MECHANISM AND KINETICS OF VINYL POLYMERISATION:

THE POLYMERISATION OF METHYL METHACRYLATE

by

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INTRODUCTION

INTRODUCTION

The polymerisation reaction of methyl methacrylate has been the subject of a great deal of research over the past twenty years or so. This may partly be due to the commercial importance of the polymer but undoubtedly has its origins from the kinetic viewpoint in the unusual effects which take place as polymer accumulates in the system. The most striking characteristic of the reaction is the large increase in polymerisation rate which occurs at the intermediate stages (about 20% conversion) in the manner of autocatalytic systems. This is also accompanied by a corresponding increase in the polymer molecular weight. The phenomenon is generally referred to as the gel effect (or sometimes the viscosity or Trommsdorff effect). The work described in this thesis is primarily concerned with such effects (a review of relevant previous work is given in a later section).

Other vinyl polymerisations, such as those of vinyl acetate and styrene, exhibit similar characteristics but not to the same degree. With particular reference to the photopolymerisation an effect peculiar to methyl methacrylate has recently been observed. This is a decrease in the intensity exponent of the rate from an initial value of 0.5 (in agreement with the usual kinetic scheme) to a value of 0.3 in the region where the rate is increasing. This has not been satisfactorily explained, and since it has important implications in relation to the fundamental kinetic scheme for the reaction it is the reason for the investigation of the high conversion polymerisation which is the subject of this thesis.

The bulk polymerisation of methyl methacrylate has been studied up to 50% conversion using the thermistor non-stationary state method. Velocity coefficients for the propagation and termination reactions have been determined from measurements of reaction rates and kinetic chain lifetimes together with rates of chain initiation. The energies of activation for these reactions have also been determined where possible.

The low values of intensity exponent referred to above have been confirmed in this work. The possibility of the increase in dark rate at high conversion causing these low values has been rejected and an explanation suggested in terms of the effect of variation in radical chain length at different irradiation intensities on the termination reaction.

The latter effects prompted a further study of the polymerisation when the polymer chain length is reduced by controlled amounts. Molecular weight variations have been produced by introduction of the chain transfer agent bromotrichloromethane (BTCM) into the polymerising system in various concentrations. The molecular weights of the products formed at different BTCM concentrations have been determined and the transfer constant deduced. Values of velocity coefficients and energies of activation have also been determined at arbitrary intervals throughout the reaction when various concentrations of BTCM are present.

A definite dependence of the rate acceleration on radical chain length is observed and a modified form of the explanation generally accepted for the gel effect has been suggested involving localised zones of high viscosity.

Striking decreases have been noted in the values of the velocity coefficients when the radical chain length is small (19 monomer units and less). These have been discussed and tentative explanations given based on the possible low initiation efficiency of BTCM at high concentrations or on a slow chain initiation step. It is possible also that some mode of radical "solvation" effect is taking place in the BTCM medium.

Similar effects have been observed in the polymerisation of <u>iso</u>-butyl methacrylate in presence of BTCM.

The Mechanism of Addition Polymerisation

Addition polymerisations involving vinyl compounds of type CH_2=CHX can proceed by either a free radical or ionic mechanism depending on experimental conditions and on the nature of the substituent X. The more usual of the two is a free radical mechanism, and, as this is relevant to the present work, it will be considered in greater detail.

Staudinger[1] in 1920 was probably the first to recognise the possibility of a free radical mechanism in connection with his work on styrene polymerisation. However the first clear and unambiguous example of a free radical mechanism for a polymerisation reaction is that given by Taylor and Jones[2] in 1930 for the polymerisation of ethylene induced by the decomposition of mercury diethyl. Since then much evidence has been adduced in support of the free radical mechanism and it is now firmly established.

The overall reaction in a radical polymerisation can be divided into four elementary steps, viz., initiation, propagation, chain transfer and termination. These processes are common to all types of chain reaction.

Initiation.

Essentially this involves the opening of the monomer double bond to produce a free radical end or unpaired electron. This is generally achieved through the agency of heat, photochemical activation or initiators such as organic peroxides and azo compounds.

In thermal initiation the following sequence of reactions is generally held to occur:

$$2\ CH_2{=}CHX \longrightarrow \dot{C}H_2CHXCH_2\dot{C}HX$$

$$\dot{C}H_2CHXCH_2\dot{C}HX + CH_2{=}CHX \longrightarrow CH_2{=}CXCH_2\dot{C}HX + CH_3\dot{C}HX$$

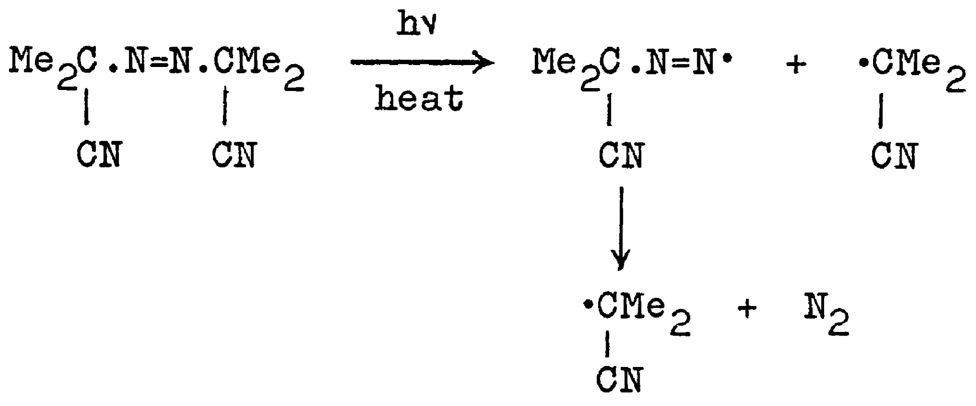
In the first step a diradical is produced by the collision and reaction of two monomer molecules. This reaction will have a high activation energy at room temperature and thus requires heat. In the second step the diradical disproportionates with monomer producing two monoradicals.

In purely photochemical initiation light of wavelength less than 3000 Å is absorbed and the associated energy opens the double bond producing monoradicals thus:

$$CH_2{=}CHX \xrightarrow{h\nu} \dot{C}H_2\dot{C}HX$$

$$\dot{C}H_2\dot{C}HX + CH_2{=}CHX \longrightarrow CH_2{=}\dot{C}X + CH_3\dot{C}HX$$

In the photoinitiator or catalyst method a compound is decomposed by heat or light to give free radicals stable enough to initiate polymerisation. For example α:α'-azobis<u>iso</u>butyronitrile decomposes thus:



$$\underset{\text{CN}}{\overset{}{Me_2C}}.N{=}N.\underset{\text{CN}}{CMe_2} \xrightarrow[\text{heat}]{h\nu} \underset{\text{CN}}{Me_2C}.N{=}N\cdot + \cdot\underset{\text{CN}}{CMe_2}$$

$$\underset{\text{CN}}{Me_2C}.N{=}N\cdot \longrightarrow \cdot\underset{\text{CN}}{CMe_2} + N_2$$

Thermally catalysed and photosensitised polymerisations are the most usual encountered in quantitative studies because it is easier to obtain reproducible results in such systems.

<u>Propagation</u>.

This step is simple and unambiguous. The monomer, once activated to the free radical state, can readily add further monomer molecules forming long chains. The reaction may be represented as,

$$R_n\cdot + M \longrightarrow R_{n+1}\cdot$$

$R_n\cdot$ represents a growing polymer radical of n monomer units.

M represents a molecule of monomer.

Chain transfer.

This is a reaction whereby the growing chain is stopped and the growth mechanism is transferred to another molecule. This may occur with monomer or with a solvent molecule. In general a hydrogen atom (or sometimes a halogen atom) is transferred from the inactive molecule to the growing radical, the solvent molecule being converted into a free radical in the process:-

$$\sim\sim\sim\, CH_2\dot{C}HX + SH \longrightarrow \sim\sim\sim\, CH_2CH_2X + S\cdot$$

The radical S• may or may not reinitiate polymerisation. In the former case the overall rate of reaction is not affected since the kinetic chain is not terminated. If reinitiation does not occur the rate will be retarded. In either case the molecular weight of the polymer formed is reduced.

The tendency of a molecule to act as a transfer agent will in general be governed by the relative ease of removal of the hydrogen atom. Compounds with a particularly labile hydrogen atom, e.g. triphenyl methane, are found to be efficient transfer agents.

Termination.

The most general mode of termination in free radical polymerisation is the mutual destruction of radicals in pairs. This can occur in either of two ways:

(a) combination,

$$R_1CH_2\dot{C}HX + R_2CH_2\dot{C}HX \longrightarrow R_1CH_2CHXCHXCH_2R_2$$

(b) disproportionation,

$$R_1CH_2\dot{C}HX + R_2CH_2\dot{C}HX \longrightarrow R_1CH_2CH_2X + R_2CH{=}CHX$$

These reactions are equivalent in a kinetic sense for two active centres are destroyed in each case. Usually one or other mechanism is preferred for a given monomer. In methyl methacrylate polymerisation the majority of radicals terminate by disproportionation[3,4].

Termination can also occur by interaction of the radicals with initiator fragments, impurities such as oxygen, or inhibitors. These reactions may be grouped under the heading of first order termination. Where this occurs to any great extent the kinetic analysis of the system is affected markedly (see page 14-19).

Kinetics of Addition Polymerisation[5].

The mechanism of addition polymerisation described in the previous section may be summarised in the following scheme:

Initiation	M	$\longrightarrow R_1\cdot$	rate = I
Propagation	$R_n\cdot + M$	$\longrightarrow R_{n+1}\cdot$	rate = $k_p[R]\,[M]$
Chain Transfer	$R_n\cdot + M$	$\longrightarrow P_n + R_1$	rate = $k_{tr}[R]\,[M]$
Termination	$R_n\cdot + R_m\cdot$	$\longrightarrow P_{(n+m)}$ or $P_n + P_m$	rate = $k_t[R]^2$

where $[M]$ = concentration of monomer.

$[R]$ = concentration of free radicals.

P = dead polymer.

I = rate of initiation

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

For the purposes of this analysis it will be assumed that chain transfer to monomer is negligible and that radical reactivity is independent of radical size[6-8], so that

$$(k_p)_1 = (k_p)_2 = \ldots\ldots (k_p)_n .$$

In the period immediately following commencement of the reaction the radical concentration will be rapidly increasing but this will very quickly approach a limiting value due to the onset of termination. Eventually a stage will be reached when the rate of production of radicals equals the rate of removal. This is the so-called stationary state. Thus at the stationary state we have,

$$\frac{d[R]}{dt} = I - k_t[R]^2 = 0 \qquad \text{..................... (1)}$$

$$\text{i.e. } [R_s] = (I/k_t)^{\frac{1}{2}} \qquad \text{..................... (2)}$$

where $[R_s]$ = concentration of radicals at the stationary state.

Before the limiting concentration $[R_s]$ of radicals is reached, i.e. in the non-stationary state, the concentration of radicals is increasing according to the equation,

$$\frac{d[R]}{dt} = I - k_t[R]^2 \qquad \text{..................... (3)}$$

Integration gives

$$\frac{1}{2}(k_tI)^{-\frac{1}{2}} \ln\left[\frac{1 + (k_t/I)^{\frac{1}{2}}\,|R|}{1 - (k_t/I)^{\frac{1}{2}}\,[R]}\right] = t + C \qquad \text{............ (4)}$$

$$\text{i.e. } \tanh^{-1}\frac{[R]}{[R_s]} = (k_tI)^{\frac{1}{2}}t \qquad \text{............ (5)}$$

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

The lifetime of the kinetic chain τ is defined as

$$\tau = \frac{\text{radical concentration}}{\text{rate of removal of radicals}} = \frac{[R_s]}{k_t[R_s]^2}$$

i.e. $$\tau = \frac{1}{k_t[R_s]} = (k_tI)^{-\frac{1}{2}} \qquad \text{.................. (6)}$$

Substituting in equation (5) gives

$$\tanh^{-1}\frac{[R]}{[R_s]} = \frac{t}{\tau} \qquad \text{.................. (7)}$$

Now the rate of polymerisation equals the rate of disappearance of monomer and we have,

$$-\frac{d[M]}{dt} = k_p[R]\,[M] \qquad \text{.................. (8)}$$

$$= k_p[R_s]\,[M]\,\tanh\left(\frac{t}{\tau}\right) \qquad \text{................ (9)}$$

Integration gives,

$$-\ln\frac{[M]}{[M_o]} = \frac{k_p}{k_t}\ln\left[\cosh(t/\tau)\right] \qquad \text{................ (10)}$$

If F = fractional conversion to polymer then,

$$\frac{[M]}{[M_o]} = 1 - F$$

$$\therefore -\ln(1-F) = \frac{k_p}{k_t}\ln\left[\cosh(t/\tau)\right] \qquad \text{................ (11)}$$

If $F \ll 1$ then, $-\ln(1-F) = F$ .... (12)

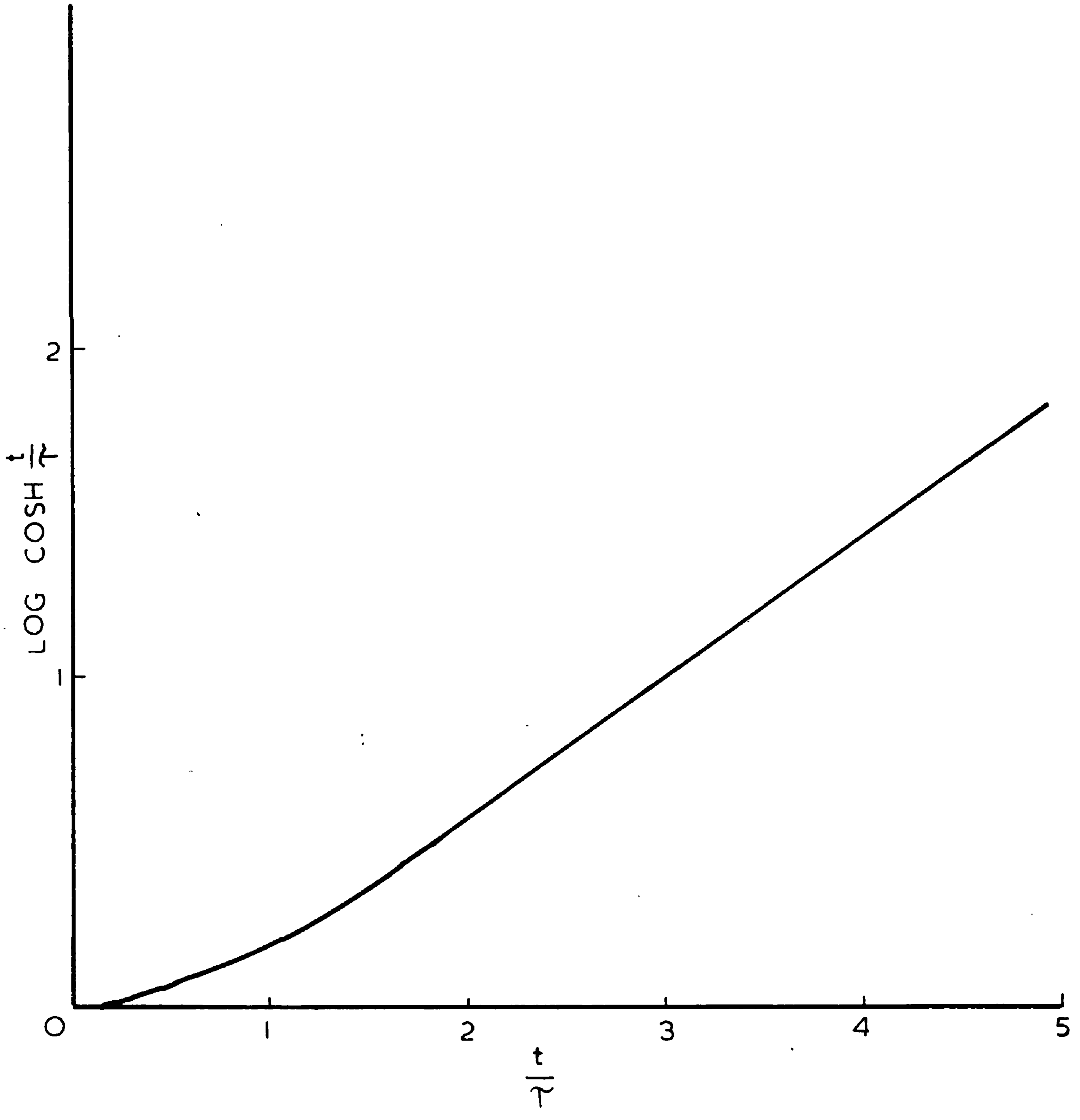
and equation (11) becomes $F = \frac{k_p}{k_t}\ln\left[\cosh(t/\tau)\right]$ .... (13)

Also when $t \gg \tau$ (i.e. during the stationary state) this approximates to

$$F = \frac{k_p}{k_t}\left(\frac{t}{\tau} - \ln 2\right) \qquad \text{................ (14)}$$

FIGURE 1

THEORETICAL PLOT OF FRACTIONAL CONVERSION AGAINST TIME



Thus a plot of fractional conversion against time will give a straight line of slope $k_p/k_t\tau$ and intercept on the time axis $t_i = \tau \ln 2$.

The lifetime can also be obtained from the decay curve when reaction is stopped since it requires a finite time for the rate to fall to zero. The radical concentration is governed by,

$$\frac{d[R]}{dt} = -k_t[R]^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

This integrates to $[R]^{-1} - [R_s]^{-1} = k_t t \quad \ldots\ldots\ldots\ldots (16)$

The rate of conversion to polymer at any stage is given by,

$$-\frac{d[M]}{dt} = k_p[R]\,[M]$$

$$\therefore \quad [R] = \frac{\text{Rate}}{k_p[M]}$$

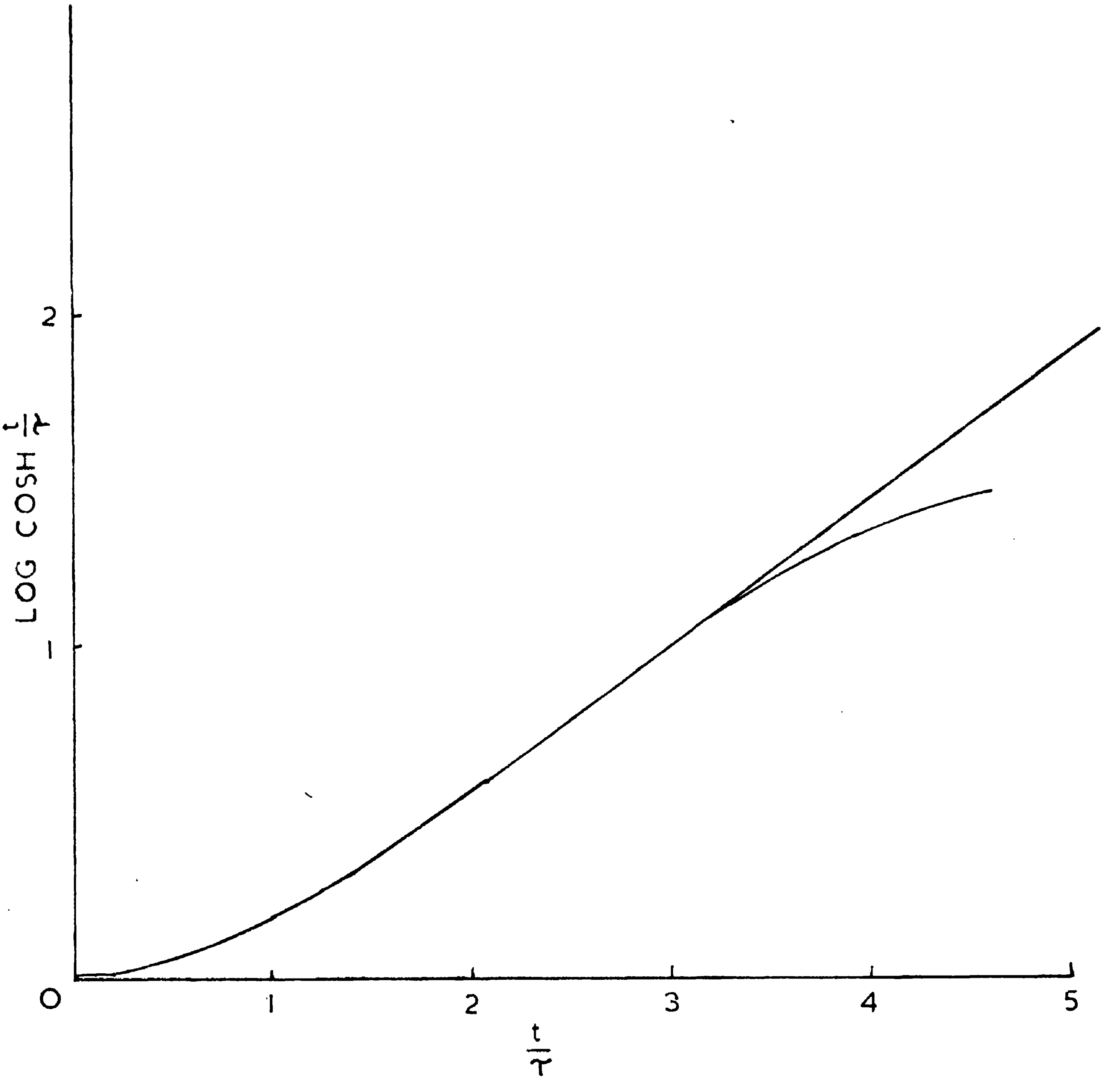
$$\therefore \quad (\text{Rate})^{-1} - (\text{Rate})_s^{-1} = \frac{k_t}{k_p[M]} \cdot t \quad \ldots\ldots\ldots\ldots (17)$$

Hence a plot of 1/Rate against time is linear with slope = $k_t/k_p[M]$. Also the rate when $t = \tau$ is $\frac{1}{2}(\text{Rate})_s$.

Thus by studying either the build up or decay period, values of the ratio k_p/k_t and of τ can be obtained. By measuring rates of initiation I under conditions that are identical k_t can be obtained from

FIGURE 2

THEORETICAL PLOT OF FRACTIONAL CONVERSION AGAINST TIME: EFFECT OF NON ADIABATIC CONDITIONS



$k_t = 1/\tau^2 I$ and hence k_p can also be calculated.

This analysis is based on the assumption of mutual termination of radicals. As indicated in the description of polymerisation mechanism, termination can also take place by a variety of first order processes. Strictly speaking this should not occur in bulk polymerisation if adequate precautions are taken to remove all impurities from the system. However in the presence of diluents of any kind first order termination may occur to some extent. This represents a mixed order termination and, as was stated previously, affects the kinetic analysis markedly. The following section suggests the corrections necessary to allow for this.

Kinetic Analysis of Mixed Order Termination

When mixed order termination occurs in a polymerisation it has been general to assume second order kinetics in deriving values of k_p and k_t. Burnett and Wright[9] have suggested a method of correcting for mixed order in relation to the rotating sector method, but even this is not entirely satisfactory since it is difficult to apply to the later stages of polymerisation.

The following method devised by Bengough[10] eliminates the errors due to the assumption of second order kinetics by introducing a correction factor.

The kinetic scheme is:

Initiation	$\left.\begin{array}{l} B + h\nu \longrightarrow C \\ C + M \longrightarrow R\cdot \end{array}\right\}$	Rate $= I$
Propagation	$R\cdot + M \longrightarrow R\cdot$	Rate $= k_p [R] [M]$
Mutual Termination	$R\cdot + R\cdot \longrightarrow$ polymer	Rate $= k_t [R]^2$
Monomer Termination	$R\cdot + M \longrightarrow$ polymer	Rate $= k_m [R] [M]$
Retarder Termination	$R\cdot + Q \longrightarrow$ polymer	Rate $= k_q [R] [Q]$
Occlusion Termination	$R\cdot + ? \longrightarrow$ polymer	Rate $= k_o [R] [?]$

where $R\cdot$ = a growing polymer radical

B = a molecule of initiator

C = a radical from the initiator

M = a molecule of monomer

Q = a molecule of retarder

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

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

$$\frac{d[R]}{dt} = I - [R]\Big[k_m[M] + k_q[Q] + k_o[?]\Big] - k_t[R]^2$$

$$= I - [R]X - k_t[R]^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (18)$$

where $X = k_m[M] + k_q[Q] + k_o[?] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$

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

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

$$\therefore [R_s] = -\frac{X}{2\,k_t} + \left[\frac{(X^2 + 4Ik_t)}{4k_t^{\,2}}\right]^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

$$= -\beta + \alpha$$

where $\beta = \frac{X}{2k_t}$ and $\alpha = \left[\frac{(X^2 + 4Ik_t)}{4k_t^{\,2}}\right]^{1/2}$

Integrating equation (20) over the period 0 to t, with the radical concentration changing from 0 initially to [R] at time t gives,

$$\alpha^{-1}\tanh^{-1}\left[\frac{[R] + \beta}{\alpha}\right] = \alpha^{-1}\tanh^{-1}(\beta/\alpha) + k_t.t \quad \ldots\ldots\ldots \quad (21a)$$

This rearranges to

$$[R] = -\beta + \alpha\tanh\left\{\alpha k_t.t + \tanh^{-1}(\beta/\alpha)\right\} \quad \ldots\ldots\ldots \quad (21b)$$

The rate of polymerisation is

$$-\frac{d[M]}{dt} = k_p[R]\,[M] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (22)$$

Substituting for [R] from equation (21b) in equation (22)

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

Integrating over the range 0 to t gives

$$\ln\left[[M_o] / [M]\right] = k_p\left[- \beta t + k_t^{-1} \ln\left\{\cosh(\alpha k_t t) + \alpha^{-1}\beta \sinh(\alpha k_t t)\right\}\right] \qquad \ldots\ldots\ldots\ldots(23)$$

where $[M_o]$ = initial monomer concentration,

$[M]$ = concentration of monomer at time t.

For values of $t \gg (\alpha k_t)^{-1}$ we have from equation (23)

$$\ln\left[[M_o] / [M]\right] = k_p(\alpha-\beta)t - (k_p/k_t) \ln\left\{2\alpha/(\alpha+\beta)\right\} \qquad \ldots\ldots\ldots\ldots(24)$$

and since $\ln\left[[M_o] / [M]\right] = - \ln (1-F)$

where F = fractional conversion of monomer to polymer,

when $F \ll 1$, $- \ln (1-F) \simeq F$ $\qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(25)$

Equation (24) then becomes

$$F = k_p(\alpha-\beta)t - (k_p/k_t) \ln\left\{2\alpha/(\alpha+b)\right\} \qquad \ldots\ldots\ldots\ldots(26)$$

This is a straight line which intercepts the time axis at $F = 0$ giving an intercept

$$t_i = \frac{\ln\left\{2\alpha/(\alpha+\beta)\right\}}{k_t/(\alpha-\beta)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(27)$$

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

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

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

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

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

$$\therefore\ n = \frac{I}{2[R_s]\alpha k_t} = \frac{I}{2\ k_t\alpha(\alpha-\beta)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (28)$$

Squaring equation (28) and substituting for α and β gives,

$$X^2 = \frac{(2n-1)^2}{n(1-n)} \cdot I \cdot k_t \quad \ldots\ldots\ldots\ldots\ldots\ldots (29)$$

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

By using the substitution $\alpha = p\beta$ where p is any integer or fraction, equations (27) and (28) can be solved to give

$$X = \frac{(2n-1)}{(1-n)t_i} \cdot \ln (1/n) \quad \ldots\ldots\ldots\ldots\ldots\ldots (30)$$

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

Substituting for X in equation (29) and solving for k_t we get

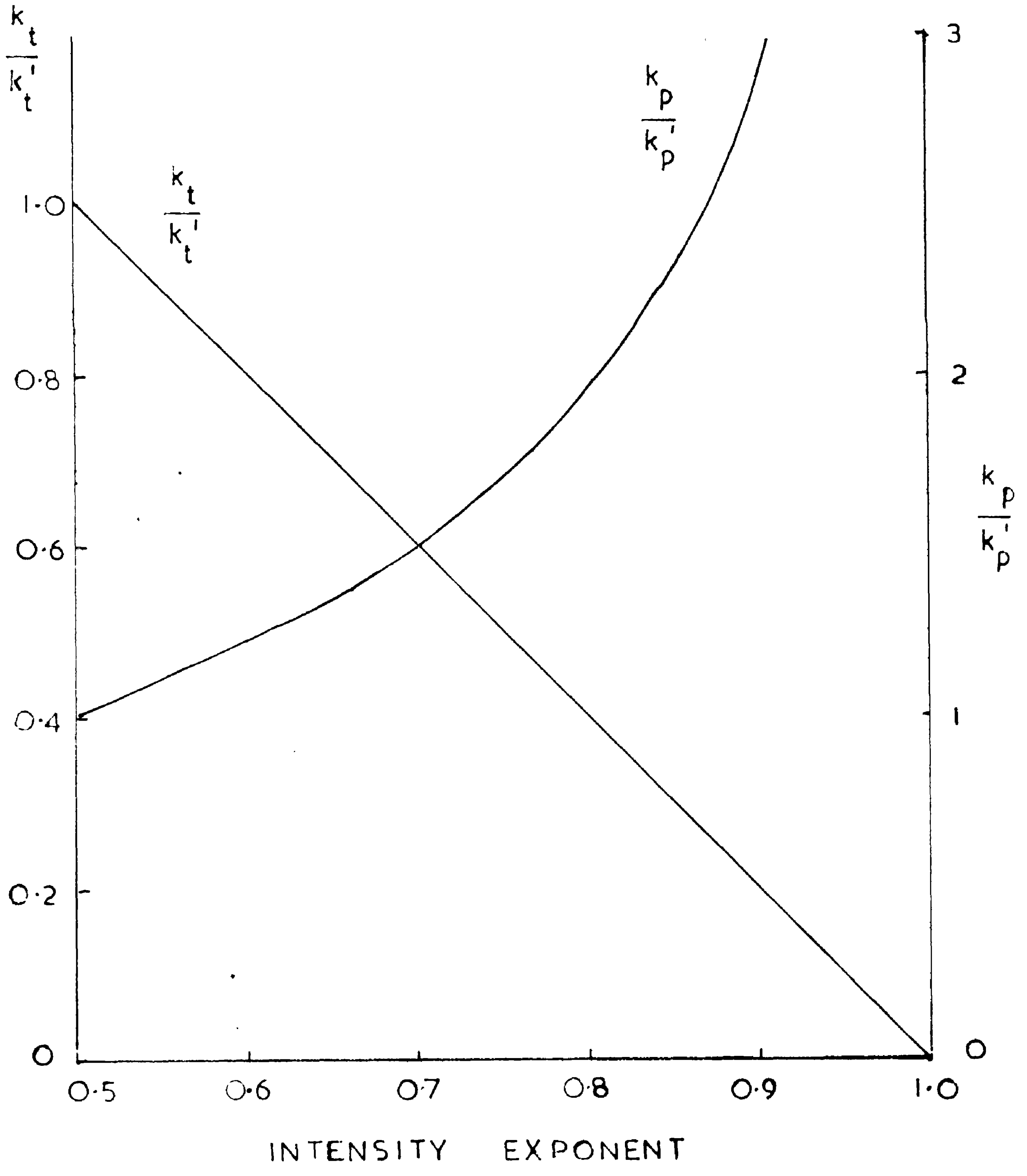
$$k_t = \frac{n \ln (1/n)^{2}}{(1-n)t_i^{2}(I)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (31)$$

Thus both k_t and X can be calculated from experimental measurements. Once X, I and k_t are known, k_p can be calculated since

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

$$\therefore\ k_p = \text{rate} / [M] \left\{ \frac{-X}{2k_t} + \frac{(X^2 + 4Ik_t)}{4k_t^{2}} \right\} \ldots\ldots\ldots (32)$$

FIGURE 3
MIXED ORDER TERMINATION CORRECTION FACTORS FOR k_p AND k_t



Solving for k_p in terms of the intensity exponent gives

$$k_p = \frac{\text{rate}}{(I/k_t)^{1/2}|M|} \cdot \left[\frac{n}{1-n}\right]^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(33)$$

Correction for the second order termination assumption.

Let k_t' be the calculated value of the coefficient for termination assuming exclusive second order termination.

Then $k_t' = \dfrac{(\ln 2)^2}{I.t_i^2}$

The correct value of k_t was given by equation (31)

The correction factor is, therefore, k_t/k_t'

$$\text{and } k_t/k_t' = \frac{n\{\ln(1/n)\}^2 \cdot (I)t_i^2}{(1-n)t_i^2 . (I) . (\ln 2)^2}$$

$$= \frac{n\{\ln(1/n)\}^2}{(1-n)(\ln 2)^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (34)$$

The correction factor for k_p is given from equation (33) as

$$k_p/k_p' = \left[\frac{n}{(1-n)}\right]^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (35)$$

Thus equations (34) and (35) give a value for the correction factor calculated solely on the basis of the intensity exponent. The correction factors for various values of n are given in figure 3.

Experimental Methods for Measuring the Non-Stationary State of Vinyl Polymerisations

This section describes experimental techniques to which the kinetic analysis of the non-stationary state, given in the preceding sections, can be applied. The duration of the non-stationary state is usually of the order of a few seconds so that conventional methods of chemical analysis cannot be used in its investigation. Recourse must be had, therefore, to physical methods capable of fine resolution in time. The following is a list of the commonly used methods.

Rotating sector method.

The idea of using intermittent illumination for the evaluation of velocity coefficients was first introduced by Briers, Chapman and Walters[11] in 1926 and later applied successfully to the liquid phase polymerisation of vinyl acetate by Burnett and Melville[12].

In this method a rotating disc with a segment of known area cut away is placed between the light source and the reaction vessel. The polymerisation rates when the sector is rotating at different speeds are determined dilatometrically. A definite transition in rate takes place when the flash time, which is a function of the speed of rotation, approaches the kinetic chain lifetime, thus enabling the latter to be determined. Since several rate determinations must be made by contraction measurements the method is time-consuming and this may result in considerable advancement of the polymerisation during the determination of a single lifetime. This can be largely eliminated using a modification of the method[13] whereby rates are measured as a function of the initial expansion under adiabatic conditions. The method is restricted to the measurement of lifetimes of the order of a few seconds. Moreover it falls down when first order termination is occurring for then the rate is independent of the flash time.

The spatial interference method[14] is similar in principle. Here the rates are determined when two beams of light of equal intensity are focussed on the polymerising system, (a) when the beams are far apart, (b) when they interfere. In (a) the rate will be the sum of that obtained with each beam individually if the time of diffusion of radicals from one zone to the other is long compared to the lifetime. In (b) the rates of initiation will be additive. Obviously the transition from one rate to the other should permit calculation of the lifetime.

