PHOTOCHEMICAL TELOMERISATION OF VINYL MONOMERS WITH BROMOTRICHLOROMETHANE.

by

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SUMMARY

Studies have been made of the telomerisation of methylmethacrylate, dichloroethylene, vinyl chloride and propylene with bromotrichloromethane under the influence of U.V. light.

PART 1.

The telomerisation of methylmethacrylate with TBr has been studied at 25, 40 and 60°C. The molecular weights of the telomers have been measured chiefly by a cryoscopic method but also by other methods such as end group analysis, radioactive tracer techniques and vapour pressure methods for purposes of comparison. Chain transfer constants, evaluated by means of a modified Mayo plot were found to be 0.149, 0.182 and 0.208 respectively at three temperatures. The difference of the activation energies for the transfer and propagation steps has been found to be +2.2 K. cals/mole. No reactivity minimum was associated with the growth of the polymethylmethacrylate radical during the initial stages of the addition reaction.

The effect of reactant concentration on reaction rate was found to be in agreement with the expected kinetic scheme.

A value of 18.35 K. cals/mole was found for the heat of reaction between bromotrichloromethane and methylmethacrylate under the conditions where 1,1 adduct is formed and was used to obtain a corrected value of 1.3×10^6 mole/litre sec. for the termination constant of the reaction involving combination of two trichloromethyl radicals.

PART 2.

Attempts have been made to find individual chain transfer constants of the growing radicals formed by reaction at 25°C between bromotrichloromethane and (a) dichloroethylene, (b) vinyl chloride and (c) propylene using vapour phase chromatographic analysis. Since the method was found to be insufficiently accurate and also limited because of lack of a sufficient number of volatile adducts, only approximate values of the chain transfer constants for 1,1 and 1,2 dichloroethylene adducts and for the 1,1 vinyl chloride adduct could be found.

In the case of vinyl chloride, telomerisation studies have also been carried out at -35°C, 0°C and 60°C.

the fact that dichloroethylene was found to react with bromotrichloromethane, although more than 200 times slower than vinyl chloride, and that a very small peak on the vapour phase chromatogram of products of reaction between vinyl chloride and bromotrichloromethane was invariably found to be present, has been taken as evidence for the formation of $CCl_3 - CHCl - CH_2Br$ derived from the "wrong way round" addition of trichloromethyl radical to vinyl chloride.

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PART 1.

INTRODUCTION

INTRODUCTION

Methylmethacrylate is an important commercial monomer and much attention has been paid to the study of the kinetics of the polymerisation reaction. The polymerisation work became more interesting from a kinetic standpoint when Norrish and Smith[1] and independently Trommsdorff[2] observed the now well known phenomenon of the "gel effect". Since then many workers have studied the polymerisation of methylmethacrylate but relatively little work has been done on its telomerisation. In part one of this thesis some results obtained on the photochemical telomerisation of methylmethacrylate with bromotrichloromethane are reported.

The telomerisation of methylmethacrylate with bromotrichloromethane has been studied by Robb and Senogles[3] and to a lesser extent by Brash[4]. This system was originally chosen because the photolysis of bromotrichloromethane is unambiguous in the region of 3650°A[5]. Also low molecular weight products are obtained in a convenient range of molar ratio of the two reactants[5]. The results of Brash[4] do not agree with those of Robb and Senogles[3], particularly with regard to the molecular weight of the low polymers prepared under identical conditions. These results also showed considerable lack of agreement in the value of the chain transfer constant both when low molecular products and when high molecular weight products are produced.

Brash's[4] work was mainly concerned with the effect of bromotrichloromethane on the gel effect in the polymerisation of methylmethacrylate, but he had done a little work at high bromotrichloromethane concentration where low polymers are produced. In the present work the initial problem was to make a careful study of the molecular weights of the products formed in this system for different bromotrichloromethane/methylmethacrylate ratios at 25°C. (This being the temperature of telomerisation used by Brash[4]. Robb and Senogles[3] studied this reaction at 30°C). The chain transfer constant was evaluated by the use of a modified Mayo plot and the results compared with those of previous workers. It was found that the results obtained were more in line with those of Brash[4]. The work was then extended to study the telomerisation, in a similar way, at 40°C and 60°C. The difference in the energy of the propagation and chain transfer reaction was obtained by the use of an Arrhenius plot. The validity of the general kinetic scheme was verified in terms of the rate dependencies of the reaction on the concentrations of the reactants. The heat of addition of bromotrichloromethane to methylmethacrylate was obtained by the dilatometric method. This enabled kinetic constants of the reactions under conditions where 1,1 adduct is formed to be calculat- from the kinetic chain life time results obtained by Brash[4].

Striking differences in the results obtained by previous workers[3,4] have been outlined. Possible errors involved in measuring molecular weight by the cryoscopic method, and by carbon, hydrogen and halogen analysis have been discussed. The views put forward have been further supported by the results obtained by the radioactive tracer technique and the vapour pressure method of determining the molecular weight of the products.

The Mechanism of the Polymerisation of Methylmethacrylate and of its Telomerisation

Polymerisation of vinyl compounds of the type $CH_2=CHX$ can take place either by an ionic or a free radical mechanism. The free radical mechanism is relevant to the work of this thesis and therefore only chain reactions proceeding by this means are considered.

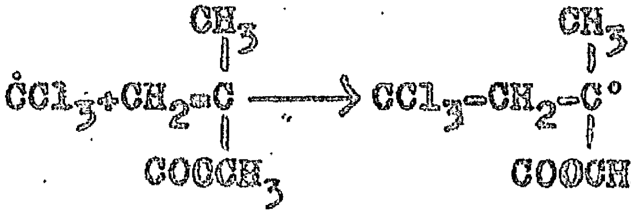
The normal kinetic scheme consists of three basic steps, initiation, propagation and termination. These are considered below in more detail.

Initiation

This is commonly achieved by heating or irradiating with U.V. light a mixture of monomer and an unstable compound which will break down to produce free radicals. In this case bromotrichloromethane acts as an initiator by decomposition as shown

$$CCl_3Br \xrightarrow{h\nu} \overset{\circ}{C}Cl_3 + Br^{\circ} \quad \ldots \quad \ldots \quad (1)$$

The free radical $\overset{\circ}{C}Cl_3$ thus produced can add to the monomer molecule in the following fashion

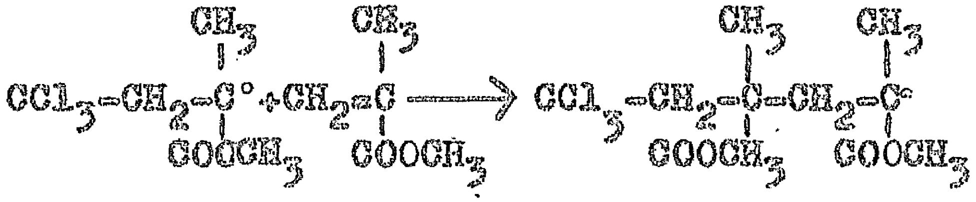


$$\overset{\circ}{C}Cl_3 + CH_2=\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \longrightarrow CCl_3-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C^{\circ}}} \quad \ldots \quad (2)$$

The rate of initiation can be denoted by I.

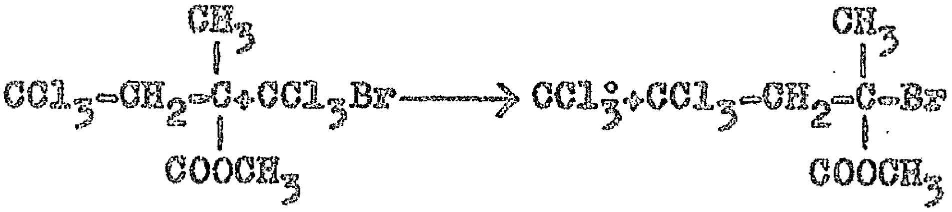
Propagation

The activated monomer radical can add successively to molecules of monomer by opening the double bond of vinyl group in the same way as the free radical produced by decomposition of the catalyst adds to the first monomer molecule



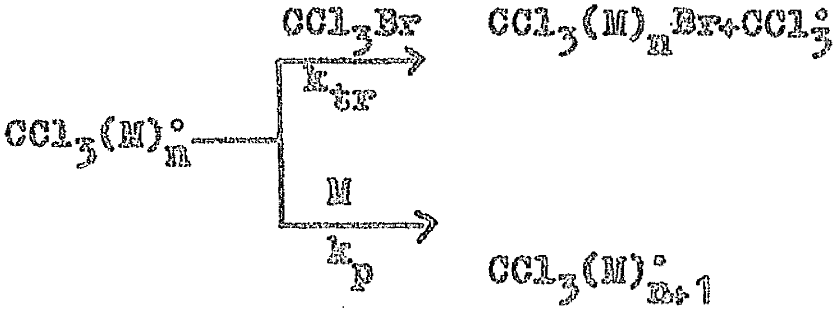
$$CCl_3-CH_2-\overset{CH_3}{\underset{COOCH_3}{C^\circ}}+CH_2=\overset{CH_3}{\underset{COOCH_3}{C}} \longrightarrow CCl_3-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2-\overset{CH_3}{\underset{COOCH_3}{C^\circ}} \quad \ldots (3)$$

The growing radical can also undergo a transfer reaction with a molecule of bromotrichloromethane. In doing so another trichloromethyl radical is generated.



$$CCl_3-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}+CCl_3Br \longrightarrow CCl_3^\circ+CCl_3-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-Br \quad ..(4)$$

Thus a growing radical containing n monomer units faces two competing reactions



$$CCl_3(M)_n^\circ \begin{cases} \xrightarrow[k_{tr}]{CCl_3Br} \quad CCl_3(M)_nBr+CCl_3^\circ \\ \xrightarrow[k_p]{M} \quad CCl_3(M)_{n+1}^\circ \end{cases}$$

where M represents a molecule of methylmethacrylate.

The ratio of the velocity coefficient for the chain transfer reaction (k_{tr}) to that for the propagation reaction(k_p)is defined as the chain transfer constant, the value of which indicates the extent to which each of the above reactions contributesto telomerisation.

Termination

The telomer chain radicals or trichloromethyl radicals can terminate by mutual destruction of radicals in pairs by any of the following three reactions.

(i) Combination of two trichloromethyl radicals

$$\overset{\circ}{C}Cl_3 + \overset{\circ}{C}Cl_3 \longrightarrow C_2Cl_6 \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

(ii) Combination of two trichloromethyl-polymethylmethacryl radicals

$$CCl_3(M)_m^{\circ} + CCl_3(M)_n^{\circ} \longrightarrow CCl_3(M)_{m+n}CCl_3 \ldots \quad (6)$$

(iii) Combination of trichloromethyl radical with a trichloromethyl-polymethylmethacryl radical

$$\overset{\circ}{C}Cl_3 + CCl_3(M)_n^{\circ} \longrightarrow CCl_3(M)_nCCl_3 \ldots \quad \ldots \quad (7)$$

Kinetically in all cases two active centres are destroyed. The conditions to favour one of these reactions in preference to the remaining two are described later.

Review of Previous Work

In any kinetic scheme for free radical polymerisation it is usual to assume that the reactivity of a growing polymer radical is independent of the chain length. The free radical intermediates in addition polymerisation are all of a similar nature but differ from one another in the number of monomer units. Thus one single velocity coefficient is used to describe all the propagation steps. The same holds for all chain transfer reactions and termination reactions. The experimental results obtained for addition polymerisation of vinyl monomers are in good agreement with the theoretical kinetic equations[6-8]. However, in some cases, particularly when kinetic equation analysis is required to evaluate rate constants for the addition step, the chain transfer step and the termination step for the first few units of monomer, these assumptions of equal reactivity are known to have failed.

Initial studies on the photochemical reactions of trichloromethyl radicals with various olefins have been reported by Kharasch. He proposed the following kinetic scheme.

$$(1)\qquad TBr \xrightarrow{k_d} T^{\circ} + Br^{\circ}$$

$$(2)\qquad T^{\circ} + M \xrightarrow{k_i} TM^{\circ}$$

$$(3)\qquad TM^{\circ}_{n} + M \xrightarrow{k_{p,n}} TM^{\circ}_{n+1}$$

$$(4)\qquad TM^{\circ}_{n} + TBr \xrightarrow{k_{tr,n}} TM_{n}Br + T^{\circ}$$

$$(5)\qquad T^{\circ} + T^{\circ} \xrightarrow{k_{t,a}} C_2Cl_6$$

$$\left.\begin{array}{ll} (6) & TM^{\circ}_{n} + TM^{\circ}_{n} \xrightarrow{k_t} \\ & TM^{\circ} + TM^{\circ} \xrightarrow{k_{tb}} \\ (7) & T^{\circ} + TM^{\circ}_{n} \xrightarrow{k_{t,c}} \end{array}\right\} \text{non radical products}$$

where T° represents the trichloromethyl radical, M the monomer and TM°_{1} the radical formed by the addition of the trichloromethyl radical to one unit of monomer molecule, TM°_{n} a similar radical to which n units of monomer molecules have been added subsequently. k_d and k_i are the velocity coefficients for the initiator decomposition reaction(1) and for the reaction(2) involving addition of trichloromethyl radical to the olefin. $k_{p,n}$ and $k_{tr,n}$ are the velocity coefficients for the propagation reaction (3) and transfer reaction (4). It will be shown later that when low molecular weight products are being formed the velocity coefficients for the propagation and the transfer step should be assigned a separate constant to characterise each individual step. i.e.

$$TM_2^{\circ} + M \xrightarrow{k_{p,2}} TM_3^{\circ}$$

$$TM_3^{\circ} + M \xrightarrow{k_{p,3}} TM_4^{\circ}$$

The velocity coefficients for the various termination steps involved are represented by $k_{t,a}$, $k_{t,b}$, and $k_{t,c}$.

By using a high TBr to olefin ratio, it is possible to make reaction (4) fast compared with reaction (2). The relative reactivities of various olefins towards the trichloromethyl radical were measured[9-11] by starting with the reactants containing excess TBr and an equivalent amount of various olefins so that the 1,1 adduct was the predominant product. The reaction was stopped after X hours and the 1,1 adduct isolated quantitatively. The amount of 1,1 adduct thus formed gave indications of the reactivity of the trichloromethyl radical with various olefins. The following table was constructed.

Table 1. Relative reactivities of trichloromethyl radical with various olefins.

OLEFIN	RELATIVE REACTIVITY
styrene	>100
butadiene	18
cyclopentadiene	4·5
1,3 cyclohexadiene	4·0
indene	3·0
2 ethyl-1 butene	1·4
β methyl styrene	1·1
1 octene	1·0
2 methyl-2-butene	0·9
cyclopentene	0·8
ethyl cinnamate	0·8
vinyl acetate	0·8
allyl chloride	0·5
allyl cyanide	0·3
cyclohexene	0·2

Melville, Robb and Tutton[12] undertook detailed investigations of the reaction between bromotrichloromethane and cyclohexene. By working with excess TBr they were able to make reaction (2) rate controlling and under these conditions the main termination reaction was due to interaction of two trichloromethyl radicals (reaction 4). They found the velocity constant for the addition of trichloromethyl radical to cyclohexene in terms of rate of initiation and $k_{t,a}$. From the value of k_i and the data in table 1 they obtained the reactivity on an absolute basis. They also determined the reaction constant $k_{tr,n}$ in terms of rate of initiation and $k_{t,b}$. This was achieved by working with excess olefin so that reaction (4) became the rate controlling step and termination of the reaction chain was then brought about by the interaction of two trichloromethyl-cyclohexyl radicals.

Melville, Robb and Tutton repeated their work on similar lines with vinyl acetate[12]. In this work they obtained the following results:

k_i = 1120 litre/mole sec
$k_{tr,n}$ = 2740 " " "
$k_{t,a}$ = 10^8 " " "

According to these results Mayo predicted[13] that since k_i and $k_{tr,n}$ are of the same magnitude, polymerisation should take place when the reaction mixture contains a large excess of vinyl acetate. However, Melville et al[12] did not obtain any polymer even with a large vinyl acetate/TBr ratio. Bengough and Thomson also showed[14] that under the conditions used by the above mentioned authors, 1,1 adduct was the major product formed. The work of Bengough and Thomson cleared up this mystery by showing[15] that the value of $k_{tr,n}$ = 2740 litre/mole sec was incorrect. In fact the results obtained on the effect of the TBr concentration on the rate showed that reaction (4) was not the rate determining step. Hence, it is not possible to measure $k_{tr,n}$ and $k_{t,b}$. However Bengough and Thomson found[14] that the order of magnitude of the ratio of velocity coefficients for chain transfer with TBr to propagation $k_{tr,n}/k_{p,n}$ changes from about 40 for small attacking radicals to about 0.6 when the grow-polymer radicals are of higher degree of polymerisation. i.e.

$$\frac{k_{tr,1}}{k_{p,1}} = 40 \quad \text{for short chain radicals}$$

$$\frac{k_{tr,n}}{k_{p,n}} = 0.6 \quad \text{for long chain radicals}$$

From the work of Bengough et al[15] k_1 is not much different from the asymptotic value of $k_{p,n}$. Thus the difference in the value of $\frac{k_{tr,n}}{k_{p,n}}$ is mainly due to a marked change in the value of $k_{tr,n}$. Thus the reactivity of radicals of very short chain lengths are quite different from the polymer type radicals in the case of transfer reaction. It is perhaps relevant to mention that Melville et al did not find[12] any changes for the termination reactions involving interaction of various size-radicals.

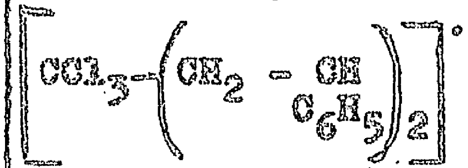
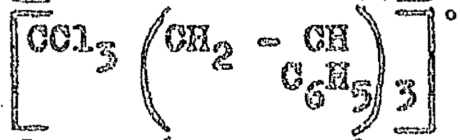
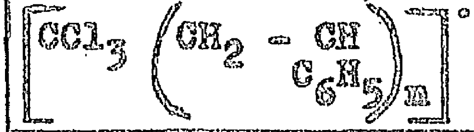
These reactivity differences were further confirmed by the work of Gregg and Mayo[16] who obtained the ratio of $\frac{k_{tr,n}}{k_{p,n}}$ (for short chain radicals) in styrene/TBr system. They obtained the following results:

Table 2. The values of $\frac{k_{tr,n}}{k_{p,n}}$ of various short chain radicals in styrene/TBr system.

Radical $\left[CCl_3 \left(CH_2 - \underset{C_6H_5}{CH}\right)_n\right]^{\circ}$	$\frac{k_{tr,n}}{k_{p,n}}$
$n = 1$	0·0006
$n = 2$	0·0025
$n = 3$	0·0070
$n > 3$	0·0115 (becomes constant)

Gregg and Mayo also found that the value of $\frac{k_{p,n}}{\sqrt{k_{t,n}}}$ remained constant over the same range of adducts. From this Mayo thought that the changes in the values of $\frac{k_{tr,n}}{k_{p,n}}$ as shown in the above table are merely due to the change in the value of k_{tr} i.e. $k_{p,n}$ remained unchanged. However, further work of Robb and Vosfi[17] indicated that in fact $k_{tr,n}$ remains unchanged and instead $k_{p,n}$ changes. This is shown in table 3.

<u>Table 3.</u> <u>Individual velocity constant of various short chain radicals in styrene/TBr system.</u>

Average Radical Size	$k_{tr,n}$ 1/m sec	$k_{p,n}$ 1/m sec	$k_{t,n}$ 1/m sec
 $\left[CCl_3-\left(CH_2-\underset{C_6H_5}{CH}\right)_2\right]^{\cdot}$	3.4×10^{2}	44	1.3×10^{8}
 $\left[CCl_3\left(CH_2-\underset{C_6H_5}{CH}\right)_3\right]^{\cdot}$	3.0×10^{2}	1.25	1.1×10^{5}
 $\left[CCl_3\left(CH_2-\underset{C_6H_5}{CH}\right)_n\right]^{\cdot}$	—	55	$2.5\times10^{7*}$

$^*k_t$ in this case

where n = number of monomer units in an average polymer molecule of high degree of polymerisation.

Robb and Vosfi[17] concluded that a reactivity minimum is associated with the growth of polystyryl radicals during the initial stages of the addition reaction.

Evidence that the reactivity of the radical is not very dependent on the number of monomer units incorporated, came from the work of Brash[4]. Working with the methylmethacrylate/TBr system, Brash[4] obtained the following values for the chain transfer constants when products of both high molecular weight and low molecular weight were produced.

	$\frac{k_{tr,n}}{k_{p,n}}$
High molecular weight products	0·05
V. low molecular weight products	0·08

Almost simultaneous work carried out independently by Robb and Senogles[3] gave rather conflicting results for the methylmethacrylate/TBr system in which only low molecular weight products were formed. Robb and Senogles found that the transfer constants for the low molecular weight products are not only different from those of high molecular weight products but also the low molecular weight products in themselves have several different values for transfer constants. They summarised their results as shown in table 4.

Table 4. The values of $\frac{k_{tr,n}}{k_{p,n}}$ for the low molecular weight products in the methylmethacrylate/TBr system.

radical	chain transfer constant $k_{tr,n}/k_{p,n}$
trimeric	0.084
tetrameric	4.6
polymeric	1.2

It would appear from the results of table 4 that in the early stages of the reaction each discrete step involving the interaction of a growing radical of the (poly) methylmethacrylate type with either methylmethacrylate or TBr would have to be assigned a specific constant.

Under identical reaction conditions Brash and Soneglee reported quite different values for the product composition. The bulk of the work described in part 1 of this thesis was done with these points in view. Much attention has been paid to the methods involved for the determination of molecular weight of the telomers as these values markedly effect the values obtained for the transfer constants.

Experiments have been repeated at various temperatures which would, it was thought, confirm the general trend of those variations of the transfer constants when low molecular weight products are formed.

THEORETICAL

The addition of bromotrichloromethane and similar halogeno-methanes to olefins has been extensively studied by Kharasch and Coworkers[18,19]. The general kinetic scheme first proposed by Kharasch and now generally accepted is given on page 8., but is repeated here for the convenience of the reader along with rates of reactions involved in each case.

	Rate Constant	Rate
(1) $TBr \xrightarrow{hv} T^\circ + Br^\circ$	k_d	I
(2) $T^\circ + M \longrightarrow TM^\circ$	k_i	$k_i[T^\circ][M]$
(3) $TM^\circ_n + M \longrightarrow TM^\circ_{n+1}$	$k_{p,n}$	$k_{p,n}[TM^\circ_n][M]$
(4) $TM^\circ_n + TBr \longrightarrow TM_nBr + T^\circ$	$k_{tr,n}$	$k_{tr,n}[TM^\circ_n][TBr]$
(5) $T^\circ + T^\circ \longrightarrow T_2$	$k_{t,a}$	$k_{t,a}[T^\circ][T^\circ]$
(6) $TM^\circ_n + TM^\circ_n \longrightarrow TM_{n+n}T$	k_t	$k_t[TM^\circ_n][TM^\circ_n]$
$TM^\circ + TM^\circ \longrightarrow T(M)_2T$	$k_{t,b}$	$k_{t,b}[TM^\circ][TM^\circ]$
(7) $T^\circ + TM^\circ_n \longrightarrow TM_nT$	$k_{t,c}$	$k_{t,c}[T^\circ][TM^\circ_n]$

Rate dependencies

Melville, Robb and Tutton[12] used the above scheme omitting reaction (3) in their study of the photochemical reaction between vinyl acetate and TBr. They deduced the following conditions.

(1) When a large excess of TBr is used in the reaction

mixture, reaction (5) is the predominant chain termination process. Also chain transfer reaction (4) is much faster than the addition reaction (2). The rate of the reaction is thus given by the addition reaction.

$$-\frac{d[M]}{dt} = k_1[T^\circ][M] \ldots \ldots \ldots \quad (8)$$

at steady state conditions

$$[T^\circ] = \sqrt{I/k_{t,a}}$$

where I = rate of initiation.

Substituting the value of $[T^\circ]$ in equation (8) we get

$$-\frac{d[M]}{dt} = k_1\sqrt{\frac{I}{k_{t,a}}}\,[M] \ldots \ldots \ldots \quad (9)$$

Since rate of initiation is directly proportional to the concentration of TBr, it follows therefore that the rate of reaction under these conditions is directly proportional to $[TBr]^{\frac{1}{2}}$ and $[M]$

(2) When a large excess of monomer is used in the reaction mixture, reaction (6) is the predominant chain termination process. In this case the chain transfer reaction (4) is the slow rate determining step. The rate of the reaction is given by

$$-\frac{d[M]}{dt} = k_{tr}\left(\frac{I}{k_{t,b}}\right)^{0.5}[TBr] \ldots \quad (10)$$

In this case the rate of reaction can be seen to be proportional to $[TBr]^{1 \cdot 5}$.

(3) It is clear that polymerisation will take place when reaction (3) is much faster than reaction (4). Under these conditions the rates of polymerisation are given by

$$-\frac{d[M]}{dt} = k_{p,m}\left(\frac{I}{k_t}\right)^{0 \cdot 5}[M] \quad \ldots \quad \ldots \quad \ldots \quad (11)$$

where k_t is the termination constant for two polymer radicals. The rate dependencies of this equation are identical to the ones mentioned in the first case when a large excess of TBr is used in the reaction mixture.

The rate dependencies on these theoretical aspects have been applied to the vinyl chloride/TBr system[20]. In this thesis similar work has been completed on the methylmethacrylate/TBr system. The results are reported in the appropriate sections.

<u>Chain transfer constant C_s</u>

Mayo[21] gave the following derivation of an equation for the transfer constant in a polymerisation system containing a chain transfer agent S and catalyst C, the general kinetic scheme being similar to the one drawn up on page 8. The derivation applies to polymerisation involving long chains and is later modified to include systems in which short chains are produced. Under steady state conditions the average degree of polymerisation $\overline{DP}$ is given by the ratio of the rate of chain growth to the rate of formation of polymer molecules.

$$\text{i.e.}\quad \overline{DP} = \frac{k_p[R_s][M]}{k_t[R_s]^2 + k_{tr}[R_s][S] + k_{tr}[R_s][M]} \quad \ldots \quad (12)$$

where k_{tr} = velocity coefficient for monomer transfer

R_s = long chain radicals

k_p = propagation constant for the addition of monomer molecules to long chain radicals

k_t = termination constant

Also at steady state $[R_s] = k_i \dfrac{[C][M]^{\frac{1}{2}}}{[k_t]^{\frac{1}{2}}}$ $\ldots$ (13)

Combining (11) and (12), we get,

$$\frac{1}{\overline{DP}} = \frac{k_t[R_s]}{k_p[M]} + \frac{k_{tr}[S]}{k_p[M]} + \frac{k_{tr}}{k_p} \quad \ldots \quad \ldots \quad \ldots \quad (14)$$

$$= \frac{(k_i k_t)^{\frac{1}{2}}[C]}{k_p[M]^{\frac{1}{2}}} + \frac{k_{tr}[S]}{k_p[M]} + \frac{k_{tr}}{k_p} \quad \ldots \quad \ldots \quad \ldots \quad (15)$$

If $\overline{DP}$ is the degree of polymerisation in the absence of solvent S i.e. at $[S] = 0$, we have,

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + \frac{k_{tr}}{k_p} \cdot \frac{[S]}{[M]}$$

$$= \frac{1}{\overline{DP}_0} + C_s \frac{[S]}{[M]} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (16)$$

From equation (15) it can be seen that the gradient of the straight line plot of $1/\overline{DP}$ against $[S]/[M]$ should yield the value of C_s.

However, the situation is a rather more complicated[21] when solvent such as TBr also acts as the initiator. In the equation (14) the value of C can be replaced by S which gives

$$\frac{1}{\overline{DP}} = k_1 \frac{[S]}{[M]} + k_2 \frac{[S]^{\frac{1}{2}}}{[M]^{\frac{1}{2}}} + k_3 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (17)$$

A similar plot of equation (16) does not give a straight line any longer. This is due to the fact that the $\overline{DP}$ is effected by the changing rate of initiation as well as by the solvent transfer reaction. Under these conditions equation (13) can be rewritten in the following form in which chain transfer with monomer has been neglected since it is negligibly small.

$$\frac{1}{\overline{DP}} = \frac{k_{tr}}{k_p} \cdot \frac{[S]}{[M]} + \frac{k_t}{k_p^2 \, [M]^2} \text{ Rate} \quad \ldots \quad \ldots \quad (18)$$

The plot of $1/\overline{DP}$ against rate at constant $[S]/[M]$ would give an intercept equal to $k_{tr}[S]/k_p[M]$ from which C_s can be calculated.

A modification of the theory for long chain polymers has to be made if we wish to apply it to low molecular weight telomers. Mayo[22] and also independently Thomson[23] have put forward such a treatment. The treatment given by Thomson is as follows.

From the competing reactions of chain transfer and propagation, we have

$$\frac{\text{chance of propagation}}{\text{chance of chain transfer}} = \frac{k_p[R_s][M]}{k_{tr}[R_s][S]} \quad \ldots \quad (19)$$

i.e. Probability of chain transfer $= \dfrac{k_{tr}[S]}{k_{tr}[S] + k_p[M]}$

and probability of propagation $= \dfrac{k_p[M]}{k_{tr}[S] + k_p[M]}$

Applying this to the present case we can calculate the number of each type of molecule which is formed.

Molecule	$\overline{DP}$ x number of molecules
$CCl_3(M)Br$	$\dfrac{1 \times k_{tr}[S]}{k_{tr}[S] + k_p[M]}$
$CCl_3(M)_2Br$	$\dfrac{2 \times k_p[M]\, k_{tr}[S]}{\{k_{tr}[S] + k_p[M]\}^2}$

$CCl_3(M)_nBr$ $$\frac{n \times k_p[M]^{n-1} \times k_{tr}[S]}{\left\{k_{tr}[S] + k_p[M]\right\}^n}$$

The overall theoretical degree of polymerisation will be obtained by taking the sum to infinity of the above series.

Let $k_{tr}[S] = A$, $k_p[M] = B$

then series Θ is represented by

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

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

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

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

where $\lambda = \dfrac{B}{A+B}$

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

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

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

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

$$\text{i.e. } \Theta = \frac{A}{A+B} \times \frac{1}{\left\{1 - B/(A+B)^2\right\}} = 1 + \frac{B}{A}$$

$$\text{i.e. } \overline{DP} = 1 + \frac{k_p[M]}{k_{tr}[S]} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (20)$$

The gradient of the plot of $\overline{DP}$ against $\frac{[M]}{[S]}$ can be identified with the value of k_p/k_{tr}, the reciprocal of which would give the value of C_s.

EXPERIMENTAL

EXPERIMENTAL

MATERIALS

Methylmethacrylate (M.M.A.)

