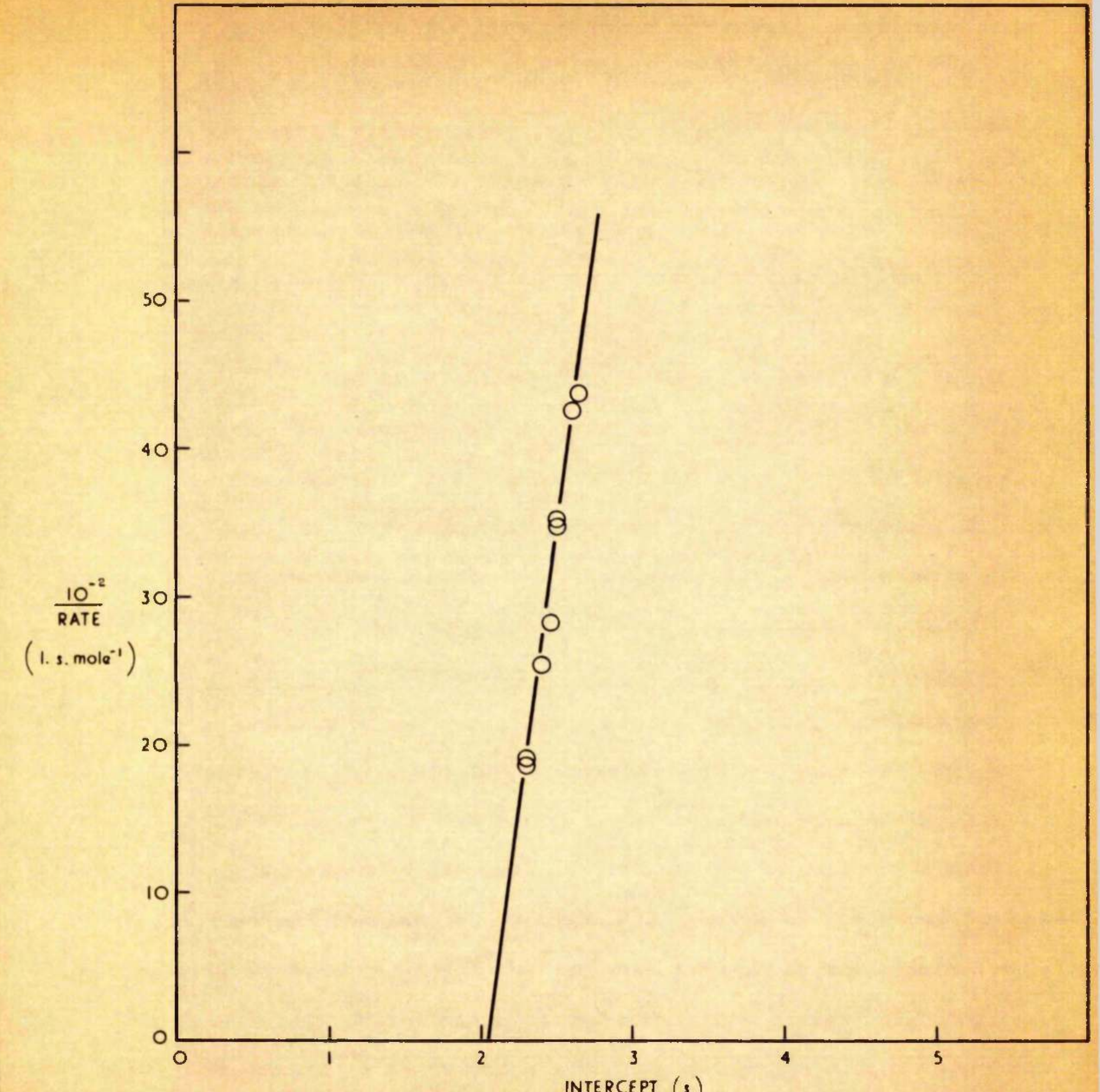


FIG. 7 TYPICAL GRAPH FOR THE DETERMINATION OF INSTRUMENT LAG AND k_p/k_t

intersection of the plot with the horizontal co-ordinate axis (Fig.7). The kinetic chain lifetime was then calculated. The second figure after the decimal point has been included in the value of the kinetic chain lifetime but only as an indication of the most probable value of the first figure, e.g. 0.4(8)s. is most probably 0.5 s., and to facilitate the deduction of other quantities from τ e.g. E_t.

The rate of reaction is relatively constant until about 20% conversion. It then begins to increase and attains a maximum value about 50% conversion [Fig. 9]. The kinetic chain lifetimes are also constant till 20% conversion, but then increase gradually as the termination step becomes more difficult due to the viscosity or gel effect [Fig.10]. The viscosity effect was first suggested by Norrish and Smith[55] to explain a pronounced increase in the rate of polymerisation of methyl methacrylate after 10% conversion. They suggested, that as the viscosity of the medium increased, the rate of termination would decrease and since the rate of propagation remains constant, the rate of reaction will increase. This was developed by Trommdorff et al.[56] who included substances to increase the viscosity of the polymerising medium and consequently obtained increased rates of reaction. The term 'gel effect' was first used by Burnett and Melville[47] who demonstrated that the gel

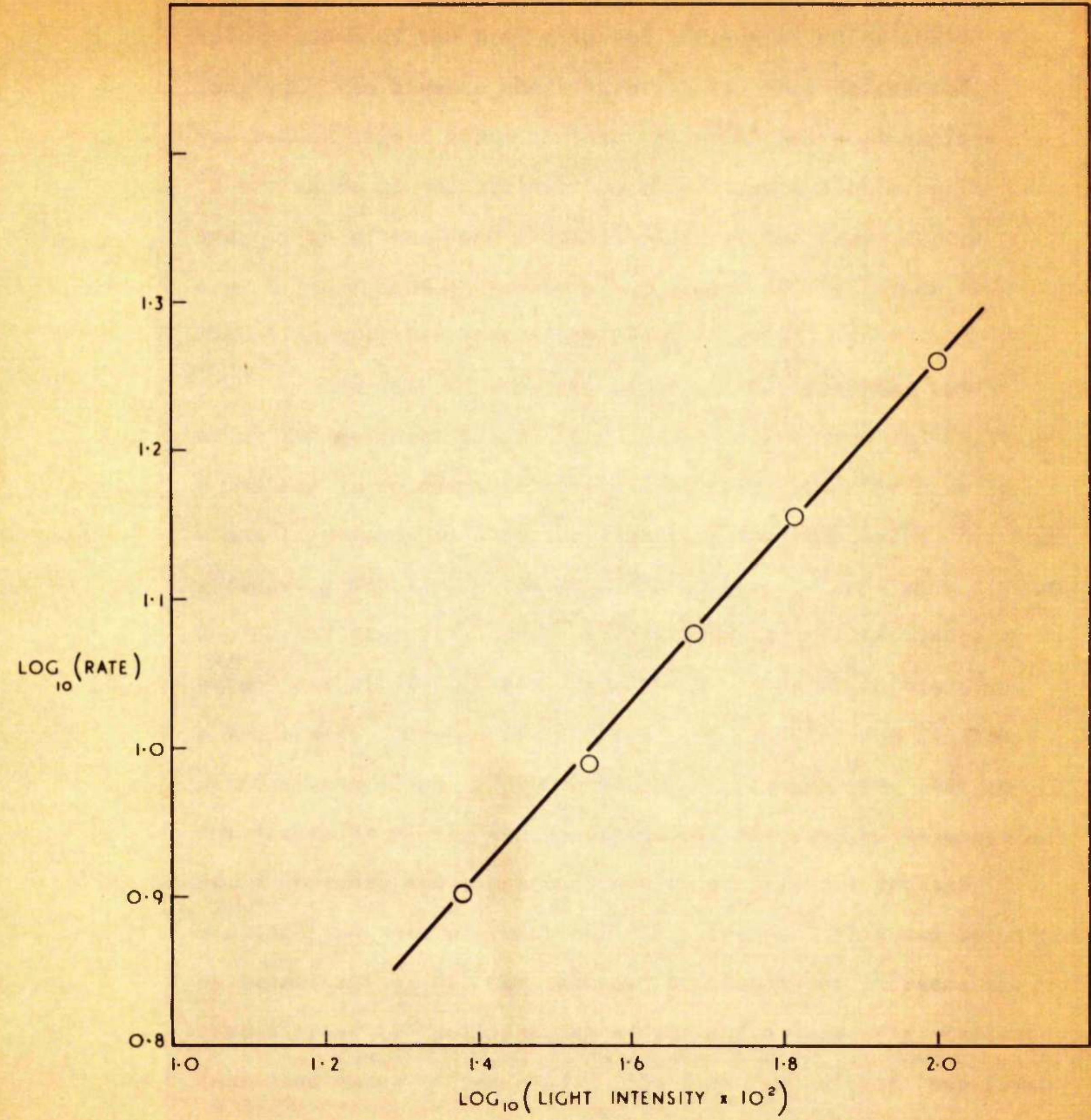


FIG. 8 TYPICAL GRAPH FOR THE DETERMINATION OF THE INTENSITY EXPONENT.

formed by the increase in viscosity of the polymerising medium caused a decrease in the rate of termination and that the onset of the gel effect could be varied using good or bad solvents.

Determination of the Intensity Exponent.

It is important to determine the nature of the termination step in a polymerisation reaction in order to apply a correct or modify an existing kinetic scheme. If, in a free radical system, termination occurs between two radicals then this is termed second order termination with respect to the radical concentration. If termination occurs between a radical and a non-radical species then the reaction is first order with respect to the radical concentration.

The relation between the rate of reaction and the incident light intensity can be expressed in the following manner,

$$\frac{Z_1}{Z_2} = \left(\frac{I_1}{I_2}\right)^m \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(19)$$

where Z_1 is the rate of reaction at light intensity I_1

and Z_2 is the rate of reaction at light intensity I_2.

m is the intensity exponent.

For second order termination where the rate is proportional to the square root of the initiator concentration (equation 2) $m = \frac{1}{2}$. For first order termination, since the rate of

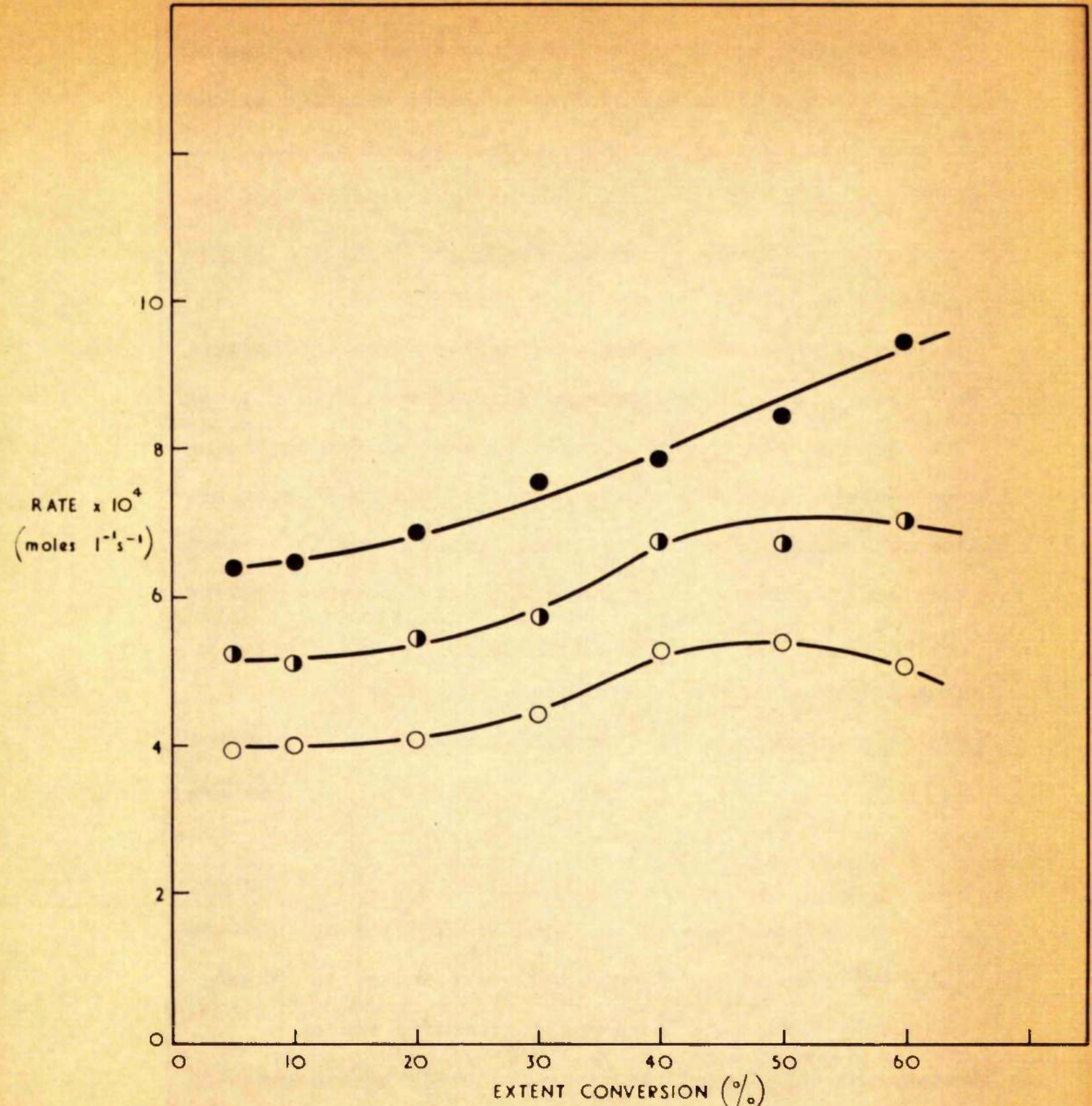


FIG. 9 BULK VINYL ACETATE POLYMERISATION. VARIATION OF RATE WITH CONVERSION

○ 25°C ◑ 35°C ● 45°C

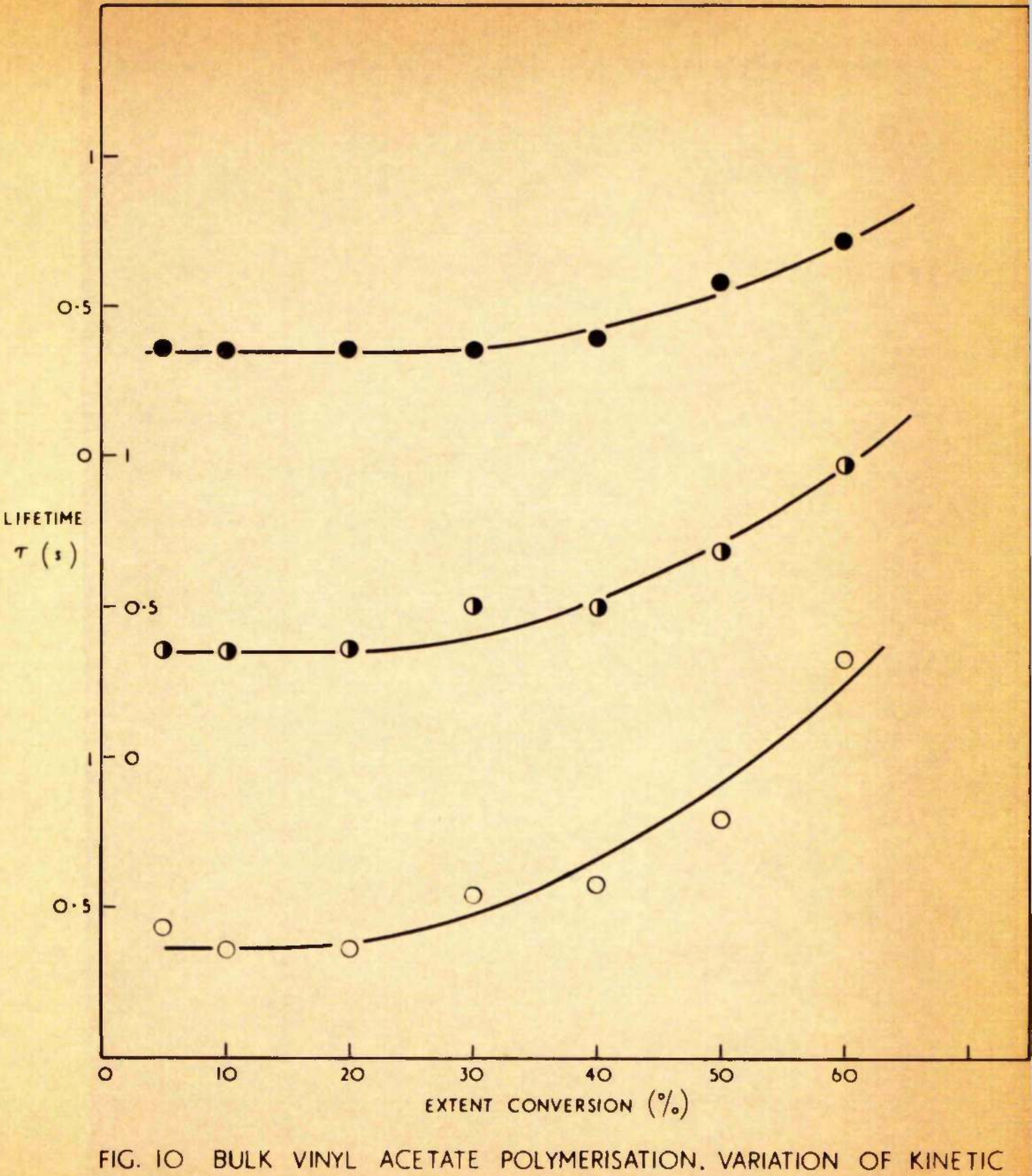


FIG. 10 BULK VINYL ACETATE POLYMERISATION. VARIATION OF KINETIC CHAIN LIFETIME WITH CONVERSION

○ 25°C ◑ 35°C ● 45°C

reaction is proportional to the initiator concentration $n = 1.0$

If the termination step is a mixture of first and second order reactions then the value of n will be between ½ and 1.0. The intensity exponent was determined from the slope of the straight line obtained by plotting log rate against l light intensity [Fig. 8].

The intensity of the incident light was varied by placing wire mesh screens in the beam of light. In all cases the thickness of the wire was less than 0.005 inches in diameter. The transmission of the screens was determined using a Unicam spectrophotometer. By measuring the intensity of light of wavelength 3650 Å falling on a photoelectric cell before and after a screen was inserted, a direct reading of the transmission was obtained. The values of the screens were 65.5%, 48.5%, 35% and 24% of the full light intensity.

Table 2 Variation of the rate and kinetic chain lifetimes with extent conversion at 25°C and at 48% full light intensity.

Extent Conversion %	Rate of Reaction $\times 10^4$ moles l^{-1} s^{-1}	Intercept s	Kinetic Chain Lifetime s
5	2.87	2.6(0)	0.5(5)
10	2.61	2.5(5)	0.5(0)
20	2.77	2.6(3)	0.5(8)
30	2.90	2.8(5)	0.8(0)
40	3.37	3.0(5)	1.0(0)
50	3.32	3.3(5)	1.3(0)
60	3.35	4.0(5)	2.0(0)

Table 2 indicates that the variations in rates of reaction and lifetimes are parallel to those at higher full light intensity. From the derived kinetics the kinetic chain lifetime is inversely proportional to the square root of the initiator concentration and consequently it increases with the decrease in light intensity.

Table 3 Intensity Exponents at 25°C. $L_2 = 0.485 L_1$.

Extent Conversion %	Rate of Reaction $\times 10^4$ Full Intensity moles l^{-1} s^{-1}	Reduced Intensity moles l^{-1} s^{-1}	Intensity Exponent
5	3.95	2.87	0.55
10	4.04	2.61	0.53
20	4.11	2.77	0.54
30	4.42	2.90	0.54
40	5.30	3.37	0.62
50	5.39	3.32	0.65
60	5.12	3.35	0.62

The intensity exponent indicates that the termination step is second order with respect to the radical concentration till 60% conversion.

Table 4 Variation of the rate and kinetic chain lifetime with extent conversion at 35°C and full light intensity.

Extent Conversion %	Rate of Reaction $\times 10^6$ moles l^{-1} s^{-1}	Intercept s	Kinetic Chain Lifetime s
5	5.25	2.3(0)	0.3(6)
10	5.15	2.3(0)	0.3(6)
20	5.47	2.3(0)	0.3(6)
30	5.75	2.4(0)	0.5(0)
40	6.77	2.4(0)	0.5(0)
50	6.75	2.5(3)	0.6(9)
60	7.04	3.0(2)	0.9(7)

With an increase in temperature from 25°C to 35°C a decrease in the gel effect would be expected. However the proportional increase in rate at 35°C is comparable with that at 25°C although the kinetic chain lifetimes at the later stages of conversion are smaller and the rate is still increasing.

Table 5 Variation of the rate and kinetic chain lifetime with extent conversion at 45°C and full light intensity.

Extent Conversion %	Rate of Reaction x 10^4 moles l^{-1} s^{-1}	Intercept s	Kinetic Chain Lifetime s
5	6.40	2.3(0)	0.3(6)
10	6.46	2.3(0)	0.3(6)
20	6.90	2.3(0)	0.3(6)
30	7.57	2.3(0)	0.3(6)
40	7.86	2.3(3)	0.4(0)
50	8.49	2.4(5)	0.6(0)
60	9.45	2.5(5)	0.7(2)

The increase in temperature brings the resultant increase in the rate of reaction [Fig. 9] and the kinetic chain lifetimes are again lower in the region of 40 to 60% conversion [Fig.10]. Although the reactions were not generally carried beyond 60% conversion, a previous experimental dilatometer had shown that the rate began to fall at 70% conversion. The gel effect does not seem to be particularly large since the proportional increase at 45°C is greater than that at 25° and 35°C.

A probable explanation for the small gel effect could be that the molecular weight of the polymer was low and the solution was consequently not as viscous. The initial rate of polymerisation was almost twice that of previous workers due to the greater intensity of the incident light and this would result in lower molecular weight polymer. This is also supported by the shortness of the kinetic chain lifetimes.

Another possible explanation is that the gel effect obtained by other workers was increased by the presence of impurities in their system. If this was so, then the value of k_p/k_t for this work should be much greater than those quoted in the literature. Since they are comparable, this explanation cannot be correct

Determination of the Velocity Coefficients of Propagation and Termination.

The ratio of the velocity coefficients was determined from the slope of the line obtained by plotting the reciprocal of the rate against the measured intercept [Fig. 7]. Since the kinetic chain lifetime has been found, the separate velocity coefficients can be calculated if the rate of initiation is known. The rate of decomposition was taken from the literature[4] and was given as 5.2×10^{-8} moles l^{-1} s^{-1} for a rate of reaction of 7.0% $hr.^{-1}$

This has been amended since the diphenyl picryl hydrazyl used contained one molecule of crystallisation of benzene. Assuming an initiator efficiency of 0.5, the corrected rate of initiation is 2.17×10^{-8} moles l^{-1} s^{-1} at 7.0% polymerisation per hour.

Since the square root of the rate of initiation is proportional to the rate of reaction, a rate of 14.2% per hour at zero conversion gives a value of 8.9 x 10^{-8} moles l^{-1} s^{-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 %	Kinetic Chain Lifetime s	k_p/k_t x 10^5	k_p l $mole^{-1}$ s^{-1}	k_t x 10^{-7} l $mole^{-1}$ s^{-1}
5	0.43	1.43	860	6.0(0)
10	0.36	1.17	1010	8.6(7)
20	0.36	1.43	1240	8.6(7)
30	0.54	2.18	840	3.8(5)
40	0.58	3.08	1030	3.3(6)
50	0.80	3.94	700	1.7(6)
60	1.33	6.27	400	0.6(4)

Determination of Energies of Activation.

The relationship between a velocity coefficient and activation energy may be expressed by the normal Arrhenius equation.

$$k = A.\ \exp^{-E/RT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(20)$$

The overall activation energy E_0 can be determined from the plot of log rate against the reciprocal of the absolute temperature [Fig. 11]. Similarly the activation energy of termination E_t can pe obtained from the slope of the straight line plot of $\log_{10}\frac{1}{\tau}$ against the reciprocal of the absolute temperature. It can also be obtained by plotting $\log_{10} {}^{k_p}/_{k_t}$ against the reciprocal of the absolute temperature [Fig.12]. Both methods have been used to obtain a value for the activation energy of termination and both values have been plotted to verify any general trend in the polymerisation.

Since the termination step is second order with respect to the radical concentration the energy of propagation E_p, can be obtained from

$$E_0 = E_p - \tfrac{1}{2}E_t \qquad \ldots\ldots\ldots\ldots\ldots\ldots(21)$$

Table 7 Variation of velocity coefficients with extent conversion at 35°C and full light intensity.

Extent Conversion %	Kinetic Chain Lifetime s	${}^{k_p}/_{k_t}$ x 10^5	k_p l $mole^{-1}$ s^{-1}	k_t x 10^{-7} l $mole^{-1}$ s^{-1}
5	0.3(6)	1.80	1560	8.6(7)
10	0.3(6)	1.62	1400	8.6(7)
20	0.3(6)	1.90	1650	8.6(7)
30	0.5(0)	2.79	1250	4.4(9)
40	0.5(0)	3.08	1380	4.4(9)
50	0.6(8)	4.35	1040	2.4(0)
60	0.9(7)	6.40	760	1.1(9)

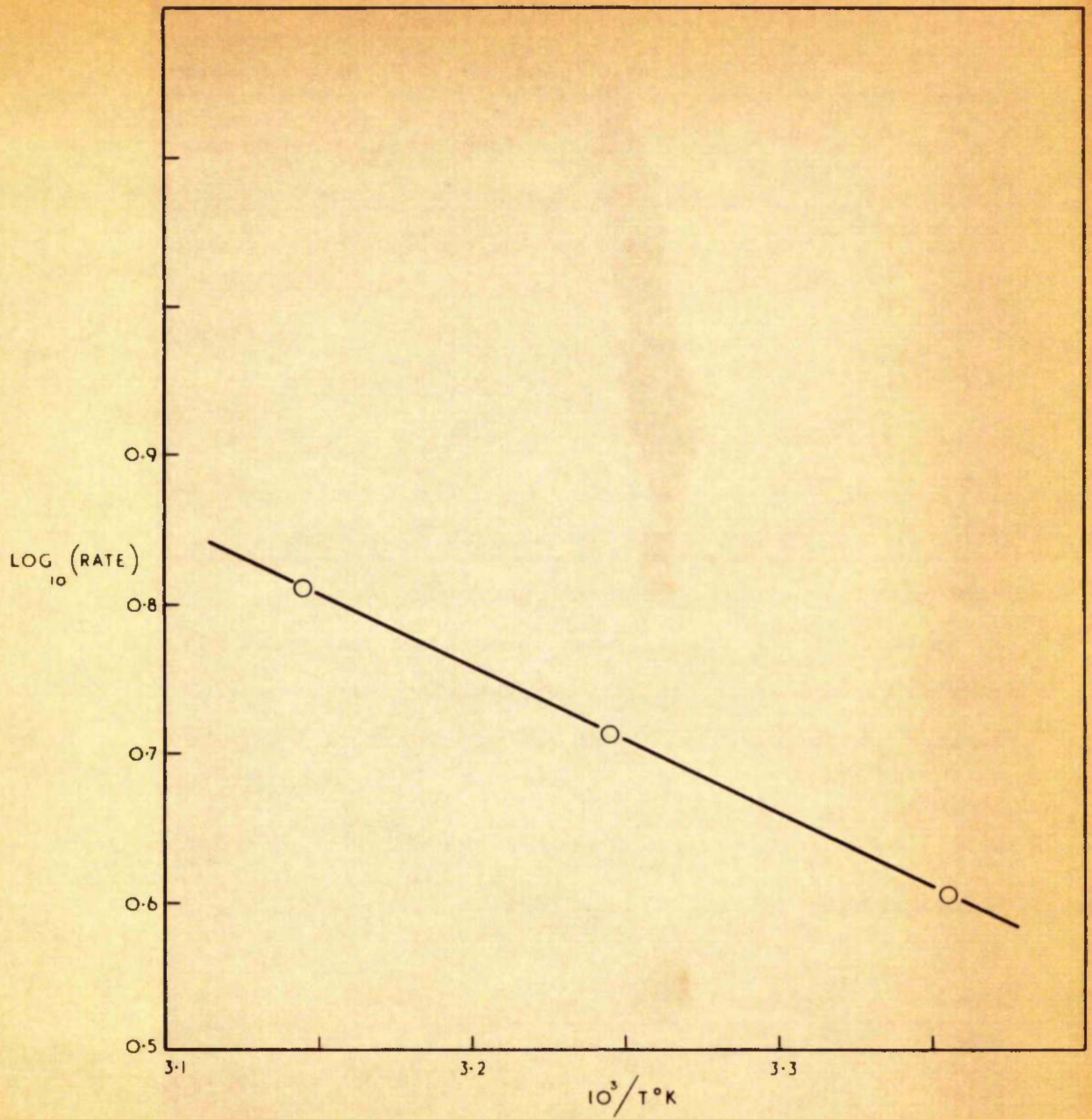


FIG. 11 TYPICAL GRAPH FOR THE DETERMINATION OF E_0.
$E_0 = 4\cdot6 \times$ GRADIENT kcal.

Table 8 Variation of velocity coefficients with extent conversion at 45°C and full light intensity.

Extent Conversion %	Kinetic Chain Lifetime s	$k_p/k_t \times 10^5$	k_p $l\ mole^{-1}\ s^{-1}$	$k_t \times 10^{-7}$ $l\ mole^{-1}\ s^{-1}$
5	0.3(6)	2.11	1830	8.6(7)
10	0.3(6)	2.42	2100	8.6(7)
20	0.3(6)	2.51	2180	8.6(7)
30	0.3(6)	2.68	2320	8.6(7)
40	0.4(0)	3.40	2440	7.1(7)
50	0.6(0)	5.15	1730	3.3(6)
60	0.7(2)	6.56	1380	2.1(7)

At all three temperatures k_p increases during the first 40% conversion and then decreases during the later stages of the polymerisation while the velocity coefficient for termination remains constant during the initial stages and then begins to decrease.

Table 9 Variation of activation energies with extent conversion.

Extent Conversion %	E_0 k.cals.	E_t derived from τ k.cals.	E_t derived from k_p/k_t k.cals.	E_p k.cals.
5	4.8	0	2.2	4.8
10	4.5	0	0	4.5
20	4.7	0	0	4.7
30	4.8	3	4.2	6.3
40	4.5	6.0	7.1	7.5
50	4.7	6.1	4.6	7.7
60	5.8	11.8	11.7	11.7

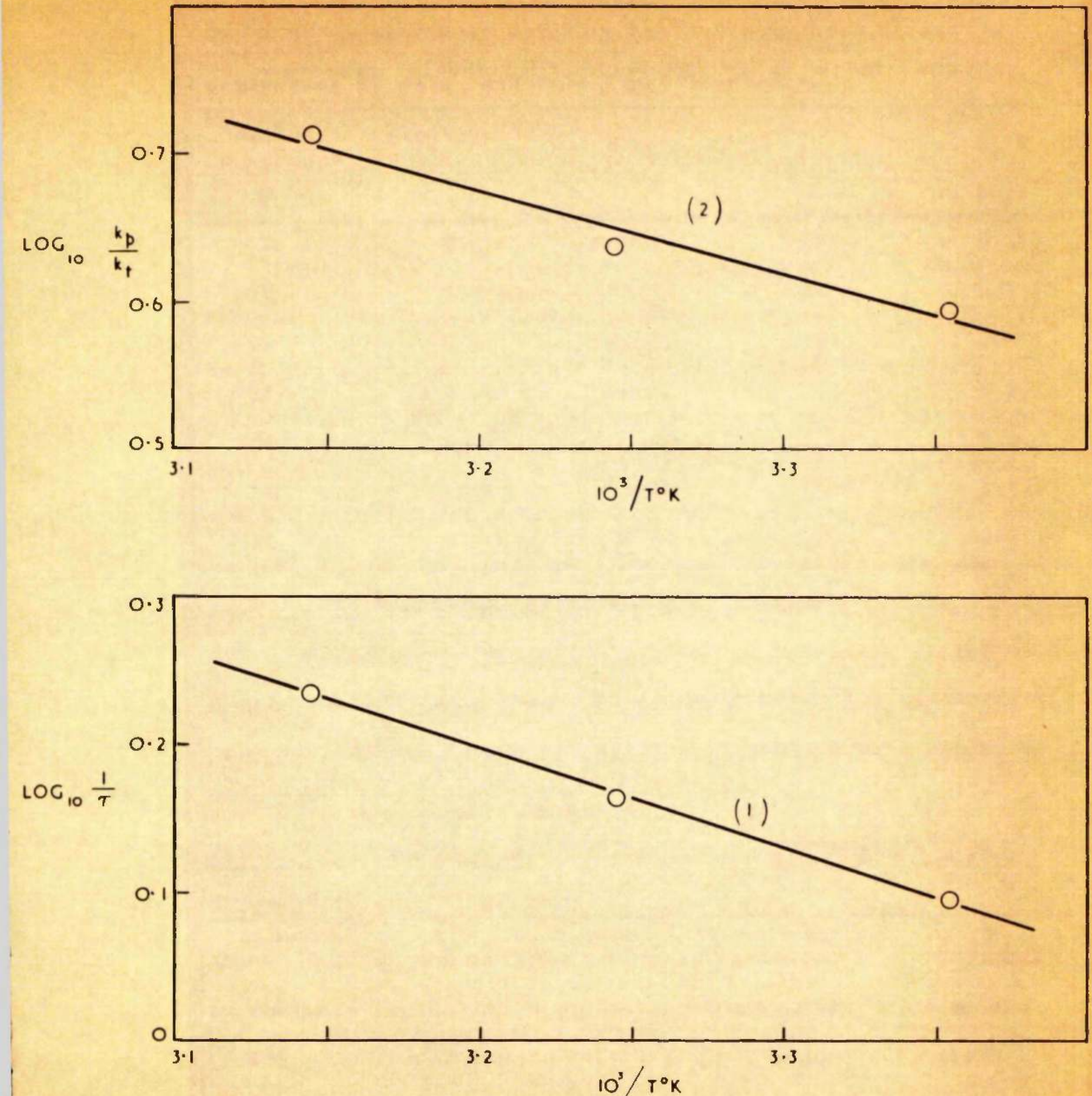


FIG. 12 TYPICAL GRAPHS FOR THE DETERMINATION OF E_t

(1) E_t = 9·2 GRADIENT kcal

(2) E_t = 2 (E_0 − 4·6 GRADIENT) kcal

The agreement between the activation energy of termination derived from the two sources is quite reasonable [Fig. 13].