These methods are not truly measurements of the non-stationary state. They involve the establishment of a pseudo-stationary state with a different associated radical concentration from the normal stationary state.

Dielectric constant method[15].

The original idea behind this method was to measure the change in dielectric constant of the medium caused by the formation of polymer. For the low conversions being dealt with, however, this was found to be small compared to the changes induced by deviation from isothermal conditions. The method was then adapted to measure the changes in dielectric constant produced by the heat of reaction under adiabatic conditions, with the change due to monomer conversion as a correction term.

Two tuned circuits, with quartz reaction vessels acting as capacitors, are balanced out initially. When one is irradiated the out of balance is amplified and recorded by an oscilloscope. The rate is measured by this means till a steady state is established and the required data are then obtained by extrapolation to the time base. High resolution is obtained of 10^{-5}°C in 10^{-4} seconds. The reactions vessels are not expendable, however, and so the method is unsuitable for use at high conversion.

Refractive index method.[16,17]

The same considerations apply here as in the previous method. Changes in refractive index caused by the formation of polymer are obscured by those due to temperature change in the exothermic reaction. The latter is therefore determined indirectly as a function of the composite refractive index change.

Use is made of a photoelectric recording interferometer of the Jamin type. Pairs of optically matched interferometer tubes are used as reaction vessels and the movement of interference fringes across the field of view of a telescope is observed when the reaction vessel is irradiated. Again the necessary data are obtained by extrapolation of the stationary state rate curve to the time base.

The method can be made extremely sensitive in time resolution (e.g. measurement of 10^{-4} °C in 10^{-2} sec. can be achieved) by the use of cine photographic recording. It is subject, however, to considerable operating difficulties, for example through the drift of fringes due to dark or thermal polymerisation and background temperature fluctuation. Also the specially designed reaction vessels make the method unsuitable for examining the gel stage of a polymerisation. It has the advantage over the dielectric constant method that it is not restricted to systems of electrically insulating liquids and could be used, for example, with electrolytes.

Thermocouple method.[18]

In the previous two methods the temperature rise due to self-heating of the reaction medium is measured indirectly as a function of some temperature-dependent property. In this method the temperature rise is measured directly by the use of a thermocouple situated at the centre of the reaction vessel. This records the adiabatic temperature rise when polymerisation takes place.

Perhaps the main improvement over the refractive index and dielectric constant methods, apart from the directness of the method, is that only the temperature rise at the centre of the vessel is recorded whereas in the other methods the average over the whole vessel is measured. In the latter case errors will obviously arise since the reaction will not remain truly adiabatic due to cooling losses at the surface. The improvement in adiabatic period in the thermocouple method means that longer lifetimes can be accurately measured. Also since the vessels are simple and inexpensive the method can be used to examine the later stages of polymerisation. A slight limitation is that systems cannot be studied which attack the metals of the junction, e.g. halogen compounds.

Thermistor method[19,20]:

This is essentially the same as the thermocouple method in which a thermistor is used as the temperature-sensitive element. It is perhaps more sensitive in temperature than the thermocouple method but since in practice this is limited by background fluctuations (see discussion) it does not represent any improvement in practice. However the resistance head is usually glass-coated so that it can be used for systems which are reactive towards metals.

The thermistor, placed at the centre of the reaction vessel, constituted one arm of a balanced Wheatstone Bridge. When reaction is initiated the balance is broken up and a signal is obtained from the bridge which can be amplified and recorded. By reason of the fact that current is flowing through the system even at the null point the thermistor is less sensitive to electrical pick-up than the thermocouple method in which the signal starts off from an absolute zero.

Since this is the method used in the present work it will be described in more detail later.

Dilatometric methods.

The measurement of the change in volume as monomer is converted to polymer is perhaps the most widely used method of measuring the reaction rate in the stationary state. Recently the method has been adapted to the measurement of the non-stationary state also[21]. The method again depends on the reaction remaining adiabatic for a period sufficiently long for the stationary radical concentration to be established. This has been possible in the present method by enclosing the dilatometer in a vacuum jacket. The physical constants for most vinyl monomers are such that the initial expansion due to heat of reaction is greater than the contraction occurring due to polymer formation. The rate and lifetime can be determined by measuring this initial expansion rate using cine photographic methods or a pen-recording voltmeter.

Another dilatometric method has been described[22] which examines the decay curve obtained in the period immediately following the end of irradiation. The analysis is based on the solution of the simultaneous differential equations governing chemical reaction and heat flow to the surroundings.

These methods have the advantage over the other methods described that they are simple and no complicated apparatus is required.

Viscosity method.[23,24]

Finally may be mentioned the viscosity method in which changes in intrinsic viscosity of a photopolymerising system are measured during the stationary state and in the period immediately following the cessation of irradiation. The use of vacuum viscometers makes the method very simple in practice but again it is unsuitable for use at high conversion.

Review of Previous Work on the "Gel Effect".

The preceding sections have dealt with the theory (and some of the experimental methods of applying it) on which the work of this thesis is based. Before going on to describe the present work in detail it will perhaps be relevant to summarise the work which has been done previously on methyl methacrylate polymerisation. Since the present investigations are primarily concerned with the gel effect the summary will be restricted to this aspect of the polymerisation.

The gel effect (sometimes known as the viscosity effect or Trommsdorff effect) is a well-known kinetic characteristic of most vinyl polymerisations and is manifested by an increase in the rate of reaction as polymer accumulates in the system. The magnitude of this autoacceleration varies from monomer to monomer but it is greatest in methyl methacrylate, the rate increasing by as much as a factor of 10 over the first 50% polymerisation. The explanations suggested for this have been notable only for their number and variety since the effect was first noted about twenty years ago.

Norrish and Brookman[25] in 1939, during a study of the thermal polymerisation of methyl methacrylate, were the first to observe the phenomenon. They supposed that the reaction became non-isothermal between 10 and 20% conversion when convection currents were suppressed by the increasing viscosity of the medium. Since the heat of reaction could not be carried away the temperature rose and with it the rate also. Thus they interpreted the effect in terms of a "thermal explosion". A similar effect was also noted in vinyl acetate polymerisation by Cuthbertson et al.[26] and the explanation given was based on the postulation of a series of consecutive reactions involving catalyst-monomer complexes which controlled initiation.

Neither of these explanations was accepted for long since it was soon discovered by Schulz and Blaschke[27,28], working on methyl methacrylate, that the acceleration was still evident even under isothermal conditions so that it should be interpreted as a real kinetic effect. These authors argued that the rate increase itself was responsible for the temperature rise and was caused by an increase in the rate of formation of active centres, i.e. by an increased rate of initiation. This view was later shown to be untenable by Trommsdorff[29] who observed that the acceleration was accompanied by a large increase in the molecular weight of the polymer formed. From the usual kinetic scheme for addition polymerisation this would be quite inconsistent with an increased rate of initiation. Trommsdorff also showed that the rate acceleration could be produced equally by adding compounds of high molecular weight (e.g. cellulose tripropionate) as well as by the polymer produced '<u>in situ</u>', and that by the introduction of small amounts of divinyl compounds (e.g. 1% of 1:3-butylene glycol dimethacrylate), which produce cross-linked three-dimensional structures, the effect was greatly increased.

An important advance was made by Norrish and Smith[30] who suggested that the rate acceleration was the result of the increase in bulk viscosity of the medium causing a fall in the value of the termination velocity coefficient, k_t. This was based on the observation that the gel effect occurred earlier at low values of temperature and initiator concentration, conditions which result in higher bulk viscosity. They tested this hypothesis further by polymerising methyl methacrylate in a range of diluents, e.g. precipitants for the polymer, poor solvents and good solvents, so that a wide variation in bulk viscosity at a given percentage conversion would be obtained. The rate and molecular weight were found to increase most with precipitants and least with good solvents. In good solvents the polymer chains were supposed to be less associated and hence more mobile and amenable to interaction.

Further work was undertaken by Schulz and Harborth[31] who confirmed that even under isothermal conditions at 50 and 70°C the rate acceleration persisted and that the molecular weight of the polymer increased in approximately the same ratio as the rate up to 40% conversion. The theory was advanced that the termination step became diffusion controlled as the bulk viscosity increased. They gave a slightly different interpretation of the results of Norrish and Smith attributing the acceleration in bad solvents to the precipitation of polymer which then absorbs monomer to give an inhomogeneous mixture corresponding in composition to high conversion. The reasons for the rate increase would then be the same as for the bulk polymerisation at high conversion.

Work of a similar nature was reported by Burnett and Melville[32] on vinyl acetate polymerisation. They observed an increase in rate at 25% conversion in the bulk reaction and earlier in the presence of <u>n</u>-hexane which is a poor solvent for the polymer. An explanation was suggested in terms of the coiling of growing polymer chains thus restricting the interaction of radical chain ends and causing a decrease in the rate of termination.

Analagous to the gel effect were observations made on the emulsion polymerisation of methyl methacrylate[33,34] and on the heterogeneous polymerisation of vinyl chloride[35] and acrylonitrile[36]. The rate in emulsion polymerisation was greatly increased compared to that in the bulk reaction and this was attributed to a reduced termination rate in micelles of high internal viscosity. The accelerating rate observed in heterogeneous polymerisations was again thought to be due to hindrance to radical-radical interaction caused by a chain transfer reaction with 'dead' polymer or by occlusion of radical chain ends in agglomerates of polymer.

Thus the qualitative picture was more or less established at this stage that the gel effect is a result of the decreased rate of termination caused by the increase in bulk viscosity of the medium. As a result of improvements in experimental techniques for studying polymerisation reactions information of a more quantitative nature was soon forthcoming. For example Matheson <u>et al</u>.[37] measured the individual velocity coefficients for the propagation and termination steps (k_p and k_t) using the rotating sector method. They found that k_t was reduced by a factor of 100 at 33% conversion while k_p remained substantially constant.

In a paper by Vaughan[38] the Rabinowitch[39] treatment of diffusion control of second order reactions was applied to the polymerisation of methyl methacrylate and the modified theory was found to predict the bulk viscosity at which the rate acceleration begins. No relation was found between solution viscosity and reaction rate, however. In a similar study by Robertson[40] it was concluded that a definite bulk viscosity must be reached before diffusion control of the polymerisation can set in.

Burnett and Loan[41] have drawn attention to the rapid fall in reaction rate to zero which occurs at about 80% conversion so that the reaction never achieves completion. The point is brought out to add weight to the diffusion control hypothesis. At these extremely high conversions the system becomes a solid gel and it is supposed that growing polymer radicals become completely immobilised and are rendered inaccessible even to monomer so that the radical concentration is effectively reduced and the reaction rate falls. It is suggested by these authors that the accelerated phase of the polymerisation does not involve a reduction in k_t but that an increase in radical concentration is brought about by the trapping of radicals in the viscous medium. At this stage monomer can still diffuse freely so that the rate is increased. but due to radical immobility the rate of termination is reduced.

Despite these arguments recent work by Bengough and Melville[42] and by Hayden and Melville[43] has shown that in the photosensitised polymerisation k_t, as measured by the thermocouple method, does in fact decrease by a factor of 100 over the first 40% conversion and by a factor of 10^5 over the first 80%. Measurements of energies of activation for the individual steps also point to a reduction in k_t. The validity of these results is thrown in some doubt by assumptions which have to be made with regard to the termination reaction. The calculations are based on the theory of the non-stationary state which assumes mutual destruction of growing radicals. This implies that the intensity exponent of the reaction rate should be 0.5 . However the above authors have observed considerable deviation from this. Although in the initial stages the exponent has the required value of 0.5 it very quickly falls off to reach a value of 0.3 at about 30% conversion. Thereafter it begins to increase and tends towards a value of unity in the final stages. If these are to be taken as true kinetic effects then the termination reaction would seem to be of third order or higher during the accelerated phase tending to first order at the later stages. A kinetic interpretation of third order termination would seem improbable and the low value of intensity exponent is thus difficult to explain. The suggestion has been made that the effect may be attributable to photochemical after effects which are most marked in methyl methacrylate polymerisation[42], but no entirely satisfactory evidence has been adduced to account for the fall in exponent and to this extent these measurements remain in doubt.

The increase in intensity exponent to unity at the later stages is fairly readily explained. This may in fact imply a gradual change to first order termination since the radicals are removed from the system simply by immobilisation in a gelled medium. Another factor tending to produce an increase in exponent is that the full stationary state rates are never achieved within the adiabatic period of the reaction at these later stages because of the enormous increase in kinetic chain lifetimes. This point will be discussed more fully in a later section (page 124).

Worthy of attention is work by Benson and North[44] in which the viscosity of the medium is accurately varied over the range 0.4 to 200 c.p. in the initial stages of the reaction by adding mixtures of polyethylene oxide - polypropylene oxide copolymers. Values of k_p and k_t are determined by a dilatometric method. It is found that k_p remains unchanged over the entire viscosity range but k_t undergoes a large reduction. The authors conclude that termination is diffusion controlled over the complete range and that k_t is proportional to the reciprocal of the first power of solvent viscosity. However no dependence of k_t on the chain length of the radicals could be observed.

In view of the findings of these more recent papers it was thought desirable in the present work to examine more precisely the reasons for the low value of intensity exponent during the accelerated phase of the reaction so that the reduced values of k_t could be placed on a sounder theoretical basis. Also it was thought advantageous to examine the polymerisation kinetics when the radical chain length is reduced by controlled amounts. As indicated in this review much work has already been carried out on the effects of added compounds of different types on the course of the polymerisation. Mostly these have been compounds which precipitate the polymer[30] or cause premature gelling through cross-linking[29,45]. A great deal of solution polymerisation has also been investigated but this has mainly been confined to the initial stages of the reaction using solvents of negligible or very low transfer constant. Hence the effects observed have been due to dilution of the medium which merely causes an indeterminate lowering of the bulk viscosity without necessarily reducing the molecular weight of the polymer to any appreciable extent.

Molecular weight reductions can be effected by the use of an efficient transfer agent. One such compound which has been used in investigations of other vinyl polymerisations is bromotrichloromethane (BTCM)[46-49]. This compound is also an excellent source of free radicals with an excitation wavelength in the region of 3300 - 3900 Å so that polymerisations can be studied using non-stationary state methods which require that photochemical initiation be used. This property of bromotrichloromethane also obviates the need for any conventional photosensitiser to be used thus dispensing with any complications which might arise from interaction of the catalyst and transfer agent. BTCM, therefore, is eminently suitable for the type of investigation undertaken in this work.

The present thesis, then, is a study of the kinetics of methyl methacrylate polymerisation in systems of the above type.

EXPERIMENTAL

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Apparatus

A line diagram of the experimental arrangement used in the non-stationary state measurements is shown in figure 4. The essential items of apparatus are the reaction vessel equipped with thermistor and situated in a constant temperature bath, an amplifier and a pen recorder.

Considerable time was spent in the design of a suitable reaction vessel to meet all requirements. The vessel shown in figure 5 is constructed in pyrex glass. The bulb A is of about 15 ml. capacity and contains the thermistor T with the resistance bead at the centre. The cunife thermistor leads are brazed to tungsten wire suitable for sealing into pyrex at S to give a vacuum tight seal. Outside the vessel the tungsten is brazed to flexible leads for making connections to the external circuit. Arms B and C, of 0.5 cm. bore, are for filling from the high vacuum line and for dilatometric contraction measurements respectively. Mercury is used as the recording liquid since the monomer-polymer mixture becomes extremely viscous at high conversion causing serious distortion of the mèniscus. This represents a

FIGURE 4

DIAGRAM OF EXPERIMENTAL ARRANGEMENT.

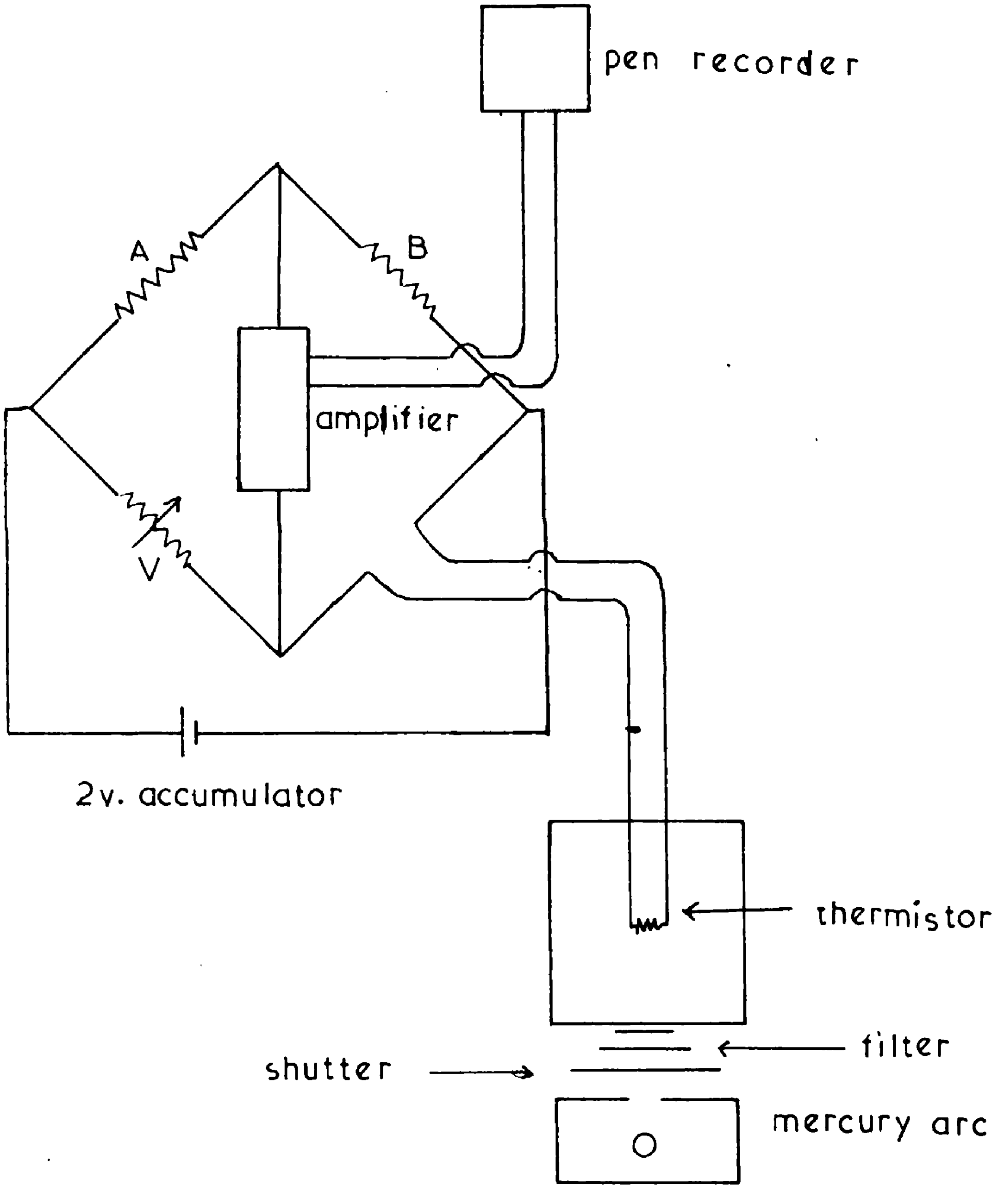
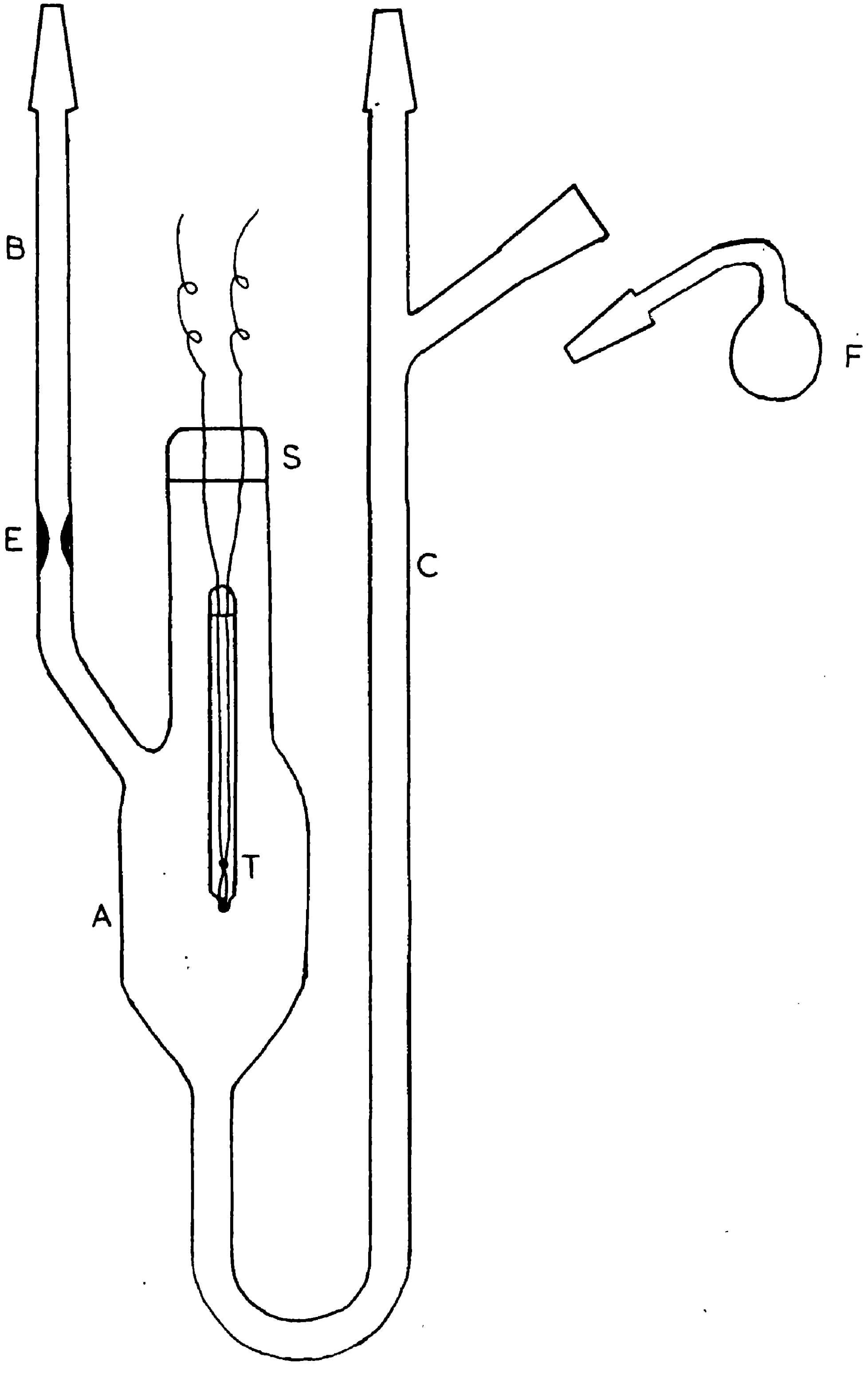


FIGURE 5

THERMISTOR REACTION VESSEL.



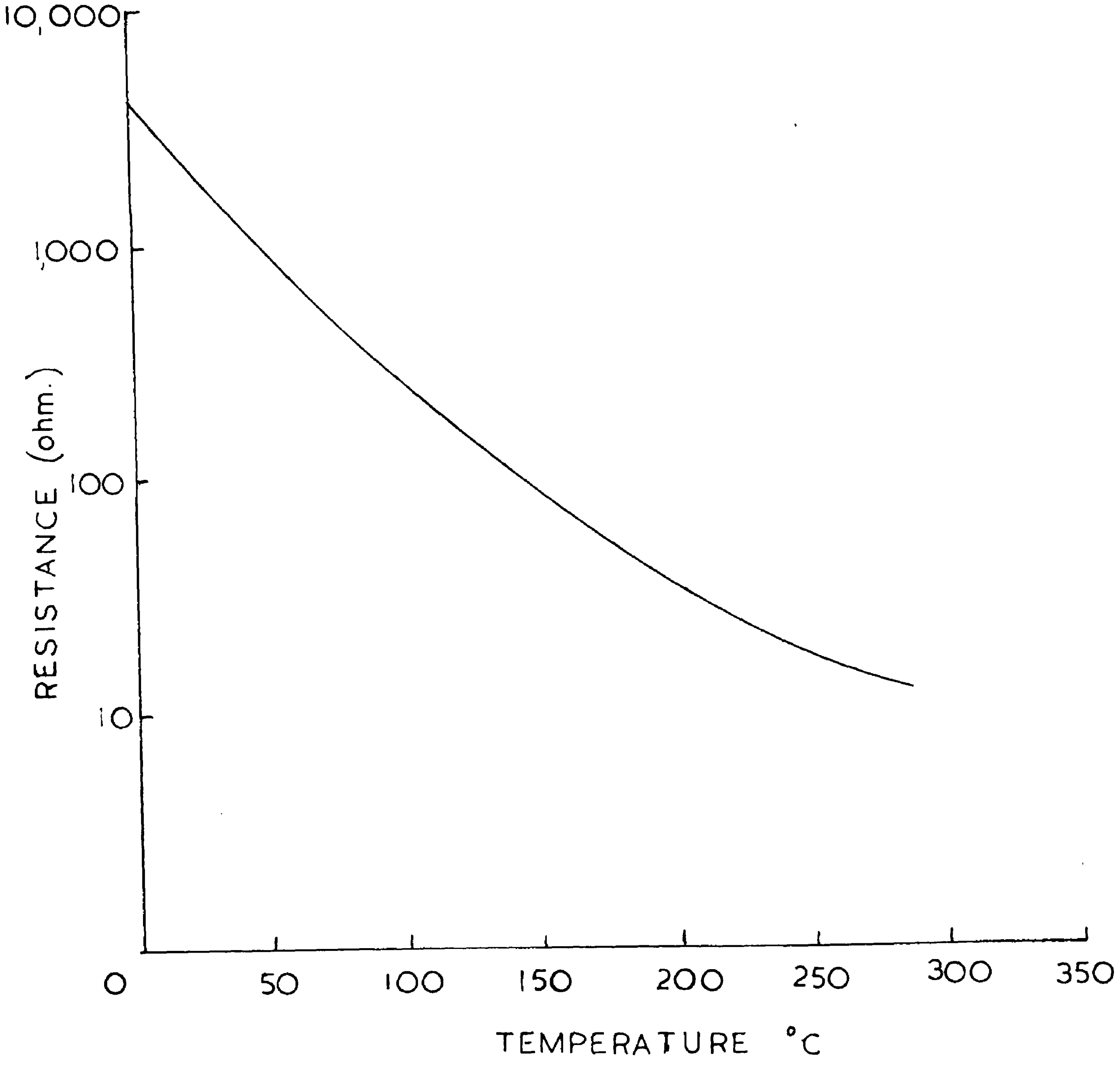
considerable improvement on other methods used in estimating conversion[42,43] which are based on time-integration of a measured rate or on gravimetric analysis which can only give an accurate estimate of the final extent conversion when the vessel is broken open. If it is not required to make contraction measurements for estimating extent of conversion the side arm C can be dispensed with.

The thermistors used were supplied by Standard Telephones and Cables Ltd. The type chosen as suitable for the present work is coded F.23. and has the temperature-resistance characteristics shown in figure 6. This is a directly heated bead type thermistor. The element consists of a very small bead of resistance material which is integrally formed on two parallel platinum wires. The platinum leads are welded to cunife leads and the assembly is sealed in a soft glass bulb. The thermistor has a resistance of about 2000 ohm. at 20°C manufactured to a tolerance of ± 20%. The maximum continuous power dissipation is 10 mW which if greatly exceeded may lead to permanent damage of the element. Apart from this the power dissipation should be kept as low as possible to avoid self-heating of the thermistor.

The external bridge circuit (figure 4) consisted of the ratio arms A and B and the variable resistance V

FIGURE 6

RESISTANCE - TEMPERATURE CHARACTERISTICS OF THERMISTORS.



which could be adjusted in stages of 0.1 ohm up to a value of 1000 ohm in balancing the bridge. A standard voltage was applied to the bridge by a 2-volt lead accumulator.

The amplifier was a Sunvic DC model, Type DCA.1, with output designed to give ± 5 milliamps into a maximum load of 5000 ohm. D.C. negative feedback is applied to the amplifier and the sensitivity is controlled by the value of the feedback resistance. This can be arranged for an input impedance ranging from 40 to 1 k.ohm in four stages. The amplifier can be used, as in the present work, to give a low impedance voltage output of up to 25 volts for full scale output (5 mA). This was adequate for the present work, and as will be explained later, the limit of temperature measurement is not controlled by the amplification obtainable but by other factors (page 119).

An Elliot pen recording voltmeter was used in conjunction with the amplifier to give a chart trace of the out of balance from the bridge. The chart speed could be readily varied from 12" per hour to 12" per minute.

The thermostat was a cylindrical water tank of pyrex glass, lagged at the base with expanded ebonite and round the sides with fibre glass contained in an aluminium jacket. The tank had suitable apertures for viewing and irradiation. The temperature was controlled by a 250-watt Robertson heater connected to a Variac transformer thus allowing variation of the background heat input. Finer control (± 0.005 °C) was achieved using in addition a 40-watt bulb heater operating on a relay circuit controlled by the conventional mercury-toluene regulator.

The source of ultra violet light for the photochemical reactions was a 125-watt Osira mercury arc, connected to a choke and capacitor. Thermal and other undesirable radiation effects were cut out by the use of a Chance OX1 filter with a band in the region of 3650 Å.

All reactions were carried out under high vacuum conditions. A vacuum line of standard design was constructed in pyrex glass with a pumping system consisting of a 3-stage mercury diffusion pump backed by an Edwards oil pump. This enabled a vacuum of 10^{-5} m.m. of mercury to be attained.

Materials.

Monomeric methyl methacrylate was obtained from I.C.I.Ltd. and washed with 10% caustic soda solution till the yellow colour in the aqueous layer had completely disappeared. This removed all but the last traces of the hydroquinone added as inhibitor. The monomer was then washed with distilled water several times and dried for 2-3 days over calcium chloride. It was then fractionally distilled under an atmosphere of nitrogen in an all-glass apparatus and the fraction boiling at 40 °C (80 m.m. mercury pressure) collected. The monomer was then transferred to the vacuum line and thoroughly outgassed by repeated freezing-pumping-thawing cycles. It was finally prepolymerised to about 5% conversion and distilled on the vacuum line immediately before use.

Monomeric iso-butyl methacrylate was similarly purified.

Bromotrichloromethane (BTCM) was supplied by Eastman Kodak Ltd. It was washed with dilute sodium carbonate solution to remove free bromine, then with distilled water and dried over calcium chloride. It was stored in the dark and subjected to distillation under reduced pressure immediately before use.

Di-t-butyl peroxide (TBP) was obtained from Laporte Chemicals Ltd. and distilled under reduced pressure (40-45 °C at 55-70 m.m. mercury) dried over anhydrous copper sulphate and stored in the dark. It was distilled again before use.

Chloroform and carbon tetrachloride used as diluents in non-stationary state measurements were of spectroscopic grade and were distilled once before use.

1:1'-diphenyl-2-picrylhydrazyl (DPPH) used in measuring rates of initiation was prepared by the method of Goldschmidt and Renn[50] and recrystallised from benzene. The product obtained is the 1:1 addition complex of DPPH and benzene.

Experimental Procedure

Calibration of thermistors.

The exact temperature coefficient of resistance was determined for each thermistor used at 25, 35 and 45 °C, the temperatures it was proposed to work at. This was done by immersing the reaction vessel, filled with an inert liquid such as benzene, in the thermostat. The thermistor was connected to the external bridge circuit as under reaction conditions and allowed to come to thermal equilibrium with the bath. The bridge was then balanced and the value of the variable resistance V (figure 4) noted. A Beckmann thermometer measured the temperature of the bath to 0.001 °C. The bath temperature was then raised by an amount such as might occur during the non-stationary state of a polymerisation reaction (0.1 to 0.2 °C) and the new balance point noted when thermal stability was again attained. This procedure was repeated for several small variations in temperature about the ambient value thus obtaining the temperature coefficient of resistance. The amplitude of the recorder deflection produced by various small changes in V (of the order of those encountered under reaction conditions) was then measured.

This enabled a direct relation between temperature change of the thermistor and recorder deflection to be obtained. A typical example of this relation is shown for the operating temperatures in figure 7. Values were found to vary by as much as 50% from one thermistor to another.

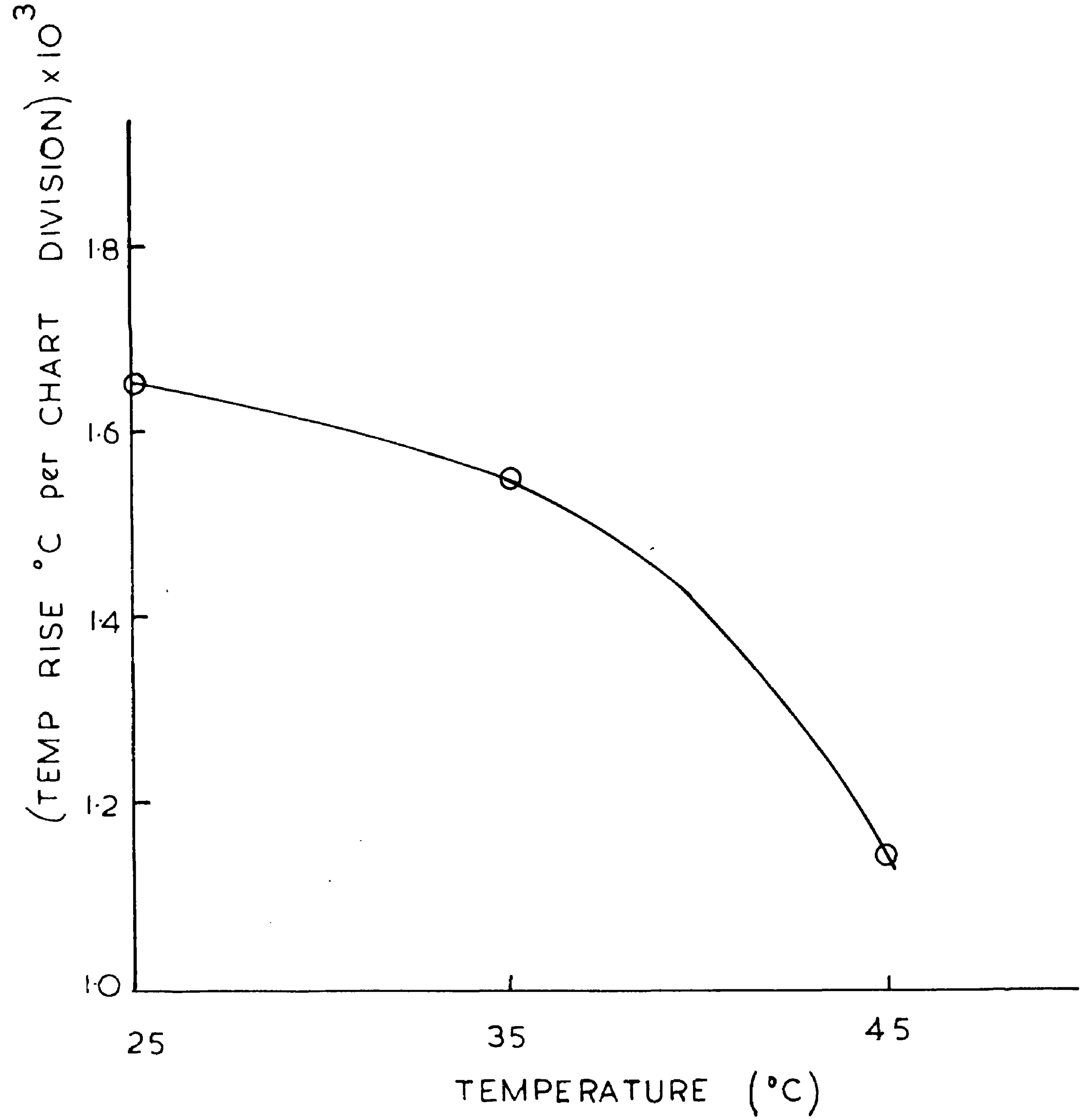
This is perhaps a more laborious method than that used for example by Fujii and Tanaka[20] in which the recorder chart is calibrated by introducing a test signal voltage through a standard resistance connected to the circuit, but it makes for simplicity in the bridge circuit and is certainly equivalent in accuracy.