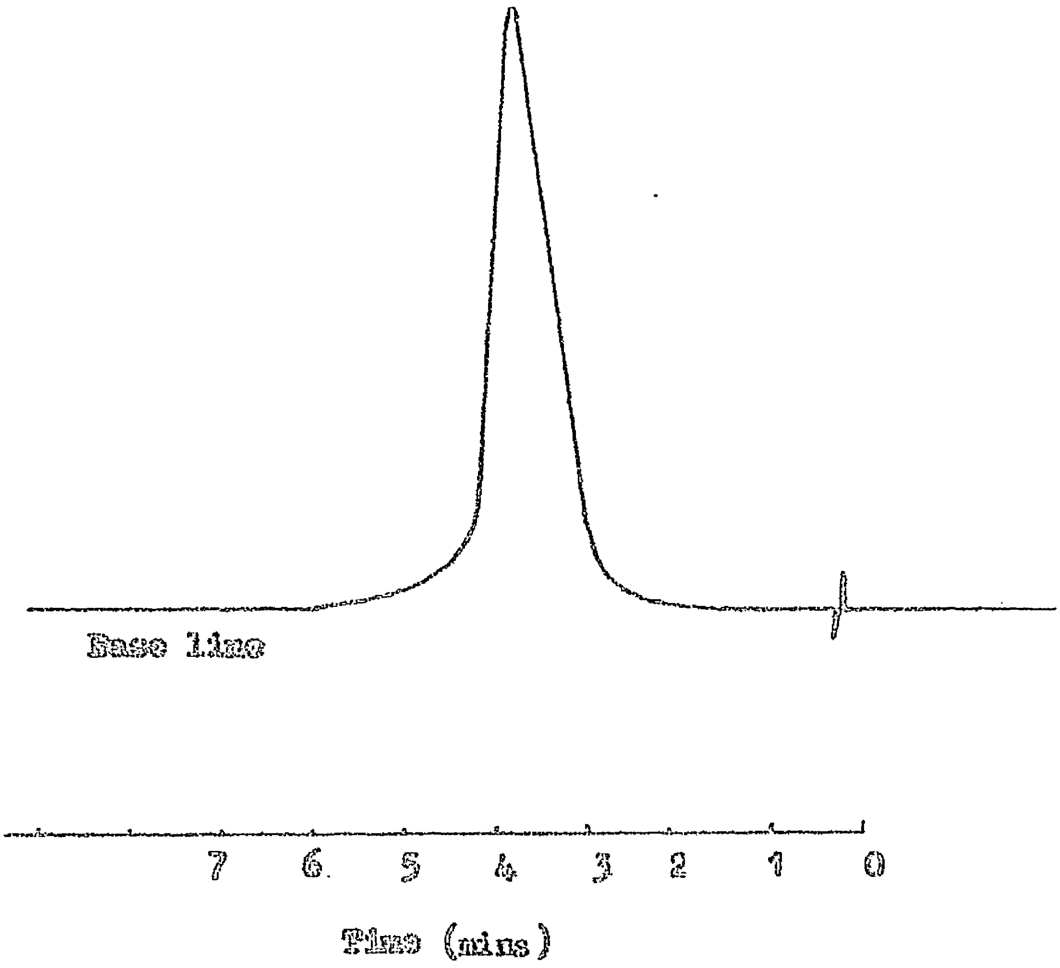
M.M.A. containing hydroquinone as inhibitor was obtained from I.C.I. Ltd. The inhibitor was removed by distilling the monomer under vacuum twice and drying for two to three days over anhydrous calcium chloride. The monomer was finally fractionally distilled under nitrogen in an all glass apparatus. The fraction boiling at 40°C (80mm. mercury pressure) was collected and transferred to the vacuum line. The monomer was thoroughly degassed by repeated freezing evacuating thawing cycles. It was finally polymerised to 5% conversion and distilled on the vacuum line immediately before being used. The monomer gave a single peak on the vapour phase chromatogram, as shown on fig. (1)

Bromotrichloromethane (TBr)

This was obtained from Eastman Kodak Ltd. It was washed with dilute sodium carbonate solution to remove any free bromine, then with distilled water and dried over calcium chloride. It was stored in the dark and distilled when required in a 2' column under

FIG. 1

Purity of M.M.A. as Indicated by
V.P.C. at 45°C



a pressure of 80mm. of mercury. The middle fraction which boiled at 43°C was collected.

Carbon Tetrachloride and Benzene

Analar grade solvents were distilled for use as non reactive diluents in studies of the effects of the bromotrichloromethane and methylmethacrylate concentrations on the rate of reaction.

Radioactive Benzene

0.5 mille-curies of benzene was supplied by the Radio-Chemical Centre, Amersham, in a break seal ampoule. This was prepared[24] by trimerisation of CH≡CH. The ampoule was attached to the vacuum line by a B.14 cone and the space above the break seal evacuated. The break seal was then broken using a stainless steel ball bearing. 15ml. degassed inactive analar benzene, was then distilled into the ampoule.

Radioactive methylmethacrylate

90 milligrames of 0.5 millicuries of methyl (C^{14}) methacrylate containing hydroquinone as inhibitor was supplied by New England Corporation, Massachusetts.. This was diluted with 10 ml. inhibitor containing inactive methylmethacrylate. Further dilutions prior to its use are described under the headings

of experimental techniques and procedure of radioactive tracer work.

APPARATUS

High Vacuum Line

The all glass high vacuum line consisted of a series of traps and high vacuum taps connected to a 3-stage mercury diffusion pump backed by an Edwards rotary oil pump. Liquid nitrogen cold traps were placed immediately before and after the mercury diffusion pump. Apeizon high vacuum grease was used on all Quick fit joints and taps. Using this system, a residual pressure of about 10^{-4}mm. of mercury, as measured by Pirani gauge, was easily achieved.

Constant Temperature Water Bath

The water bath was a cylindrical Pyrex glass tank of about 25 litre capacity. This was surrounded by an aluminium jacket with observation and irradiation windows. The annular space between the tank and the jacket was filled with asbestos wool lagging. A mercury/toluene regulator operated a low power heater to give temperature control of about ± 0.005°C at the bath temperature of 25°C. Constant temperature distribution was ensured by vigorous stirring when working at higher temperature (e.g. 40°C and 60°C), a larger 2 KW heater connected through a Variac controller was used to raise the bath temperature to, and maintain it approximately 1°C below required temperature, the final temperature being achieved by the low power heater, and controlled by the mercury/toluene regulator.

Irradiation

The source of irradiation for the photochemical reaction was a 125 W Osira high pressure mercury vapour lamp which was stabilised with a capacitor and choke.

Cryoscopic Cell

Considerable time was spent in the design of a suitable apparatus which would give reproducible results, since the values obtained for the chain transfer constant depend directly upon the molecular weight measurement. The apparatus (fig. 2) eventually used was essentially a small detachable cell (A) surrounded by two air jackets (B and C). The outside jacket (C) could be evacuated to provide better insulation. A calibrated thermistor (D) of low heat capacity was attached through a Wheatstone Bridge circuit (fig. 3). The vessel was stirred by means of a rotating magnet placed below the cooling bath which turned a small glass covered magnet (E) situated in the cell. The

FIG. 2

Cryoscopic Cell

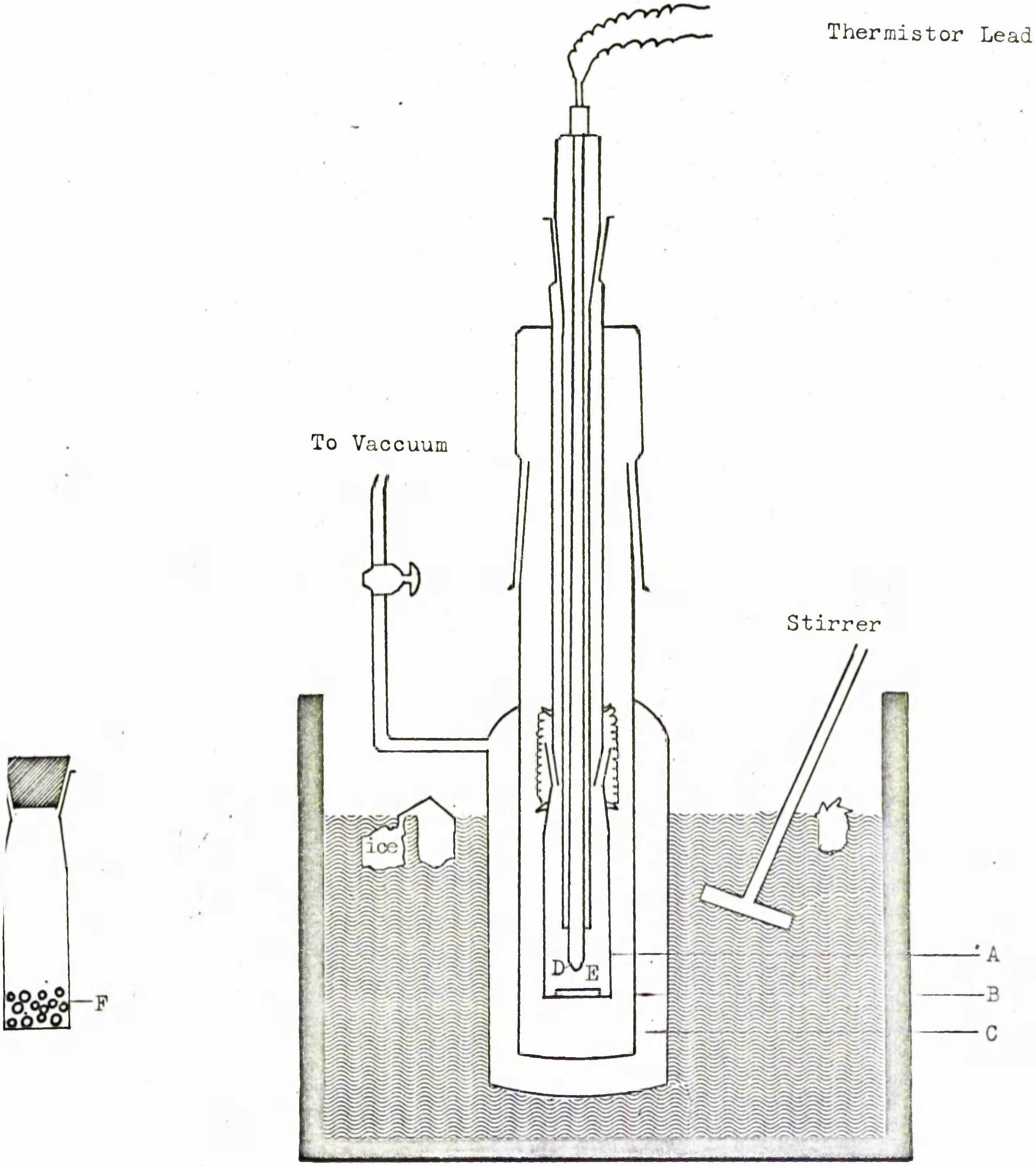
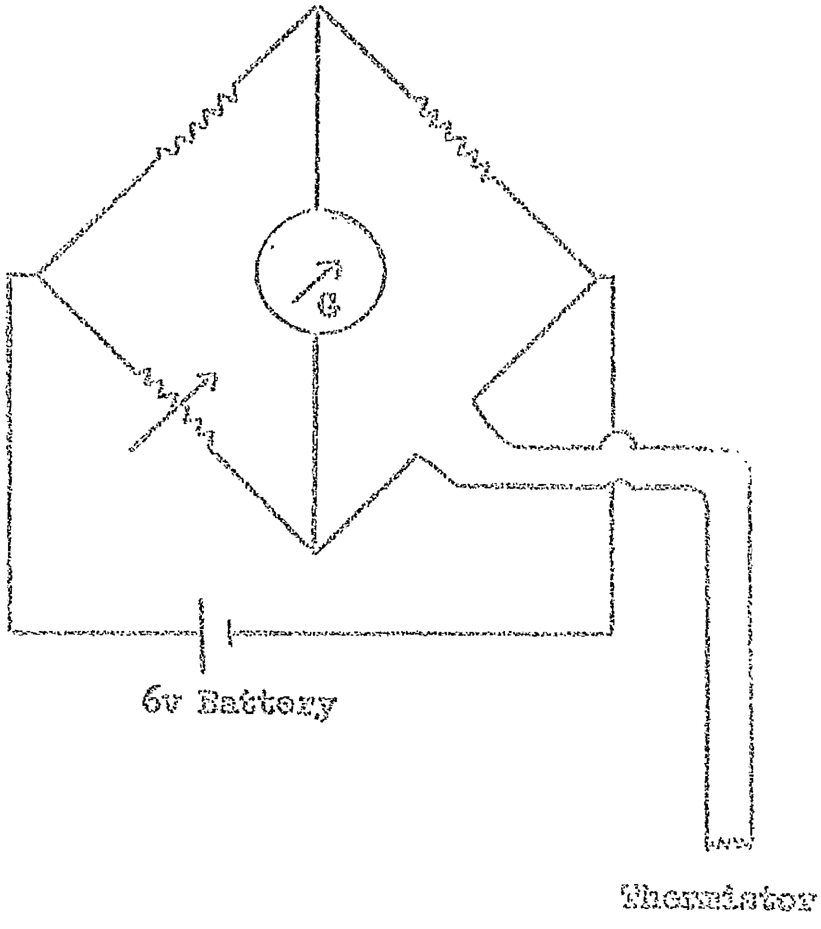


FIG. 3

Wheatstone Bridge Circuit



G - Galvanometer

cell could be detached and weighed at any time throughout the experiment. A replacement cell F containing anhydrous calcium chloride was used to hold the thermistor assembly during the weighing operation.

U.V. Shutter

A quick moving shutter operated by an electromagnet was placed between the lamp and the reaction vessel and used in the experiments in which the heat of addition of bromotrichloromethane to methylmethacrylate was determined.

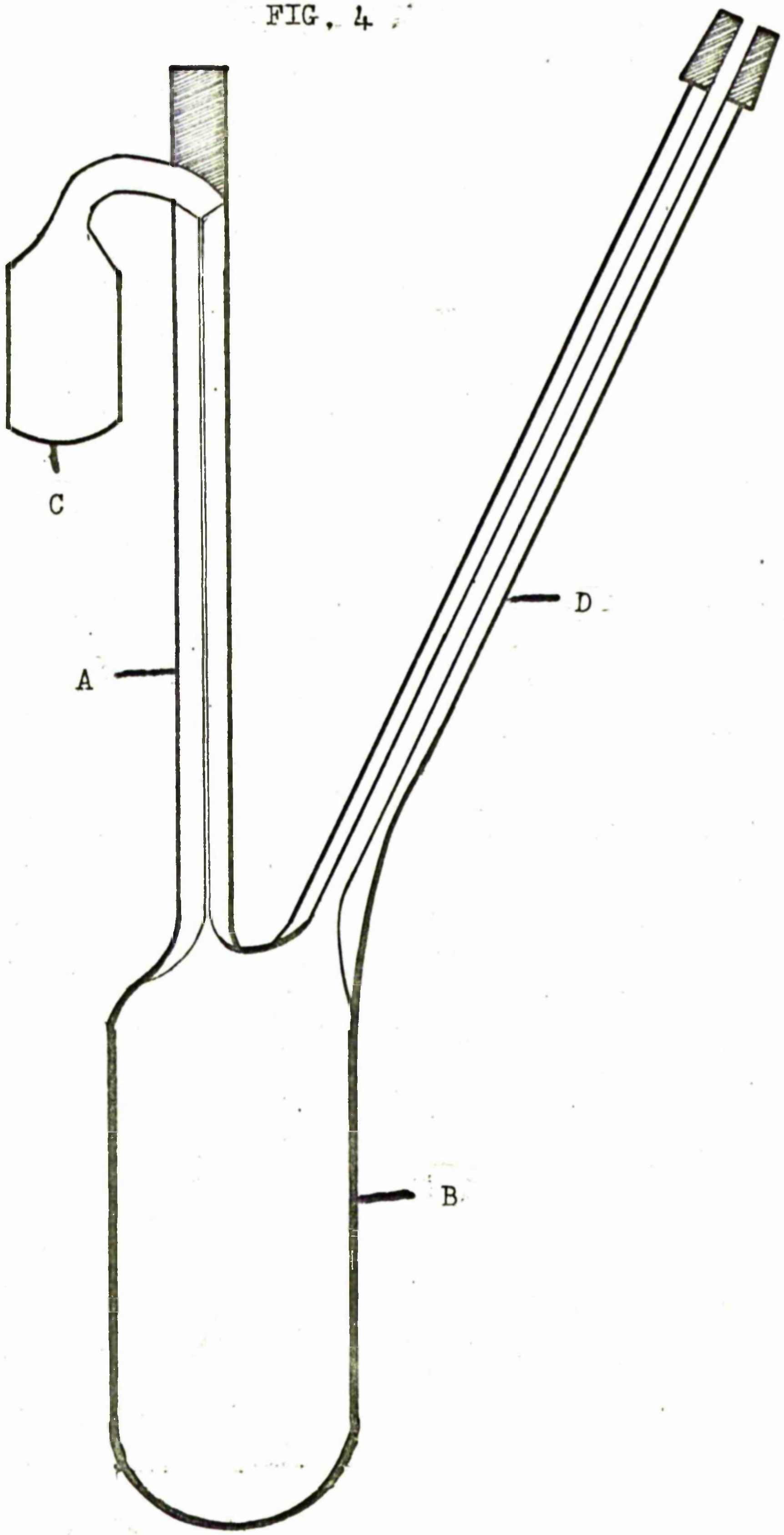
Dilatometers.

The dilatometers were made from Pyrex glass and consisted of cylindrical bulbs of approximately 4-10 ml. capacity, surmounted by Verdia capillary stem of 1.5 mm. diameter. The Verdia capillary was attached to a constriction for flame sealing under vacuum and a B.10 ground glass cone for connecting to the vacuum line.

For the work which involved determination of heat of reaction, a special dilatometer (fig. 4) was used. A very fine capillary (A) of 0.4 mm. bore was connected at one end to the dilatometer bulb (B) of approximately 30 ml. capacity and at the other, to

Dilatometer for the Determination of Heat of Reaction

FIG. 4



an overflow bulb (C). For connection to the vacuum line by B.10 cone, a side arm capillary (D) of larger bore was used. This overcame the practical problem of the slow distillation of the monomer into the dilatometer through the very fine capillary tube. The large volume bulb and very fine capillary were used to increase the sensitivity of measurements of contraction or expansion in the capillary under adiabatic conditions. When the level in the capillary had fallen outside the capillary, more material was added from the overflow bulb.

PROCEDURE

The filling of dilatometers.

The dilatometers were cleaned with concentrated nitric acid followed by water, acetone, and finally dried on the vacuum line. They were then calibrated by filling with A.R. acetone from a burette graduated in 0.05 ml. divisions. Bromotrichloromethane was introduced directly into the dilatometers from a graduated burette. The dilatometer was then attached to the vacuum line and its contents degassed by repeated freezing, evacuating and thawing cycles. The calculated quantity of monomer was then distilled in from a neighbouring graduated reservoir on the vacuum line.

Rate measurements

Sealed dilatometers were immersed in the water bath at the required temperature. About 15 to 20 minutes was allowed for thermal equilibrium before commencing irradiation with light of greater than 3000°A. The distance between the U.V. lamp and the dilatometer was kept constant in all the experiments. The movement of the meniscus in the dilatometer was followed with a cathetometer. A typical reaction run is shown in fig. (5) from which the reaction rate can be determined in terms of contraction per unit volume.

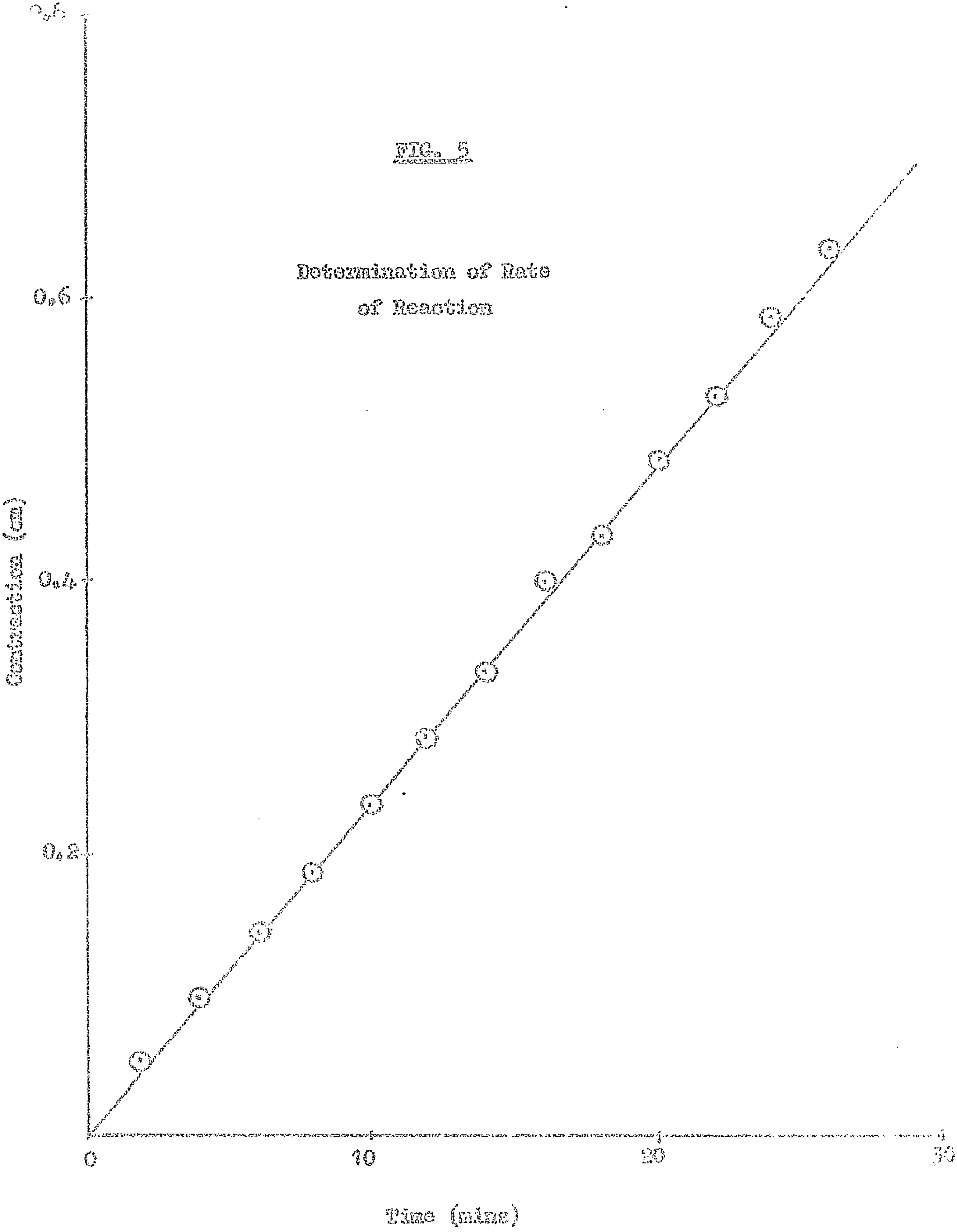


FIG. 5

Determination of Rate of Reaction

Isolation of the products

After the required contraction had occurred the dilatometer was broken open and its contents emptied into a flask which was then fitted to the vacuum line to pump off the unreacted reactants. The high boiling liquid or solid products were then dissolved in benzene and freeze dried. The freeze dried products, of $\overline{DP}$ = 4 to 5, were subjected to one of the following treatments:

(a) Heated at 40°C for 1 hour or

(b) Heated at 60°C for 1 hour or

(c) Freeze dried twice more and then heated to 60°C for 1 hour. Molecular weight measurements and weight loss results showed that the products as obtained after a single freeze drying, did not alter by further freeze drying and/or heating. The products, however, improved markedly after the first freeze drying in their physical form. Products prior to freeze drying gave inconsistent values for molecular weight and were difficult to handle due to their somewhat sticky physical nature. Hence, after distilling the unreacted reactants, one freeze drying was adopted as standard procedure for isolation of products. The products were stored in the dark for molecular weight measurements.

Senoglos[5], when studying a similar system, isolated his products merely by distilling off the unreacted reactants on the vacuum line.

Molecular Weight determination

Depression of the freezing point due to Roult's law[25-27] offers one of the most convenient methods for the determination of molecular weight. This method depends on the fact that when a telomer is dissolved in a suitable solvent e.g. benzene, the vapour pressure of the benzene is lowered by a characteristic amount. This in turn results in depression of the freezing point of the solution which is related to the molecular weight by the following equation.

$$\Delta T = \frac{K \times W_1 \times 100}{M_1' \times W_2} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (21)$$

where, ΔT = freezing point depression (°C)

W_1 = weight of telomer (gms)

W_2 = weight of benzene (gms)

M_1' = molecular weight of telomer

Since the behaviour of most solvents approaches the ideal at extreme dilution, it follows that the depression determined in practice is very small. Accurate measurement is thus essential. At such dilutions the presence of even traces of moisture from atmosphere has marked effect on reproducibility of the results.

Calibration of the thermistor.

A Beckman differential thermometer was set to give a reading at the freezing point. A larger cell (fig. 6) which enabled the thermometer bulb to be fully immersed, was used. The thermistor was carefully attached to the Beckman thermometer and inserted into the cell containing a small magnet for stirring. The apparatus complete with its two jackets was lowered into the ice and water cooling bath to cool slowly. The freezing point was recorded on the Beckman and thermistor. This procedure was repeated a number of times by addition of a few milligrames of pure monochloro 2,4 dinitro-benzene to obtain the calibration curve (fig 7) shown later, in the section containing results.

Drying of Benzene.

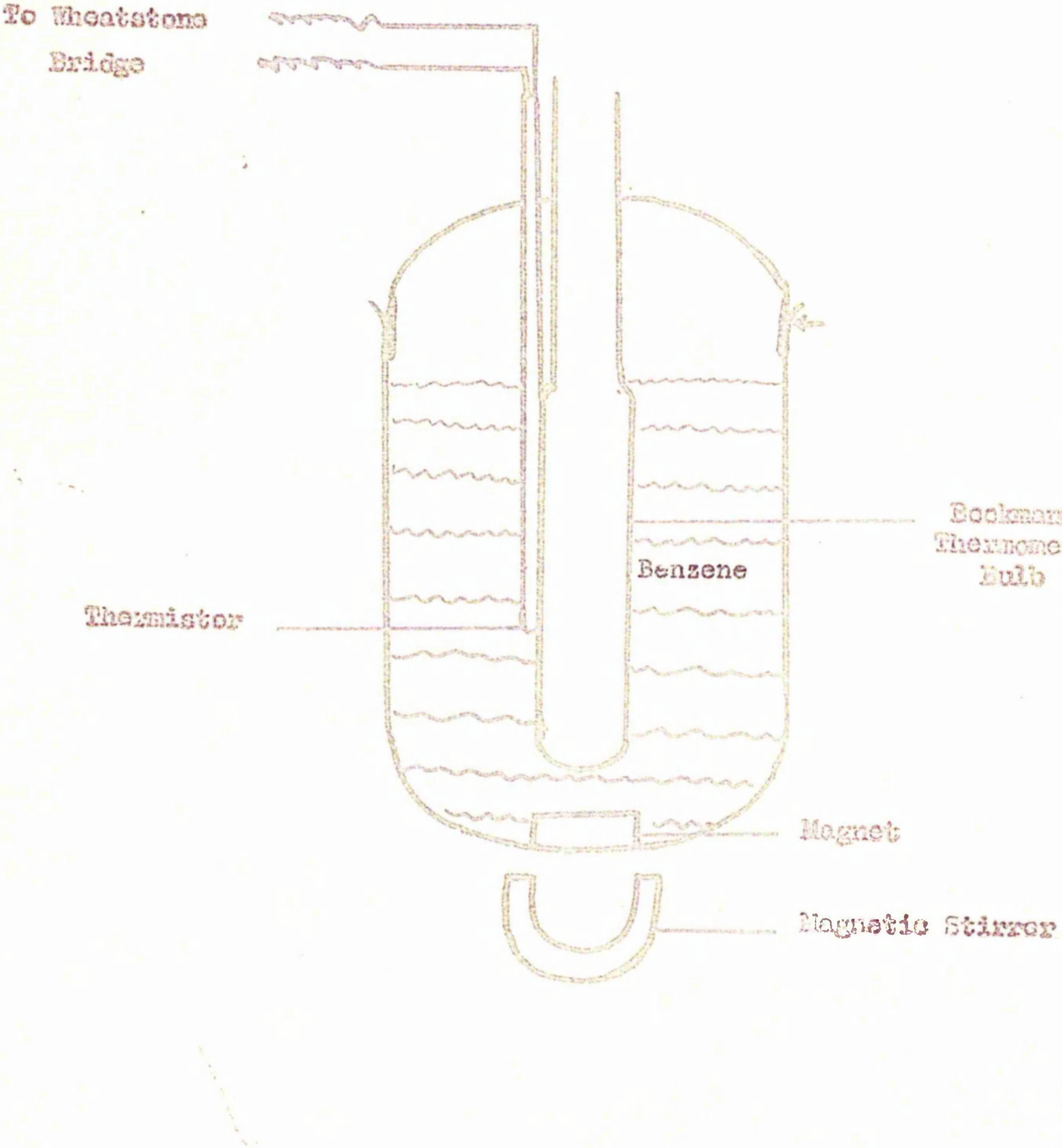
Molecular weight grade benzene was dried over molecular sieve type 5 A (aluminium calcium silicate) for four days. The molecular sieves had been predried at 400°C for 12 hours and were stored in a vacuum desiccator over phosphorus pentoxide.

Depression Constant.

About 2ml. of dried benzene was weighed directly

FIG. 6

Thermistor Calibration Apparatus



in-to the cell. The freezing point was determined as above. About 10 mg. of chemically pure monochloro 2,4 dinitro-benzene, whose molecular weight is known, was added and freezing point determined again. When the cell was detached for weighing, a replacement cell containing calcium chloride was attached to the guide tube containing the thermistor (fig. 2). The stopper from the calcium chloride cell was used to keep the experimental cell sealed during weighing operations. The constant K was then calculated from the relationship given by the equation (21). Substituting the value of K, unknown molecular weights of telomers were determined by following the same procedure as for the constant K.

Other experimental techniques used were the determination of heat of addition of trichloromethyl radical to methylmethacrylate by dilatometric method, and the determination of molecular weight by radio tracer technique. These will be described later in the appropriate sections dealing with the results of the experiments.

RESULTS

RESULTS

Calibration of Thermistor.

The procedure described on page 36 was used. The results obtained are given in table 5, which shows the variation of the resistance of the thermistor with temperature, as recorded by the differential Beckmann thermometer. Benzene was employed as a solvent and 1 chloro-2,4 dinitro-benzene was added progressively to lower the freezing point.

Table 5. Variation of thermistor resistance with temperature.

Change in temperature °C	Resistance in ohms	Change in temperature °C	Resistance in ohms
0	2856.5	0.572	2800.5
0.132	2844.2	0.661	2792.2
0.240	2832.3	0.812	2778.8
0.300	2827.5	0.913	2769.2
0.333	2824.1	1.178	2745.0
0.461	2811.9		

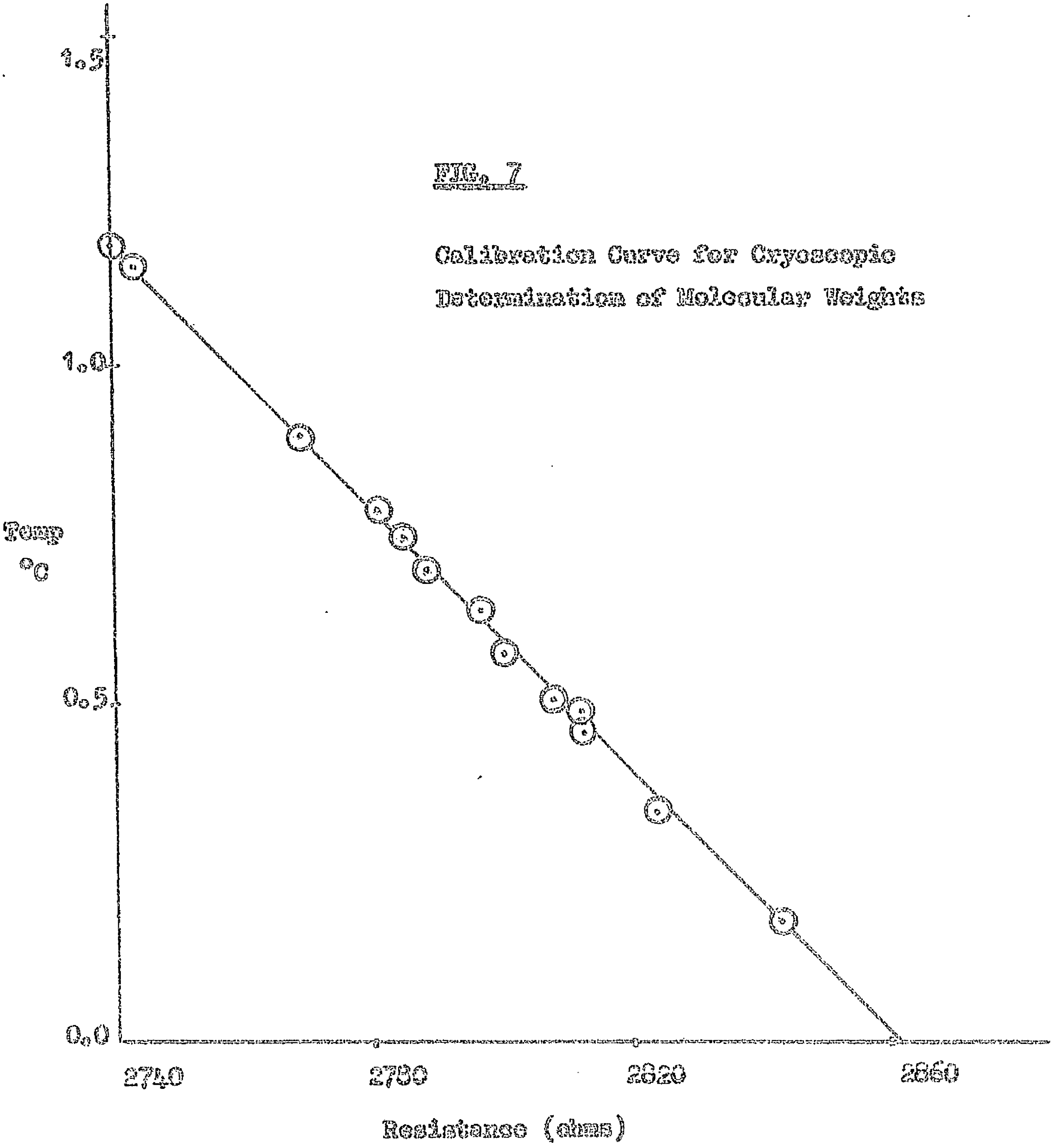


FIG. 7

Calibration Curve for Cryoscopic Determination of Molecular Weights

From the results and the graph shown in fig. 7. it can be seen that a straight line relationship exists between the resistance of the thermistor and the change in temperature recorded by the Beckman thermometer in the range 4.5 to 5.5°C. From this graph, a +1 ohm change of resistance was calculated to be equivalent to a change of -0.0104°C.

