THE PHOTOCHEMICAL TELOMERISATION OF METHYL METHACRYLATE

A thesis submitted by

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SYNOPSIS

The photochemically initiated polymerisation-transfer reaction between bromotrichloromethane and methyl methacrylate has been studied. Under suitable conditions low polymers of methyl methacrylate can be produced, and quantitative element analysis or vapour phase chromatography can be used to determine their composition. Correlation of the latter with feed composition enables values of Mayo's transfer constant (C) to be found for methyl methacrylate type radicals of different size. These values can be resolved into their component propagation and specific transfer rate constants by determining overall reaction rates, rates of initiation, and the life-time of the appropriate sized radical. Dilatometry has been used to obtain these latter measurements, the techniques of radical scavenging and intermittent illumination being utilised to evaluate the initiation rate and the radical lifetime respectively.

It was found that in going from the trimeric radical to the tetrameric there is a pronounced increase in reactivity in the debromination reaction, though a subsequent drop occurs when the radical becomes still larger. Propagation and termination reactivities for the corresponding radicals are, however, independent of radical size. The results are discussed.

ACKNOWLEDGMENTS

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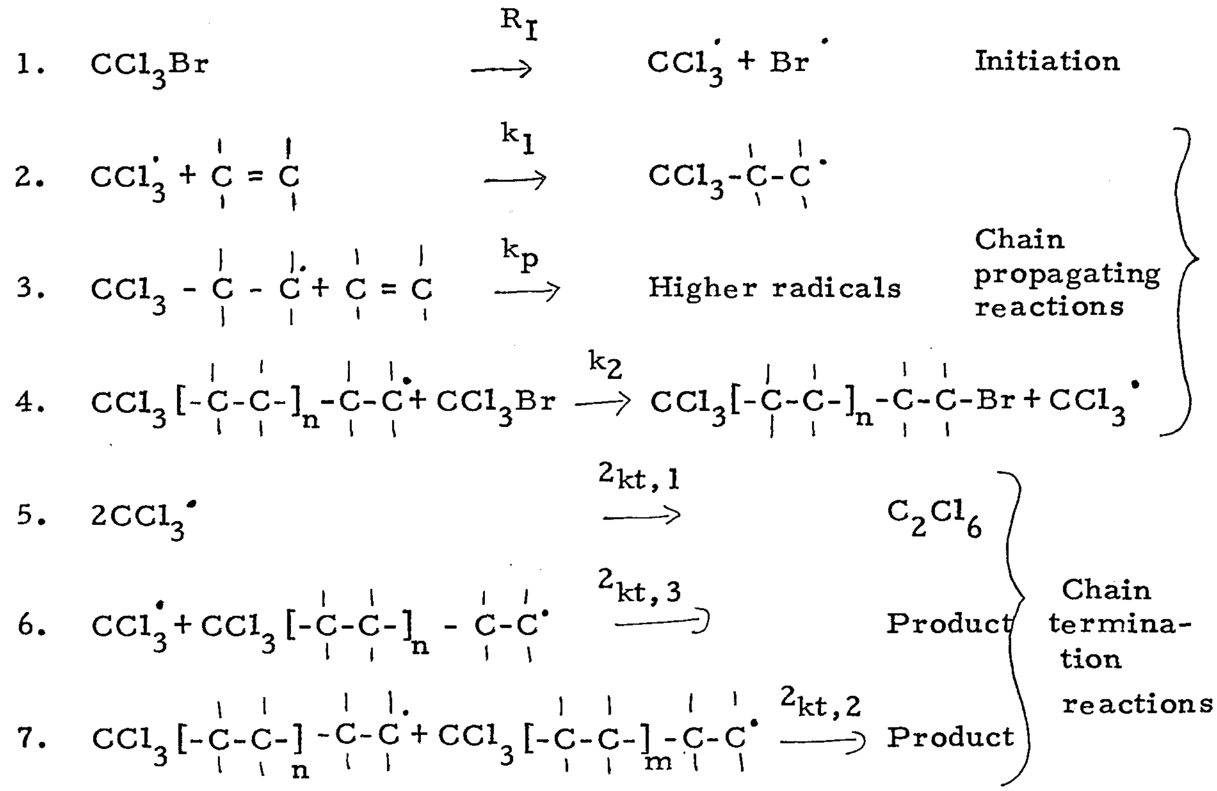
CONTENTS

CHAPTER I

INTRODUCTION

Workers in the field of chemical kinetics have established that many reactions proceed through highly reactive intermediates known as 'free radicals'. These intermediaries are a distinct and separate species from the relatively stable substances from which they are derived, and undergo specific reactions at specific rates independent of their origin. Many such reactions have been studied and quantitative data has been obtained for specific 'radical-molecule' reactions and also for specific 'radical-radical' reactions. In particular, studies of reactions involving a common discrete molecule with different free radicals or vice versa, have given very useful data, enabling numerous radical and molecule reactivities in specific reactions to be compared directly.