Filling of reaction vessels.

Vessels of the type shown in figure 5 were filled as follows. Mercury was poured into the side arm C till the U-bend was filled to the bottom of the bulb A. The remaining volume of the vessel up to the constriction E was determined by running in acetone from a burette. The vessel was then emptied and cleaned with conc. nitric acid followed by water and acetone, and finally dried by prolonged pumping on the vacuum line. The same amount of mercury as used in the calibration was then poured in again and the required quantity of peroxide catalyst introduced through limb B using a micrometer syringe.

FIGURE 7

TYPICAL CALIBRATION CURVE FOR THERMISTORS.



The vessel was attached to the vacuum line at the cone joints on B and C and the mercury and catalyst degassed. Monomer was then distilled in through limb B from a graduated reservoir on the vacuum line to fill the space up to E at 25°C, the standard operating temperature. The constriction at E was then collapsed and sealed off. Mercury from the bulb F was poured in to fill limb C as far as possible before disconnecting the vessel from the vacuum system.

When diluents such as BTCM, chloroform and carbon tetrachloride were also required these were added and degassed in the same way as described for the mercury and catalyst before distilling in the monomer.

Where large amounts of BTCM were required the mercury seal type of vessel could not be used since mercury is rapidly attacked under these conditions. In these cases the U-bend and side arm C were not included in the design and only the bulb A was filled with reaction mixture. Extent of conversion had then to be estimated by integration of the rate recorded by the thermistor.

Procedure for measurement of the non-stationary state.

The thermistor leads external to the reaction vessel were insulated and rubber tubing was pushed over the seal S to prevent contact of the leads with the thermostat water. The leads were then soldered into the bridge circuit and the vessel clamped rigidly and reproducibly in the thermostat. The amplifier and mercury arc were switched on and left for one hour to attain thermal stability, by which time the reaction vessel should also be in thermal equilibrium with the bath.

After the bridge was balanced and the recorder chart set moving at a speed of 12" per minute the shutter was opened by hand as the pen passed a suitable mark on the recorder chart. The rise in temperature of the reaction mixture was observed on the recorder chart and when a steady rate of increase was established the reaction was stopped by replacing the shutter. A typical chart trace obtained in this way is shown in figure 8. A period of at least 15 minutes was allowed to elapse before any further measurement was made. This period is to allow thermal equilibrium to be re-established and its length will depend on the kinetic chain lifetime and the thermal conductivity of the reaction medium.

Such measurements were repeated at different light intensities by inserting wire gauze screens or photographic plates of known transmission factor in the light

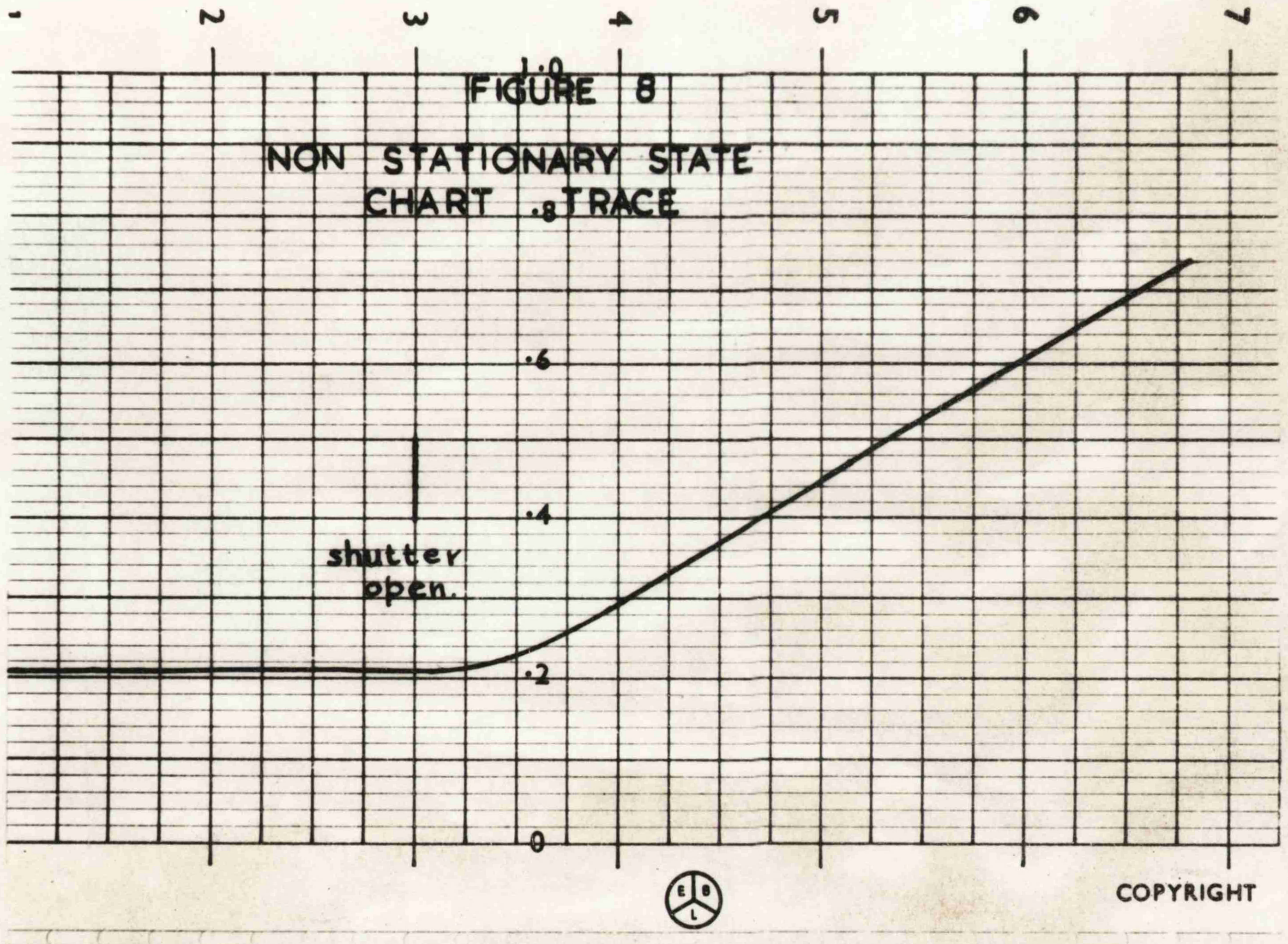


FIGURE 8

NON STATIONARY STATE CHART TRACE

beam. This permits estimation of the intensity exponent of the rate. Also by plotting reciprocal rate against time-intercept the instrument lag is obtained from the value of the intercept at infinite rate. Each individual measurement of rate and lifetime was repeated at least three times to ensure reproducibility. To obtain activation energies similar measurements were made at 25, 35 and 45°C.

The reaction mixture was then continuously irradiated, recording the temperature variations with the thermistor, till a suitable extent of conversion was reached and the complete set of non-stationary state measurements repeated. In order to cut down dark rate when a set of measurements at one conversion was not completed, the reaction vessel was kept in a drikold-acetone freezing mixture overnight and at weekends. Even so dark rate is considerable at the later stages and it becomes difficult to associate one set of measurements with a particular extent of conversion since the polymerisation may advance during the long periods which have to be left between measurements.

Moreover it was found that at about 50% conversion in the bulk polymerisation the reaction mixture, which had become a solid gel, parted from the walls of the vessel or formed internal cavities at various locations so that after this stage accurate estimation of the extent of conversion was not possible by contraction measurements. The final extent could be checked by weighing a slice of the polymer before and after pumping off residual monomer under vacuum.

Also, if a cavity were formed between the light source and the thermistor the non-uniform light path produced might cause various internal reflections or some scattering of light. This would produce unpredictable variations in reaction rate. For these various reasons measurements were seldom taken beyond about 50% conversion since the results would be almost meaningless.

Measurement of dark rate.

This was carried out using dilatometers of similar design to those used in the non-stationary state work (figure 5). No thermistor was necessary and the limb C was replaced by narrow bore capillary (0.2 m.m.) to enable accurate contraction measurements to be made. The use of this mercury seal dilatometer enables the dark rate to be followed right through to the later stages by continually topping up the capillary with mercury.

Other experimental techniques used were the determination of rates of initiation using an inhibitor, DPPH, and the determination of molecular weights of polymers by viscometry and by cryoscopic methods. These will be described later in the appropriate sections dealing with the results of the experiments.

EXPERIMENTAL

RESULTS

I. The Bulk Polymerisation of Methyl Methacrylate

It was desired to cut down the thermal or "dark" rate as far as possible so that a set of measurements could be completed without the polymerisation advancing to any appreciable extent. This was specially important during the later stages when the dark rate is high. As mentioned in the introduction it was also desirable to minimise these photochemical after effects from the point of view of rendering the calculation of individual velocity coefficients on a theoretically sound basis.

A search of the literature revealed that the use of the catalyst di-t-butyl peroxide would be eminently suitable in this respect since it has a negligible thermal decomposition rate at temperatures below 80°C[51], which was well above the working temperatures envisaged.

The initial step in the photochemical decomposition[52] is the scission of the -O-O- bond to give two t-butoxy radicals. These may disproportionate or abstract hydrogen from a substrate to give fresh radicals thus:

$$(CH_3)_3CO.OC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO\cdot$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2CO + CH_3\cdot$$

$$(CH_3)_3CO\cdot + (CH_3)_3CO.OC(CH_3)_3 \longrightarrow (CH_3)_3C.OH + (CH_3)_3COOC(CH_3)_2\dot{C}H_2$$

The lifetime of these radicals, of whatever species, is sufficiently long to allow polymerisation to be initiated.

The U.V. absorption spectrum was checked down to 3200 Å and is shown in figure 9. The measurements were made on a 0.6 mole $l.^{-1}$ solution in methyl methacrylate. Cells of 2 cm. path length were used in a Unicam spectrophotometer. The spectrum shows that there is no structural absorption in the wavelength range measured and ensures the absence of internal filter or "skin" effects at the principal wavelength of the mercury arc (3650 Å) for solutions at least up to 0.6 mole $l.^{-1}$.

Preliminary experiments.

Rates of polymerisation were determined at various catalyst concentrations by a simple dilatometric technique using vessels of about 10 ml. capacity with capillary stems of 2 m.m. bore. This was necessary in order to check on the catalyst exponent and to ensure that the monomer purification procedure was adequate. The results also serve to establish a suitable catalyst concentration for use in the non-stationary state experiments.

FIGURE 9
ABSORPTION SPECTRUM OF
DI-t-BUTYL PEROXIDE.

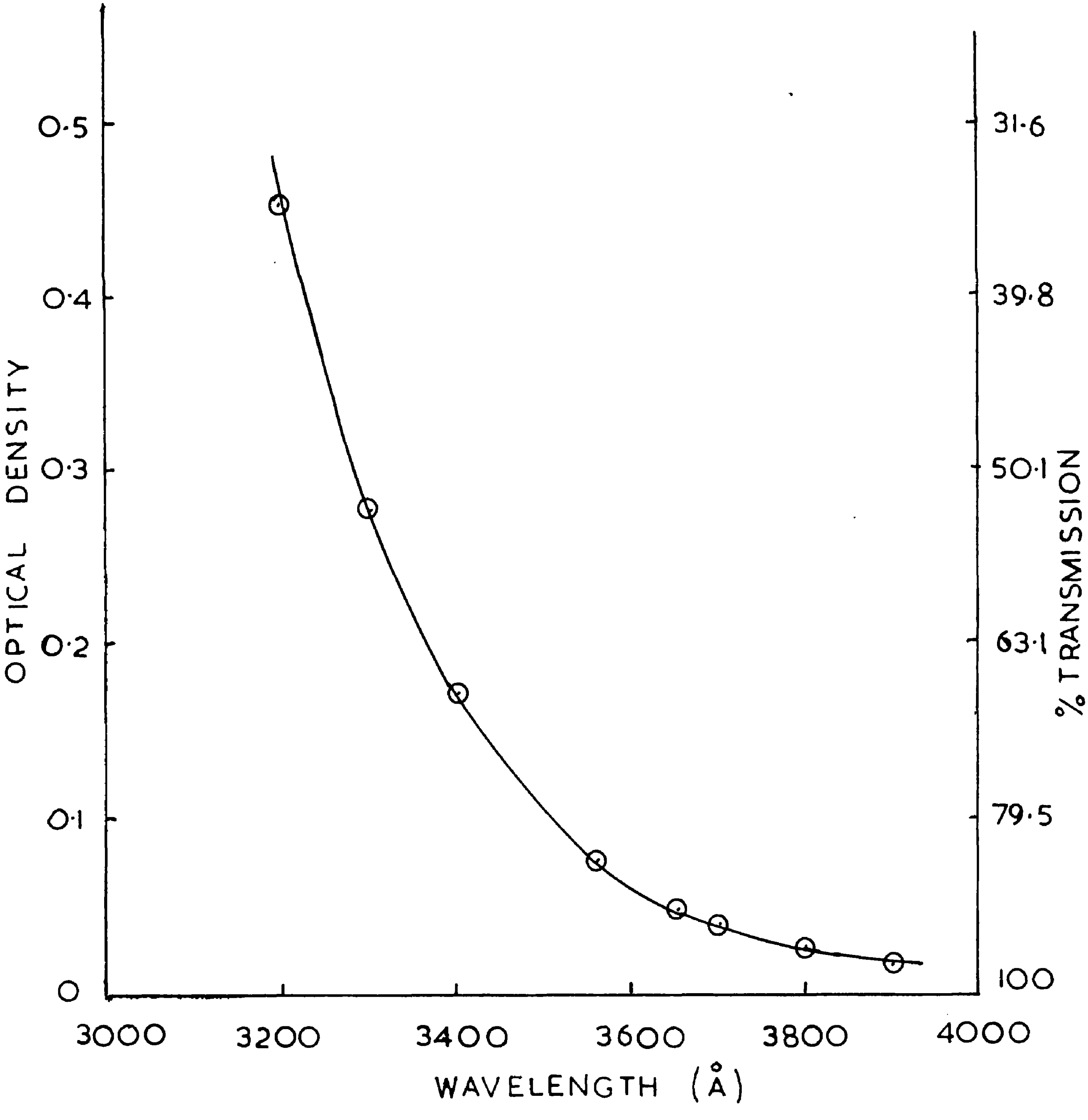


FIGURE 10

DEPENDENCE OF RATE ON CONCENTRATION OF CATALYST

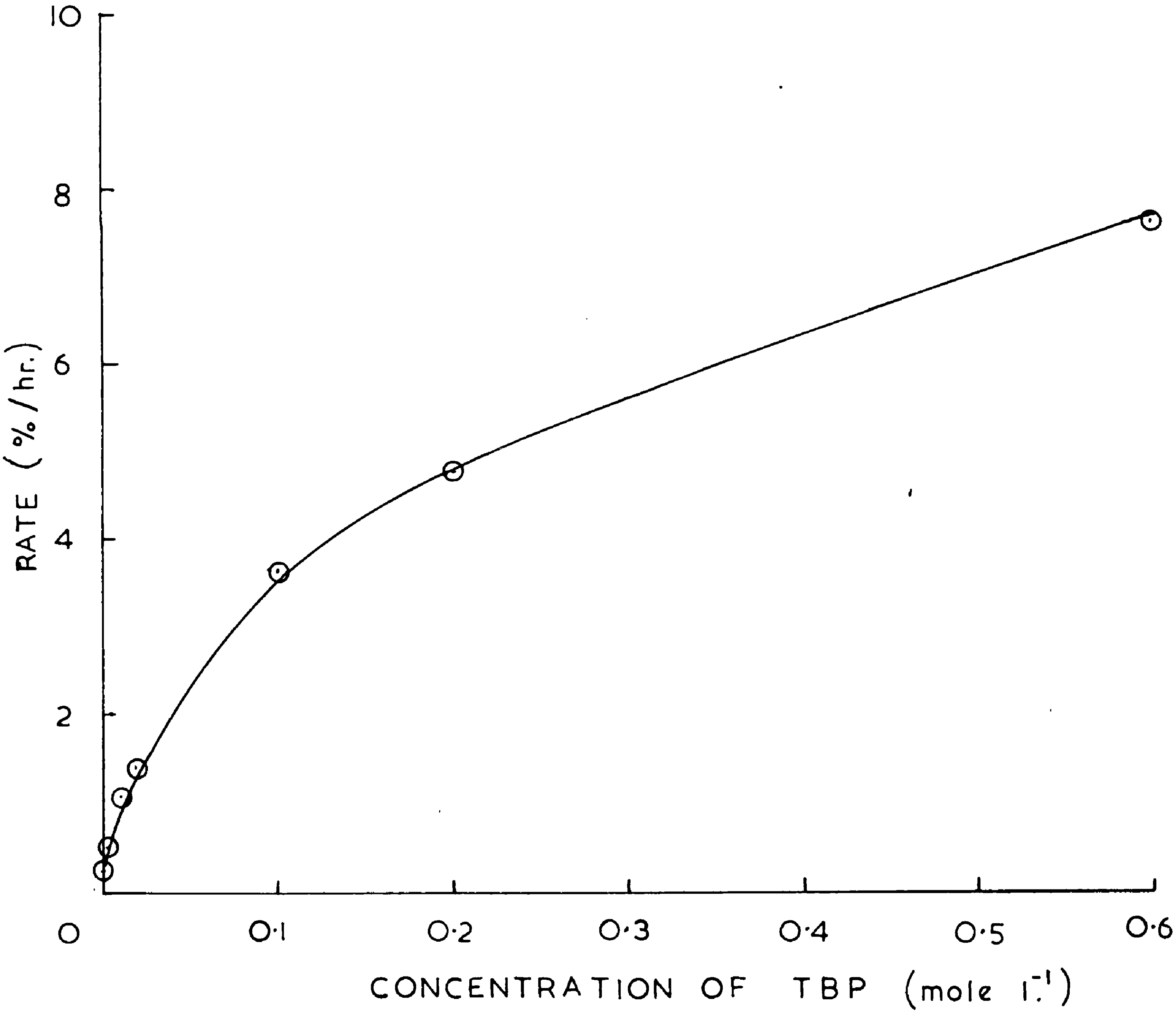
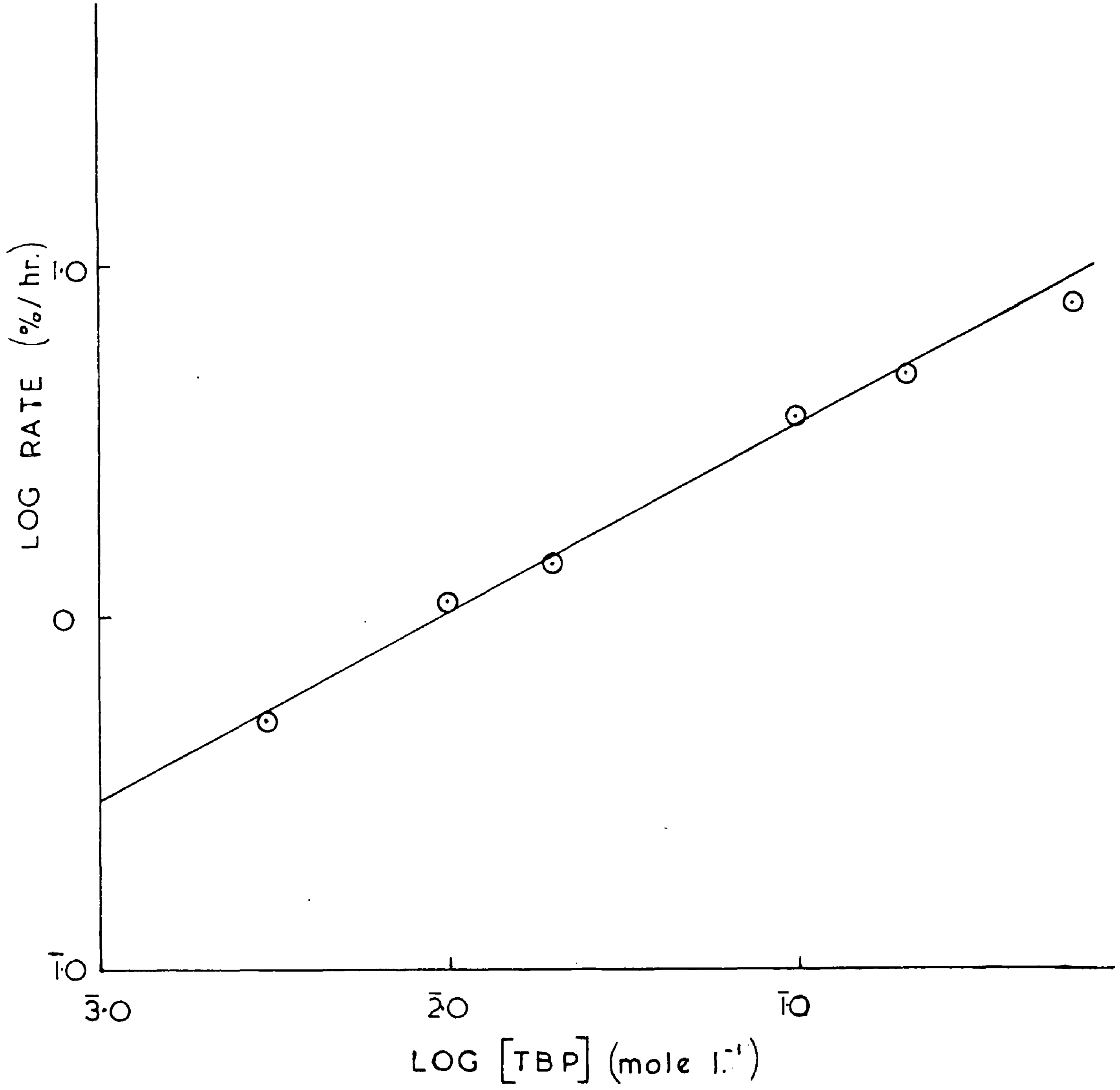


FIGURE 11

DEPENDENCE OF RATE ON . CONCENTRATION OF CATALYST



The results are shown in graphical form in figures 10 and 11. It will be seen that the plot of log rate against log catalyst concentration gives a straight line of slope 0.53 thus indicating the half-order dependence on initiator concentration required for second-order termination by the usual kinetic scheme (Page 10).

Rates of reaction were followed to about 5% conversion and remained steady during this time indicating that no peroxide-forming impurities were present, and since there was no inhibition period the adequate purification of the monomer was established.

From figure 10 it can be seen that a rate of about 1% polymerisation per hour was obtained at a concentration of TBP of 0.01 mole $l.^{-1}$. This was considered a suitable initial rate since increases of up to tenfold had to be allowed for in the gel stage. Hence this concentration of initiator was chosen for non-stationary state measurement of the bulk polymerisation.

Results of non-stationary state measurements.

Table 1. Variation in rate and lifetime with extent conversion at 25°C and full irradiation intensity.

Extent Conversion %	Rate of Reaction % /hr.	Lifetime sec.
0	0.94	3.5
12	1.75	4.7
15	1.76	8.1
17	2.74	9.7
22	4.84	11.4
30	6.43	16.4
37	10.60	20.2
45	9.75	36.1

In common with the findings of other workers it can be seen that the rate undergoes a large increase over the first 50% conversion. The increase starts almost from the beginning of the reaction becoming very pronounced after about 20% conversion and producing a tenfold increase by about 40%. The lifetime shows similar trends as the polymerisation proceeds. These variations are the expected consequences of the gel effect.

Table 2. Variation in rate and lifetime with extent conversion at 25°C and reduced irradiation intensity.

Extent Conversion %	Rate of Reaction % /hr.	Lifetime sec.
0	0.55	8.4
12	1.23	8.7
15	1.24	15.4
17	1.93	14.7
22	3.34	19.8
30	4.24	22.7
37	7.95	36.0
45	5.12	95.0

From Table 2 it can be seen that variations in rate and lifetime show similar trends to those observed at full light intensity.

Measurements were not carried out beyond about 50% conversion. Apart from the fact that extent of conversion could not be accurately estimated beyond this stage (see page 49) it became impossible to measure lifetimes accurately since these were so long that the stationary state could not be established during the adiabatic period of the system. Even those quoted beyond 30% conversion should be regarded as minimum values only. The high dark rate at this stage also meant that by the time a set of measurements could be completed the polymerisation could advance by as much as 20% thus making interpretation of results impossible.

In addition to those already presented measurements of rate and lifetime were in fact made at several light intensities to permit calculation of intensity exponents and to obtain data for the variation of measured intercept with rate. As has been explained the latter is necessary for the determination of instrument lag. The calculation of intensity exponent and instrument lag will now be considered in turn.

Intensity exponent of the rate.

Let m_1 and m_2 be the fractional rates of reaction under irradiation intensities L_1 and L_2 respectively. If the rate of initiation is proportional to light intensity then, in general, we have:

$$m = k_p \sqrt{\frac{KL}{k_t}}$$

$$= K' \sqrt{L}$$

where K and K' are constants.

i.e. $$\frac{m_1}{m_2} = \left[\frac{L_1}{L_2}\right]^{1/2}$$

That is, rate should be proportional to the square root of the light intensity using the kinetic scheme on page 10 . Allowing for deviation from second order termination, we have, in general,

$$\log \frac{m_1}{m_2} = n \log \frac{L_1}{L_2}$$

where n is the intensity exponent of the rate. Thus by determining the rate at different intensities and plotting log rate against log intensity a straight line of slope n should be obtained.

Plots of this type for the bulk polymerisation of methyl methacrylate are shown in figure 12.

Wire gauze screens or photographic plates were inserted in the light beam to produce variation in irradiation intensity. The transmission factors were determined at 3650 Å using a Unicam spectrophotometer. Transmission did not in fact vary appreciably over a fairly wide range of wavelength.

FIGURE 12

INTENSITY EXPONENT PLOTS FOR BULK POLYMERISATION.

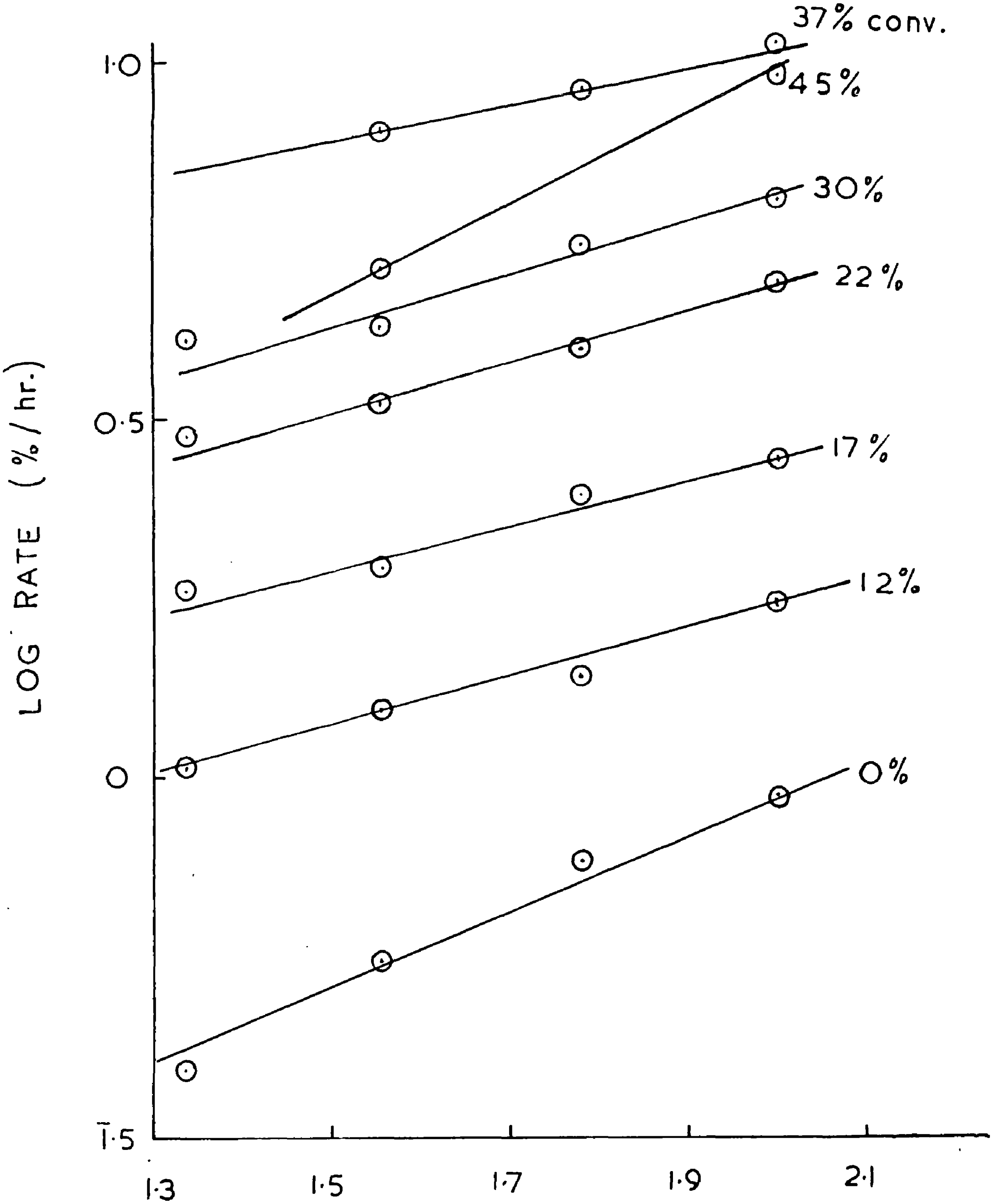


Table 3. Values of intensity exponents at different extents of conversion in the bulk polymerisation of methyl methacrylate.

Extent Conversion %	Rate (%/hr.) at relative intensity of: 100%	60.4%	35.9%	21.7%	Intensity Exponent
0	0.94	0.76	0.55	0.39	0.52
12	1.75	1.35	1.23	1.04	0.34
15	1.76	1.53	1.24	1.00	0.35
17	2.74	2.44	1.93	1.82	0.34
22	4.84	3.97	3.34	2.99	0.36
30	6.43	5.56	4.24	4.09	0.40
37	10.60	9.84	7.95	-	0.28
45	9.75	-	5.12	-	0.63

It will be seen that the intensity exponent has a value of 0.5 initially and decreases to between 0.3 and 0.4 up to nearly 40% conversion, then increasing rapidly to a value greater than 0.5. The significance of these values will be discussed later.

It should be mentioned that the number of rate measurements was minimised at the later stages since speed of manipulation was essential in order that measurements could be associated with a given extent of conversion.

Calculation of instrument lag.

The measured intercept X on the recorder chart can be represented by:

$$X = C + \tau \ln 2$$

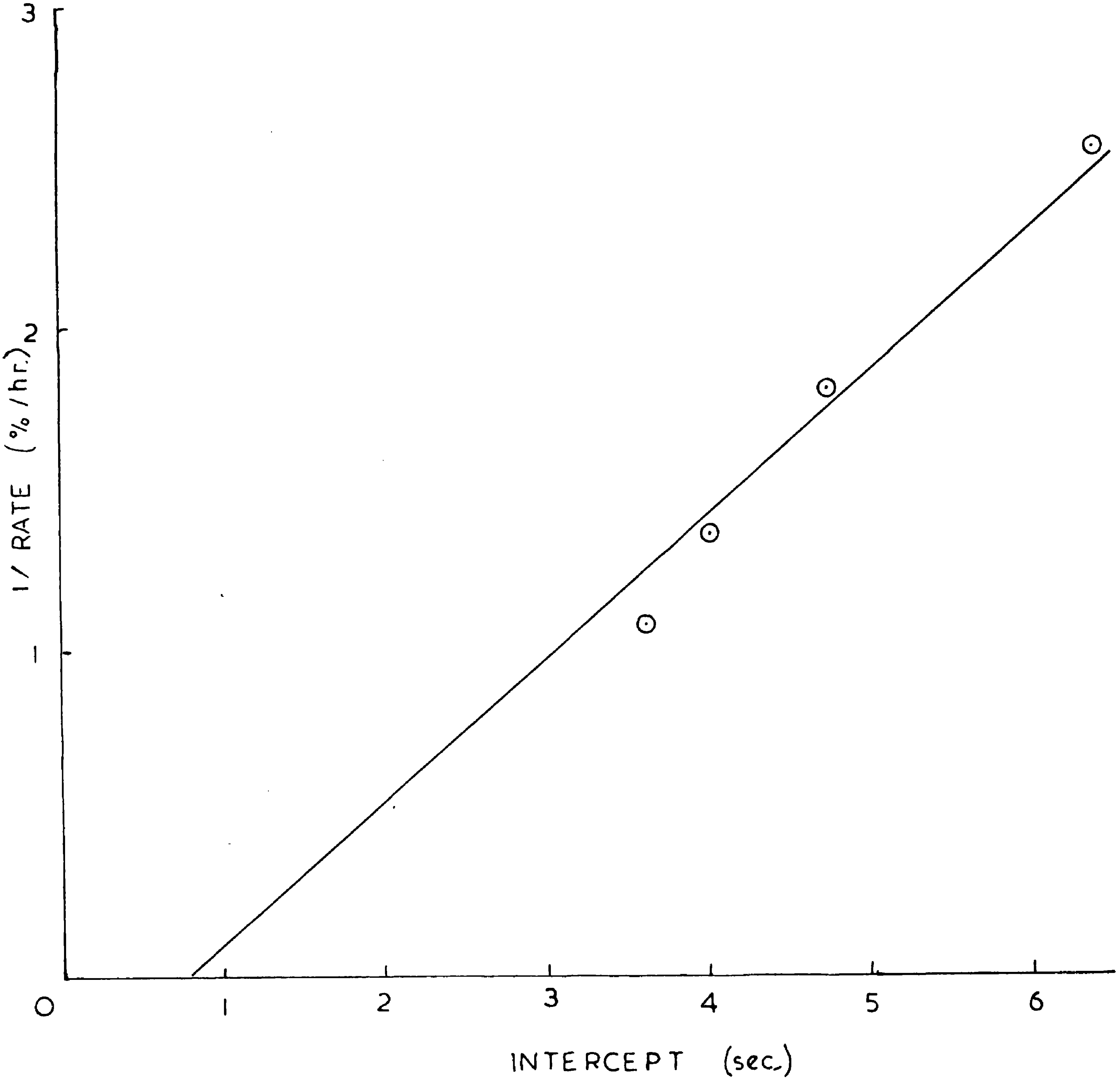
where C is the lag in response of the circuit from the instant light reaches the thermistor element till the recorder pen responds. At infinite rate of reaction τ will become theoretically equal to zero and in this case, X = C. Thus by plotting reciprocal rate against measured intercept C can be obtained from the intercept at 1/rate = 0.