Determination of depression constant K.

The depression constant was determined as described on pages 36 and 37. Benzene and 1 chloro-2,4 dinitrobenzene were employed as solvent and solute respectively. Table 6 shows the calculation of the depression constant K from the values of the freezing point depressions at different dilutions.

Table 6. Calculation of depression constant. Resistance at the freezing point of brnzene is equal to 2787.7 ohms. Weight of salute (W_1) is equal to 0.0465 gms.

Weight of benzene (W_2) gms.	Resistance ohms	Increase in resistance ohms	Depression (ΔT) °C	K
4.4014	2813.9	26.2	26.2 x 0.0104	50.2
5.8356	2807.4	19.7	19.7 x 0.0104	50.1
7.5342	2803.2	15.5	15.5 x 0.0104	50.3

Mean K = 50.2

The accuracy of the depression constant and the procedure in general was tested by comparing the molecular weights obtained by this method, and as calculated from the molecular formulae, for the following materials.

Table 7. Comparison of molecular weights.

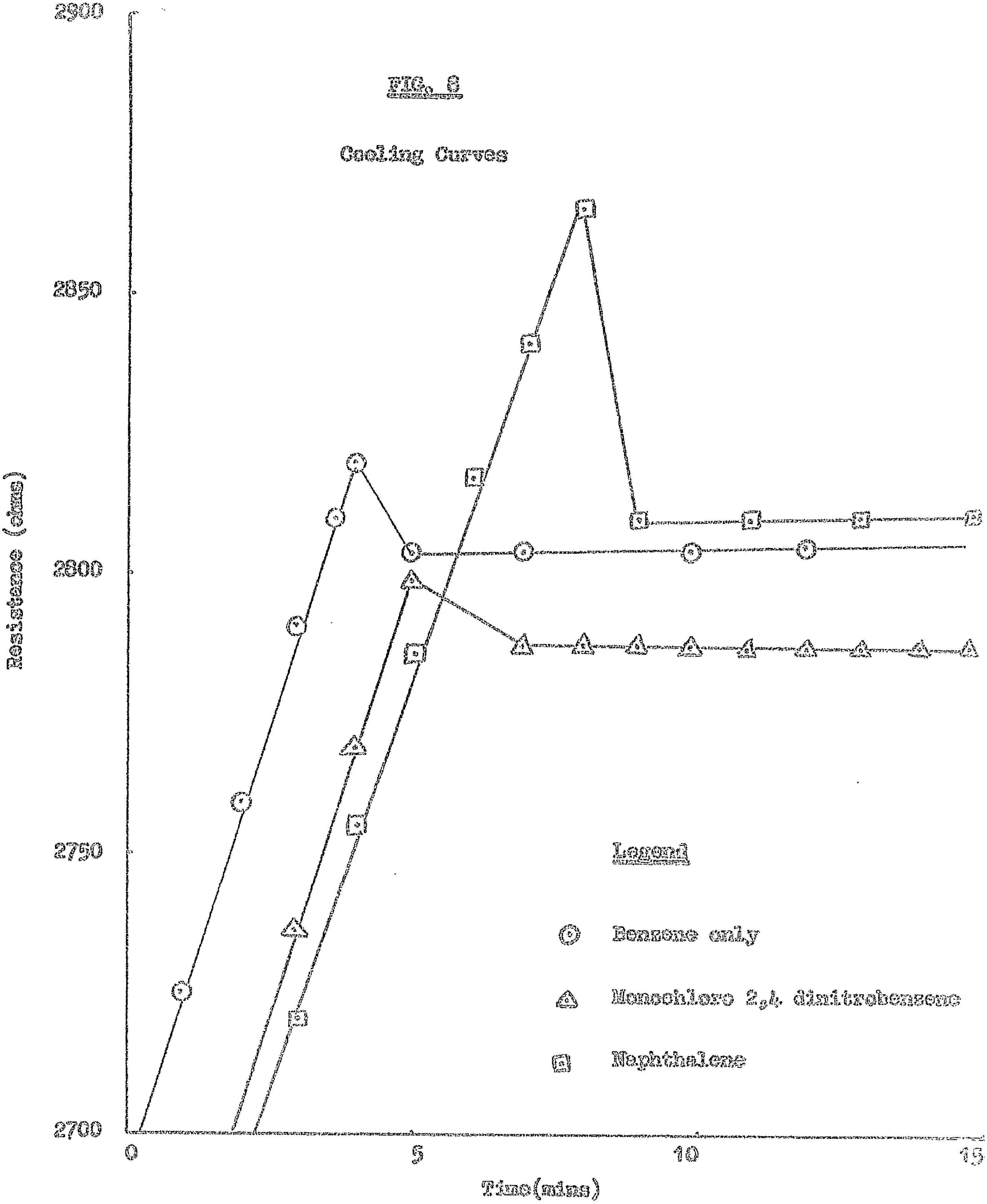
	Cryoscopic	Theoretical
(Naphthalene)	129.7	128.2
TBr	196.8	198.0
1 chloro-2,4 dinitro-benzene	201.2	202.6

The values given are the mean results of five determinations, which were found to show a deviation of less than 3%. It can be seen from Table 7 that there is a good agreement between the values of molecular weights obtained cryoscopically and those obtained theoretically. Hence, this procedure was adopted as being satisfactory for the determination of the molecular weights of the telomers.

Typical cooling curve (fig. 8) shows the expected degree of super cooling immediately prior to freezing.

FIG. 8

Cooling Curves



Intensity Exponents

The nature of the radical termination step can be found out by measuring the rate dependence on the intensity of U.V. irradiation. The intensity exponent can be evaluated by measuring the rate of reaction for various light intensities. The rate of any photochemical reaction is expressed as

$$\text{Rate} = k \times (\text{Intensity})^{x} \times \text{concentration terms} \qquad (22)$$

where k = a proportionality constant

x = intensity exponent

For fixed concentrations of reactants, it can readily be shown that x is given by

$$x = \frac{\log R_1/R_2}{\log I_1/I_2} \quad \ldots\ \ldots\ \ldots\ \ldots\ \ldots \quad (23)$$

The light intensity was changed by inserting a screen of known transmission between the vessel and the source of irradiation. The transmission of the screens was obtained by measuring the intensity of light of wave length 3650°A falling on a photoelectric cell before and after the screen was inserted as a direct reading on a Unicam spectrophotometer. Intensity exponents were calculated from equation (23) and also graphically from equation (22). An average value of the rates before and after the screen insertion was taken as the rate at full intensity (fig. 9). The plot of log rate against log intensity for two reaction systems of methylmethacrylate/TBr 10/1 and 1/1 feed ratio at 25°C is shown in fig. 10. The effect of the intensity of irradiation on the rate of reaction for experiments with 1/1 molar mixtures of methylmethacrylate/TBr at 25°C is given in table 8.

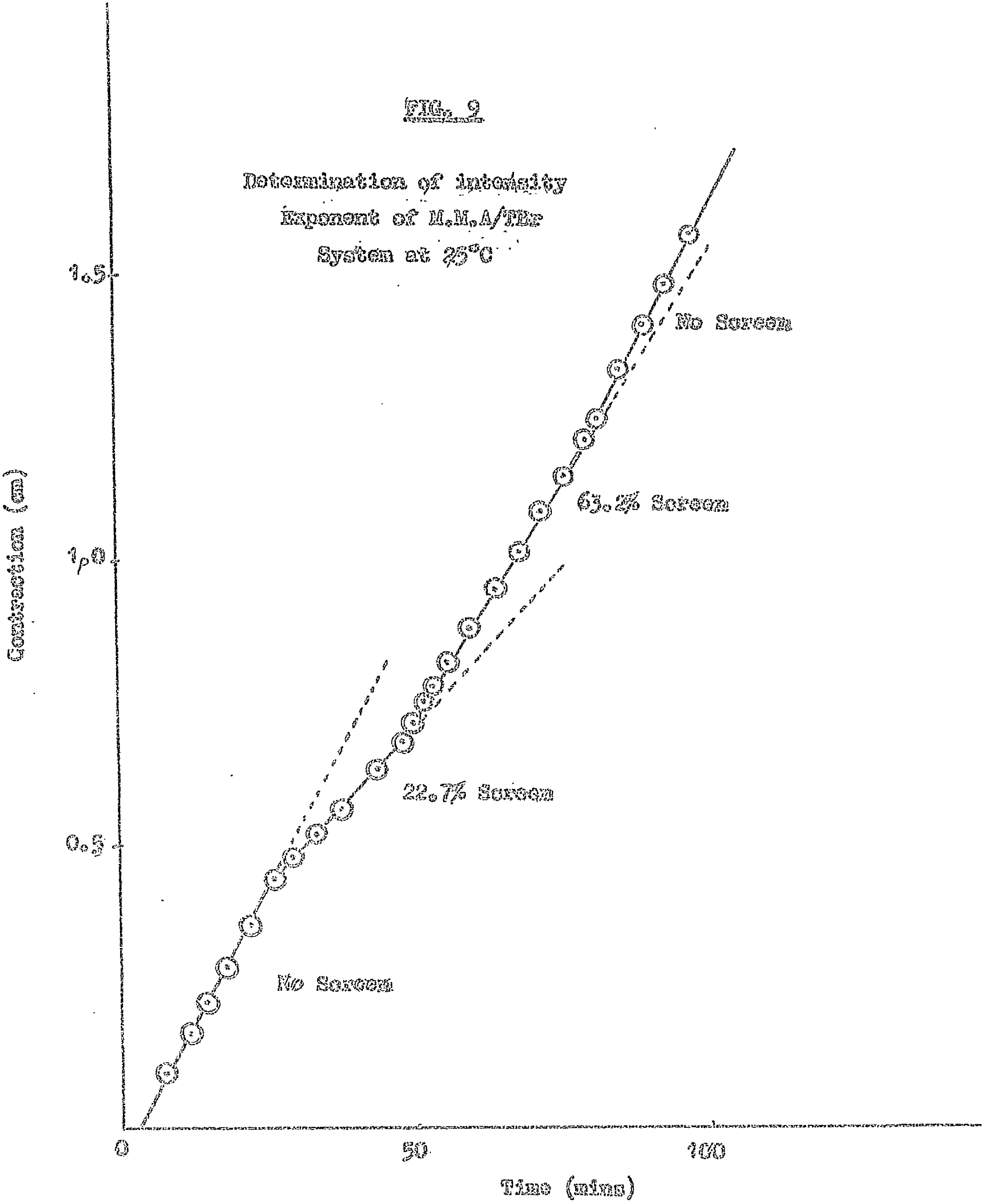
Table 8. The effect of intensity of irradiation on the rate of telomerisation of a 1/1 molar mixture of methylmethacrylate/TBr.

% Transmission T	log T	(Rate x 10) % per hour contraction	log (Rate x 10)
100.0	2.0000	11.5	1.060
63.2	1.8002	8.65	0.937
50.0	1.6990	8.15	0.918
37.0	1.5740	6.76	0.836
25.5	1.4060	5.50	0.748

Intensity exponents have been determined experimentally at different temperatures using two different feed mixtures of methylmethacrylate and TBr and a third containing added carbon tetr.chloride. The results of these determinations are shown in table 9.

FIG. 9

Determination of Intensity Exponent of M.M.A/TBr System at 25°C



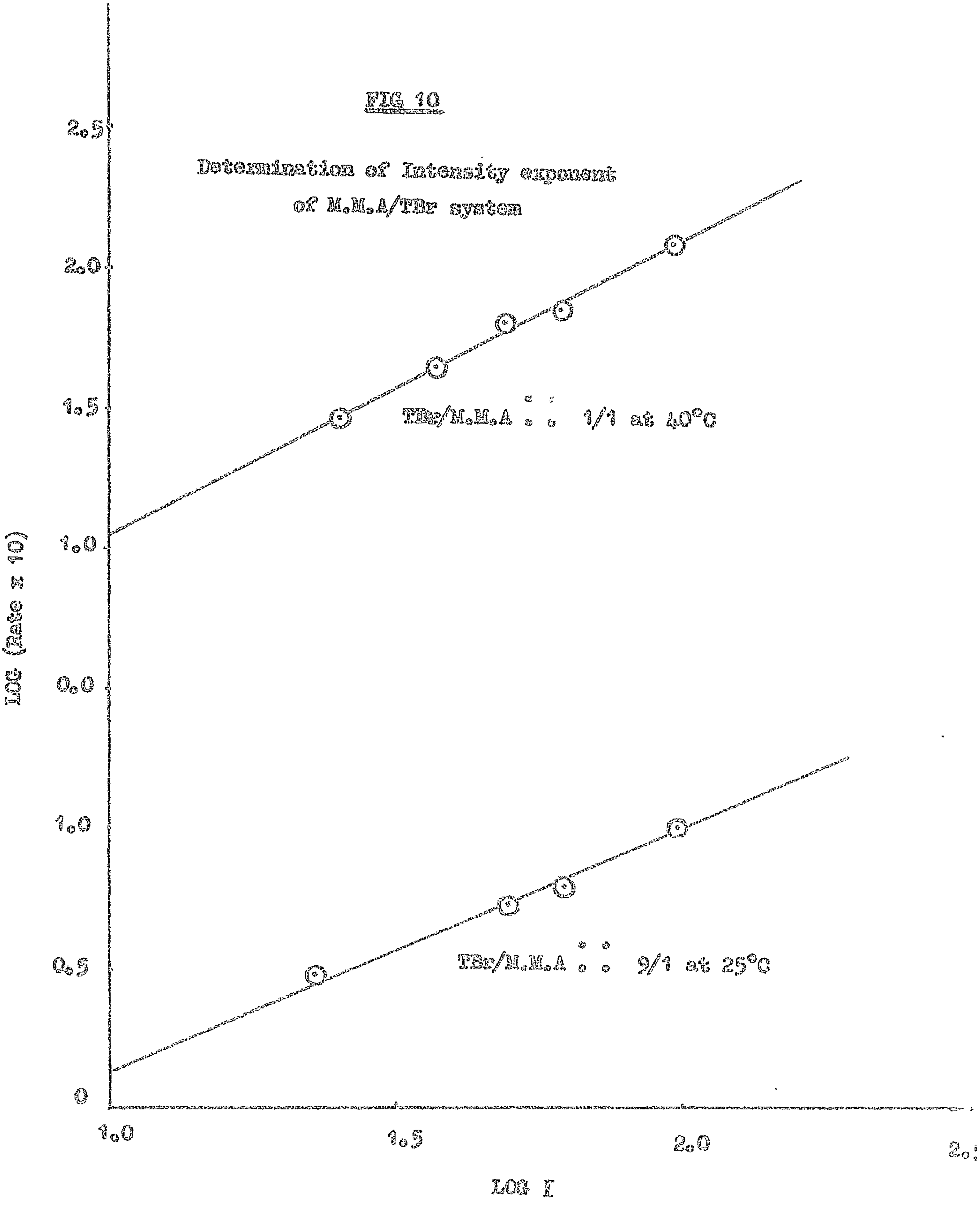


FIG 10

Determination of Intensity exponent of M.M.A/TBr system

Table 9. Determination of intensity exponents with differing feed ratios of the reactants and temperatures.

[TBr]	[M.M.A.]	Solvent carbon tetrachloride	Temperature °C	x
9	1	0	25	0.44
1	1	0	25	0.55
9	1	0.3	25	0.50
1	1	0	40	0.51
9	1	0	60	0.52

Evidently there is a little deviation in values of the intensity exponents under the conditions used.

The telomerisation of methylmethacrylate with TBr at 25°C.

The equation derived on page 25 (equation 20), for the evaluation of the transfer constant in the telomer range requires a knowledge of the values of $\overline{DP}$ with varying TBr/M.M.A. ratios. Table 10 shows these results, which were obtained by using the experimental set-up and procedure described in the experimental section.

The rates of telomerisation, which were also followed, are included in this table as percentage per hour contraction, since the densities of products other than the 1,1 adduct were not known, and the absolute rates could not be calculated. The reactions were allowed to proceed until the observed contraction corresponded to that estimated for approximately 6 - 8% conversion. The reactions were stopped at this stage simply by switching off the U.V. light. It was presumed that the ratio of the concentrations of the reactants did not change appreciably at such low conversions.

Table 10. Variation of molecular weight and reaction rate with feed composition at 25°C.

Feed molar ratio [M.M.A]/[TBr]	Feed molar ratio [TBr]/[M.M.A]	Molecular weight	$\overline{DP}$	Rates % per hour contraction
0.102	9.760	335	1.350	1.140
0.125	8.000	302	1.020	1.470
0.200	5.000	411	2.110	0.905
0.333	3.000	473-500	2.73-3.0	1.037
0.666	1.500	690	4.900	1.050
1.000	1.000	942-1020	7.40-8.20	1.185
1.500	0.666	1210-1290	10.1-10.9	1.180
2.000	0.500	1610	14.10	0.920
4.160	0.240	1580	13.80	1.002

Table 10 shows, in general, a steady increase in the value of the molecular weight, with the increasing M.M.A./TBr ratio. Fig. 11 shows the plot of $\overline{DP}$ against

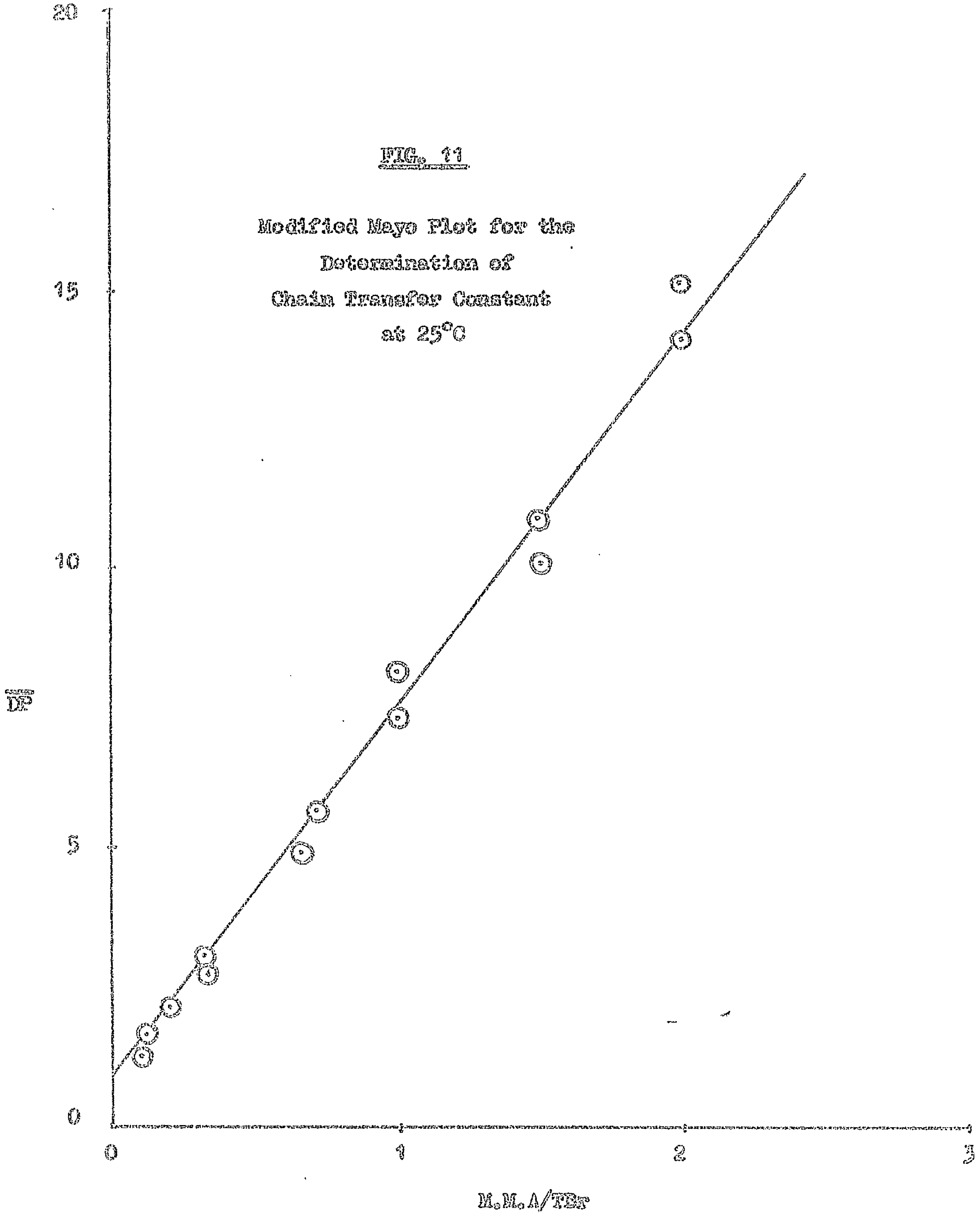


FIG. 11

Modified Mayo Plot for the Determination of Chain Transfer Constant at 25°C

M.M.A./TBr ratio. The rates, however, do not appear to be related to the feed ratio, and in fact, vary very little from a constant value. The deviation from the trend of increasing molecular weights for the feed ratios of M.M.A./TBr of 2.000 and 4.160 can perhaps be attributed to the difficulties in measuring extremely small freezing point depressions for high molecular weights.

Unless stated otherwise, all the molecular weights have been determined cryoscopically. In a few cases molecular weights were also determined by

(1) Vapour pressure method.

(2) Carbon, hydrogen and total halogen analysis method.

(3) Radio-active tracer techniques.

Comparison of the results obtained by these methods will be given in the discussion.

Melting points were also determined on some of the products. Table 11 shows their values together with visual observations on physical appearance of the product as made by the author and those reported by Senogles[5].

Table 11. Properties of telomers

$\overline{DP}$	Melting point °C	Physical appearance of the product	Appearance of the product reported by Senogles[5]
1-1.5	——	viscous liquids	liquids
2.2	——	sticky resin like	"
2.46	35 ± 2	fluffy white powder	viscous liquids
4.25	57 ± 2	"	flakes
4.9	64 ± 2	"	"
8.0	91 ± 2	"	"
16.35	111 ± 3	"	"

Table 11 shows clear differences of physical appearance of the products especially in the lower $\overline{DP}$ range. For example whereas Senogles[5] has reported a $\overline{DP}$ of 2.46 for his viscous liquid products, it has been found in this work that such a product has a $\overline{DP}$ of 1 to 1.5 and that a product of $\overline{DP}$ 2.46 is in the form of solid flakes of melting point 35°C.

The telomerisation of methylmethacrylate with TBr at 40°C.

Experiments were repeated to study the variation of the molecular weight of the product with varying molar ratios of TBr and M.M.A. at 40°C. The results are shown in table 12 where once again the rates of reaction are also reported.

Table 12. Variation of molecular weight and reaction rate with feed composition at 40°C.

Molar ratio [M.M.A]/[TBr]	Molar ratio TBr/M.M.A.	Molecular weight	$\overline{DP}$	% per hour contraction
0.095	10.560	335	1.350	——
0.200	5.000	400	2.000	1.895
0.400	2.500	570	3.700	1.865
1.000	1.000	910	7.100	1.830
1.500	0.666	1,100	9.000	1.730

As at 25°C the molecular weight increases steadily with increase in M.M.A./TBr ratio and the rate is not greatly affected by the change in mole ratio in the feed. Fig.12 shows the plot of $\overline{DP}$ against M.M.A./TBr ratio. The results of table 11 and table 12 show the expected decrease in molecular weight with increasing temperature at all feed ratios. This is attributed to the fact that the rate of transfer of the growing radical with a TBr molecule increases more than the propagation rate. This will be shown by the results obtained for the difference of activation energy of the two competing reactions.

The telomerisation of methylmethacrylate with TBr at 60°C.

Similar experiments were performed at 60°C. The results obtained are shown in table 13.

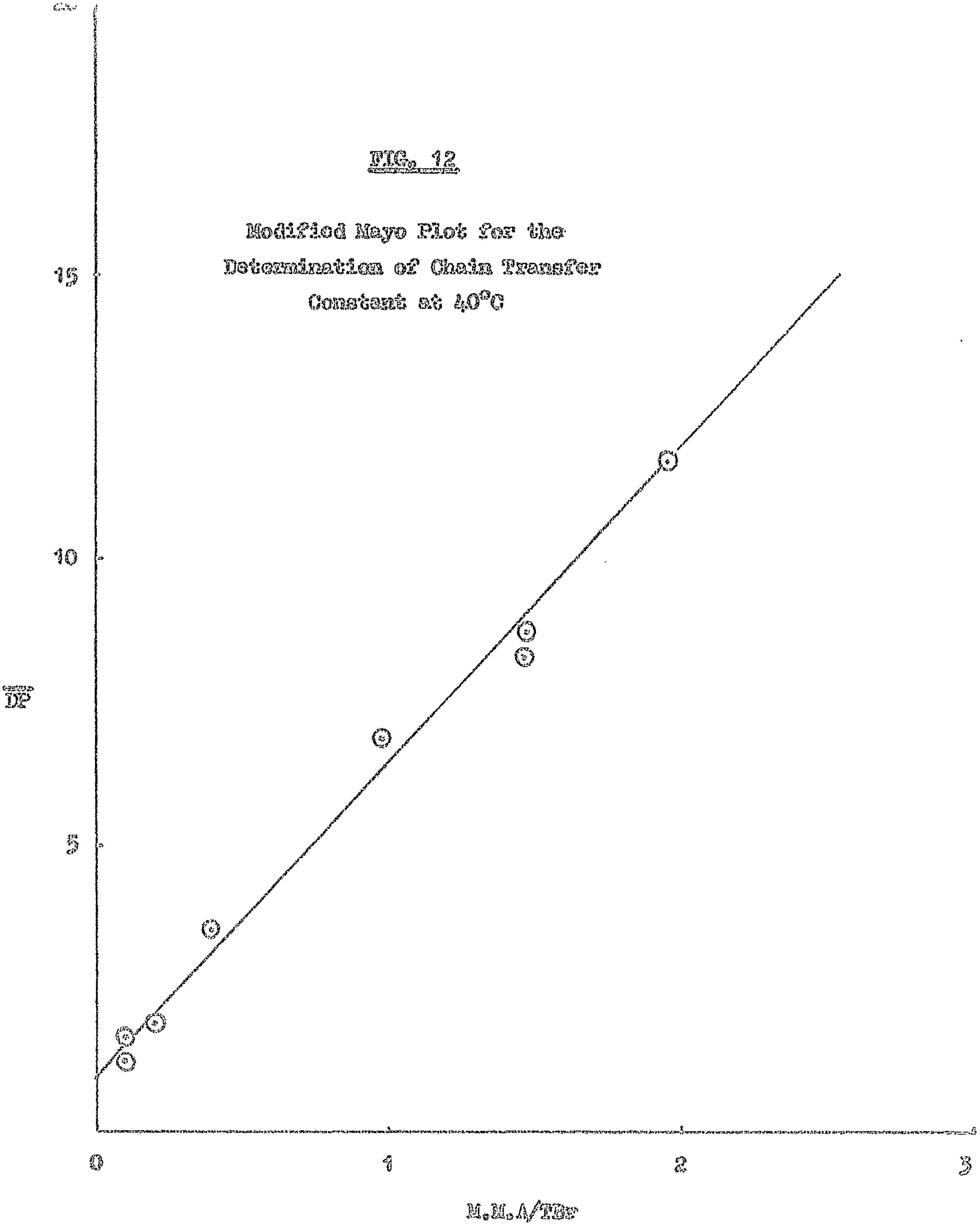


FIG. 12

Modified Mayo Plot for the Determination of Chain Transfer Constant at 40°C

Table 13. Variation of molecular weight and reaction rate with feed composition at 60°C.

Molar ratio [M.M.A]/[TBr]	Molar ratio [TBr]/[M.M.A]	Molecular weight	$\overline{DP}$	% per hour contraction
0.100	10.000	320	1.20	4.36
0.333	3.000	572	3.72	3.49
0.400	2.500	540	3.40	—
0.650	1.540	637	4.37	—
1.020	0.980	755	5.25	—
1.500	0.666	1090	8.90	3.14
6.000	0.167	985	7.85	2.30

The results in this table repeat the pattern seen in table 11 and table 12. There is a general increase in the values of molecular weights with increasing M.M.A./TBr ratio and the rates show a less significant variation, though it could be suggested that there is decrease in rate with decreasing TBr/M.M.A. ratio. Fig. 13 shows the plot of $\overline{DP}$ against M.M.A./TBr ratio. A comparison of the results of table 13 with those of tables 11 and 12 again show the expected decrease in molecular weights with increasing temperature. Further, it can be seen that there is the expected increase in rate with increasing temperature for the mixtures of the same composition.

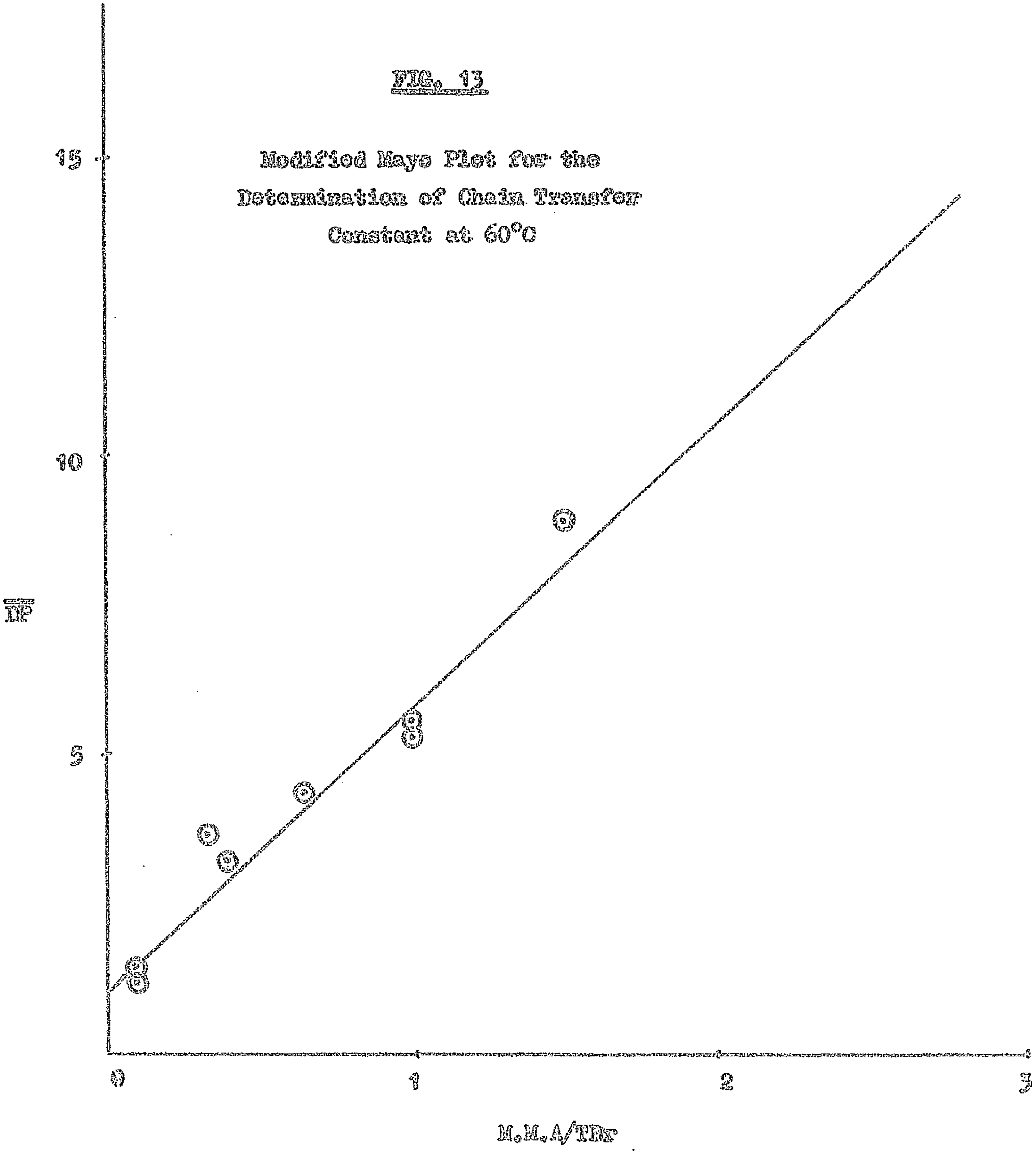


FIG. 13

Modified Mayo Plot for the Determination of Chain Transfer Constant at 60°C

Measurement of molecular weights by radioactive tracer techniques.