Discussion of the bulk polymerisation of vinyl acetate.

The most obvious feature in the bulk polymerisation is the obvious lack of gel effect in the early stages. Previous workers have noted an immediate acceleration in rate especially at 25°C and a greater proportional increase in the rate at the lower temperatures. This has not occurred in this work since the rate at 25°C is almost constant for the first 20% conversion and the rate at 45°C over the same period has increased. If the gel effect was operative then the lifetimes would also increase and the velocity coefficient for termination should fall due to termination becoming more difficult. Neither has occurred. Also monomer diffusion is not affected as k_p appears to increase at all temperatures. Since the gel effect is a viscosity effect the system must consist of monomer and low molecular weight polymer and the solution viscosity must be less than that obtained by previous workers.

After 30% to 40% conversion the value of k_t begins to decrease due to the reaction mixture becoming viscous and making it more difficult for the polymer radicals to diffuse together and terminate. There is a corresponding increase in the value of the kinetic chain lifetimes which one would expect

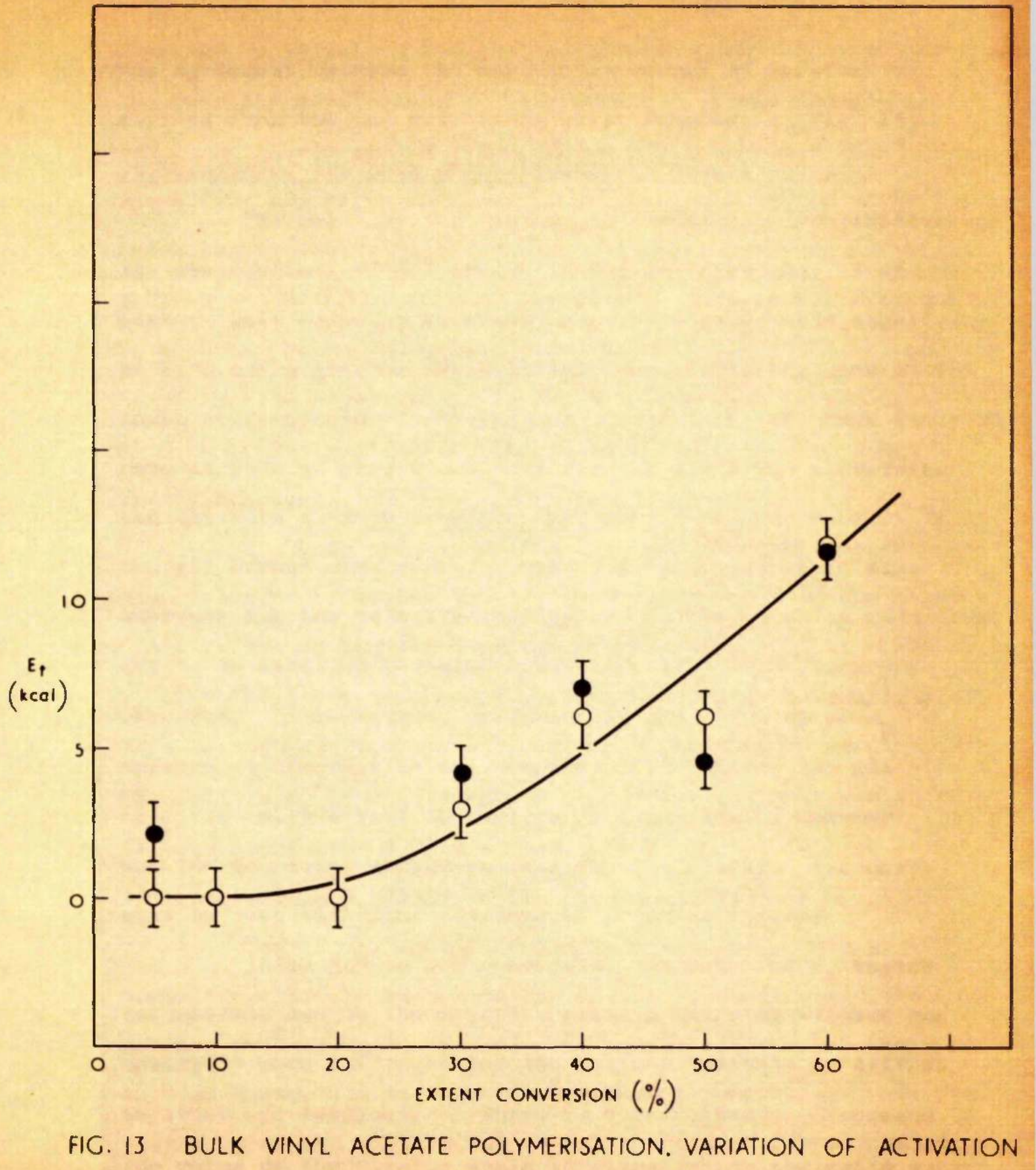


FIG. 13 BULK VINYL ACETATE POLYMERISATION. VARIATION OF ACTIVATION ENERGY OF TERMINATION WITH CONVERSION

○ E_t FROM $\frac{1}{T}$ ● E_t FROM k_p/k_t

from the relationship between the kinetic chain lifetime and the velocity coefficient of termination. These changes are reflected in the activation energies. With the increase in the difficulty of termination of the radicals E_t begins to increase from the zero value it had during the initial stages of the polymerisation while E_p also increases. However the increase in E_t does not cause any marked lowering of E_0 [Fig. 14] since there is as large a proportional increase in the rate of reaction at 45°C as there is at 25°C. The value of E_0 therefore remains fairly constant.

At 50 to 60% conversion the increasing viscosity of the system is reflected in the increase in value of the kinetic chain lifetimes and the decrease in value of k_t. The value of k_p also falls due to monomer diffusion becoming more difficult. This is not particularly apparent from the rate of reaction since the fall in k_t is sufficient to counteract the decrease in k_p. This is demonstrated by the fact that E_0 begins to rise since the increase in E_p compensates for the increase in E_t.

Therefore, initially the bulk polymerisation of vinyl acetate appears to be a reaction mixture through which the monomer polymer chain radicals can easily diffuse and the reaction is then controlled by individual chemical properties. As the viscosity of the mixture increases the rate of polymerisation

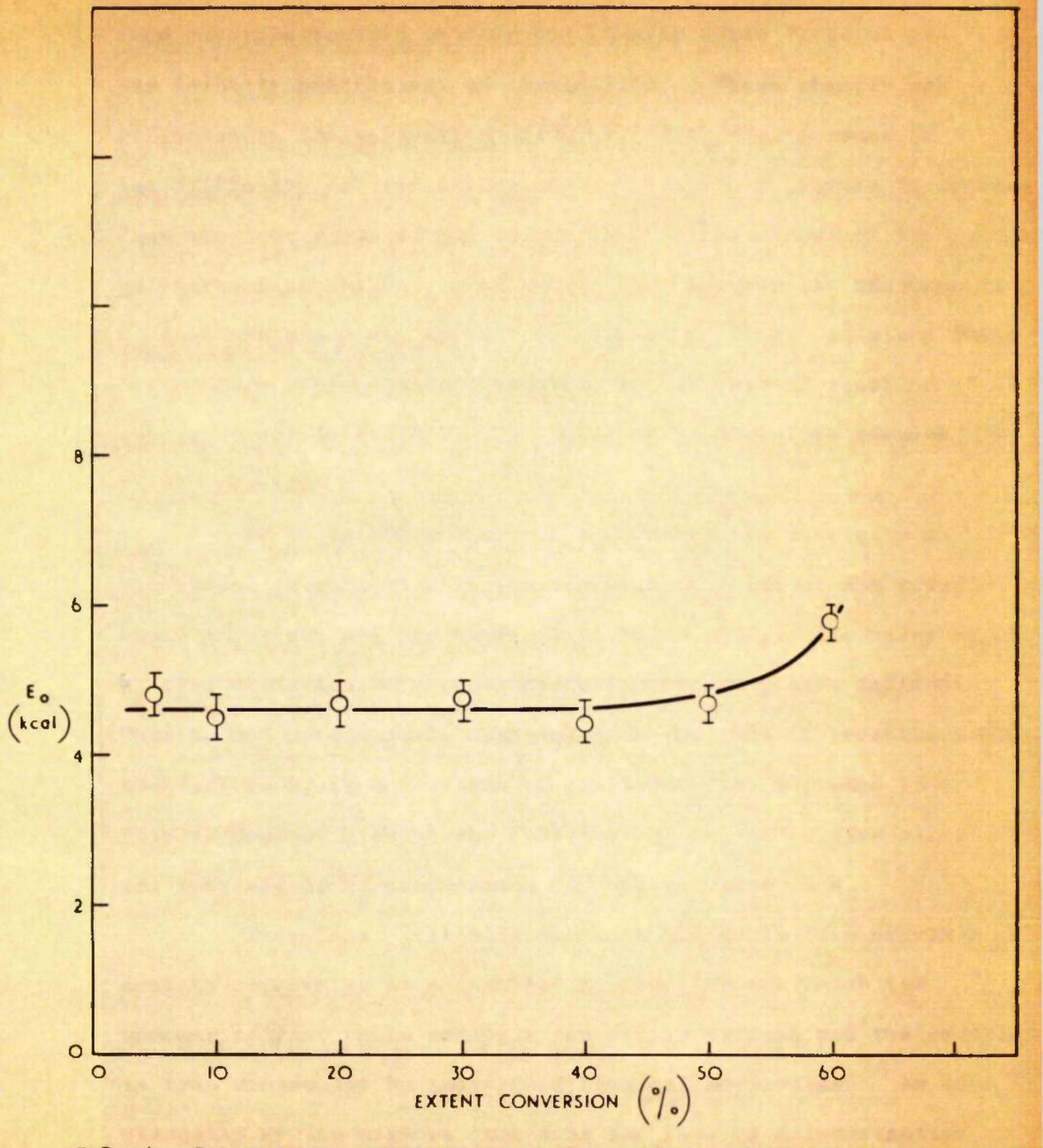


FIG. 14 BULK VINYL ACETATE POLYMERISATION. VARIATION OF ACTIVATION ENERGY E_0 WITH CONVERSION

increases as it becomes more difficult for the radicals to diffuse together and terminate. As the viscosity of the system increases and the concentration of monomer decreases with conversion the diffusion of monomer becomes controlled and the rate of propagation falls. When this occurs the rate of reaction will begin to fall with increasing conversion.

Comparison of Results with Literature Values.

It is worthwhile to compare the velocity coefficients and activation energies obtained especially as there is a marked decrease in the gel effect. The values for k_p and k_t are in reasonable agreement with those obtained by other workers.

Table 10 Velocity coefficients for the photo-initiated bulk polymerisation of vinyl acetate at 25°C.

Reference	k_p $l\ mole^{-1}\ s^{-1}$	$k_t \times 10^7$ $l\ mole^{-1}\ s^{-1}$
This work	860	6.0
Bengough and Melville[4]	895	2.4
Bengough and Ferguson[8]	1090	14.6

A similar comparison between the overall and termination activation energies demonstrates that these are in good agreement with the published literature values.

Table 11 Activation energies for the initial stages of the bulk polymerisation of vinyl acetate for the range 25°C to 45°C.

Reference	E_0 k.cals.	E_t k.cals.
This work	4.8	0
Bengough and Melville[3]	4.2	1
Bengough and Ferguson[8]	5.8	0.8
Burnett and Melville[47]	4.4	0
Dixon-Lewis[48]	3.2	0
Matheson et al.[40]	4.7	5.2

The value of E_t calculated by Matheson et al would appear to be very high. This was obtained from the sector method where there can be a factor of 2 in error in the determination of the kinetic chain lifetime depending on the accuracy with which the practical curve can be fitted to the theoretical curves. Apart from this result there is good agreement with the other literature data.

Polymerisation of Vinyl Acetate in the Presence of Benzene.

In the following section the results of the polymerisation of vinyl acetate in the presence of benzene will be examined in an attempt to ascertain the manner in which the solvent retards the reaction. The monomer was polymerised in the presence of 2.5, 5 and 20% v/v benzene. Since it was very difficult to duplicate the kinetic chain lifetimes where the rate was as low as 3×10^{-8} moles $l^{-1} s^{-1}$ no greater dilution was attempted. It was also calculated that in the presence of 20% benzene most of the initiator was being consumed at these lower rates though this will be commented upon in the appropriate section.

The Polymerisation of Vinyl Acetate in the presence of 2.5 v/v Benzene.

The calculation to obtain the rate of polymerisation (Appendix 2) involves a knowledge of the specific heats of the species present in the system. While the addition of a small quantity of solvent does not particularly alter the specific heat factor for a monomer-polymer system, the effect is considerable when larger quantities of solvent are present. It was assumed that the specific heat of the mixture varied linearly with the amount of benzene present. The initiator concentration was 4×10^{-3} moles l^{-1}.

Table 12 Variation of rate and kinetic chain lifetime with extent conversion at 25°C and full intensity.

Extent Conversion %	Rate of Reaction $\times 10^4$ moles l^{-1} s^{-1}	Intercept s	Kinetic Chain Lifetime s
5	2.52	0.6(4)	0.9(2)
10	2.46	0.5(0)	0.7(2)
20	2.47	0.5(0)	0.7(2)
30	2.75	0.4(5)	0.6(5)
40	2.66	0.5(0)	0.7(2)
50	2.65	0.8(0)	1.1(5)
60	2.91	1.3(0)	1.8(8)

The effect of the addition of only 0.281 moles l^{-1} of benzene is quite marked. The rate of reaction [Fig.15] is considerably reduced while the kinetic chain lifetimes are greater at each particular conversion [Fig. 16]. Although the rate of reaction is retarded, the gel effect is still present. The proportional increase in the rate, however, is not so great as that noted for the bulk polymerisation.

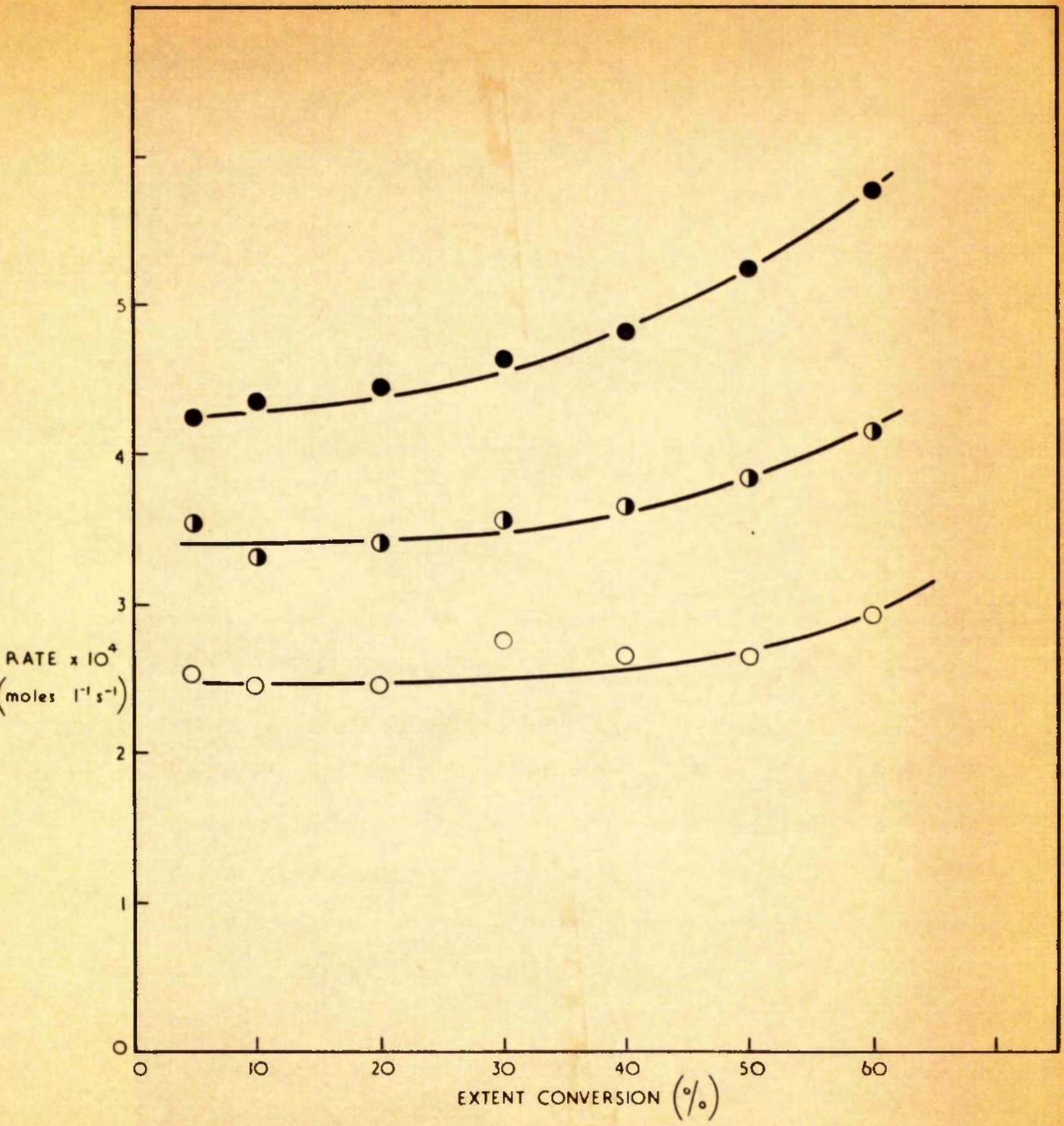


FIG. 15 VINYL ACETATE PLUS 2·5% BENZENE. VARIATION OF RATE WITH CONVERSION

○ 25°C ◑ 35°C ● 45°C

Table 13 Variation of rate and kinetic chain lifetime and intensity exponenet at 25°C and reduced light intensity. L_2 = 0.485 L_1.

Extent Conversion %	Rate of Reaction x 10^4 moles l^{-1} s^{-1}	Kinetic Chain Lifetime s	Intensity Exponent s
5	1.58	1.4(4)	0.59
10	1.67	1.1(5)	0.59
20	1.65	1.1(0)	0.63
30	1.75	1.1(0)	0.62
40	1.67	1.2(3)	0.62
50	1.72	1.8(0)	0.62
60	1.86	2.9(6)	0.60

The rate at this reduced light intensity is naturally lower than at 100% intensity while the kinetic chain lifetimes are correspondingly longer. Although the intensity exponent is rather greater than 0.5 it would seem more probable that the termination step is second order with respect to the radical concentration as has been found by other workers.[1,8] Bengough and Ferguson[3] obtained an intensity exponent of 0.7 for this particular concentration of benzene and assumed that mixed order termination was occurring. However, since the best intensity exponent obtained for the bulk polymerisation was 0.54 and allowi

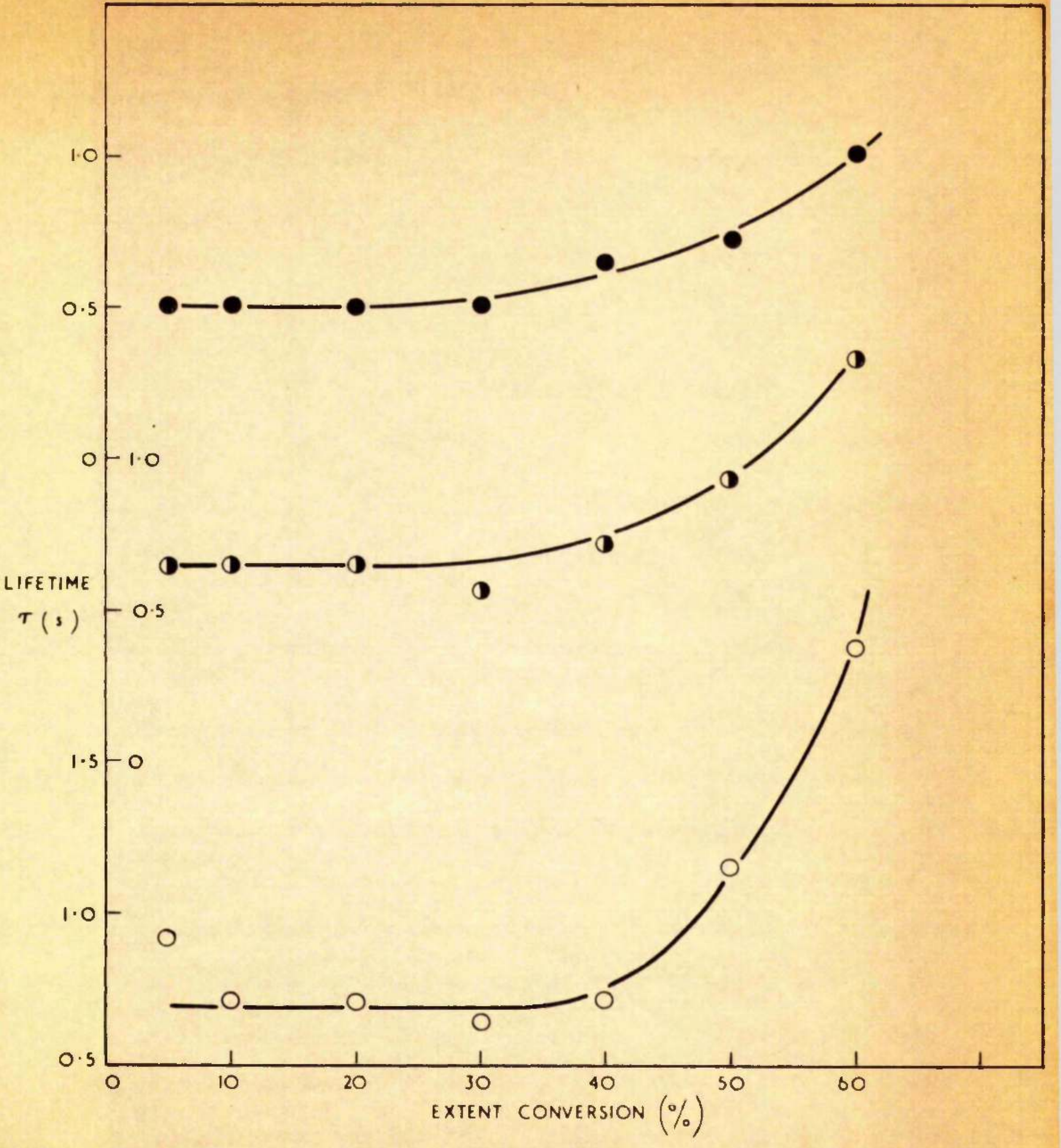


FIG. 16 VINYL ACETATE PLUS 2·5% BENZENE. VARIATION OF KINETIC CHAIN LIFETIME WITH CONVERSION

○ 25°C ◑ 35°C ● 45°C

for experimental error, the value of 0.59 can be taken as a reasonable indication of second order termination. It can only be assumed that the high intensity exponent obtained by Bengough and Ferguson was the result of some impurity being present in the system

<u>Table 14</u> Variation of rate, kinetic chain lifetime and intensity exponent at 35°C and full light intensity.

Extent Conversion %	Rate of Reaction x 10^4 moles l^{-1} s^{-1}	Intercept s	Kinetic Chain Lifetime s	Intensi Exponen
5	3.52	0.4(5)	0.6(5)	0.59
10	3.31	0.4(5)	0.6(5)	0.55
20	3.41	0.4(5)	0.6(5)	0.55
30	3.56	0.4(0)	0.5(6)	0.58
40	3.65	0.5(0)	0.7(2)	0.60
50	3.85	0.6(5)	0.9(4)	0.59
60	4.17	0.9(3)	1.3(4)	0.67

The rate of reaction [Fig.15] at 35°C is greater than at 25°C for similar conditions while the proportional drop in rate compared with the bulk polymerisation is the same for both temperatures. The kinetic chain lifetimes are again greater at all conversions than those of the bulk polymerisation [Fig.16].

Table 15 Variation of rate, kinetic chain lifetime and intensity exponent at 45°C and full light intensity.

Extent Conversion %	Rate of Reaction x 10^4 moles l^{-1} s^{-1}	Kinetic Chain Lifetime s	Intensity Exponent
5	4.22	0.5(0)	0.61
10	4.36	0.5(0)	0.63
20	4.45	0.5(0)	0.59
30	4.63	0.5(0)	0.55
40	4.81	0.6(5)	0.64
50	5.24	0.7(2)	0.60
60	5.78	1.0(0)	0.67

The kinetic chain lifetimes follow a similar pattern to those in the bulk polymerisation. They are constant till 30% conversion when they begin to increase. They are, of course, greater than the values obtained for the kinetic chain lifetimes of the bulk polymerisation at the same conversion. The increase in the kinetic chains lifetimes at the later stages of conversion would indicate the occurrence of a slight gel effect.

Table 16 Variation of velocity coefficients with extent conversion at 25°C and full illumination.

Extent Conversion %	$k_p/k_t \times 10^6$	k_p $1\ mole^{-1}\ s^{-1}$	$k_t \times 10^{-7}$ $1\ mole^{-1}\ s^{-1}$
5	2.11	280	1.3(2)
10	1.46	320	2.1(6)
20	1.42	310	2.1(6)
30	1.80	480	2.6(7)
40	1.85	400	2.1(6)
50	2.97	250	0.8(8)
60	5.11	160	0.3(2)

Both k_p and k_t follow a similar pattern to that followed by the corresponding velocity coefficients in the bulk polymerisation. The value for the velocity coefficient of propagation rises from the initial stages of the polymerisation till about 40% conversion when it begins to decrease. Both coefficients have lower values than in the bulk polymerisation indicating that both propagation and termination steps are not occurring as easily.

Table 17 Variation of velocity coefficients with extent conversion at 35°C and full illumination.

Extent Conversion %	$k_p/k_t \times 10^5$	k_p l $mole^{-1}$ s^{-1}	$k_t \times 10^{-7}$ l $mole^{-1}$ s^{-1}
5	2.00	530	2.6(7)
10	2.43	650	2.6(7)
20	1.69	450	2.6(7)
30	2.06	730	3.5(4)
40	2.51	540	2.2(6)
50	3.30	420	1.2(8)
60	5.27	330	0.6(3)

Table 18 Variation of velocity coefficients with extent conversion at 45°C and full illumination.

Extent Conversion %	$k_p/k_t \times 10^5$	k_p l $mole^{-1}$ s^{-1}	$k_t \times 10^{-7}$ l $mole^{-1}$ s^{-1}
5	2.16	950	4.4(0)
10	1.85	625	3.3(7)
20	2.62	1150	4.4(0)
30	2.11	930	4.4(0)
40	2.94	785	2.6(7)
50	3.51	760	2.1(6)
60	5.67	625	1.1(0)

The velocity coefficients of propagation and termination at 35° and 45°C exhibit a similar pattern with respect to their counterparts in the bulk polymerisation.

The activation energies for this polymerisation were derived from the same sources as those for the bulk polymerisation. Thus E_p can be derived from $E_0 = E_p - \frac{1}{2}E_t$ since we have assumed that the termination step is in fact second order with respect to the radical concentration.

Table 19   Variation of activation energies with extent conversion.

Extent Conversion %	E_0 k.cal.	E_p k.cal.	E_t from τ k.cal.	E_t from k_p/k_t k.cal.
5	5.4	9.4	11.2	9.7
10	5.7	8.9	6.4	8.5
20	5.3	8.7	6.8	6.3
30	5.2	7.7	4.9	6.5
40	6.0	8.0	3.9	8.0
50	6.5	11.0	8.9	9.1
60	6.9	12.9	11.9	11.9

There would appear to be a larger variation in E_t derived from the two different sources than there was for the bulk polymerisation [Fig. 17].

Normally E_t is obtained from the plot of $\log_{10}\frac{1}{\tau}$ against

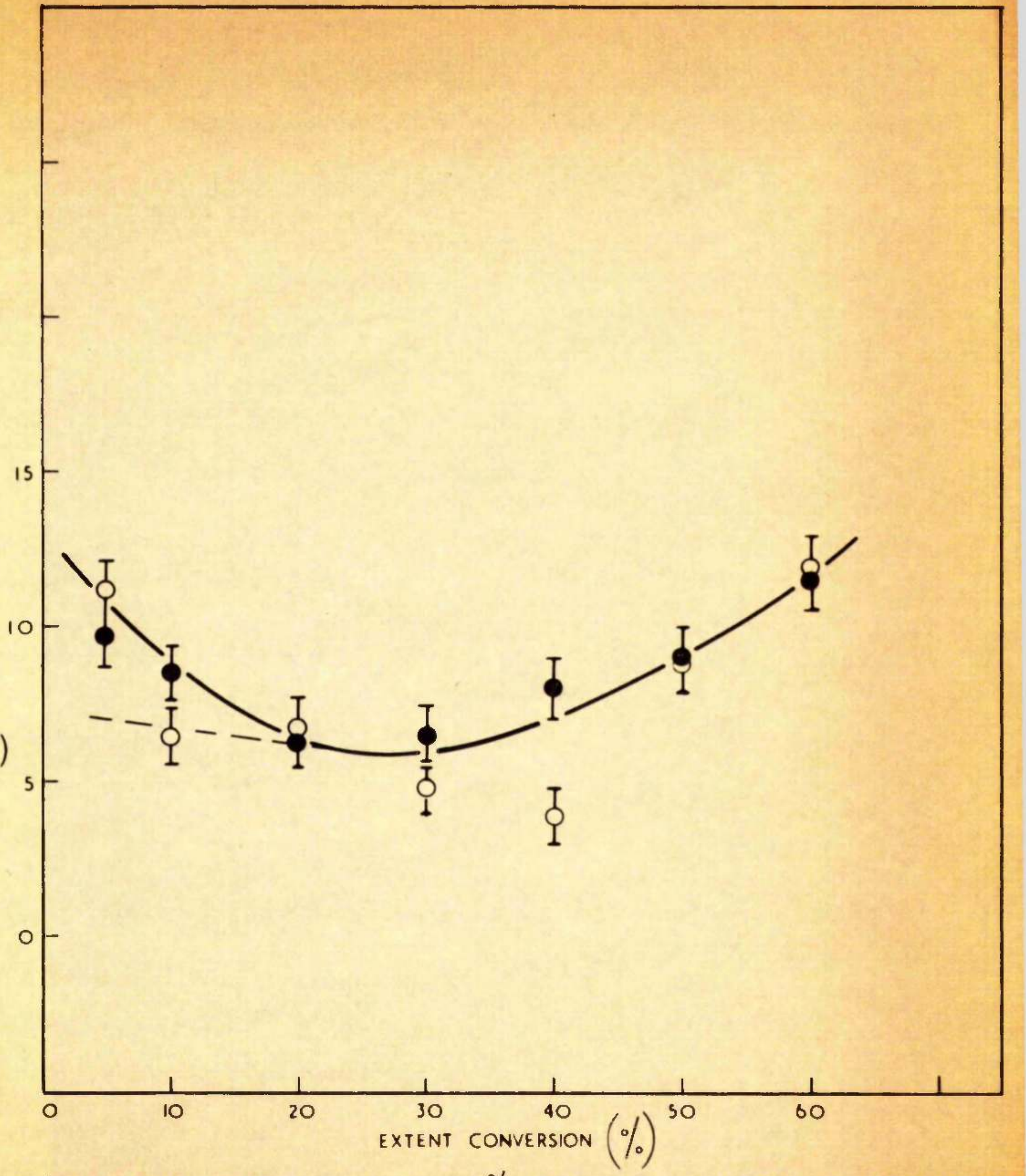


FIG. 17 VINYL ACETATE PLUS 2·5% BENZENE. VARIATION OF ACTIVATION ENERGY OF TERMINATION WITH CONVERSION

○ E_t FROM $\frac{1}{T}$ ● E_t FROM k_p/k_t

the reciprocal of the absolute temperature. However this value of τ is obtained from only one point on the plot of $\frac{1}{\text{Rate}}$ against the measured intercept. It was thought that it would be better to obtain an average result from the slope of this straight line rather than an individual result for a single point on it. The value of E_t is then obtained by solving the two simple equations:-

$$E_p - \tfrac{1}{2}E_t = E_0,$$

$$E_p - E_t = Z.$$

Z is the value of $E_p - E_t$ obtained from the slope of the straight line plot of $\log_{10} k_p/k_t$ against the reciprocal of the absolute temperature. Any error in selecting the correct line from the plot of $\frac{1}{\text{Rate}}$ against the measured intercept or in determining the overall activation energy E_0 [Fig.18] will consequently be reflected in the final value of E_t.