From the theory given on pages 10–13 the slope of this plot will be proportional to k_t/k_p so that the plot affords a means of obtaining an average value of the ratio. An example of such a plot is shown in figure 13. It was found that the lag varied usually between 1 and 2 sec. and had to be determined for each set of measurements since it affects considerably the values of derived lifetimes.

It should perhaps be pointed out at this stage that the plot of 1/rate against intercept should, strictly speaking, be linear only when termination is second order. If deviation in intensity exponent from 0.5 represents a true kinetic effect then the

FIGURE 13

TYPICAL PLOT FOR DETERMINATION OF INSTRUMENT LAG & k_p/k_t



proportionality between 1/rate and τ falls down. This can be seen from the following considerations.

Let z be the order of termination. Then from the usual kinetic scheme we have:

$$\text{Fractional rate} = k_p [R_s]$$

$$\tau = \frac{[R_s]}{k_t [R_s]^z} = \frac{1}{k_t [R_s]^{z-1}}$$

$$\therefore \qquad [R_s] = \left\{\frac{1}{k_t \tau}\right\}^{1/(z-1)}$$

$$\text{so that} \quad \frac{1}{\text{rate}} = \frac{1}{k_p} (k_t . \tau)^{1/(z-1)}$$

$$\text{i.e.} \quad \frac{1}{\text{rate}} \propto \tau^{1/(z-1)}$$

Thus a plot of 1/rate against time-intercept will be linear only if z = 2. It will be a rising curve concave or convex to the "time-intercept" axis as z decreases or increases below or above 2.

The uncertainty in measurement of lifetime was found to obscure any such effects in practice and best straight lines were always drawn through the experimental points.

Table 4. Values of k_p/k_t at different extents of conversion 25°C.

Extent Conversion %	Rate %/hr.	Lifetime sec.	$\frac{k_p}{k_t} \times 10^5$
0	0.94	3.5	0.91
12	1.75	4.7	2.28
15	1.76	8.1	3.96
17	2.74	9.7	7.38
22	4.84	11.4	15.3
30	6.43	16.4	29.3
37	10.60	20.2	59.5
45	9.75	36.1	97.7

Since k_p/k_t is in effect the product of rate and lifetime the increase of the ratio reflects the effect of conversion on the rate and lifetime combined.

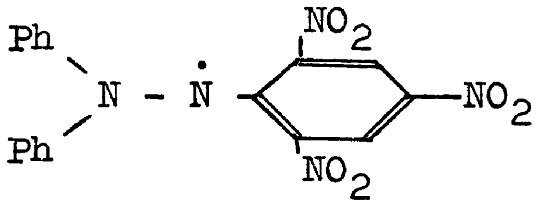
Determination of the individual velocity coefficients for the propagation and termination reactions.

In addition to the value of k_p/k_t obtained from non-stationary state measurements, another relation between k_p and k_t must be determined before their separate values can be found. By measuring the rate of chain initiation I, k_t can be calculated from the relation:

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

Hence k_p can be calculated also.

The rate of initiation was measured using the radical inhibitor 1:1'-diphenyl-2-picrylhydrazyl (DPPH). This is an extremely stable free radical of structure:

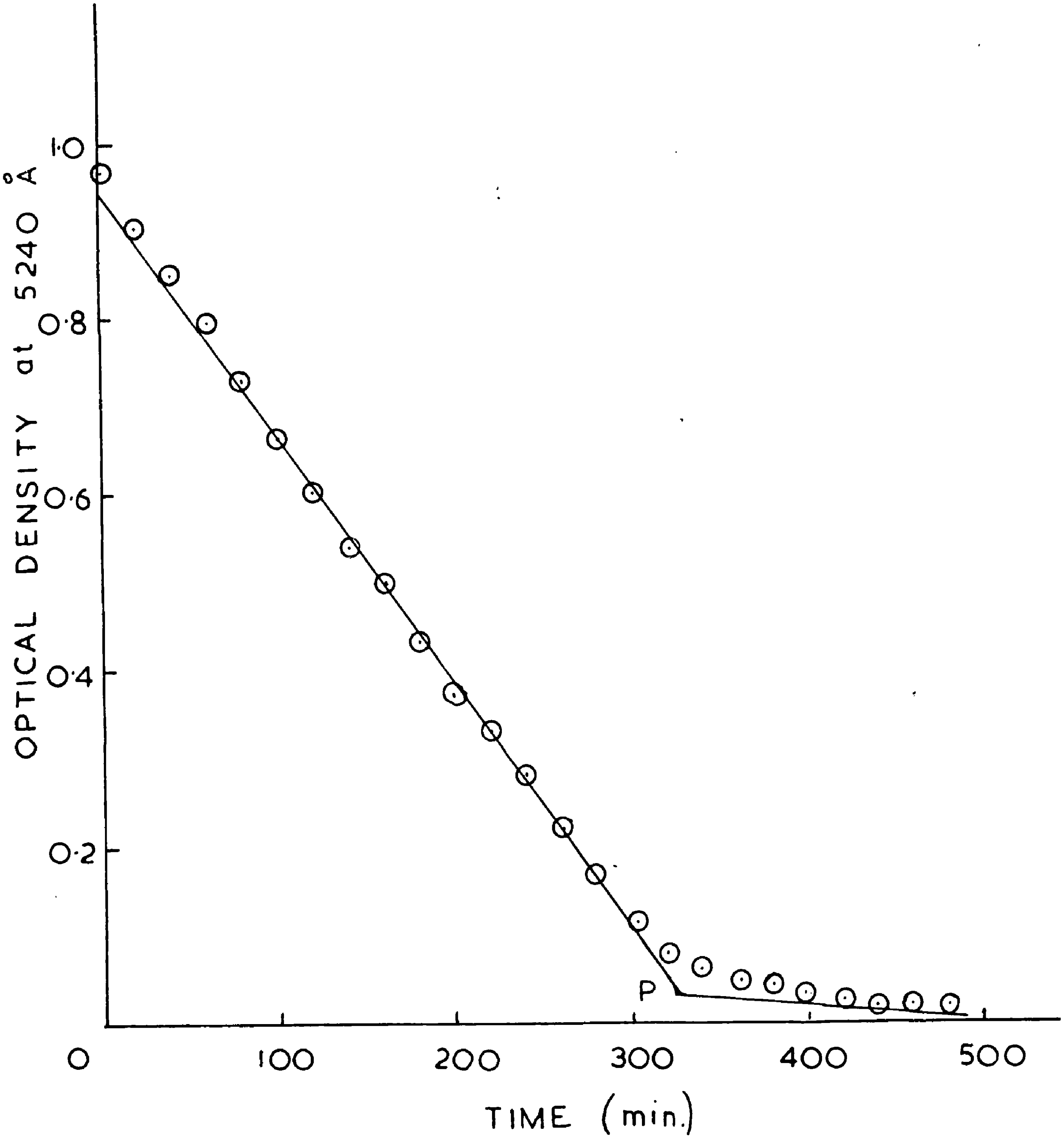


The basic principle of the method is to measure the rate of disappearance of DPPH under reaction conditions and equate this to the rate of chain initiation.

In the present work this was done by finding the rate of removal of DPPH colour (purple) from DPPH-catalyst-monomer mixtures under reaction conditions. A Unicam SP1400 spectrophotometer was used for this purpose, the measurements being made at 5240 Å. Graphs of solution optical density against time have the form shown in figure 14. The optical density shows a fairly sharp break and the end-point of the inhibition period is found by extrapolating the two parts of the curve to meet at P. For ideal inhibition behaviour the optical density would remain steady after point P had been reached. The fact

FIGURE 14

TYPICAL CURVE SHOWING RATE OF REMOVAL OF DPPH IN MONOMER-TBP SYSTEM.



that it continues to decrease at a reduced rate shows that a certain amount of secondary reaction is taking place.

The rate of initiation I is then calculated from the expression

$$I = \frac{\text{concentration of DPPH (mole l.}^{-1}\text{)}}{\text{period of inhibition (sec.)}}$$

Experiments were conducted at several different concentrations of DPPH and the inhibition period was found to be proportional to DPPH concentration. The rate of initiation at a concentration of di-t-butyl peroxide of 0.01 mole l.$^{-1}$ was calculated as 2.74×10^{-9} mole l.$^{-1}$sec.$^{-1}$

In calculating the rate of initiation it must be assumed that each DPPH radical reacts with one other radical, potentially a chain starter. There is in fact some doubt as to the validity of this. Bawn and Mellish[53] have claimed that this is the case in their studies of the decomposition of benzoyl peroxide and azobis*iso*butyronitrile in the presence of DPPH. In the latter case, however, it has been shown by Hammond, Sen and Boozer[54] that one DPPH radical may react with several initiator radicals through the regeneration of DPPH by subsequent reactions. In view of the conflicting experimental evidence no a priori judgement can be made on this point though the results quoted in the present work, which do not allow for any such effects, should be treated with the appropriate reserve.

In addition to this, doubt always arises as to the initiation efficiency, i.e. as to how many of the radicals produced in the system are successful in starting polymer growth. There are alternative reactions which the initiator radicals may undergo, e.g. recombination by a cage mechanism[55]. Efficiency of initiation has in fact been measured for some catalyst-monomer systems but no experimental data are available on the system under consideration. Hence initiation efficiency has been tacitly assumed to be 100%. In view of the fact that most systems investigated appear to have efficiencies between 50 and 100% this may introduce uncertainty up to a factor of 2 in k_t but it will be constant for all values quoted so that comparisons will not be imparied.

Table 5. Values of k_p and k_t for the bulk polymerisation of methyl methacrylate at 25°C. Rate of initiation = 2.74×10^{-9} mole $l.^{-1}sec.^{-1}$

Extent Conversion %	Rate %/hr.	sec.	$10^5 \times \frac{k_p}{k_t}$	k_p	$10^{-7} \times k_t$ $l.mole^{-1} sec^{-1}$
0	0.94	3.5	0.91	270	2.98
12	1.75	4.7	2.28	377	1.65
15	1.76	8.1	3.96	220	0.56
17	2.74	9.7	7.38	288	0.39
22	4.84	11.4	15.3	428	0.28
30	6.43	16.4	29.3	410	0.14
37	10.60	20.2	59.5	530	0.09
45	9.75	36.1	97.7	292	0.03

Since it was not possible to determine rates of initiation at the later stages of the polymerisation this has been assumed to be constant throughout. It will be seen from the results that k_t decreases by a factor of about 100 over the first 50% conversion while k_p remains constant within experimental error (see discussion).

Effect of temperature on the course of the polymerisation.

Measurements similar to those already described were made at 35 and 45°C. Essentially this was to permit calculation of the activation energy of the reaction but it also serves to show the effect of temperature or, indirectly, of temperature dependent variables, such as viscosity, on the course of the reaction.

Table 6. Variation of rate and lifetime with conversion at 35°C and full irradiation intensity.

Extent Conversion %	Rate %/hr.	Lifetime sec.	$\frac{k_p}{k_t} \times 10^5$
0	1.23	3.0	1.03
15	2.64	9.3	6.78
17	3.46	7.9	7.6
30	7.95	17.1	37.8
37	10.7	13.2	39.2

Values of rate show parallel increases with those at 25°C (Table 1) but lifetimes, perhaps a more fundamental criterion of the gel effect, do not show such marked increases as at the lower temperature.

Table 7. Variation of rate and lifetime with conversion at 45°C and full irradiation intensity.

Extent Conversion %	Rate %/hr.	Lifetime sec.	$\frac{k_p}{k_t} \times 10^5$
0	1.54	3.9	1.66
15	3.97	9.0	9.92
17	4.21	6.8	7.95
30	9.15	13.1	33.3
37	8.04	8.7	19.4

Again the trends in rate and lifetime are similar to those at lower temperatures with the lifetime showing slightly less dependence on conversion as the temperature increases. The number of measurements at higher temperatures was restricted over the range of the polymerisation for reasons already given (page 58).

Calculation of energies of activation.

Velocity coefficients for the individual steps of the reaction may be expressed in the form:

$$k = Ae^{-E/RT}$$

where A is the Arrhenius or frequency factor

E is the energy of activation.

The overall rate of polymerisation may be written:

$$\text{Rate} = k_p\sqrt{\frac{k_i}{k_t}} \cdot \left[\text{concentration term}\right].$$

$$\therefore \ln \text{rate} = K + \left[-\frac{E_p}{RT} + \frac{1}{2}\frac{E_t}{RT} - \frac{1}{2}\frac{E_i}{RT}\right]$$

where K is a constant and E_p, E_t, E_i are the activation energies of propagation, termination and initiation respectively.

$$\text{i.e. } 2.3 \log \text{rate} = K - \frac{E_o}{RT}$$

$$\text{where } E_o = E_p - \tfrac{1}{2}E_t + \tfrac{1}{2}E_i$$

Hence a plot of log rate against 1/T will be a straight line of slope $-E_o/2.3R$

Also from the kinetic scheme on page 10 we obtain

$$\tau = (1/k_tI)^{\frac{1}{2}}$$

$$\therefore \tau^{-1} = (k_tI)^{\frac{1}{2}}$$

$$= (A_t . e^{-E_t/RT} . I)^{\frac{1}{2}}$$

$$\therefore \ln \tau^{-1} = K' - \frac{1}{2}\frac{E_t}{RT}$$

where K' is a constant.

Thus a plot of log $^{-1}$ against 1/T should give a straight line of slope $-\frac{1}{2} \cdot \frac{E_t}{2.3R}$.

Since E_i in a photopolymerisation can be assumed equal to zero then $E_o = E_p - \frac{1}{2}E_t$

FIGURE 15
TYPICAL GRAPH FOR
DETERMINATION OF E_0

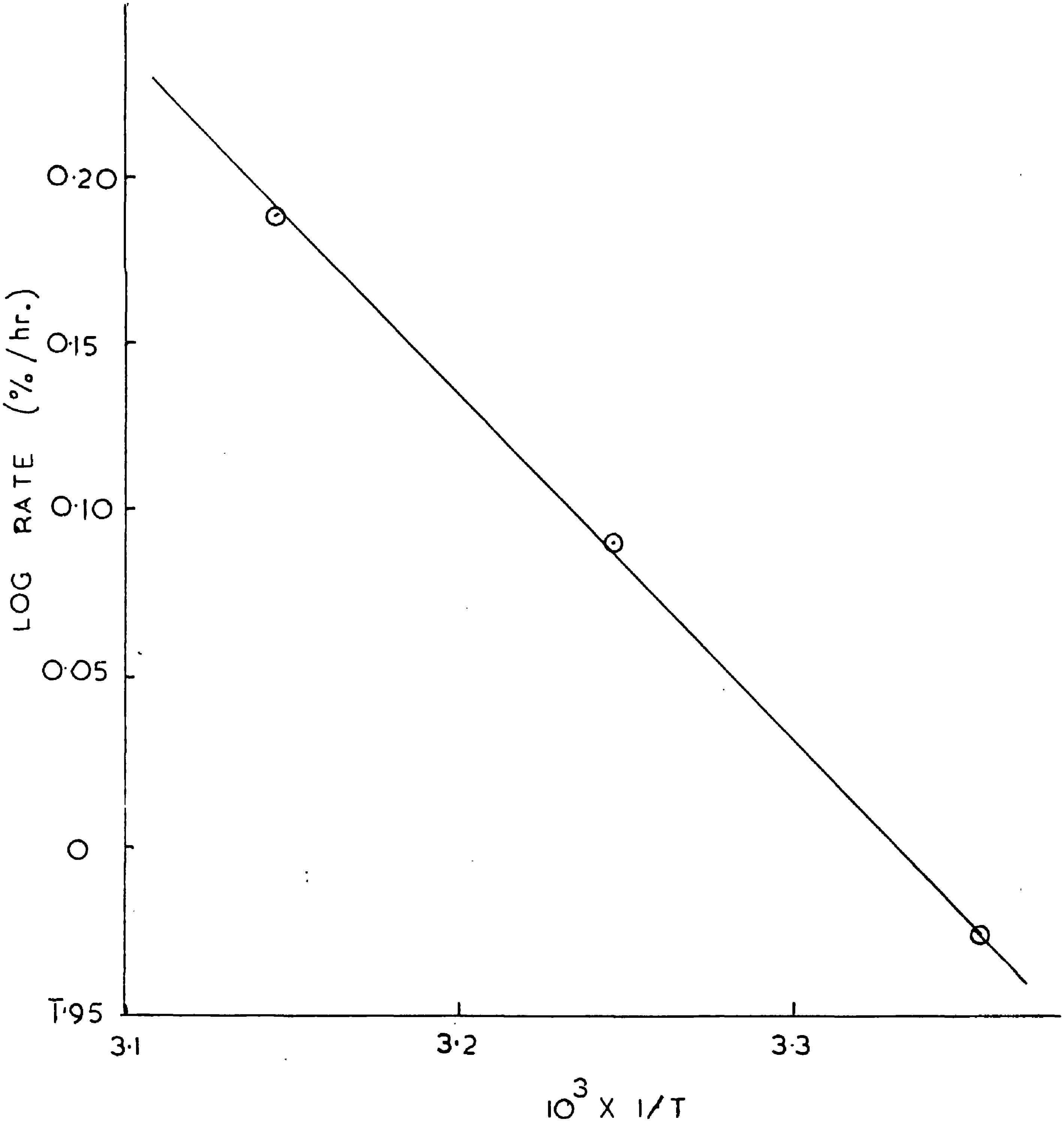
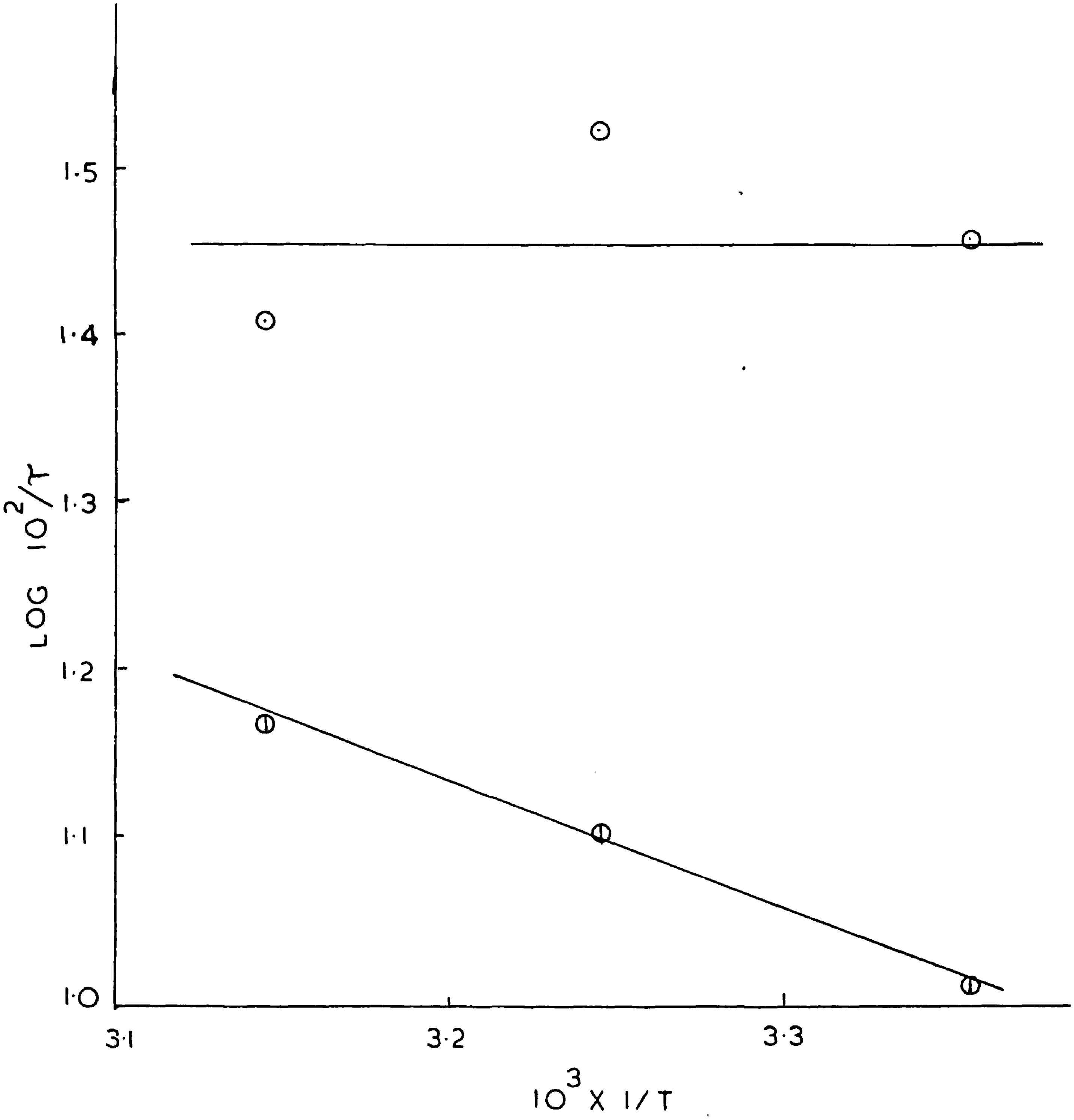


FIGURE 16

TYPICAL PLOTS FOR DETERMINATION OF E_t



Thus it is possible to obtain values of E_p and E_t by measuring rate and lifetime at different temperatures. Typical activation energy plots for E_o and E_t are shown in figures 15 and 16. The plots for E_t show considerable scatter especially when the lifetimes are short (upper line) and in this case such scatter has been taken to indicate little or no variation of τ with temperature so E_t is quoted as zero. When lifetimes become longer, as in the later stages, such plots become more reliable (lower line) although the low values of intensity exponent at this stage which cast a doubt on the order of termination make the variation of τ with temperature suspect as a means of calculating E_t.

Table 8. Variation of activation energies with conversion calculated over the range 25 to 45°C

Extent Conversion %	E_o	E_t	E_p
	kcal. per mole.		
0	4.7	0	4.7
15	7.6	0	7.6
17	4.1	6.7	7.5
30	3.5	3.3	5.2
37	-1.0	16.7	7.4

E_o appears to increase at first and then gradually decreases reaching a negative value at about 40% conversion. E_t gradually increases from an initial value of zero to a value of about 17 kcal. at 40% conversion. These changes reflect the gradual retardation of the termination reaction in the gel stage of the polymerisation.

It is now possible to obtain an overall picture of the course of polymerisation over the range of conversion measured.

Table 9. Summary of kinetic data for the bulk polymerisation of methyl methacrylate. Rate of initiation $= 2.74 \times 10^{-9}$ mole $l.^{-1} sec.^{-1}$

Extent Conversion %	Rate %/hr.	Lifetime sec.	$10^5 \frac{k_p}{k_t}$	k_p (l. mole^{-1} sec.$^{-1}$)	10^{-7} k_t	E_o (kcal)	E_t	Intensity Exponent
0	0.94	3.5	0.91	270	2.98	4.7	0	0.52
12	1.75	4.7	2.28	377	1.65	-	-	0.34
15	1.76	8.1	3.96	220	0.56	7.6	0	0.35
17	2.74	9.7	7.38	288	0.39	4.1	6.7	0.34
22	4.84	11.4	15.3	428	0.28	-	-	0.36
30	6.43	16.4	29.3	410	0.14	3.5	3.3	0.40
37	10.60	20.2	59.5	530	0.09	-1.0	16.7	0.28
45	9.75	36.1	97.7	292	0.03	-	-	0.63

Results of dark rate measurements.

As mentioned previously one of the peculiar and so far unexplained features of the photopolymerisation of methyl methacrylate is the decrease in intensity exponent to about 0.3 during the accelerated phase of the reaction. This has been confirmed in the present work. The effect has been tentatively attributed to the effects of the very marked dark rate associated with methyl methacrylate polymerisation[42].

The adoption of the mercury seal type of dilatometer described on page 49 enables accurate contraction measurements to be made into the gel stage of the reaction so that the dark rate can be studied by a simple dilatometric method at this stage. Using this technique several investigations of the dark rate were made under conditions identical to those in the non-stationary state experiments.

The rate under full illumination intensity was measured firstly. The light was then cut off and the contraction followed till a steady rate of reaction, the dark rate, was established. This sometimes took several hours to attain. This procedure was repeated at different extents of conversion throughout the polymerisation.

The results of these experiments are summarised in

FIGURE 17

VARIATION OF LIGHT & DARK RATES WITH EXTENT CONVERSION AT 25°C.

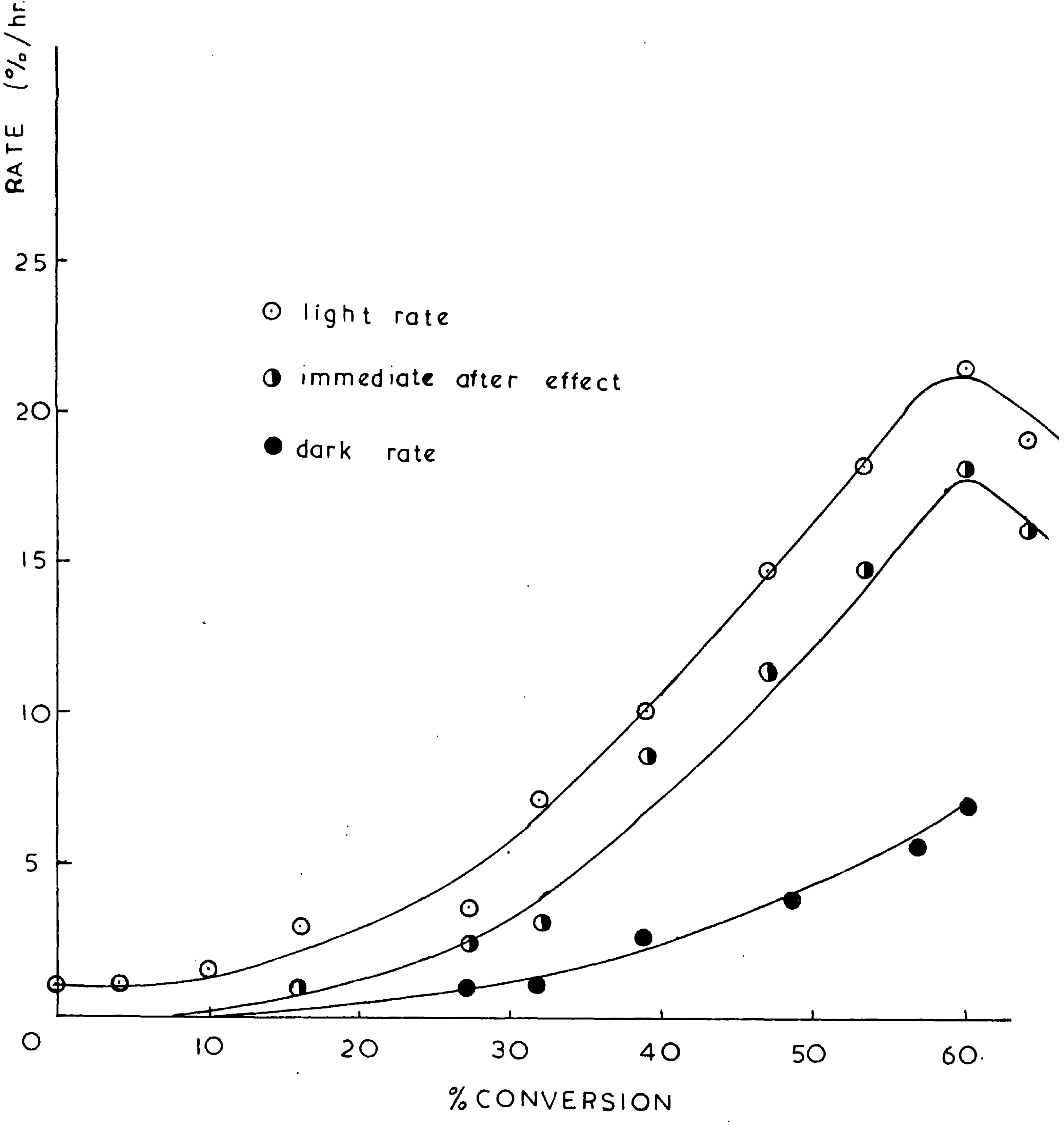


figure 17. The upper curve shows the rate of reaction at full irradiation intensity. The middle curve shows the average rate over a period of about 20 minutes after irradiation has ceased and it should be borne in mind that part of the contraction measured during this stage will be due to cooling of the reaction mixture. The lower curve shows the steady dark rate eventually reached.

It will be evident from the preceding paragraphs that it was not possible to measure light and dark rates at precisely the same extents of conversion. However the curves, as shown, are fairly smooth making comparisons quite reasonable.

The dark rate is seen to be immeasurably small up to about 10% conversion and thereafter increases considerably. The following table shows the ratio of dark to light rate at various extents of conversion.

% Conversion	0	10	20	30	40	50	60
Ratio of dark to light rate	0	0	0.14	0.21	0.23	0.26	0.33

Thus as the polymerisation advances the dark rate becomes an increasingly significant fraction of the overall rate. The implications of this for the non-stationary state results will be discussed in a later section.

II. The Polymerisation of Methyl Methacrylate in Presence of the Chain Transfer Agent Bromotrichloromethane

As mentioned in the introduction bromotrichloromethane (BTCM) acts as a chain transfer agent in vinyl polymerisation. It has therefore been used in the present work to examine the changes in the course of methyl methacrylate polymerisation when the polymer molecular weight is reduced by known amounts. The kinetics of the reaction have been studied over a range of BTCM concentration from about 0.09 to 9 mole $l.^{-1}$; the accompanying change in the molecular weight of the products is from approximately 160,000 to 600 corresponding to chain lengths of 1600 and 4 respectively.

Since BTCM gives rise to free radicals, $\dot{C}Cl_3$ and $\dot{B}r$, by photochemical excitation the reaction can be studied as a purely binary system without the complicating influence of a photosensitiser. Indeed during preliminary experiments in which the system was studied in the presence of di-t-butyl peroxide the reaction rate was found to be slower than when BTCM was added alone, showing that some interaction may be taking place between the peroxide and the BTCM.

Experiments for measuring the non-stationary state of the reaction were carried out under identical conditions to those used in the bulk polymerisation. The introduction of 'inert' diluent must be allowed for in calculating rates of reaction from the temperature rise measured by the thermistor. This is readily done from a knowledge of the specific heats of the reactants. In making such corrections it has been assumed that the specific heat of mixtures of BTCM and methyl methacrylate varies linearly with their composition.

A. The polymerisation of methyl methacrylate in presence of BTCM at a molar ratio of reactants of 100 : 1 .

Table 10. Variation in rate and lifetime with extent of conversion at 25°C and full irradiation intensity

Extent Conversion %	Rate of Reaction %/hr.	Lifetime sec.
0	1.64	1.1
7	1.28	0.9
11	1.49	0.9
17	1.56	1.6
21	2.77	4.1
30	3.96	3.9

It can be seen from Table 10 that the rate and lifetime show substantial increase as the polymerisation proceeds but this is not so marked as in the bulk polymerisation. Over the first 30% conversion the rate increases by a factor of about 2.5 and the lifetime by a factor of 4. The corresponding increases in the bulk polymerisation are 6- and 5-fold respectively. Thus the gel effect, though still in evidence, is now much less pronounced. It will be noted also that the rate decreases slightly over the first 17% conversion before the gel acceleration becomes obvious so that the conditions producing the gel effect are much longer in developing than in the bulk polymerisation where the rate starts to increase almost from the beginning.

Table 11. Variation in intensity exponent with extent of conversion at 25°C.

Extent Conversion %	Rate (%/hr.) at relative intensity: 100%	60.4%	35.9%	21.7%	Intensity Exponent
0	1.64	1.32	1.02	0.83	0.47
7	1.28	0.94	0.76	0.57	0.51
11	1.49	1.01	0.88	0.66	0.52
17	1.56	1.17	0.92	0.68	0.52
21	2.77	2.18	1.62	1.32	0.51
30	3.96	2.88	2.20	1.64	0.55

The intensity exponent is seen to show little or no variation over the first 30% conversion. Thus the curious drop to 0.3 which takes place in the bulk polymerisation over this range of conversion is not observed. From the values in Table 11 termination may be assumed to be predominantly second order.

Values of the ratio k_p/k_t were calculated as in the bulk polymerisation from the slope of the plot of reciprocal rate against measured intercept.

Table 12. Variation of the ratio k_p/k_t with extent of conversion at 25°C and full irradiation intensity

Extent Conversion %	Rate %/hr.	Lifetime sec.	$\frac{k_p}{k_t} \times 10^5$
0	1.64	1.1	0.48
7	1.28	0.9	0.33
11	1.49	0.9	0.36
17	1.56	1.6	0.69
21	2.77	4.1	3.07
30	3.96	3.9	4.30

Again the ratio k_p/k_t shows a slight initial decrease up to about 10% conversion and then increases to about 9 times its initial value at 30% conversion. The increase is thus delayed in its onset and of much smaller magnitude than for the bulk polymerisation.