Since accurate measurements of the molecular weights of telomers were of prime importance, radioactive tracer techniques were employed to

(a) obtain molecular weights of a representative range of telomers prepared by using radioactive methyl (C 14) methacrylate with inactive bromotrichloromethane, and compare them with the values of molecular weights obtained by cryoscopic, vapour pressure and elemental analysis methods The results obtained by the two latter methods are reported in the discussion.

(b) investigate the purity of telomers by using radioactive benzene and radioactive methyl (C 14) methacrylate and ascertaining whether these reagents were completely removed by vacuum distillation. Radioactivity was measured by scintillation counting, in which use is made of the photons created when a suitable luminescent material is excited by nuclear radiation. These photons are converted into electrons, at the cathode of a photomultiplier tube. Multiplication of these electrons in the photomultiplier gives rise to electrical pulses which can be recorded on a scaler and timing unit (described later). Each isotope produces a typical pulse dependent on its energy output:

differentiation between spurious pulses and those due to the presence of isotopes is made by the use of a discriminator.

Experimental procedure and equipment.

The liquid scintillation medium used was supplied by Nuclear Enterprises Ltd. and consisted of a toluene solution containing 3 gms. per litre 2,5 diphenyloxazole and 0.1 gms. per litre diphenyloxazolyl benzene. The sample whose radioactivity was to be determined was contained in a flat bottomed silica cell of 18 ml. capacity, which was aluminised on the outside to give maximum light reflection. The aluminium coating was protected by the use of an epoxy resin finish. 20 cs. grade silicone oil, also obtained from Nuclear Enterprises Ltd., was used to act as the optical coupler between the cell bottom and the cathode of the photomultiplier tube. The sample cell was filled with 5 ml. of the liquid scintillator and 5 ml. of benzene solution. For calibration purposes these 5 ml. of benzene contained a known amount of radio benzene or radio M.M.A. When radioactivity of the telomer was to be obtained, the solution was of 5 ml. inactive benzene plus approximately 20 milligrams of the radioactive telomer. The polythene cap was then replaced on the cell which was then placed in the scintillation head unit and dark adapted for 20 minutes to minimise residual phosphorescence.

The scintillation head unit is essentially a 'castle' with 2 inches of lead shielding fitted with a special rotary light locking device. This device permits operation of the assembly in daylight without exposing the photomultiplier to the light when changing the cells. This means that the tube dark current is allowed to reach the lowest level possible, making for improved accuracy and lowering the background activity. Also, the high voltage supply to the photomultiplier tube may be left connected when the samples are being changed. Since the photomultiplier tube gain varies as a function of the 8th power of the applied high voltage, no variation in the high voltage supply is obviously desirable. Any variation in output due to temperature changes was avoided by continuously passing cold water through copper coils surrounding the photomultiplier tube.

A Nuclear Enterprise 5202 Fairstein amplifier with a gain setting from 0.4 - 200 was used to amplify the output from the photomultiplier.

The pulses from the main amplifier pass into a single channel height analyser. Since each isotope emits a specific quantum of energy, a pulse peculiar to that isotope is obtained. This instrument can be set so that it will only accept pulses whose amplitude is representative of the particular isotope being counted. The required gate width and pulse height for C 14 counting are noted below.

Stabilised High Voltage	0.740	K. volts
Amplification	50 x 1	
Pulse Height	30	
Gate Width	30	

The pulse in its final form is relayed to the scaler type No. 1009 F and timing unit No. N108 A which were supplied by Dynatron Electronics. The time unit could be used to switch off the scaler either at a pre-set time or after a preset number of counts have been recorded. The time unit has a maximum time store of 99,999 seconds and a maximum count store of 99,999 counts

Results using radioactive benzene

Experiments were carried out to establish if any benzene was incorporated in the telomers during the freeze drying process. The stock solution of benzene which was used for freeze drying the telomers was made up by diluting 0.1 cc. of strongly radioactive benzene (see page 27) with 100 cc. of inactive benzene. For calibration purposes 1 cc. of the stock solution was further diluted with 99 cc. of inactive benzene.

A calibration curve (fig 14) was obtained.

A sample of telomer of $\overline{DP} = 7$ whose molecular weight had been determined cryoscopically was divided into two parts. One part of this sample was freeze dried from ordinary inactive benzene and the other half was freeze dried from the stock solution of radioactive benzene. The following results were obtained on the subsequent activity of the two parts.

(1) activity of 0.0050 gms. of telomer freeze dried from inactive benzene = 0.5 cps.

(2) activity of 0.0050 gms. of telomer freeze dried from radioactive benzene = 0.7 cps.

(3) activity of the 0.0050 gms. of telomer used in (2), freeze dried from radioactive benzene, subsequently freeze dried from inactive benzene = 0.7 cps.

From the calibration curve this increase of activity was found to correspond to 2.3×10^{-4} gms. of benzene. This led to the conclusion that there was 0.6 moles of benzene present in 1 mole of the telomer. These results will be discussed in detail in the discussion.

Results using radioactive M.M.A.

The stock solution of radioactive M.M.A. was prepared by adding 0.2 ml. of highly radioactive M.M.A. (see page 27) to a 100ml. graduated vessel and making

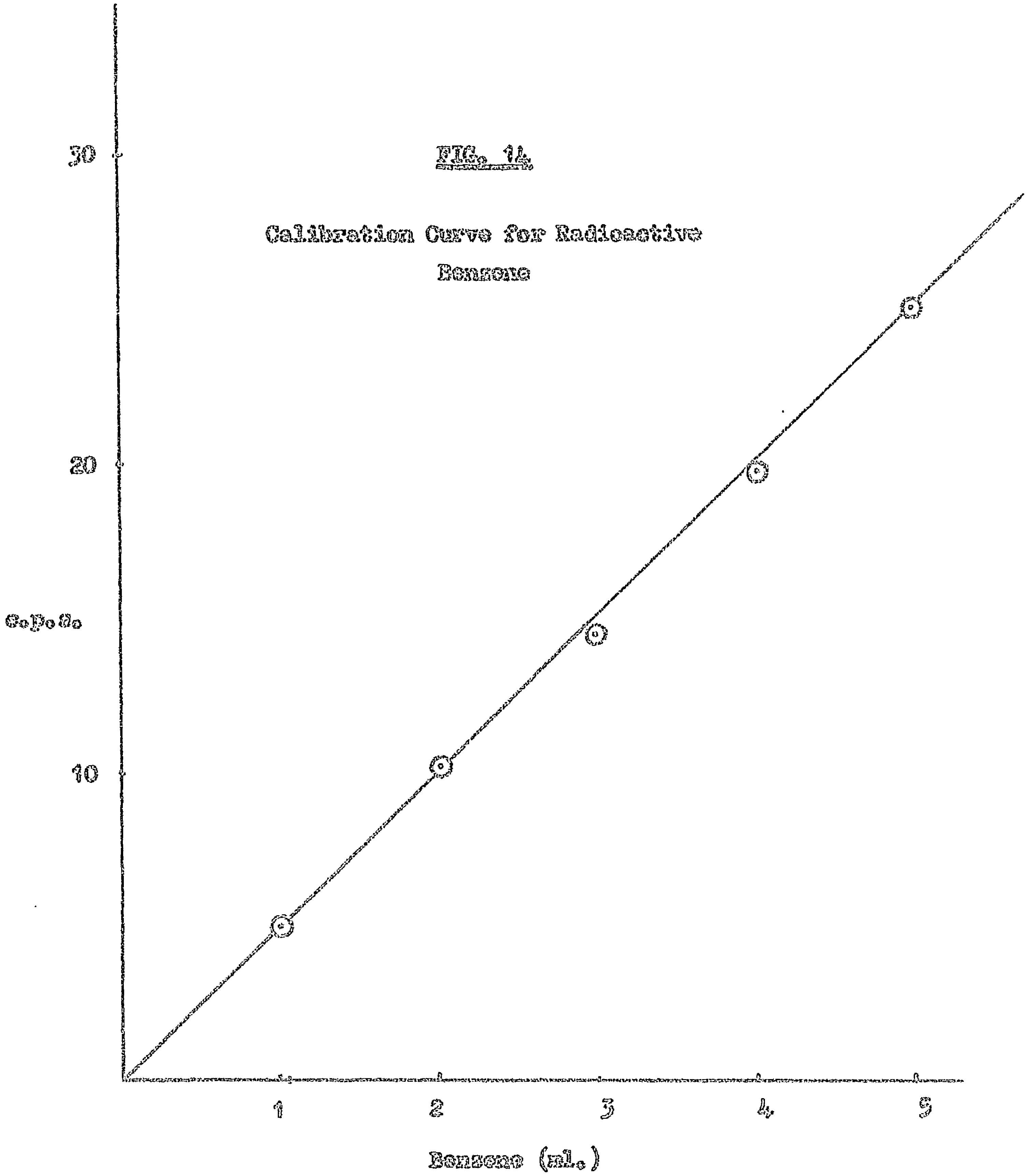


FIG. 14
Calibration Curve for Radioactive Benzene
30
20
10
C.P.M.
1
2
3
4
5
Benzene (ml.)

it up to the mark with inactive inhibitor-containing M.M.A. For calibration purposes, it was found necessary to further dilute 1 ml. of this stock solution to 100 ml. with inactive benzene, this being used in preference to M.M.A. on account of the quenching effect obtained when using the latter diluent. The calibration curve obtained is shown in fig. 15.

The stock solution was used to prepare radioactive telomers at different temperature in the presence of varying quantities of TBr for molecular weight determinations. The results obtained are shown in table 14, which also gives molecular weights measured cryoscopically on inactive samples prepared under identical conditions.

Table 14. Molecular weights obtained by radioactive tracer technique.

[M.M.A.]/[TBr]	Preparation temperature ^{o}C	Molecular weight by R.A. tracer technique	Molecular weight cryoscopically
0.200	25	450	411
0.333	25	580	500
1.000	60	800 - 1000	755

The same stock solution of radioactive M.M.A. was also used to dissolve a previously prepared inactive telomer

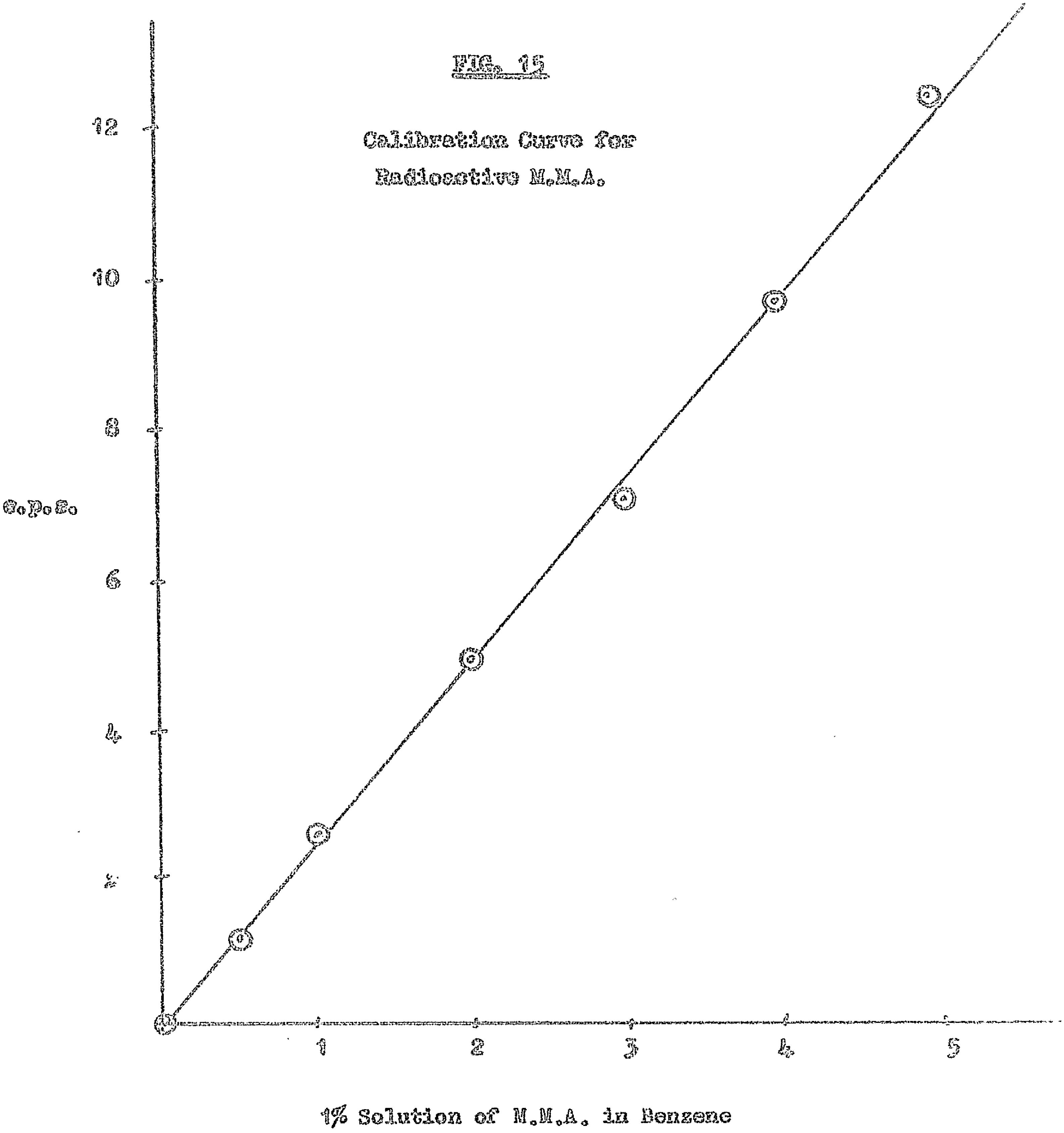


FIG. 15

Calibration Curve for Radioactive M.M.A.

($\overline{DP}$ = 7). From this solution, the radioactive M.M.A. was then distilled off on the vacuum line for 4 hours. The activity of the 0.00208 gms. telomer was found to have increased by 0.198 cps. after the treatment with radioactive M.M.A. This was calculated to correspond to approximately 1 molecule of M.M.A. to 1 molecule of telomer.

Calculations for chain transfer constants.

The following equation for the determination of chain transfer constant for short chain polymers has been derived on page 25.

$$\overline{DP} = \frac{k_{p,n}[M]}{k_{tr,n}[S]} + 1$$

In fig. 11, fig. 12 and fig. 13, $\overline{DP}$'s are plotted against M.M.A./TBr ratio (feed composition) for the values obtained at 25°C, 40°C, and 60°C respectively. (See tables 10, 12, and 13). As required by theory, the experimental points lie on straight lines which intersect the ordinate at $\overline{DP} = 1$. The gradient of these lines can be identified with the value of $k_{p,n}/k_{tr,n}$ at the experimental temperature. The values of $C_s = k_{tr,n}/k_{p,n}$ can thus be readily obtained. Table 15 shows these results together with some additional data used to construct the Arrhenius plot for determining activation energy.

Table 15. Chain transfer constants at 25°C, 40°C, and 60°C together with activation energy data.

Temperature °C	$\frac{k_{p,n}}{k_{tr,n}}$	$\frac{k_{tr,n}}{k_{p,n}}$	$\frac{1}{\text{Abs. Temp.}}$ $(^{\circ}K)^{-1}$	$\log\left[\frac{k_{tr,n}}{k_{p,n}} \times 100\right]$
25	6.7	0.149	0.00336	1.174
40	5.5	0.182	0.00319	1.260
60	4.8	0.208	0.00305	1.318

Calculation of activation energy

The relationship between the velocity coefficient and activation energy is expressed by the Arrhenius equation

$$k = A_1 e^{-E/RT} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (24)$$

where k is the velocity constant of the reaction, A_1 is the frequency factor, representing the total frequency of encounters between the reacting species, E is the energy of activation for the reaction, T is the absolute temperature at which the reaction occurs, and R is the molar gas constant.

The Arrhenius equation for transfer and propagation reaction can be written as

$$k_{tr,n} = A_{tr,n} e^{-E_{tr,n}/RT} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (25)$$

$$k_{p,n} = A_{p,n} e^{-E_{p,n}/RT} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (26)$$

From equations 25 and 26 we obtain

$$\log_{10} \frac{k_{tr,n}}{k_{p,n}} = \frac{1}{2.303RT} (E_{p,n} - E_{tr,n}) \quad \ldots \quad (27)$$

where suffixes $t_{r,n}$ and p,n refer to transfer and propagation respectively.

Fig. 16 shows the plot of log $k_{tr,n}/k_{p,n}$ against 1/T (see table 1) for the temperature range 25°C to 60°C.

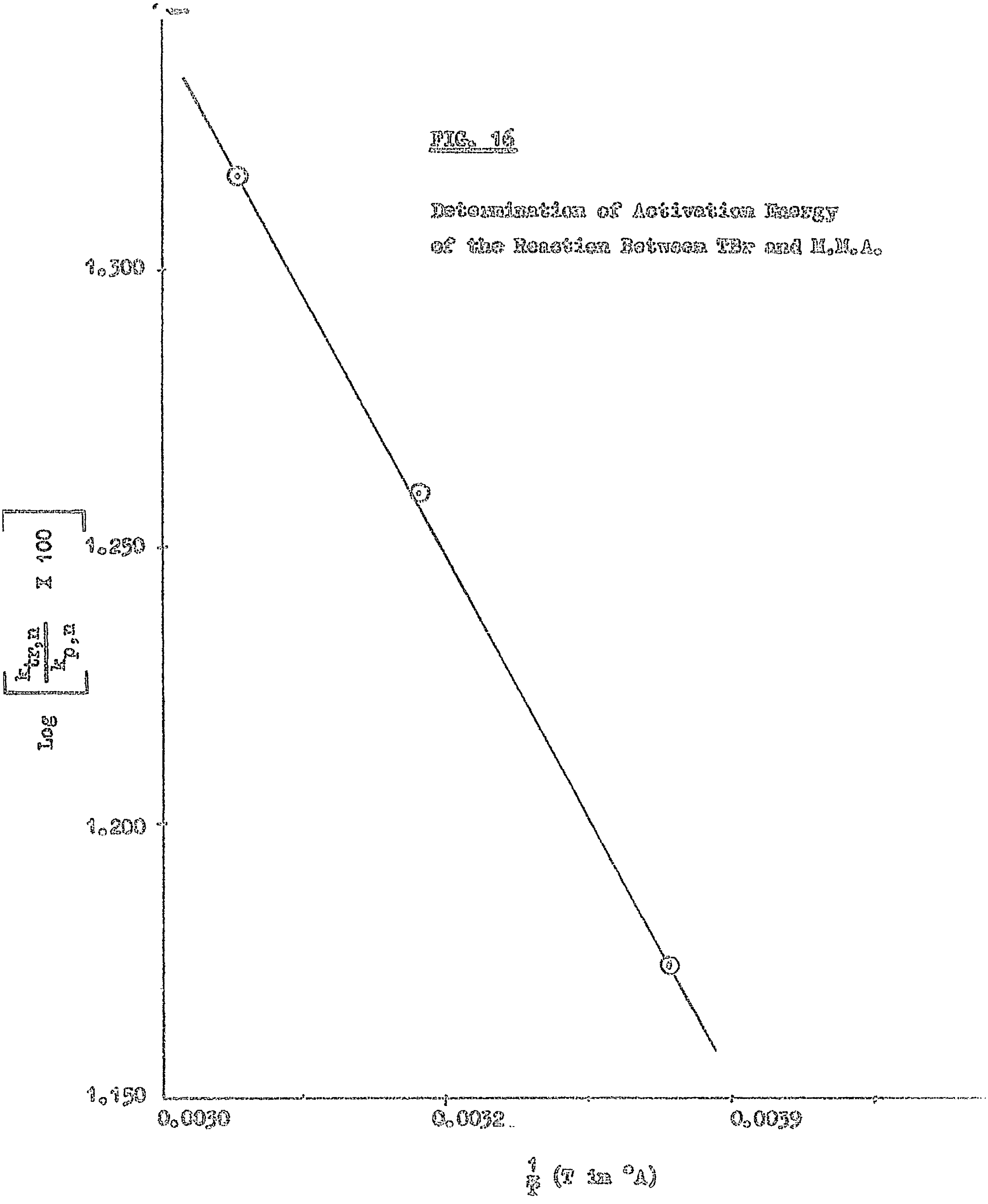


FIG. 16

Determination of Activation Energy of the Reaction Between TBr and M.M.A.

Equation 27 gives the slope of this line as $E_{p,m} - E_{tr,m}/2.303$

This led to the value of

$E_{tr,m} - E_{p,m} = +2.2$ K cals/mole

Specific gravity of 1,1 adduct.

A 10:1 molar mixture of TBr and M.M.A. was irradiated in a dilatometer of 3 mm. capillary to 100% conversion. The total contraction for 100% conversion was followed over a period of three days, after which no further contraction took place. The molar ratio of [TBr] / [M.M.A.] increased as more and more 1,1 adduct was formed. This resulted in a building up of the [TBr] / [M.M.A.] mole ratio and since 1,1 adduct is the lowest addition product possible, at still higher [TBr] / [M.M.A.] ratio the same product will be produced. The specific gravity of the 1,1 adduct, thus isolated, was calculated to be 1.65 from the total contraction measurements.

A check was made by determining the specific gravity with a 1 ml. pyknometer. This gave a value of 1.63. The average value of 1.64 has been used for further calculations in this thesis.

Rate dependencies on reactant concentrations.

It has been shown in the kinetic scheme on page 18 that the rate of reaction would vary as follows.

(1) Absolute rate would be proportional to $[TBr]^{0.5}$ and

[M], when addition of trichloromethyl radical to monomer is the rate controlling step.

(2) Absolute rate would be proportional to $[TBr]^{1.5}$ when transfer with TBr is the rate controlling step.

(3) Absolute rate would be proportional to $[TBr]^{0.5}$ and [M] where polymerisation is the chief reaction.

It may be assumed from the reaction scheme that excess of TBr or excess of M.M.A. will produce conditions (1) and (3) respectively while (2) may possibly be produced in the intermediate stages.

These assumptions have been investigated by studying the effect of reactant concentration on the rate of reaction. In a two component liquid system, it is not possible to vary the concentration of one reactant without automatically varying the concentration of the other. Bengough and Thomson[20] have used benzene as a non reactive diluent to make similar studies of the vinyl chloride and TBr system. However, when benzene was used with the M.M.A./TBr system the results obtained, shown in table 16, indicated that the rates did not vary as expected from theory. It was therefore concluded that benzene may have some interfering reaction with the M.M.A./TBr system.

Table 16. The effect of excess TBr concentration on the fractional rate of reaction using benzene as a diluent at 25°C.

[M.M.A] m/1	[TBr] m/1	% per hour contraction
0.738	8.86	1.02
"	8.71	1.03
"	7.75	1.02
"	6.65	1.02
"	5.91	1.04

Table 17. The effect of M.M.A. concentration on the rate of reaction using benzene as a diluent at 25°C (excess TBr).

[TBr] m/1	[M.M.A] m/1	% per hour contraction
7.75	0.632	1.03
"	0.738	1.02
"	0.884	1.04
"	0.980	1.09

It can be seen from table 16 and table 17 that the molar ratio range was varied within the conditions where 1,1 adduct is the predominant product (case 1). It should be noted too, that, in both these tables, the rate quoted is the fractional rate. Since the absolute rate is proportional to the product of the fractional rate and the M.M.A. concentration, it can be seen that in table 16, where the M.M.A. concentration is invariant, the fractional rates are in fact proportional to the absolute ones, and do not show the variation with TBr concentration which is predicted by the above theory. This may be attributed to the interference by the diluent benzene. As will be pointed out in the discussion, radioactive benzene studies showed that benzene was being incorporated in the telomers in some chemically bonded form which made it impossible to distil it off on the vacuum line, even after pumping for up to two days. On the strength of these results it may appear that benzene is reacting with M.M.A. in preference to TBr, thus keeping the rate of reaction constant even when TBr concentration is varied from 8.86 to 5.90 m/l.

In table 17, on the contrary, where the M.M.A. concentration varies, it is necessary to estimate the product of fractional rate and M.M.A. concentration to compare the values of absolute rate. When this is done, it can be seen that the absolute rate is virtually proportional to M.M.A. concentration as would be suggested by the theory. Owing to the deviation from the expected course of the reaction when the TBr concentration was varied, an alternative diluent was sought.

It was hoped that carbon tetrachloride whose molecular species resemble those of TBr in chemical structure would be a satisfactory diluent. Neither benzene nor carbon tetrachloride gave rise to any apparent contraction when photolysed in the presence or absence of TBr for 2 hours, but, even if there was any small decomposition due to photochemical excitation or transfer reaction in the case of carbon tetrachloride, this would result only in the generation of trichloromethyl radicals. Since the reaction mixture already contained these species, the system would not have any added impurity. The results obtained with carbon tetrachloride are shown in table 18 and table 19.

Table 18. The effect of TBr concentration on the rate of reaction using carbon tetrachloride as a diluent at 25°C.

[M.M.A.] m/1	[TBr] m/1	$\frac{[TBr]}{[M.M.A.]}$	$\sqrt{[TBr]}$	Rate % per hour contraction	approx. DP
0.738	9.070	12.30	3.01	1.050	1
"	7.750	10.50	2.78	0.970	1
"	7.020	9.50	2.66	0.950	1
"	5.910	8.00	2.44	0.820	1
"	3.240	4.40	1.80	0.650	2.3
"	1.000	1.35	1.00	0.510	4.9
"	0.468	0.63	0.68	0.420	14
"	0.250	0.27	0.50	0.333	20
"	0.112	0.15	0.33	0.250	60
"	0.040	0.05	0.20	0.204	>60
"	0.000	0.00	0.00	0.107	—

This table covers the results of a series of experiments in the presence of diluent carbon tetrachloride using a constant concentration of M.M.A., and TBr concentrations ranging from nil to a 12 fold excess. As the concentration of TBr is reduced it ca be seen that there is a concomitant reduction in the rate. It should be noted that a fractional rate of 0.107%/hour is observed in the absence of TBr due to photopolymerisation of M.M.A.

In view of the wide range of TBr to M.M.A. concentration, the results in this table should be able to be used to distinguish the different rate controlling steps outlined on pages 18 - 20. This has been done in fig. 17 in which fractional rate has been plotted against $\sqrt{[TBr]}$, and which shows that the results do in fact fall into three sections indicated by the straight lines OA and BC and the curve AB. The straight line BC represents the range where 1,1 adduct is produced. In the range where average $\overline{DP}$ is 14 or above the plot is identified with the other line OA of different gradient i.e. this is identical with the polymerisation reaction. This falls well within expected theoretical aspects.

The significance of these results will be further dealt with in the discussion.

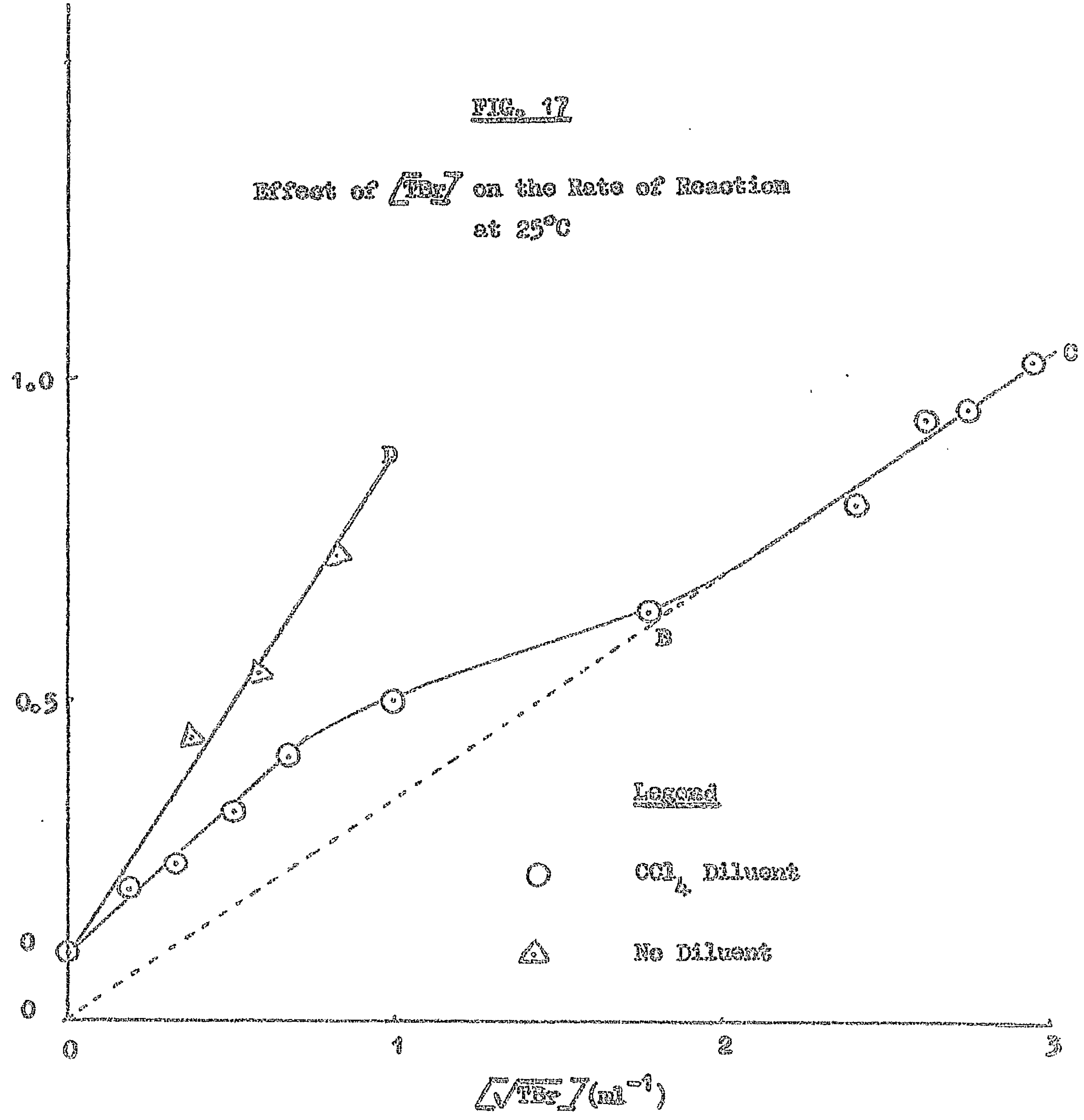


FIG. 17

Effect of [TBr] on the Rate of Reaction at 25°C

Table 19. **The effect of varying M.M.A. concentration on the rate of reaction, using carbon tetrachloride as a diluent at 25°C, and constant excess TBr concentration.**

[TBr] m/l	[M.M.A.] m/l	[TBr] / [M.M.A.]	% per hr. contraction
7.75	0.632	12.27	1.002
7.75	0.738	10.50	1.003
7.75	0.980	7.92	0.980

The results of this table show that absolute rates (which are proportional to the product of M.M.A. concentration and fractional rate) are proportional to the M.M.A. concentration over the M.M.A. concentration range from 0.980 to 0.632 m/l. The dependence of rates on M.M.A. concentration is satisfactorily established by using either of the diluents (benzene or carbon tetrachloride). Experiments were also repeated by using a Chance OX1 filter to see if this relationship holds when light of 3650°A in predominance is used. Table 20 shows the results obtained.

Table 20. **The effect of varying M.M.A. concentration on the rate of reaction using carbon tetrachloride as a diluent and OX1 filter at 25°C. (Constant excess TBr concentration)**

[TBr] m/l	[M.M.A.] m/l	[TBr]/[M.M.A.]	% per hr. contraction
7.75	0.632	12.27	0.79
7.75	0.738	10.50	0.79
7.75	0.980	7.92	0.79

As expected the % per hour contraction has decreased due to the decrease in light intensity but it remains constant over the [TBr]/[M.M.A.] molar ratio range of 12.27 to 7.92.

Experiments were repeated in the absence of any diluent at very high concentrations of methymethacrylate. The results obtained are summarised in table 21.

Table 21. The effect of TBr concentration on the rate of reaction in the absence of diluent at high concentrations of M.M.A. at 25°C.