Discussion of the Polymerisation of Vinyl Acetate in the Presence of 2.5 v/v Benzene.

The most striking feature of the polymerisation is the marked decrease in the rate of reaction for the addition of such a small quantity of solvent. At all three temperatures the initial rate is only approximately 3/8 of the corresponding bulk polymerisation rate. The gel effect is still operating in the system for the rates of reaction increase with conversion. The values for the kinetic chain lifetimes are greater than the corresponding

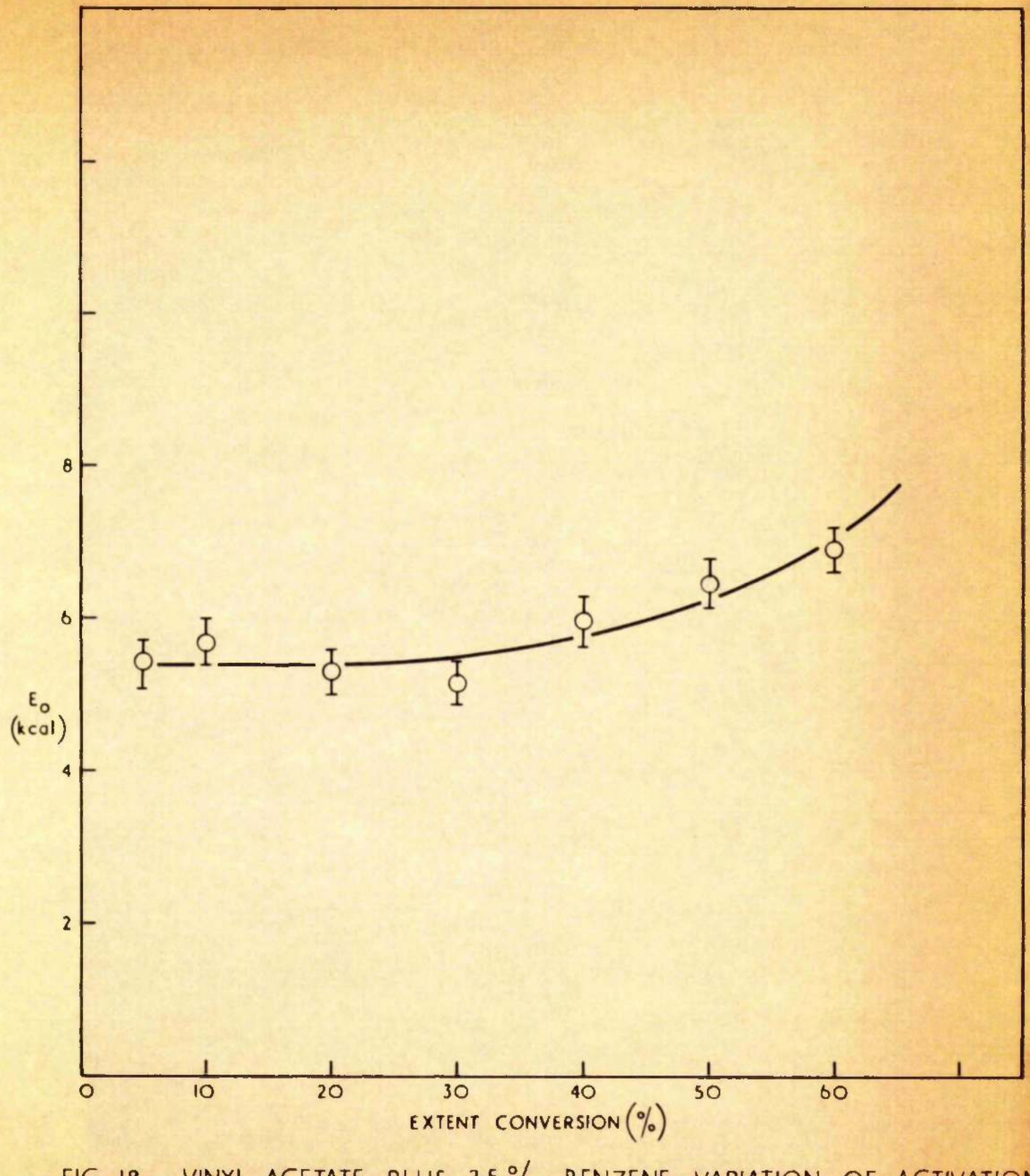


FIG. 18 VINYL ACETATE PLUS 2·5 % BENZENE. VARIATION OF ACTIVATION ENERGY E_0 WITH CONVERSION

values in the bulk polymerisation but exhibit the same pattern of behaviour i.e. the value remains constant till about 40% conversion when they begin to increase.

There is also a very close resemblance when the velocity coefficients of propagation and termination are considered. They are lower in value than their counterparts in the bulk polymerisation but rise and fall in a similar manner.

A comparison between the activation energy of termination for the two systems illustrates that the addition of the solvent radically alters the polymerisation process. For the initial stages of the bulk polymerisation E_t is zero. But for the addition of 2.5% benzene E_t varies between 10 and 6 k.cals., although the dotted line in Fig.17 indicates a more probable value for E_t at these initial stages of conversion. Since E_0 is slightly greater than for the bulk polymerisation this represents an increase of at least 3 k.cals. in E_p. This rise in E_p and E_t indicates that the addition of solvent makes the propagation and termination steps more difficult. This would appear to be independant of the gel effect since the pattern followed by the velocity coefficients is similar to that of the bulk polymerisation.

Polymerisation of Vinyl Acetate in the presence of 5% v/v Benzene

The concentration of benzene was increased from 2.5% to 5% to obtain the effect of benzene concentration on the rate of reaction and the kinetic chain lifetime. The specific heat of the mixture was corrected for the presence of the solvent and the true rate of reaction obtained.

Table 20 Variation of rate, kinetic chain lifetime and intensity exponent at 25°C and full light intensity.

Extent Conversion %	Rate of Reaction, moles l^{-1} s^{-1}	Kinetic Chain Lifetime s	Intensity Exponent
5	1.97	0.7(2)	0.66
10	1.84	0.7(2)	0.63
20	1.74	0.7(2)	0.60
30	1.85	0.7(9)	0.62
40	2.05	0.8(7)	0.60
50	2.06	1.0(0)	0.58
60	2.20	1.8(0)	0.60

There is a further decrease in the rate of polymerisation with the increase in concentration of the solvent. The initial rate of polymerisation is now $\frac{1}{8}$ of the rate obtained for the bulk polymerisation at a similar conversion [Fig. 19]. Although there is a further reduction in the rate the addition of further solvent has not eradicated the gel effect. There is still an increase in the rate of polymerisation although Bengough and

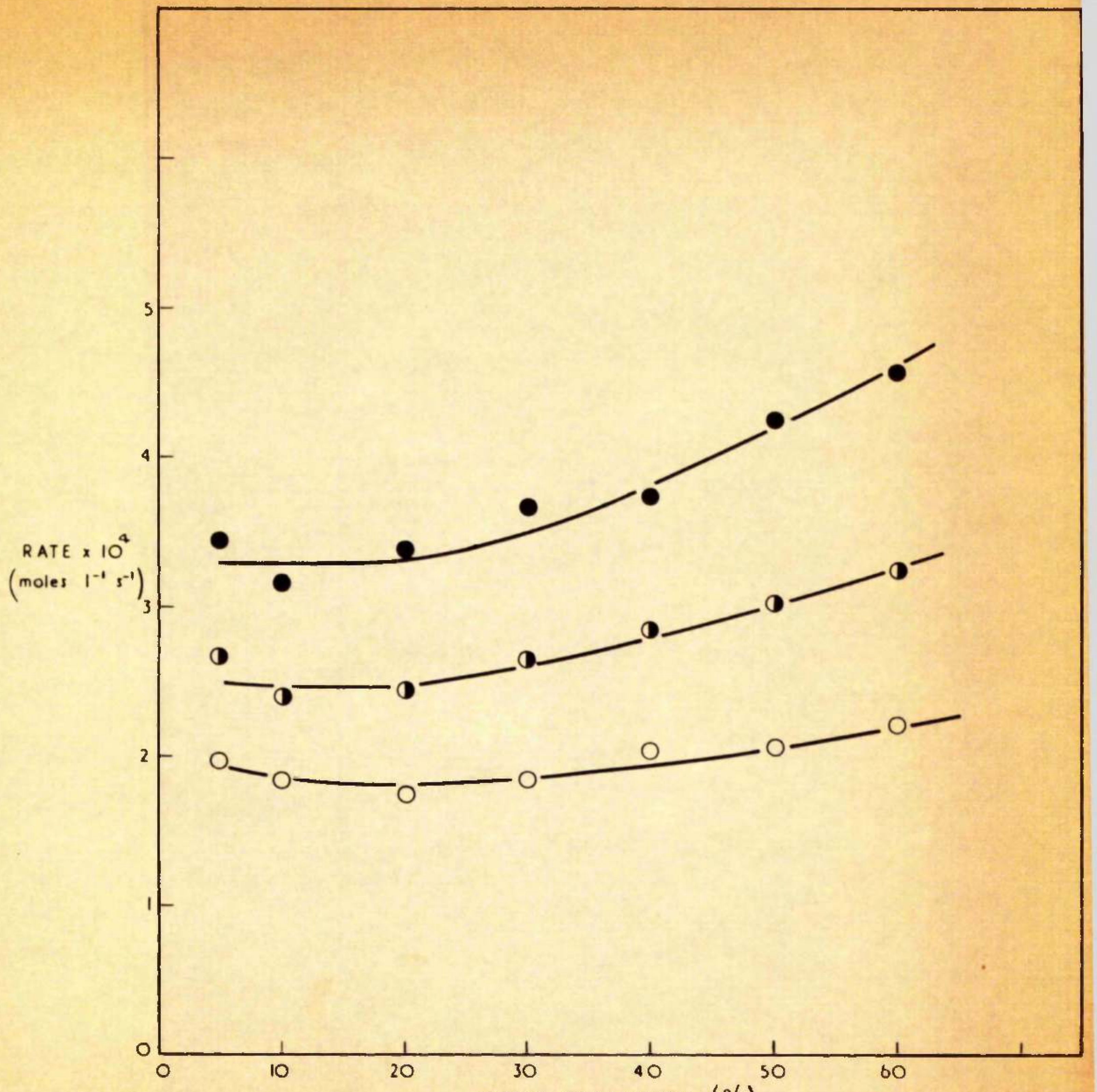


FIG. 19 VINYL ACETATE PLUS 5% BENZENE. VARIATION OF RATE WITH CONVERSION

○ 25°C ◐ 35°C ● 45°C

Ferguson[3] did not obtain this.

The value of the kinetic chain lifetime appears to have increased slightly with the addition of more solvent and is again constant during the initial stages of polymerisation [Fig.20]. The intensity exponent is in the region of 0.6 and the termination reaction is assumed to be second order with respect to the radical concentration.

Table 21 Variation of rate, kinetic chain lifetime and intensity exponent at 35°C and full light intensity.

Extent Conversion %	Rate of Reaction x 10^4 moles l^{-1} s^{-1}	Kinetic Chain Lifetime s	Intensity Exponent
5	2.68	0.5(8)	0.65
10	2.40	0.5(0)	0.62
20	2.44	0.6(1)	0.60
30	2.64	0.6(8)	0.57
40	2.85	0.7(2)	0.57
50	3.02	0.6(5)	0.58
60	3.26	1.5(0)	0.55

The drop in the initial rate of polymerisation is maintained. The rate however continues to increase with conversion so the gel effect is still operating on the system.

The kinetic chain lifetimes would seem to have decreased when compared with the corresponding values at

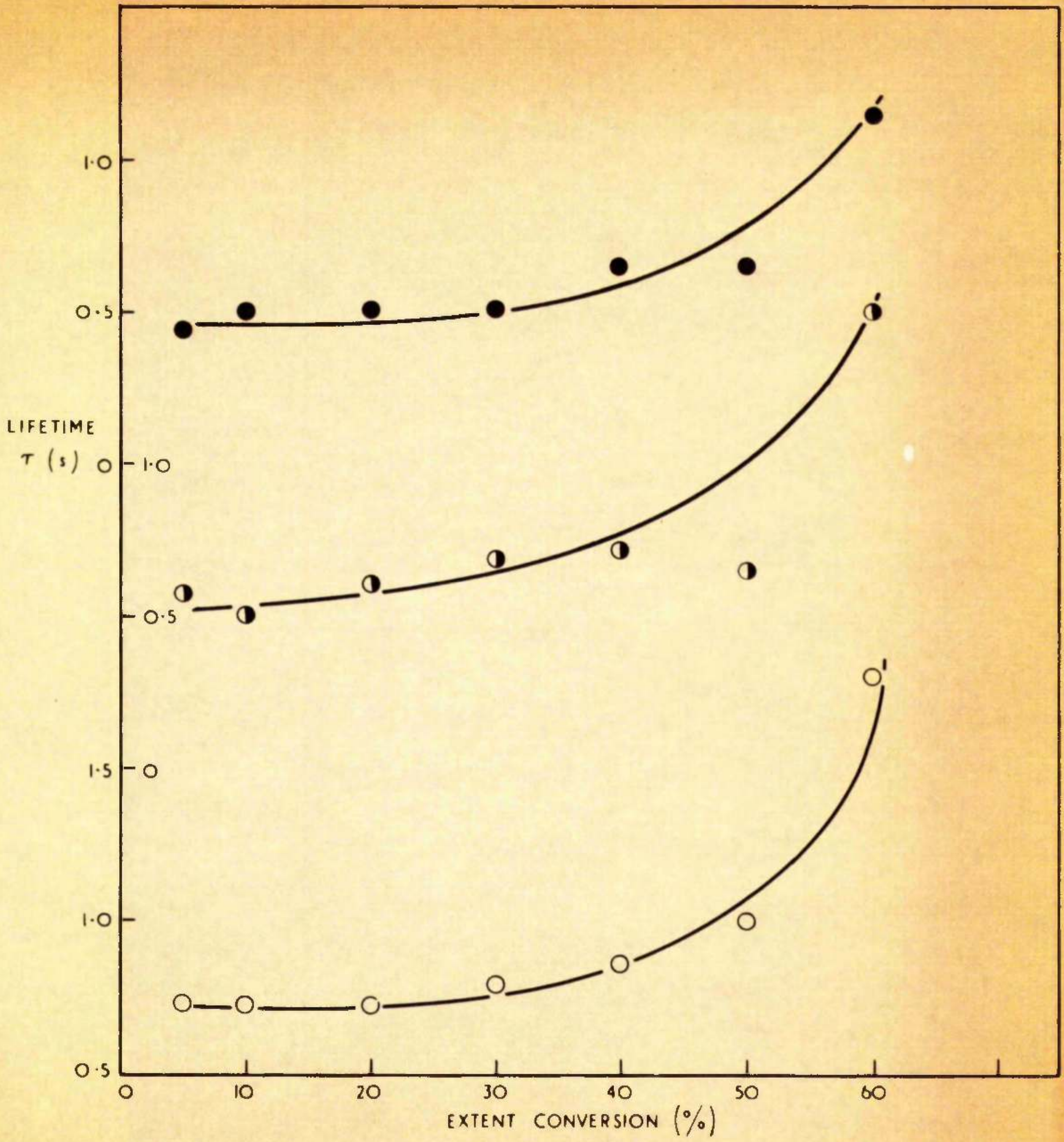


FIG. 20 VINYL ACETATE PLUS 5% BENZENE. VARIATION OF KINETIC CHAIN LIFETIME WITH CONVERSION

○ 25°C ◑ 35°C ● 45°C

2.5% benzene. Considering the experimental error which is involved in the system it seems more probable that the values for 2.5% and 5% benzene are the same at all three temperatures [Figs 16 and 20].

Table 22 Variation of rate, kinetic chain lifetime and intensity exponent at 45°C and full light intensity.

Extent Conversion %	Rate of Reaction $\times 10^4$ moles l^{-1} s^{-1}	Kinetic Chain Lifetime s	Intensity Exponent
5	3.43	0.4(5)	0.62
10	3.16	0.5(6)	0.59
20	3.38	0.5(0)	0.59
30	3.66	0.5(0)	0.61
40	3.74	0.6(5)	0.53
50	4.26	0.6(5)	0.60
60	4.57	1.1(5)	0.60

Table 23 Variation of velocity coefficients with extent conversion at 25°C and full light intensity

Extent Conversion %	$k_p/k_t \times 10^5$	k_p l mole^{-1} s^{-1}	$k_t \times 10^{-7}$ l mole^{-1} s^{-1}
5	1.34	290	2.2
10	1.31	280	2.2
20	1.18	250	2.2
30	1.40	300	1.8
40	1.68	250	1.5
50	1.83	200	1.1
60	3.83	130	0.3

The trend that the results at 2.5% and 5% benzene are similar is maintained in the velocity coefficients especially with respect to k_p.

Table 24 Variation of velocity coefficients with extent conversion at 35°C and full light intensity.

Extent Conversion %	$k_p/k_t \times 10^5$	k_p $\text{l mole}^{-1}\,\text{s}^{-1}$	$k_t \times 10^{-7}$ $\text{l mole}^{-1}\,\text{s}^{-1}$
5	1.06	355	3.4
10	1.10	485	4.4
20	1.44	430	3.0
30	1.82	435	2.4(6)
40	1.85	400	2.2
50	1.98	530	2.7
60	4.70	235	0.5

Table 25 Variation of velocity coefficients with extent conversion at 45°C and full light intensity

Extent Conversion %	$k_p/k_t \times 10^5$	k_p $\text{l mole}^{-1}\,\text{s}^{-1}$	$k_t \times 10^{-7}$ $\text{l mole}\,\text{s}^{-1}$
5	1.60	960	6.0
10	1.60	700	4.4
20	1.63	720	4.4
30	1.86	820	4.4
40	2.62	700	2.7
50	2.65	710	2.7
60	5.21	440	0.8

Comparison between the velocity coefficients at 35° and 45°C for 2.5 and 5.0% benzene confirms that any difference in value for a particular conversion is within experimental error. The activation energies E_0 and E_t [Figs 21 and 22] as would be expected, are also comparable [Figs. 21, 22 with Figs. 17 and 18].

Table 26 Variation of activation energies with extent conversion.

Extent Conversion %	E_0 k.cals.	E_t from τ k.cals.	E_t from k_p/k_t k.cals.
5	5.7	9.8	8.5
10	6.1	6.8	8.0
20	6.6	6.8	6.6
30	6.6	6.7	11.1
40	6.3	5.7	6.7
50	7.3	7.0	7.8
60	7.8	8.8	9.5

The only obvious difference between the polymerisation of vinyl acetate in 2.5% benzene and 5% benzene is a definite reduction in the rate of polymerisation. The percentage of benzene in the reaction mixture was therefore increased to 20% to find the effect of this larger dilution of the monomer.

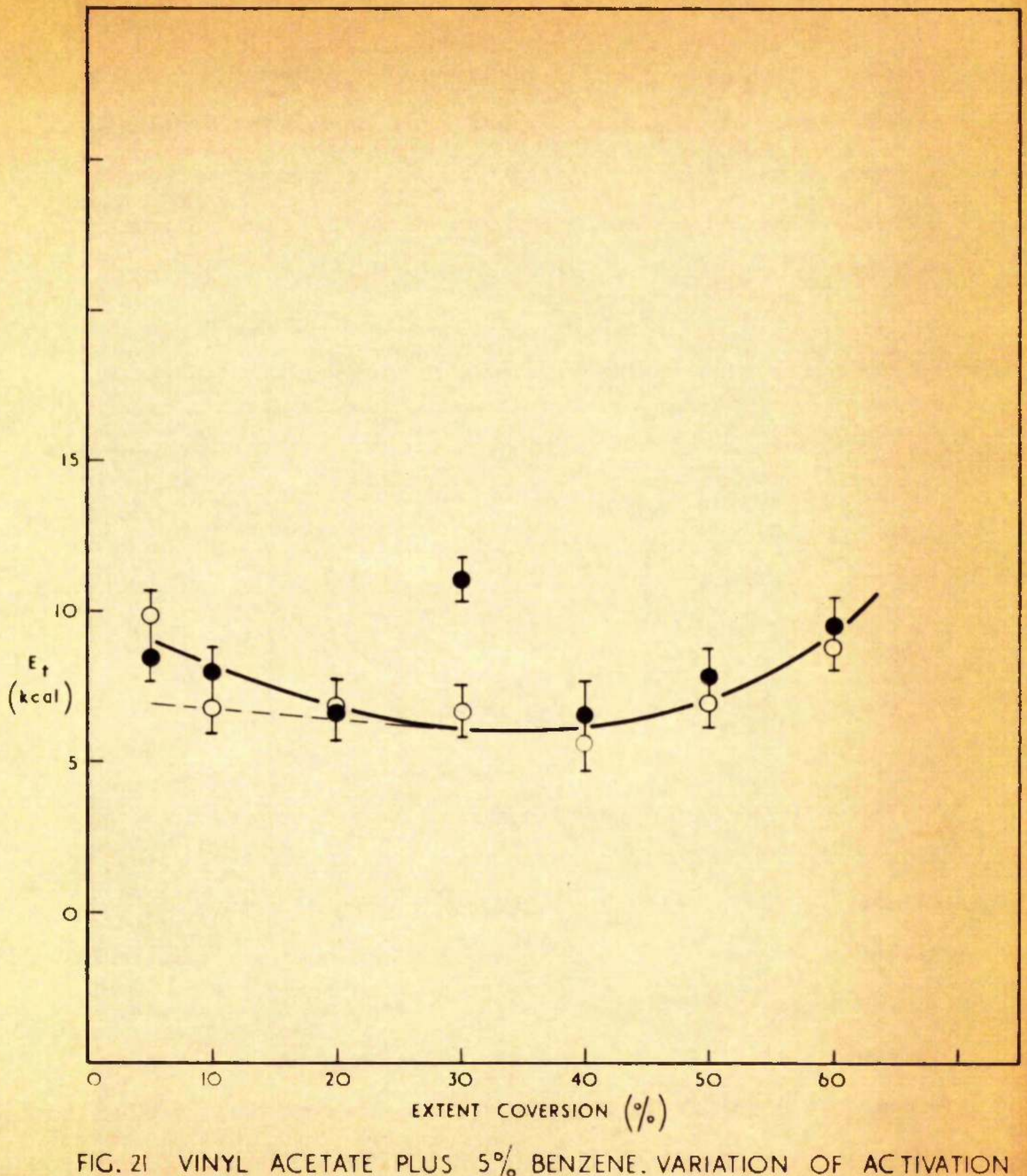


FIG. 21 VINYL ACETATE PLUS 5% BENZENE. VARIATION OF ACTIVATION ENERGY OF TERMINATION WITH CONVERSON

○ E_t FROM $\frac{1}{\tau}$ ● E_t FROM k_p/k_t

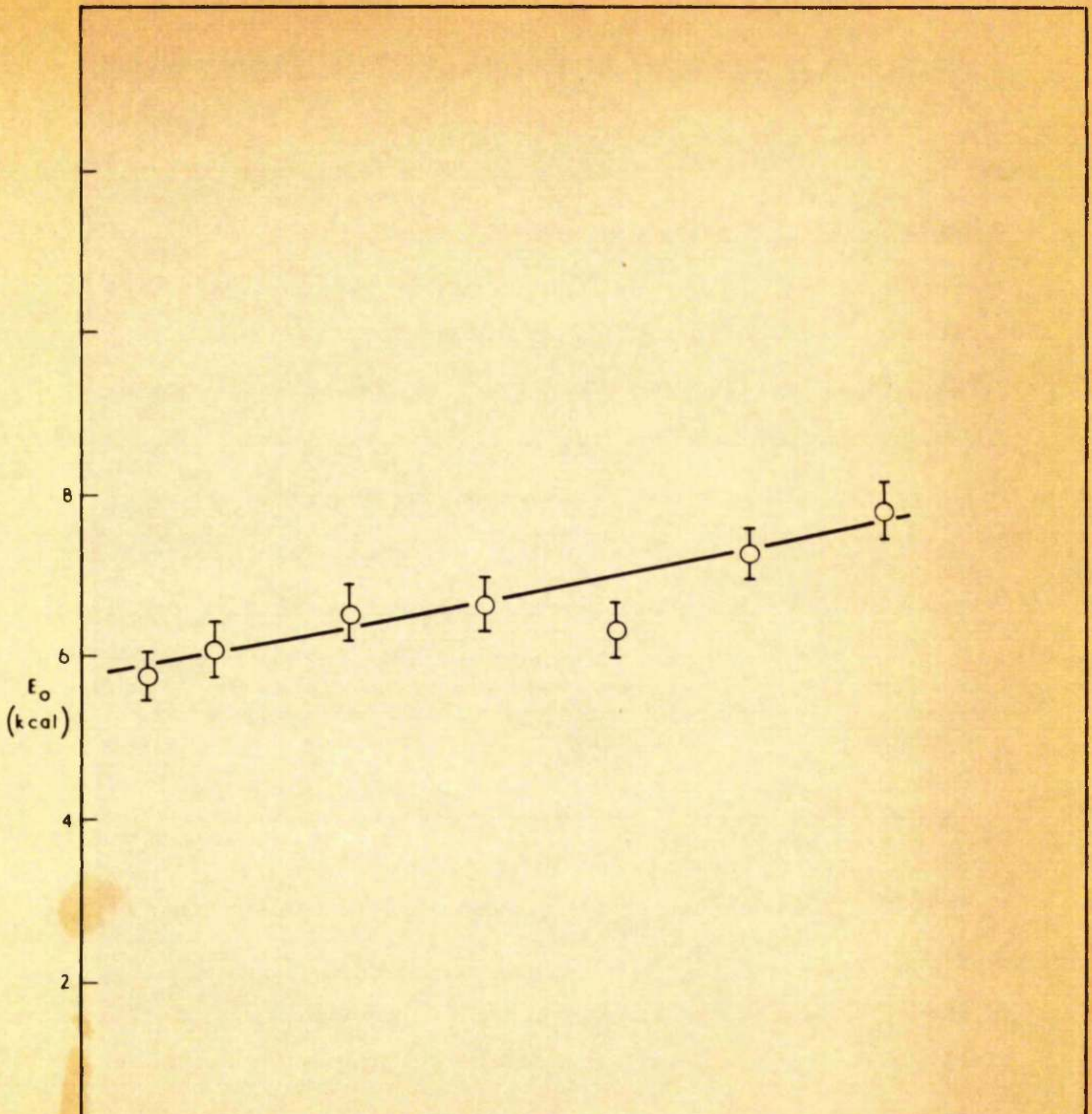


FIG. 22 VINYL ACETATE PLUS 5% BENZENE. VARIATION OF ACTIVATION ENERGY E_0 WITH CONVERSION

Polymerisation of Vinyl Acetate in the presence of 20% v/v Benzene.

The addition of 5% v/v benzene in place of 2.5% benzene to vinyl acetate caused a decrease in the rate of reaction but the other physical properties did not alter very significantly. Also, with these very small quantities of solvent, the dilution effect was very slight. To study this effect, and in an attempt to alter the kinetic chain lifetimes, etc. vinyl acetate was polymerised in the presence of 20% v/v benzene with an initiator concentration of 4×10^{-3} moles l^{-1}

Table 27. Variation of rate, kinetic chain lifetime and intensity exponent at 25°C and full light intensity.

Extent Conversion %	Rate of Reaction $\times 10^5$ moles l^{-1} s^{-1}	Kinetic Chain Lifetime s	Intensity Exponent
5	5.54	1.1(0)	0.71
10	4.71	1.3(7)	0.69
20	3.63	1.4(4)	0.65
30	3.25	1.2(3)	0.63
40	2.82	1.1(5)	0.63
50	2.48	1.6(2)	0.58
60	2.15	2.9(0)	0.51

The trend in the previous rates of reaction is reversed by the increased addition of solvent. The gel effect, which caused the increase in the rate of polymerisation has apparently been suppressed and the rate of reaction falls from zero conversion [Fig. 23]. The continuous fall in the rate of reaction is surprising. However, the rate of reaction at this dilution is extremely low and consequently the initiator may be partially consumed as the reaction proceeds. If we assume that an overall rate of reaction of 5×10^{-8} moles l^{-1} s^{-1} is applicable for all three temperatures and all intensities of incident light, then the time to reach 40% conversion

$$= \frac{40}{2.09} \doteqdot 19 \text{ hr.}, \text{ since } 5 \times 10^{-8} \text{ moles } l^{-1} s^{-1}$$

is equivalent to 2.09% polymerisation hr^{-1}.

Substituting for an initiator concentration of 4×10^{-3} moles l^{-1} and a rate of initiation of $2 \times 8.9 \times 10^{-9}$ moles l^{-1} s in the equation $I = 2\, k_D[\text{initiator}]$ we obtain a value of 1.11×10^{-8} s^{-1} for k_D where k_D is the velocity coefficient for the decomposition of the initiator. The concentration of the initiator can be obtained from the equation for a 1st order reaction, namely $C = C_0 e^{-k_D t}$ where C_0 is the original catalyst concentration. From this, at 40% conversion, the catalyst concentration is 1.87 moles l^{-1}. Since the rate of reaction is proportional to the concentration of initiator to the power ½ the decrease in the rate may be a result of this loss of initiator in the system.