Determination of rates of initiation.

The rates of initiation in the BTCM-methyl methacrylate system were again determined using DPPH as a radical inhibitor. Since measurement of the velocity coefficients was to be undertaken over a wide range of BTCM concentration it was necessary to determine rates of initiation over as much of this range as possible.

In the use of DPPH in photochemical reactions, however, there is a limit on the concentration of radical generator which can be adequately dealt with. This arises as follows.

The extinction coefficient of DPPH is extremely high so that unless the concentration of solutions is kept very low any incident radiation will be almost entirely absorbed at the glass-liquid interface. This internal filter effect will produce completely meaningless results and to avoid this in the present system it was found necessary to keep the concentration of DPPH below about 8×10^{-5} mole $l.^{-1}$ With this limit on the DPPH concentration it is then required to reduce the concentration of initiator to such a value that inhibition

FIGURE 18

TYPICAL EXAMPLE OF INHIBITION PERIODS PRODUCED BY DPPH.

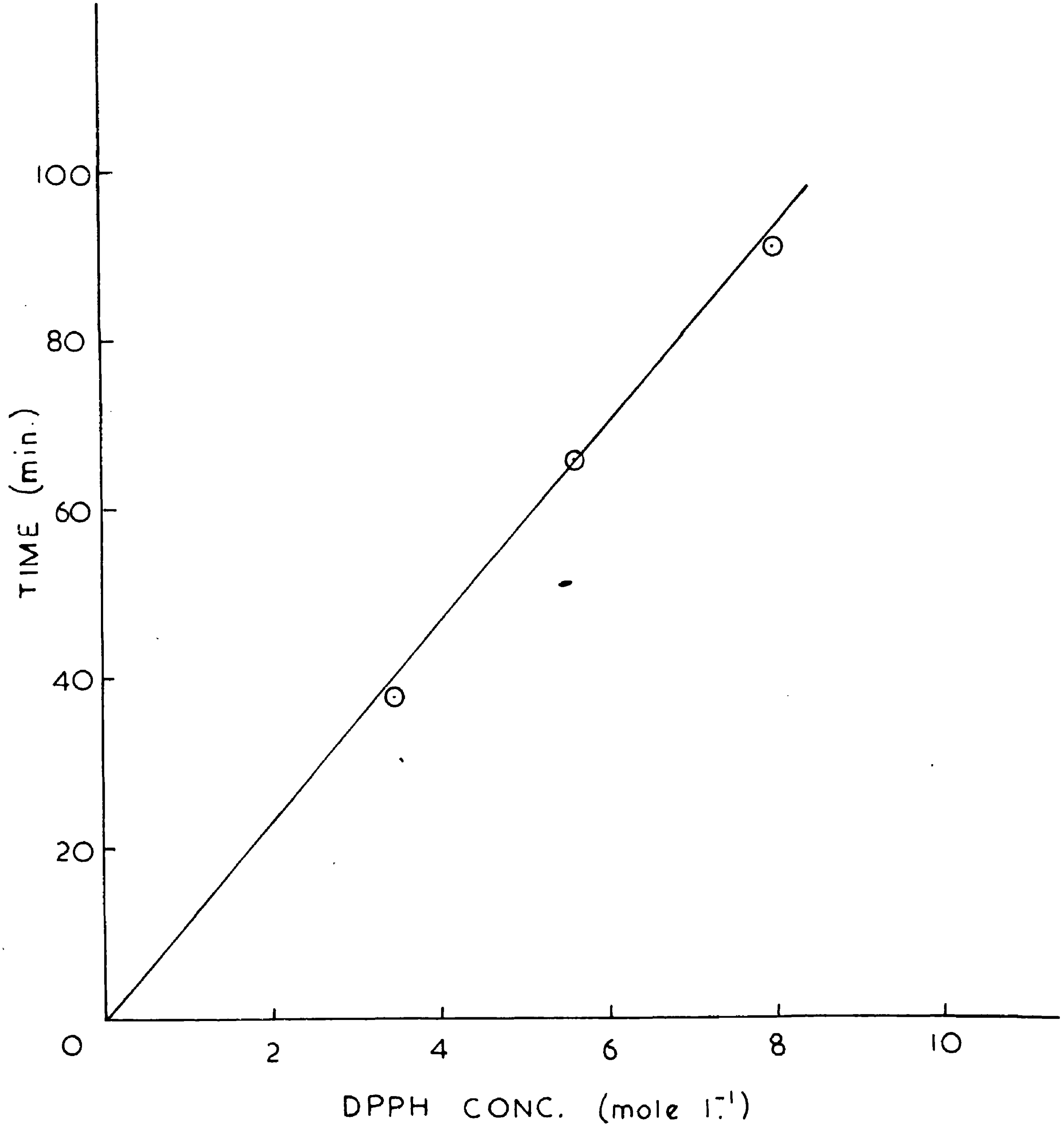
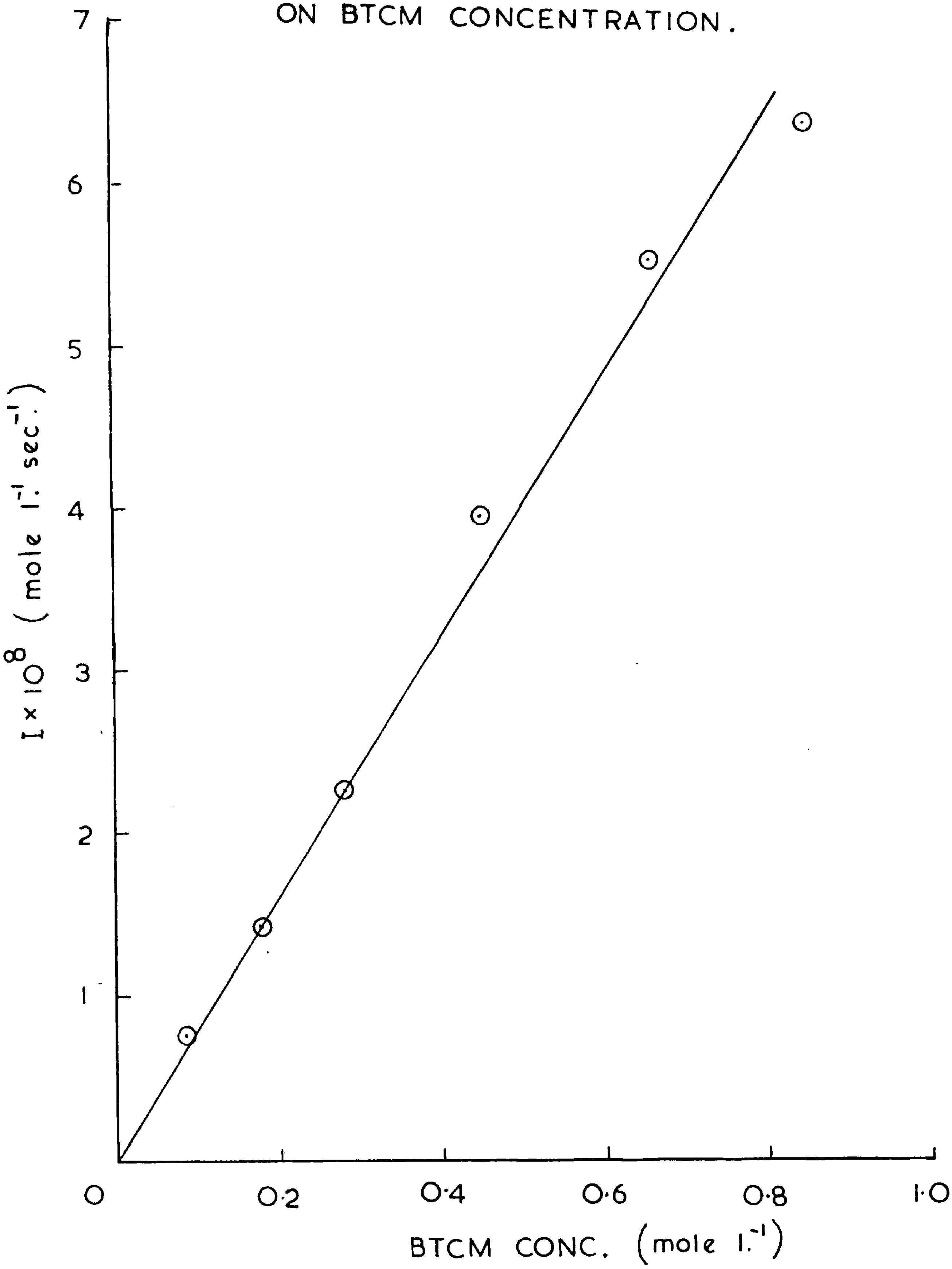


FIGURE 19

DEPENDENCE OF RATE OF INITIATION I ON BTCM CONCENTRATION.



periods of reasonable duration are produced. Taking these as 20 minutes minimum it was found that the upper limit on the BTCM concentration which could be safely used was about 0.8 mole $1.^{-1}$, corresponding to a molar ratio of monomer to BTCM of 10:1 .

The measurements were again carried out using the absorptiometric technique described previously, the inhibition periods being determined from optical density - time curves. For each concentration of BTCM used inhibition periods were determined at several concentrations of DPPH. A typical example of the type of relation obtained is shown in figure 18. DPPH thus shows ideal inhibitor behaviour in this system producing inhibition periods proportional to the concentration.

The results of the measurement of rates of initiation is summarised in graphical form in figure 19. The rate of initiation is proportional to the BTCM concentration over the range measured and the relationship can be expressed in the form:

$$I = 8.76 \times 10^{-8} \text{ BTCM}$$

where I is the rate of initiation in mole $1.^{-1}$sec.$^{-1}$ and BTCM is expressed in mole $1.^{-1}$

At concentrations of BTCM greater than those measured, the above proportionality was taken to hold good and rates of initiation in these cases were obtained by extrapolation.

Using these values of initiation rate it is now possible to determine the individual velocity coefficients for propagation and termination as for the bulk polymerisation.

Table 13. Variation of individual velocity coefficients with extent conversion at 25°C. Rate of initiation = 8.1 x 10^{-9} mole $l.^{-1}$ sec.$^{-1}$

Extent Conversion %	$10^5 \times \frac{k_p}{k_t}$	k_p	$k_t \times 10^{-7}$
		l. mole^{-1}	sec.$^{-1}$
0	0.48	490	10.2
7	0.33	500	15.2
11	0.36	546	15.2
17	0.69	335	4.83
21	3.07	228	0.74
30	4.30	348	0.81

The value of k_p is seen to remain substantially constant while k_t shows a decrease by a factor of about 10 over the first 30% conversion after remaining constant to about 11% conversion.

Effect of temperature on the course of the reaction.

Non-stationary state measurements of reaction rate and lifetime were again carried out at temperatures of 35 and 45°C to determine the energies of activation of the individual steps in the reaction.

Table 14. Variation of rate and lifetime with extent conversion at 35°C and full irradiation intensity.

Extent Conversion %	Reaction Rate %/hr.	Lifetime sec.	$10^5 \times \frac{k_p}{k_t}$
0	1.97	1.0	0.55
17	1.73	1.6	0.77
30	4.08	2.3	2.60

Table 15. Variation in rate and lifetime with extent conversion at 45°C and full irradiation intensity.

Extent Conversion %	Reaction Rate %/hr.	Lifetime sec.	$10^5 \times \frac{k_p}{k_t}$
0	2.21	1.0	0.62
17	2.00	1.5	0.83
30	4.34	1.8	2.17

The relative increase of rate and lifetime is seen to be gradually diminished as the temperature increases so that the gel effect becomes less evident at higher temperatures. These measurements lead to values of energies of activation E_o and E_t obtained respectively from the plots of log rate and log $1/\tau$ against $1/T$.

Table 16. Variation in energies of activation with extent conversion over the temperature range 25 to 45°C

Extent Conversion %	E_o	E_t	E_p
	kcal.	per mole.	
0	3.0	0	3.0
17	2.5	0	2.5
30	0.5	13.5	7.3

The initial values of E_o and E_t are substantially the same as in the bulk polymerisation. As polymerisation proceeds E_o decreases and presumably becomes negative eventually. E_t shows the opposite behaviour, increasing from an initial value of zero to a value of 13.5 kcal. at 30% conversion. The relative increase is however less than in the bulk polymerisation again indicating that the gel effect is less pronounced in this reaction.

Table 17. Summary of kinetic data for the polymerisation of methyl methacrylate in the presence of 1 mole % of BTCM at a rate of initiation of 8.1 x 10^{-9} mole $l.^{-1}$ $sec.^{-1}$

Extent Conversion %	Reaction Rate %/hr.	Life-time sec.	$10^5 \frac{k_p}{k_t}$	k_p (l.mole^{-1}	10^{-7} k_t sec.$^{-1}$)	E_o (kcal)	E_t	Intensity Exponent
0	1.64	1.1	0.48	490	10.2	3.0	0	0.47
7	1.28	0.9	0.33	500	15.2	-	-	0.51
11	1.49	0.9	0.36	546	15.2	-	-	0.52
17	1.56	1.6	0.69	335	4.83	2.5	0	0.52
21	2.77	4.1	3.07	228	0.74	-	-	0.51
30	3.96	3.9	4.30	348	0.81	0.5	13.5	0.55

In summarising the results for this reaction it may be said that the characteristics are very similar to those exhibited in the bulk polymerisation and any differences are of degree only. Thus the gel effect is still in evidence though to a much modified extent. There is no reduction in the value of intensity exponent as observed in the bulk polymerisation and termination would seem to be accurately bimolecular over the range of conversion studied.

B. The polymerisation of methyl methacrylate in the presence of BTCM at a molar ratio of reactants of 10:1

Table 18. Variation in rate and lifetime with extent conversion at 25°C and full irradiation intensity

Extent Conversion %	Reaction Rate %/hr.	Lifetime sec.	$10^5 \times \frac{k_p}{k_t}$
0	4.08	0.3	0.34
15	2.97	1.4	1.15
22	4.94	0.9	1.23
40	12.1	5.6	18.8

At this concentration of BTCM the molecular weight of the polymer is of the order of 24,000 compared to 1.5 x 10^6 in the bulk polymerisation and 1.6 x 10^5 in the reaction at 100:1 molar ratio of monomer : BTCM. The average polymer chain length is thus reduced further by a factor of about 7.

From Table 18 it will be seen that the initial value of the rate is greater by a factor of 2 than the rate for the reaction at 100:1 molar ratio. This is most probably due to the increased rate of initiation. The trend in the value of the rate with conversion is similar to that shown in the reaction at 100:1 molar ratio, i.e., an initial decrease followed by an increase by a factor of 3 at 40% conversion. The lifetime has a lower initial value than for the previous reactions but shows the same gradual increase with conversion. This increase is less marked than for either the bulk polymerisation or the reaction at 100:1 molar ratio of reactants. It should also be pointed out that any increase in rate and lifetime is delayed till about 20% conversion.

Table 19. Variation in intensity exponent with extent conversion at 25°C.

Extent Conversion %	Rate (%/hr.) at relative intensity: 100%	60.4%	35.9%	21.7%	Intensity Exponent
0	4.08	2.89	2.20	1.61	0.60
15	2.97	2.38	1.69	1.30	0.57
22	4.94	3.27	2.33	1.58	0.73
40	12.1	8.69	5.50	4.02	0.78

The intensity exponent for this reaction shows considerable deviation from 0.5 and tends to increase with conversion. Thus the results obtained in the bulk polymerisation are completely reversed. The values of intensity exponent show that some first order termination may be taking place, implying that appropriate correction should be made to the values of individual velocity coefficients calculated on the basis of second order termination. This is demonstrated in the following tables.

Table 20. Variation of individual velocity coefficients with extent conversion at 25°C. Rate of initiation = 7.5×10^{-8} mole $l.^{-1}$ $sec.^{-1}$

Extent Conversion %	$10^5 \times \frac{k_p}{k_t}$	k_p	$10^{-7} \times k_t$
		$l.mole^{-1}.sec.^{-1}$	
0	0.34	503	14.8
15	1.15	78	0.68
22	1.23	203	1.65
40	18.8	75	0.04

Table 21. Velocity coefficients corrected for mixed order termination.

Extent Conversion %	$10^5 \times \frac{k_p}{k_t}$	k_p	$10^{-7} \times k_t$
		$l.mole^{-1}.sec.^{-1}$	
0	0.52	613	11.8
15	1.51	89	0.59
22	3.66	325	0.89
40	69	137	0.02

From Tables 20 and 21 it can be seen that k_p fluctuates to some extent as the reaction proceeds showing, if anything, a slight decrease with conversion. It is, however, doubtful if any significance should be attached to this in view of the probable errors involved in the measurements (see discussion). The value of k_t, on the other hand, shows a definite decrease by a factor of 500 over the first 40% conversion so that the gel effect is still operative in this reaction.

<u>Effect of temperature on the course of reaction</u>.

Table 22. Variation in rate and lifetime with conversion at 35 and 45°C and full irradiation intensity.

	Extent Conversion %	Rate %/hr.	Lifetime sec.
35°C	0	5.70	0.4
	15	3.09	1.9
	22	5.23	1.0
	40	12.7	4.9
45°C	0	6.25	0.6
	15	3.41	1.9
	22	6.3	0.8
	40	13.6	3.3

As in the previous reactions studied the effect of raising the temperature is to reduce the increase of rate and lifetime as the reaction proceeds.

Table 23. Values of energies of activation at various extents of conversion over the temperature range 25 to 45°C.

Extent Conversion %	E_o	E_t	E_p
		kcal.	per mole
0	4.1	0	4.1
15	1.5	0	1.5
22	2.4	0	2.4
40	0.9	10	5.9

The initial value of E_o is similar to those for the previous reactions and again shows a gradual decrease with conversion. From a comparison of the values of lifetime in Tables 18 and 22 it will be seen that there is no significant trend in lifetime with temperature up to 20% conversion. The value of E_t up to this stage has therefore been quoted as zero. At 40% conversion the lifetime decreases quite markedly with temperature increase giving a value of E_t of 10 kcal.

It should also be noted at this point that the intensity exponents for this reaction indicate that mixed order termination is occurring so the slope of the usual plot for E_t, i.e. $\log \tau^{-1}$ against $1/T$, has no theoretical interpretation and will almost certainly not give the correct value of E_t. However the slope of this line gives a measure of the temperature coefficient of τ^{-1} and as such has been quoted here.

Table 24. Summary of kinetic data for the polymerisation of methyl methacrylate in presence of BTCM at a molar ratio of reactants of 10:1. Rate of initiation = 7.5 x 10^{-8} mole $l.^{-1}$ $sec.^{-1}$

Extent Conversion %	Rate %/hr.	Lifetime sec.	$10^5 \frac{k_p}{k_t}$	k_p l.mole^{-1}sec.$^{-1}$	10^{-7} k_t	E_o kcal.	E_t	Intensity Exponent
0	4.08	0.3	0.52	613	11.8	4.1	0	0.60
15	2.97	1.4	1.51	89	0.59	1.5	0	0.57
22	4.94	0.9	3.66	325	0.89	2.4	0	0.73
40	12.1	5.6	69	137	0.02	0.9	10.0	0.78

Again this reaction shows similar trends to those already studied. The further reduction in molecular weight is thus not sufficient to eliminate the gel effect completely but only serves to delay its onset. A notable difference in this reaction is the change to mixed order termination.

C. The photochemical reaction of methyl methacrylate with BTCM at a molar ratio of reactants of 1:1.

When the reactants are present in equimolar proportions it is found that the average molecular weight of the products is reduced to 2100 so that high molecular weight materials are no longer formed. Hence the reaction might be better termed "telomerisation" than "polymerisation". As a photochemically initiated chain process, however, it is similar to polymerisation in mechanism, and comparison to the previous reactions is therefore justified.

The value of molecular weight quoted above implies an average chain length of 19 monomer units so that the predominant reaction from a thermo-chemical viewpoint is still the joining together of chains of monomer molecules. Thus in calculating the values of reaction rate from non-stationary state data the heat of reaction has been assumed equal to that for the bulk polymerisation of methyl methacrylate. Rate values derived from contraction data confirm that no significant error is introduced through the adoption of this value.

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

Extent Conversion %	Reaction Rate %/hr.	Lifetime sec.	$10^5 \times \frac{k_p}{k_t}$
0	8.01	2.1	4.71
30	3.38	4.5	4.22
40	2.24	5.4	3.38
47	2.24	6.3	3.93
56	1.45	4.8	1.93

In this reaction the initial value of the rate is higher than in previous reactions due presumably to the increased rate of initiation as the BTCM concentration is raised. The trend in rate with conversion is completely reversed compared to the bulk polymerisation and those reactions with smaller concentrations of BTCM. No gel acceleration is observed and instead the rate gradually decreases as reaction proceeds. This may possibly be attributable to a dependence of the rate on monomer concentration. The lifetime has a higher initial value compared to the reactions at lower BTCM concentration and remains more or less steady as the reaction proceeds, showing if anything a slight increase.

Table 26. Variation in intensity exponent with extent conversion at 25°C.

Extent Conversion %	Rate of reaction (%/hr.) at relative intensity of: 100%	60.4%	35.9%	21.7%	Intensity Exponent
0	8.01	5.82	4.49	3.27	0.56
30	3.38	2.72	2.04	1.56	0.50
40	2.24	1.69	1.39	1.09	0.47
47	2.24	1.42	0.91	0.57	0.86
56	1.45	1.01	0.64	0.46	0.81

It will be seen that the intensity exponent has an initial value of about 0.5 which is steady up to 40% conversion but thereafter increases rapidly towards unity. It should be pointed out that the rate becomes extremely small when conversion reaches about 50% thus making the measurements subject to some uncertainty. The inaccuracy in these values could give rise to the apparent increase in intensity exponent at the later stages. The decreasing rate also puts a limit on the extent of conversion to which measurements can be made. Beyond about 60% conversion the rate becomes immeasurably low and variation with intensity almost undetectable making the measurement of lifetimes impossible.

From the values of intensity exponent in Table 26 termination would appear to be second order up to 40% conversion tending to become first order thereafter.

Table 27. Variation in values of individual velocity coefficients with extent conversion at 25°C. Rate of initiation = 4.25 x 10^{-7} mole $l.^{-1}sec.^{-1}$

Extent Conversion %	$10^5 \times \frac{k_p}{k_t}$	k_p	$10^{-7} \times k_t$
		$l.mole^{-1}.sec.^{-1}$	
0	4.71	25.0	0.053
30	4.22	5.06	0.012
40	3.38	2.70	0.008
47	3.93	2.36	0.006
56	1.93	1.93	0.01

Table 28. Variation in velocity coefficients corrected for mixed order termination.

Extent Conversion %	$10^5 \times \frac{k_p}{k_t}$	k_p	$10^{-7} \times k_t$
		$l.mole^{-1}.sec.^{-1}$	
0	6.09	28.0	0.046
30	4.22	5.06	0.012
40	3.38	2.70	0.008
47	27.5	5.51	0.002
56	10.2	3.88	0.004

It can be seen from Table 28 that the values of k_p and k_t show significant deviation from those of the previous reactions studied. In the initial stages k_p is reduced by a factor of about 10 compared to the bulk polymerisation and by a factor of about 20 compared to the reactions with 1 and 10 mole per cent of BTCM. k_p shows a drop by a factor of 5 at 30% conversion and remains fairly constant thereafter. The initial value of k_t is reduced by a factor of 60 compared to the bulk polymerisation and by a factor of about 200 compared to the reactions at lower BTCM concentration. The value is gradually reduced as the reaction progresses reaching about 1/10 of its initial value at 50% conversion. The discussion of these results is deferred to a later section.

Effect of temperature on the course of the reaction.

Table 29. Variation in rate and lifetime with extent conversion at 35 and 45°C and full irradiation intensity.

	Extent Conversion %	Reaction Rate %/hr.	Lifetime sec.
35°C	0	13.0	1.8
	30	5.0	3.8
	40	3.96	4.2
	47	3.41	5.1
	56	2.26	4.7
45°C	0	19.40	1.6
	30	7.04	3.2
	40	5.39	3.3
	47	4.90	4.6
	56	2.87	4.7

The variations in rate and lifetime are similar at 35 and 45°C to those taking place at 25°C (Table 25), the rate gradually decreasing and the lifetime showing a very slight increase with extent of conversion. The ratio of the initial to the final rate measured is almost identical at 25, 35 and 45°C showing that the rate is not affected by properties of the medium, such as viscosity, which are temperature-dependent.

Table 30. Variation in energies of activation with extent conversion over the temperature range 25 to 45°C.

Extent Conversion %	E_o	E_t kcal. per mole	E_p
0	9.8	4.9	12.3
30	8.3	8.1	12.3
40	8.4	10.1	13.4
47	8.1	8.7	12.5
56	6.6	1.1	7.1

The initial value of the overall energy of activation E_o is greater by a factor of about 2 than the values found in the previous reactions but unlike these it remains substantially constant over the range of conversion measured. The same remarks are valid as to the theoretical significance of the quoted values of E_t as for the previous reaction. E_t appears to increase up to about 40% conversion and then starts to decrease again with a very sharp drop to 1 kcal. at about 60% conversion. At the initial stage of the reaction E_t has in this case a significant value whereas in the bulk polymerisation and in those reactions where low concentrations of BTCM are present E_t is initially zero.

Table 31. Summary of kinetic data for the reaction of methyl methacrylate and BTCM for a molar ratio of reactants of 1:1 at 25°C. Rate of initiation = 4.25×10^{-7} mole l.$^{-1}$ sec.$^{-1}$

Extent Conversion %	Reaction Rate %/hr.	Life-time sec.	$10^5 \frac{k_p}{k_t}$	k_p l.mole^{-1}sec.$^{-1}$	10^{-7} k_t	E_o kcal.	E_t	Intensity Exponent
0	8.01	2.1	6.09	28.0	0.046	9.8	4.9	0.56
30	3.38	4.5	4.22	5.06	0.012	8.3	8.1	0.50
40	2.24	5.4	3.38	2.70	0.008	8.4	10.1	0.47
47	2.24	6.3	27.5	5.51	0.002	8.1	8.7	0.86
56	1.45	4.8	10.2	3.88	0.004	6.6	1.1	0.81

The characteristics of this reaction differ markedly from those already studied in two main respects. Firstly the absolute values of the velocity coefficients and energies of activation show considerable deviation from the "normal" values. Secondly their variation with extent conversion is reversed and the gel effect exhibited by the other reactions is completely removed.

D. The photochemical reaction of methyl methacrylate and BTCM at a molar ratio of reactants of 10:1 excess BTCM.

This reaction has been studied in order to ascertain whether the velocity coefficients and energies of activation show the same "abnormal" values as those for the reaction at 1:1 ratio of reactants or whether they revert to the values found for the reactions producing long chain polymers. The average chain length of the products in this reaction is about 4 monomer units.

The reaction has been studied only at the initial stage for comparison with the other reactions, the later stages being no longer of interest since the gel effect is eliminated.

Table 32. Summary of results for the reaction at a molar ratio of monomer:BTCM of 1:10 at 25°C. Rate of initiation is 7.98×10^{-7} mole $l.^{-1}sec.^{-1}$

Reaction Rate %/hr.	Life-time sec.	$10^5 \frac{k_p}{k_t}$	k_p	$10^{-7}\ k_t$	E_o	E_t	Intensity Exponent
			l. mole^{-1}sec.$^{-1}$		kcal.per mole		
11.5	2.7	13.9	18.1	0.013	9.1	6.2	0.61

It can be seen from these results that the rate continues to increase as the concentration of BTCM rises and the lifetime also shows a slight increase over the value at 1:1 molar ratio of reactants. The values of k_p and k_t are, if anything, slightly lower than those of the previous reaction while the activation energies are higher. Thus as the polymer chains are shortened still further the velocity coefficients appear to decrease while activation energies increase.

In view of the value of intensity exponent obtained, k_p and k_t have been corrected for mixed order termination and are shown thus in Table 32.

E. Determination of the transfer constant in the reaction between methyl methacrylate and bromotrichloromethane.

The transfer constant in a polymerisation or kindred free-radical chain reaction is defined as the ratio of the velocity coefficient for transfer to that for propagation (see introduction, page 10). Where a solvent is present in such a reaction the growing radicals may obviously react with either a monomer or a solvent molecule or, in other words, these two species will be in competition for the radicals.

The two reactions, propagation and transfer, may be represented thus:

Propagation $R_n\cdot + M \longrightarrow R_{(n+1)}\cdot$ Rate = $k_p[R]\ [M]$

Transfer $R_n\cdot + S \longrightarrow P_n + S\cdot$ Rate = $k_{tr}[R]\ [S]$

where the symbols have their usual meaning.

Thus the transfer constant $C_s = k_{tr}/\ k_p$ ....(36)

The value of C_s will give an indication of the extent to which each of the above reactions contributes in perpetuating the kinetic chain. This is obviously important to know in any kinetic analysis of such a system and hence justifies determination of the transfer constant. As will be seen below this necessitates determination of polymer molecular weights. Since these were of interest in themselves in the present case in order that kinetic data could if possible be correlated, the measurements involved in determination of the transfer constant become doubly important.

The following derivation of an equation for C_s is due to Mayo[56].

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

$$\text{i.e.}\quad \overline{DP} = \frac{k_p\ [R_s]\ [M]}{k_t[R_s]^2 + k_{tr}[R_s]\ [S] + k'_{tr}\ [R_s]\ [M]} \qquad \text{....(37)}$$

where k'_{tr} = velocity coefficient for monomer transfer

$$\text{Now } [R_s] = \left\{\frac{k_i [C]\ [M]}{k_t}\right\}^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(38)$$

where C = concentration of catalyst.

$$\therefore \qquad \frac{1}{\overline{DP}} = \frac{k_t [R_s]}{k_p [M]} + \frac{k_{tr} [S]}{k_p [M]} + \frac{k'_{tr}}{k_p} \qquad \ldots\ldots\ldots\ldots(39)$$

$$= \frac{(k_i\ k_t)^{1/2} [C]^{1/2}}{k_p [M]^{1/2}} + \frac{k_{tr} [S]}{k_p [M]} + \frac{k'_{tr}}{k_p} \qquad \ldots\ldots(40)$$

If $\overline{DP}_o$ = the degree of polymerisation when [S] = 0, then

$$\frac{1}{\overline{DP}_o} = \frac{(k_i\ k_t)^{1/2} [C]^{1/2}}{k_p [M]^{1/2}} + \frac{k'_{tr}}{k_p} \qquad \ldots\ldots\ldots\ldots(41)$$

Substituting this value in equation (40) we have

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_o} + \frac{k_{tr}}{k_p} \cdot \frac{[S]}{[M]}$$

$$= \frac{1}{\overline{DP}_o} + C_s \frac{[S]}{[M]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(42)$$

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

In the present work where the reaction is also initiated by the solvent, S becomes synonymous with C and equation (40) becomes,

$$\frac{1}{\overline{DP}} = \frac{(k_t\ k_i)^{1/2} [S]^{1/2}}{k_p\ [M]^{1/2}} + \frac{k_{tr} [S]}{k_p [M]} + \frac{k'_{tr}}{k_p} \ldots\ldots\ldots(43)$$

$$= K_1 \left\{\frac{[S]}{[M]}\right\} + K_2 \left\{\frac{[S]}{[M]}\right\}^{1/2} + K_3 \quad \ldots\ldots\ldots(43a)$$

where K_1, K_2 and K_3 are constants.

A plot of $1/\overline{DP}$ against $[S]/[M]$ will not be linear and the above analysis falls down in this case. The fundamental error is that the molecular weight and $\overline{DP}$ are affected by the changing rate of initiation as well as by the solvent transfer reaction.

Equation (39) can also be written in the form:

$$\frac{1}{\overline{DP}} = \frac{k_{tr}}{k_p} \cdot \frac{[S]}{[M]} + \frac{k_t}{k_p{}^2 [M]^2} \cdot \text{Rate} \quad \ldots\ldots\ldots(44)$$

(Monomer transfer is omitted, being regarded as negligibly small.)

By keeping $[S]/[M]$ constant and varying the rate a linear relation should be obtained between $1/\overline{DP}$ and rate. The intercept on the ordinate from a plot of $1/\overline{DP}$ against rate should then yield the value of $\frac{k_{tr}}{k_p} \frac{[S]}{[M]}$. Hence C_s can be calculated.

The above theory holds when long chain polymers are being produced but requires modification for the case of short chain products. The following theory has been derived by Mayo[8] and independently by Thomson[48].

As already stated the transfer and propagation reactions will be in competition in perpetuating the kinetic chain. Thus we have:

$$\frac{\text{Chance of propagation}}{\text{Chance of transfer}} = \frac{k_p[R_s][M]}{k_{tr}[R_s][S]}$$

$$\text{i.e.} \quad \text{Probability of propagation} = \frac{k_p[M]}{k_{tr}[S] + k_p[M]}$$

$$\text{and} \quad \text{probability of transfer} = \frac{k_{tr}[S]}{k_{tr}[S] + k_p[M]}$$

From these relations we can calculate the number of each type of molecule which is formed. Using the case of methyl methacrylate (MMA) and BTCM we have:

Molecule	DP x number of molecules
$CCl_3(MMA)Br$	$\frac{1 \times k_{tr}[S]}{k_{tr}[S] + k_p[M]}$
$CCl_3(MMA)_2Br$	$\frac{2 \times k_p[M] \cdot k_{tr}[S]}{\{k_{tr}[S] + k_p[M]\}^2}$
$CCl_3(MMA)_nBr$	$\frac{n \times k_p[M]^{n-1} k_{tr}[S]}{\{k_{tr}[S] + k_p[M]\}^n}$

The overall theoretical $\overline{DP}$ will be obtained by taking the sum to infinity of the above series.

If $k_{tr}[S] = A$, $k_p[M] = B$ and the series is represented by Q, then

$$Q = \frac{A}{(A + B)} + \frac{2AB}{(A + B)^2} + \frac{3AB^2}{(A + B)^3} + \cdots\cdots$$

$$= \frac{A}{A+B}\left[1 + \frac{2B}{A+B} + \frac{3B^2}{(A+B)^2} + \frac{4B^3}{(A+B)^3} + \ldots\ldots\right]$$

$$= \frac{AC}{A + B}$$

where $C = 1 + 2\lambda + 3\lambda^2 + 4\lambda^3 + \ldots\ldots$

where $\lambda = B / A+B$

Now $\lambda C = \lambda + 2\lambda^2 + 3\lambda^3 + \ldots\ldots\ldots$

$$\therefore C(1-\lambda) = 1 + \lambda + \lambda^2 + \lambda^3 + \ldots\ldots$$

$$= \frac{1}{1 - \lambda}$$

$$\therefore \quad C = \frac{1}{(1- \lambda)^2}$$

$$\therefore \quad Q = \frac{A}{A + B} \times \frac{1}{\{1 - B/(A + B)\}^2} = 1 + \frac{B}{A}$$

i.e. $\overline{DP} = 1 + \frac{k_p}{k_{tr}} \frac{[M]}{[S]}$

or $\frac{1}{\overline{DP}-1} = \frac{k_{tr}}{k_p} \frac{[S]}{[M]}$ ....(45)

Hence by plotting $1/(\overline{DP}-1)$ against $[S] / [M]$ a straight line of gradient C_s should be obtained. The similarity in form between equations (45) and (42) will be noted.