[M.M.A.] m/l	[TBr] m/l	[TBr]/[M.M.A.]	$\sqrt{[TBr]}$	% per hr. contraction
8,42	1.00	0.119	1.000	0.780
8,74	0.66	0.017	0.814	0.738
9.03	0.36	0.075	0.600	0.540
9.20	0.16	0.040	0.400	0.455
9.36	0.00	0.000	0.000	0.107

These results show similar trend to those of the experiments carried out in carbon tetrachloride diluent where M.M.A. was in excess (table 18). The results have been added to fig. 17 as a straight line OD. It is interesting to note that the slope of OD is not the same as that of OA possibly due the much higher concentrations of M.M.A. but that the same fractional rate was found in the absence of TBr.

Heat of addition of 1,1 adduct of TBr and M.M.A.

A number of calorimetric methods have been reported for measuring heats of reactions adiabatically[28-30] or isothermally[31]. The heat evolved is measured directly or indirectly as a function of some physical property at a fixed extent of reaction. Direct measurement of the temperature rise in the reaction vessel using a thermistor[32,33] or a thermocouple method[34] has been reported. These methods are usually complicated in that they involve use of intricate apparatus and lengthy procedures. Due to its simplicity and good reproducibility, a dilatometric method[35] has been used in the present work. Reaction vessels of the kind as described on page 31 (fig. 4) have been employed. A molar ratio of TBr and M.M.A. of 10 : 1 has been used which according to table 10 produces 1,1 adduct at 25°C.

Measurement of heat of reaction.

The measurement of volume contraction by means of a dilatometer is widely used for determining reaction rates under stationary state. The dilatometric method is also now used to follow volume changes in non-stationary state[35,36,37]. This involves measuring the rate of expansion (ϵ) due to self heating during the first 10 - 20 seconds (assumed to be adiabatic) and the rate of contraction (z) due to reaction under thermal steady state conditions. Instead of the initial rate of expansion (ϵ), the initial post irradiation rate of contraction (y), due to cooling may also be used. The method is obviously limited to photoinitiated reactions.

Theoretical[35]

The following derivation of an equation by Bengough[35] enables heat of reaction to be evaluated from the ratio of ϵ/z.

In a chemical reaction such as the reaction of TBr and M.M.A., the total change in volume is due to

(a) an expansion produced by the heat generated in the reaction

(b) a contraction due to difference of density of the polymer and the monomer

(c) and a contraction due to the heat loss to the surroundings.

The overall rate of contraction (c) can be written as

$$c = z + y - \epsilon \quad \dots \quad \dots \quad \dots \quad \dots \quad 27.$$

Both Z and ϵ are clearly proportional to the rate of reaction and, for a polymerisation proceeding at a rate of x'% per second, are given by the following equations

$$Z = x'(\rho - \rho')/\rho' \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 28.$$

$$\epsilon = x'\Delta H\alpha/sM' \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 29.$$

where ΔH = heat of reaction in cals/mole.

α = coefficient of expansion of monomer.

M' = molecular weight of monomer.

s = specific heat of monomer.

ρ = density of monomer.

ρ' = density of product formed.

Dividing 28 and 29 and solving for H, we get,

$$\Delta H = \frac{\epsilon s M'(\rho - \rho')}{Z \alpha \rho'} \quad \text{cals/mole}$$

The value of ϵ was evaluated from the following two methods.

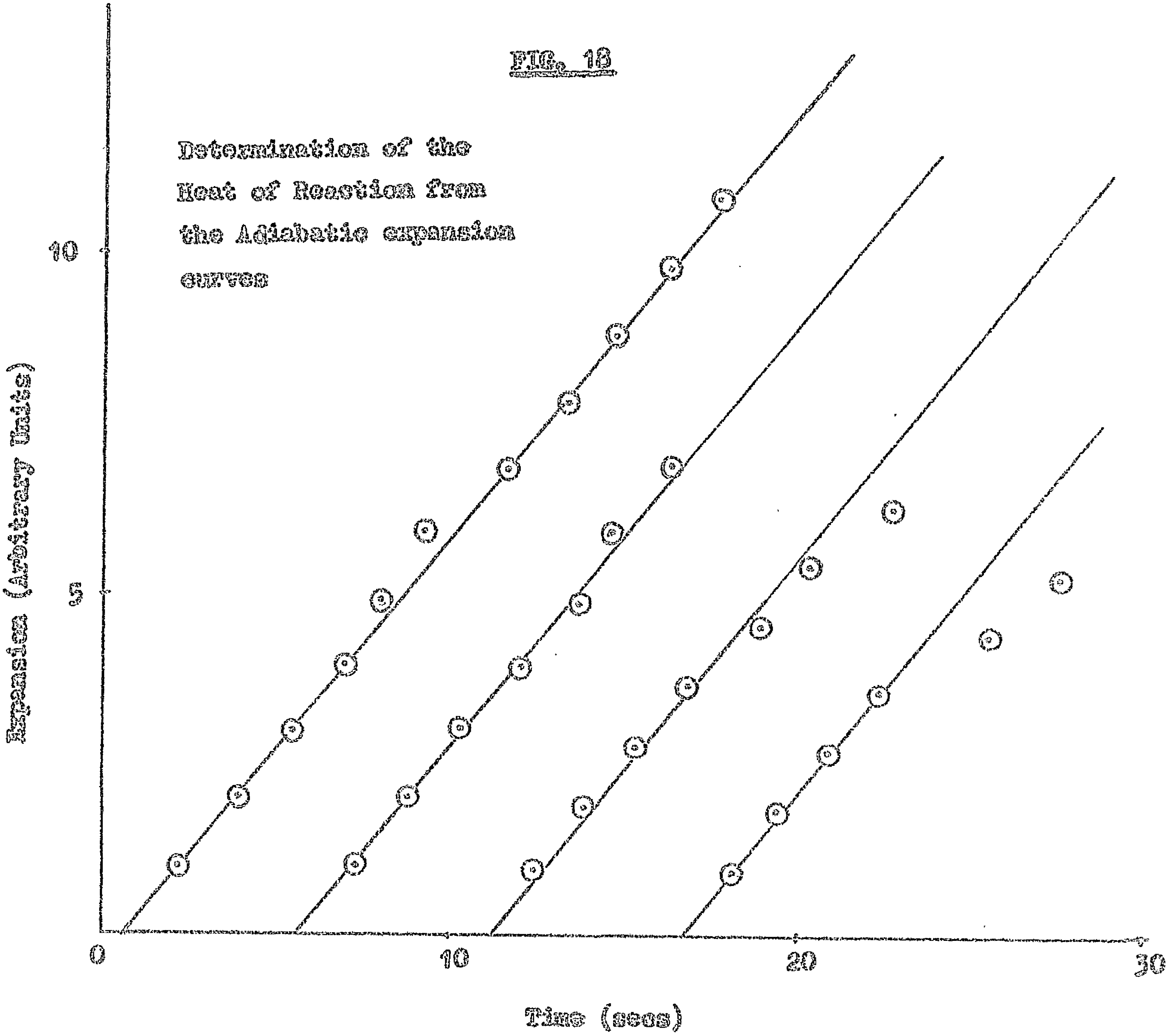
(a) <u>Direct measurement of ϵ from the initial rate of expansion.</u>

The usual method of following the movement of the meniscus with a cathetometer is unsatisfactory to measure rates under adiabatic conditions which last for

10 - 20 seconds. The system used here to record the movement of the meniscus during adiabatic conditions consisted of a cathetometer in which the cross wire of the eye piece had been replaced by a calibrated scale, and a strip chart time recorder fitted with a depressing key. As the meniscus crossed suitable marked division on the scale in the eye piece, the time was recorded by depressing the key which applied a voltage to the pen recorder. When the dilatometer had reached thermal equilibrium in the water bath at 25°C., the cathetometer was focused on the meniscus and set to read a convenient division on the calibrated scale in the eye piece. The irradiation was then commenced by depressing another button which operated the U.V. shutter electromagnetically. Fig. 19 shows some measurements of the expansion immediately after the irradiation has commenced. The lines are reasonably parallel which indicates good reproducibility. After about 6 - 10 secs. the rate of expansion fell off due to heat losses. The adiabatic duration time can be prolonged by using vacuum jacketed dilatometers or by using larger dilatometer bulbs made from thicker glass. This would necessitate,

FIG. 18

Determination of the Heat of Reaction from the Adiabatic expansion curves



however, prolonged thermal equilibrium times for following stationary state rates. The results from these rates give the value of $\epsilon - z$. The value of ϵ can be calculated since z is readily obtained from the gradient of the stationary state rate plot (fig. 18). These values are tabulated in table 23.

(b) Direct measurement of ϵ from the initial cooling contraction rate.

The irradiation was continued for about 15 minutes to reach steady state conditions. The rate z was obtained by following contraction under steady state. (curve OA, fig. 19). The irradiation was then cut off. Contraction as a function of time was measured immediately following the end of irradiation. This is shown by the curve AB in fig. 19, the gradient of which gave the direct value of ϵ. These values are also tabulated in the table 23.

Mean values of specific heat, specific gravity etc. of the reactants.[37]

The equation derived earlier for the heat of reaction is

$$\Delta H = \frac{\epsilon}{z} \left\{ \frac{sM'(\rho - \rho')}{\alpha \rho'} \right\}$$

As there are two reactants, the heat capacity (sM'),

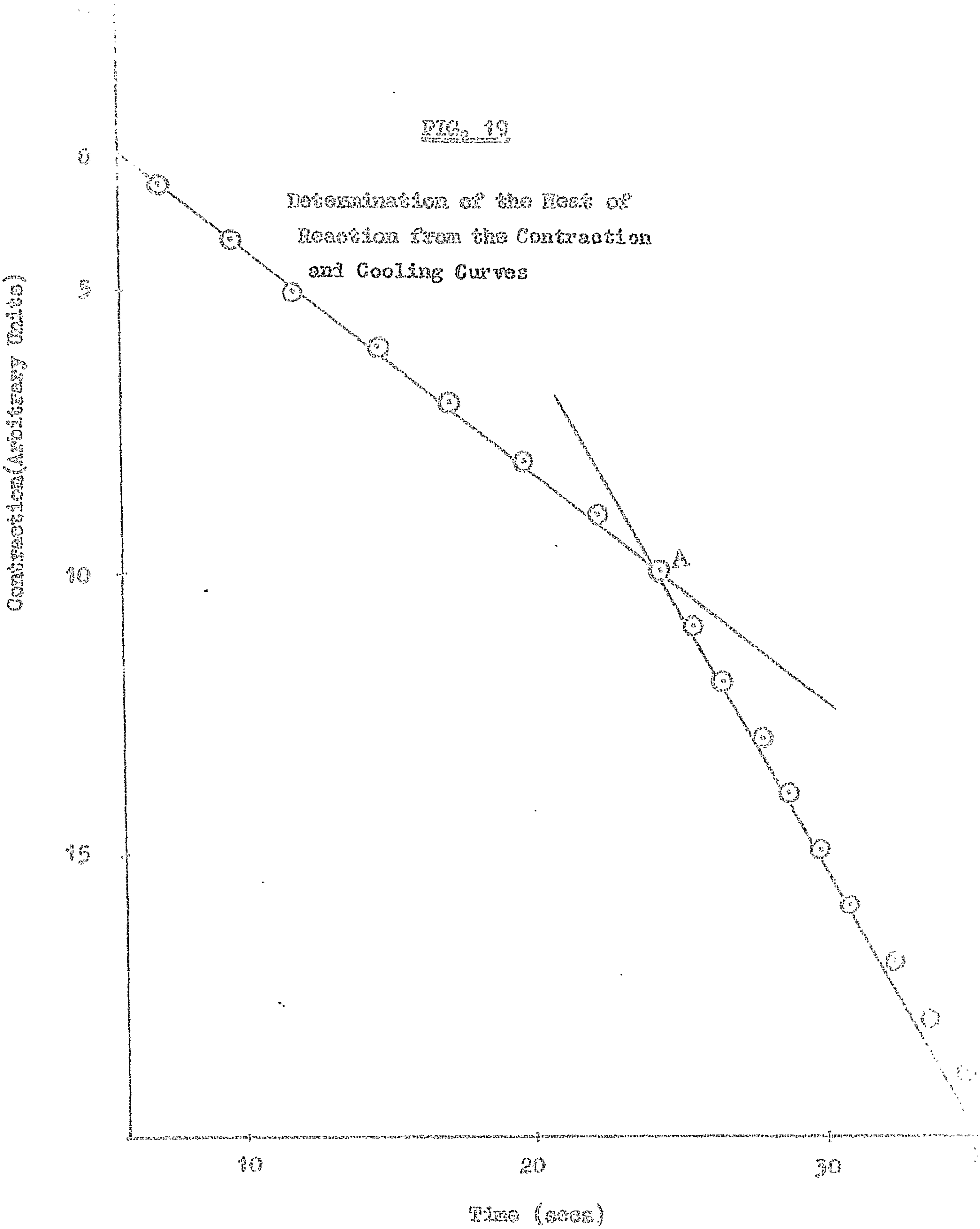


FIG. 19

Determination of the Heat of Reaction from the Contraction and Cooling Curves coefficient of expansion and specific gravity now refer to the reactant as a whole. Since the reaction mixture contained 10 moles of TBr and 1 mole of M.M.A the mean heat capacity is given by $10M_1s_1 + M_2s_2$, the coefficient of expansion by

$$(10M_1\alpha_1/\rho_1 + M_2\alpha_2/\rho_2)/(10M_1/\rho_1 + M_2/\rho_2)$$

the specific gravity of the system before reaction by

$$(10M_1 + M_2)/(10M_1/\rho_1 + M_2/\rho_2)$$

and specific gravity of the system after reaction by

$$(9M_1 + M_3)/(9M_1/\rho_1 + M_3/\rho_3)$$

where suffixes 1, 2 and 3 refer to TBr, M.M.A. and 1,1 adduct respectively.

The physical constants required in the calculation of ΔH are given in table 22. Since the density of 1,1 adduct was not available in the literature, it was determined as described earlier. Coefficients of expansion were measured dilatometrically in the usual way.

Table 22. Physical constants for TBr, M.M.A. and 1,1 adduct.

	TBr	M.M.A.	1,1 adduct
Molecular weight	198	100.11	298.11
Specific heat	0.18	0.49	—
Coefficient of expansion	1.062×10^{-3}	1.24×10^{-3}	—
Specific gravity	2.006	0.936	1.64

Table 23. Heat of formation of 1,1 adduct of TBr and M.M.A., $sM'(\rho - \rho')/\alpha\rho' = -7925$, mole ratio TBr/M.M.A. = 10/1

ϵ	initial expansion rate $\epsilon - z$	reaction rate z	cooling rate ϵ/z	ΔH K. cals/mole
—	5.0	11.7	2.34	18.55
—	4.6	10.0	2.17	17.20
—	4.7	11.0	2.34	18.55
6.2	5.0	11.2*	2.24	17.75
6.2	4.6	10.8*	2.34	18.55
6.4	4.8	11.2*	2.34	18.55
—	4.1	9.4	2.29	18.14

* The value of ϵ has been calculated from the values obtained for

$$\epsilon - z \text{ and } z$$

The values of expansion are quoted in arbitrary units.

Table 23 indicates that the values of ϵ/z are in close agreement and reproducible. From the results in the above table, the mean value for heat of addition is 18.35 K. cals/mole.

DISCUSSION

DISCUSSION

Preparation of Telomers.

A number of chain transfer agents are available for the preparation of M.M.A. compounds e.g. mercaptans, tetrabromoethane and bromotrichloromethane. However, the M.M.A./TBr system was chosen in the first place to clarify differences of results obtained by previous workers. TBr is also perhaps the most suitable chain transfer agent for telomerisation studies of M.M.A. Its excitation wave length is from 3300 to 3900°A and since the C - Br bond is weaker than the C - Cl bond, it follows that photolysis could yield an equal number of bromine and trichloromethyl radicals. When isolating the products, TBr, being volatile, is easy to remove by distillation on the vacuum line. Telomerisation carried out with TBr always gives end groups which are halogen in character. This is quite useful for determination of molecular weights etc. by end group analysis methods.

However, one problem in handling TBr is that it attacks mercury slowly and thus prolonged contact of its vapour with the mercury of the mercury diffusion pump must be avoided. This can easily be achieved by using liquid nitrogen as a coolant in the traps immediately before and after the mercury diffusion pump.

Limitations in the preparation of telomers.

As the reaction proceeds, continuous changes in the molar ratio of the reactants take place. If the amount of M.M.A. is small compared with TBr then there will be a large deviation from the original concentration of the reactants. This is demonstrated in the following table.

Table 24. Concentration changes in the M.M.A./TBr system during telomerisation.

Quantities of TBr and M.M.A. reacted (moles)	[M.M.A.] moles	[TBr] moles	[TBr]/[M.M.A.]
0	1.00	20.00	20.0/1
0.25 moles TBr 0.25 moles M.M.A.	0.75	19.25	26.4/1
0.50 moles TBr 0.50 moles M.M.A.	0.50	19.50	39.0/1

% conversions were therefore carefully watched and kept below 7% of the reactant present in lowest concentration, so that final concentrations of the reactants were not very different from the initial concentrations.

When appreciable quantities of telomers were required for the determination of physical properties such as density, molecular weight, very large dilatometers (up to 100 mls.) had to be used since the reaction had to be stopped below 7% conversion.

Telomers of $\overline{DP}$ less than 1.5 were viscous resin-like materials and were very difficult to handle for weighing out into cryoscopic cells for the determination of molecular weight. Thus the results with these materials are liable to be less accurate than for the solid telomers.

<u>Density of 1.1 adduct.</u>

This was determined by reacting M.M.A. and TBr in molar ratio of 1/10 and completing the reaction to 100% conversion over 3 days continuous irradiation. As the reaction proceeded it resulted in a build up of the [TBr]/[M.M.A.] mole ratio and since 1,1 adduct is the lowest addition product possible, at still higher [TBr]/[M.M.A.] ratios, the same product was produced. The density of 1.63 g/ml was found on the isolated product using a 1 ml. pyknometer. It must be pointed out that such a long irradiation would perhaps result in the formation of some hexachloroethane (produced by termination reaction between two trichloromethyl radicals). From the values of rate of initiation[4] = 7.98×10^{-7} mole/litre sec. and termination constant $k_{t,a} = 1.3 \times 10^{5}$ mole/l. sec., it was estimated that over the irradiation period of 3 days 0.64 mole/litre of hexachloroethane may have been produced.

The value of density was therefore also determined by total contraction measurements over 100% conversion. This was, however, found to be 1.65 g/ml which is in excellent agreement with the value obtained by the pyknometer method. Bengough and Thomson obtained the densities of 1,1 adducts for vinyl chloride[20] with TBr and vinyl acetate[14] with TBr. Table 25 shows the comparison of these values with the corresponding polymers.

Table 25. Comparison of densities of 1,1 adducts of some vinyl monomers with TBr and the corresponding monomers and polymers.

	density of monomer at 25°C. g/ml	density of 1,1 adduct at 25°C. g/ml	density of polymer at 25°C. g/ml	density of 1,1 adduct/ density of polymer
M.M.A.	0.936	1.640	1.190	1.38
vinyl chloride	0.905	1.825	1.403	1.30
vinyl acetate	0.925	1.660	1.187	1.39

It can be seen from these results that the value obtained for the density of 1,1 adduct of M.M.A. with TBr is in keeping with the values for the 1,1 adducts of vinyl chloride and vinyl acetate with TBr.

Molecular weight measurements cryoscopically.

Sources of Errors.

The classical Beckman procedure[39] is too insensitive for the present measurements, since low depressions are produced because of the higher molecular weight of the telomers being measured. Refinements on these methods have been made by use of a calibrated thermocouple[40] or a resistance thermometer[41] and more recently a thermistor[42-44]. The latter method was further refined by the design of the apparatus used in this work (see page 30). General sources of errors such as condensation of moisture from the atmosphere, interference due to crystallisation and heat of fusion were minimised. Since strong hydrogen bonding groups such as OH, NH, NH_2 and COOH are not present in M.M.A. and also benzene a non polar solvent has been used, problems due to association of the molecules have not been experienced.

Precision, accuracy and sensitivity.

The spot galvanometer used to deduct the null point permitted the measurement of resistance changes to the nearest 0.1 ohms. Reproducibility of repetitive readings was however not good since even the very minute traces of moisture condensing from the atmosphere depressed the freezing point. Also during the freezing process the plot of time against temperature is not a straight line parallel to the time axis (fig. 20.), a continuous gradual drift being produced due to a lowering of the temperature in the cell. All measurements were therefore made immediately after the freezing process had commenced. Measurements of the molecular weights of naphthalene, TBr and monochloro-2,4 dinitro benzene were repeated 5 times for each experiment. This showed that the error was within 3%. Accuracy on higher molecular weight telomers was difficult to evaluate since samples of suitable substances of known molecular weights in these regions are difficult to obtain.

Comparison of results on telomerisation of methylmethacrylate/TBr system with previous workers.

As indicated earlier, considerable differences

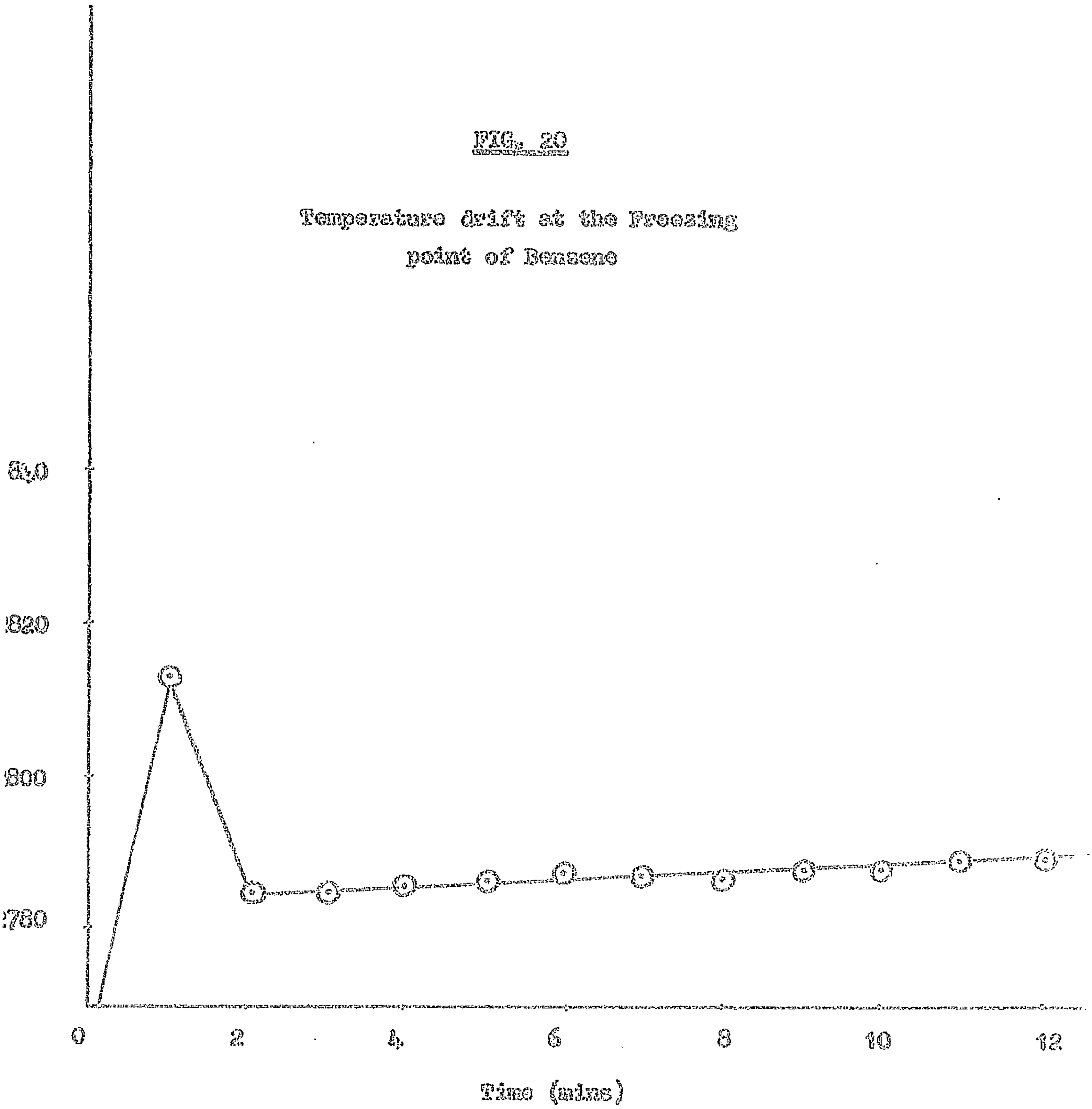


FIG. 20

Temperature drift at the Freezing point of Benzene exist between these results and those obtained by Robb and Senogles[3] and also independently by Brash[4]. Table 26 shows a comparison between the results of these workers.

<u>Table 26.</u> <u>Relationship between the molar ratios of the reactants and $\overline{DP}$ of the products isolated.</u>

$\frac{[M]}{[TBr]}$	$\overline{DP}$ (This work)	$\overline{DP}$ (Robb and Senogles)[3]	$\overline{DP}$ (Brash)[4]
0.054	—	2.425	—
0.102	1.35	—	4
0.114	—	2.850	—
0.125	1.02	—	—
0.133	—	3.500	—
0.199	—	3.900	—
0.200	2.11	—	—
0.303	—	3.950	—
0.333	2.73-3.0	—	—
0.562	—	3.950	—
0.666	4.90	—	—
0.768	—	4.000	—
1.000	7.40-8.20	3.950	19
1.500	10.1-10.9	—	—
2.000	14.10	5.150	25
2.220	—	5.500	—
2.900	—	5.150	—
3.080	—	5.600	—
4.160	13.80	—	—
5.070	—	6.725	35
6.820	—	7.900	—
10.900	—	12.050	—

From this table it can be seen there are differences both in the values and the trends of the values of $\overline{DP}$ for approximately the same ratio of the reactants. It should be pointed out that the telomerisation was carried out at 30°C by Robb and Senogles[3] as against 25°C by Brash[4] and in this work. This, however, could not be expected to account for such differences as can be seen from the results at 40°C and 60°C (see tables 12 and 13). Further discrepancies between this work and that of Robb and Senogles[3] have been noted in the physical appearance of the telomers thought to be of the same molecular weight. Whereas all products except those of $\overline{DP} < 1.5$ obtained during this work were white fluffy powder like materials, Robb and Senogles[3] found that the products of up to 2.5 $\overline{DP}$ were viscous liquids and up to 4.0 $\overline{DP}$ were gel like solids. Melting points of the solids obtained in this work have been shown in table 11. These results show that the melting points of these telomers increases from 35°C to approximately 111°C for telomers of the $\overline{DP}$ range 2 to 16.5. From table 26 it is interesting to note that, for ratios of M.M.A./TBr from 0.054 to 0.333, molecular weights obtained in this work are less than those obtained by Robb and Senogles[3]. This trend reverses itself for molar ratios of 0.333 onwards.

Isolation of products.

Details of the isolation process have already been mentioned. Since product purity is of the utmost importance in the molecular weight measurements, efforts have been made in the course of this work to study and compare methods used both here and by Robb and Senogles[3].

In an effort to check the values obtained in this work, molecular weights on some randomly selected samples of telomers were measured by several different methods.

(a) Cryoscopic - using benzene as solvent.

(b) Vapour pressure - using benzene as solvent.

(c) Carbon, hydrogen and halogen analysis. The ratio of carbon/total halogen and % carbon was selected in preference to carbon/hydrogen or other ratios to overcome the possibility of the product being hygroscopic.

(d) Radioactive tracer technique.

Also some samples which had been allowed to remain at room temperature for approximately one year in the dark had their molecular weights redetermined cryoscopically to see whether any changes in structure occurred during this time. These results are shown in table 27.

Table 27. Showing the values of molecular weights obtained by various methods.

[M.M.A]/[TBr]	preparation temp. °C	Molecular weight values					
		cryoscopic		vap. pr.	R. A. tracer	analysis	
		initial value	after one year			C/Hal.	%C
0.200	40	400	510	680	—	1,030	980
0.200	25	411	—	471	450	—	—
0.333	25	500	540	—	580	—	—
0.400	60	540	656	800	—	960	1,100
1.000	60	755	840	1,075	900	2,150	2,200
2.000	25	1,610	—	1,861	—	2,550	—

It can be seen from table 27 that there is a tendency for slight increase in the value of molecular weight when telomers were stored over a period of one year in the dark. It would seem that there is a reasonable agreement between the results obtained by cryoscopic, vapour pressure and radioactive tracer methods, but there is substantial discrepancy with the results obtained by the analysis method. This led to the suggestion that benzene may have been incorporated in the telomer as benzene of crystallisation during the freeze drying process. To clarify this point experiments were carried out using radioactive benzene as solvent for the telomer in the freeze drying process. These experiments showed that there was a significant increase in the radioactivity of the telomer after the freeze drying, suggesting that benzene was in fact incorporated in the telomer. From the increase in radioactivity of the telomer, whose molecular weight was known from cryoscopic measurements, it was possible to determine the amount of benzene being incorporated. For example, in one case for 0.0050 gms. of telomer of $\overline{DP} = 7.0$, back ground counts before freeze drying were 0.5 cps. and after freeze drying 0.7 cps. From the calibration curve of radioactive benzene, it was known that 73 cps. $\equiv$ 0.1 cc of benzene. It can be readily shown that the increased activity of 0.2 cps. represents 2.8 x 10^{-4} cc benzene which is present in 0.0050 gms. of telomer of average molecular weight 900. It follows that the telomer ($\overline{DP}$ = 7) contained approximately 0.6 molecules of benzene per molecule of telomer. The elemental analysis of this particular sample showed that it contained 54% carbon, which corresponds to $\overline{DP}$ of 20. Telomers of molecular weight 900 ($\overline{DP}$ = 7) should however have 48% carbon value, but the presence of benzene of crystallisation would increase its carbon content as shown by the following table.

Table 28. Showing increase in % carbon content in telomer of $\overline{DP}$ = 7.0 with increasing molecules of benzene of crystallisation.

	% carbon value
Telomer + no benzene	48.0%
Telomer + 0.5 molecules of benzene	49.5%
Telomer + 1 molecule of benzene	51.0%
Telomer + 2 molecules of benzene	55.0%

This table shows that just under two molecules of benzene of crystallisation would have to be present per molecule of telomer to give a product containing 54% carbon. 0.6 moles of benzene of crystallisation were found experimentally.

Since benzene is a solvent for the cryoscopic method, its presence in the telomer would only slightly affect the value of depression of the freezing point and hence molecular weight should not be altered significantly. The same argument would apply to the determination of molecular weight by the vapour pressure method. Robb and Senogles[3] used the elemental analysis method for determining their molecular weight but since they did not freeze dry their products, the molecular weight values should not have been affected by the presence of benzene of crystallisation.

An examination of table 26 indicates that for when the feed ratio of [M.M.A.] / [TBr] is greater than 1, values of $\overline{DP}$ obtained by Robb and Senogles[3] are lower than those obtained in this work and even lower than those of Brash[4]. For example at [M.M.A.] / [TBr] ratio = 2 the $\overline{DP}$ obtained by Robb and Senogles[3] is 5 compared with 25 obtained by Brash's work[4] and 14 obtained in this work. This latter value is achieved by Robb and Senogles[3] only when using a six fold increase in the feed ratio. This led to further experiments to see if residual M.M.A. and TBr were being completely removed by their method of isolation of the telomers. By redissolving some telomer in radioactive M.M.A. and pumping off this M.M.A. in the normal manner for 4 hours to constant weight, it was found that there was an increase in the radioactivity of the telomer after this, but not quite so much as if the product were subsequently freeze dried. The following results were obtained on one such sample.

Background activity of the telomer = 0.5 cps.

0.0020 gms. of telomer (treated with radioactive M.M.A.) without freeze drying = 0.698 cps.

0.0020 gms. of telomer subsequently freeze dried = 0.55 cps.

It was calculated that the increase in activity of 0.198 cps. corresponded to 1 mole of unreacted M.M.A. per molecule of the telomer (DP = 7). Since the radioactive M.M.A. contained inhibitor, this increase in activity could not be due to polymerisation of added radioactive M.M.A. in the telomer. Some caution must be exercised in comparing these results with those of Robb and Senogles[3], since the latter workers carried out their evacuation for a period of 16 hours and there must be an inevitable difference in the vacuum conditions used. This may also explain why the molecular weight of the telomers increases on aging which can perhaps be due to post telomerisation of traces of unreacted M.M.A.