The rate of reaction is also proportional to the concentration of monomer. This will decrease as the conversion

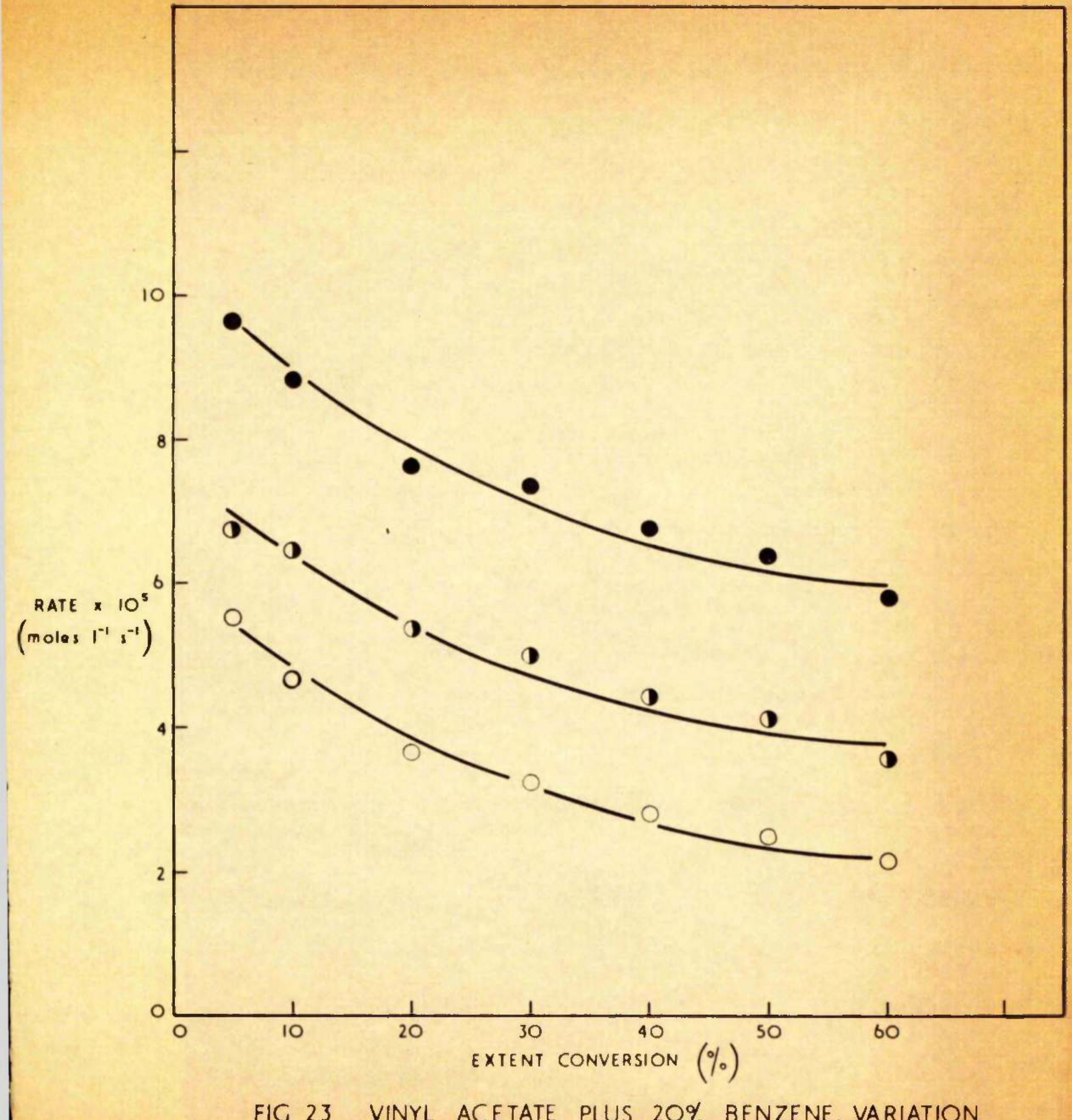


FIG 23 VINYL ACETATE PLUS 20% BENZENE. VARIATION OF RATE WITH CONVERSION

○ 25°C ◑ 35°C ● 45°C

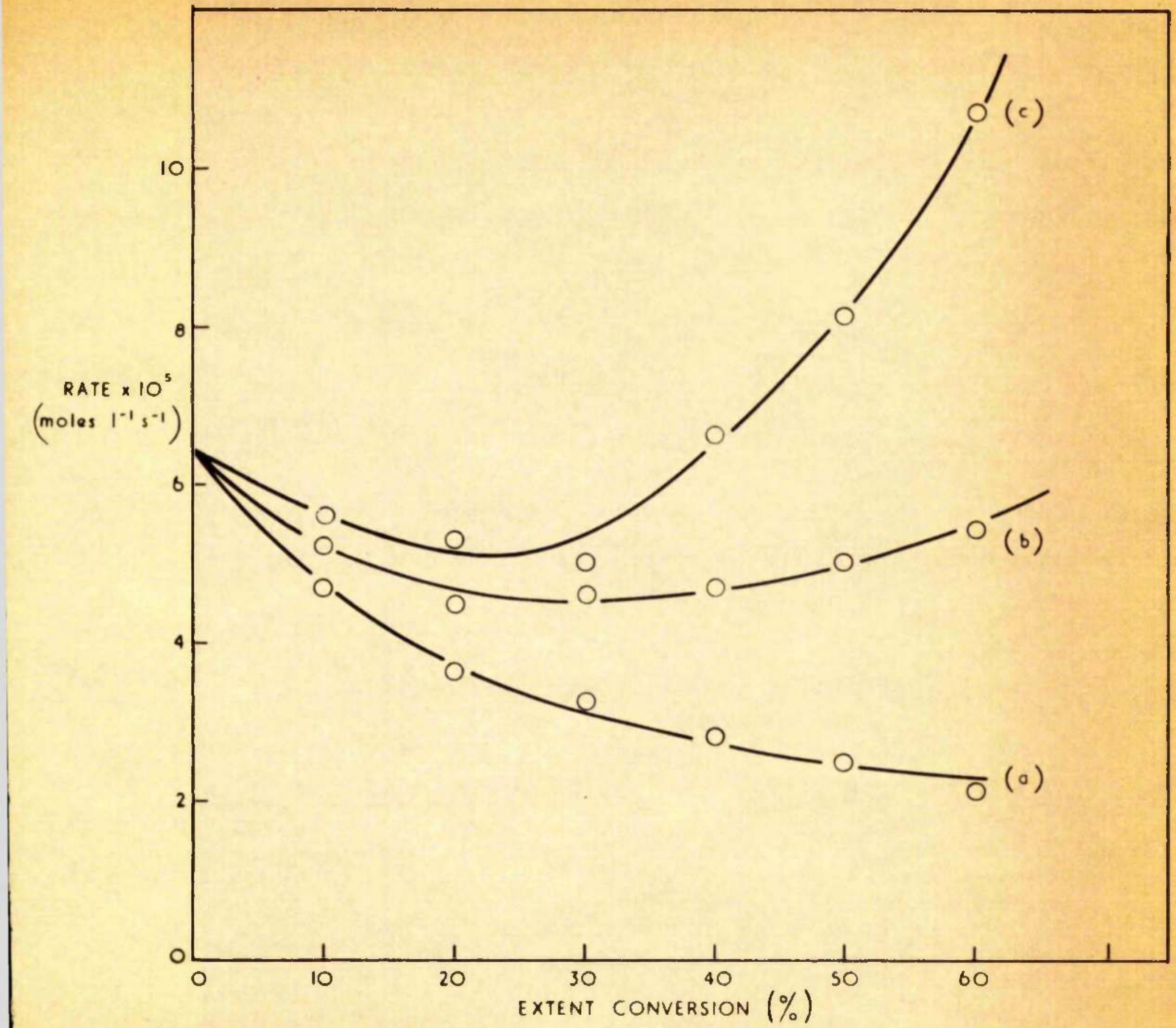


FIG 24 VINYL ACETATE PLUS 20% BENZENE

(a) ORIGINAL RATES AT 25°C FROM THERMOCOUPLE VESSEL

(b) RATES CORRECTED FOR DECREASE IN MONOMER CONCENTRATION

(c) RATES CORRECTED FOR DECREASE IN MONOMER AND CATALYST CONCENTRATION increases and so a correction must be applied for this effect. Consider the rate at 60% conversion:-

the rate of reaction at 60% conversion = 2.15 moles 1^{-1} s^{-1};

at zero conversion, the monomer is 80% of the reacting mixture, therefore at 60% conversion, the monomer is 32% of the reacting mixture.

Therefore the rate, corrected for the decrease in monomer

$$\text{concentration} = 2.15 \times \frac{80}{32} \text{ moles } 1^{-1} s^{-1},$$

$$= 5.27 \text{ moles } 1^{-1} s^{-1}.$$

If we assume that the initiator concentration has fallen to 1×10^{-3} moles 1^{-1} at 60% conversion, applying a further correction

$$\text{the rate of reaction} = 5.37 \times \frac{\sqrt{4}}{\sqrt{1}} .$$

$$= 10.7 \text{ moles } 1^{-1} s^{-1}.$$

<u>Table 28</u> Rates of reactions at 25°C and full light intensity corrected for a decrease in monomer and initiator concentration.

Extent Conversion %	Original Rates x 10^5 moles 1^{-1} s^{-1}	Rate x 10^5 after correction for monomer concentration moles 1^{-1} s^{-1}	Rate x 10^5 after correction for initiator and monomer concentration moles 1^{-1} s^{-1}
0	6.4	6.4	6.4
10	4.71	5.2	5.6
20	3.63	4.5	5.3
30	3.25	4.6	5.0
40	2.82	4.7	6.6
50	2.48	5.0	8.1
60	2.15	5.4	10.7

To explain this table of results it is necessary to assume initially that the initiator concentration is constant throughout the reaction. If the dilution effect of the solvent is sufficiently great to suppress the gel effect the actual rate of reaction should fall gradually from zero conversion due to a fall in monomer concentration. However, after correcting for this effect the rate of reaction still tends to fall from the initial rate of 6.4×10^{-6} moles $l^{-1} s^{-1}$. It should be noted that the plot increases after a minimum at 30% conversion.

Considering the original calculation in this section it seems reasonable to correct for a loss in initiator concentration. The chief problem associated with this calculation is determining the initiator value at any particular conversion. If we assume that the concentration of initiator has fallen to 1 x 10 moles l^{-1}, at 60% conversion the corrected rate of reaction is the one shown in the above table i.e. 10.7 moles $l^{-1} s^{-1}$. If we assume that the concentration at 60% conversion is 2×10^{-3} moles l^{-1} the corrected rate of reaction is 6.4 moles $l^{-1} s^{-1}$. It can be seen that the corrected rate is very sensitive to the choice of initiator concentration. The increase in the rate of reaction after 30% conversion is now more noticeable and indicates that the gel effect in the system has not been entirely suppressed despite the fact that benzene is a good solvent for polyvinyl acetate. It is difficult to gauge the extent of the effect since the increase is dependant on the initiator concentration chosen.

Due to the inaccuracy involved, the corrections for the decrease in monomer and initiator concentrations have only been applied to the results in Table 27 to demonstrate that the gel effect may still be operating on the system.

The increase in solvent concentration resulted in an increase in the values of the Kinetic chain lifetime [Fig.25]. At most conversions a value for E_t, which was in reasonable agreement with one derived from $^{k}p/k_t$, could be obtained from the calculated lifetimes. But at 50% and 60% conversion the values of the kinetic chain lifetimes at 25°C were too low to comply with those at 35°C and 45°C at a similar conversion. Therefore, the values of the kinetic chain lifetime which are quoted in Table 27 at 50% and 60% conversion are interpolated from the plot of $\log_{10} \frac{1}{\tau}$ against the reciprocal of the absolute temperature.

During the initial stages of polymerisation the value of the intensity exponent is rather high for the termination step to be second order with respect to the radical concentration. It was assumed that this was due to trace impurities and that the termination step was still second order.

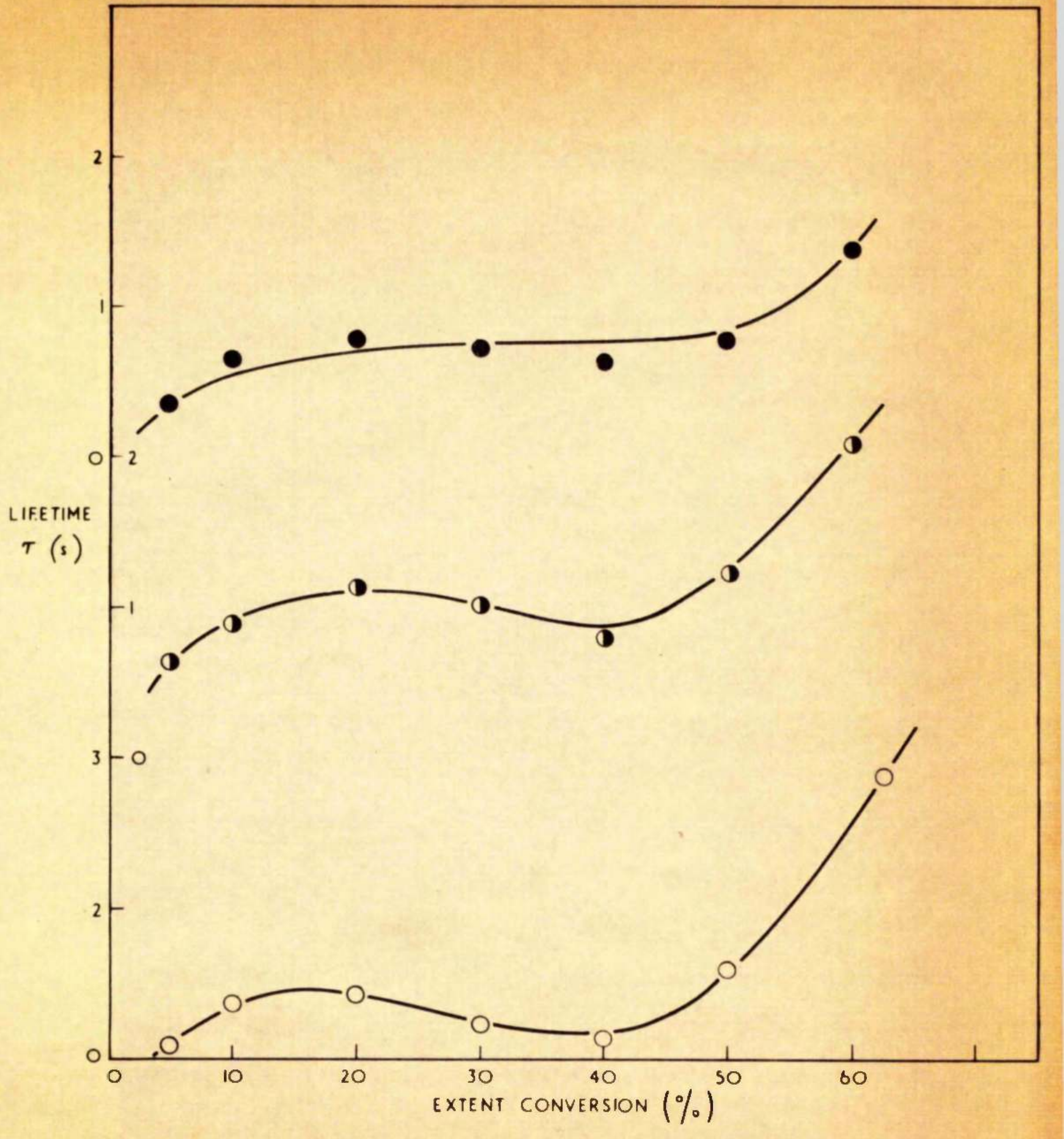


FIG. 25 VINYL ACETATE PLUS 20 % BENZENE. VARIATION OF KINETIC CHAIN LIFETIME WITH CONVERSION

○ 25°C ◐ 35°C ● 45°C

Table 29 Variation of rate of reaction, kinetic chain lifetime and intensity exponent at 35°C and full light intensity.

Extent Conversion %	Rate of Reaction x 10^6 moles l^{-1} s^{-1}	Kinetic Chain Lifetime s	Intensity Exponent
5	6.77	0.6(5)	0.59
10	6.45	0.9(0)	0.63
20	5.36	1.1(5)	0.59
30	4.99	1.0(5)	0.60
40	4.46	0.8(0)	0.50
50	4.16	1.2(3)	0.53
60	3.59	2.1(0)	0.56

Again there is an appreciable drop in the rate of reaction as the conversion increases [Fig.23] and the same corrections apply to this as to the decrease at 25°C. The kinetic chain lifetimes are greater than those found for a 5% benzene solution. The assumption, that the termination step is still second order with respect to the radical concentration, is verified by the intensity exponents obtained.

Table 30 Variation of rate of reaction, kinetic chain lifetime and intensity exponent at 45°C and full light intensity.

Extent Conversion %	Rate of Reaction $\times 10^5$ moles $l^{-1} s^{-1}$	Kinetic Chain Lifetime s	Intensity Exponent
5	9.64	0.3(6)	0.59
10	8.83	0.6(7)	0.59
20	7.64	0.8(0)	0.54
30	7.36	0.7(2)	0.54
40	6.76	0.6(5)	0.55
50	6.37	0.8(0)	0.56
60	5.80	1.4	0.58

A similar decrease in rate is obtained at 45°C and the kinetic chain lifetimes are greater than with 5% benzene. The intensity exponents are in accord with second order termination.

Table 31 Variation of velocity coefficients at 25°C and full light intensity.

Extent Conversion %	$k_p/k_t \times 10^3$	k_p l mole^{-1} s^{-1}	$k_t \times 10^{-6}$ l mole^{-1} s^{-1}
5	6.73	62	9.2(9)
10	7.04	42	5.9(9)
20	5.27	28	5.4(1)
30	2.98	4	1.3(5)
40	2.09	18	8.5(0)
50	1.58	7	4.2(8)
60	3.15	4	1.3(4)

The values for the velocity coefficients are lower than the corresponding values at 5% benzene indicating that the propagation and termination steps have become more difficult by increasing the concentration of solvent.

Table 32 Variation of velocity coefficients at 35°C and full light intensity.

Extent Conversion %	k_p/k_t x 10^6	k_p l $mole^{-1}$ s^{-1}	k_t x 10^{-7} l $mole^{-1}$ s^{-1}
5	2.91	78	2.6(7)
10	7.61	105	1.3(9)
20	7.96	70	0.8(5)
30	6.80	70	1.0(2)
40	4.39	75	1.7(5)
50	5.51	40	0.7(5)
60	6.70	17	0.2(5)

Table 33 Variation of velocity coefficients at 45°C and full light intensity.

Extent Conversion %	k_p/k_t x 10^6	k_p l $mole^{-1}$ s^{-1}	k_t x 10^{-7} l $mole^{-1}$ s^{-1}
5	5.03	440	8.6(8)
10	5.99	150	2.5(0)
20	6.80	120	1.7(5)
30	5.33	115	2.1(4)
40	5.02	135	2.6(8)
50	5.19	90	1.7(5)
60	6.52	40	0.6(0)

The velocity coefficients at 35°C and 45°C confirm that the addition of further solvent makes the propagation and termination steps more difficult. This is also reflected in the values of the activation energies.

Table 34 Variation of activation energies with extent conversion.

Extent Conversion %	E_0 k. cals.	E_t from k_p/k_t k. cals.	E_t from τ k.cals.
5	5.4	7.2	12.0
10	6.1	9.1	13.0
20	7.3	9.9	12.0
30	8.1	5.1	10.3
40	8.6	11.8	10.4
50	9.3	13.3	12.0
60	9.7	5.4	12.0

The overall activation energy of the system increases with extent conversion [Fig.26]. At some conversions the difference between the values of E_t derived from k_p/k_t and E_t derived from τ are quite appreciable [Fig.27] although the general trend is again of an increase in value with conversion. No actual line has been drawn showing the variation in E_t with conversion. Instead, it is considered more reasonable to assume that the value of E_t at any particular conversion will be in the area bounded by the two broken lines. Since the overall activation energy and the activation energy of termination both increase with conversion, E_p must also follow this pattern.

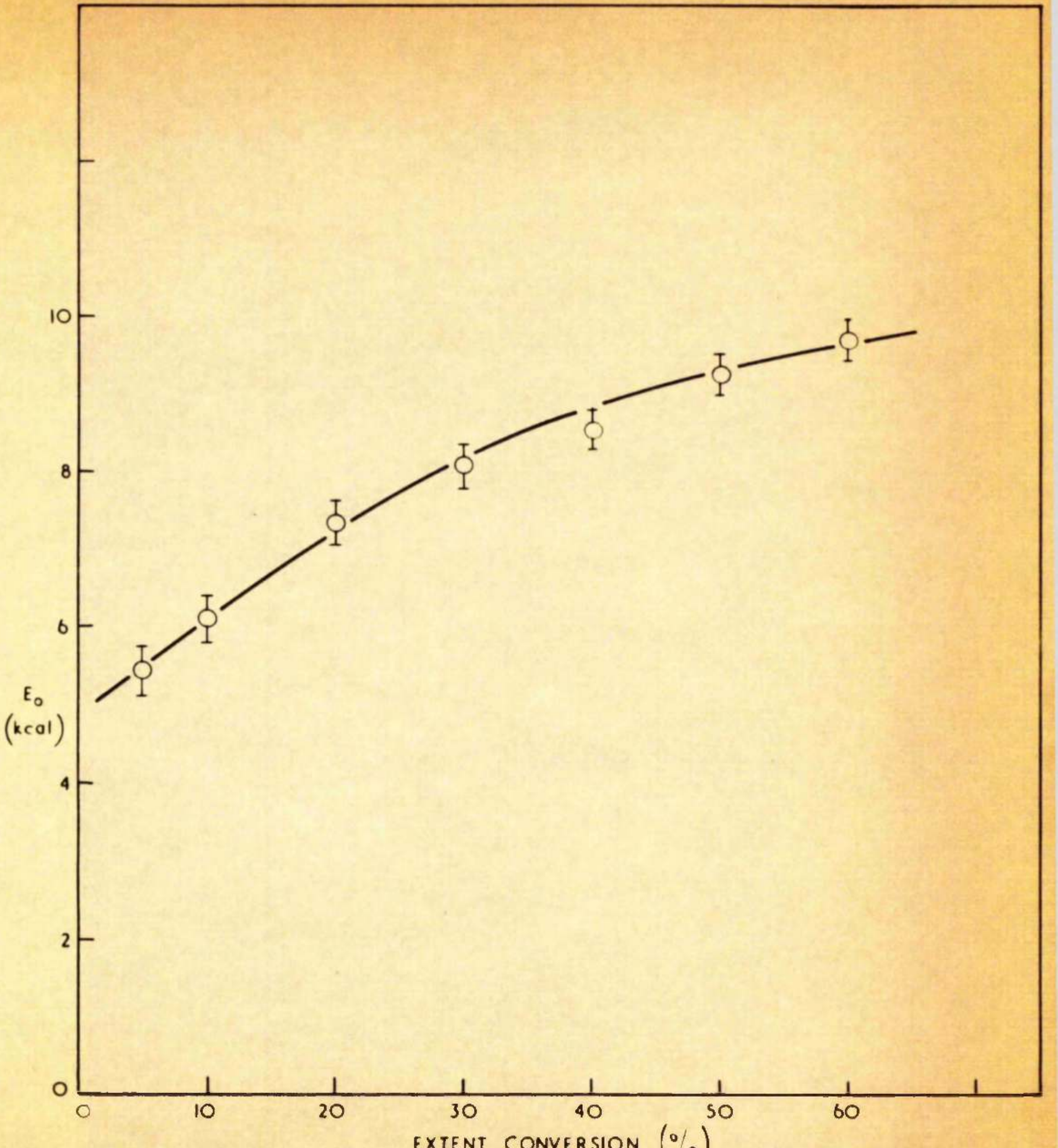


FIG 26 VINYL ACETATE PLUS 20% BENZENE. VARIATION OF ACTIVATION ENERGY E_o WITH CONVERSION

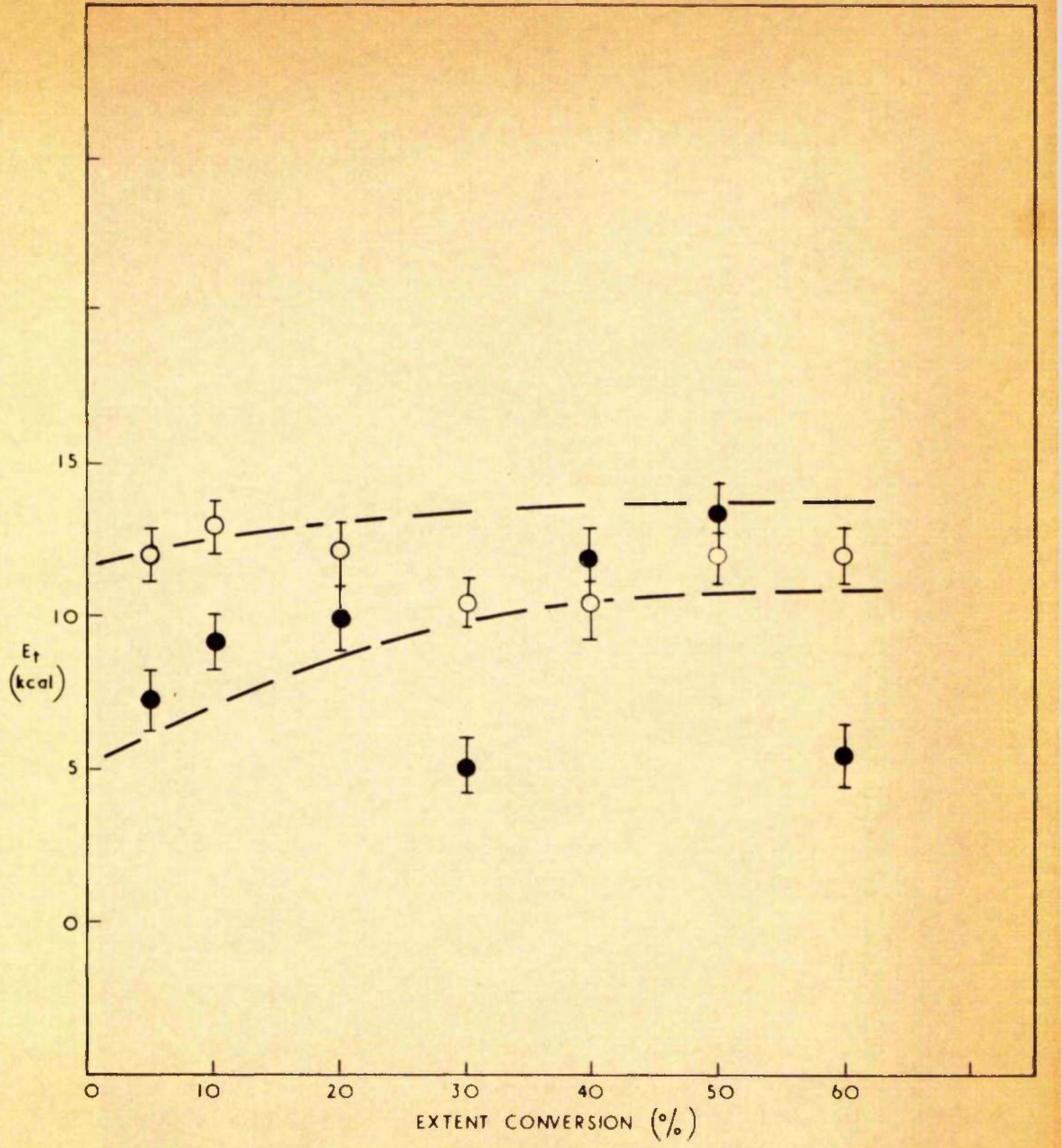


FIG 27 VINYL ACETATE PLUS 20% BENZENE. VARIATION OF ACTIVATION ENERGY OF TERMINATION WITH CONVERSION

○ E_t FROM $\frac{1}{T}$ ● E_t FROM k_p/k_t

Although the second decimal figure has been quoted regularly for kinetic chain lifetimes, rates of reaction and velocity coefficients in all sections, little reliance can be placed upon it. It has been included to give an indication of the value of the next digit and to facilitate the calculation of further quantities e.g. the overall activation energy and the activation energy of termination.

The non-stationary state results have been reviewed in sections determined by the concentrations of solvent. The variation in physical constants at particular conversions for varying concentrations of solvent will be demonstrated in the discussion of results.

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

The ratio of the velocity coefficient of transfer to the velocity coefficient of propagation is termed the transfer constant and is often denoted by C_s.

If the transfer reaction is

$$R^{\circ} + S \longrightarrow P + S^{\circ} \qquad \text{Rate} = k_{tr}[R^{\circ}][S]$$

then the transfer constant $C_s = k_{tr}/k_p$.

The polymerisation of vinyl acetate in the presence of various quantities of benzene was carried out at different temperatures. From the transfer constants at these temperatures a value for the activation energy of transfer was obtained.

The following method of deriving an equation to determine C_s was developed by Mayo.[23]

The degree of polymerisation $\overline{DP}$ is the ratio of the rate of growth of the polymer chain to the rate of termination of the chain,

i.e. $$\overline{DP} = \frac{k_p[R^\circ]_s[M]}{k_t[R^\circ]_s^2 + k_{tr}[R^\circ]_s[S] + k_{tr'}[R^\circ]_s[M]} \quad ..(22)$$

where $k_{tr'}$ = velocity coefficient of monomer transfer. (The other symbols have already been defined).

From equation (1) $[R^\circ]_s = \frac{I^{1/2}}{k_t^{1/2}}$,

$$\therefore \frac{1}{\overline{DP}} = \frac{k_t^{1/2} I^{1/2}}{k_p[M]} + \frac{k_{tr}}{k_p}\frac{[S]}{[M]} + \frac{k_{tr'}}{k_p}. \quad ....(23)$$

Let $\overline{DP}_0$ = The degree of polymerisation when $[S] = 0$,

$$\therefore \frac{1}{\overline{DP}_0} = \frac{k_t^{1/2} I^{1/2}}{k_p[M]} + \frac{k_{tr'}}{k_p}.$$

$\therefore$ Substituting $\frac{1}{\overline{DP}_0}$ in equation (23) gives

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + \frac{C_s[S]}{[M]}. \quad ....(24)$$

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

Before C_s can be determined the molecular weight of the polymer has to be found. The following section describes how this was accomplished.

Determination of Molecular Weights of the Polymer.

The intrinsic viscosity η_i of a dilute polymer solution is related to the weight average molecular weight M_w of the polymer by the modified Staudinger equation which is expressed as;

$$\eta_i = K.M_w^{\alpha}$$

where K and α are constants for the polymer-solvent system.

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 flow time t for the solution to the flow time t_0 for the solvent gives the relative viscosity.

$$\text{i.e.} \quad \eta_r = \frac{t}{t_0}$$

and the specific viscosity $\eta_{sp} = \eta_r - 1$.

The ratio of the specific viscosity to the concentration of the polymer, expressed in gms/100 ml., is then plotted against the concentration.

$$\text{Since } \left[\eta_i\right] = \lim_{C \to 0} \frac{\eta_{sp}}{C}$$

the intrinsic viscosity is obtained by extrapolation to zero concentration.

From light scattering measurements of a series of low conversion polyvinyl acetates, both fractionated and unfractionated, Stockmayer and Howard[57] obtained the following equations:

$$\log \bar{M}_v = 5.44 + 1.4 \log [\eta_i] , \quad \ldots\ldots\ldots(25)$$

where $\bar{M}_v$ = viscosity average molecular weight

$$\text{and} \quad \frac{\bar{M}_v}{\bar{M}_n} = 1.85 , \quad \ldots\ldots\ldots\ldots(26)$$

where $\bar{M}_n$ = number average moleculareweight

and from these derived the relationship that

$$\log \overline{DP}_n = 3.24 + 1.40 \log [\eta_i] .$$

The number average degree of polymerisation was obtained from this relationship and plotted against $\frac{[S]}{[M]}$ to obtain the chain transfer constant C_s.

Experimentel Determination of Transfer Constants.

The polymerisation experiments were carried out in ordinary dilatometers of approximately 15 ml. capacity and 1.5 mm. veridia stems. The dilatometers were calibrated with acetone (A.R. grade reagent) and the initiator introduced in a chloroform solution such that the initiator concentration was 4×10^{-3} moles l^{-1}. The solvent was pumped off on the vacuum line and a known quantity of purified benzene added to the dilatometer. This was thoroughly degassed by freezing, evacuating and heating up to room temperature until all the air was removed. The required quantity of monomer was then distilled into the dilatometer which was sealed under vacuum. The vessel was placed in a thermostatically controlled bath and the polymerisation taken to be about 7% conversion. That data of Starkweather and Taylor[20] and the interpolation of Matheson <u>et al.</u>[46] were used to calculate the densities of vinyl acetate monomer and polymer and from this it was calculated that at 25°C, 100% conversion was equivalent to 22.1% contraction.

The contents of the dilatometer, vinyl acetate, benzene and polymer were dissolved in 100 ml. of benzene [A.R. grade reagent] in a 1 litre round bottom flask. The solution was frozen on the sides of the flask by rotating it in an acetone-dricold mixture.

The flask was attached to the vacuum line and evacuated. The benzene sublimed, taking with it the residual monomeric vinyl acetate while the cooling induced by the sublimation kept the mixture frozen on the sides of the flask. After 6 hr. the flask was removed from the vacuum line and the polymer was free from benzene.

The polymer had been originally precipitated to remove any initiator but it was found that this made no difference to the intrinsic viscosity.

Viscosity Measurements.

A known weight of polymer, about 0.05 gm., was dissolved in 50 ml. of acetone [A.R. grade reagent] and filtered. The intrinsic viscosity of each polymer was determined using a Ubbelohde viscometer modified so that the polymer solutions could be diluted *in situ*.

Temperature	Intrinsic Viscosity	Molecular Weight $\times 10^5$	$\frac{S}{M}\%$	$C_s \times 10^4$
	2.15	5.07	0	
25°C	1.93	4.36	2.5	11.5
	1.68	3.58	5	
	1.10	1.99	20	
	2.16	5.11	5	
35°C	1.41	2.81	15	11.0
	0.99	1.71	25	
	2.21	5.27	2.5	
45°C	1.74	3.76	5	12.0
	1.12	2.03	20	

From Fig.28 it will be seen that the plot of $\log_{10} C_s$ against the reciprocal of absolute temperature is a horizonal line.

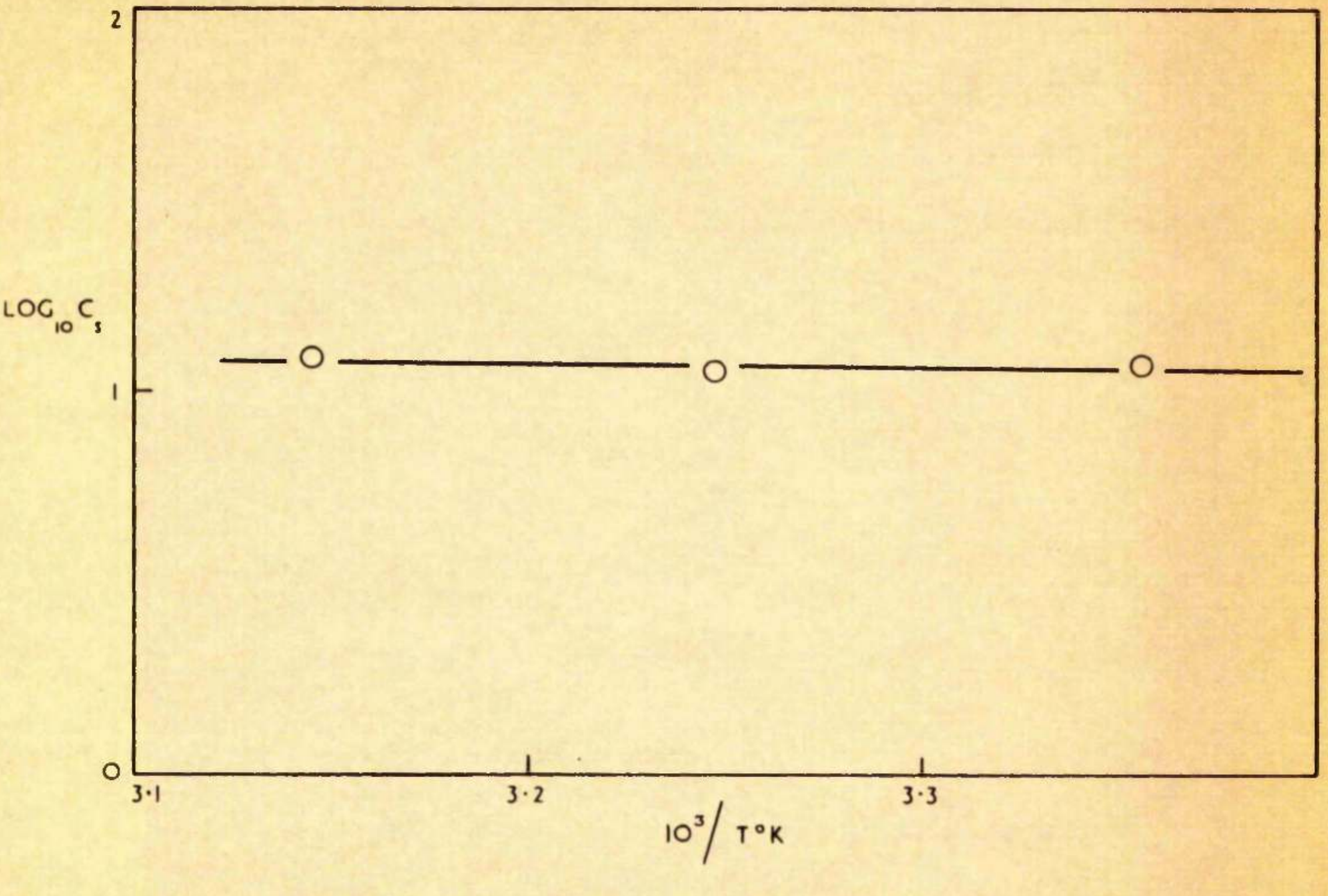


FIG 28 DETERMINATION OF $E_p - E_{tr}$

C_s is the ratio of k_{tr}/k_p. Using the Arrhenius relationship that $k = Ae^{-E/RT}$, the equation

$\log_{10} k_{tr}/k_p = \frac{1}{2.303RT}(E_p - E_{tr})$ + Constant, can be developed, where E_{tr} is the activation energy of the transfer reaction. Therefore, if $\log_{10} C_s$ is plotted against the reciprocal of the absolute temperature, a value of $E_p - E_{tr}$ can be obtained from the gradient of the straight line [Fig.28].