Experimental determination of molecular weights.

From the above theory it will be obvious that for a value of C_s to be obtained molecular weight determinations must be made on various polymer samples. In the present work two methods have been used for this depending on the value of the molecular weight. In the case of high polymers, molecular weights were determined viscometrically and for materials of low molecular weight (less than about 4000) a cryoscopic method was used. These will be described in turn.

Determination of molecular weights by the viscometric method.

Solutions of high molecular weight polymers are obviously much more viscous than the pure solvent. Staudinger[57] was the first to suggest that this relative increase in viscosity could be related quantitatively to the molecular weight of the polymer. The original Staudinger equation has had to be modified in the light of later experimental results but his general hypothesis has been extensively confirmed. Since the theory of solution viscosities is still in a formative stage the method does not yield an absolute value of molecular weight but must be calibrated for a given polymer-solvent system by reference to one of the absolute methods such as light scattering or osmometry. However, because of its experimental simplicity, it is perhaps still the most widely used method for determining molecular weights.

The increase of viscosity of a polymer solution over that of the pure solvent may be expressed as a fraction, the specific viscosity, η_{sp}.

$$\text{i.e.} \quad \eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = \eta_r - 1$$

where η_r = relative viscosity ($= \eta / \eta_o$)
The specific viscosity is dependent on the concentration and in order to define a quantity characteristic of a given molecule in a solvent it is necessary to take the initial slope of the η_{sp} against concentration curve.

$$\text{i.e.} \quad \lim_{C \to 0} \eta_{sp}/C = \lim_{C \to 0} \ln \eta_r/C = [\eta]_i$$

This limiting value of η_{sp}/C at infinite dilution is called the intrinsic viscosity $[\eta]_i$ and a plot of η_{sp}/C against C gives $[\eta]_i$ at $C = 0$.

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

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

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

The relation used in the present work was derived by

Fox et al.[58] from light scattering measurements as

$$[\eta]_i = 0.57 \times 10^{-4} M_w^{0.76}$$

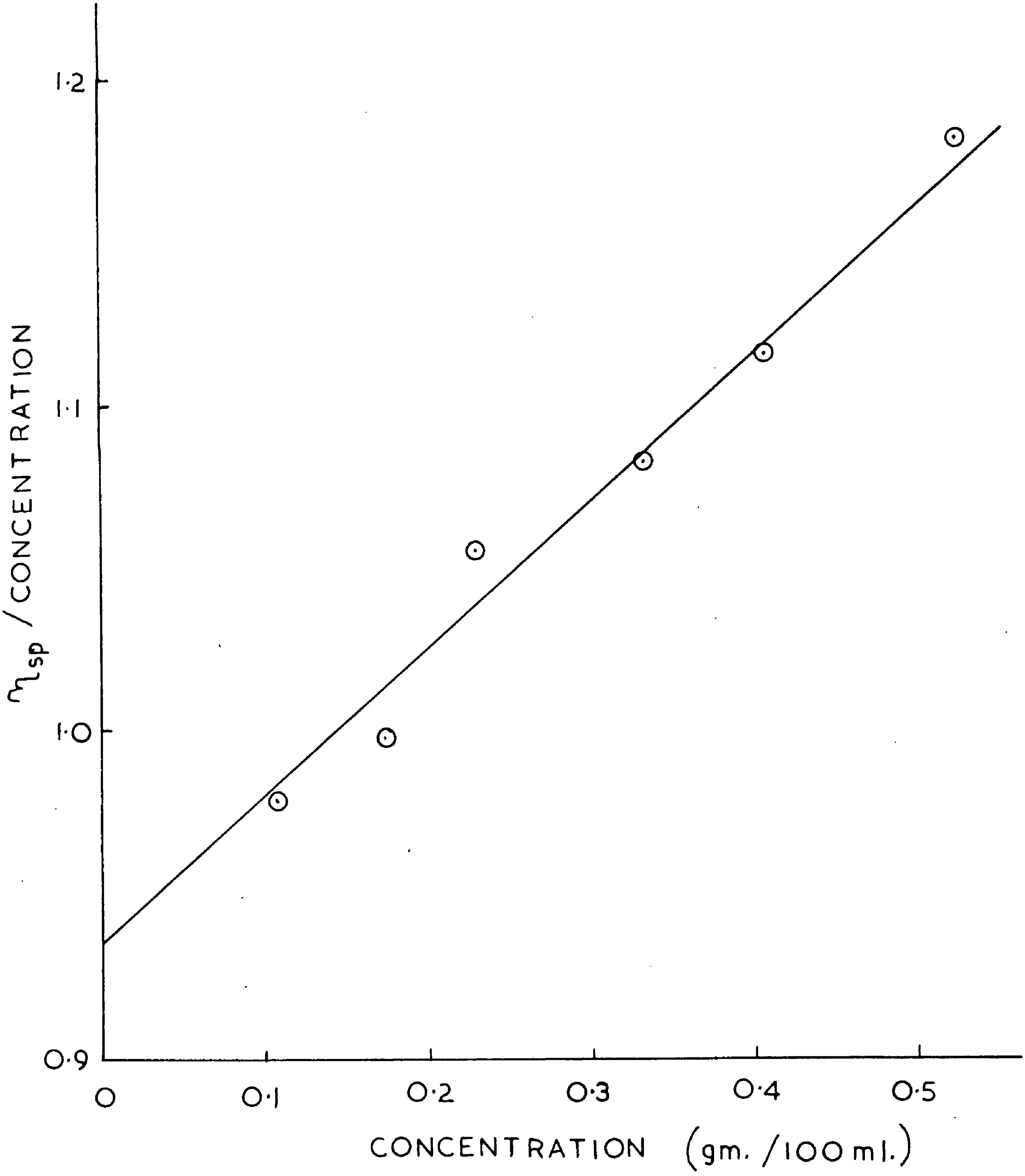
for polymethylmethacrylate in benzene solution at 25°C. M_w is the weight average molecular weight and can be converted to number average M_n using the relation $M_n:M_w = 1:2$ for the most probable molecular weight distribution[59].

Experimental procedure.

The appropriate quantities of BTCM and monomer were condensed into dilatometers of about 20 ml. capacity under vacuum. The mixtures were then polymerised to about 5% conversion at 25°C and contraction measurements of the rate were made. The contents of each dilatometer were transferred in turn to the high vacuum line and as much as possible of the unreacted material removed by overnight pumping. The residue was dissolved in about 5 times its own volume of benzene and the polymer precipitated by pouring into methanol. The polymer was then dried overnight under vacuum, redissolved in benzene and freeze-dried. This procedure gave a highly porous polymer sample which was readily soluble in benzene even at high molecular weight. Solutions of the polymer in benzene were then made up (about 1 g. per 100 ml.) and their viscosities measured to infinite dilution using a modified

FIGURE 20

TYPICAL INTRINSIC VISCOSITY DETERMINATION.



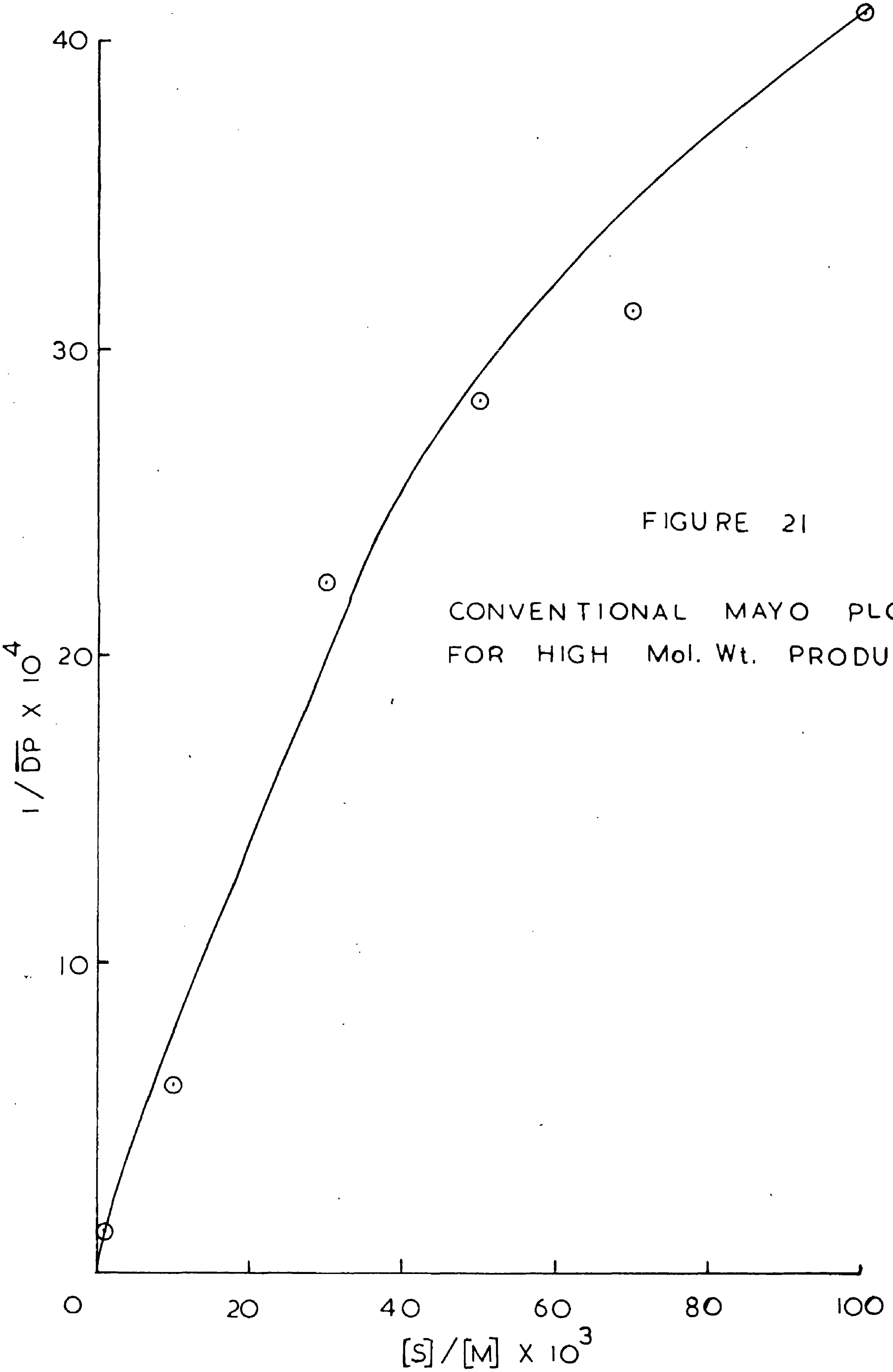
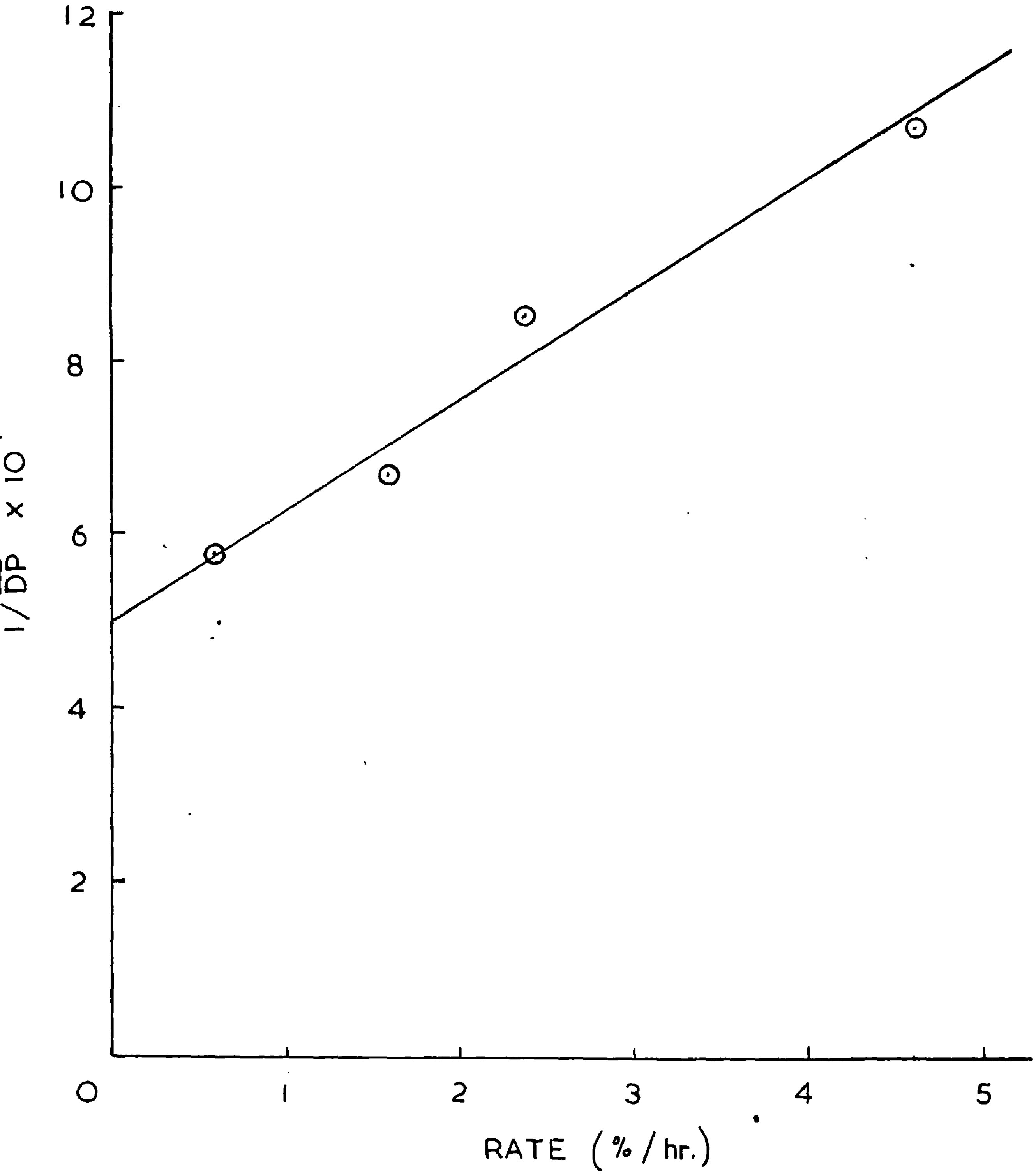


FIGURE 21

CONVENTIONAL MAYO PLOT FOR HIGH Mol. Wt. PRODUCTS.

FIGURE 22

MAYO PLOT FOR DETERMINATION OF TRANSFER CONSTANT AT A RATIO $[S]/[M] = 10^{-2}$.



Ubbelohde viscometer at 25°C. This type of viscometer enables dilution to be carried out *in situ*.

Results of molecular weight determination by viscometry.

The molecular weights of the polymers formed by reaction of mixtures of monomer and BTCM ranging from 1000:1 to 10:1 molar ratio of reactants were measured by the above method. The results are shown in graphical form in figures 20-22. Figure 20 shows a typical intrinsic viscosity plot and the conventional Mayo plot of figure 21 shows the curvature predicted by equation (43).

As mentioned above the transfer constant for the present system was determined by measuring polymer molecular weight as a function of reaction rate. This was carried out at a fixed molar ratio of monomer to BTCM of 100:1, the rate being varied by changing the intensity of irradiation over a 20-fold range. The results are shown in figure 22 from which it can be seen that the predicted linearity of equation (44) is confirmed. The intercept obtained from figure 22 gives rise to a transfer constant C_s of 0.05.

Determination of molecular weights by the cryoscopic method.

This method depends on the fact that one mole of a solute lowers the freezing point of the solvent by a characteristic amount. The freezing point of the solvent and dilute solutions of the polymer are determined from cooling curves and the molecular weight is calculated from an equation of the form,

$$M = K_f \frac{w}{\Delta T \ W}$$

where w = weight of polymer, W = weight of solvent, ΔT = freezing point depression and K_f is an experimentally determinable constant, the cryoscopic constant.

The main requirement of the method is, therefore, the ability to measure small differences in temperature with sufficient accuracy to enable materials of fairly high molecular weight to be dealt with. In the present work a thermistor bridge circuit was used as a temperature detector in much the same way as in the non-stationary state experiments. A spot galvanometer was used for balancing instead of the DC amplifier. A special cryoscopic cell was also used which incorporates magnetic stirring and is vacuum jacketed to ensure uniform slow cooling.

The bridge circuit was calibrated by measuring the resistance change produced in the thermistor as the freezing point of benzene was lowered by introducing weighed

FIGURE 23

CALIBRATION CURVE FOR CRYOSCOPIC DETERMINATION OF MOLECULAR WEIGHTS.

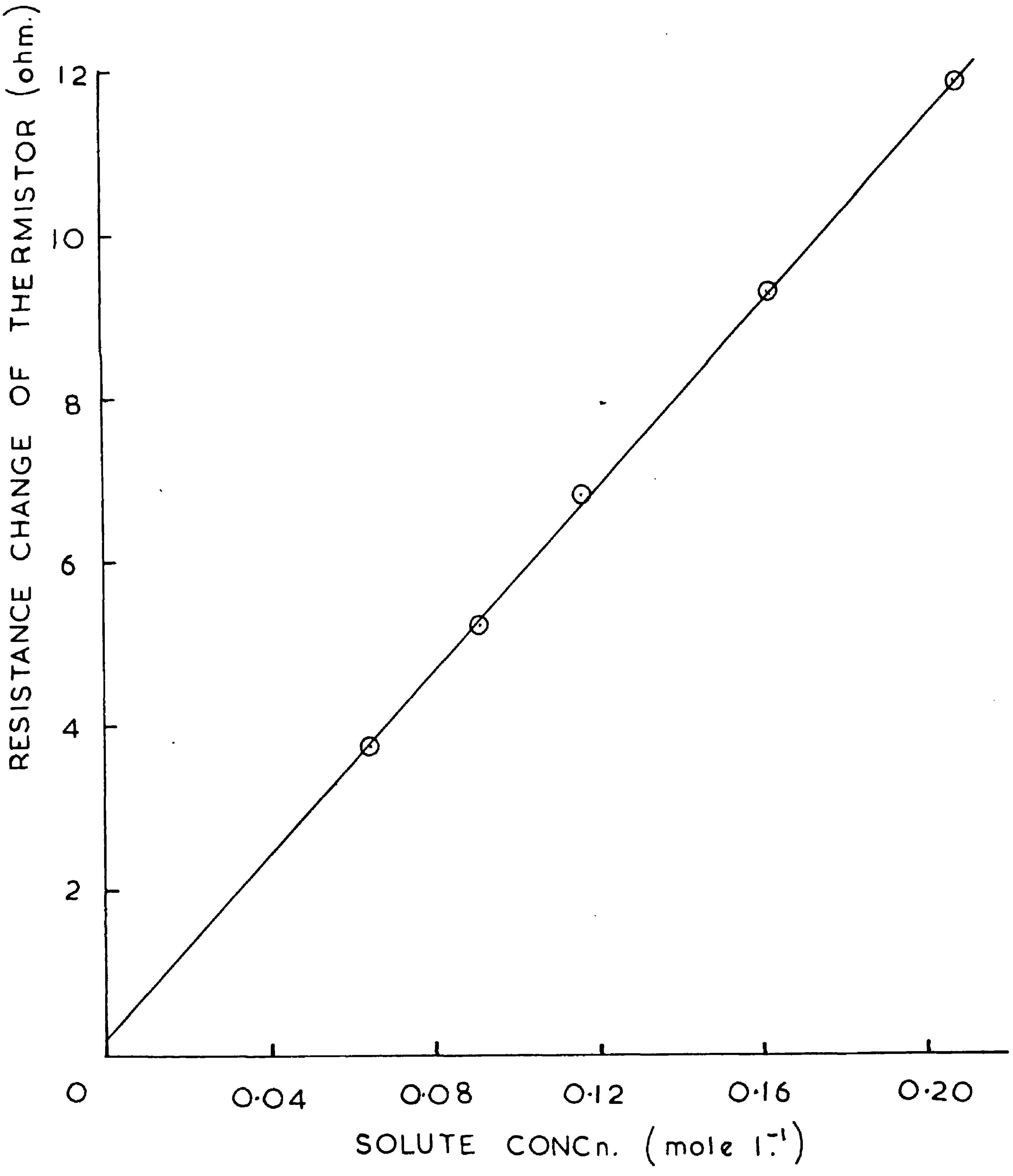


FIGURE 24

TYPICAL COOLING CURVES FOR DETERMINATION OF FREEZING POINT DEPRESSION.

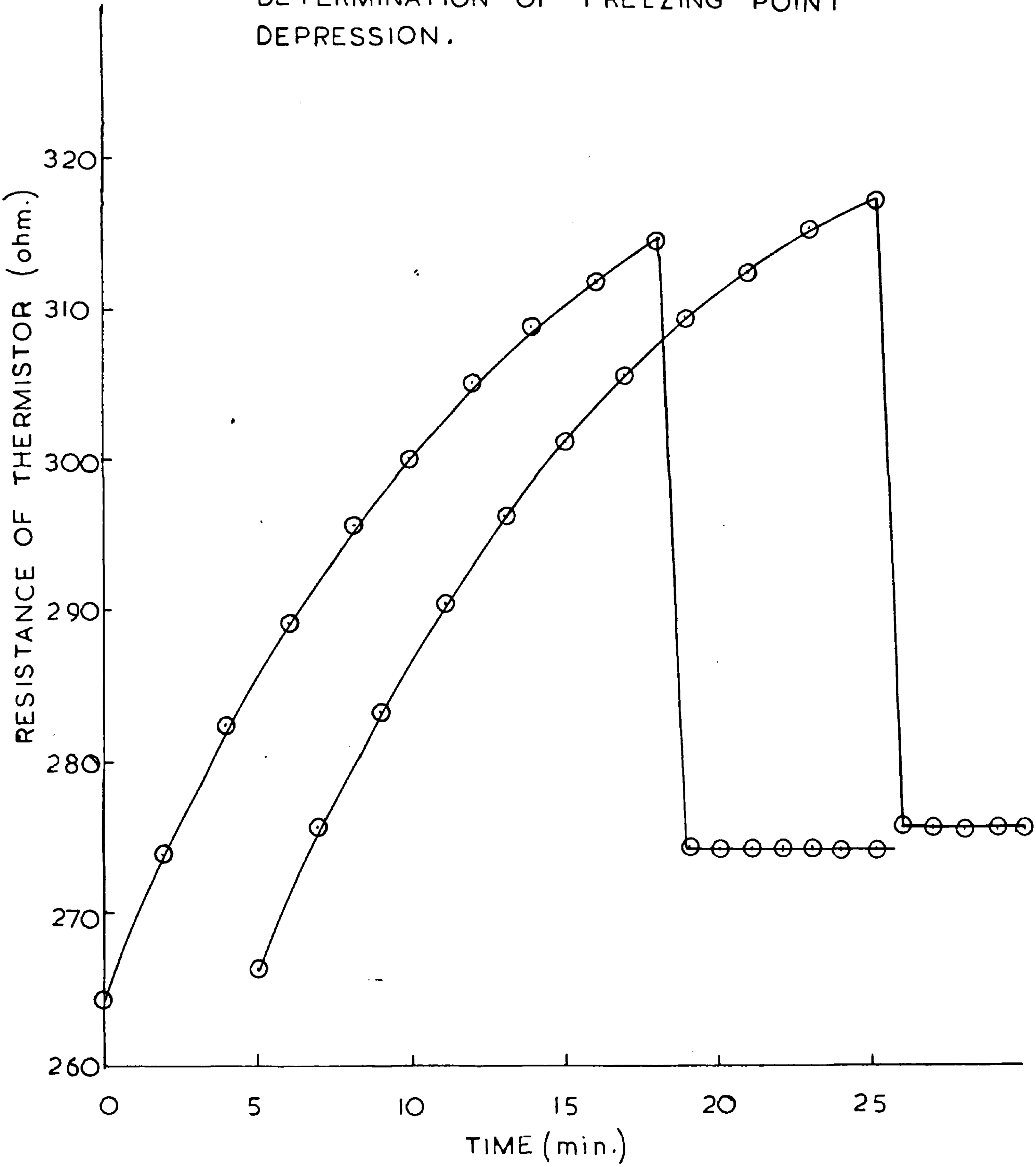
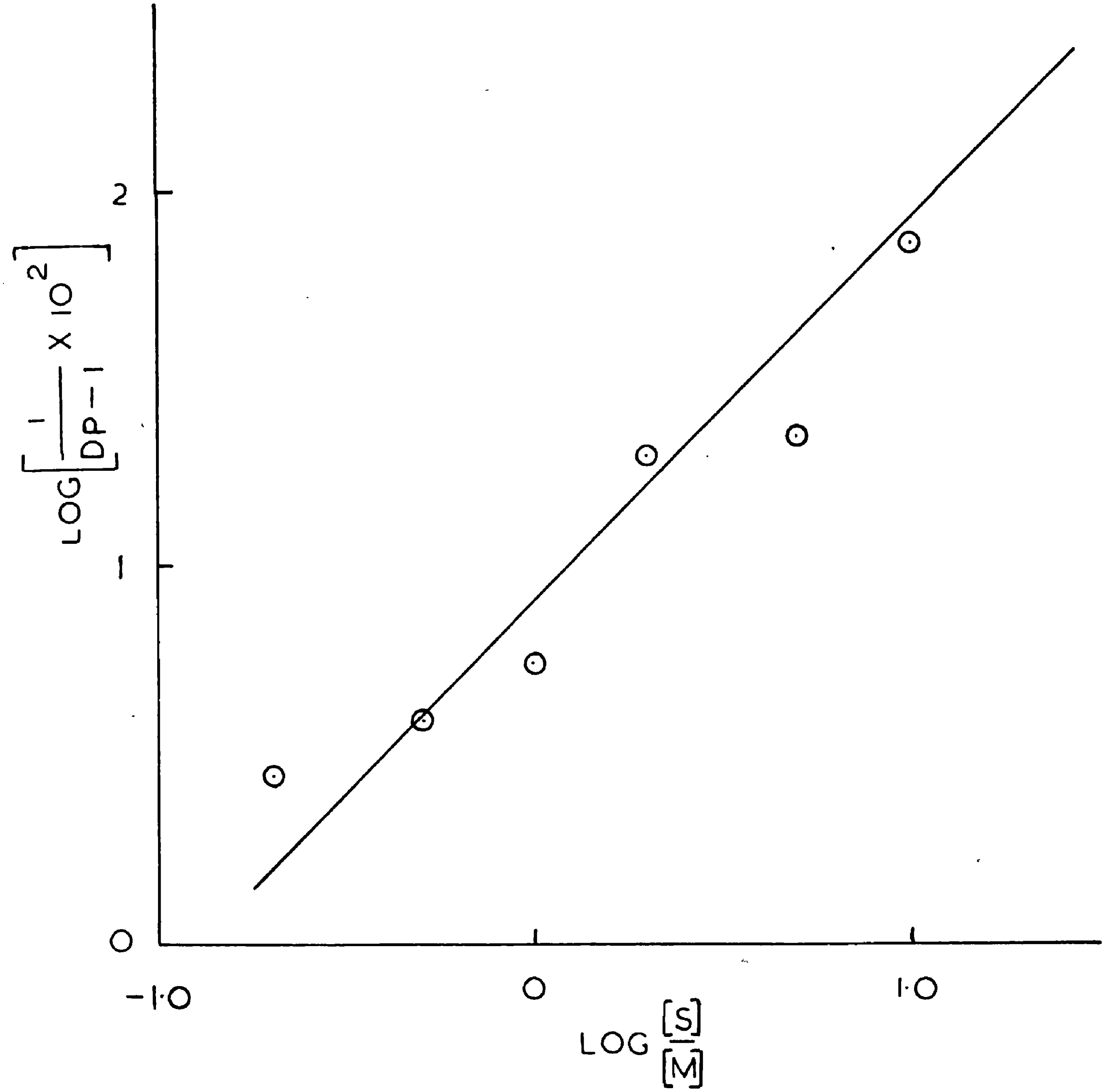


FIGURE 25

MODIFIED MAYO PLOT FOR LOW Mol. Wt. PRODUCTS



quantities of a standard substance (2:6-di-methyl naphthalene) of known molecular weight. A typical calibration curve is shown in figure 23. From this type of curve values of K_f can be calculated for any given sample of solvent.

Polymer samples were prepared by a similar method to that used in the viscometric experiments with the exception that the precipitation step was omitted so that low molecular weight fractions soluble in methanol would not be lost.

Freezing point determinations were made on dilute solutions (less than 1% w/w) of the polymer in benzene. The cryoscopic cell was immersed in an ice bath and slowly cooled to the freezing point while stirring the solution. The depression was determined at several polymer concentrations. Typical cooling curves are given in figure 24. These show the expected degree of supercooling immediately prior to freezing.

Results.

The molecular weights of the products from reaction of mixtures of methyl methacrylate and BTCM ranging from 5:1 to 1:100 molar ratio of reactants were determined by this method. The results are shown in figure 25 which is a modified Mayo plot based on the theory given on page 103. As required by the theory the experimental points lie on a straight line of unit gradient. The value of log k_{tr}/k_p is obtained from the intersection of the extrapolated line with the ordinate at $\log [S]/[M] = 0$. This leads to a value of C_s of 0.08.

The transfer constant is thus low and substantially constant over the complete range of BTCM concentration studied, showing that the propagation step is the predominant one in the growth of the kinetic chain.

It is perhaps of interest to note that a confirmation of the value of the rate of initiation can be obtained from the molecular weight measurements.

Equation (44) gives,

$$\frac{1}{\overline{DP}} = \frac{k_{tr}}{k_p}\frac{[S]}{[M]} + \frac{k_t}{k_p^2 [M]^2} \cdot \text{Rate}$$

The slope of the line obtained by plotting $1/\overline{DP}$ against rate will therefore give a value of $k_t/k_p^2[M]^2$ and hence a value of $k_p/k_t^{1/2}$, and since

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

then I can be determined from molecular weight measurements also if it is assumed that no monomer transfer is occurring.

The data from figure 22 give a value of I of 8.74×10^{-9} mole $1.^{-1}$ sec.$^{-1}$, obtained by assuming disproportionation as the termination mechanism. This compares well with the value of 8.1×10^{-9} mole $1.^{-1}$ sec.$^{-1}$ obtained by inhibition measurements.

III. The Polymerisation of Methyl Methacrylate in the Presence of Chloroform and Carbon Tetrachloride.

The peculiar kinetic effects observed in the presence of BTCM at high concentration, viz., the large reduction in k_p and k_t compared to the values in the bulk polymerisation, are not easily explained (see discussion) and it was considered possible that these effects might be due to the change in reaction medium caused by the introduction of high concentrations of BTCM. To test this hypothesis as far as possible analogous reactions were carried out in the presence of molecular species resembling BTCM in chemical structure. These are chloroform and carbon tetrachloride. These compounds do not give rise to free radicals by photochemical excitation so that small quantities of initiator were also added to give a measurable rate of reaction.

Polymerisation of methyl methacrylate in the presence of chloroform.

Since it was desired to compare the velocity coefficients with those of previous reactions studied at the initial stage only, non-stationary state measurements were confined to this stage of the reaction. The reaction mixture consisted of 1 mole methyl methacrylate per mole of chloroform. Di-t-butyl peroxide (0.01 mole $l.^{-1}$) was used as initiator. The results are summarised in the following table.

Table 33. Kinetic data for the polymerisation of methyl methacrylate in presence of chloroform at 25°C.

Reaction Rate %/hr.	Life-time sec.	$10^5 \frac{k_p}{k_t}$	k_p l.mole^{-1}	10^{-7} k_t sec.$^{-1}$	E_o kcal.	E_t	Intensity Exponent
2.72	2.10	2.30	1200	5.22	3.7	0	0.69

The rate of initiation was calculated from the results obtained previously for di-t-butyl peroxide. The intensity exponent deviates considerably from the value of 0.5 required for exclusive second order termination and the velocity coefficients shown have been corrected to allow for this.

It will be seen from Table 33 that the velocity coefficients do not show the "abnormally" low values exhibited in the reaction at high BTCM concentration. k_p has a somewhat higher value than in the bulk polymerisation while k_t is substantially the same. The energies of activation also have the usual values for methyl methacrylate polymerisation.

Polymerisation of methyl methacrylate in presence of carbon tetrachloride.

In this reaction the photosensitiser was BTCM used at sufficiently low concentration not to affect the reaction medium. The reaction mixture consisted of 1 mole monomer, 0.9 mole carbon tetrachloride and 0.1 mole BTCM. Table 34 shows the results obtained.

Table 34. Kinetic data for the polymerisation of methyl methacrylate in presence of carbon tetrachloride photosensitised with BTCM at 25°C.

Reaction Rate %/hr.	Life-time sec.	$10^5 \frac{k_p}{k_t}$	k_p l.mole^{-1}	10^{-7} k_t sec.$^{-1}$	E_o kcal.	E_t	Intensity Exponent
5.45	1.32	2.00	246	1.23	3.4	0	0.51

From the above table it can be seen that the values of the velocity coefficients in presence of carbon tetrachloride are very similar to those for the bulk polymerisation.

Molecular weights of the products were also obtained for these reactions. The $\overline{DP}$'s determined by viscosity measurements were 9,300 for the chloroform system and 250 for the carbon tetrachloride reaction.

In the first case the only transfer taking place will be to $CHCl_3$ which must be very slight. In the second case about 5 mole per cent of BTCM is present and the $\overline{DP}$ of the product compares with the value obtained in the methyl methacrylate - BTCM system at a molar ratio of reactants of 20:1.

Thus although these reactions simulate the conditions of medium in the BTCM - methyl methacrylate reaction they do not produce the same short-chain polymers.