Since no radioactive TBr was available similar studies could not be carried out to ensure that no unreacted TBr was trapped in the telomer.

From the above discussion it would appear that the cryoscopic method, vapour pressure and radioactive tracer methods lead to the most reliable values of the molecular weight of the telomers which have been freeze dried.

Chain transfer constants.

As previously noted the results shown in table 26 show differences in the trends of the values of $\overline{DP}$ with increasing feed ratio. These differences are clearly reflected in the modified Mayo plot (fig. 21). This plot shows that whereas the results obtained in

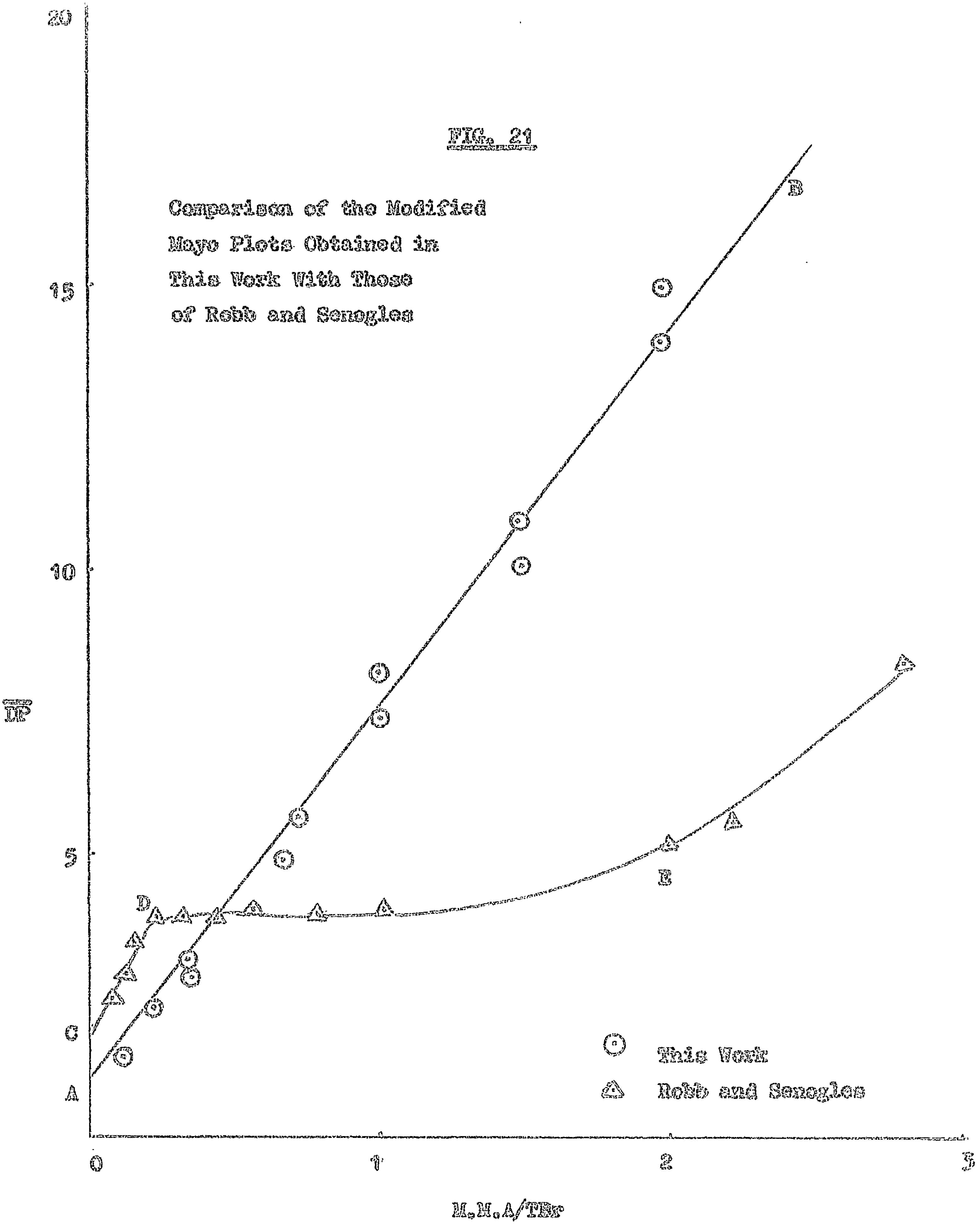


FIG. 21

Comparison of the Modified Mayo Plots Obtained in This Work With Those of Robb and Senogles this work lie on a single straight line AB of slope 0.149, those of Robb and Senogles[3] can be represented by 3 distinct lines of 3 different slopes. The line DE indicates that in going from M.M.A./TBr ratios of 0.1 to 1.0, the $\overline{DP}$ remains virtually constant, while for the same range of feed ratios the DP increases 7 fold in this work. Using Robb and Senogles'[3] results, the value of the chain transfer constant for telomer of $\overline{DP}$ greater than 4 is 1.2, whereas the results of this work give a single value of 0.149 for the whole range of $\overline{DP}$s studied. This is in closer agreement with the results of Brash[4], who measured the chain transfer constants for both high and low molecular weight products and obtained values of 0.05 and 0.08 respectively, and with Robb's results for up to trimeric radicals which can be seen in the following table.

Table 29. Values of chain transfer constants for different size radicals.

Radical size	Robb & Senogles[3]	This work	Brash[4]
trimeric	0.084	0.149	0.080
tetrameric	4.600	0.149	0.080
tetrameric - 20	1.200	0.149	0.080
polymeric	1.200	———	0.050

Thus it can be seen that there is a general agreement in the values of the chain transfer constant in the lower range - i.e. less than trimeric radicals - but it is difficult to explain the differences between the results when higher radicals are involved.

Telomerisation at 40°C and 60°C.

The pronounced variation in the value of chain transfer constants as indicated by Robb and Senogles[3] in their work with the M.M.A./TBr system and by Robb and Vosfi[17] in their work with the styrene/TBr system did not show up on the modified Mayo plot (fig. 12 and fig. 13) for the telomerisation reactions carried out at 40°C and 60°C. In fact results obtained at these temperatures are in general agreement with the parallel results obtained at 25°C except that the slope of the lines is different, this being expected from the energy of activation considerations.

Activation Energy.

The Arrhenius plot (fig. 16) for the difference in activation energy of propagation and of transfer reactions leads to an $E_{tr,n} - E_{p,n}$ value of 2.2 K cals. Although only 3 points have been plotted, the plot can be seen to be of good linearity and as such should yield a reasonably accurate $E_{tr,n} - E_{p,n}$ value. When dealing with the system where 1,1 adduct is the major product formed, the symbols $E_{tr,n}$ and $E_{p,n}$ would change to $E_{tr,1}$ and E_1 respectively, $E_{tr,1}$ being the energy of activation for the reaction

$$CCl_3M^{\circ} + CCl_3Br \longrightarrow CCl_3MBr + \overset{\circ}{C}Cl_3$$

and E_1 the energy of activation for the reaction

$$\overset{\circ}{C}Cl_3 + M \longrightarrow CCl_3M^{\circ}$$

Brash[4] obtained the overall activation energy E_0 and the activation energy $E_{t,a}$ for the termination of two trichloromethyl radicals from non-stationary state measurements. The value of E_1 can be calculated from the relationship

$$E_0 = \frac{E_I}{2} + E_1 - \frac{E_{t,a}}{2} \qquad \ldots \quad \ldots \quad \ldots \quad 30.$$

which is applicable to the present system since the termination step is second order with respect to radical concentration as will be shown later. E_I the energy of activation for initiation can be assumed to be equal to zero for phototelomerisation.

By substituting the value of E_1 in the $E_{tr,1} - E_1$ value obtained in this work, it is possible to evaluate individual values of $E_{tr,1}$ and E_1. The following table thus gives the values of activation energy for different steps involved in the reaction scheme.

Table 30. Values for the activation energy of individual steps of the kinetic scheme.

Reaction step	Reference	Activation energy K. cals/mole
E_o	4	9.1
$E_{t,a}$	4	6.2
E_1	calculated	12.2
$E_{tr,1}$	this work	14.4

Since trichloromethyl radical is more stable than any long chain polymer type radical formed by the subsequent addition of monomer units to the initiating radical, it would be expected that E_1 (the activation energy for addition of trichloromethyl radical to monomer) and $E_{t,a}$ (activation energy for the mutual interaction between two trichloromethyl radicals) would be considerably higher than the activation energies of the propagation and termination reactions involving growing chains ($E_{p,n}$ and $E_{t,b}$). Moreover, the activation energy of propagation might be expected to decrease as the number of monomer units added to the initiator fragment increased. This effect can be seen from the following table. (The values of $E_{t,b}$ and $E_{p,n}$ as obtained by Brash[4] have been added).

Table 31. Activation energies for different size radicals.

$\frac{[TBr]}{[M.M.A.]}$	$\overline{DP}$ of products	Radical species	E_i K. cals/mole	$E_{t,a}$ K. cals/mole
10/1	1.2	$\overset{\circ}{C}Cl_3$	12.2	6.2
1/10	240	$CCl_3(M)^{\circ}_{n}$	4.1	0
1/100	1600	$CCl_3(M)^{\circ}_{n+m}$	3.1	0

Melville, Robb and Tutton[12] working on the vinyl acetate/TBr system obtained

$E_{tr,1} = 7.5$ $\quad$ $E_1 = 6.1$

It is difficult to explain why the activation energy for the addition of the trichloromethyl radical to M.M.A. is 12.2 K. cals/mole whilst the addition of the same radical to vinyl acetate required only 6.1 K. cals/mole.

Verification of the kinetic scheme.

Before the individual reaction rate constant can be evaluated, it is necessary to verify that the kinetic scheme (page 8) applies to the TBr/M.M.A. system.

Intensity exponent.

Table 9. shows that at molar ratios of M.M.A./TBr = 1/10 and 1/1, the value of the intensity exponent lies between 0.44 and 0.53. This value for the intensity exponent is unchanged even when telomerisation is carried out at 40°C, 60°C and in the presence of carbon tetrachloride as a non reactive diluent. If termination proceeds via reaction scheme 1 to 7 then the rate will be proportional to the square root of initiation which in turn is directly proportional to the intensity of light. Since the value of intensity exponent is approximately 0.5 over this range of concentration of reactants and this temperature of telomerisation, it would indicate that the chain termination reaction proceeds by the mutual interaction of the chain carrier radicals. This is in agreement with the kinetic scheme (reactions 4,5 and 7). It should be pointed out that carbon tetrachloride was used as a solvent because, if chain transfer reaction

were to occur, the resulting radical would still be a propagating trichloromethyl radical.

Rate dependencies on concentration of reactants.

The effect of reactant concentration on the rate of reaction was studied over a wide range of concentrations. Experiments were carried out both in the presence and absence of diluent. These results are shown in fig. 17. The plot of the fractional rate against $\sqrt{[TBr]}$ is the straight line BC in the range where 1,1 adduct is produced. In the range where $\overline{DP}$ is 14 or above, the plot is identified with another straight line OA of a different gradient. The intermediate points do not form a linear plot. These can be interpreted in detail by splitting the graph into three parts.

(1) The plot OA shows that the rate is proportional to $\sqrt{[TBr]}$ at low TBr concentrations. The molecular weight measurements showed that polymers of $\overline{DP}$ = 14 or above are produced in this range. It has already been pointed out that this is possible in a system of propagation reactions of type

$$TM^{\circ} + M \longrightarrow T(M)^{\circ}_2$$

$$T(M)^{\circ}_n + M \xrightarrow{k_{p,n}} T(M)^{\circ}_{n+1}$$

Under these conditions the rate is clearly given by

$$-\frac{d[M]}{dt} = k_{p,n}\sqrt{\left(\frac{I}{k_t}\right)}[M]$$

Since the radiation is absorbed weakly by the TBr, the rate of initiation I is directly proportional to the TBr concentration

$$\therefore -\frac{d[M]}{dt} = k_{p,n}\sqrt{\left(\frac{[TBr]}{k_t}\right)}[M]$$

This is in agreement with the plot OA which shows a linear relationship between the rate and $\sqrt{[TBr]}$ From the above equation the absolute rate is expected to depend directly on the monomer concentration. The results of table 19 show that this is in fact so. This establishes the fact that in the system where high molecular weight products are produced (i.e. at low concentration of TBr), the rate is given by the proposed equation 10 given in the kinetic scheme on page 19. When the concentration of TBr is zero a fractional rate of 0.107 is obtained due to phototelomerisation of M.M.A. Bengough and Thomson[20] when studying the vinyl chloride/TBr system, found that the rate at TBr concentration = 0 was also zero, since vinyl chloride does not polymerise directly with the light of wave length 3650°A.

(2) The plot BC (fig. 17) shows the relationship between fractional rate and $\sqrt{[TBr]}$ in the region where TBr is in much higher concentrations than M.M.A. The scatter of the points which forms the straight line BC is notably greater than for those which form the plot of OA. This is due to the lower accuracy of the concentration rate dependence determination for the reactant which is in excess, since it is only possible to make relatively small % changes in its concentration. This results in a relatively small change in the rate. The molecular weight measurements showed that in this range of molar ratio of reactants, products of $\overline{DP}$ = 1 to $\overline{DP}$ = 2.5 were obtained. This suggests that the chain transfer reaction 4 is fast compared with the reaction 2 representing the addition of trichloromethyl radical to M.M.A., and hence the latter step is rate controlling. The rate is then given by

$$-\frac{d[M]}{dt} = k_1\sqrt{\left(\frac{I}{k_{t,a}}\right)}[M]$$

$$= k_1\sqrt{\left(\frac{[TBr]}{k_{t,a}}\right)}[M]$$

Once again if the rate is represented by the above equation the absolute rate should then also be directly dependent on the concentration of monomer (i.e. the fractional rate will be independent of monomer concentration). Table 19 shows that the fractional rates are indeed independent of monomer concentration. Similar results have also been obtained by Bengough and Thomson^{20} when working with the vinyl chloride/TBr system. However, in their work the slope of line OA is less than the slope of AB which is in contrast to the present findings.

(3) The region AB is obtained in the intermediate concentration range of TBr where before the transfer reaction can become rate controlling, the propagation reaction becomes so significant that the reaction product is no longer 1,1 adduct. It can be seen from the graph that the rate is no longer proportional to $\sqrt{[TBr]}$.

Rate dependencies in the absence of diluents.

It was found that at high M.M.A. concentration, the square root dependence of the rate on the TBr concentration was obeyed even when no diluent was used. This is shown by the line OD in fig. 17. This meant that as the TBr concentration was changed, the M.M.A. concentration automatically altered but the M.M.A. concentration was relatively so high as to change little.

The slope of the line OD clearly shows increased fractional rates for equivalent TBr concentrations compared with the fractional rates obtained in the presence of non reactive diluent carbon tetrachloride.

The heat of addition of trichloromethyl radical to M.M.A.

When working with high TBr concentrations to produce very low molecular weight products, Brash[4] evaluated various reaction constants involved in the reaction scheme (page 8) which has now been shown to be applicable to the system studied in the present work. He evaluated the rate constants by the use of non stationary state data in which he assumed that the heat of reaction was equal to that for the bulk polymerisation of methylmethacrylate (where high polymers are produced).

Bengough and Thomson[14] working with the vinyl acetate/TBr system found that the heat of addition of trichloromethyl radical to vinyl acetate was in fact significantly higher than the heat of the normal polymerisation reaction in which polyvinyl acetate is produced. Similarly, working with the vinyl chloride/TBr system, Bengough and Thomson[20] found that almost parallel differences were obtained in this system. In the present work the author has obtained the value for the heat of addition of trichloromethyl radical to methylmethacrylate, and the comparison of this value with that of the heat of polymerisation of M.M.A. shows that a similar trens is maintained. In general it may be said that in the three cases considered above, the heat of addition of trichloromethyl radical to the vinyl monomer is approximately 30 - 40% higher than the corresponding value for the heat of polymerisation. The following table demonstrates these differences.

Table 32. Comparison of heat of addition of trichloromethyl radical to vinyl monomer and the corresponding heat of polymerisation.

Monomer	Heat of polymerisation K. cals/mole	Heat of addition	App. % increase
vinyl chloride	18-19	25.6-27.6	40%
vinyl acetate	21.4	27-28	29%
M.M.A.	13.5	18.35	36%

Evaluation of rate constants.

From his non stationary state results, Brash[4] obtained a rate of 11.5% per hour for a molar ratio of TBr/M.M.A. of 10/1. In calculating this rate he used a value of 13.5 K. cals/mole as the heat of reaction, this being the heat of polymerisation for M.M.A. The value of the heat of addition of a trichloromethyl radical to M.M.A. has been found to be 18.35 K. cals/mole in this work. Thus it is possible to correct the reaction rate and the reaction rate constants obtained by Brash[4] as follows.

$$\text{corrected rate} = \frac{13.5}{18.5} \times 11.5 \quad \% \text{ per hour}$$

$$= 8.7 \% \text{ per hour}$$

Brash[4] obtained $\frac{k_1}{k_{t,a}} = 13.9 \times 10^{-5}$

As this was obtained directly from rate and kinetic chain lifetime measurements it can be corrected for the new corrected rate.

$$\frac{8.7}{11.5} \times 13.9 \times 10^{-5} = 10.3 \times 10^{-5}$$

The values for k_1 and k_t were found by Brash[4] to be 18.1 and 1.3×10^{-5} l. mole^{-1} sec^{-1} respectively. Since $k_{t,a}$ depends only on the rate of initiation and kinetic chain lifetime τ, there will be no change in its value due to the change in the value of the rate. By substituting the value of $k_{t,a}$ in the equation

$$\frac{k_1}{k_{t,a}} = 10.3 \times 10^{-5}$$

one obtains a corrected value of $k_1 = 13.4$ l. mole^{-1} sec^{-1}. The value of $k_{tr,n}$ ($n = 1$ in this case) then becomes 1.99 l. mole^{-1} sec^{-1} since $k_{tr,n}/k_1 = 0.149$ (see page 56.). The following table can be constructed to compare the values of k_1 and $k_{tr,n}$ obtained by Robb and Senogles[3], Brash[4] and in the present work.

Table 33. Comparing values of k_1 and $k_{tr,n}$ of present work with previous workers.

	This work	Brash[4] (corrected for new ΔH)	Robb and Senogles[3]
$\frac{k_{tr,n}}{k_1}$	0.149	0.08	0.083
k_1 l/m.sec	13.4	13.4	160
$k_{tr,n}$ "	1.99	1.07	13.3

The value for the rate constant for the termination of two trichloromethyl radicals by mutual termination ($k_{t,a}$) has been obtained by various workers in different systems. A comparison of these values with that of Brash's[4] value shows that they differ by a factor of at least 100. This is seen from the following table.

Table 34. Showing values of k_t as obtained in different systems by various workers.

Workers	References	System studied	$k_{t,a}$ 1/m. sec.
Robb, Melville & Tutton	12	vinyl acetate/TBr	1.0×10^8
Bengough & Thomson	14	vinyl acetate/TBr	1.06×10^8
Robb & Senogles	3	M.M.A./TBr	1.6×10^7
Brash	4	M.M.A./TBr	1.3×10^5
Robb & Vosfi	17	styrene/TBr	2.1×10^9
Kirkham & Robb	45	styrene/TBr	5×10^8
Robb, Melville & Tutton	12	cyclohexene/TBr	1.0×10^8
P. Goldfinger et al	46	estimated from chlorination of chloroform	1×10^9*
Tedder & Walton	47	ethylene/TBr	$\sim 1 \times 10^{10}$*
Bengough & Thomson	20	vinyl chloride/TBr	1.06×10^8

* These reactions were carried out in gas phase.

From the expression $k_{t,a} = 1/I\tau^2$, it can be seen that either a 100 fold decrease in the value of I or 10 fold decrease in the value of τ would be required to make the values of Brash[4] comparable with the other workers. A check was made to obtain approximate values of the kinetic chain lifetime τ from the expansion data of experiments carried out to determine the heat of addition of trichloromethyl radical to M.M.A. The plot (fig.22) shows that the line intersects the time axis at about 1.25 secs. after the commencement of irradiation. Although the intercept cannot be determined accurately by this method,[36] it gives some indication of the value of τ, which was found to be 1.8 secs. by this method. From the results of fractional rates in table 18, and the density of the 1,1 adduct, the absolute rate was calculated for the reaction of a similar feed ratio. Using the value of k_i = 13.4 l. mole^{-1} sec^{-1} and the absolute rate, the value of k_t was found to be 1.02×10^6 l. mole^{-1} sec^{-1}.

This value lies midway between those of Robb and Senogles[3] and Brash[4]. With regard to the value of I, while it is unlikely that the efficiency of initiation is 100%, (assumed by Brash[4]) it seems even more improbable that the efficiency could be as low as 1%. It would also seem from this table that $k_{t,a}$ for gas phase reactions is different from that for liquid phase reactions. This is to be expected since Brash[4] obtained

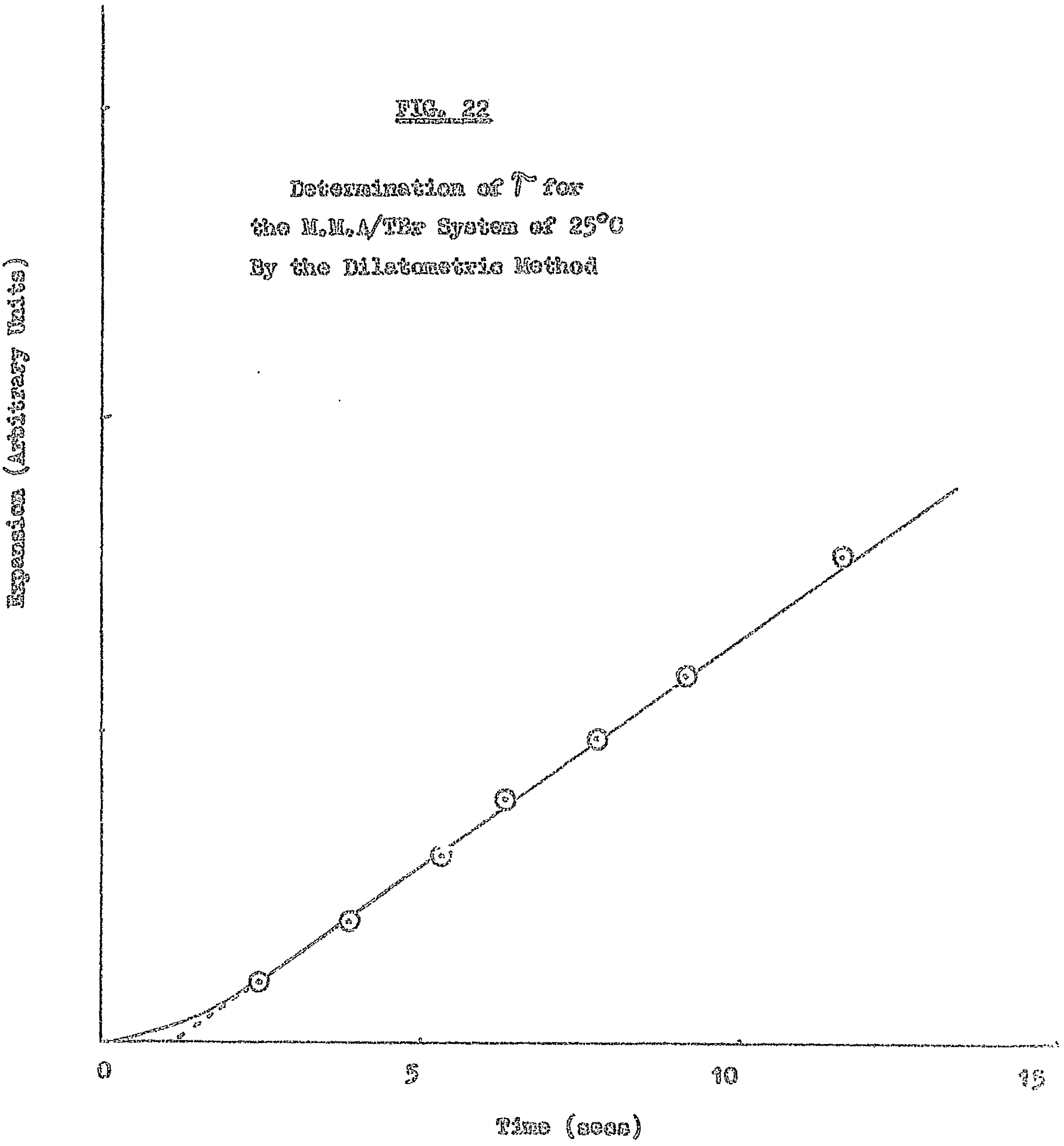


FIG. 22

Determination of τ for
the M.M.A/TBr System of 25°C
By the Dilatometric Method

an energy of activation for combination of $\dot{C}Cl_3$ of 6.2 K.cals/mole. This is in contrast to the view of Tedder and Walton that this activation energy is approximately zero, which would result in little difference in $k_{t,a}$ values at different temperatures.

PART 2

INTRODUCTION

INTRODUCTION

Work carried out using M.M.A. reported in part 1 enabled a value for the chain transfer constant of a growing telomer radical, at different sizes, to be calculated. It was decided to extend the work to other vinyl monomers to see whether the same constancy in chain transfer constant values would be observed. Since, as has already been discussed, the original results using M.M.A. were in disagreement with those of Robb, it was decided at the same time to vary the method of determining the chain transfer constant from the usual molecular weight determination methods to some alternative method.

The method of vapour phase chromatography was selected since it would be possible, from a knowledge of the relative amount of products formed, to estimate chain transfer constants for varying radical sizes. Viz:-

For a reaction of a one monomer unit radical:

$$\frac{\text{1,1 adduct formed}}{\text{total amount of one unit radical reacted}} = \frac{k_{tr,1} \cdot S}{k_{tr,1}S + k_{p,1}M}$$

and

$$\frac{\text{2 unit radical formed}}{\text{total amount of one unit radical reacted}} = \frac{k_{p,1}M}{k_{tr,1}S + k_{p,1}M}$$

For reaction of a 2 unit radical

$$\frac{\text{1,2 adduct formed}}{\text{total amount of 2 unit radical reacted}} = \frac{k_{tr,2}S}{k_{tr,2}S + k_{p,2}M}$$

$$\therefore \frac{\text{1,1 adduct formed}}{\text{1,2 adduct formed}} = \frac{k_{tr,1}S(k_{tr,2}S + k_{p,2}M)}{k_{tr,2}S(k_{tr,1}S + k_{p,1}M)} \times \frac{k_{tr,1}S + k_{p,1}M}{k_{p,1}M}$$

$$= C_{tr,1}\left(\frac{S}{M} + \frac{1}{C_{tr,2}}\right) \quad \ldots \quad \ldots \quad \ldots \quad (31)$$

Thus by plotting the ratio of TBr to monomer against the relative amount of 1,1 and 1,2 adduct formed, a straight line graph should be obtained of slope equal to $C_{tr,1}$ and intercept equal to $C_{tr,1}/C_{tr,2}$. The values for $C_{tr,3}$, $C_{tr,4}$ .... can be found similarly.

While vapour phase chromatography is useful in demonstrating the relative quantities of substances present in a mixture, it is necessary that these constituents be relatively low boiling substances or stable at their boiling points for the technique to be applied successfully. This meant that it was not possible for the technique to be used for the analysis of the reaction products from the telomerisation of M.M.A. with TBr unless special modifications were carried out on the column[5], since, as can be seen from the table 11 on page 46, most of the products of this reaction are high boiling solids. It was therefore decided to try to extend the studies of the kinetics of the telomerisation to vinyl monomers the products of which might be expected to have relatively low boiling points and do not decompose at or below these boiling points. Vinyl chloride was first selected, anticipating that the gaseous monomer would yield a series of low boiling products. The vapour phase chromatographic studies showed however that only 1,1 adduct, 1,2 adduct and 1,3 adduct could be detected. Since these products resulted in 3 peaks on the vapour phase chromatogram, it was possible to demonstrate the relative amount of these adducts formed at different temperatures, in order to support the previously obtained evidence for the M.M.A./TBr system that there was increasing predominance of chain transfer over propagation as the temperature was increased.

Attention was turned to the telomerisation of propylene with TBr as this again was expected to yield volatile products, but it was shown that the only liquid product from the reaction to give a peak on the vapour phase chromatogram was 1,1 adduct.

While the work with vinyl chloride was being carried out, Tedder and Walton published their work on the orientation of free radical to olefins[48,49]. They claimed that it is possible for an initiating radical to attack an unsymmetrical vinyl monomer from either end. This can be expressed by the following two equations.

1) $R^{\circ} + XCH = CH_2 \longrightarrow X\overset{\circ}{C}H - CH_2R \longrightarrow XYCH - CH_2R$

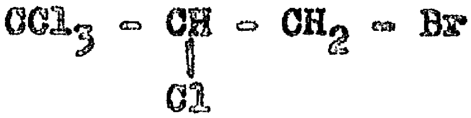
2) $R^{\circ} + XCH = CH_2 \longrightarrow RXCH - \overset{\circ}{C}H_2 \xrightarrow{RY} RXCH - CH_2Y$

where R is a free radical derived from a chain transfer agent RY.

This led to an extension of the vapour phase chromatographic work to determine if any evidence could be found for the appearance of reaction 2 in addition to the usually assumed initiation (reaction 1).

To establish the possibility of such a reaction, work was carried out with 1,2 dichloroethylene (structurally similar at both ends to the substituted end of vinyl chloride) and TBr. The fact that reaction was found to occur between these two (albeit at 227 times slower rate than the normal addition of $\overset{\circ}{C}Cl_3$ to vinyl chloride) has been taken as evidence that it would be possible for $\overset{\circ}{C}Cl_3$ formed by photolysis of TBr, to take part in reaction 2.

Small peaks in the vapour phase chromatograms of the products of reaction between TBr and vinyl chloride were interpreted in this light as being due possibily to



$$CCl_3 - \underset{\displaystyle Cl}{\underset{|}{CH}} - CH_2 - Br$$

EXPERIMENTAL

EXPERIMENTAL

MATERIALS

Vinyl Chloride (VCl)

A cylinder of vinyl chloride was kindly supplied by British Geon Ltd. The gas was condensed in a vacuum line trap cooled by liquid nitrogen. The solid was liquified by raising the temperature to -78°C using an acetone/drikold bath and degassing was carried out by freezing, evacuating, thawing cycles in the usual way. The monomer was then purified by trap to trap distillation.

1,2 Dichloroethylene (D.C.E.)

A mixture of cis and trans 1,2 dichloroethylene was obtained from B.D.H. Vapour phase chromatographic results indicated that this mixture contained approximately 40% of the trans and 60% of the cis form. The mixture was fractionally distilled in a 2 foot Podbielniak column and the following fractions were obtained.

	Temperature range °C	Fractions
1)	47 - 49	Trans form(b.p. 48.4°C
2)	50 - 54	Intermediate Fraction
3)	54 - 58	" "
4)	58 - 61	cis form (b.p. 60.1°C)

The first and the fourth fractions were used for some particular experiments while most of the work was carried out using the original 40/60 trans/cis mixture after distillation.

Propylene

A cylinder of propylene was made available through the kindness of I.C.I., Ltd. The gas was condensed in a vacuum line trap cooled by liquid nitrogen, the only coolant capable of solidifying the monomer. Degassing was carried out by trap to trap distillation. The monomer was finally stored as a gas in a 10 litre bulb connected to the vacuum line.

Ethylene

A cylinder of ethylene was purchased from British Oxygen Ltd. and was used as supplied for reaction with TBr.

APPARATUS

Irradiation

Since the reaction between D.C.E. and TBr is very slow, a more powerful U-shaped arc tube (Hanovia UVS 220), fitted with an intensity stabiliser was used throughout the experiments described in part 2 of this thesis.

PROCEDURE

Isolation of the Products

(a) Vinyl chloride/TBr and Propylene/TBr Products

The dilatometers were cooled in drikold/acetone mixture before breaking them open. The contents were transferred to a small sample bottle which was left open to the atmosphere at room temperature until all the vinyl chloride or propylene had evaporated off. These were then stored in the dark for vapour phase chromatographic studies. The unreacted TBr was not removed by vacuum distillation since some 1,1 adduct also distilled off. Attempts to distil off TBr by vacuum fractional distillation also proved unsuccessful.

(b) D.C.E./TBr Products

Products were concentrated on the vacuum line by distilling off unreacted TBr and D.C.E. The distillate was checked by vapour phase chromatographic studies to ensure that, apart from unreacted TBr and D.C.E., no other products distilled over.