From the plot, $E_p - E_{tr} = 0$

From the bulk polymerisation $E_p = 4.8$ k.cals.

$\therefore E_{tr} = 4.8$ k.cals.

RADIOACTIVE TRACER EXPERIMENTS

Vinyl acetate was polymerised in the presence of radio active benzene to determine quantitatively the number of benzene molecules present in each polymer chain. The variation in the results of other workers has already been discussed and in this case the radio benzene was purified by the growth of a single crystal.

Experimental Details.

0.5 Mille-curies of benzene, prepared[49] from the trimerisation of $^{14}\mathrm{CH}\equiv{}^{14}\mathrm{CH}$, was supplied by the Radio-Chemical Centre, Amersham, in a break seal ampoule. This was attached to the vacuum line by a B14 cone and the space above the break-seal evacuated. 15 ml. of inactive benzene, purified by single crystal growth, was degassed in a neighbouring reservoir on the vacuum line. The break seal was then broken using a stainless steel ball bearing and the inactive benzene was distilled into the ampoule using liquid nitrogen as coolant. The solvent was then distilled to and fro between the reservoir and the ampoule to ensure that the 15 ml. of benzene contained as much activity as possible.

Two crystal growth tubes, approximately 1.5 cm. in diameter were filled with the active solvent and single crystals grown as previously described. One of the crystals obtained was used for this series of experiments while the other was stored in a deep freeze for future use.

5 ml. of active benzene from the single crystal were added to a 25 ml. graduated vessel and made up to the mark with inactive purified benzene and this solution provided the solvent for the polymerisation experiments. This was an extremely active sample and was too active to calibrate, especially by gas counting. Using a micrometer syringe, 0.1 ml. of the solvent from the single crystal were added to a 50 ml. graduated vessel which contained about 49 ml. of pure benzene. It was made up to the mark and well shaken. This solution was much less active and consequently there was less danger when working with it. More dilute solutions of known concentration were prepared using this 50 ml. solution as stock and these were used to construct a calibration curve to determine the activity of the benzene used in the polymerisation experiments.

The activity, both of the solvent and the polymer, was obtained by two methods:-

(i) Conversion by combustion to carbon dioxide and the activity of the resultant gas determined in a Geiger tube, and

(ii) addition of the solvent or polymer solution to a scintillation medium and the activity determined from the number of photons created when the scintillator is excited by the nuclear radiation.

Preparation of Radio-Active Polymers.

Vinyl acetate was polymerised in the presence of 2.5%, 5% and 20% v/v radio-active benzene. The polymerisation of vinyl acetate with 5% v/v radio solvent was carried out in a non-stationary state dilatometer of the type that has been previously described, while the other two polymerisation reactions were carried out in ordinary dilatometers. The polymers were then prepared by the method described for the determination of chain transfer constants.

A sample of the distillate from each freeze drying operation was taken and the activity of the solvent determined by scintillation counting. The freeze drying process was repeated until there was no indication of activity in the distillate. Generally the process had to be repeated 4 times.

The molecular weights of the resultant radio-active polymers were determined by viscosity measurements in a modified Ubbelohde viscometer.

Gas Counting

If benzene labelled with C^{14} is polymerised in the presence of vinyl acetate and a number of benzene units are incorporated in the polymer molecule then the chemical composition of the polymer can be written as $(C_4H_6O_2)_n(C_6H_6)_m$ where n is the average degree of polymerisation $\overline{DP}_n$, and m is the number of benzene fragments per polymer molecule.

Since the benzene is labelled with C^{14}

$$\frac{\text{Specific activity of carbon in polymer}}{\text{Specific activity of carbon in benzene}} = \frac{6m}{4n + 6m}.$$

If the molecular weight of the polymer is large, 4n is much greater than 6m and the equation becomes

$$\frac{\text{Specific activity of the polymer}}{\text{Specific activity of the benzene}} = \frac{6m}{4n}.$$

$\therefore$ The number of fragments of benzene, m =

$$\frac{4\ n \times \text{specific activity of the polymer}}{6 \times \text{specific activity of the benzene}}.$$

The activity of the solvent and polymer can be found by combusting the materials in a stream of oxygen and filling a Geiger tube to a fixed pressure with the resulting carbon dioxide gas. If a constant voltage is applied across the elctrodes of this tube the number of electrical pulses or counts obtained in a definite interval of time is a measure of the activity of the gas

Combustion Procedure.

The combustion of both the polymer and the benzene was carried out in a Baird and Tatlock rapid micro-combustion unit. The essential feature of this unit is the combustion chamber which is provided with baffle plates, where complete combustion of the sample occurs without the use of a catalyst.

Oxygen for the combustion is purified by passing it through a preheater tube at approximately 700°C and through scavenging tubes containing anhydrone and soda asbestos. The gas then passes through a rotameter and the flow of oxygen into the quartz combustion tube is maintained at a rate of 50 ml./min. by means of a screw clip.

The technique for the combustion of the solvent is now described in detail as two serious explosions occurred before the method was evolved.

A piece of glass tubing, 0.3 mm. in diameter was sealed at one end and a few crystals of potassium chlorate inserted into it. The other end of the tubing was drawn to a fine capillary so that the main body of the vessel was approximately 1.5 cm. in length. The central area of the vessel was heated gently in a small gas flame, withdrawn and the capillary placed in the solvent which was to be oxidised. As the vessel cooled a small quantity of the solvent was drawn into the tube. The vessel was centrifuged so that the contents were thrown to the sealed end and no liquid remained in the capillary. It was then inserted into the quartz combustion tube until it was approximatel 10 cm. from the entrance of the combustion chamber. The sample burner was lit and adjusted to give the smallest possible flame. It was slowly moved forward until it was about 1 cm. behind the sealed end of the vessel. In this position there was sufficient heat present to vaporise the benzene very slowly. As there was no large concentration of benzene vapour now being carried into the combustion chamber, no explosions were experienced.

By contrast, the polymer was burnt in an open platinum boat. The movable burner was now advanced until it was underneath the boat and the flame gradually increased until the sample was completely vaporised.

The vapours passed into the baffled combustion tube, maintained at approximately 900°C, where complete combustion occurred. The gases then passed over a roll of silver gauze heated to approximately 700°C where any halogen or sulphur oxidation products were retained.

The remaining products of the combustion were water vapour, oxides of nitrogen, carbon dioxide and excess oxygen. These gases were passed into an anhydrone tube to remove any water vapour, through a tube containing granules of basic manganese dioxide to remove any oxides of nitrogen and then through another anhydrone tube to remove any remaining traces of water vapour.

The carbon dioxide and excess oxygen were passed through a spiral coil [Fig.29] which was cooled by liquid oxygen and open to the atmosphere via a 2-way T. tap. When all the carbon dioxide had condensed, the coil was isolated

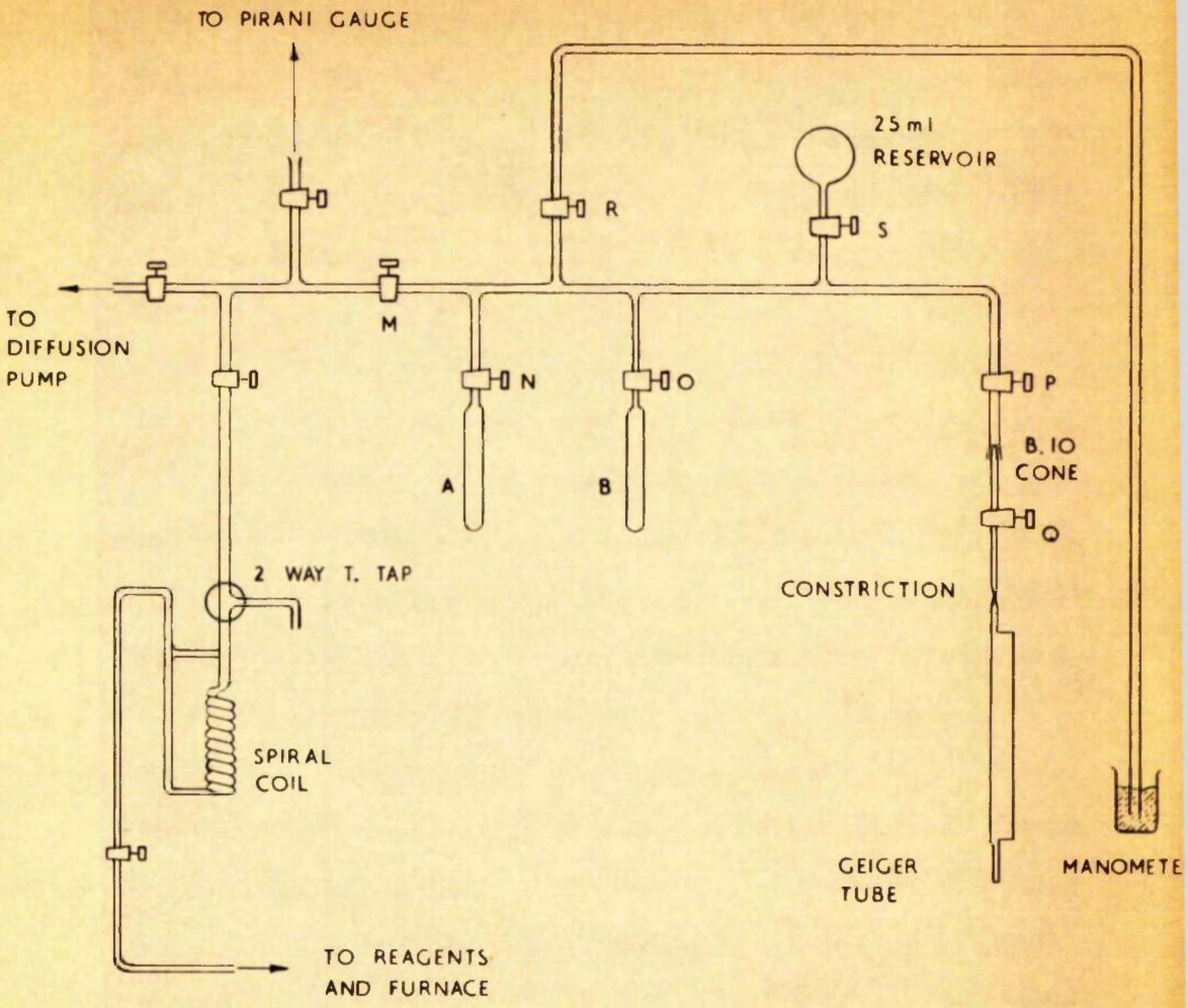


FIG 29 COMBUSTION AND MEASUREMENT APPARATUS FOR GAS COUNTING

from the furnace and opened slowly to the vacuum system using the 2-way T tap. The carbon dioxide was thoroughly degassed and collected in a receiving tube A on the vacuum line, and kept surrounded by liquid oxygen. Approximately 2 ml. of carbon disulphide [A.R. grade reagent] were placed in another trap B and thoroughly degassed.

The Geiger tube was attached to the vacuum line and the total system evacuated for 1 hr. With vacuum taps M, O and Q closed and taps P,R and S open the carbon dioxide was admitted into the system. A cathetometer was focussed on the mercury meniscus in the 2.5 mm. capillary tubing manometer and tap N was closed when this had fallen 15 cm. Tap Q was then opened very carefully and closed when the meniscus had risen 6 cm. No difficulty was encountered in measuring the pressure to within 0.001 cm. using the cathetometer. If the measurement was incorrect then the gas could be recondensed and the procedure repeated. The remaining carbon dioxide was recondensed in trap A and the measured quantity of gas frozen at the foot of the Geiger tube. The same procedure was repeated for carbon disulphide but in this case only 3 cm. of gas were admitted to the Geiger tube. It was more difficult to control the addition of the carbon disulphide and once it was in the tube no further adjustment could be made.

The mixture of gases was thoroughly degassed to remove any air which had leaked into the system during the measurement procedure. This also served to mix the vapours. The gas mixture was then frozen in the foot of the Geiger tube and the system evacuated until the reading on the Pirani gauge was 10^{-4} mm. of mercury. The tube was then sealed off at the constriction.

Carbon dioxide alone is a poor counting gas and its behaviour is not improved by the addition of the usual quenching vapours such as alcohol or xylene. However, it has been found that the addition of carbon disulphide vapour produces a mixture with good counting characteristics.[58,59]

Counting Equipment.

The circuit diagram for the gas counting equipment is shown in Fig. 30.

The probe unit, type No. 1104, supplied by Ericsson Telephones Ltd., is designed to minimise counting errors, which are liable to occur in a Geiger-Muller tube. The main sources of error are spurious pulses which may arise in the tube, and the unknown dead time of the tube. With this unit the counting of spurious pulses is prevented by a reduction in voltage brought about by a quench pulse while the dead time is replaced by the quench pulse.

The stabilised power unit, type No. N103, supplied by

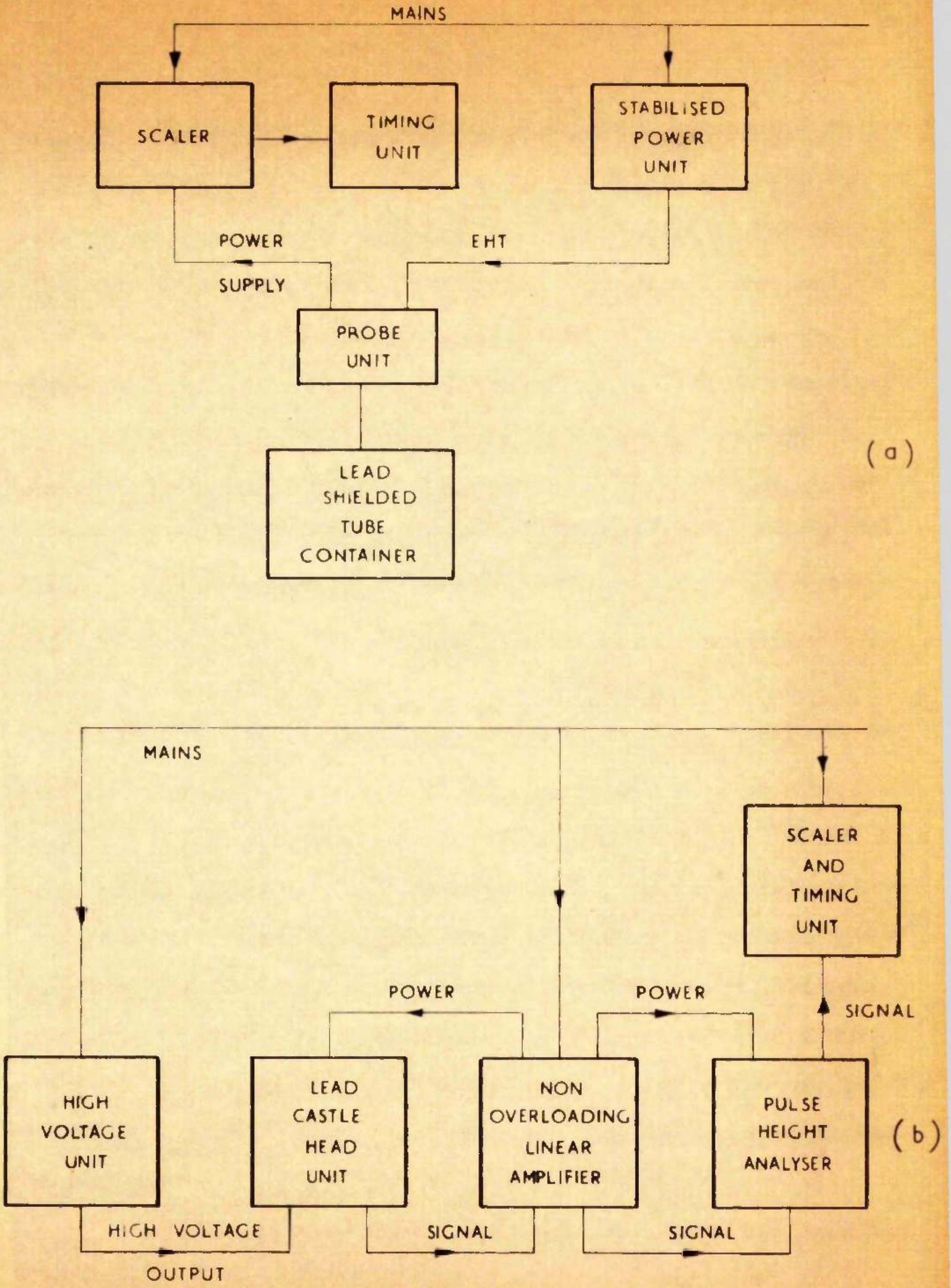


FIG 30 CIRCUIT DIAGRAMS FOR (a) THE GAS AND (b) THE SCINTILLATION COUNTING EQUIPMENT

Dynatron Radio is designed to give a stable source of high voltage free from ripples and pulses, and produces a variable stabilised voltage from 300 to 3,300 volts at a positive or negative potential with respect to the chassis.

The scaler, type No. 1009E, was also obtained from Dynatron Radio. The function of this unit is to count random or regular electrical impulses whose amplitude is greater than some predetermined value in the range + 5 and + 50 volts. The electrical impulses to be counted can be fed directly to the normal input circuit or derived from a probe unit. The pulses are applied to the discriminator. The discriminator bias may be set at any value between + 5 and + 50 volts so that pulses below this predetermined value can be rejected.

The paralysis time on the scaler can be preset in steps over a range extending from 5 to 10,000 micro-seconds. This circuit causes the scaler to become ineffective for the preset period immediately after it has been triggered by a pulse. This facility is used to avoid the spurious discharges which can occur in a Geiger-Muller tube.

The scaling unit was operated in conjunction with a cooling unit to ensure a minimum temperature increase within the scaler.

The Timing Unit, type No. N108A, was also supplied by Dynatron Radio. It was used to switch off the scaler either at a preset time or after a preset number of counts had been recorded. The unit has a maximum time store of 99,999 seconds and a maximum count store of 999,999 counts.

Counting Procedure

The Geiger tube was placed in a lead shielded box and connected to the probe unit, the inner wire of the coaxial cable being linked to the thin wire anode of the tube. The minimum voltage required to cause a discharge was found. The vapour mixture was allowed to age for 4 hr. at a voltage slightly above the threshold voltage. The plateau region [Fig.31] was established by counting at 20 volt intervals for 3000 seconds. When the mid-point of the plateau had been found the sample was counted at this particular voltage for at least 10,000 seconds. It is necessary to count for a fairly long period of time since the discharges occur in a random manner and short counts can give very misleading results. Before counting the instruments were switched on and allowed to stabilise for 1 hr.

Various dilutions of the calibration solution were burnt and a plot of counts per minute against dilution obtained [Fig.32].

In order to interpret the results, it is necessary to know the background activity. This is the activity associated with the materials of construction of the Geiger-Muller tube,

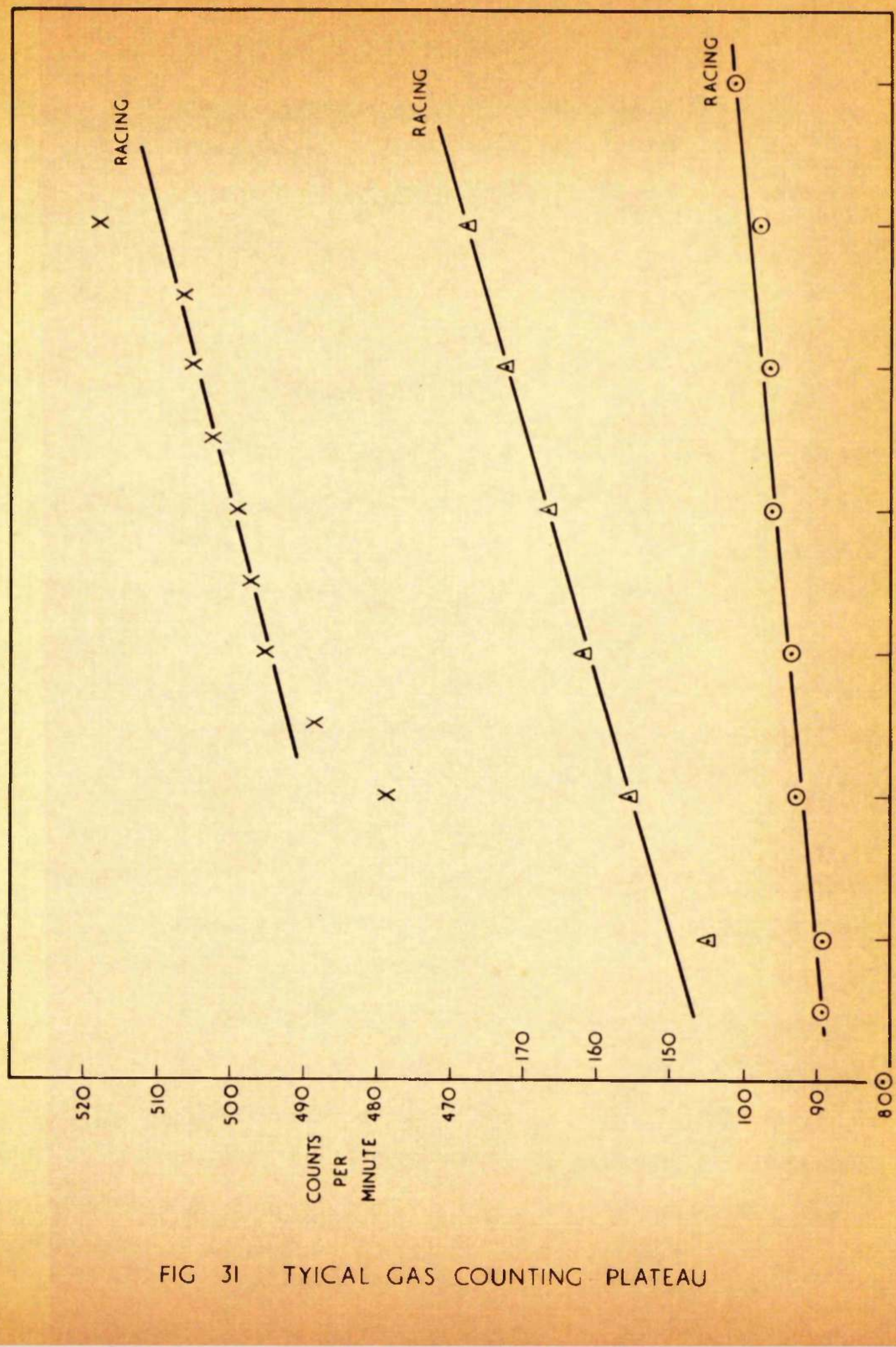


FIG 31 TYICAL GAS COUNTING PLATEAU

the penetration of ionising radiations through the walls of the tube and the natural activity of the polymer and benzene. It was measured by (1) allowing a piece of dricold to vaporise in the combustion tube and (2) combusting a sample of inactive polymer and counting in the normal way. The background count obtained was found to be constant within the limits of experimental accuracy.

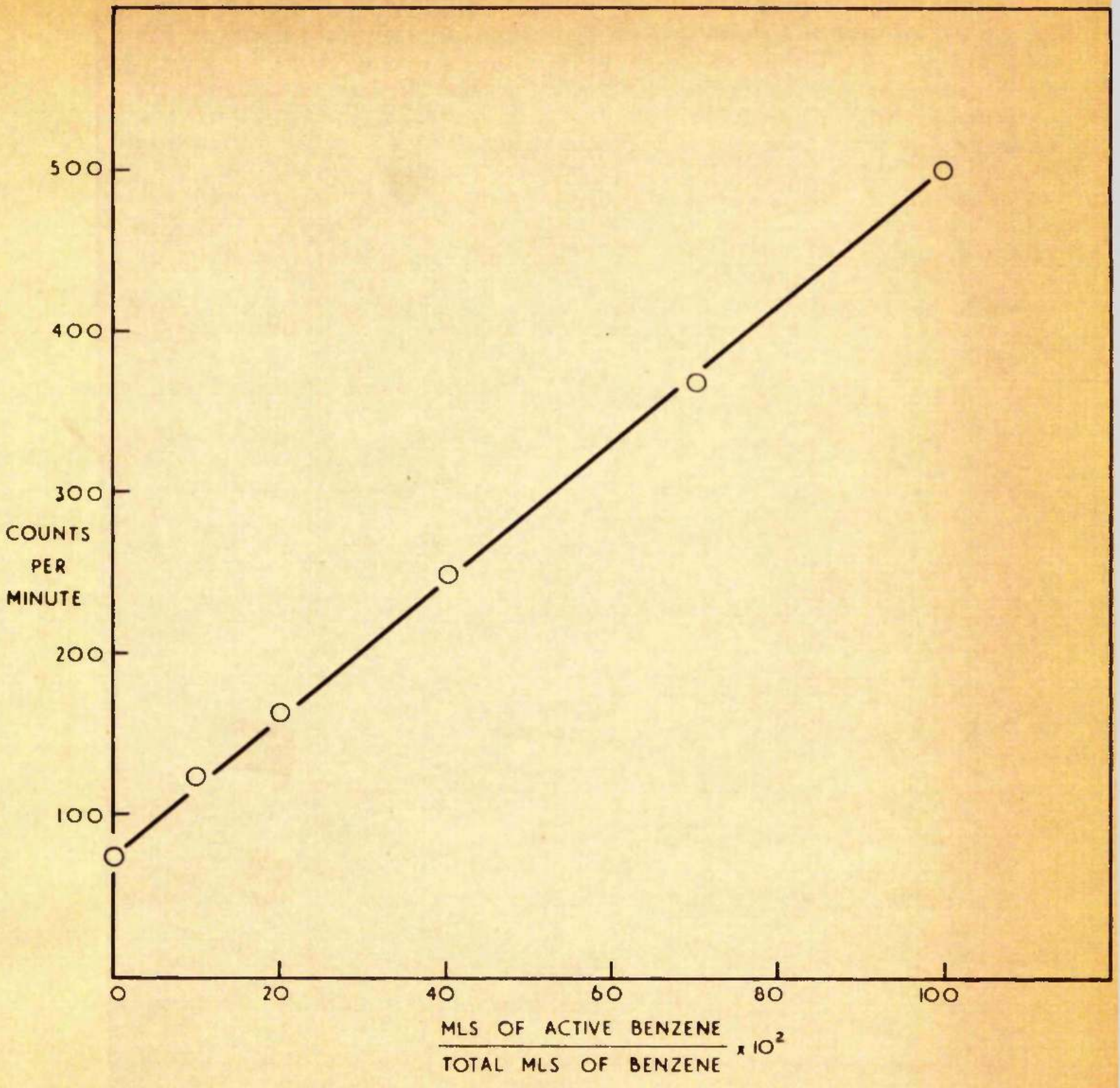


FIG 32 CALIBRATION CURVE FOR THE ACTIVITY OF BENZENE BY GAS COUNTING

Scintillation Counting

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

Experimental Procedure and Equipment

In this work the scintillation medium used was a liquid scintillator supplied by Nuclear Enterprises Ltd. The sample to be assayed for activity is contained in a silica cell of 18 ml. capacity which is aluminised on the outside to give maximum light reflection. The aluminium coating is protected with an expoxy resin finish and the cells have an optically flat bottom to prevent bubble formation in the coupling medium. A silicone oil, supplied by Nuclear Enterprises Ltd., is the optical coupler between the cell bottom and the cathode of the photomultipler tube.

5 ml. of the liquid scintillator were pipetted into a

sample cell and to this 5 ml. of benzene solution were added. For calibration purposes, these 5 ml. of benzene contained a know amount of radio benzene obtained from the calibration stock solution [Fig. 33]. When assaying the polymer, the solution was of inactive benzene containing 20 milligrams of the radioactive polymer. The cell was then placed in the scintillation head unit and dark adapted for 20 min. to minimise residual phosphorescence.

The scintillation head unit is essentially a 'castle' with 2 inches of lead shielding. The principal feature of this 'castle' is a special rotatory light locking device which permits operation of the assembly in daylight without exposure of the photomultiplier tube to the light when changing the cells. In practice this means that the tube dark current is allowed to reach the lowest level, making for improved accuracy and lowering the background activity. Another advantage gained from this device is that the high voltage supply to the photomultiplier tube may be left connected when the samples are being changed. Since the photomultiplier tube gain varies as a function of the 8th power of the applied high voltage, no variation in the high voltage supply is obviously desirable. To avoid any variations in output due to temperature changes, the

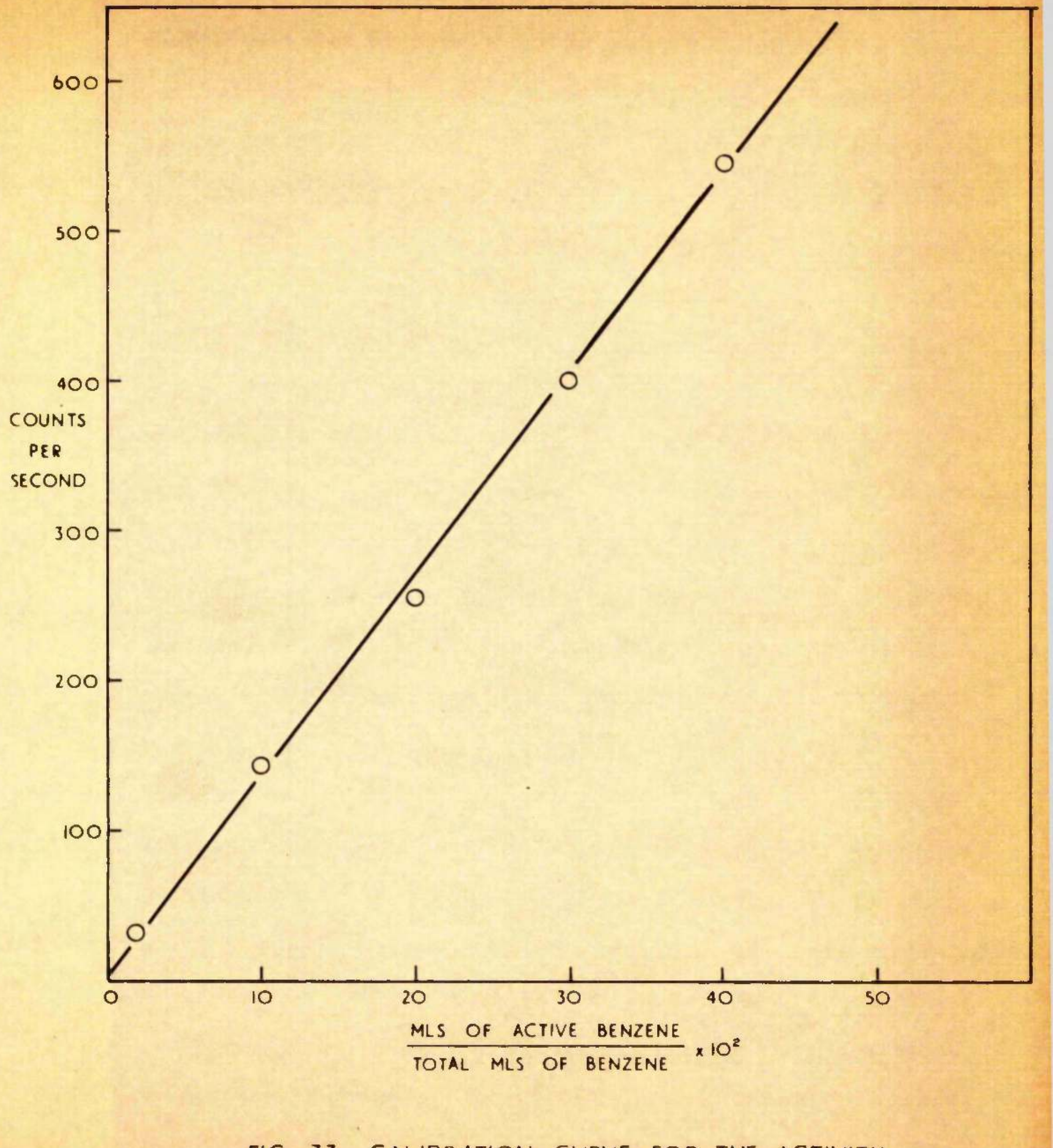


FIG 33 CALIBRATION CURVE FOR THE ACTIVITY OF BENZENE BY SCINTILLATION COUNTING

photomultiplier tube was cooled by a continuous supply of water passing through copper coils which surrounded it.