IV. The Polymerisation of *iso*-Butyl Methacrylate in the Presence of BTCM.

By way of further investigation of the "abnormal" low values of the velocity coefficients at high BTCM concentration in the polymerisation of methyl methacrylate it was decided to study the polymerisation of another methacrylate monomer under similar conditions to determine whether this effect is a general property of methacrylate esters. This has been done using *iso*-butyl methacrylate at two concentrations of BTCM. Firstly the reaction has been studied at a molar ratio of monomer to BTCM of 100:1. This should give velocity coefficients similar to those in the bulk polymerisation of *iso*-butyl methacrylate. Secondly, velocity coefficients have been determined at a molar ratio of 1:1, monomer:BTCM thus simulating conditions under which k_p and k_t have abnormal values in the methyl methacrylate - BTCM system.

The principal results are shown in Table 35. Again no measurements were carried out beyond the initial stage of the reactions.

Table 35. Kinetic data for the polymerisation of iso-butyl methacrylate in presence of BTCM at 25°C.

Mol ratio monomer: BTCM	Rate %/hr.	Life-time sec.	$10^5 \frac{k_p}{k_t}$	k_p l.mole^{-1}sec^{-1}	10^{-7} k_t	E_o kcal.	E_t	Intensity Exponent
100:1	3.10	0.7	5.8	4870	8.4	5.2	0	0.86
1:1	7.3	1.3	7.34	68.3	0.093	6.3	0	0.72

The values of $\overline{DP}$ at 100:1 and 1:1 ratios are 2,350 and 17 respectively.

In calculating the rate from the non-stationary state temperature rise, values for the specific heat and heat of polymerisation of iso-butyl methacrylate have had to be assumed since these are not available in the literature. An average value of specific heat for most vinyl monomers is about 0.5 and this has been used in the present case. The heat of polymerisation has been taken as 13.0 kcal.per mole, the value used for methyl methacrylate. If anything this value may be slightly high since the larger ester group will cause further stretching of alternate -C-C- bonds in the polymer chains. Rates were also determined by dilatometric measurements using values of monomer and polymer density of 0.8858 and 1.045 g./ml. respectively[60]. The rates determined by the two methods agree to within 10%, showing that the velocity coefficients may be in error to a corresponding extent. Since only a comparison is required between the values at 100:1 and 1:1

molar ratios of reactants the adoption of the values of heat of polymerisation and specific heat quoted above is justified.

Rates of initiation were calculated using the relation established for the methyl methacrylate reaction. This may also introduce errors since DPPH appears to be dependent on medium conditions for its inhibitor action[48].

The results in Table 35 should be considered in the light of these possible limitations.

On examination of Table 35 it should firstly be noted that intensity exponents for this reaction are high and the velocity coefficients have been appropriately corrected to allow for mixed order termination.

At the 100:1 ratio the absolute values of the velocity coefficients and particularly k_p are rather higher than those for the methyl methacrylate reaction or than those of other methacrylate monomers so far measured[61]. The same significant decrease in k_p (almost 100-fold) and k_t (100-fold) is observed in this reaction when the concentration of BTCM is high and short chain polymers are also produced in this case. The values of activation energies are similar to those for methyl methacrylate.

DISCUSSION

DISCUSSION

Before proceeding to any detailed discussion of results or conclusions to be drawn therefrom it will be of advantage to consider at this point the limitations of the thermistor method. In this way it will be more readily obvious what significance should be attached to any variations in measured quantities and in the more fundamental constants derived from them. The quantities measured directly by this method are reaction rate and lifetime of the kinetic chain. These will be considered in turn.

Rate measurement.

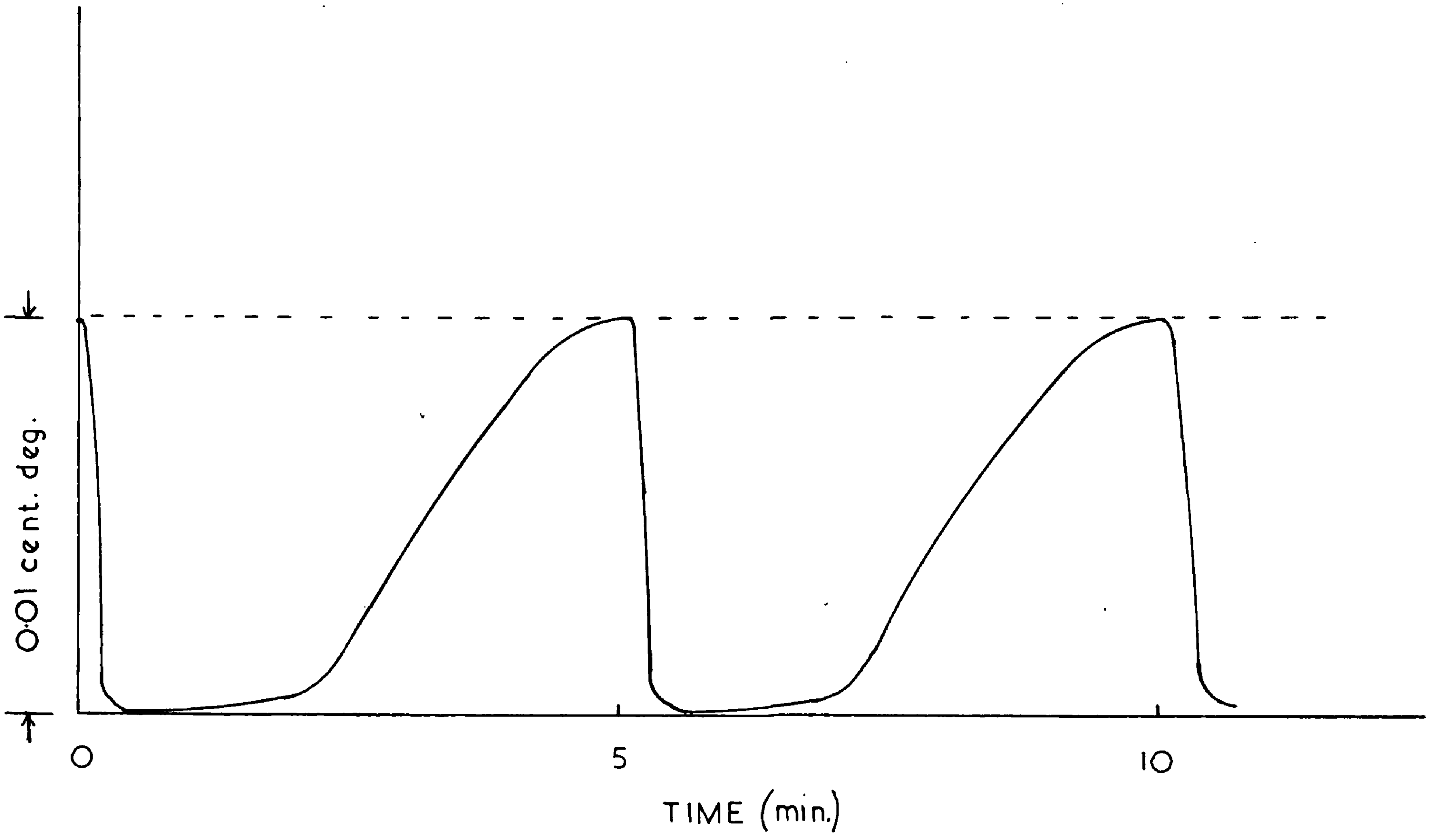
Essentially this involves the measurement of temperature increase as a function of time. The limit of temperature measurement is governed by the maximum amplification of the out of balance signal from the bridge which can be obtained. This must be considered against background temperature fluctuations.

It was found that with the type of amplifier used (Sunvic DCA.1) only one amplification range was suitable for measuring the temperature changes associated with the systems studied. This corresponded to the highest gain practicable against thermostat fluctuations. When polymerisations were followed through to the autoaccelerated phase this single amplification range had to be used for measuring rates which differed by as much as a factor of 10. Hence the rate at the initial stage of the reaction had to be kept as small as possible. The rate used in the bulk polymerisation, for example, was about 1% per hr. corresponding to a rate of temperature increase of about 0.022°C in 30 sec. or 7.3×10^{-4} °C per sec. This represents about the lowest rate which could be measured with any degree of reproducibility. The ultimate resolution in temperature and time are somewhat better than this. For example a typical result from the calibration of thermistor temperature rise against recorder deflection is 0.0176 °C per cm. Supposing that the amplitude of the recorder chart can be measured to 0.2 m.m. the lower limit of temperature sensitivity is 3.5×10^{-4} °C and if 0.2 m.m. can be measured on the time axis also this represents 0.04 sec. with the chart moving at 12" per minute.

The thermostat control band was of the order of ± 0.005°C under optimum conditions, i.e. when operating at or very near the ambient temperature. Any great

FIGURE 26

WAVE FORM OF TEMPERATURE FLUCTUATIONS IN THERMOSTAT



deviation from these conditions resulted in considerable widening of the band and produced a large increase in the frequency of the temperature oscillations. These oscillations could be measured and recorded by the thermistor itself and gave rise to a wave form of the approximate nature shown in figure 26.

The curve is shown for ideal operating conditions. The best point at which to make non-stationary state measurements is at the bottom of the troughs when the temperature remains sensibly steady for a period of about 2 minutes. Since a single non-stationary state measurement requires usually about 30 sec. to record the thermostat fluctuations should be negligible during this time. Hence the possible temperature measurement is not restricted with respect to these background variations. Under the worst operating conditions encountered in the present work (45°C) the frequency and amplitude of temperature oscillations were about doubled compared to those at 25°C. Even so a period of about one minute at the bottom of the troughs, when the temperature remains steady, suffices for most measurements required except perhaps those in the very late stages of the bulk polymerisation. In the latter case, however, the thermal conductivity of the highly viscous mixture is so reduced that small variations in the thermostat temperature take almost infinite time to be reflected in the thermistor and so do not affect the measurements.

As mentioned in the experimental section rates of reaction were each checked several times. From the scatter of results obtained on any one rate the maximum probable error in the rate measurements is about 5%. This occurs with the lowest values measured.

Lifetime measurement.

The accuracy of this is governed by some of the factors involved in the discussion of rate measurement. The main requirements are a steady base line on the recorder chart prior to reaction and the minimum of interference during the run from electrical pick-up or background temperature variation.

Given these conditions it is possible to make a fairly accurate extrapolation of the rate curve to obtain the time-intercept and hence the lifetime. Theoretically there should be no limit on the smallest lifetime which can be measured by this system provided recording apparatus of sufficient sensitivity in time is used. For the Elliot recorder used in this work the absolute limit of time resolution has been shown to be about 0.04 sec.

However it has been found that with lifetimes of 1 second or less the probable error as calculated from the scatter of results can be as much as ± 50%. This is a consequence of the difficulty in obtaining a precise indication of the opening of the shutter and of the variation in the response lag of the system from thermistor to recorder.

In some of the trial experiments with this system an electrically operated shutter was arranged to give a small pip on the recorder chart to indicate the commencement of reaction. This was found to displace the pen from its true baseline resulting in large fluctuations in values of measured intercept; these were especially significant for short lifetimes of the order of 1 second. Better reproducibility was obtained by using a simple manually operated shutter but even so the results are not reliable to better than 50%.

As indicated previously the lag in response of the system was determined by measuring the rate and intercept at different intensities of irradiation. The line obtained by plotting reciprocal rate against intercept was extrapolated to infinite rate when the value of the intercept is equivalent to the lag. The response time of the amplifier is quoted by the makers as 0.1 sec. but the recorder has a much larger value, about 1 second. The total lag was found usually to lie between 1 and 2 seconds, and was presumably varying from one measurement to the next. (This could be caused for example by differing amounts of ink in the bucket pen and by slight variations in its balance.) Since an average value of the lag has to be calculated from a whole series of measurements errors are obviously introduced and again these will become important where very short lifetimes are concerned.

Taking all these factors into consideration the lower limit on measurable lifetimes is probably of the order of 1 second and even these will be reliable only to ± 50%. Conditions producing such short lifetimes were therefore avoided where possible.

The upper limit on the lifetimes which can be measured using the present system is governed by the adiabatic period of the reaction in the vicinity of the thermistor element. From the curve shown in figure 2 it can be seen that as soon as the reaction becomes non-adiabatic the plot of temperature (corresponding to fractional conversion) against time deviates from a straight line and gradually levels off to a steady maximum value depending on the rate of reaction. The theory of the non-stationary state given on pages 11-13 requires that a period equal to three times the lifetime should elapse before this curve attains linearity. If the reaction becomes non-adiabatic before this then linearity will never be attained and measurement of the lifetime will be impossible by the present method. It is generally considered that the adiabatic period should be of the order of 5 times the lifetime in order to obtain reliable extrapolations of the steady rate. The adiabatic period produced by normal experimental conditions in the present work was generally about 30 sec. in the initial stages of the reaction so that lifetimes up to 6 sec. could be measured. In the autoaccelerated phase of reaction values up to 30 sec. have been quoted and although the adiabatic period increases considerably at this stage when heat transfer due to convection is largely eliminated, these should be regarded as minimum values since the stationary rate is not fully achieved before cooling takes place.

It has been claimed by Hayden and Melville[43] making similar measurements with a thermocouple that the half-life of heat of the system can be increased to 1500 seconds, allowing for the measurement of lifetimes up to 300 seconds. This is achieved by enclosing the reaction vessel in a vacuum jacket. Lifetimes of this order would be encountered only in the gel stage of the bulk polymerisation when the rate may be as high as 10% per hr. To obtain one recorder trace under these circumstances would require 3000 secs. (allowing time for thermal equilibrium with the thermostat to be re-established before the next chart trace is taken). Assuming that a minimum of three such measurements is required for determination of the lag the time needed to measure a single lifetime would be about 2½ hours. During this time the polymerisation would have advanced some 12% exclusive of dark reaction and it would thus be impossible to associate the results with a precise extent of conversion. In this respect such measurements would seem pointless as applied to the present system.

The probable error associated with the general magnitude of lifetime measured in this work will at best be about ± 20%. This results in errors of ± 50% in the values of the individual velocity coefficients k_p and k_t. (It should be noted, moreover, that uncertainty from other sources such as rate of initiation measurements has not been taken into account.) Thus from the point of view of rate and lifetime measurements alone, experimental error can account for a factor of about 2 in the values of k_p and k_t so that no variation within this range can be considered significant.

The Bulk Polymerisation of Methyl Methacrylate.

The bulk polymerisation was studied in the present work for two main reasons: (1) To provide a basis of comparison of experimental variables and derived kinetic constants with those obtained in the presence of various diluents. Although the kinetics of methyl methacrylate polymerisation has been studied many times in the past strict comparison of results is only possible when conditions (e.g. temperature, irradiation intensity, optical system if photochemically initiated) are identical and one experimental method, in this case the thermistor method, is consistently used. (2) To make a further investigation of the hitherto unexplained decrease in the value of the intensity exponent in the region of 20 to 40% conversion.

The former aspect of the work requires little comment. The results of the present work are in reasonable agreement with those of other workers. The following table gives a comparison of the published values of velocity coefficients for propagation and termination at the initial stages of reaction. The results have been corrected to 15°C using a value of 3.7 kcal./mole for E_p and zero for E_t.

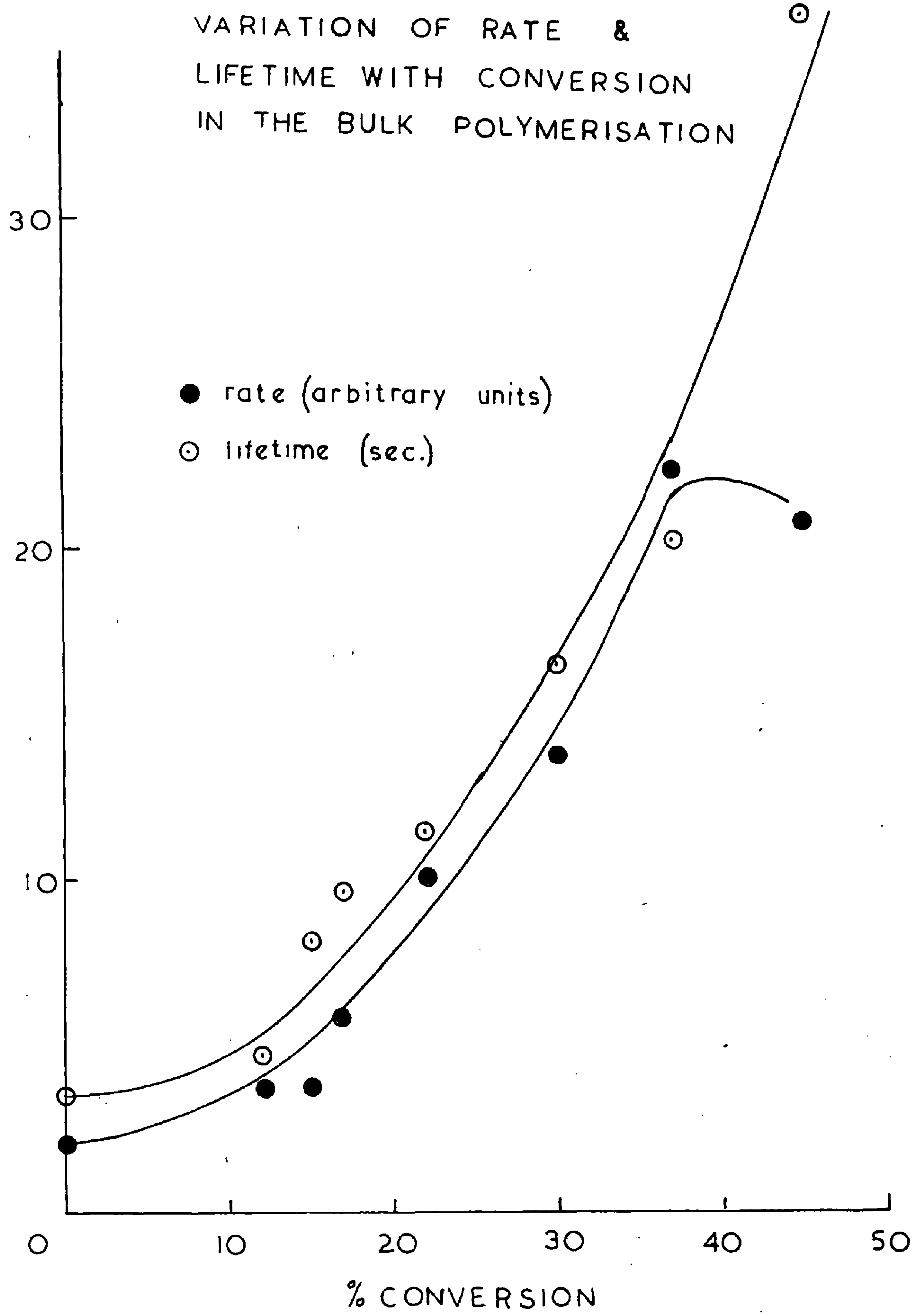
Table 36. Velocity coefficients for propagation and termination in methyl methacrylate polymerisation at 15°C.

Reference	Method of determining τ	$10^5 \frac{k_p}{k_t}$	k_p l.mole^{-1}sec.$^{-1}$	10^{-7} x k_t l.mole^{-1}sec.$^{-1}$
this work	thermistor	0.738	220	2.98
62	thermistor	0.54	-	-
43	thermocouple	0.742	328	4.42
42	thermocouple	1.33	74	0.56
16	refractive index	0.61	-	-
63	viscosity	2.20	59	0.27
64	sector	1.40	-	-
65	sector	0.79	180	2.27
66	sector	0.89	410	4.46
67	sector	0.39	258	6.6
37	sector	0.85	208	2.44

The agreement among these values is good considering the wide range of methods used for determining lifetimes and rates of initiation. This may be taken as confirmation of the validity of the thermistor method as used in the present work.

The variation in rate and lifetime with conversion

FIGURE 27



VARIATION OF RATE & LIFETIME WITH CONVERSION IN THE BULK POLYMERISATION is clearly illustrated in figure 27. Both quantities increase by a factor of about 10 up to 50% conversion. The reasons for limiting measurements to this stage of the reaction have been given variously in different sections of the thesis but may be conveniently summarised here: (a) the impossibility of measuring lifetimes because their high values beyond 50% conversion are incompatible with adiabatic requirements, (b) the formation of cavities in the polymerising mixture which renders rate measurements of the photochemical reaction extremely uncertain, (c) the high dark rate at this stage making it impossible to assign a set of results to a precise extent of conversion, (d) the impossibility of estimating extent of conversion with any degree of reliability. For these various reasons any results obtained beyond about 50% conversion would be worthless.

One further point may be mentioned in connection with the results for the bulk polymerisation. The autoacceleration of the rate was first noted in methyl methacrylate polymerisation and is without doubt most marked for this monomer. However the same effect can be observed to a lesser degree in other vinyl monomers which are similar to methyl methacrylate in chemical constitution and polymerisation mechanism.

Among these are vinyl acetate and styrene; the rate in the vinyl acetate reaction, for example, increases only by a factor of 2 at its greatest value[68]. The explanation usually given for the rate acceleration is that the increased viscosity of the system retards diffusion of the macro-radicals to such an extent that the termination reaction becomes diffusion-controlled. This seems somewhat inadequate in view of the fact that the viscosity of the reaction mixture for the other monomers mentioned is not greatly different from that of methyl methacrylate. The question of why the latter monomer shows a gel effect to such a marked degree does not seem to have received a great deal of attention. Indeed reference to it can be found only in a paper by Norrish and Smith[30] in which it is suggested that termination is further restricted in methyl methacrylate polymerisation because the polymer chains are extremely rigid. This is held to decrease the collision frequency of chain ends as compared to other polymerising systems in which kinking of the chains at certain points along their length can take place. In view of the lack of experimental evidence this explanation must be regarded as purely tentative.

It is not proposed to give any a priori reasons for the peculiarity of methyl methacrylate in this respect. Certainly there seems to be no unifying principle which can correlate the behaviour of all vinyl monomers at higher conversions. It is possible that absolute values of polymer chain length may have some bearing. For example the monomer transfer coefficient k'_{tr} in vinyl acetate polymerisation is high. Kwart et al.[69] quote a value of 0.23 while according to Matheson et al.[37] the value for methyl methacrylate is 0.74×10^{-4} l.mole^{-1} sec.$^{-1}$. Thus if monomer transfer is the controlling factor in polymer chain length there will be a difference of almost 10^4 between these two systems under a given set of conditions. On the other hand k'_{tr} for styrene[5] is of the same order as that for methyl methacrylate. However k_p for styrene is low so that higher initiator concentrations (producing smaller $\overline{DP}$) are necessary to produce a given rate.

The dependence of gel effect on polymer chain length will be discussed more fully in a later section.

Discussion of intensity exponent.

The main point at issue in these investigations is the reason for the fall in intensity exponent to values of less than 0.5. Interpreted as a true kinetic effect this implies an order of termination greater than 2 with respect to polymer radicals and so invalidates the kinetic scheme on which the non-stationary state theory is based. As the idea of third order termination cannot be supported on any theoretical ground an explanation of the low intensity exponents must be sought elsewhere. As mentioned in the introduction Bengough and Melville[42] have suggested that these low values may be due to the peculiar photochemical after effects shown in this polymerisation. It is conceivable that these effects may overlap with the normal photo-initiated reaction and so cause the usual relation between rate and irradiation intensity to break down. This idea has received some attention in the present work. It may be relevant at this point, therefore, to review some of the observations which have been made on these photochemical after effects or 'dark reaction' by other workers.

It is well-known that in the photoinitiated polymerisation of methyl methacrylate there is a high associated 'dark rate'. The mechanism of the process giving rise to this is obscure but in systems where a photosensitiser is present it may be attributable to initiation by thermal decomposition of the catalyst.

The dark reaction was first referred to by

Melville[70] in a study of the vapour phase polymerisation of methyl methacrylate when it was observed that polymerisation continued for long periods after irradiation ceased. This was explained by postulating that the active centres in this dark reaction are not free radicals but "activated double bonds" capable of promoting chain growth. These reaction chains were supposed to be of infinite lifetime so that no termination ever occurred.

This theory was rejected by Bamford and Dewar[63] who attributed the dark rate to the formation of a catalyst by ultra-violet irradiation. They found that the catalyst was destroyed by prolonged heating. These ideas were confirmed by later work of Mackay and Melville[71] who concluded that in the polymerisation photosensitised with benzoyl peroxide a substance was formed which was capable of thermal dissociation at room temperature to produce radicals. They were led to believe that the only difference between the dark and light reactions in this case was in the initiation step.

In a paper by Shantarovich[72] the dark rate is found to follow a half-order dependence on the polymer concentration showing that the associated reaction is autocatalytic in the same way as the normal polymerisation. The dark reaction is interpreted by that author as being the development of the "spatially branched structure of the polymer" as opposed to the "generation and propagation of chains" which is supposed to constitute the light reaction.

The results on the dark reaction obtained in this work show that the rate increases more or less in parallel with the light rate through the autoaccelerated phase, thus indicating that both reactions have similar mechanisms. The implications of the high dark rate at the later stages of the polymerisation will now be considered.

As shown in the result section the ratio of dark to light rate gradually increases throughout the period of the acceleration. True values of intensity exponent should only take account of the pure photoreaction so that when a dark rate is contributing to the overall measured rate errors are introduced. This can be seen from the following considerations.

Let R_l = light rate, R_d = dark rate, L = light intensity.

In a normal polymerisation where dark rate is negligible we have,

$$\frac{(R_l)_1}{(R_l)_2} = \left(\frac{L_1}{L_2}\right)^n$$

where n = true value of intensity exponent.

If a significant dark rate operates independently then the total polymerisation rate will be the sum of the rates due to photochemical and dark initiation,

$$\text{i.e.}\quad R_o = R_1 + R_d$$

$$\therefore\quad \frac{(R_o)_1}{(R_o)_2} = \frac{(R_1)_1 + R_d}{(R_1)_2 + R_d}$$

since the dark rate is presumably independent of irradiation intensity.

Taking a typical case in the present reaction at about 30 to 40% conversion when $R_d = \frac{1}{4} R_1$ we have,

$$\frac{(R_o)_1}{(R_o)_2} = \frac{\frac{5}{4}(R_1)_1}{(R_1)_2 + \frac{1}{4}(R_1)_1}$$

$$= \frac{5}{4(L_2/L_1)^n + 1}$$

$$\therefore \log\left[(R_o)_1/(R_o)_2\right] = \log 5 - \log\left[4(L_2/L_1)^n + 1\right]$$

The apparent measured value of intensity exponent is given by

$$\frac{\log\left[(R_o)_1/(R_o)_2\right]}{\log\,(L_1/L_2)} = \left\{\log 5 - \log\left[4(L_2/L_1)^n + 1\right]\right\} \Big/ \log(L_1/L_2)$$

Taking the value of the true exponent n to be 0.5 and $L_1 = 2L_2$ the value of the measured exponent will be 0.385, decreasing as the ratio L_1/L_2 increases. Hence on this basis the low values of intensity exponent can be almost quantitatively explained.

The question then arises as to whether dark rate is included in the overall rate measurements. By the nature of the thermistor method any steady background rate of polymerisation, giving rise to an increase of temperature, will be balanced out in the bridge circuit before irradiation begins. Thus it may be that the rate due to photochemical initiation alone is measured. This idea was tested in the following way.

The intensity exponent was first of all measured in the normal way by balancing the bridge when no irradiation was taking place and then finding the rate at various irradiation intensities. Secondly the intensity exponent was determined after a steady background rate had been established by inserting several gauze screens between the mercury arc and the reaction vessel, thus making an optical combination of low transmission. The bridge was balanced and the rate determined by withdrawing the screens one by one from the light beam (all screens being replaced between rate measurements). In a typical experiment of this kind the intensity exponents obtained by these procedures were 0.52 and 0.89 respectively. Thus it can be seen that the effect of balancing out a steady heat flow due to an independent source of reaction is to increase rather than decrease the intensity exponent. The normal dark rate would be a much smaller fraction of the overall rate than that produced artificially in the above experiment but nevertheless these results show that the true exponent may be even lower than reported in this work. The same considerations are valid for the thermocouple method used by the other workers who have observed a decrease in exponent[42,43].

It may be concluded, then, that the low values of intensity exponent would be accounted for by dark rate only if this is measured in combination with the light rate. Since this is not the case in the present system such an explanation must be rejected.

It is possible that the exponent may be lowered by the effects of rate of initiation on the radical chain length. The smaller the rate of initiation, i.e. the lower the irradiation intensity, the greater is the $\overline{DP}$ of the polymer formed. It will be more difficult for long chains to diffuse through the polymer-monomer matrix so that on the basis of diffusion controlled termination the overall polymerisation rate should be faster at the low intensities than could be expected under normal conditions. A practical consequence of this would be that the plot of 1/rate against intercept measured at different intensities would not be a straight line but a curve convex to the intercept axis. In other words the ratio k_p/k_t would increase as the intensity decreased. The results of the present work give no definite evidence that this is so. Plots of k_p/k_t at different intensities have no well-defined trend but merely reflect the scatter of results which is due, presumably, to the uncertainty in lifetime measurements indicated previously. Nevertheless although undetectable by this means differences in chain length may well contribute to the low exponents. The point will be referred to again when the high conversion polymerisation in presence of bromotrichloromethane is discussed.

In conclusion it may be said that no completely satisfactory explanation of exponents less than 0.5 can be found. They would seem at least to be the result of prevailing experimental conditions rather than of any fundamental change in the reaction kinetics. If this basic premise is accepted then calculations of individual velocity coefficients based on the mutual destruction of radicals in pairs is valid and the decrease in k_t as polymerisation proceeds, observed by many workers, is a real effect.

The Polymerisation of Methyl Methacrylate in Presence of Bromotrichloromethane.

This reaction will be discussed from two points of view. Firstly will be considered the effect of BTCM on the course of the polymerisation as polymer accumulates in the system and secondly the modifications in kinetic constants at the initial stage of reaction as the concentration of BTCM is increased.

As has already been explained the former aspect of the work was concerned with the effect on the auto-accelerated phase of the polymerisation of reducing the chain length of the polymer. It was hoped, moreover, to reduce the polymer chain length without diluting the reaction medium to any appreciable extent. This has been achieved by the use of BTCM.

Halogenated methanes, and in particular BTCM, have been used in connection with a number of other olefins both from a preparative point of view and in kinetic studies[73-76]. The following kinetic scheme was first proposed by Kharasch.

Initiation 1. $CCl_3Br \longrightarrow \dot{C}Cl_3 + Br\cdot$

Propagation steps

2. $CCl_3\cdot + M \longrightarrow CCl_3M\cdot \qquad k_i$

3. $CCl_3M_r\cdot + M \longrightarrow CCl_3M_{r+1}\cdot \qquad k_p$

4. $CCl_3M_r\cdot + CCl_3Br \longrightarrow CCl_3M_rBr + CCl_3\cdot \qquad k_{tr}$

$$\begin{array}{c}\text{Termination}\\ \text{steps}\end{array}\left\{\begin{array}{lll} 5.\ 2\,CCl_3\cdot & \longrightarrow & C_2Cl_6 \\ 6.\ CCl_3M_r\cdot + CCl_3M_n\cdot & \longrightarrow & \text{products} \\ 7.\ CCl_3M_r\cdot + CCl_3\cdot & \longrightarrow & \text{products}\end{array}\right\}\quad k_t$$

For olefins which do not polymerise reaction 3 does not occur. In this case the kinetic chain will be sustained entirely by the chain transfer reaction 4 and the products of the reaction will be exclusively the 1:1 adduct of BTCM and olefin. For polymerisable monomers competition will take place between reactions 3 and 4 and the extent to which each reaction participates in chain propagation will be controlled by the relative reactivities of monomer and BTCM towards the growing polymer radicals. In the case of methyl methacrylate the ratio of the velocity coefficients for these reactions, i.e. the transfer constant k_{tr}/k_p has been shown to be small with an average value of 0.065 over the complete range of BTCM concentration studied. Thus the kinetic chain will be propagated almost exclusively by reaction 3.

The value quoted for k_{tr}/k_p gives rise to the following values of $\overline{DP}$ at different concentrations of BTCM.

FIGURE 28

VARIATION OF RATE WITH CONVERSION
AT VARIOUS MONOMER : BTCM RATIOS.