Vapour phase chromatography

Efforts were made to carry out quantitative analysis of the products on the Griffon and George Mk IIB instrument in which a thermal conductivity type detector is used. Nitrogen was used as the carrier gas at a flow rate of 1.2 litre/hour. The column, 200 cms in length, and 6 mm in diameter, was made of pyrex glass. It was filled with Celite 545 using silicone (E301) as stationary phase. The response of the detector is directly proportional to the thermal conductivity of the vapour, and it was therefore possible to estimate quantitatively the products of the reaction by measuring the areas under the peaks of the chromatograms. This was achieved by approximating the peaks to triangles by drawing tangents at the point of inflection and obtaining the area of the triangle as ½ base x altitude. The identity of the products was determined by comparing their retention times with authentic materials under identical conditions. When the authentic material was not available, attempts were made to prepare it synthetically.

The sample was injected through a serum cap by means of a 10 μl hypodermic needle. In most cases 1μl of the sample was introduced but greater quantities of up to 5 μl had to be injected to detect certain smaller components.

A number of runs were done to find a suitable temperature at which all the components of the reaction products could be resolved without causing any product decomposition. The temperature required was found to be 175°C for the products of the D.C.E./TBr system and 220°C for the products of both the VCl/TBr and the propylene/TBr system.

Apart from the temperature differences all other conditions were kept constant throughout all the experiments. These conditions are summarised below.

column = 20% High vacuum silicone grease E301 on Celite 545 mesh (80 - 120).
nitrogen flow = 1.2 l/hr.
inlet pressure = 53.5 mm
outlet pressure = 43.6 mm
sample size = 2 µl
attenuation = 3
detector current = 100 Milliamp
chart speed = 1.01 cm/minute.

RESULTS

RESULTS

Experiments with the D.C.E./TBr system.

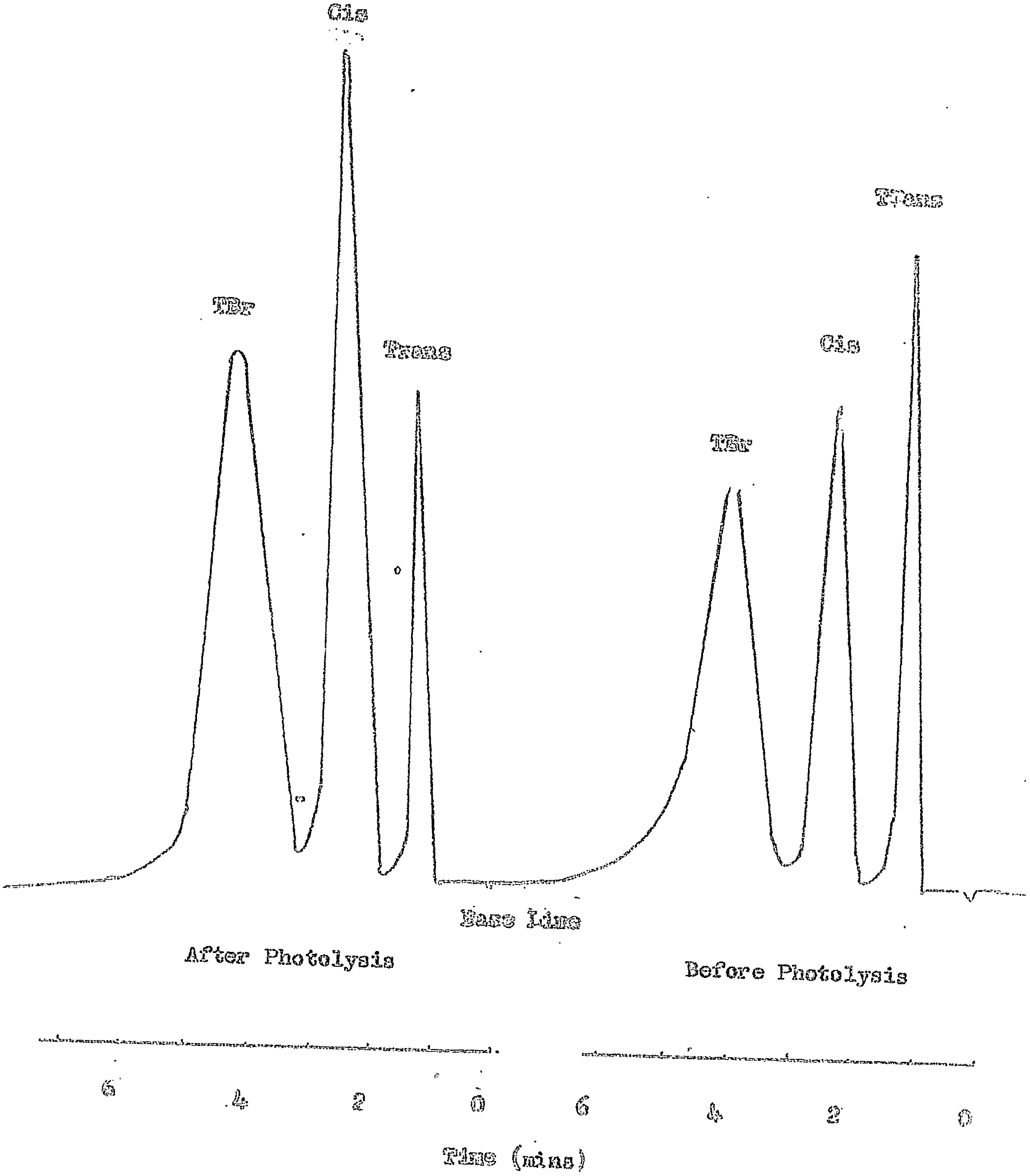
This system was chosen in the first instance, as has already been stated, to determine the possibility of reaction occurring between a trichloromethyl radical derived from TBr and the chlorine carrying carbon atom of the vinyl chloride molecule. It was also hoped to make a study of the chain transfer constant in this system and the rates of reaction for comparison with VCl under identical conditions.

In the course of preliminary work with D.C.E. it was necessary to look more closely at the individual reactions of the cis and the trans forms.

The vapour phase chromatogram at 23°C of the pure D.C.E. used showed 2 peaks, the first to appear being attributed to the lower boiling trans form and the latter to cis. Whenever the mixture of cis and trans forms was reacted, it was observed that the peak due to the trans form was significantly reduced while that due to the cis form was relatively unchanged, (cf. fig. 23 for reaction mixture consisting of 1:1 D.C.E. and TBr irradiated for 16 hours at room temperature), indicating that reaction was indeed taking place, but that

FIG. 23

V.P.C. Showing The Preference of TBr To React With Trans D.C.E.



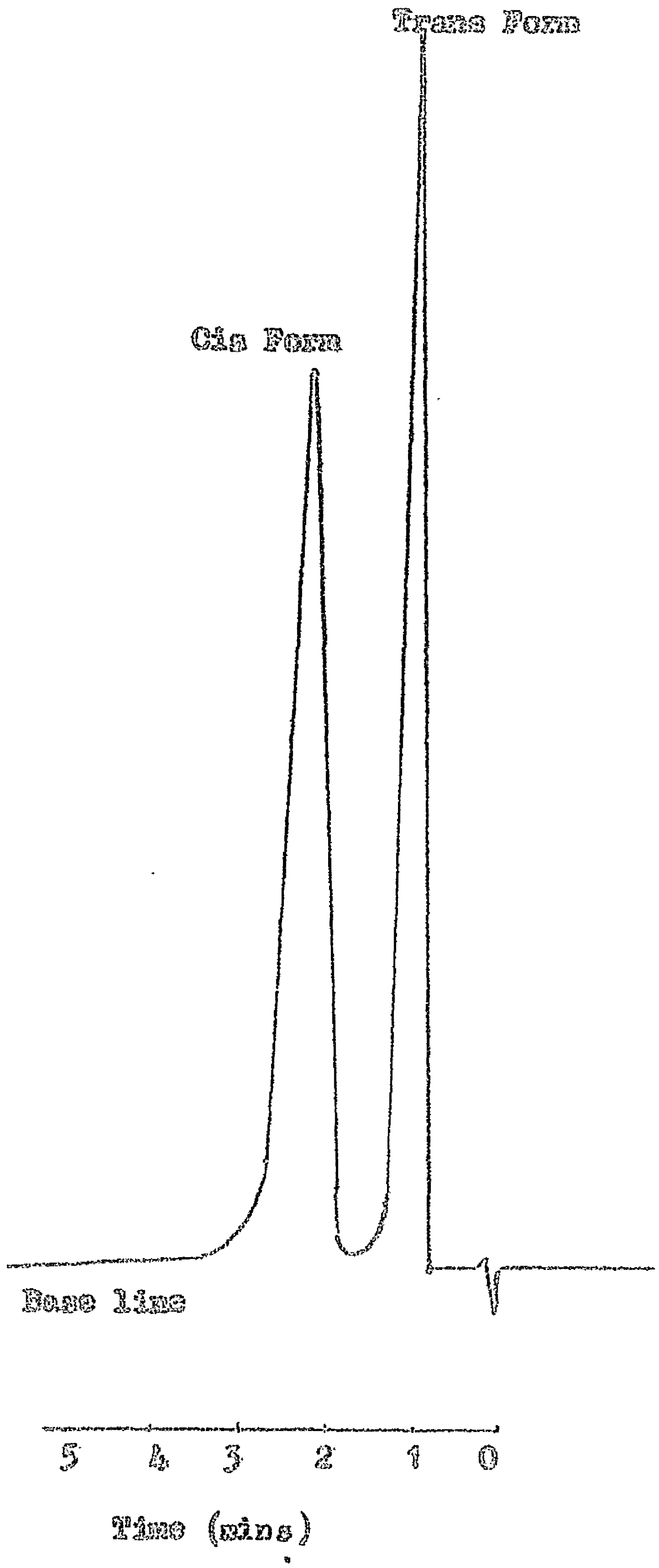
the trans form was reacting preferentially. Fig. 23 does not show the peaks due to the reaction products since the chromatogram was obtained at 23°C which is too low to produce vapours from the products. A check was made to exclude the possibilities of transformation of trans form to cis form due to irradiation without the presence of TBr. As is shown in fig. 24 there was no change in the relative concentrations of trans and cis forms when D.C.E. was irradiated for 16 hours at 25°C.

A mixture of cis form (obtained by fractional distillation) and TBr was irradiated at 25°C. It was found to react, but extremely slowly. Even after 18 days of irradiation there was still a small peak due to unreacted D.C.E. It was therefore decided to ignore the reaction with cis form in future considerations.

Fig. 25, representative of the results obtained for the reaction mixture containing 1:1 molar ratio of D.C.E. to TBr, irradiated for 24 hours at 25°C, shows the following peaks (table 35). Products were isolated as described earlier on page 117.

FIG. 24

V.P.C. of D.C.E.
at 23°C



<u>FIG. 25</u>

V.P.C. of The Reaction Products

of D.C.E. and TBr at 175°C

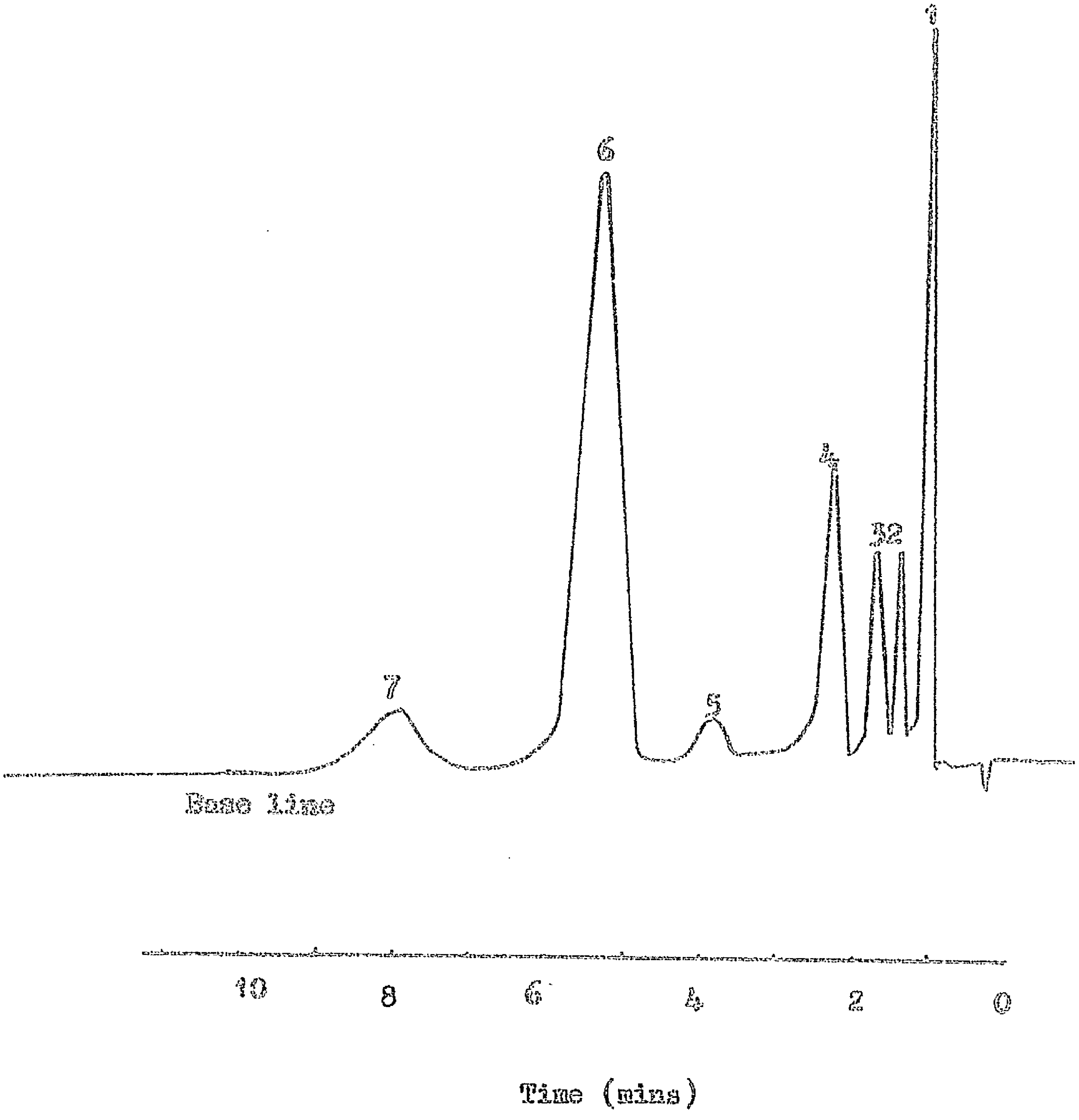


Table 35. Interpretation of peaks in fig.25.

Serial number	Retention time -cm*	Area of peak	Identity
1	0.80	runs off chart	TBr
2	1.20	0.260	?
3	1.50	0.330	?
4	2.00	1.200	DBDCE or HCE
5	3.60	0.125	?
6	5.10	5.120	1,1 adduct
7	7.70	0.540	1,2 adduct

* Speed of chart = 1.01 cm/minute.

As noted, the designation of the overlapping peaks due to dibromodichloroethane (DBDCE) or hexachloroethane (HCE) was determined by prior calibration with pure substances, the former prepared by bromination of D.C.E. and the latter being available. Unknown peaks 2 and 5 in fig.25 were thought to be due to unsaturated decomposition products since the bromination of the reaction mixture resulted in the disappearance of such peaks. Peak 4 remained unreacted after bromination and as such remained unaccounted for. Possible suggestion regarding the nature of the substances causing these peaks will be discussed later.

From the "area of peak" column it can be seen that while the peaks due to D.C.E., which at high temperature overlap one another giving rise to a single peak, are not evident, it is obvious that significant quantities of TBr remained even after distillation. Peak 4 is attributable to equal quantities of DBDCE and HCE as expected from the reaction scheme on page 8. It is evident that there is 10 times more 1,1 adduct formed than 1,2 adduct.

Intensity Exponent.

The intensity exponent was determined at 25°C for the reaction mixture which contained 10/1 molar ratio of [TBr]/[D.C.E.]. The results are shown in table 36.

Table 36. Variation of rate with varying light intensity.

% light intensity	$\sqrt{\text{\% light intensity}}$	rate % telomerisation per hour	rate/ $\sqrt{\text{intensity}}$
100.0	10	0.135	0.0135
50.0	7.06	0.101	0.0141
33.5	5.78	0.072	0.0125
22.7	4.77	0.053	0.0111

From the above results and equation 23 given on page 41 the mean value of the intensity exponent was found to be 0.533. The plot of the square root of intensity against the rate gave a straight line as shown fig. 26. It can also be seen that the value of rate/$\sqrt{\text{intensity}}$ is reasonably constant.

Telomerisation of D.C.E. with TBr at 25°C.

Experiments were carried out to study the quantitative variation of products obtained with varying feed ratios of D.C.E. and TBr. Results obtained after 24 hours irradiation are shown in table 37.

Table 37. Quantitative variation of reaction products with feed composition at 25°C.

$\frac{[TBr]}{[D.C.E]}$	Areas of the peaks in cm^2			(B)/(A)	(B)/(C)
	DBDCE + HCE (A)	1,1 adduct (B)	1,2 adduct (C)		
13/1	1.000	8.30	0.00	8.30	∞
10/1	0.630	3.74	0.00	5.94	∞
5.2/1	1.500	7.20	0.42	4.90	17.20
1/1	1.200	5.12	0.54	4.27	9.49
1/3	0.690	2.40	0.96	3.48	2.48
1/10	1.147	1.50	2.38	1.02	0.63
1/30	1.125	0.36	3.14	0.32	0.11
1/100	2.800	0.50	3.80	0.18	0.13

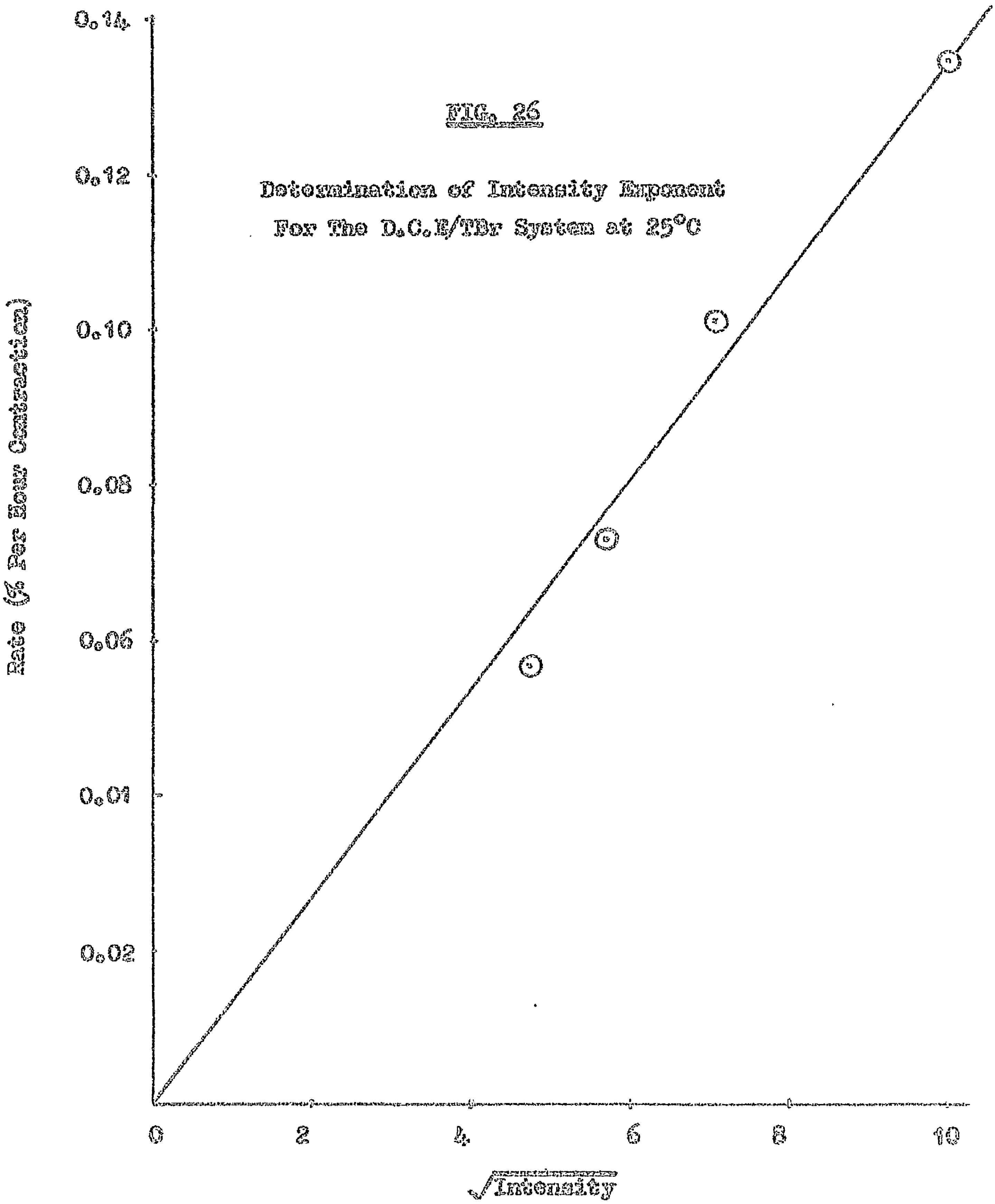


FIG. 26

Determination of Intensity Exponent For The D.C.E/TBr System at 25°C

It can be seen that the quantity of 1,1 adduct formed tends to decrease as the relative amount of D.C.E. in the feed mixture increases, and this is accompanied by an opposite trend in the amount of 1,2 adduct formed. Deviations from these trends may be due to inconsistency in the amount of sample chromatographed, since, while there appears to be little regularity in the amount of (DBDCE plus HCE) formed, the comparisons of peak areas show steady trends. To be in keeping with the reaction scheme on page 8, the amount of (DBDCE plus HCE) formed relative to the total amount of the adduct products should be constant for varying TBr/D.C.E. values. This is concordant with the results in table 37 for TBr/D.C.E. equal to 13/1 to 1/1, where the sum of 1,1 and 1,2 adduct formed represents the total adduct product and the ratio of this to (DBDCE plus HCE) is essentially constant in the range 4 - 8. At high D.C.E. concentrations, (TBr/D.C.E. equal to 1/1 to 1/100) 1,1 and 1,2 adducts are not the only products, the amount of 1,1 adduct formed being reduced accordingly.

A graph (fig. 27) of 1,1 adduct formed/1,2 adduct formed versus [TBr]/[D.C.E.] has been drawn in the light of equation 31 on page 111 and interpreted to yield

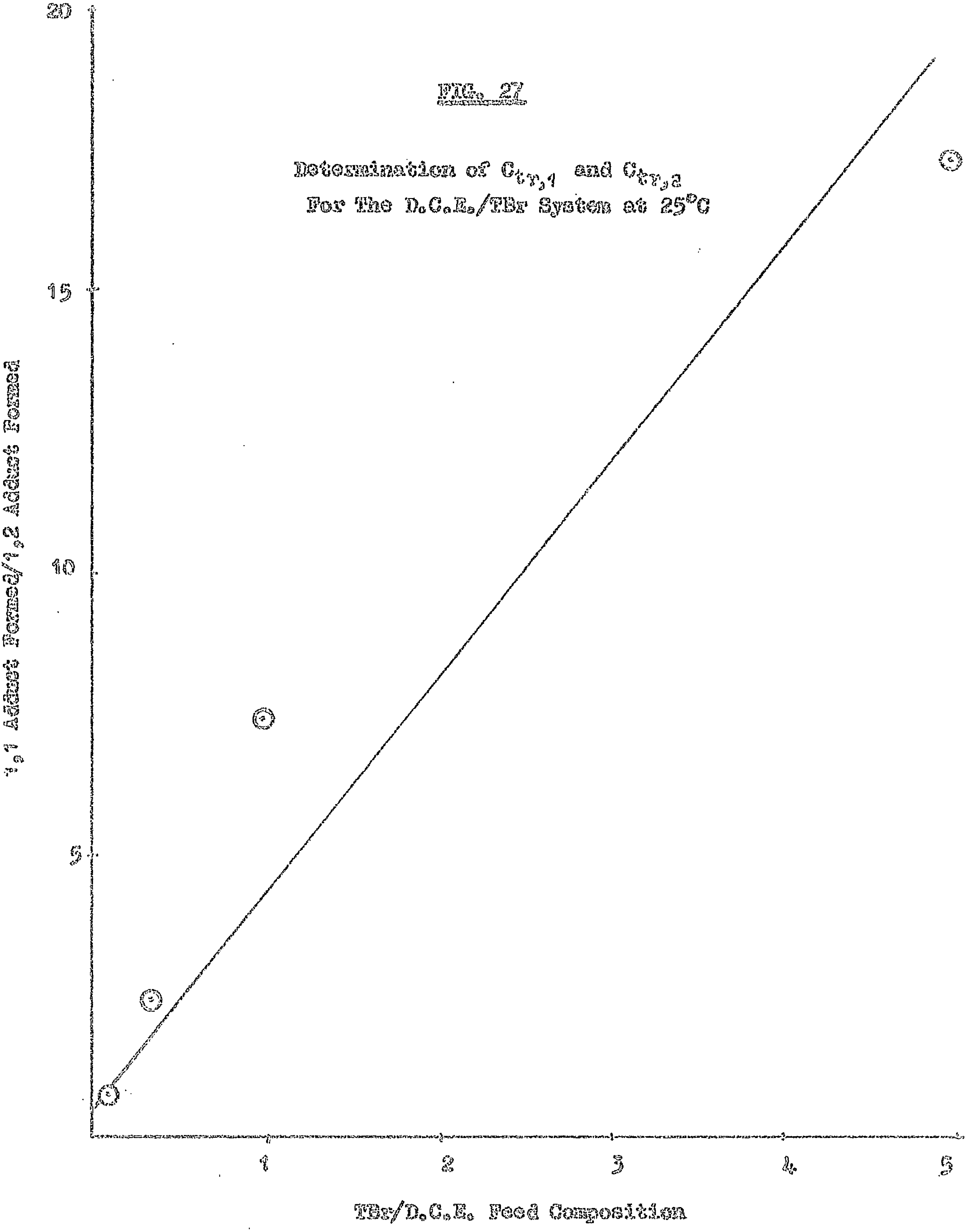


FIG. 27

Determination of $C_{tr,1}$ and $C_{tr,2}$ For The D.C.E./TBr System at 25°C values of $C_{tr,1} = 4.6$ and $C_{tr,2} = 7.0$, though these values are not extremely accurate for reasons presented in the discussion.

Molecular weight of the products prepared by using TBr/D.C.E. feed ratio of 13/1 and 10/1 at 25°C.

The mean value for the molecular weight of these products was found to be 284 cryoscopically and 296 by the vapour pressure method. Since the theoretical value of the molecular weight for the 1,1 adduct is 295, it was assumed that the reaction products did not contain any other high molecular weight products which, if present, would not show on the chromatogram due to low volatility or decomposition.

Specific gravity of the 1,1 adduct.

The specific gravity of the 1,1 adduct was found to be 1.96 by using a 1 ml pyknometer. This value has been used to calculate the rate of reaction in terms of % telomerisation/hour which was to be compared with the rate of reaction in the VCl/TBr system under identical conditions.

Rates of reaction.

The rates of reaction were determined under conditions where 1,1 adduct was the predominant product formed. These results are shown in table 38.

Table 38. **Rates for the reaction between TBr and D.C.E. where only 1.1 adduct is formed.**

[TBr] m/l	[D.C.E.] m/l	Rates % telomerisation/ hour
9.00	1.700	0.19
9.17	0.945	0.13

Experiments with the VCl/TBr system.

Reactions involving telomerisation of VCl with TBr were carried out under identical reaction conditions to those used in the studies of D.C.E. in order to show comparability of rate measurements. Vapour phase chromatographic analysis of the products of the reactions using a 5/1 molar ratio of VCl to TBr gave rise to a chromatogram (fig.28). The identity of the peaks in this figure is given by table 39.

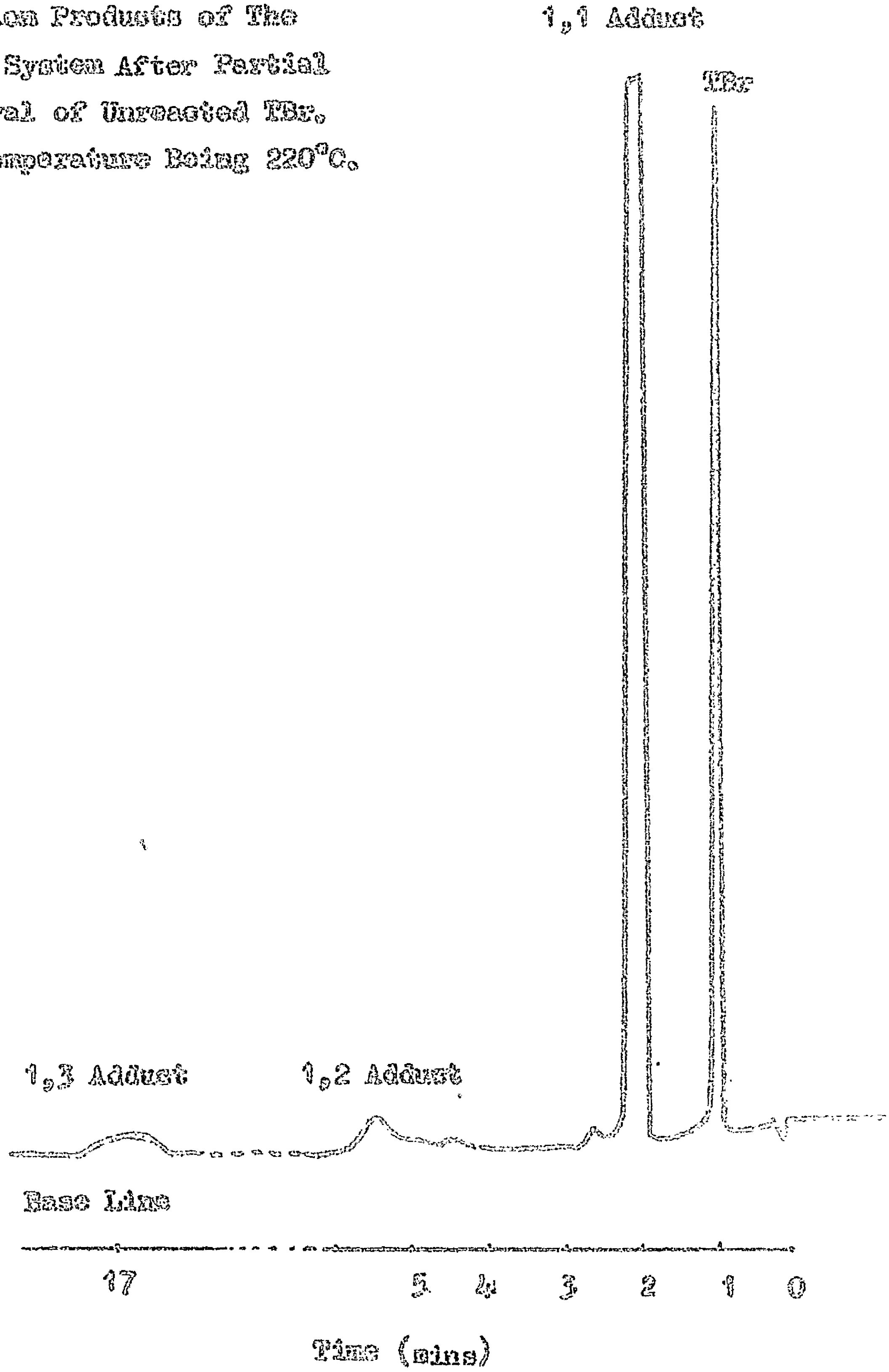
Table 39. Interpretation of the peaks in fig.28.