Many studies have been made of radical additions to a double bond. Thus Melville and Robb[1] investigated the reaction of atomic hydrogen, effectively the simplest of radicals, with various double-bonded compounds. Recently bromotrichloromethane (BTM) has been recognised as a convenient source of radicals and Kharasch and other workers have studied the reactions of these radicals with various olefins.[2,3,4,5,6,7] In the presence of ultra-violet light (3300 - 3900 Å) BTM photolyses to give two unlike entities, a trichloromethyl radical and a bromine atom. Energy considerations indicate that the mode of breakdown and the nature of the radicals produced are quite unambiguous. Kharasch was more interested in the reactions from an organic preparative point of view, but nevertheless he postulated the following kinetic scheme and obtained some semi-quantitative data:—



1. $$CCl_3Br \xrightarrow{R_I} CCl_3^{\bullet} + Br^{\bullet}$$ Initiation

2. $$CCl_3^{\bullet} + C = C \xrightarrow{k_1} CCl_3\text{-}C\text{-}C^{\bullet}$$

3. $$CCl_3 - C - C^{\bullet} + C = C \xrightarrow{k_p} \text{Higher radicals}$$

4. $$CCl_3[-C-C-]_n-C-C^{\bullet} + CCl_3Br \xrightarrow{k_2} CCl_3[-C-C-]_n-C-C-Br + CCl_3^{\bullet}$$

Chain propagating reactions (2–4)

5. $$2CCl_3^{\bullet} \xrightarrow{2k_{t,1}} C_2Cl_6$$

6. $$CCl_3^{\bullet} + CCl_3[-C-C-]_n - C-C^{\bullet} \xrightarrow{2k_{t,3}} \text{Product}$$

7. $$CCl_3[-C-C-]_n-C-C^{\bullet} + CCl_3[-C-C-]_m-C-C^{\bullet} \xrightarrow{2k_{t,2}} \text{Product}$$

Chain termination reactions (5–7)

When the olefin is not a monomer reaction (3) does not occur and n = m = o. In general Kharasch did not work with monomers but when he did the accumulation of higher molecular weight products was noted,[2,7] as predicted in the kinetic scheme. However, even at low BTM to monomer molar rates, yields of 1 : 1 addition products were high. Similar reactions were studied with various other halomethanes and olefins, a similar type of mechanism operating.[3,7,8,9,10] Various simple observations were noted, for example:[10] —

(a) With a system of carbon tetrabromide and styrene a greater percentage of 1 : 1 adduct was obtained than with equivalent amounts of carbon tetrachloride and styrene. The kinetic scheme predicts this, reaction (4) of the competitive reactions (3) and (4) being more favoured with the carbon tetrabromide system, because the C-Br bond is weaker than the C-Cl.

(b) The fact that reaction (4) was more favoured with a carbon tetrabromide-styrene system than with one of bromoform and styrene was explained by the fact that the C-Br bond in bromoform is less susceptible to attack than the same bond in carbon tetrabromide.

The reactivities of various olefins to trichloromethyl radicals were compared[4,5,6] by mixing equivalent amounts of the olefins with excess BTM and allowing an initiated reaction to proceed to 50% conversion. Excess BTM ensured that with most monomers no polymerisation occurred and only 1 : 1 adducts were isolated. Furthermore, it meant that reaction (4) was in general much faster than reaction (2), the latter being therefore the rate controlling step. Comparison of the amounts of the various 1 : 1 adducts isolated was clearly therefore a comparison of the rates of addition, or reactivities, of various olefins with trichloromethyl radicals. Thus the following reactivity table was obtained, the olefin 1-octene being selected as a reactivity standard.

The Relative Reactivities of Olefins Towards a Free Trichloromethyl Radical

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-Methylstyrene	1.1
1 Octene	1.0
2 Methyl-2-butene	0.9
Cyclopentene	0.8
Ethylcinnamate	0.8
Vinylacetate	0.8
Allyl chloride	0.5
Allyl cyanide	0.3
Cyclohexene	0.2

Melville, Robb and Tutton[11] examined the photochemical reaction of bromotrichloromethane and cyclohexene in detail. They verified Kharash's kinetic scheme and by working with excess BTM were able to make reaction (2) rate controlling. Reaction rates were observed dilatometrically and under the above conditions k_1 was evaluated in terms of $2k_{t,1}$ and the rate of initiation. The termination constant was determined by performing rotating sector experiments, and the rate of initiation by using an inhibitor. Thus k_1 was obtained. In a similar manner measurement of overall rate, termination constant $k_{t,2}$ and the rate of initiation, when working with a system of excess olefin, enabled k_2 to be found. Also by working in intermediate conditions where neither reaction (2) or (4) is rate controlling, $k_{t,3}$, the mixed termination constant, was obtained using the previously determined values for the other rate constants. Thus all rate constants for the system were evaluated. Having obtained the rate constant for the reaction between trichloromethyl radicals and cyclohexene (k_1), the reactivity table of Kharasch was examined and expressed on an absolute basis.