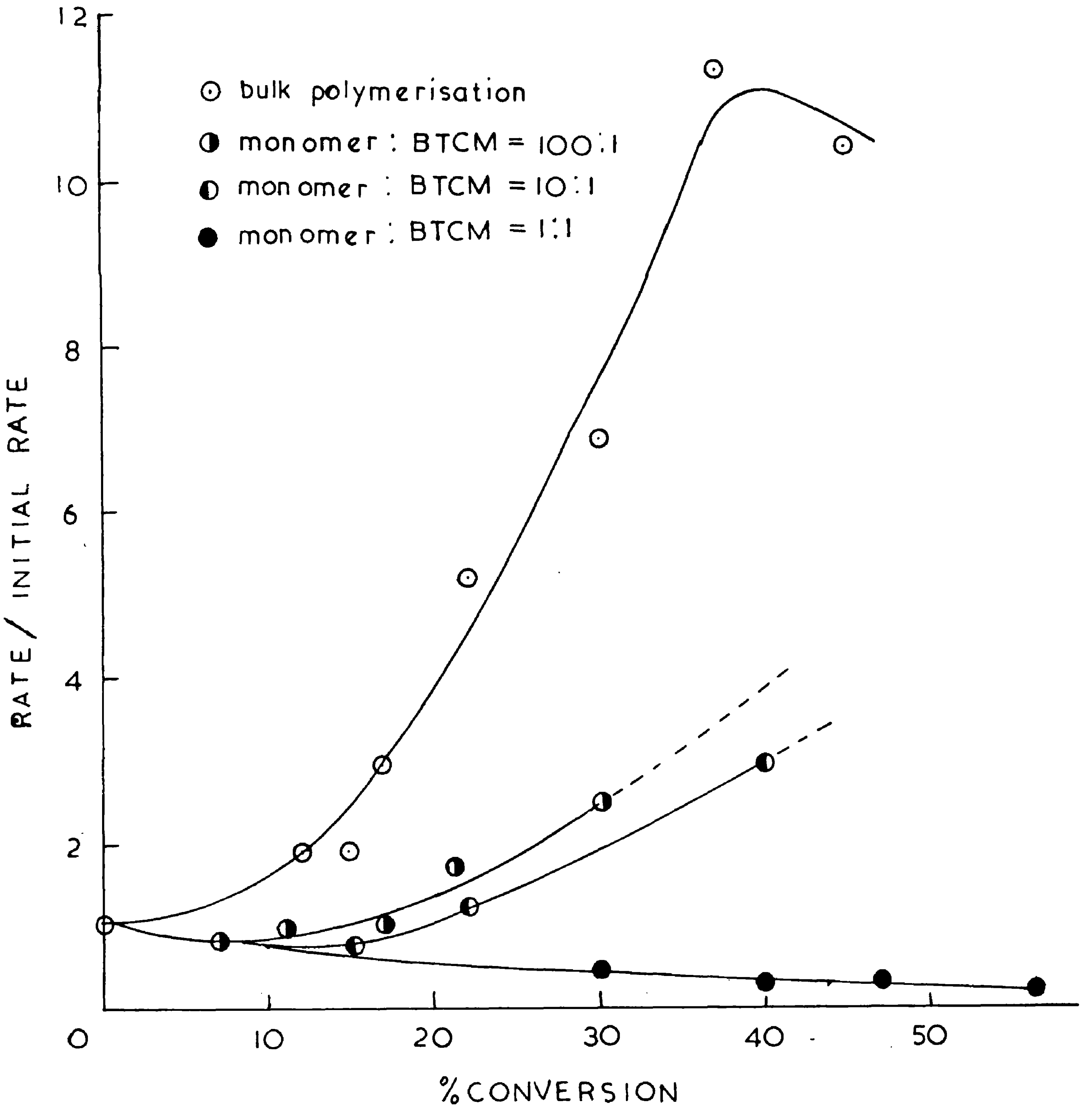
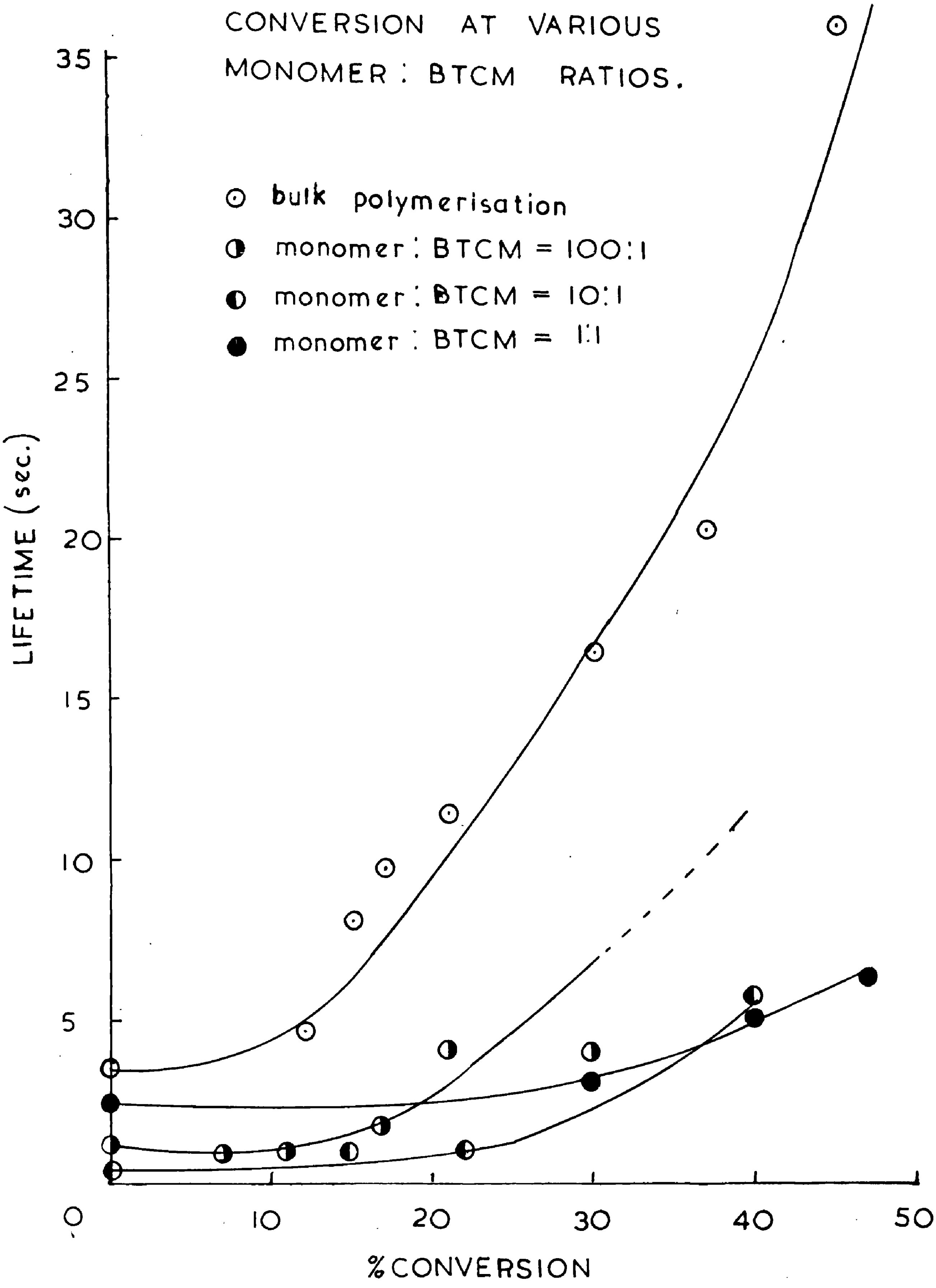


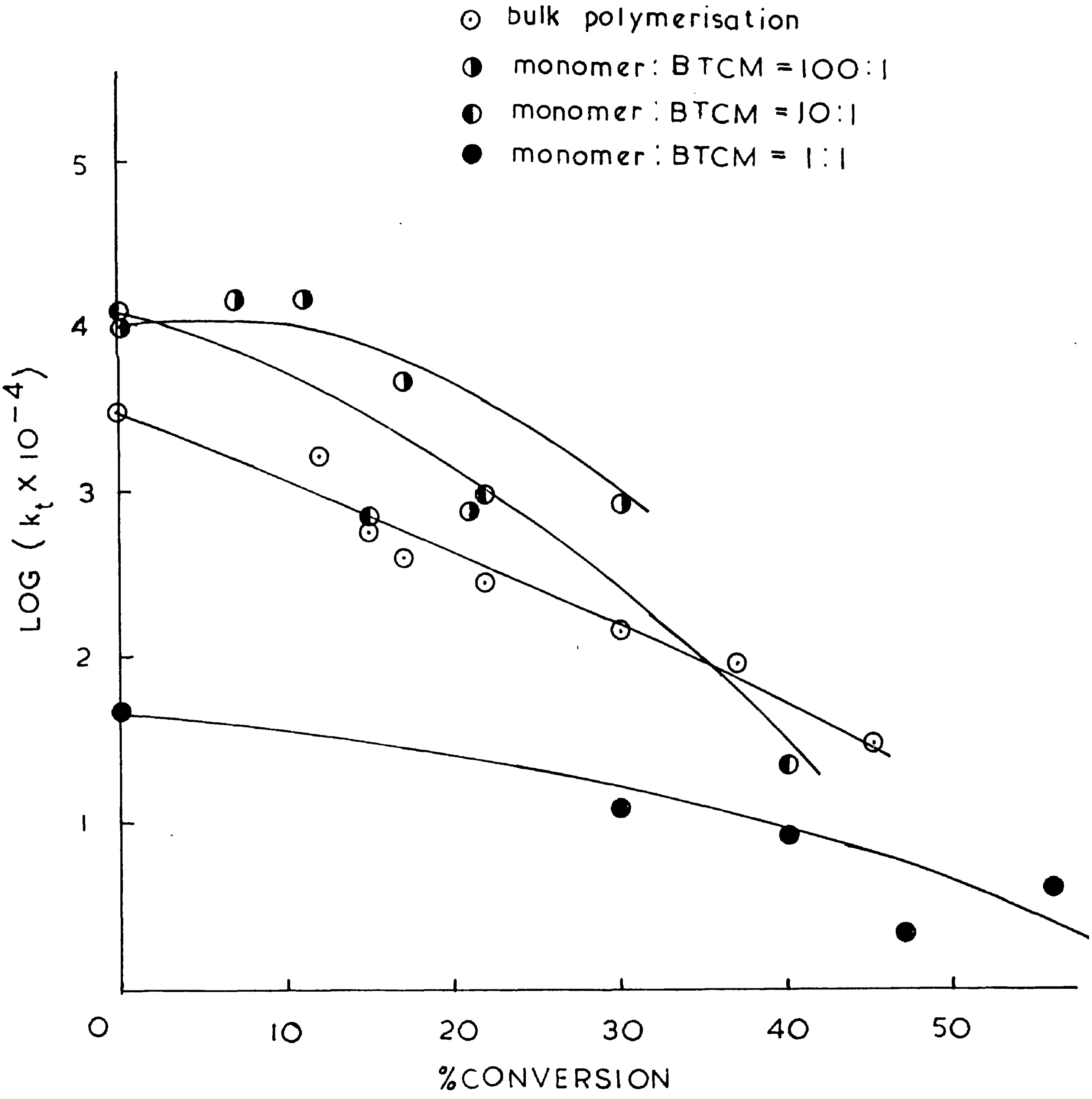
FIGURE 29



VARIATION OF LIFETIME WITH CONVERSION AT VARIOUS MONOMER : BTCM RATIOS.

FIGURE 30

VARIATION OF k_t WITH CONVERSION AT VARIOUS MONOMER : BTCM RATIOS.



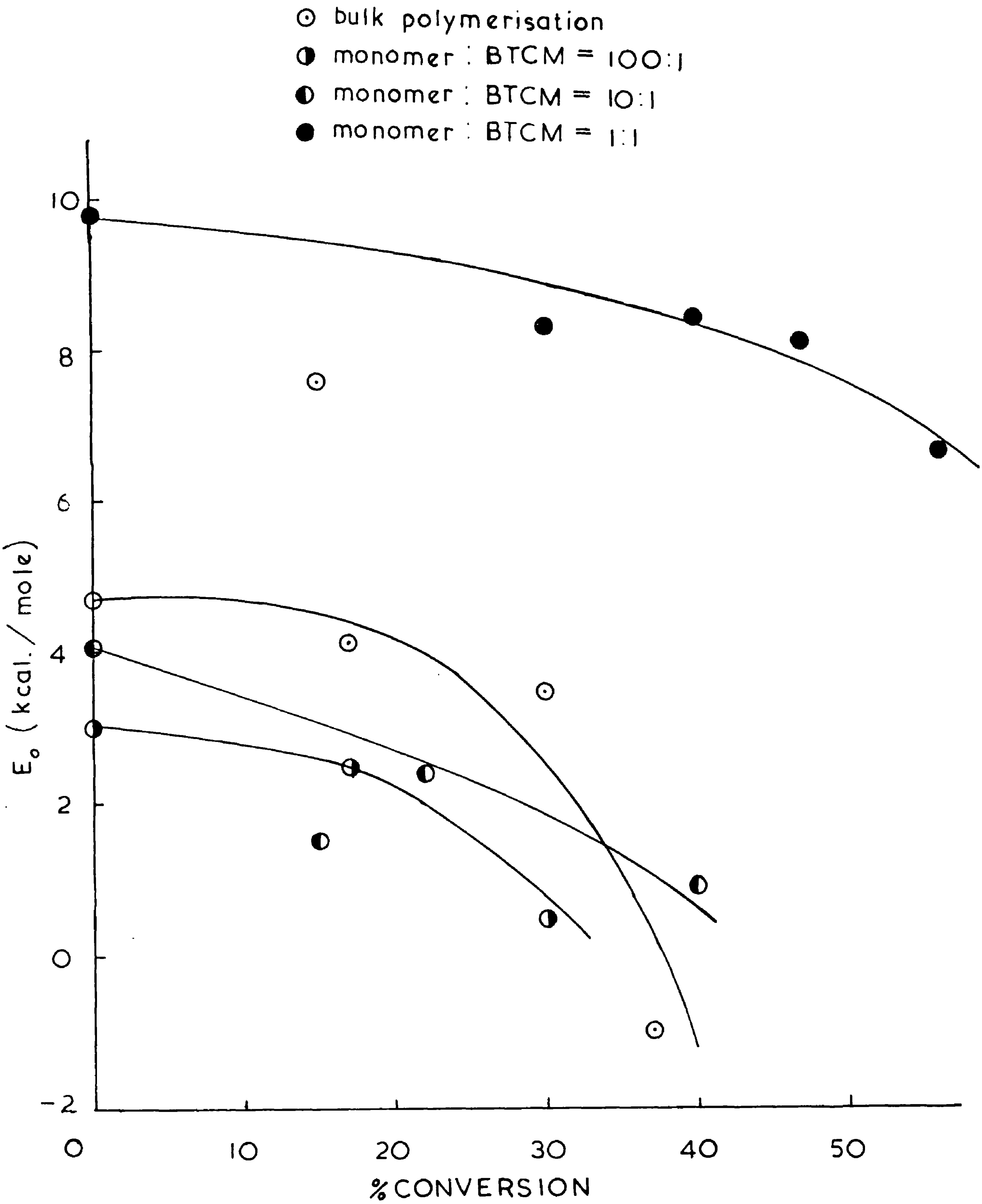
Molar ratio monomer : BTCM	BTCM concn. mole $1.^{-1}$	Average $\overline{DP}$ of product
Bulk polymerisation	0	15,000
1000 : 1	0.0093	8,800
100 : 1	0.0922	1,650
10 : 1	0.8555	240

Hence the chain length can be reduced substantially (but still kept within the high polymer range) without the necessity of diluting the medium to any appreciable extent. The effect of so reducing the chain length on the reaction kinetics is shown in figures 28-30, in which the course of polymerisation is compared at various molar ratios of monomer to BTCM. From these graphs the following table can be constructed.

Molar ratio monomer:BTCM	Bulk polymerisation	100:1	10:1	1:1
Avge. $\overline{DP}$ of products	15,000	1,650	240	19
$\frac{\text{Rate at 30\% conv.}}{\text{initial rate}}$	7.4	2.5	2.0	0.43
$\frac{\text{Lifetime at 30\% conv.}}{\text{initial lifetime}}$	4.7	4.0	6.5	1.3
$\frac{k_t \text{ at 30\% conv.}}{k_t \text{ initially}}$	0.047	0.075	0.025	0.59

FIGURE 31

VARIATION OF E_o WITH CONVERSION AT VARIOUS MONOMER : BTCM RATIOS.



phenomenon of a negative temperature coefficient for an exothermic reaction is displayed in the bulk polymerisation at about 40% conversion but negative values of E_o are not reached when BTCM is present for then E_t does not increase to the same extent. This is shown in the flattening out of the curves in figure 31 as the BTCM concentration increases. Again this shows that the gel effect is greatly reduced when the polymer chain length is cut.

It may also be pointed out that the intensity exponents in presence of BTCM do not show the peculiar low values in the gel stage which are characteristic of the bulk polymerisation. This may be due to either or both of two effects. Firstly it may be postulated that a critical chain length exists below which small differences in $\overline{DP}$ produced by variation in irradiation intensity do not affect the radical diffusion coefficients. Above the critical value, which is presumably reached in the bulk polymerisation, the differences in radical $\overline{DP}$ are sufficient to affect their diffusion rates. This theory, of course, provides further support for the explanation of low intensity exponents based on differences in chain length controlling the diffusion rates of radicals.

However a second, and perhaps more likely, reason why exponents do not exhibit values less than 0.5 in the BTCM reaction is that mixed order termination in this case is tending to increase the exponent thus obscuring any decrease which might be simultaneously occurring.

The results of this thesis tend to support the theory of the gel effect based on diffusion controlled termination but indicate that some slight modification is necessary. In so far as diffusion control is held to depend on the bulk viscosity of the medium the theory is in some doubt since the viscosities of the reaction mixtures at high conversion in the bulk polymerisation and in the reaction at 100:1 or 10:1 molar ratio of monomer to BTCM are not greatly different. Hence on the basis of viscosity alone there is no reason why the gel effect should not be equally evident in all of these reactions. On the other hand it may be that the rate determining step in the termination reaction is the diffusion of radical ends out of localised coiled polymer aggregates and not the diffusion of complete radical entities in the medium. This would imply a dependence of termination rate on radical $\overline{DP}$ as observed in this work. It could then be that the viscosity of the medium controls the reaction only on the micro scale where localised zones become sufficiently viscous to intensify the coiling of chains. The bulk viscosity on this hypothesis is not a fundamental factor in the control of termination except possibly when it becomes sufficiently high to obscure effects on the micro scale. An analogy can be seen between these ideas and the theories of heterogeneous polymerisation and similar ideas have been expressed in a recent paper by North and Reed[77].

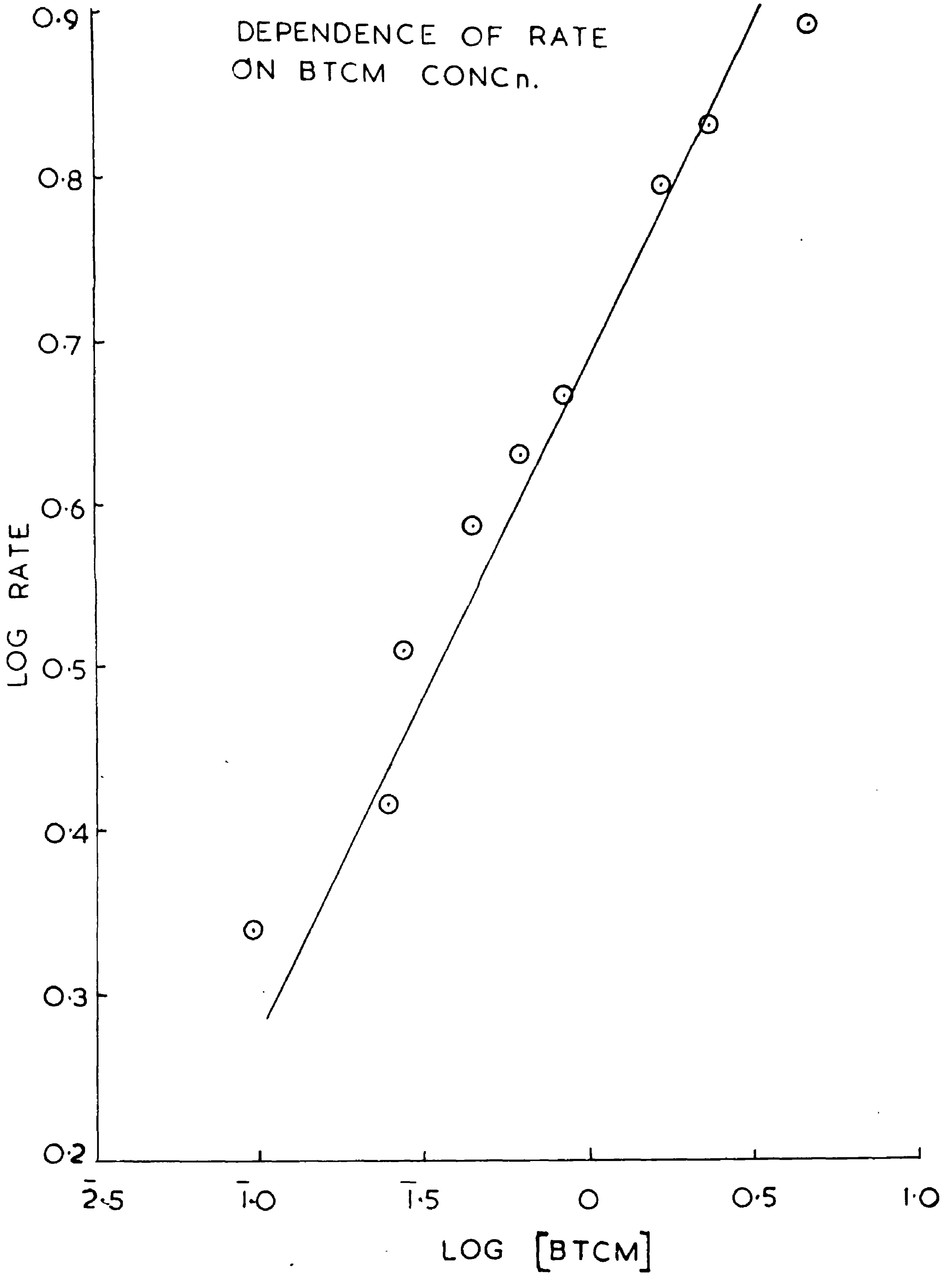
Dependence of kinetic constants on the concentration of BTCM

The polymerisation in presence of BTCM will now be discussed in terms of the results obtained in the initial stages as a function of BTCM concentration without regard to the high conversion stages of the reaction.

The dependence of reaction rate on BTCM concentration was found by plotting "log rate" against "log BTCM " (figure 33). The slope of the straight line obtained is 0.43 and this is taken to indicate a half-order dependence of rate on BTCM concentration. This is consistent with the reaction scheme on page 140.

The principal feature of this reaction which it is desired to discuss concerns the variation in the velocity coefficients with BTCM concentration. The results are

FIGURE 33


DEPENDENCE OF RATE
ON BTCM CONCn.
LOG RATE
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
$\bar{2}$·5
$\bar{1}$·0
$\bar{1}$·5
0
0·5
1·0
LOG [BTCM]

clear from the following table.

Table 37. Values of velocity coefficients at various BTCM concentrations at 25°C for the initial stages of reaction.

Molar ratio monomer:BTCM	Avge. $\overline{DP}$ of radicals	k_p l.mole^{-1}	k_t 10^{-7} sec.$^{-1}$
Bulk polymerisation	15,000	270	2.98
100 : 1	1,650	490	10.2
10 : 1	240	613	11.8
1 : 1	19	28.0	0.046
1 : 10	3.6	18.1	0.013

It will be seen from this table that the values of k_p and k_t show parallel changes as the BTCM concentration increases and the average radical chain length decreases. With a little added BTCM there is a slight increase compared to the values for the bulk polymerisation. For k_p this is within the experimental error of the method and no significance is attached. The corresponding increase in k_t is by a factor of four which is somewhat greater than can be accounted for by the probable errors. It is caused essentially by a decrease in the kinetic chain lifetime which does not quite correspond to the increase in the rate of initiation. It may well be, however, that the shorter chains produced in these reactions have intrinsically shorter lifetimes. In addition there is now the possibility of cross termination between $\dot{C}Cl_3$ radicals and polymer radicals taking place. This will presumably be faster than the straight termination between two polymer radicals, resulting in an increase in the measured value of k_t.

The changes in k_p and k_t when high polymeric products are no longer produced are the most striking of all. In passing from a 10:1 to 1:1 molar ratio of monomer:BTCM k_p decreases by a factor of 20 and k_t by a factor of 200. The effect on k_t is seen to be produced by an increase in the rate of initiation and an increase in the lifetime. Since the ratio k_p/k_t falls only by a factor of 10 this implies a 20-fold decrease in k_p.

In the usual kinetic analysis of polymerisation reactions radical reactivity is generally assumed to be independent of radical size. However this would appear to be completely unjustified in the present case. The reactivity of short compared to long radicals is drastically reduced both towards monomer molecules in the propagation step and towards other radicals of the same type in the termination reaction.

This is not an entirely new phenomenon in olefin-BTCM interaction. Robb and Vofsi[49] claim a similar effect takes place in the BTCM-styrene system and observe a reactivity minimum in the region of trimeric styrene radicals. In this case, however, k_t alone decreases passing through a minimum value and regaining a 'normal' value as the size of the radical decreases below 3. No satisfactory explanation of these results is given.

Values of radical $\overline{DP}$ were not actually measured by these authors but were calculated as a function of the molar ratio of BTCM to monomer ($[S]/[M]$) from theoretical considerations. It is pointed out that each monomer addition step (and each termination involving radicals of different size) should have a specific velocity coefficient, viz., $(k_p)_1$, $(k_p)_2$, $(k_p)_3$ etc. and "average apparent" values are assigned to these for a given $[S]/[M]$ ratio. In view of the distribution in radical $\overline{DP}$ which will be obtained at any one $[S]/[M]$ ratio the measured velocity coefficients will consist of contributions from a wide range of $\overline{DP}$ and hence it is felt that to quote values of velocity coefficients associated exclusively with dimeric, trimeric etc. radicals is doubtful.

However for the purposes of the present discussion these considerations draw attention to the essentially statistical nature of the k_p and k_t values reported. The possibility exists that the propagation constant k_p may have a minimum value at some specific stage in the polymer chain growth causing a slow step in this process. If chain transfer were more favourable at this stage then polymer growth would cease and the kinetic chain would be continued by a transfer step. However the ratio k_{tr}/k_p does not alter so on this hypothesis k_{tr} would have a minimum also. Such a slow step would be rate determining and would cause a reduction in the average propagation coefficient measured. Reasons for such a minimum in reactivity are, however, not apparent.

Considering the termination step in more detail it can be seen from the reaction scheme that there are three principal possibilities i.e. reactions 5, 6 and 7. This assumes that termination is bimolecular and the intensity exponents are close enough to 0.5 to justify this assumption by and large. In a system such as the present one these reactions will be competitive so that the fastest of the three will predominate.

In the region of high polymer production the rate controlling termination step should be the interaction of two polymer radicals (reaction 6) while in the region where low molecular weight products are formed the predominant step would be expected to be reaction 5. These deductions are based purely on the relative concentrations of the species which would be expected under these conditions. Melville et al.[47] have based their kinetic analysis of the BTCM - vinyl acetate reaction on these assumptions. They also claim that the termination velocity coefficient for the interaction of two $\dot{C}Cl_3$ radicals (reaction 5) is greater than that for the reaction of two polymer radicals (reaction 6) and that the coefficient for the cross termination (reaction 7) is greater than either. The latter observation is in accord with the general rules of free radical chemistry.

If these ideas of radical reactivity are applied to the methyl methacrylate reaction a faster termination should have been expected at higher BTCM concentration rather than the slower one which is observed. The reduction in k_t in this system is also the opposite effect to that observed in the methyl methacrylate-n-butyl mercaptan reaction by Fujii et al.[78] They find that reductions in chain length produced by the mercaptan give rise to higher values of k_t.

The results of the present work would therefore seem to contradict those of other workers studying similar reactions. It has not been possible to explain this satisfactorily but the following paragraphs indicate some of the explanations which might be advanced to account for these anomalous results.

Initiation efficiency considerations.

Initiation efficiency has been tacitly assumed to be 100% in this work in the absence of any quantitative evidence to the contrary. If it should be less than 100%, however, the true rate of initiation would inevitably be lower than the measured value so that the derived value of k_t would be increased. To account completely for the decrease in k_t the initiation efficiency would have to be as low as 0.5% compared to a value of 100% at the lower BTCM concentrations. A difference in efficiency as great as this is inconceivable. However it is possible that some re-combination of primary radicals (e.g. $\dot{C}Cl_3$ + Br, $\dot{C}Cl_3$ + $\dot{C}Cl_3$, Br· + Br·) may occur which would be intensified at higher BTCM concentration, so this may partly explain the low values of k_t under these conditions. The measured value of rate of initiation does not affect the value of the ratio k_p/k_t which is derived purely from the rate and kinetic chain lifetime. Therefore assumption of 0.5% efficiency would imply an increase of 200 times in the derived value of k_p. Since k_p/k_t in fact increases by a factor of 10 in the change from 10:1 to 1:1 molar ratio of reactants the value of k_p at 1:1 ratio would become 10 times its "normal" value. At any rate the result of assuming an efficiency of initiation less than 100% would be to increase both k_p and k_t.

It should be pointed out in connection with the initiation reaction that both $\dot{C}Cl_3$ and Br· radicals have been assumed to start chains, there being no reason to suppose otherwise. This is mentioned since the inhibitor method used for determining rates of initiation will measure the rate of production of all radicals in the system.

Postulation of a slow chain initiation step.

The question of initiation efficiency may be regarded from a slightly different point of view. If it is postulated that the reaction,

$$\dot{C}Cl_3 + M \longrightarrow CCl_3M\cdot$$

i.e. reaction 2, is very slow then the true chain initiation step is slow even though the decomposition of CCl_3Br is 100% complete and no recombination of primary radicals takes place.

The overall rate of reaction can be expressed in the form

$$-\frac{d[M]}{dt} \propto k_i[\dot{C}Cl_3][M] \quad + \quad k_p[R\cdot][M]$$

where $[R\cdot]$ is the concentration of all radicals other than $\dot{C}Cl_3$.

If reaction 2 is very slow then the concentration of $\dot{C}Cl_3$ radicals will tend to build up particularly when short chains are being produced and transfer becomes important. In the case of the 10:1 ratio of monomer to BTCM there will be only one slow step per 240 and at 100:1 ratio only one per 1650. However at the 1:1 ratio there will be one slow step in every 19. At this stage the term in $[R\cdot]$ may become negligible due to the build up of $[\dot{C}Cl_3]$ so that the rate is controlled by reaction 2. This will have the effect of reducing the measured value of "k_p" which in these circumstances would not be the coefficient for propagation in polymerisation but for addition of $\dot{C}Cl_3$ to monomer.

As a consequence of the build up of $\dot{C}Cl_3$ radical concentration the termination step 5, i.e. dimerisation of $\dot{C}Cl_3$ radicals, must be the main one. Therefore to account for the observed reduction in k_t by this theory it must also be assumed that the value of k_t for reaction 5 as reported by Melville _et al_.[47] and Thomson[48] is high by a factor of about 100.

Reaction medium.

The possibility of a change in reaction medium due to the increased concentration of BTCM has also been considered. The type of effect visualised is on the model of a cage mechanism whereby the radical chain ends become surrounded by a cage of solvent (i.e. BTCM) molecules which prevents access of the monomer or of other radicals. The rates of propagation and termination would then depend on the diffusion rates of monomer into the cage and radicals out of the cage respectively.

The experiments using chloroform and carbon tetrachloride to simulate the medium conditions were designed to test this. These experiments could not prove positively that such an effect does take place but might provide some support for it. However the results do not provide such support and, indeed, show that the velocity coefficients have "normal" values in the presence of equivalent concentrations of $CHCl_3$ and CCl_4. This does not entirely discount the cage theory for the radical chain lengths produced in the $CHCl_3$ and CCl_4 reactions are much longer than in the case of BTCM so that conditions are not identical. Moreover the same reductions in k_p and k_t are observed when methyl methacrylate is replaced by iso-butyl methacrylate so it is felt that BTCM may be specific in this respect.

Activation energy considerations.

Before concluding these discussions it should be pointed out that the activation energy of the termination reaction has a value of 5 kcal./mole at the 1:1 ratio of reactants compared to a value of zero at the 100:1 and 10:1 ratios. Hence the exponential term accounts completely for the reduction in k_t and the frequency factor does not change. It had been surmised that retardation of the termination step might be due to steric effects such as, for example, large $\dot{C}Cl_3$ radicals being hindered by their size in their approach to each other or to polymer radicals. Certainly models of the various species show that no such steric factors exist as the activation energies suggest.

In conclusion it must simply be said that very short chain radicals in this system seem to grow and terminate more slowly than very long ones. The precise reasons for this remain obscure but it may be due partly to the effects of recombination of primary radicals and partly to a slow initiation step. Some mode of radical "solvation" effect may also be occurring.

Suggestions for Further Work

As has been implied in the foregoing discussion it is difficult to determine the effect of polymer chain length on the course of the polymerisation by the use of chain transfer agents as in the present work. Separation of the effects due to dilution, however small, and those due to changes in molecular weight is almost impossible. A more profitable approach may lie in the introduction of quantities of polymer of known molecular weight. For example mixtures of monomer and polymer corresponding to given extents of conversion could be polymerised a further few per cent and the differential change in molecular weight determined. This could be done for a wide range of starting mixture compositions and also of polymer molecular weight. The practical and theoretical difficulties involved would be considerable but it is felt that this approach might lead to a more fundamental explanation of the gel effect in terms of molecular weight changes.

With regard to the 'abnormal' low values of k_p and k_t in the BTCM system it might be possible to provide some evidence for the slow initiation step postulated in the above discussion.

According to the arguments given with regard to the build up of $\dot{C}Cl_3$ radical concentration, there should be some fairly critical chain length at which the reaction,

$$\dot{C}Cl_3 + M \longrightarrow CCl_3M\cdot$$

becomes rate determining. This implies that there should be a fairly narrow range of reactant concentration over which the change from high to low values of k_p and k_t takes place. Hence if the velocity coefficients were determined at intermediate molar ratios between 10:1 and 1:1 monomer : BTCM it would be possible to see whether such a change does take place and in what chain length region.

Evidence for the slow initiation step might also be provided by studying the polymerisation of methyl methacrylate in the presence of some diluent which is a source of $\dot{C}Cl_3$ radicals but is not also a transfer agent. In this way the CCl_3 radical concentration would not build up to a value where reaction 2 becomes rate determining and long polymer chains would be produced. Such a system should exhibit 'normal' values of velocity coefficients. A compound such as $Ph_3C - CCl_3$, if it could be prepared, might be suitable for investigations of this kind.

APPENDIX

Determination of rate of reaction from recorder chart trace.

From a typical chart trace for the bulk polymerisation a slope of 0.42 chart divisions / sec. was obtained. The corresponding calibration for the thermistor was 1.65×10^{-3} °C / chart division.

$$\therefore \left.\begin{array}{l}\text{rate of temperature}\\ \text{rise of reaction}\\ \text{mixture}\end{array}\right\} \frac{d(\Delta\theta)}{dt} = 1.65 \times 10^{-3} \times 0.42^{\circ}\mathrm{C/sec.}$$

$$= 6.925 \times 10^{-4}\ {}^{\circ}\mathrm{C/sec.}$$

$$\left.\begin{array}{l}\text{Heat of polymerisation of}\\ \text{methyl methacrylate}\end{array}\right\} (\Delta H) = 13.0\ \text{kcal./mole}$$

$$\left.\begin{array}{l}\text{Specific heat of methyl}\\ \text{methacrylate}\end{array}\right\} (S) = 0.49\ \text{cal./gm.}$$

$$\text{Molecular weight} \quad (M) = 100$$

While the system remains adiabatic the heat liberated by the reaction will be absorbed completely by the reaction mixture, so that,

$$R.\Delta H = MS.\frac{d(\Delta\theta)}{dt}$$

where R = fractional rate of reaction / sec.

$$\therefore \quad R = \frac{MS}{\Delta H} \cdot \frac{d(\Delta\theta)}{dt}$$

$$= \frac{100 \times 0.49}{13{,}000} \times 6.925 \times 10^{-4} \ /\ \text{sec.}$$

$$= 2.61 \times 10^{-6}/\text{sec.}$$

$$= 0.94\% /\text{hr.}$$

The relation between reaction rate and temperature rise is thus

$$1\ \% /\text{hr.} \equiv 7.37 \times 10^{-4}\ {}^{\circ}\text{C/sec.}$$

When calculating reaction rates at different temperatures the change in thermistor calibration had to be allowed for. After the initial stage, the difference in specific heats of monomer and polymer was also taken into account, and similar corrections were made when mixtures of monomer with an 'inert' diluent were being studied.

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