The output from the photomultiplier was amplified by a standard Nuclear Enterprise 5202 Fairstein amplifier with a maximum available gain of 5×10^4. This gain is continuously variable down to a value of about 50.

The resultant pulses from the main amplifer pass into a single channel pulse height analyser. Since each isotope emits a specific quanta of energy, a pulse peculiar to that isotope is obtained. By selecting appropriate settings, this instrument will only accdpt pulses which are representative in amplitude of the particular isotope which is being counted. The required gate width and pulse height to apply this discrimination for C^{14} are noted below.

The pulse in its final form is then relayed to the scaler and timing units which have been previously discussed with respect to the gas counting equipment.

The best settings for counting the C^{14} isotope were found to be:-

Stabilised High Voltage	0.64 K.volts.
Amplification	50 x 1
Pulse Height	30
Gate Width	30

The power for the stabilised voltage, the amplifier, scaler and timing unit were switched on andallowed to stabilise for 20 min. prior to any determinations being made. The E. H. was then switched on andafter 10 min. the assay was begun. Occasionally erratic results were obtained i.e. the count began to race intermittently. This was found to be due to pulsing in the stabilised voltage. It was eradicated by switching the E. H. T. off, leaving it for 30 min. and then switching the voltage back on. Although this appeared to be rather a crude method of eradicating the pulsing in the system it was generally effective. The silicon oil in the well was replenished, in subdued lighting, after 40 or 50 samples had been assayed.

Results

(a) From the gas counting calibration curve [Fig. 32];

Count for the oxidation of calibration stock

$= 500$ counts min.$^{-1}$

Background Count $= 72$ counts min.$^{-1}$

$\therefore$ Count due to activity alone $= 428$ counts min.$^{-1}$

$\therefore$ Activity of benzene used in polymerisation experiments $= 428 \times \frac{50}{0.1} \times \frac{1}{5}$

$= 4.28 \times 10^4$ counts min.$^{-1}$

2.5% v/v benzene

$\overline{DP}_n$ of polymer = 4.25×10^3.

Specific Activity of Benzene = 4.28×10^4 counts min^{-1}.

Specific Activity of Polymer = 84 − 72 = 12 counts min^{-1}.

∴ Number of benzene fragments $= \dfrac{4 \times 12 \times 4.25 \times 10^3}{6 \times 4.28 \times 10^4}$

$= \underline{\underline{0.79}}$

5% v/v benzene

This polymerisation was carried out in a non-stationary state vessel and the results obtained at 5% conversion are as follows.

Temperature °C	Rate of Reaction × 10^4 moles l^{-1} s^{-1}	Intensity Exponent	Kinetic Chain Lifetime s
25	1.80	0.63	0.65
35	2.48	0.63	0.54
45	3.38	0.64	0.50

Temperature °C	$k_p/k_t \times 10^6$	$k_t \times 10^7$ l mole^{-1} s^{-1}	E_0 k.cals.	E_t from $\frac{1}{\tau}$ k.cals.	E_t from $k_p/$ k.cals.
25	8.36	1.27	5.98	9.9	7.8
35	8.96	5.9			
45	12.3	4.4			

The results are in reasonable agreement with those obtained with ordinary benzene.

$\overline{DP}_n$ of the Polymer = 3.44×10^3.

Specific Activity of the Benzene = 4.28×10^4 counts min^{-1}.

Specific Activity of the polymer = 88 - 72

= 16 counts min^{-1}.

$\therefore$ The number of benzene fragments $= \frac{4 \times 16 \times 3.44 \times 10^3}{6 \times 4.28 \times 10^4}$

= 0.86

20% v/v benzene

$\overline{DP}_n$ of the Polymer = 1.99×10^3.

Specific Activity of the polymer = 42 counts min^{-1}.

$\therefore$ The number of benzene fragments = 1.31

(b) Scintillation Counting

From the calibration curve for the stock radio active benzene solution [Fig.33] it can be calculated that the activity of the benzene used in the polymerisation experiments

$= 675 \times 2 \times 500 \times \frac{1}{5}$ counts sec^{-1}

$= 13.5 \times 10^4$ counts sec^{-1}.

The background count was 0.13 counts sec^{-1}.

For 2.5 v/v benzene

Specific Activity of the polymer = 42.9 counts sec^{-1}.

$\overline{DP}_n$ of the polymer = 4.25×10^3.

$\therefore$ The number of benzene fragments $= \frac{4 \times 42.9 \times 4.25 \times 10^3}{6 \times 13.5 \times 10^4}$

= 0.90

For 5% v/v benzene

Specific Activity of the polymer = 56.9 counts $\sec^{-1}$

$\overline{DP}_n$ of the polymer = 3.44×10^3

$\therefore$ The number of benzene fragments $= \dfrac{4 \times 56.9 \times 3.44 \times 10^3}{6 \times 13.5 \times 10^6}$

$= 0.97$

For 20% v/v benzene

Specific Activity of the polymer = 143 counts $\sec^{-1}$

$\overline{DP}_n$ of the polymer = 1.99×10^3.

$\therefore$ The number of benzene fragments = 1.71

It is rather surprising that the results from the scintillation counting are greater than those from the gas counting determinations since the latter is thought to be the most accurate method for tracer analysis. This would indicate that the results from the gas counting determinations are low. This could result from the presence of air which was occluded in the polymer.

Despite this error the maximum number of fragments present in each polymer chain is 1.7. According to the normal kinetics schemes, there should be 1 fragment per polymer chain if chain transfer is occurring and a number in excess of this if the retardation is due to copolymerisation. Therefore, although there is possibly a small amount of copolymerisation, the more probable step for inclusion of benzene units in the polymer chain is chain transfer.

Acetylation of Benzene

Breitenbach et al.[7] claimed that the radio-active determinations of Stockmayer et al.[5] were vitiated by the presence of acetylenic impurities in the radio-active solvent. In an attempt to substantiate this theory, radio-active benzene was treated with radio-active acetylene and vinyl acetate was polymerised in the presence of 2.5% v v of this contamined solvent.

0.1 mille curies of acetylene from a break seal ampoule were added to about 8 ml. of radio-active benzene by the procedure described at the beginning of this section. The benzene was the highly active solvent used in the polymerisation experiments and after contamination with acetylene was calibrated by scintillation counting. Vinyl acetate was polymerised at 25°C in the presence of 2.5% v v of this acetylenic benzene at an initiator concentration of 4×10^{-3} moles litre^{-1} and the polymer isolated by freeze drying, using the procedure previously described. 20 mille grams of the polymer were dissolved in 5 mls of inactive benzene and the activity of the polymer found by scintillation counting. Using the calculations previously outlined there appeared to be 7.4 fragments of benzene present per polymer molecule.

A single crystal of the contaminated benzene was grown and the solvent obtained from the optically clear crystal was used in a polymerisation reaction similar to the experiment described above. The activity of the solvent and of the polymer were again determined by scintillation counting and these corresponded to 0.92 fragments of benzene per polymer chain which was in good agreement with the previous determination of this polymer by scintillation counting.

From these results it is clear that the presence of acetylene does increase the activity in the polymer and this would substantiate the results and theory of Breitenbach. However the results of Stockmayer et al.[5] which led to the theory of copolymerisation were supposed to be due to only traces of acetylenic products in their benzene. In this work 0.1 millicuries of acetylene were deliberately added to benzene and only an increase of 7 times the activity in the polymer was obtained. If the increase in activity in the polymer is obtained by a copolymerisation mechanism then these results would indicate that the process does not occur very readily, at least at 25°C and 2.5% benzene. If the process did occur easily then the increase should have been much greater with such a strong sample of solvent. This experiment also demonstrates the ability of the single crystal growth technique to remove impurities from the solvent.

DISCUSSION AND CONCLUSIONS

Before discussing the results which have been obtained it is important to realise the type and magnitude of errors which are incurred with the use of the thermocouple method for non-stationary state measurements.

Some other methods, which have been used by various workers to evaluate the velocity coefficients, have a greater sensitivity than the non-stationary state thermocouple mechanism e.g. Grassie and Melville's[31] refractometric method can detect a temperature change of 10^{-4} °C in 10^{-2} sec., while the dielectric constant method can give a temperature resolution of 10^{-5} °C in 10^{-6} sec. However the increasing accuracy of measurement during the non-stationary state period is offset by the greater experimental difficulty and the more complex equipment required for these methods.

The thermocouple is probably the most useful method to use for evaluating velocity coefficients but, as in all such systems, there are certain difficulties and limitations in its use.

Temperature Measurement.

The temperature was recorded by a thermocouple at the centre of the reaction mixture in a soda vessel. In fact the signal obtained by the pen voltmeter recorder was due to opposing electromotive forces from two thermocouples, namely the one mentioned above and a 'cold' junction in the evacuated space in the side arm. Therefore, any random temperature fluctuations in the bath would be reflected in the trace obtained on the pen recorder voltmeter. The bulk of the heat required to maintain the temperature of the bath was supplied by the background heater while the remainder was supplied by a 40 watt light bulb which just flickered on and off. With this arrangement the apparent fluctuation of temperature in the bath was 0.001°C.

The noise level of the Tinseley D.C. amplifier corresponded to a temperature fluctuation of 0.00014°C and this represents the ultimate limit of temperature measurement even with increased thermostatic control.

The electromotive force-temperature relationship was obtained from the literature. Bengough and Melville[4] have shown that the rates obtained with copper constantan thermocouple are in good agreement with rates of reaction obtained using platinum-platinum rhodium thermocouples and with rates measured dilatometrically. This would indicate that the electromotive force-temperature relationship is quite reliable.

After considering all the variables the final limit of temperature measurement is about 0.001°C.

Measurement of the Kinetic Chain Lifetime.

Errors in the measurement of kinetic chain lifetimes are due to two factors,

(a) inaccuracy in the extrapolation of the stationary state-time curve, and

(b) variation in the instrument lag as time proceeds.

The start of the reaction was indicated by a pip on the recorder chart. If the amplification applied to the system was large then the pip increased in size and the pen did not always return to the original base line. This tended to increase the value obtained for the lifetime. However the rates of reaction obtained in this work were approximately twice those of other workers, Consequently this error did not interfere with the results until vinyl acetate was polymerised in the presence of 20% v/v benzene, where the amplification was about 1 μ volt equal to 7 or 8 chart divisions for low intensity runs.

The extrapolation of the stationary state-time curve depends on the length of time the reaction in the vicinity of the time curve remains adiabatic. 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 Υ, becomes a straight line showing a constant rate of increase in temperature [Fig. I]. This will continue until the reaction becomes non-adiabatic [Fig. 2]. If the period for which the reaction is adiabatic is less than 3τ a straight line will not be attained, the initial upward curve going through a point of inflection to a downward curve. For most monomers the reaction mixture in the area of the thermocouple remains constant for about 30 sec. Since the value of the kinetic chain lifetime in this work was never greater than 9 sec, it was not necessary to employ any special techniques to ensure adiabatic conditions. In many polymerisations, lifetimes of 50 sec and above do occur and vacuum jacketed dilatometers have been used to increase the adiabatic period.

Variation in the instrument lag from run to run probably results in the greatest error. The response times of the amplifier is 0.04 seconds and that of the thermocouple due to its small heat capacity will also be very short. The lag of the pen recorder is very much greater, about 1 sec. and can vary with the amount of ink in the pen reservoir although care was taken to keep the reservoir topped up during a series of runs. These combined lags give a delay in recording the full signal of up to several seconds; in this work 2.1sec.

To obtain accurate values the radical lifetime should be about 2 to 3 seconds. Since they were generally shorter than this it required several determinations at each stage to get a reliable figure. However, despite all the care taken with measurements etc. there was a variation of up to ± 10% in the estimation of the intercept from successive determinations of the same reaction. But the points which are plotted in the $\frac{1}{\text{Rate}}$ against measured intercept graphs [Fig. 7] are the average of at least 3 separate determinations. In Fig. 7 the intercept on the time axis corresponding to the instrument lag is 2.1 sec. and it is seen that this could vary by about ± 0.2sec.although the slope of the graph would only be slightly varied, in fact about 5%. For this reason this straight line plot was used to determine the values of the kinetic chain lifetimes which were used in calculating E_t in this work.

The best value for the rate of reaction at a particular conversion was obtained from the plot of log rate against log intensity [Fig.8]. The logarithm of this value was plotted with those obtained for the two other temperatures against the reciprocal of the absolute temperature to determine E_0 [Fig.11]. If the value for the rate of reaction was in good agreement with the other two it was used to determine the kinetic chain lifetime from the straight line plot of $\frac{1}{\text{Rate}}$ against the measured intercept. The actual calculation resulted in the kinetic chain lifetime being quoted to two figures after the decimal point. Since it is obvious from the inaccuracies in the system that the kinetic chain lifetime cannot be determined to more than ± 0.05sec little reliance can be placed on the second figure. However it does facilitate the calculation of E_t, etc. and for this purpose it has been left in the text. The same argument applies to the rate of reaction.

The kinetic chain lifetime is calculated from the plot of $\frac{1}{Rate}$ against the measured intercept from which the value of $^{k}p/k_t$ is also obtained. Therefore, the values of E_t obtained from the kinetic chain lifetime and from $^{k}p/k_t$ should be comparable [Fig.12]. But the determination of E_t from $^{k}p/k_t$ involves both E_0 and the accurate estimation of the gradient for the value of $^{k}p/k_t$. Consequently there is generally a difference in the values of the activation energy of termination calculated from the two sources. In all the activation energy plots the calculated value lies at the centre of the circle. A slight variation of the gradient of the line could give a maximum or minimum value and the extent of this has been indicated by the protruding lines.

The Influence of Benzene on the Polymerisation of Vinyl Acetate.

Previously the action of benzene on the polymerisation of vinyl acetate was reviewed in a separate section according to the concentration of solvent present in the reaction mixture. These results will now be reviewed collectively to show the effect of an increasing concentration of solvent on the rates of reaction. It is hoped by studying the results in this manner to obtain a clearer picture of the process which causes the marked retardation of the rate of polymerisation.

This retardation of the rate of polymerisation is the most striking feature of the work. The rate of reaction for the bulk polymerisation is halved by the addition of 5% v/v of the solvent while 20% reduces it tenfold [Figs. 34, 35, 36].
The values for these plots are given below to eliminate continual reference to previous sections.

Rates of Reaction (moles. $l.^{-1}$ $s.^{-1}$) x 10^3 at 25°C and full light intensity.

Concentration of Benzene moles. $l.^{-1}$	 %	Conversion 10%	 30%	 60%
0	0	4.0	4.4	5.1
0.28	2.5	2.5	2.8	2.9
0.56	5	1.80	1.9	2.2
2.24	20	0.47	0.33	0.22

Rates of Reaction (moles. $l.^{-1}$ $s.^{-1}$) x 10^4 at 35°C and full light intensity.

Concentration of Benzene moles. $l.^{-1}$	 %	Conversion 10%	 30%	 60%
0	0	5.2	5.8	7.0
0.28	2.5	3.3	3.6	4.2
0.56	5	2.4	2.6	3.3
2.24	20	0.65	0.5	0.36

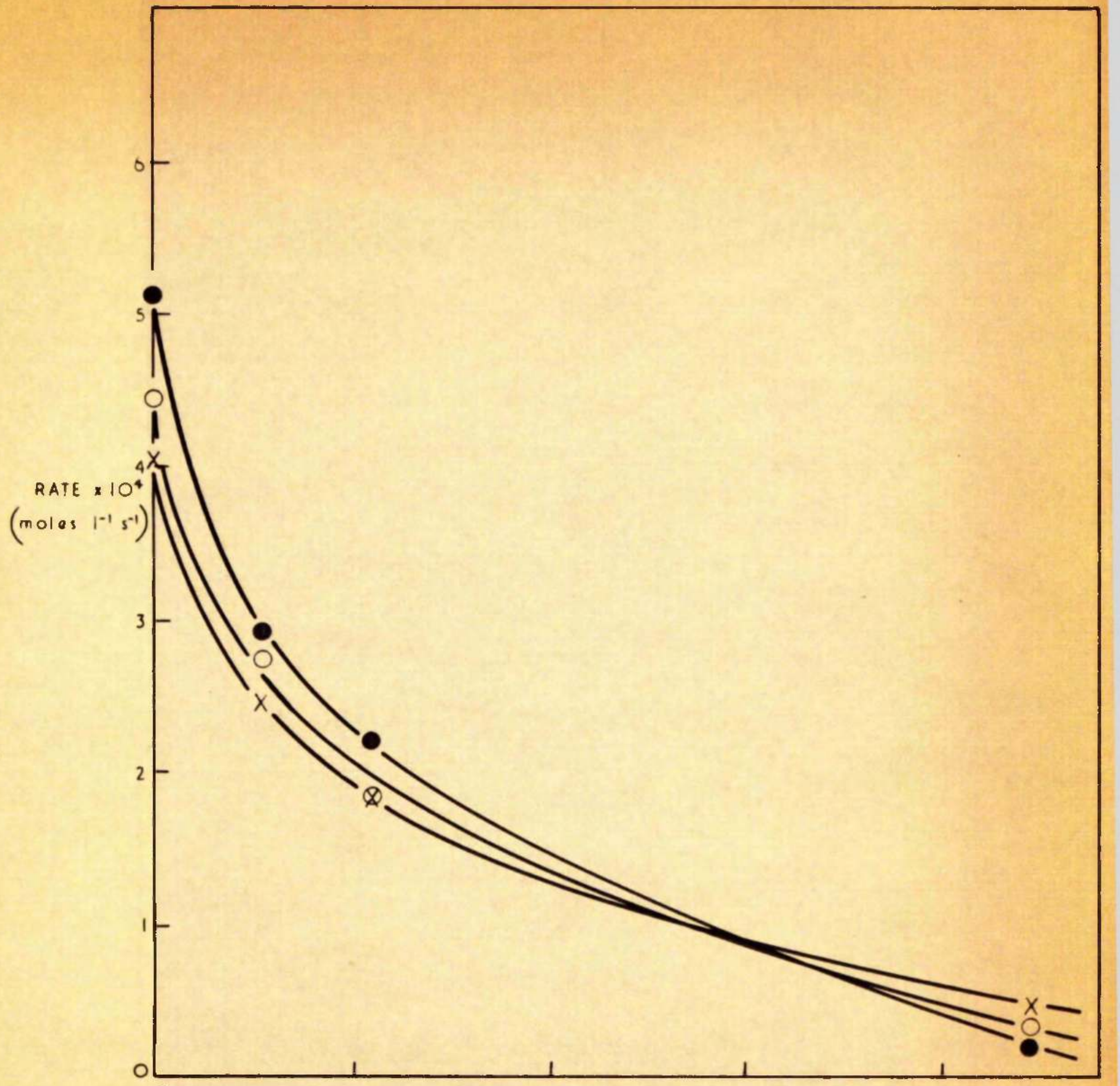


FIG 34 VARIATION OF RATE WITH BENZENE CONCENTRATION AT 25

X 10% CONVERSION
O 30% CONVERSION
● 60% CONVERSION

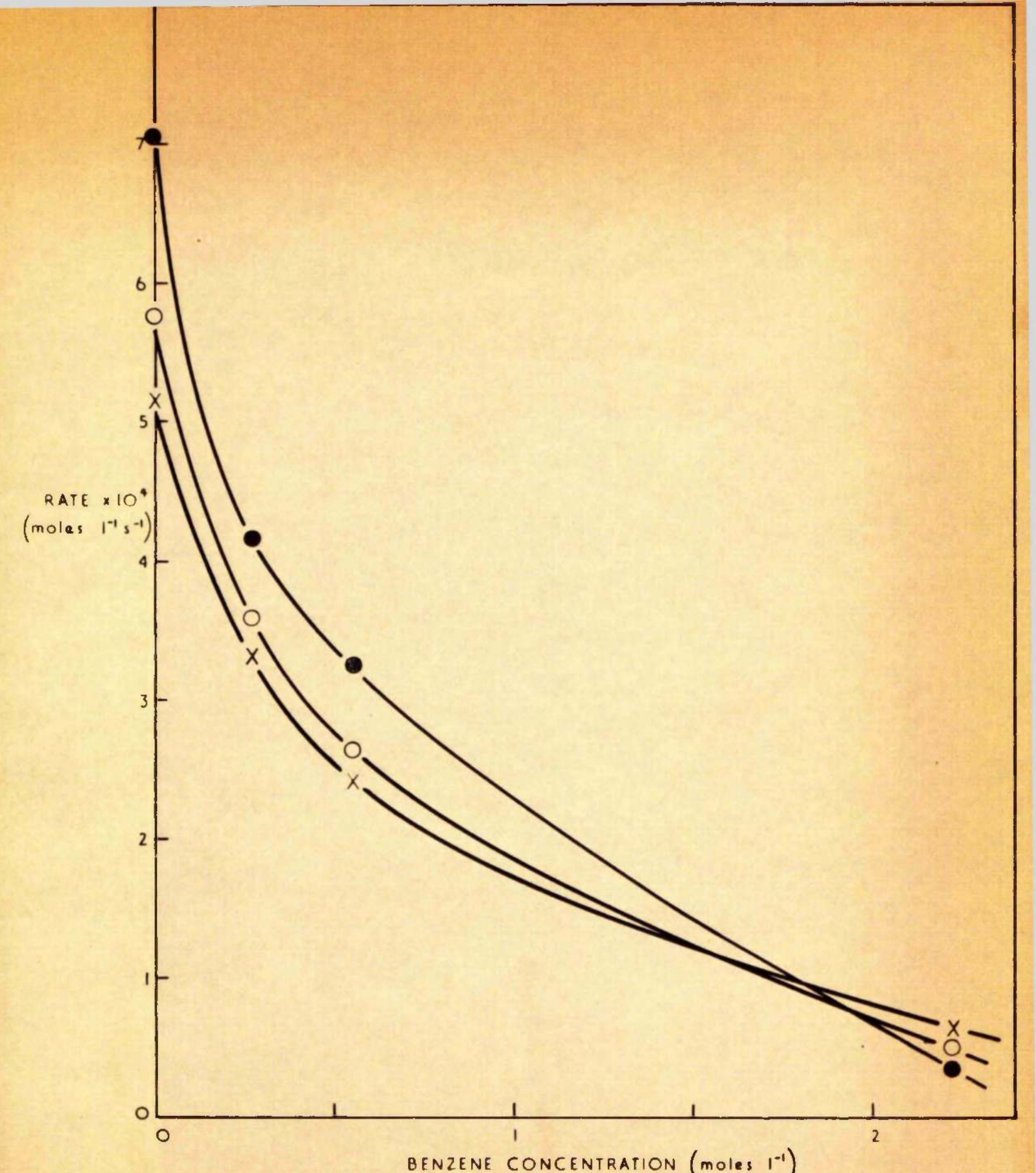


FIG 35 VARIATION OF RATE WITH BENZENE CONCENTRATION AT 35°

X 10% CONVERSION
○ 30% CONVERSION
● 60% CONVERSION

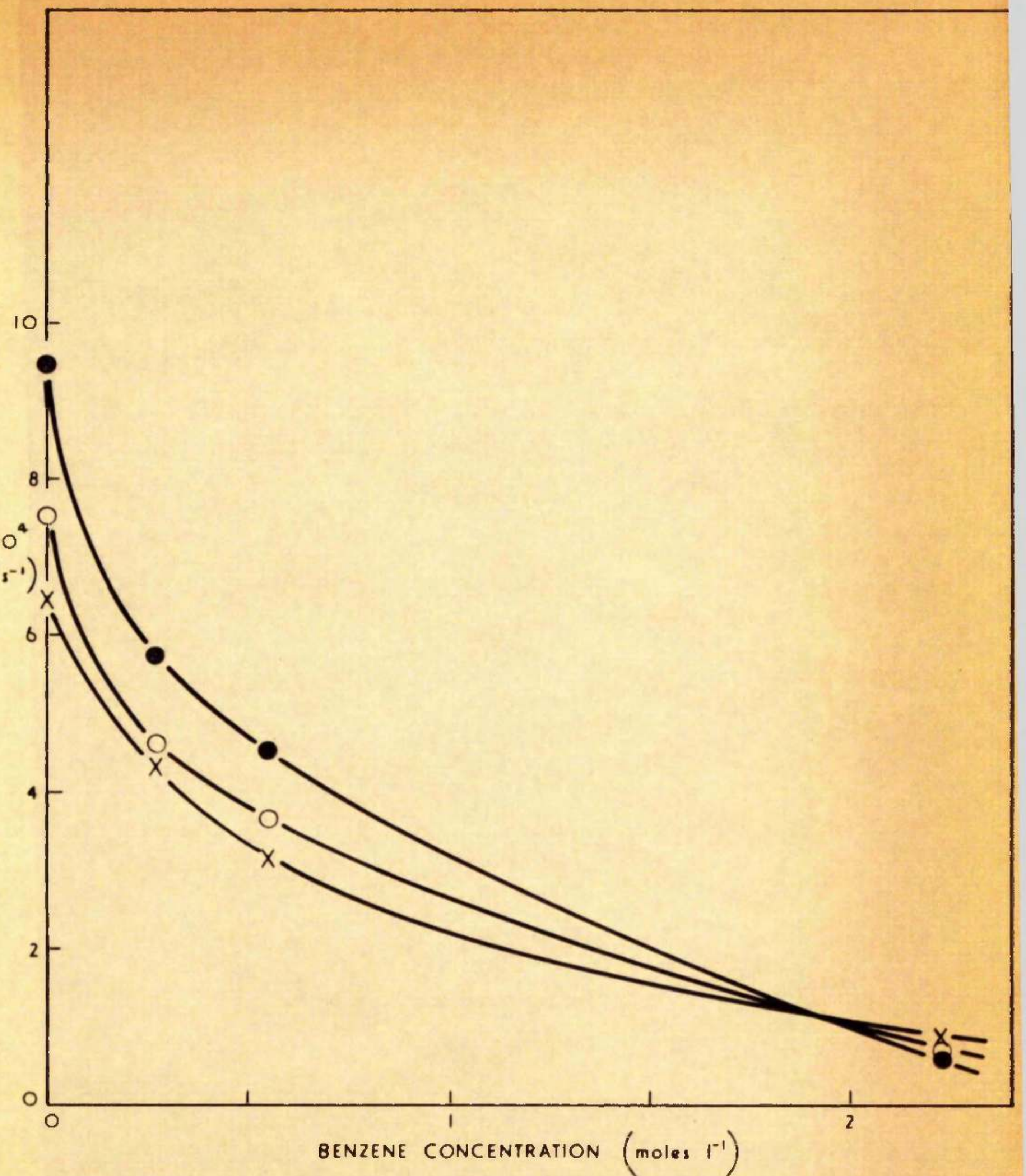


FIG 36 VARIATION OF RATE WITH BENZENE CONCENTRATIONS AT 45°C

X 10% CONVERSION

O 30% CONVERSION

● 60% CONVERSION

Rates of Reaction (Moles. l^{-1} s^{-1}) x 10^4 at 45°C and full light intensity.

Concentration of Benzene moles. l^{-1}	%	Conversion 10%	30%	60%
0	0	6.5	7.6	9.5
0.28	2.5	4.4	4.6	5.8
0.56	5	3.2	3.7	4.6
2.24	20	0.88	0.74	0.58

The rates of reaction increase from 10% conversion to 60% conversion at all temperatures and percentages. The exception to this rule is at 20% benzene where the converse would seem to apply. But after correction for a decrease in monomer and initiator concentration, the rate of reaction at 60% conversion could possibly be as large as 1.07 x 10^4 moles l^{-1} s^{-1} (page 74 So the rates of reaction at 20% benzene probably increase from 30% conversion. Since the rate of reaction should fall due to a decrease in monomer concentration, this increase in the rate of reaction from 10% to 60% conversion indicates that the gel effect is operating on the system up till 60% conversion.