The work was then repeated with the monomer vinyl acetate[11] (VA). Even with excess olefin (molar ratio = $\frac{100}{1}$) the 1 : 1 adduct only is obtained[12] and therefore all rate constants were determined as with cyclohexene. Thus k_2 was found to be 2740 litres/mole/sec. If no polymerisation is to occur, it can be seen by consideration of the competing reactions (3) and (4) that $k_2 (CCl_3Br) \gg k_p(\text{Monomer})$. Now the normal accepted value of kp in vinyl acetate polymerisation is 1100 litres/mole/sec. Using this value and that determined for k_2, it is obvious that the above expression is not valid with high monomer to BTM molar ratios. In fact polymerisation should occur, and the rate of monomer disappearance should have some dependency on monomer concentration. That experiment was in disagreement with these predictions indicated that the value used for k_p was incorrect.

In free radical polymerisation reactions the reactive radical intermediates are all of a similar type - they are organic radicals built up of the same structural units, but comprise different numbers of these units depending on the number of propagation reactions undergone by each initial radical. Any kinetic treatment must take into account the reactions of radicals of all sizes, and it is generally assumed that the reactivity of a given type of radical is independent of its length so that, for example, a single velocity constant will characterise all the propagation steps occurring in the polymerisation of a given monomer. Undoubtedly this assumption is valid when radicals are large and evidence has been obtained in support of this.[13,14,15] However it has for a long time been considered that this generalisation may break down when the radicals are very small and less than ten monomer units in length. The work of Melville Robb and Tutton on the photochemical reaction of BTM and vinyl acetate clearly indicates that this is so. If in the polymerisation of vinyl acetate the growing polymer radical is much less reactive when very small, then clearly the value of kp to be used in comparing competing reactions (3) and (4) in Kharasch's kinetic scheme must be far less than the value obtained from normal polymerisation studies, where radical sizes are very great. Only if this is so, will theoretical considerations agree with the experimental results.

Thus definite evidence was obtained for propagation reactivity changes in small polyvinyl acetate type radicals. In the same system the mutual termination constant for $CCl_3VA^{\bullet}$ radicals was found and agreed reasonably well with that for polyvinyl acetate radicals. This indicates that unlike propagation constants, termination constants may not change with small radical size, though this is not certain for small radicals greater than $CCl_3VA^{\bullet}$ were not studied.

Further evidence for reactivity changes in growing small polymer radicals was obtained by Mayo. Gregg and Mayo[16] polymerised styrene in the presence of carbon tetrachloride as a transfer agent. Monomer and transfer agent compete for the polymer radicals, and by adjusting their relative concentrations, the molecular weight of the polymer can be controlled. Kharasch's kinetic scheme is applicable and kinetic analysis indicates that the following equation is valid:

$$\frac{1}{\overline{P}} = \frac{k_2(S)}{k_p(M)} + \frac{1}{\overline{P}_o}$$

where (S) = conc. of transfer agent
(M) = conc. of monomer
$\overline{P}$ = average degree of polymerisation
$\overline{P}_o$ = average degree of polymerisation in the absence of transfer agent
and k_2, k_p have the same significance as before.

Mayo and Gregg obtained degrees of polymerisation, measured by viscosity experiments, varying from a hundred to many thousands. The ratio, $\frac{k2}{kp}$ and the overall second order rate constant $\frac{kp}{(2\,kt,2)^{\frac{1}{2}}}$ (termination occurring between polymer radicals), were found to be constant over this range. They concluded that in all probability the individual rate constants were invariable, i.e. no reactivity changes occurred.

Mayo then extended the investigation to cover very low degrees of polymerisation.[17] These he now determined by chlorine analysis and again obtained values for $\frac{k2}{kp}$ and $\frac{k_p}{(2\,kt,2)^{\frac{1}{2}}}$, for different average adduct compositions. The latter ratio was found to be constant but $\frac{k_2}{k_p}$ varied in the following manner:-

Radical $[CCl_3\text{-}(CH_2CHC_6H_5)_n]^{\bullet}$	$\frac{k_2}{kp}$
$n = 1$	.0006
$n = 2$	.0025
$n = 3$	.007
$n > 3$	Becomes constant and = .0115

Because $\frac{kp}{(2kt,2)^{\frac{1}{2}}}$ was constant over the same range of adducts Mayo thought that changes in k2, the radical transfer constant, probably accounted for the observed changes in $\frac{k2}{kp}$. He thought kp was probably independent of radical size.