Serial number	Retention time arbitrary units	Identity
1	0.85	TBr
2	1.70	1,1 adduct
3	2.10	unknown
4	3.90	unknown
5	4.20	1,2 adduct
6	15.20	1,3 adduct

The possible reaction products dibromo vinylchloride (DBVCl) and HCE were found independently to have retention times of 1.1 and 1.5 units respectively and

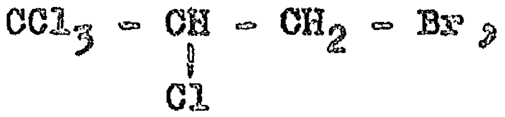
FIG. 28

Typical V.P.C. of The Reaction Products of The VCl/TBr System After Partial Removal of Unreacted TBr. Column Temperature Being 220°C.



can be seen to be absent from the products chromatographed to give fig.26

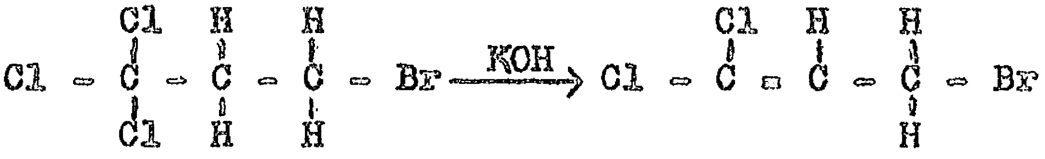
Since, as will be postulated in the discussion, the unknown peak of retention time 2.1 unit may be due to



$$\mathrm{CCl_3-CHCl-CH_2-Br},$$

efforts were made to prepare this compound by the following reaction scheme:

$\mathrm{CCl_3-CH_2-CH_2-Br}$ was prepared by bubbling ethylene into a stirred excess of TBr exposed to U.V. light. The 1,1 adduct of ethylene was isolated by vacuum fractional distillation and its purity checked by vapour phase chromatography. This product was then treated with alcholic KOH to dehydrochlorinate it viz.



$$\mathrm{Cl-CCl_2-CH_2-CH_2-Br \xrightarrow{KOH} Cl-CCl=CH-CH_2-Br}$$

(A)

This step was not successful however. In the course of the reaction a strong smell of HBr was detected and when, after distillation, the products were chromatographed it was not found possible to obtain a single peak attributable to (A). At this stage it was intended to chlorinate the product (A) to give CCl_3 - $CHCl$ - CH_2Br, but owing to the impurities present with the product (A), chlorination resulted in a mixture which gave no conclusive peaks.

In a further effort to justify the attribution of peak 3 to 1-bromo, 2-chloro, 3-trichloropropane (CCl_3 - $CHCl$ - CH_2Br), measurements were made of this peak relative to that due to the normal 1,1 adduct, since it would be expected that these would be in constant ratio regardless of initial reactant ratios. Because of the great differences in peak size, it was not possible to measure these ratios directly. Instead a 1 μl sample of the reaction mixture was chromatographed and the ratio of the areas of peaks due to 1,1 and 1,2 adduct was measured. A further 5 μl sample was then introduced in the column and from the resulting chromatogram, the ratio of the areas of the peaks due to 1,2 adduct and anticipated 1-bromo, 2-chloro, 3-trichloropropane, was measured. It was thus possible to calculate the ratios of the peaks due to the normal 1,1 adduct and the anticipated 1-bromo, 2-chloro, 3-trichloropropane. The results obtained can be seen in table 40.

Table 40. The ratio of areas of peaks due to normal 1,1 adduct and 1-bromo, 2-chloro, 3-trichloropropane at varying feed ratio.

[TBr]/ [VCl]	$\frac{\text{1,1 adduct area}}{CCl_3CHClCH_2Br\text{ area}}$
5/1	256
2/1	200
1/5	320
1/10	334

It will be observed that the above ratios are substantially constant and slight deviation could be due to the number of steps involved in the measurement.

Specific gravity of the 1,1 adduct.

Using a 1 ml pyknometer the specific gravity was found to be 1.87.

Rate measurements.

It was of interest to measure rates of the overall reaction in terms of % telomerisation/ hour for purposes of comparison with those of the reaction between TBr and D.C.E. Table 41 shows these results.

Table 41. Overall reaction rates at varying concentrations of VCl and TBr.

[TBr] ml^{-1}	[VCl] ml^{-1}	% telomerisation/ hour
9.25	0.95	29.5
8.65	1.79	27.2
7.00	4.23	23.2
5.82	5.98	17.8

Clearly there is a reduction of rate as the TBr content of the initial mixture is reduced. A comparison of the rates of reactions between VCl/TBr system and D.C.E./TBr is given in the discussion.

The telomerisation of vinyl chloride with TBr at 25°C.

In keeping with the studies of telomerisations of M.M.A. and D.C.E., measurements have been made at 25°C of the relative amounts of various adducts formed as can be seen in table 42.

Table 42. Telomerisation products at varying feed ratio.

$\frac{[VCl]}{[TBr]}$	Area of peaks cm^2			A/B
	1,1 adduct A	1,2 adduct B	1,3 adduct	
1/10	1.85	0.02	—	91.3
1/5	3.03	0.12	—	87.0
1/2	2.31	0.22	—	10.3
1/1	2.13	0.54	—	3.95
5/1	1.38	2.88	0.40	0.48
10/1	1.32	3.84	0.62	0.344
20/1	0.64	2.70	1.00	0.237
50/1	0.07	0.66	0.03	0.0105

It can be seen that at high TBr concentrations very little 1,2 adduct and no 1,3 adduct are formed. In fact 1,3 adduct is formed only when there is a five fold excess of VCl to TBr. Also the relative amount of 1,1 adduct formed is lowered as the TBr content of the initial mixture is reduced. To enable chain transfer constants to be evaluated for different sized radicals as outlined on page 111, a graph of TBr/VCl versus 1,1 adduct formed/1,2 adduct formed (fig. 29) has been drawn from the data in table 42. This can be seen to be a straight line of slope approximately 5, equal to the value of $C_{tr,1}$. It can be seen however

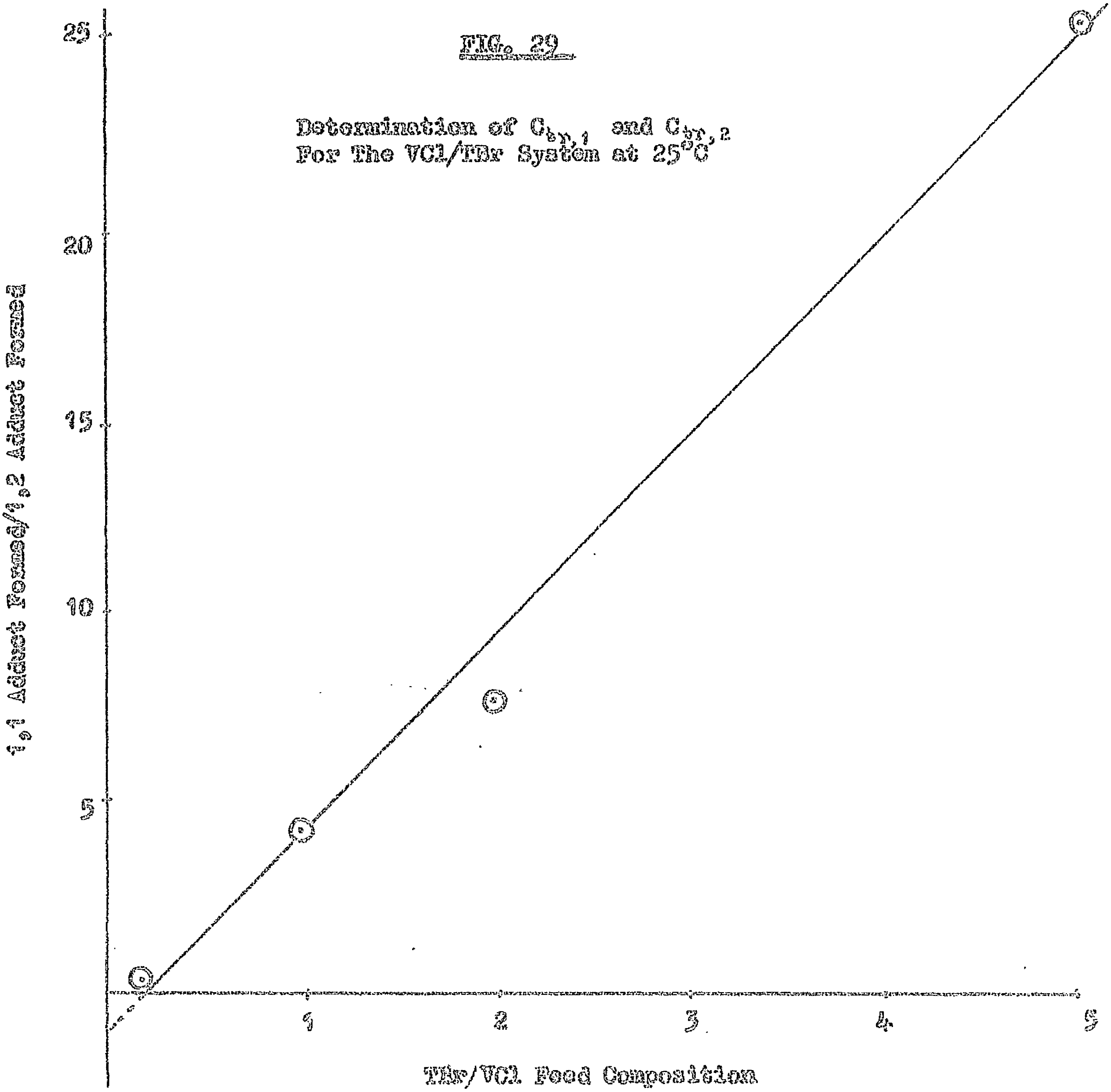


FIG. 29

Determination of $C_{br,1}$ and $C_{br,2}$ For The VCl/TBr System at 25°C that experimental error is such as to make an accurate determination of slope and of intercept (to yield a value of $C_{tr,2}$) difficult, since $C_{tr,2}$ is not expected to be negative.

Further studies were made at varying temperatures to measure the relative amounts of 1,1 and 1,2 adducts formed at varying VCl to TBr ratios. These results are shown in table 43.

Table 43. Relative amounts of 1,1 and 1,2 adducts formed at varying temperature and concentration of reactants.

	$\frac{\text{Area of 1,1 adduct peak}}{\text{Area of 1,2 adduct peak}}$			
$\frac{[VCl]}{[TBr]}$	-35°C	0°C	25°C	60°C
1/1	4.80	4.20	3.92	6.72
10/1	0.43	0.54	0.34	0.55
50/1	0.21	0.16	0.10	0.23

Comparison of results in the range 25 - 60°C show an increase in the 1,1 adduct formation at higher temperature. However, the results at 0°C and -35°C do not fit into this expected pattern.

Molecular weight of the products prepared by using TBr/VCl feed ratio of 10/1 and 5/1 at 25°C.

The following results were obtained.

Cryoscopically = 261.5

Vapour pressure method = 303.0

Theoretical value for the 1,1 adduct = 261.0

From these results it would appear that 1,1 adduct is the predominant product formed within the range of reactant ratios mentioned above.

Telomerisation of propylene with TBr at 25°C.

It was hoped that the propylene/TBr system would produce a series of relatively low boiling liquid adducts which would result in the formation of a corresponding number of peaks. From the area of these peaks it was hoped to get the chain transfer constants for each of these individual steps. However, the results obtained covering a 1/3 to 10/1 range of propylene/TBr ratios indicated that only 1,1 adduct was formed. This can be seen by reference to fig. 30. The molecular weights of the products were also determined and are given in table 44.

FIG. 30

V.P.C. of The Reaction Product
of The Propylene/TBr System at 220°C

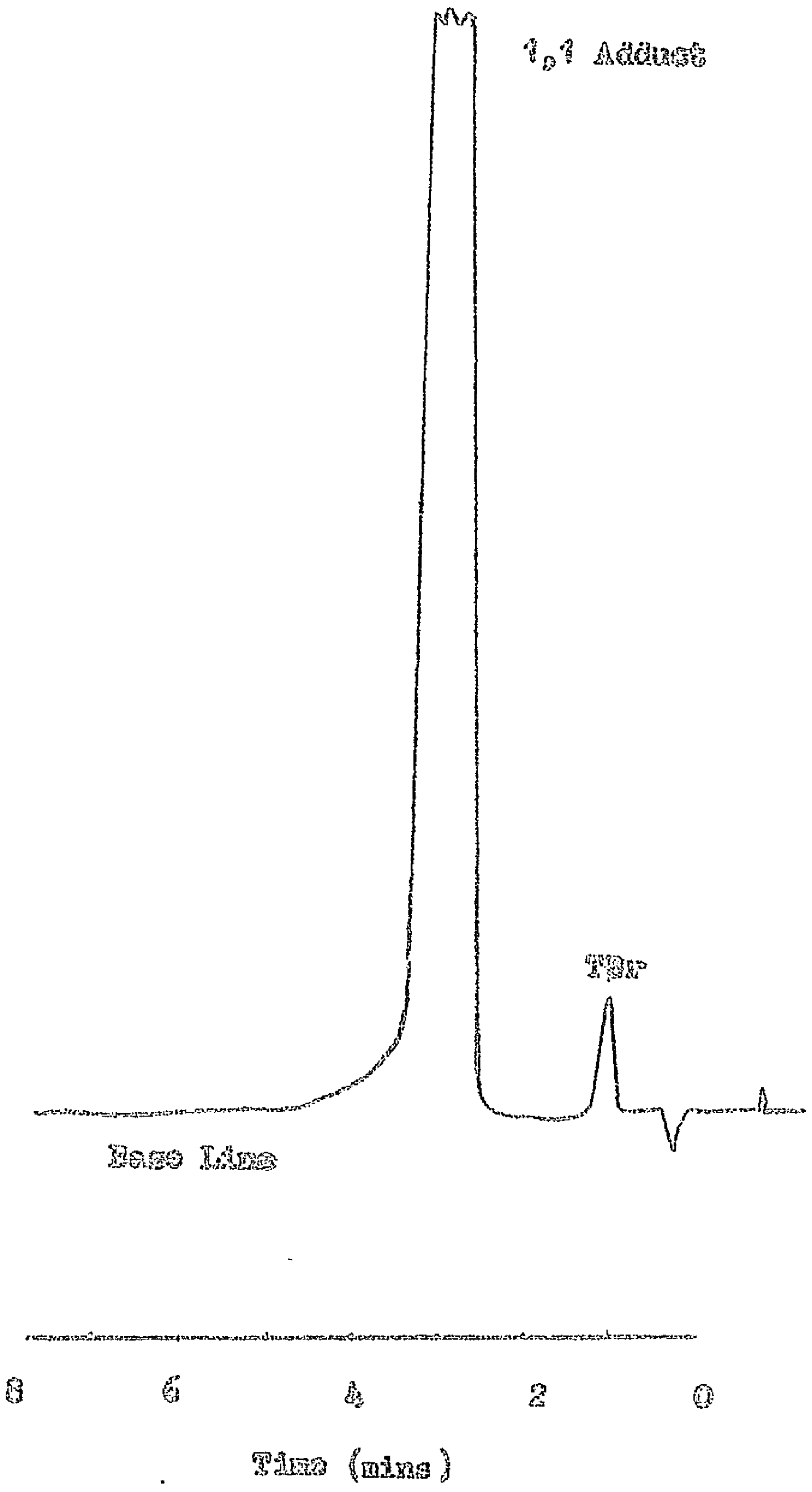


Table 44. Molecular weights of products of reaction between propylene and TBr at various initial ratios.

$\frac{[\text{propylene}]}{[\text{TBr}]}$	Number of peaks	Molecular weight	Calculated molecular weight
1/3	1	260	241
1/1	1	258	241
3/1	1	265	241
10/1	1	270	241

Work with this system was therefore abandoned.

DISCUSSION

DISCUSSION

Limitation of vapour phase chromatographic method.

As has already been pointed out by a previous worker^{50}, with a detector dependant on measurement of a gas property such as thermal conductivity, small changes in the conditions of flow of the carrier gas or fluctuations in the temperature measurement, can produce signals comparable in size of those of the eluted vapours. This was overcome by repeating measurements several times and taking the mean values. Also, it has been assumed that all the reaction products chromatographed are of similar thermal conductivity in relating peak areas to the amount of product produced.

Consideration of results with D.C.E.

It has been noted that during the early stages of the work it was found that the trans form of D.C.E. reacted preferentially with TBr, reaction with the cis form being insignificant. In an effort to explain this difference in reactivity, molecular models of the adducts made from cis and trans form were constructed which could be represented as in fig 31 and fig. 32.

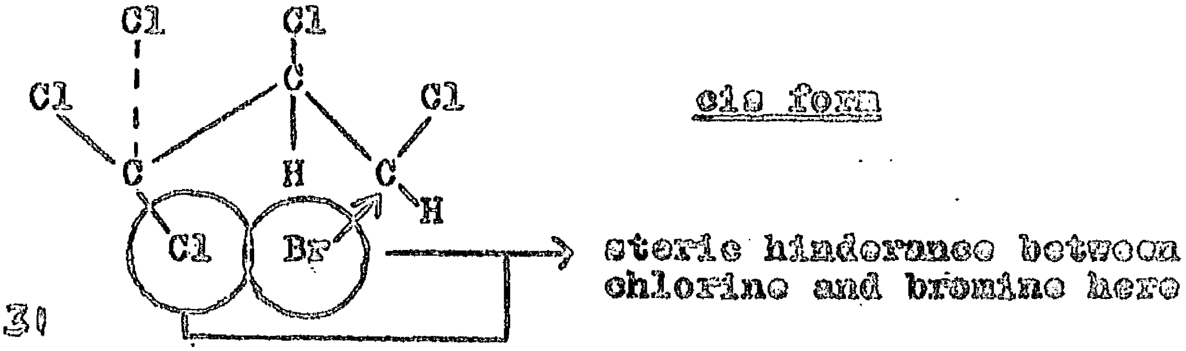


Fig. 31

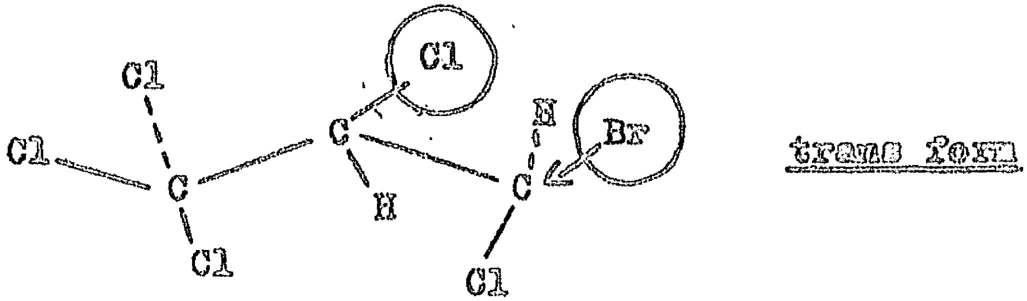
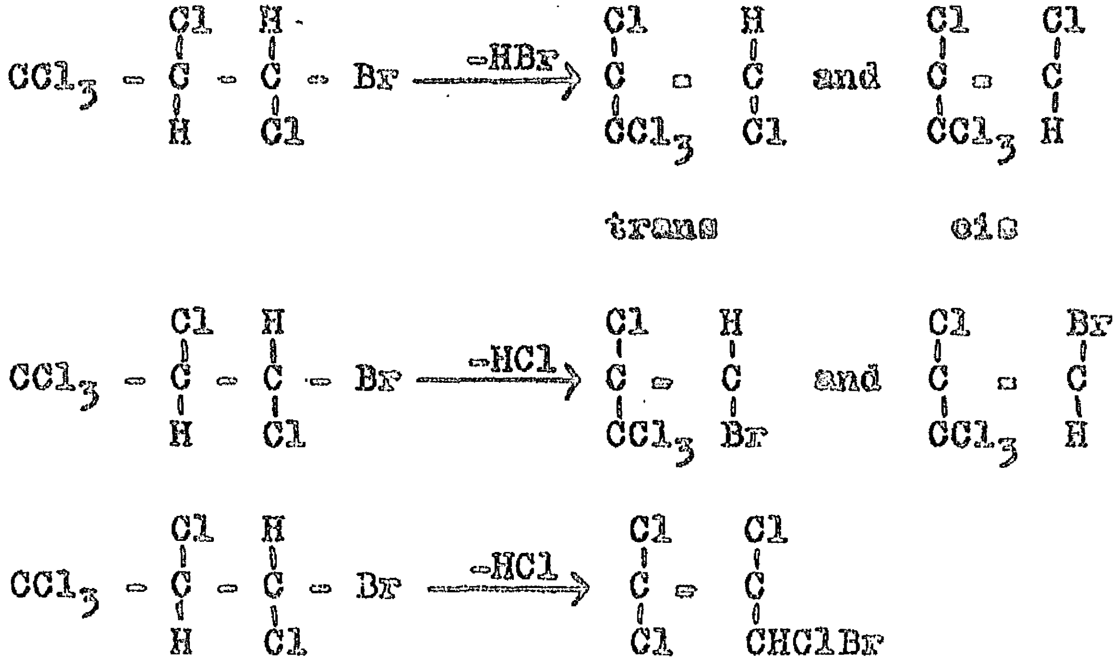


Fig. 32

From these it can be seen that while there is no difference as regards steric hinderance for the addition of CCl_3 radical to either form, the subsequent addition of a bromine atom to the model is sterically hindered in the case of the cis form. The reaction might therefore not be expected to take place. This attack on trans rather than cis is common in copolymerisation[51].

Unknown peaks in the chromatograms of the reaction products which have been attributed to unsaturated decomposition products could be due to materials formed by the following possible scheme.



(1) $$CCl_3-\underset{H}{\overset{Cl}{C}}-\underset{Cl}{\overset{H}{C}}-Br \xrightarrow{-HBr} \underset{CCl_3}{\overset{Cl}{C}}=\underset{Cl}{\overset{H}{C}} \text{ and } \underset{CCl_3}{\overset{Cl}{C}}=\underset{H}{\overset{Cl}{C}}$$

trans cis

(2) $$CCl_3-\underset{H}{\overset{Cl}{C}}-\underset{Cl}{\overset{H}{C}}-Br \xrightarrow{-HCl} \underset{CCl_3}{\overset{Cl}{C}}=\underset{Br}{\overset{H}{C}} \text{ and } \underset{CCl_3}{\overset{Cl}{C}}=\underset{H}{\overset{Br}{C}}$$

(3) $$CCl_3-\underset{H}{\overset{Cl}{C}}-\underset{Cl}{\overset{H}{C}}-Br \xrightarrow{-HCl} \underset{Cl}{\overset{Cl}{C}}=\underset{CHClBr}{\overset{Cl}{C}}$$

Since more than 1 peak is obtained it might be expected that the cis and trans isomers play a part. It is perhaps significant that bromination of reaction products results in the disappearance of these unknown unsaturated peaks and an increase in the single peak attributed to HCE and DBDCE. While bromination of the suggested products would not yield DBDCE, it is possible that the bromination of cis and trans forms of the suggested products could yield a single peak having the same retention time as DBDCE.

Considerations of results with VCl.

The ratio of 1,1 adduct and 1,2 adduct formed at -35, 0, 25 and 60°C.

It is difficult to draw firm conclusions from the results of relative amount of 1,1 and 1,2 adducts formed at varying temperatures, in view of the experimental errors involved. This work was undertaken for purposes of comparison with the results of M.M.A/TBr system, where $\overline{DP}$ was taken as a measure of the relative amount of different sized adducts formed. The results with M.M.A. and VCl may be compared over the temperature range 25 - 60°C where both sets of results show an increase in the 1,1 adduct formation. It was not possible to extend the studies with VCl to temperatures above 60°C due to the explosion hazard, and the results obtained by extending the range to -35°C are erratic.

Unknown peak.

It might have been possible to account for the unknown peak in the VCl reaction product chromatogram in an analogous manner to those peaks arising when D.C.E. was used, by attributing it to an unsaturated decomposition product. No attempt was made to study the effect on the peak of bromination of the reaction product. This was the only unknown peak to arise under normal conditions. After concentration of reaction products, a second unknown peak was produced (fig. 33) but this has likewise been attributed to a head to head addition product, in this case CCl_3 - $CHCl$-CH_2 - CH_2 $CHCl$ Br or CCl_3 CH_2CHCl $CHCl$ CH_2Br etc. etc.

It seems more likely that these unknown peaks are due to the formation of head to head addition products rather than decomposition products since

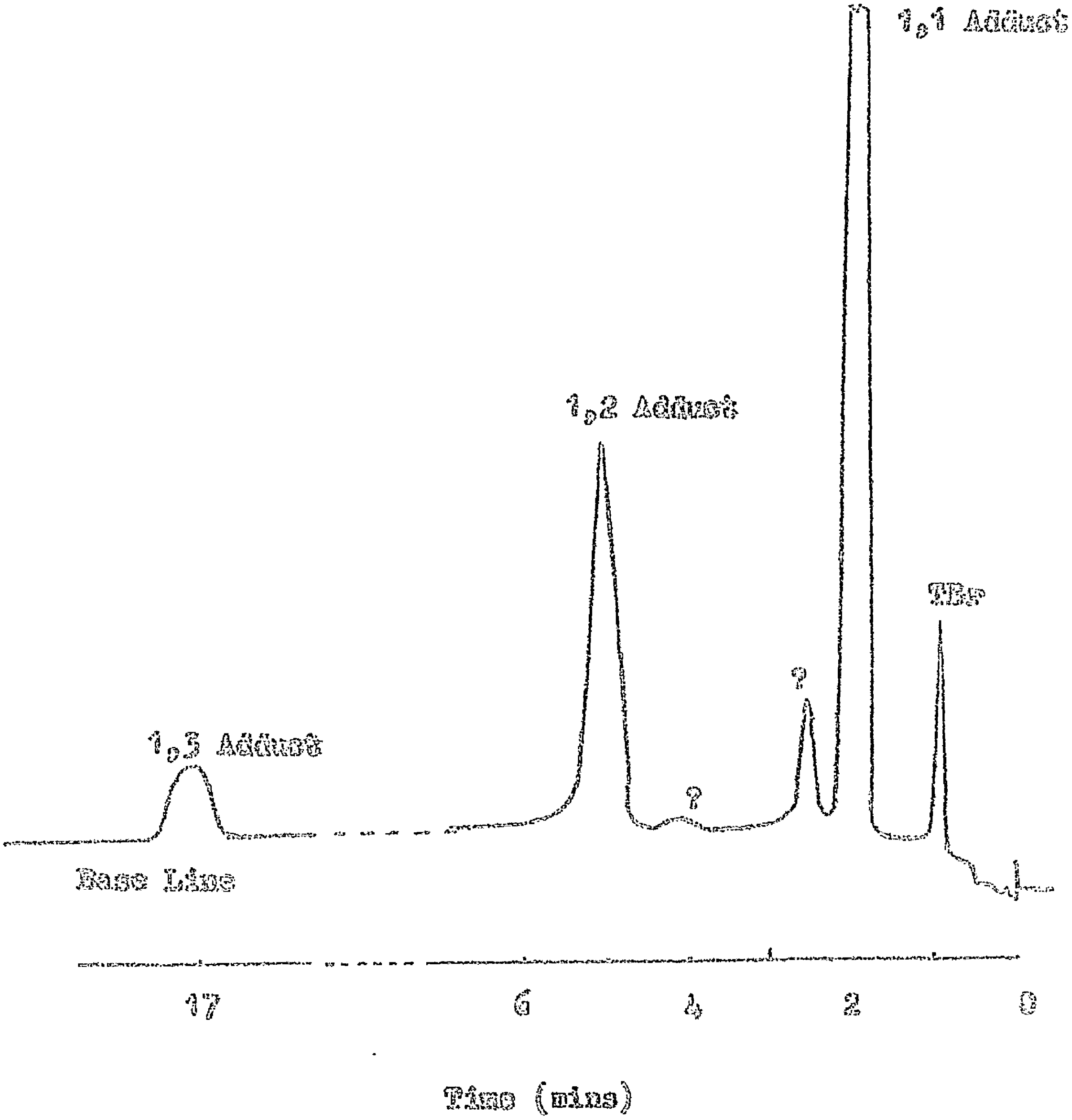
(a) not only does the ratio of unknown peak area to that of normal 1,1 adduct remain substantially constant over a wide range of initial reactant compositions but this ratio is also the same as the ratio of the rates of reaction between D.C.E. and TBr, (which has been assumed to be representative of head to head addition) and between VCl and TBr. This is brought out in the following table which compares the rates of reaction of TBr with D.C.E. and VCl under similar conditions of monomer and TBr concentration, light intensities and temperature.

<u>Table 45.</u> <u>Comparison of rates of reaction of D.C.E./TBr and VCl/TBr system at 25°C.</u>

System	[VCl] ml^{-1}	[D.C.E.] ml^{-1}	[TBr] ml^{-1}	Product formed	Rates % telomerisation per hr.	Rate VCl/TBr / Rate D.C.E./TBr
D.C.E./TBr	——	0.945	9.17	1,1 adduct	0.13	227
VCl/TBr	0.95	——	9.25	"	29.5	

FIG. 33

V.P.C. Of Reaction Products
Of VCl/TBr System After Almost
Complete Removal of Unreacted TBr
Column Temperature Being 220°C



The value of 227 given in the last column of this table should be compared with the values of approximately 300 given in table 40 for the relative peak areas.

(b) The unknown peak (attributed to $CCl_3CHClCH_2Br$) and the peak attributed to the normal 1,1 adduct are very close together as would be expected if the species were of identical molecular weight. The second unknown peak, which arises after the concentration of reaction products (fig. 33), is close to that attributed to the normal 1,2 adduct lending strength to the idea that it could be due to a similar species.

(c) As discussed in the results the only other possible products i.e. HCE and dibromovinyl chloride have their retention times significantly earlier than the 1,1 adduct or the unknown peaks.

However, since the attempts to prepare head to head adduct were unsuccessful, it was not possible to calibrate the chromatogram or to obtain NMR spectra. Attempts to isolate 1,1 adduct produced via wrong way addition, by preparative gas chromatographic techniques also failed due to its volatility being too close to the normal 1,1 adduct .

The formation of head to head polyvinylchloride (PVC) may be of industrial importance since it has been reported[52] that, whereas head to tail PVC starts to decompose at 230°C and dehydrochlorination proceeds rapidly until almost all the HCl available in PVC is lost, the head to head PVC decomposes at a lower starting temperature but at a lower rate than head to tail PVC.

Consideration of results with propylene.

It is evident that the radical produced by the addition of trichloromethyl radical to propylene is very much more reactive towards TBr than other monomers considered in this thesis. This may be compared with the reactivity of the corresponding radical formed from vinyl acetate[12, 14, 15]. Even at 100/1 molar ratio of vinyl acetate to TBr, 1,1 adduct is the predominant product.

General.

From the work carried out it can be seen that M.M.A., VCl and D.C.E. all seem to adhere to the kinetic scheme given on page 8.

Suggestions for future work.

The importance of removal of reactants from M.M.A./TBr telomers before determination of its molecular weight has already been stressed. Experiments using radioactive benzene and M.M.A. have shown that the last traces of these reagents were exceedingly difficult to remove from the telomers obtained in the M.M.A./TBr system. It would be of interest to make similar studies with radioactive TBr to see whether the telomers after the isolation process are completely free from unreacted TBr. It has also been seen that molecular weights determined by the radioactive tracer technique are in good agreement with those obtained cryoscopically. Detailed studies of molecular weight determinations by these techniques may be quite fruitful in confirming the trends of the conflicting results that have been obtained in this work and by other workers[34].

In VCl/TBr system work, the unknown peak attributed to "the wrong way addition" of trichloromethyl radical to vinyl chloride molecule remains a subject of doubt. Further attempts should be made either to prepare $CCl_3 - CHCl - CH_2Br$ synthetically or isolate the product under the unknown peak in a sufficiently pure form. Comparison of retention times of synthetically prepared

$CCl_3CHCl - CH_2Br$ with that of the unknown peak, or the NMR studies made on the product giving rise to the unknown peak, would obviously be important factors in deciding whether the unknown peak is due to the formation of $CCl_3 - CHCl - CH_2Br$ in the VCl/TBr system.

Very recently it has been reported[53] that the trichloromethyl radical attacks monomers such as $CHF = CH_2$ and $CF_2 = CH_2$ on the substituted carbon atom of the vinyl monomer.

As in the case of VCl and D.C.E. the possibility of such so called "wrong way round addition" in other asymetrically substituted vinyl monomers, i.e. M.M.A., propylene, acrylonitrile, styrene etc. could be explored by comparing their rates of reaction with TBr and those of the corresponding symetrically 1,2 disubstituted vinyl monomers. The relationship between such irregularities in the structure of a polymer molecule and the physical properties would seem most important for industrial polymers.

It has not been possible to obtain individual chain transfer constants when low molecular weight products are being produced. Two of the major difficulties experienced may be overcome by

(a) choosing systems which would result in a series of low boiling and stable products. These are however difficult to predict since it has been found that gaseous monomers do not necessarily result in a series of suitable volatile adducts. Furthermore when a gaseous monomer may yield a series of adducts (as eg. ethylene[49]) the vapour pressure of liquid at normal working temperature is so high as to present risks of explosions. Gas phase studies might be more fruitful.

(b) Using a more refined detector system in the vapour phase chromatographic studies such as a β -ray ionisation detector[50] which is known to have the advantage of producing peaks whose areas could be interpreted more accurately.

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