It can be seen in Figs. 37, 38, 39 and 40 that the value of k_p at 0, 2.5%, 5% and 20% benzene is generally constant till about 40%, when it begins to decrease due to monomer diffusion becoming more difficult and causing a reduction in the rate of propagation. This is offset by a corresponding

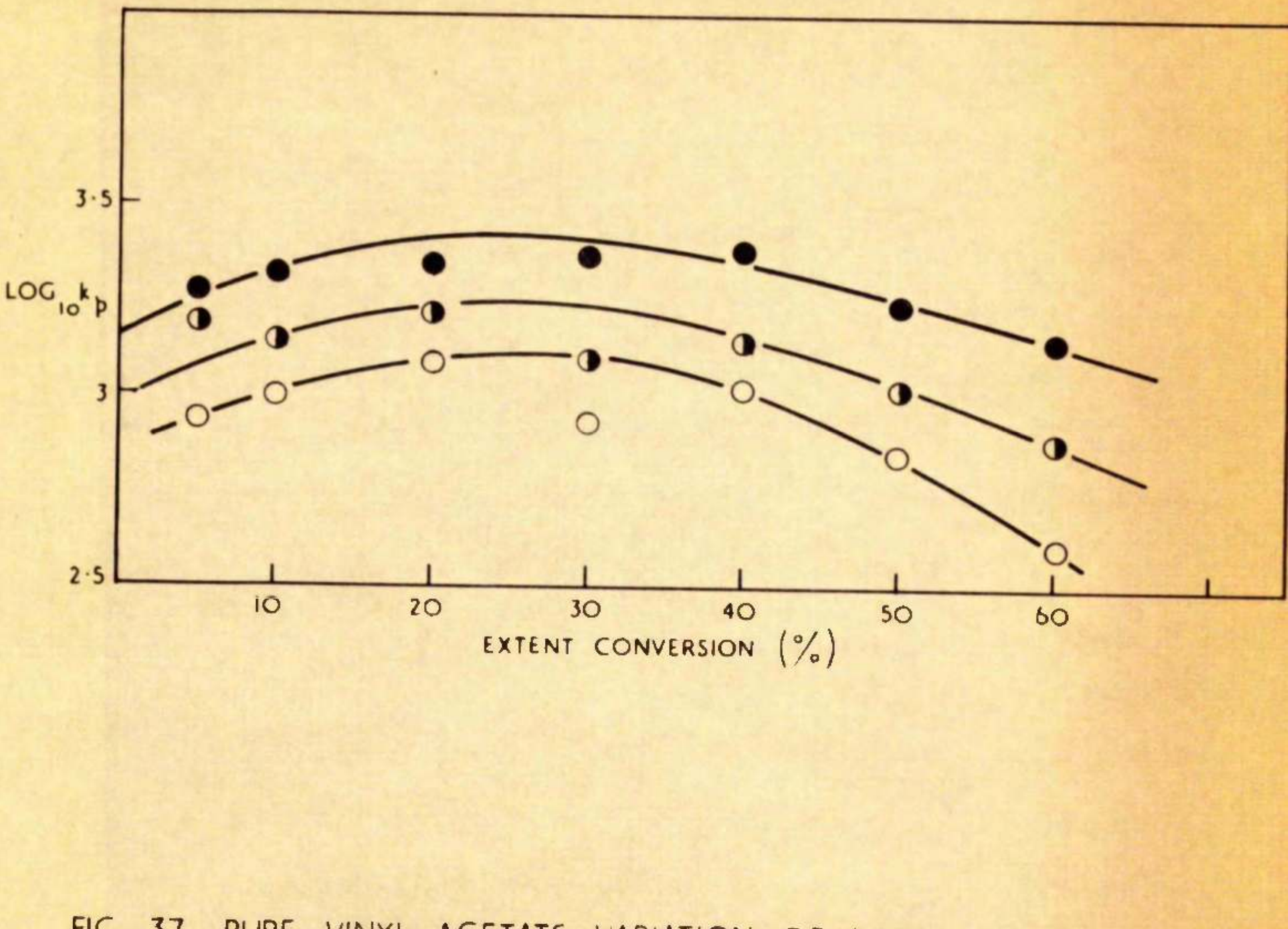


FIG 37 PURE VINYL ACETATE. VARIATION OF LOG$_{10}$ k_p WITH CONVERSIC

○ 25°C ◑ 35°C ● 45°C

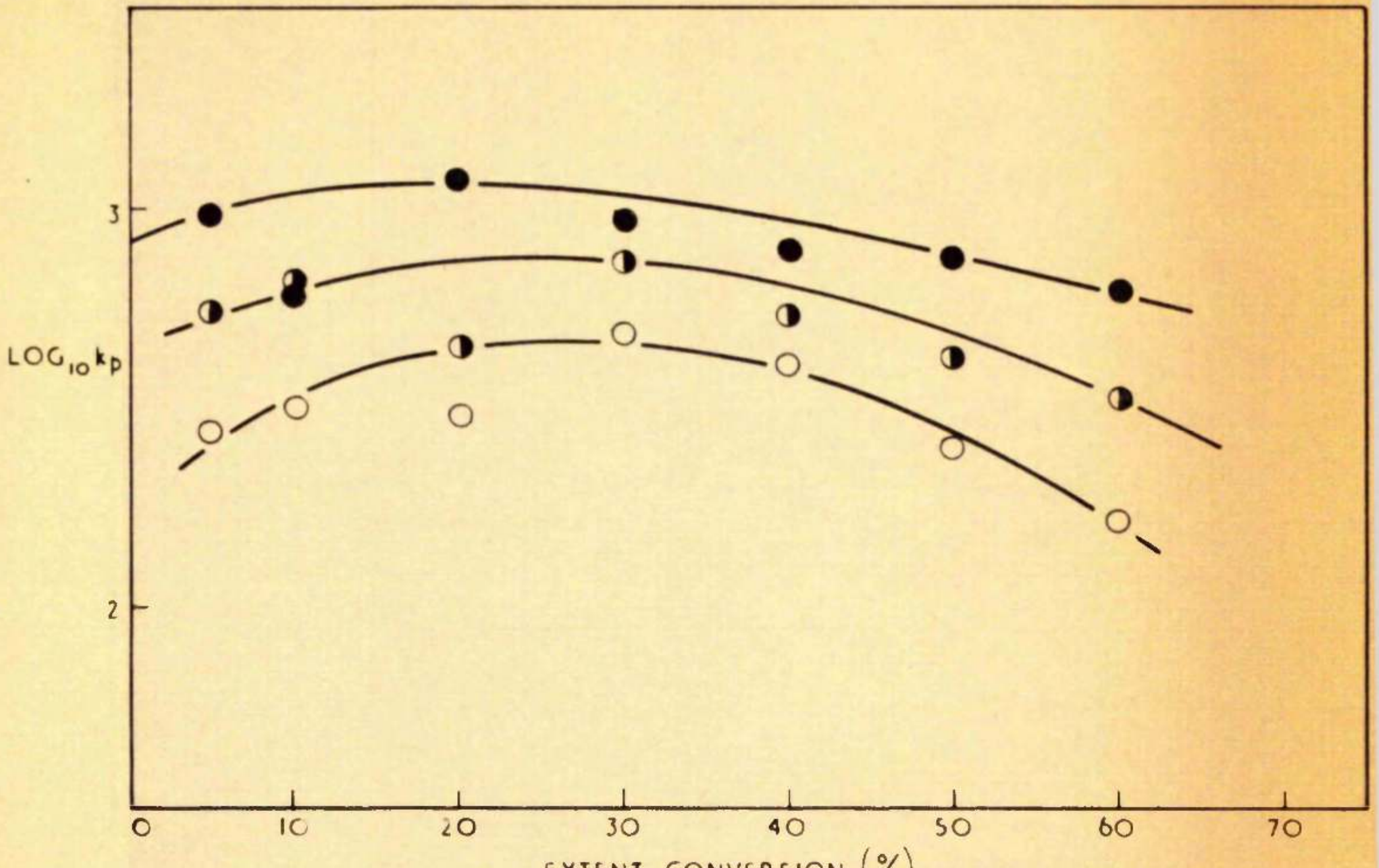


FIG 38 VINYL ACETATE PLUS 2·5% BENZENE. VARIATION OF LOG$_{10}$ k_p WITH CONVERSION

○ 25°C ◑ 35°C ● 45°C

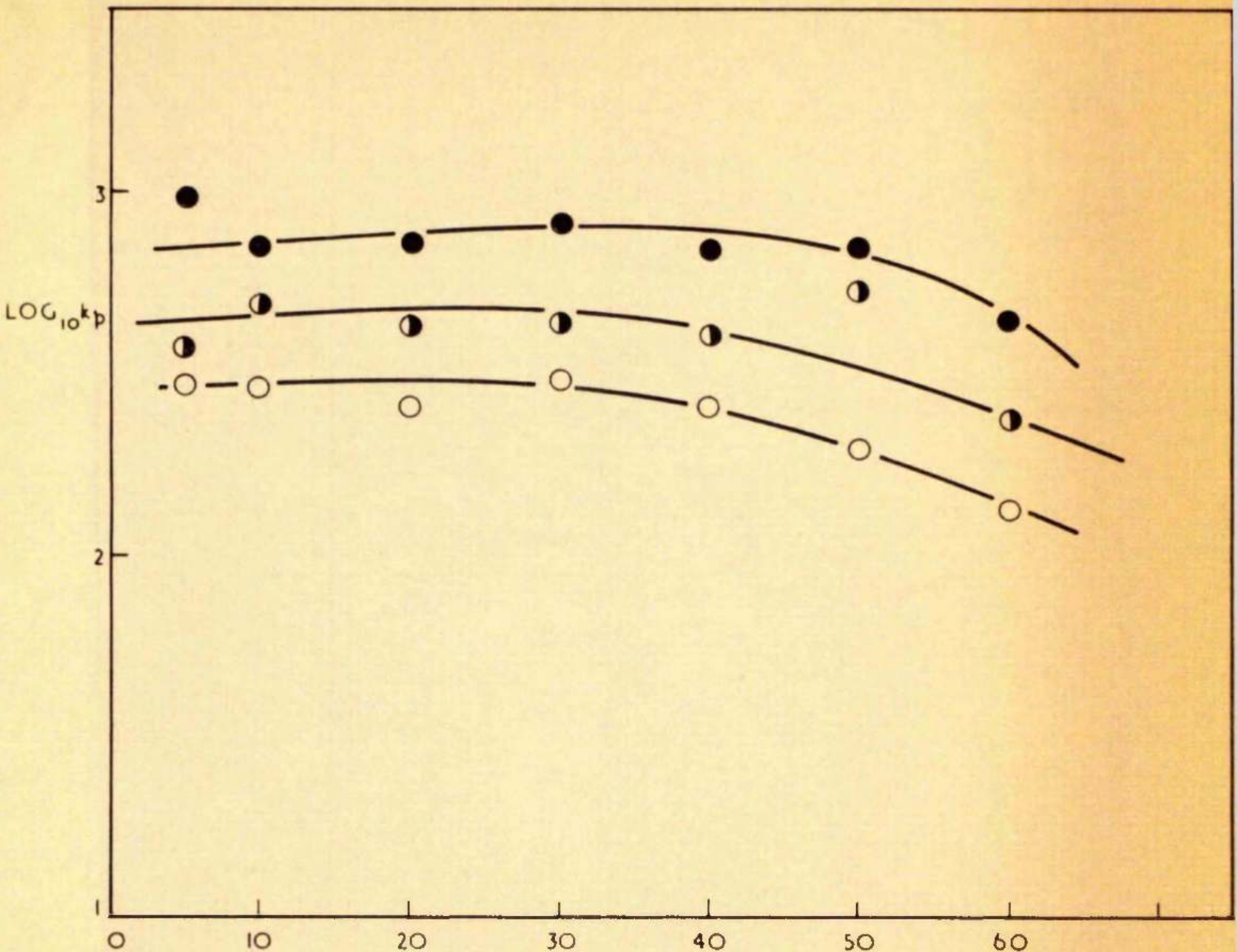


FIG 39 VINYL ACETATE PLUS 5% BENZENE. VARIATION OF LOG$_{10}$ k_p WITH CONVERSION

○ 25°C ◑ 35°C ● 45°C

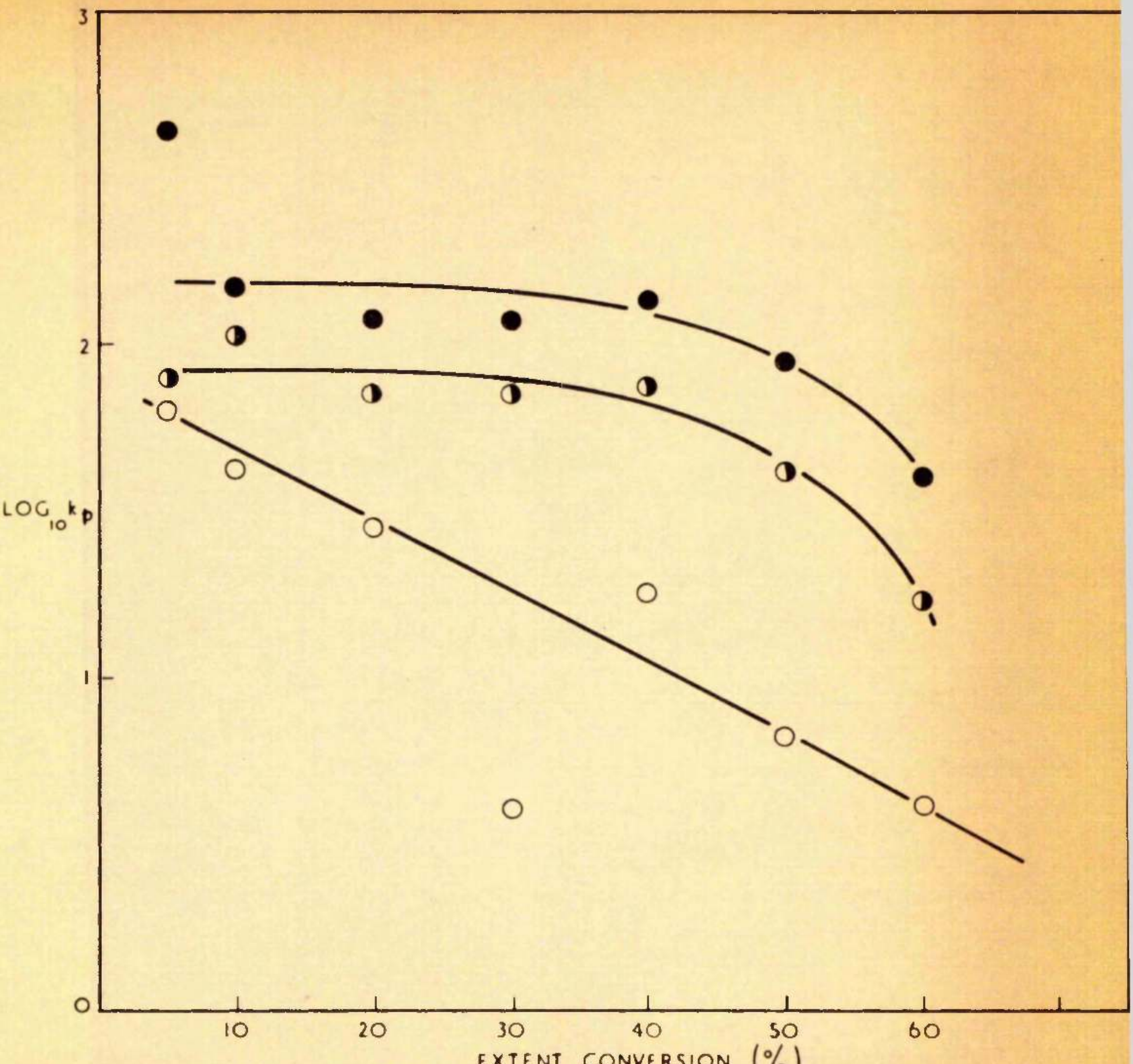


FIG 40 VINYL ACETATE PLUS 20% BENZENE. VARIATION OF LOG$_{10}$ k_p WITH CONVERSION

○ 25°C ◑ 35°C ● 45°C

fall in k_t. As the viscosity of the reaction mixture increases it becomes more difficult for the radicals to diffuse together to terminate and the rate of termination falls and with it the value of k_t

If the gel effect is operating in this way then this should be clearly demonstrated by the value of the kinetic chain lifetimes which are given below.

Kinetic Chain Lifetime(s) at 25°C and full light intensity

Concentration of Benzene		Conversion		
moles. l^{-1}.	%	10%	30%	60%
0	0	0.3(6)	0.5(4)	1.3
0.28	2.5	0.7(2)	0.6(5)	1.9
0.56	5	0.7(2)	0.7(9)	1.8
2.24	20	1.4	1.2	2.9

Kinetic Chain Lifetime(s) at 35°C and full light intensity

Concentration of Benzene		Conversion		
moles. l^{-1}.	%	10%	30%	60%
0	0	0.3(6)	0.5	0.9(7)
0.28	2.5	0.6(5)	0.5(6)	1.3
0.56	5	0.5(8)	0.6(9)	1.5
2.24	20	0.9(0)	1.1	2.1

Kinetic Chain Lifetimes at 45°C and full light intensity

Concentration of Benzene		Conversion		
moles. $l.^{-1}$	%	10%	30%	60%
0	0	0.3(6)	0.3(6)	0.7(2)
0.28	2.5	0.5(0)	0.5(0)	1.0
0.56	5	0.5(0)	0.5(0)	1.2
2.24	20	0.6(7)	0.7(2)	1.40

From the above tables and Figs. 41, 42 and 43, it is clear, that at the same temperature and percentage solvent, the kinetic chain lifetimes increase from 10% to 60%. There are specific points where this is not correct but the plots confirm that this is the general trend. Despite the fact that the concentration of the solvent has been doubled, the kinetic chain lifetimes for 2.5% and 5% benzene at all three temperatures are very similar. This is quite surprising considering that there is a marked drop in the rate.

Since the gel effect is a viscosity effect, an increase in the concentration of solvent would presumably dilute the reaction mixture and enable the chain radicals to terminate more quickly. But an examination of the above tables demonstrates that this does not occur. There is, at all three temperatures and conversions, an increase in the values of the kinetic chain lifetimes as more solvent is added to the

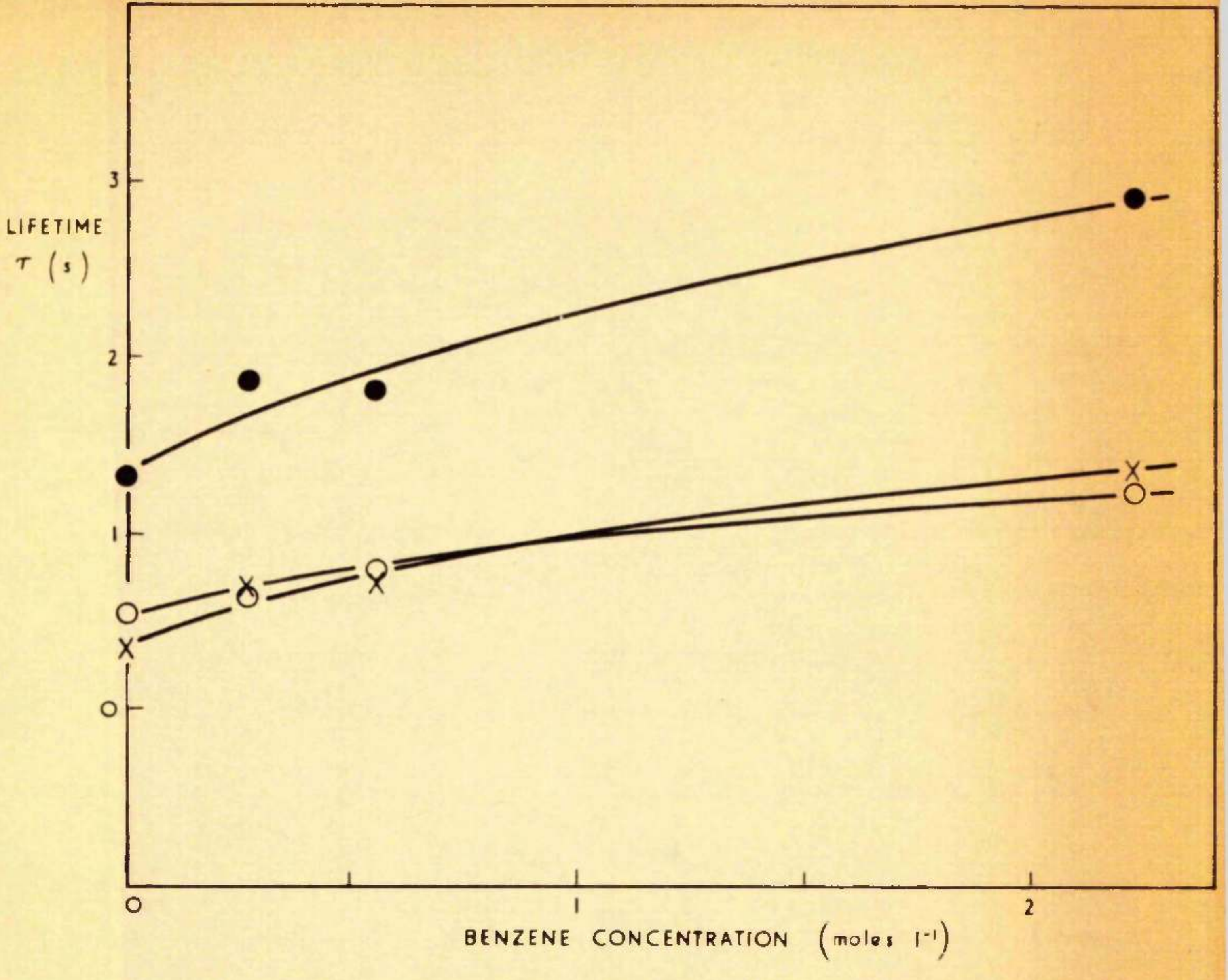


FIG 41 VARIATION OF KINETIC CHAIN LIFETIME τ WITH BENZENE CONCENTRATION AT 25°C

X 10% CONVERSION

○ 30% CONVERSION

● 60% CONVERSION

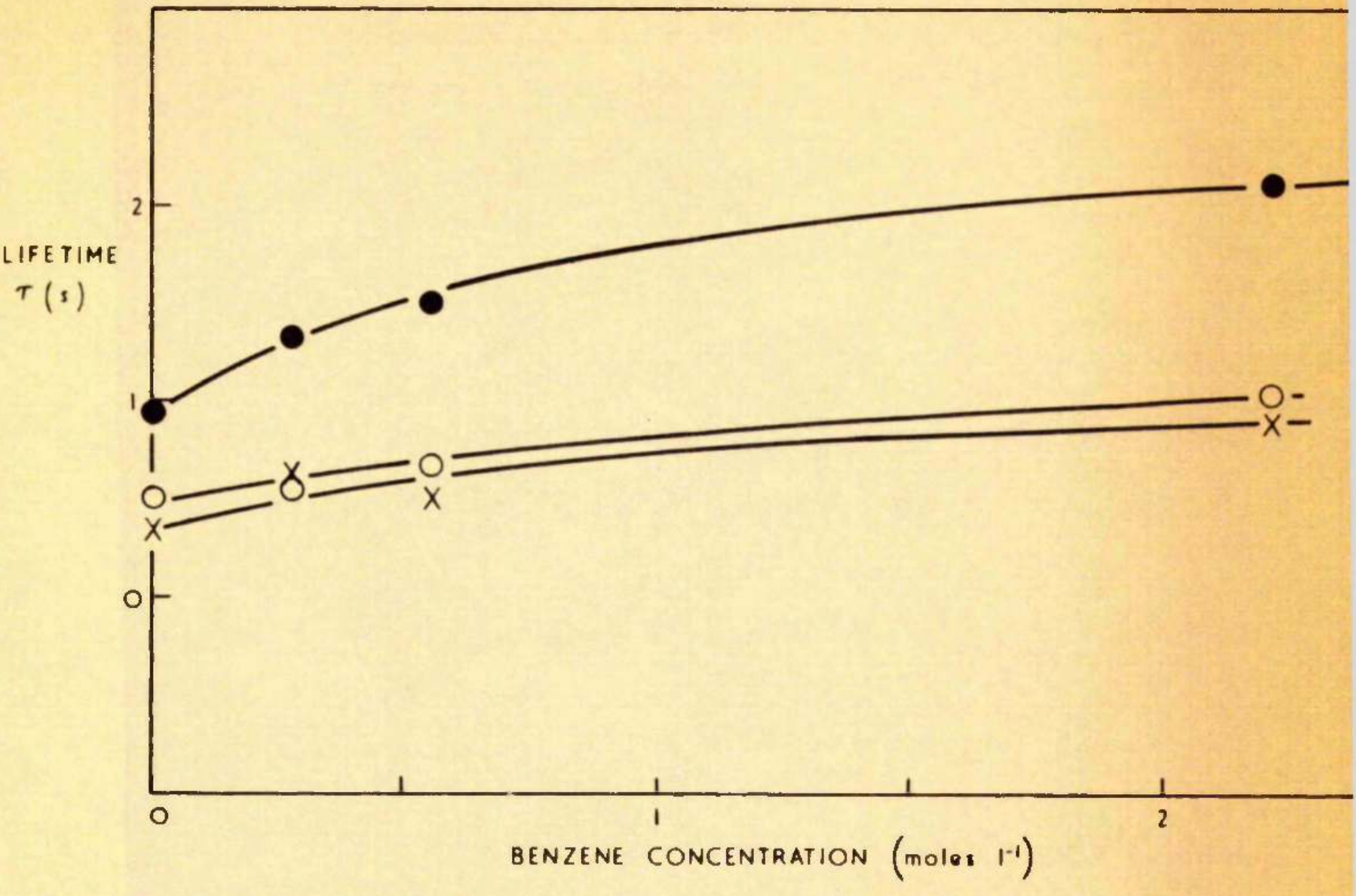


FIG 42 VARIATION OF KINETIC CHAIN LIFETIME τ WITH BENZENE CONCENTRATION AT 35°C

X 10% CONVERSION
○ 30% CONVERSON
● 60% CONVERSION

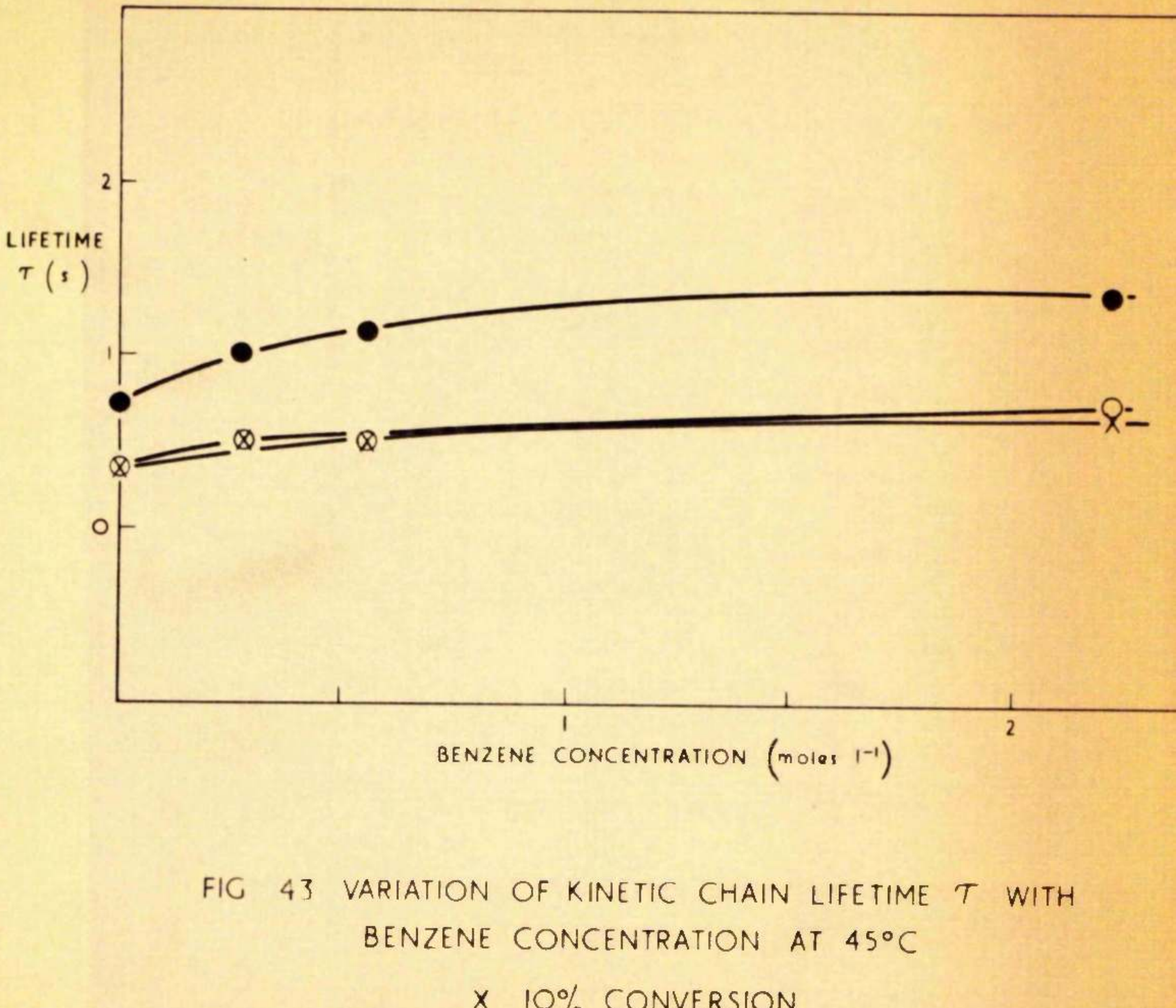


FIG 43 VARIATION OF KINETIC CHAIN LIFETIME τ WITH BENZENE CONCENTRATION AT 45°C

X 10% CONVERSION

O 30% CONVERSION

● 60% CONVERSION

system. Therefore, in addition to altering the physical state of the reaction mixture, the solvent is altering the chemical processes which control the polymerisation reaction.

Since the kinetic chain lifetime is inversely proportional to the velocity coefficient of termination, these changes in Υ with conversion should be reflected in k_t.

Variation of the velocity coefficient of termination (l. mole.$^{-1}$ s.$^{-1}$) x 10^{-7} at 25°C

Concentration of Benzene		Conversion		
mole. l.$^{-1}$	%	10%	30%	60%
0	0	8.6(7)	3.8(5)	0.6
0.28	2.5	2.1(6)	2.6(7)	0.3(2)
0.56	5	2.1(6)	1.7(9)	0.3(5)
2.24	20	0.6	0.1(4)	0.1(4)

Variation of the velocity coefficient of termination (l. mole.$^{-1}$ s.$^{-1}$) x 10^{-7} at 35°.

Concentration of Benzene		Conversion		
mole. l.$^{-1}$	%	10%	30%	60%
0	0	8.6(7)	4.5	1.2
0.28	2.5	2.6(7)	3.5(5)	0.63
0.56	5	4.4	2.3(9)	0.45
2.24	20	1.3(9)	1.0	0.25

Variation of the velocity coefficient of termination ($l.mole.^{-1}s.^{-1}$ x 10^{-7} at 45°C

Concentration of Benzene		Conversion		
$mole.\ l.^{-1}$	%	10%	30%	60%
0	0	8.6(7)	8.6(7)	2.2
0.28	2.5	3.3(7)	4.4	1.1
0.56	5	4.4	4.4	0.85
2.24	20	2.5	2.1(7)	0.60

These results are plotted in Figs. 44, 45 and 46. At the same temperatures and concentration of solvent the value of k_t falls from 10% to 60% conversion. This decrease in value corresponds to the increase in value of the kinetic chain lifetime over a corresponding range. This fall in k_t indicates that the activation energy of termination is increasing and consequently that the termination step is becoming more difficult. This supports the theory of the gel effect operating on the system and increasing in effect with increasing conversion.

But k_t is also decreasing with the increase in concentration of solvent in the reaction mixture and so the value of E_t must also increase i.e. if the solvent concentration is increased the termination step becomes more difficult. The most significant feature is the drop in k_t with the addition of only 2.5% v v benzene. This quantity of solvent could not

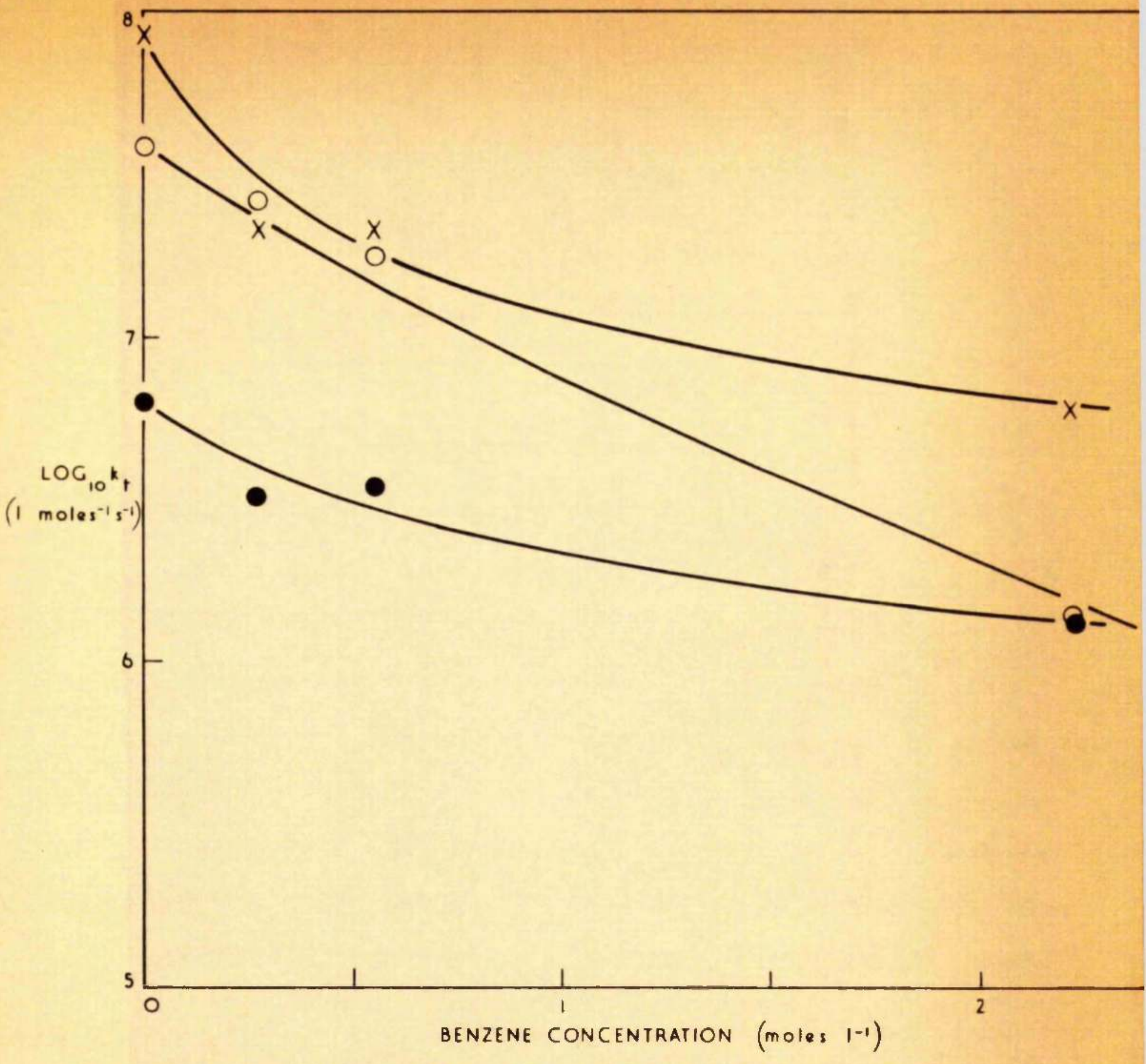


FIG 44 VARIATION OF LOG$_{10}$ k_t WITH BENZENE CONCENTRATION AT 25

X 10% CONVERSION

O 30% CONVERSION

● 60% CONVERSION

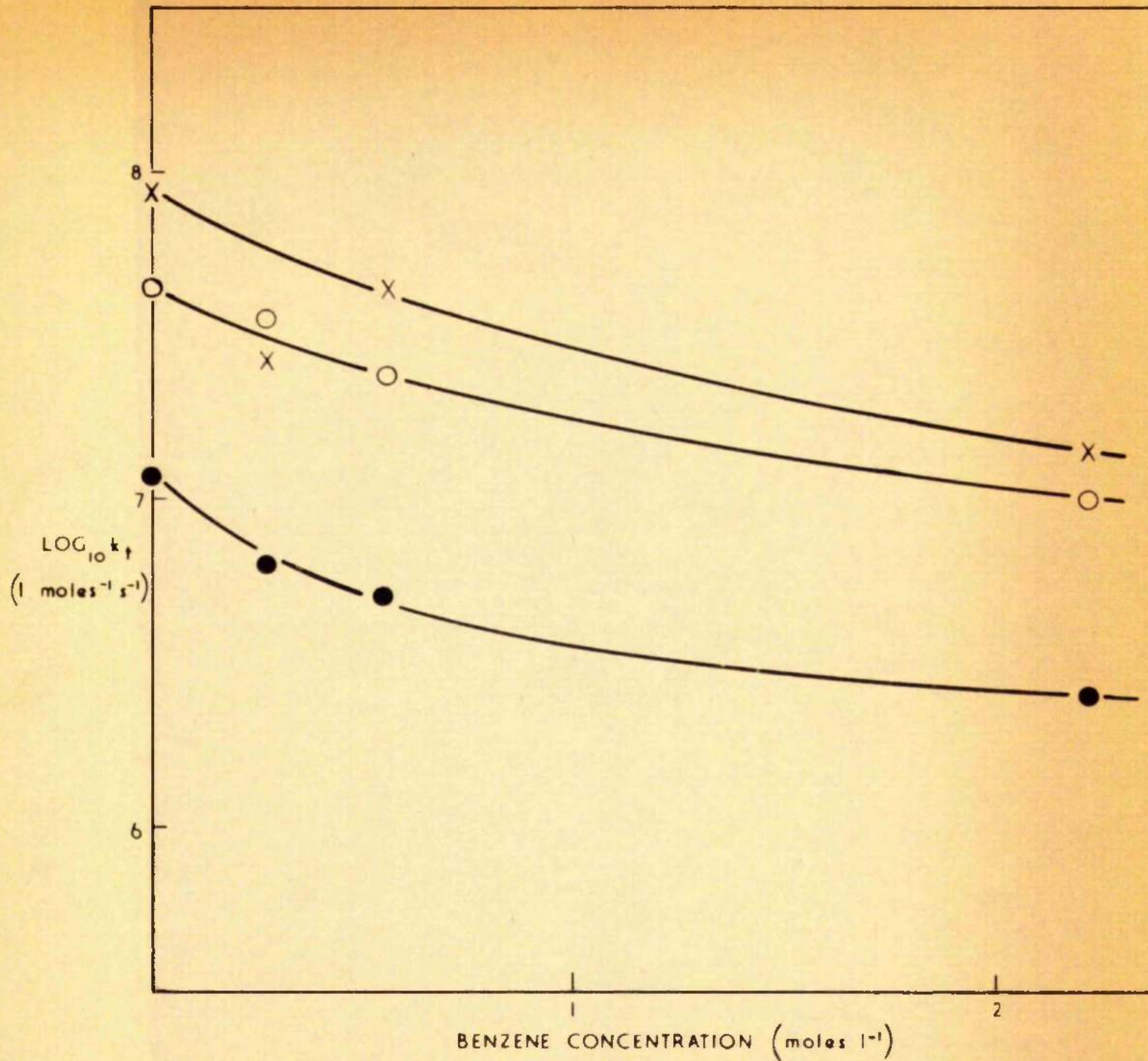


FIG 45 VARIATION OF LOG$_{10}$ k$_t$ WITH BENZENE CONCENTRATION AT 35

X 10% CONVERSION

O 30% CONVERSION

● 60% CONVERSION

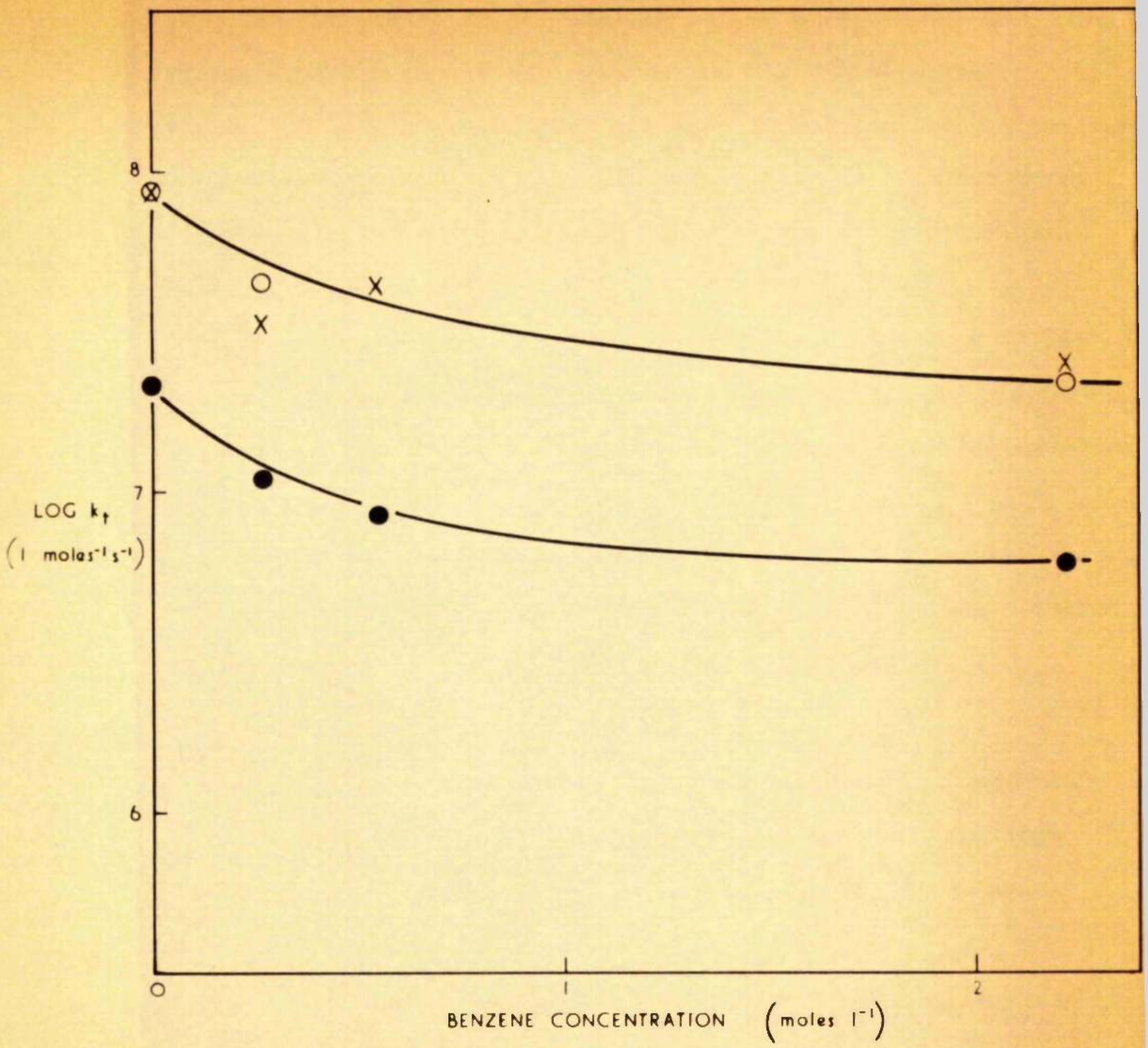


FIG 46 VARIATION OF LOG$_{10}$ k_t WITH BENZENE CONCENTRATION AT 45°

X 10% CONVERSION

○ 30% CONVERSION

● 60% CONVERSION

alter the viscosity of the mixture to any great extent but it has caused a marked increase in the activation energy of termination. The addition of solvent, since it is not acting a diluent, is making the chemical process of termination more difficult. Possible reasons for this effect will be discussed at a later stage.

The variation in the overall activation energy of the system with concentration is shown in Fig. 47. At all percentage conversions the overall activation energy increases with addition of solvent.

The assumption has been made throughout this work that th rate of termination is second order with respect to the catalyst concentration and consequently the equation

$$E_0 = E_p - \tfrac{1}{2}E_t \qquad \ldots\ldots\ldots\ldots\ldots(21)$$

is applicable to this system. Since both E_0 and E_t increase with the addition of solvent, E_p must also increase and this is demonstrated by the decrease in the values of k_p in the following tables.

Variation in the velocity coefficient of propagation at 25°C.

Concentration of Benzene		Conversion		
moles. l.$^{-1}$	%	10%	30%	60%
0	0	1010	840	400
0.28	2.5	320	480	160
0.56	5	280	300	130
2.24	20	40	4	4

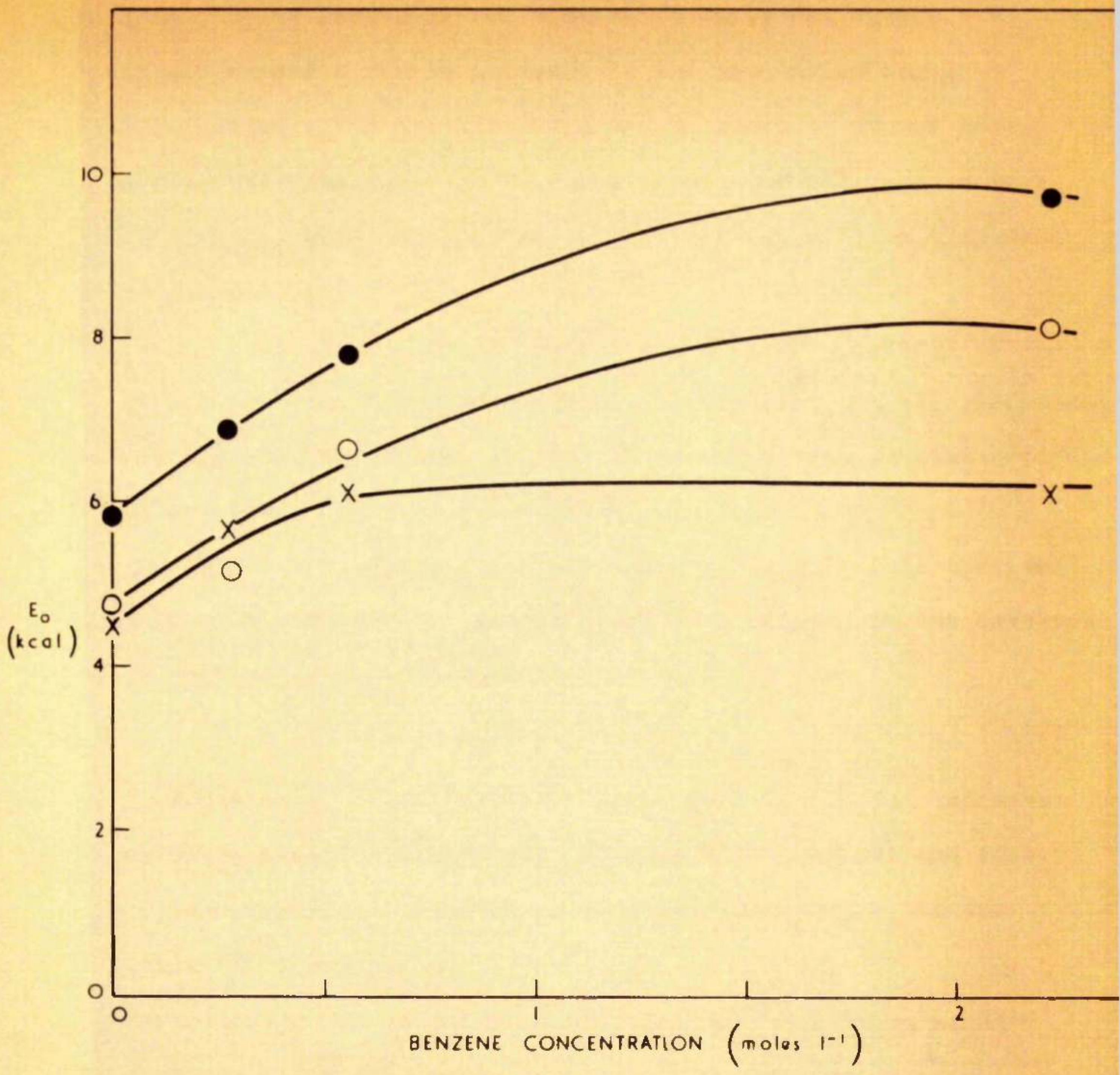


FIG 47 VARIATION OF ACTIVATION ENERGY E_o WITH BENZENE CONCENTRATION

X 10 % CONVERSION

O 30 % CONVERSION

● 60 % CONVERSION

Variation in the velocity coefficient of propagation at 35°C

Concentration of Benzene		Conversion		
mole. l.$^{-1}$	%	10%	30%	60%
0	0	1400	1250	760
0.28	2.5	650	730	330
0.56	5	490	430	230
2.24	20	105	70	17

Variation in the velocity coefficient of propagation at 45°C

Concentration of Benzene		Conversion.		
mole. l.$^{-1}$	%	10%	30%	60%
0	0	2100	2320	1380
0.28	2.5	950	930	630
0.56	5	710	820	440
2.24	20	150	115	40

The decrease in k_p is quite obvious from the above tables. The most significant feature is the magnitude of the difference in the values for the bulk polymerisation and the addition of 2.5% solvent to the reaction mixture. This cannot be assigned to any variation in the gel effect. Therefore the solvent is altering the process of propagating the chain length. There is another distinct decrease in the value of k_p when the concentration of the solvent is increased from 5% to 20%. If we assume that an average value for k_p at 5% benzene is 600 l. moles.$^{-1}$ s.$^{-1}$ while at

20% benzene it is 60 $l.mole^{-1}s^{-1}$, what does this decrease in value mean? The process involving the solvent molecule and the propagating chain radical is the same in both cases. But the chances of the reaction occurring between a radical and a solvent molecule are obviously greater with 20% benzene. This is reflecte in the values of the propagation coefficient since it takes $^{8}/_{10}$ times longer to propagate the chain at 20% benzene than it does at 5% benzene.

From this review of the relevant data, any explanation of the reaction between the solvent and the growing vinyl acetate chain radical must account for the following;

(1) fall-off in the rate of polymerisation with increasing benzene concentration,

(2) increase in the kinetic chain lifetime with increasing benzene concentration,

(3) increase in the overall activation energy E_0 with increasing benzene concentration,

(4) increase in the activation energy of termination E_t, which corresponds to an increase in the kinetic chain lifetime,

(5) an increase in the activation energy of propagation E_p with increasing concentration of benzene.

Before proposing a kinetic scheme to account for these facts, a review will be made of kinetic schemes proposed by other workers for similar systems.

The Retarder Action of Benzene on Vinyl Acetate Polymerisation

A kinetic analysis of the polymerisation of vinyl acetate in benzene is complicated by the number of different reactions that can occur.

The polymerisations were initiated by the action of ultraviolet light on azobiscyclohexane carbonitrile. This produces free radicals which, in bulk polymerisation, can react with another of the same kind or with a molecule of monomer to initiate a chain. The situation is more complicated by the presence of solvent. In this case the following reaction can occur.

$$R_c^{\circ} + M \longrightarrow R_1^{\circ} \qquad \ldots\ldots\ldots\ldots\ldots \quad (I)$$

$$R_c^{\circ} + S \longrightarrow S^{\circ} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (II)$$

$$R_c^{\circ} + R_c^{\circ} \xrightarrow[\text{Combination}]{\text{Disproportionation}} \text{Unreactive products} \quad (III)$$

where R_c° is a radical derived from the initiator. Since reaction II does not occur in bulk polymerisation it is possible that the efficiency of initiation will be reduced. Bevington[18] has shown that this remains constant over a wide range of solvent concentration and the rate of initiation has assumed to be constant in this work.

The radical chain produced in I can react as follows

Rate

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

$R_n^\circ + M \rightarrow P + R_1^\circ$ $k_{tr}[R^\circ][M]$ .... (V)

$R_n^\circ + B \rightarrow S^\circ$ $k_{tr'}[R^\circ][B]$ .... (VI)

where B is a molecule of benzene.

S is a solvent radical.

Reaction VI can take place by various mechanisms which will be shown below.

The polymer chain radical can be terminated by combination or disproportionation as outlined previously [page 7]. The solvent radical, however, can react in a number of ways.

Rate

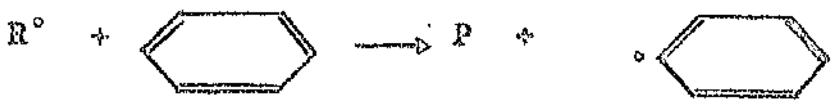
$S^\circ + M \quad R^\circ$ $k_{ri}[S^\circ][M]$ .... (VII)

$S^\circ + R^\circ \quad$ Polymer $k_{t_1}[S^\circ][R^\circ]$ .... (VIII)

$S^\circ + S^\circ \quad$ Stable Product $k_{t_2}[S^\circ]^2$ .... (IX)

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

(VIa)



(VIb)

Allen, Merret and Scanlan,[39] who investigated the polymerisation of vinyl acetate in isopropyl benzene and dihydromyrcene considered that the S° radical was formed by a chain transfer process. Having obtained an intensity exponent of 0.75, they concluded that the radicals produced from the solvent were resonance stabilised to an extent which made them slow to re-initiate with the unreactive vinyl acetate monomer and were frequently lost from the system by termination. However degradative chain transfer would be associated with an increase in the rate of termination and hence a decrease in γ . This has not been found in this work.

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 (c) a chain carrier, Burnett and Loan[1] also developed an equation for the rate. They used this equation to show that the variation in the apparent order of reaction with respect to the monomer concentration was due to the various concentration ranges used by different workers. Not only were they able to demonstrate this, but their kinetic scheme yielded theoretical curves for the rate of polymerisation of vinyl acetate in benzene which were very similar to the practical ones. However they obtained an extremely high value of 24 k.cals. for the addition of a phenyl radical to a monomer. Barson, Bevington and Eaves,[62] using C^{14} labelled benzoyl peroxide as an initiator of vinyl acetate polymerisation, found that the phenyl radical is an efficient initiator. This would indicate that the idea of chain transfer being the source of the S° radicals was wrong for the phenyl radical would require to be unreactive to account for the strong retardation of the rate in the presence of benzene.

Jenkins[40] suggested that the weakness in Burnett and Loan's kinetic scheme was that they equated the rate of formation of the S° radicals to the rate of re-initiation

i.e. $k_{tr}[R^\circ][B] = k_{ri}[S^\circ][M]$ .... (27)

Jenkins stated that this represented the condition that a negligible proportion of the solvent radicals participated in the termination reactions and if nearly all the transfer radicals were to undergo re-initiation then the retardation would be relatively weak. But equations of this form are common in copolymerisation kinetic schemes which have been used successfully to explain retardations in rates of reaction. He also based his velocity coefficients for the termination reactions on 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,[63] this is doubtful. Therefore reaction (VIII) probably occurs more easily than reaction (IX) and so a similar number of R° radicals are removed from the system when S° radicals are terminated by this reaction. If we assume that reaction (VI) occurs quickly and reaction (VII) is a slow step, then a large number of S° radicals will begin to build up in the system . Since another R° radical is removed whenever an S° radical terminates, the number of S° radicals in the system could rapidly increase while the number of R° radicals falls. When the system had reached a steady condition the ratio of the concentration of S° radicals to benzene concentration could equal the ratio of concentration of R° radicals to the monomer concentration.

$$\text{i.e.} \quad \frac{[R^\circ]}{k_{ri}\,[M]} = \frac{[S^\circ]}{k_{tr}[B]} \qquad \ldots\ldots\ldots\ldots(28)$$

$$\therefore \quad k_{tr}\,[R^\circ][B] = k_{ri}[S^\circ][M]$$

This is Burnett and Loan's original equation (equation 27) Therefore, this relationship could hold even though the S° radicals were participating in the termination reaction.

From his kinetic scheme Jenkins developed the following equation for the velocity coefficient of transfer with a solvent.

$$k_{tr} = \frac{(Ik_t)^{1/2}}{2[S]} \cdot \left(\frac{1}{\lambda} - \lambda \right) \qquad \ldots\ldots\ldots\ldots \quad (29)$$

using the normal symbols with

$$\lambda = \frac{m.[M_0]}{m_0[M]}$$

where m and m_0 are the rates of polymerisation in the presence and absence, respectively, of solvent.

Since the polymerisation reactions in this work were photo-initiated, the rate of initiation has been considered to be constant. k_t in equation (29) is the velocity coefficient for termination in the bulk polymerisation and the value of k_t does not vary much with temperature in this reaction. The expression $\frac{(Ik_t)^{1/2}}{2[S]}$ can be replaced by K, which is a constant for any given polymerisation at any particular extent conversion. So equation (29) can be rewritten,

$$k_{tr} = K \left(\frac{1}{\lambda} - \lambda \right) \qquad \ldots\ldots\ldots\ldots \quad (30)$$

Equation (30) seems to provide a reasonable method of calculating k_{tr}. However it is possible to express k_{tr} in the form,

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

The plot of $\left(\frac{1}{\lambda} - \lambda\right)$ against the reciprocal of the absolute temperature should give a value for E_{tr}. A horizontal plot is obtained using the results from this work indicating that E_{tr} is zero. In fact we have shown that E_{tr} is positive having a value of 4.8 k.cals (page 87) which is correct since the amount of transfer increases when the temperature is increased. So Jenkin's kinetic scheme, which is based on chain transfer followed by termination, must be wrong. It would also result in an increase in the rate of termination which would be reflected in a decrease in the kinetic chain lifetime. This has not been found.

Other evidence also tends to suggest that the theory of chain transfer is incorrect. It has been demonstrated that E_0 increases with the amount of benzene present during the polymerisation of vinyl acetate (Fig. 47). At the same time the rate of reaction falls due to retardation occurring more frequently. If the retardation reaction was due to chain transfer, E_0 in the presence of benzene would be less than E_0 in the bulk reaction. E_0 would decrease throughout the polymerisation of vinyl acetate in the presence of benzene since E_{tr} would be a negative term in the equation relating E_0 to E_p, E_t and E_{tr}.

In view of this evidence it must now be assumed that the transfer theory of retardation is wrong. Since the S° radical is not created by chain transfer it must be created by addition of a benzene molecule to the growing polymer. This step should occur quite quickly since it is, in effect, addition across a double band. If this is the case, the question of which reaction does cause the retardation remains to be answered.

A possible explanation for the retardation in rate is that after addition of the solvent molecule to the growing chain radical (VIb) reinitiation takes place. The radical formed by addition would be more stable than a phenyl radical and consequently the energy of re-initiation would be high.

This slow re-initiation step has already been used to justify Burnett and Loan's kinetic scheme and would obviously cause a retardation in the rate of reaction. It would also explain the increase in the kinetic chain lifetimes in solution. An increase in the kinetic chain lifetime would indicate a reduction in the rate of termination which would normally be accompanied by an increase in the rate of reaction. However, as we have previously shown, there would be a large increase in the number of S° radicals in the system if the re-initiation reaction was a slow step. This would lead to a decrease in R° radicals. Since only R° radicals are active in propagating, the rate of reaction will drop as they decrease and both the overall activation energy and the activation energy of propagation will increase. The decrease in τ as the temperature increases is probably due to the S° radicals becoming more reactive. The remaining question is whether the re-initiation step is by a copolymerisation process or by chain transfer with the monomer.

Stockmayer *et al.*[8] used the kinetic scheme developed by Kice[64,65] to explain their results obtained from the polymerisation of vinyl acetate in benzene at 60°C. They obtained chain transfer constants derived from the molecular weights of the polymer and from the rates of reaction, these being 1.2×10^{-4} and 2.0×10^{-3} respectively. Using $C_{tr} = 2 \times 10^{-3}$ they calculated that the possible combined cyclohexadiene residues to be about 2% but could not detect these by combustion analysis, determination of unsaturation by iodine monochloride or by infrared spectroscopy. They polymerised vinyl acetate in the presence of radioactive benzene at a ratio of 1:9. From the determinations of activity in the polymer from this one experiment they considered that the variation in chain transfer constants could be explained if benzene copolymerised with vinyl acetate. Breitenbach *et al.*[6] duplicated these radio-tracer experiments and from the activity in these polymers together with determinations of chlorine in chlorinated polymers concluded[66] that no copolymerisation was occurring.

The radio tracer results in this thesis indicate that the number of fragments per polymer molecule does tend to increase as the concentration of benzene in the system is increased. The number of fragments per polymer chain, however is no greater than 2 which indicates that only a slight degree of copolymerisation is occurring at 25°C with 20% benzene in the system. This conclusion must also be considered with care since the molecular weight of the polymers was obtained from viscosity measurements which are very susceptible to errors. Since the molecular weight of the polymer is in the numerator of the equation relating the number of fragments per polymer chain to the activity of the polymer (page 91), a variation in DP_n will influence the final result. The results at 2.5% and 5% benzene are definitely in favour of a chain transfer mechanism.

Another feature of this work is the apparent independence of the transfer constant on temperature. This is rather surprising. It may be that the activation energy for the addition of monomer to a chain radical is similar to that for the addition of a benzene molecule since they both involve addition to a double bond.

In conclusion, the evidence from this work suggests that the 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. From the radio-tracer experiments the re-initiation step, at the temperature and dilutions used, appears to be by chain transfer with monomer.

SUGGESTIONS FOR FURTHER WORK

Since there appeared to be an increase in the fragments of benzene present in the polymer chain at higher solvent concentrations, further tracer experiments with an increased concentration of solvent seem necessary. These could be conducted both at 25°C and 60°C to determine whether copolymerisation takes place at both or neither temperature with an increased concentration of solvent.

It would also be interesting to polymerise vinyl acetate in the presence of vinyl monomers containing aromatic rings e.g. styrene and vinyl benzoate. It may be that the low rate of reaction encountered in the copolymerisation of styrene with vinyl acetate is due to ring addition and not to the stability of the styryl radical. If radio-active styrene were used then more accurate information could be gained about the reactivity ratios of the system.

These experiments would follow as a logical extension of this work and provide more information about this particular type of polymerisation.

APPENDIX I

Determination of the Freezing Point and Mole Percentage Impurity from the plot of resistance against time

Time mins.	Resistance ohms.	Time mins.	Resistance ohms.	Time mins.	Resistance ohms.
0	302.1	14	364.1	28	364.57
1	312.3	15	363.42	29	364.66
2	319.5	16	363.40	30	364.78
3	329.0	17	363.48	31	364.99
4	336.3	18	363.64	32	365.29
5	342.0	19	363.75	33	365.38
6	347.3	20	363.85	34	365.51
7	352.4	21	363.94	35	365.69
8	356.3	22	364.04	36	365.96
9	359.6	23	364.14	37	366.44
10	363.75	24	364.24	38	366.65
11	366.40	25	364.36	39	367.03
12	368.8	26	364.44	40	367.32
13	371.4	27	364.50	41	367.74

The following formulae were obtained from page 195 of Physico Chemical Calculations by Guggenheim and Prue[64]

Mole Fraction Impurity $x = \dfrac{A}{\dfrac{1}{T_1 - T_3} - \dfrac{1}{T_1 - T_2}}$

where T_1 = Temperature at time = 0

T_2 = Temperature at time = t

T_3 = Temperature at time = 2t

and $A = \dfrac{S_f}{R.T_0} = \dfrac{H_f}{R\,T_0^{\,2}}$

H_f C_6H_6 ^{67} = latent heat of fusion = 30.3 cal.g^{-1}

where S_f C_6H_6 ^{64} = entropy of fusion = 8.44 cal deg.$^{-1}$ mole^{-1}

T_0 C_6F_6 ^{64} = 278.58°K

R = 1.987 cals. mole^{-1}

The thermistor used in the experiment was calibrated from 0°C to 10°C and the relationship $\log_{10}$ resistance = − 0.0196 obtained.

From the plot

Time mins.	Resistance ohms.	Log Resistance
16(T_1)	363.40	2.5604
29(T_2)	364.70	2.5619
42(T_3)	367.95	2.5758

$$\therefore\ T_1 - T_2 = 2.5604 - 2.5619 = \frac{-0.0014}{-0.0196} = 0.07142$$

$$T_1 - T_3 = 2.5604 - 2.5758 = \frac{-0.0154}{-0.0196} = 0.7856$$

$$\therefore \quad X = \frac{0.01525}{\frac{1}{0.07142} - \frac{2}{0.7856}} = \frac{0.01525}{14.01 - 2.546} = 0.00127.$$

∴ Mole Fraction Impurity = 0.001311

= 0.1311%

∴ Percentage Purity = 99.87.

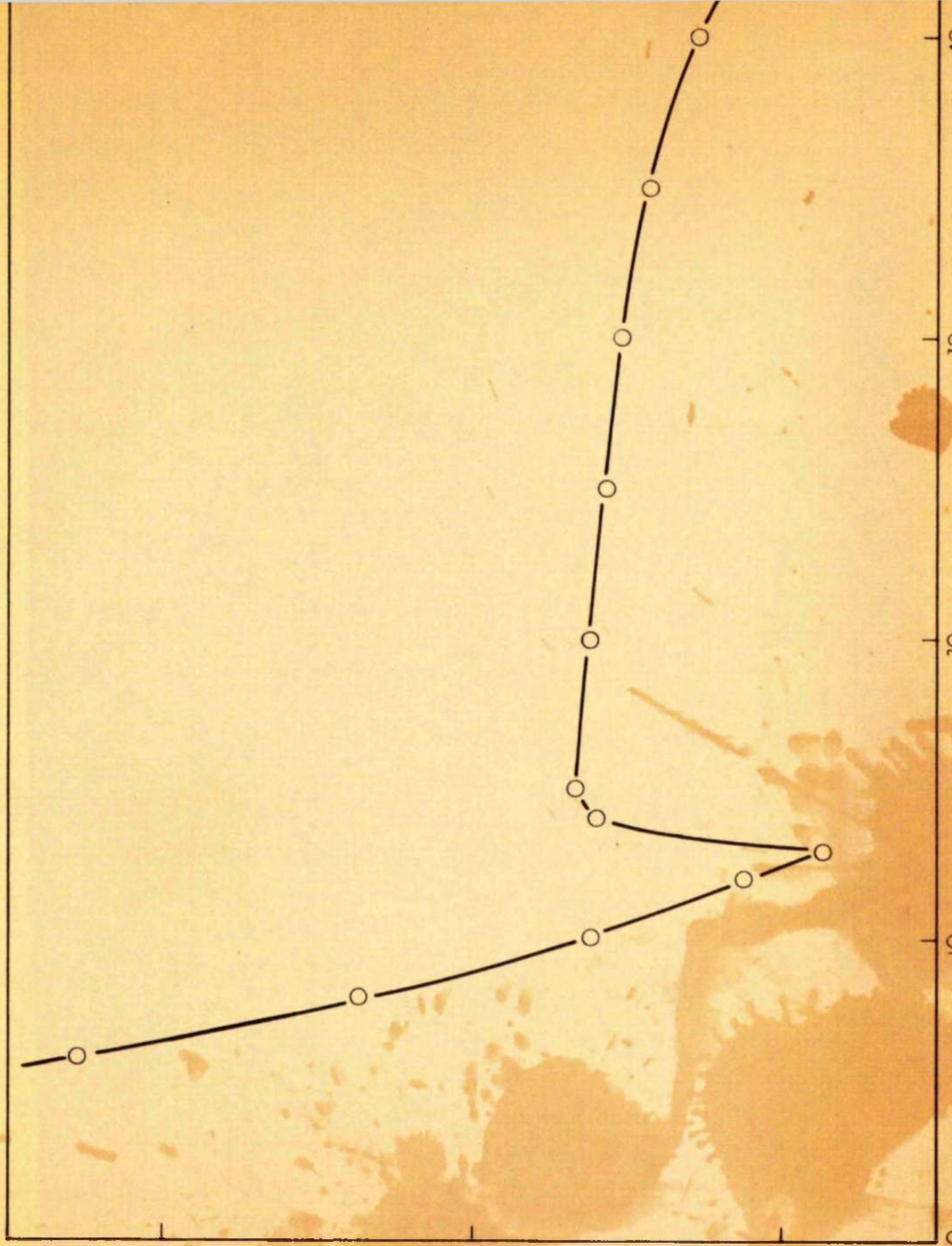


FIG 48 PLOT FOR DETERMINATION OF FREEZING POINT AND MOLE % PURITY OF BENZENE

APPENDIX II

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

From a typical chart trace a slope of 3.1×10^{-1} divisions $sec.^{-1}$ was obtained. The calibration curve showed that at the amplification used 10 μ volts was equivalent to 7.2 chart divisions, and since 40 $\mu v = 1°C.$,

Rate of temperature rise of polymerising mixture $= \dfrac{3.1 \times 10^{-1}}{0.72 \times 40}$ °C sec^{-1}

$= 10.75 \times 10^{-3}$ °C sec^{-1}

From the literature values[67]:

Heat of polymerisation of vinyl acetate, = 21.3 k.cals. $mole^{-1}$

Specific heat of monomeric vinyl acetate, = 0.47 cal. $gm.^{-1}$

Molecular weight of vinyl acetate, = 86

$\therefore$ Heat required to raise the temperature of 1 mole through 1°C $= 86 \times 0.47$ cals.

$= 40.4$ cals.

$\therefore$ 100% hr. reaction would raise the temperature $= \dfrac{21.3 \times 10^{3}}{40.4 \times 3}$ °C sec^{-1}

$= 1.47 \times 10^{-1}$ °C sec^{-1}

$\therefore$ Rate of Polymerisation $= \dfrac{10.75 \times 10^{-3}}{1.47 \times 10^{-1}}$ % $hr.^{-1}$

$= 7.31\%\ hr^{-1}$

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

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

This relationship was corrected as conversion proceeded to allow for the specific heats of the monomer and polymer and for the presence of solvent.

Consider the polymerisation of vinyl acetate in the presence of 20% v/v benzene:

Specific Heat of monomer = 0.47 cal $\mathrm{gm.}^{-1}$

Specific Heat of polymer = 0.39 cal $\mathrm{gm.}^{-1}$

Specific Heat of benzene at 25°C = 0.41 cal $\mathrm{gm.}^{-1}$

Original weight of monomer = 9.35 gm.

Weight of solvent = 2.48 gm.

At 20% conversion

$$\therefore \ 7.48 \times 0.47 + 1.87 \times 0.39 + 2.48 \times 0.41 = \text{Specific Ht} \times 11.83$$

$$3.52 + 0.73 + 1.02 = \text{Specific Ht} \times 11.83$$

$$\therefore \ \text{Specific Heat} = 0.445 \ \text{cal gm.}^{-1}$$

$\therefore$ The previous calculation was corrected by inserting 0.445 cal $\mathrm{gm.}^{-1}$ for 0.47 cal $\mathrm{gm.}^{-1}$

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