Robb and Vofsi[18] determined the individual transfer, propagation and termination constants for the average radicals CCl_3-$St_2^{\bullet}$ (distyrl) and $CCl_3St_3^{\bullet}$ (tristyrl). They used a system of BTM and styrene and obtained values for $\frac{k2}{kp}$ and $\frac{kp}{(2\,kt,2)^{\frac{1}{2}}}$ for the above radicals in a similar manner to Mayo. Measurement of respective termination constants by rotating sector experiments, enabled all the individual constants to be calculated. The following values were obtained:—

Av. radical size	$\overline{k_2}$ (ℓ/m/sec.)	$\widetilde{kp}$ (ℓ/m/sec.)	$\widetilde{kt,2}$ (ℓ/m/sec.)
$CCl_3St_2^{\bullet}$	3.4×10^2	44	1.3×10^8
$CCl_3St_3^{\bullet}$	3.0×10^2	1.25	1.1×10^5

Thus contrary to Mayo's deductions a change in propagation constant took place. kt,2 changed mutually so as to keep the ratio, $\frac{kp}{(2kt,2)^{\frac{1}{2}}}$, constant and k2 did not change. Furthermore, the values of kp and kt,2 associated with the average distyrl radical were not far removed from the asymptotic values of the constants, as obtained from styrene polymerisation data (55 and 2.5×10^7 respectively at 30°C). Both these constants fell off sharply when the radical chain length increased by an average single styrene unit but on further radical growth they must approach the asymptotic value. Thus it was concluded that a reactivity minimum is associated with the growth of the polystyrl radical during the initial stages of the addition reaction. This is in agreement with the work of Sivertz who studied the photochemical addition of various mercaptans to olefins.[19,20,21,22,23] He obtained values of the termination constant and the styrene propagation constant for the n-butylmercaptostyryl radical, and these were far greater than the corresponding rate constants for the macrostyryl radical.

Eaves[24] also obtained evidence of reactivity changes in growing small polymer radicals. He studied the mechanism of transfer in the polymerisation of styrene using a doubly labelled transfer agent, triphenyl methane (TPM). Polymerisation was initiated with various thermal initiators, benzene being used as an inactive solvent. The triphenyl methane was labelled with C^{14} in the benzene rings, and tritium was used instead of the alkyl hydrogen. The kinetic scheme is essentially that of Kharasch:—

$$\text{Initiator} \xrightarrow{R_I} R^\bullet$$

$$R^\bullet + M \longrightarrow P^\bullet$$

$$P^\bullet + M \xrightarrow{k_p} P^\bullet$$

$$P^\bullet + {}^*\varphi_3 H^* \xrightarrow{k_2} PH^* + \varphi_3^{*\bullet}$$

$$\varphi_3^{*\bullet} + M \xrightarrow{k_1} P^{*\bullet}$$

+ the usual termination steps.

Mayo's equation applies, the degrees of polymerisation being effectively determined by radioactive techniques. Tritium assays gave one set of results and C^{14} another, and thus for a fixed $\frac{(\text{Monomer})}{(\text{TPM})}$ two independent values for $\frac{k2}{kp}$ were obtained. These values did not agree but this is expected because of an isotope effect. However, both values were much higher than literature values[25] and this must be explained. It was subsequently shown that transfer also occurred between initiator radicals and transfer agent and thus some of the polymer chains would contain labelled TPM groups not derived from a transfer reaction of polymer radicals. This would give a high result for $\frac{k2}{kp}$ as calculated by C^{14} assay. A similar explanation would not account for the high value obtained by tritium assay, and experiment indicated that no tritium exchange took place with ordinary hydrogen atoms. The average kinetic chain length in these experiments was about ten, and therefore a large fraction of the polymer radicals would have chain lengths considerably shorter than this. Thus it was suggested that changes in radical reactivity with these small radicals accounted for the high value obtained for $\frac{k2}{kp}$. Further experimental evidence fitted this argument for $\frac{k_2}{kp}$ increased with decreasing monomer concentration, a factor which decreases the small average degree of polymerisation. The ratio also varied with the initiator used and with small radicals the influence of end groups is to be expected. However, the individual constants were not evaluated and therefore propagation and transfer reactivities of different sized radicals could not be compared.

The work of Robb and Vofsi showed that in the trichloromethyl initiated polymerisation of styrene, there is a pronounced decrease in radical reactivity in the propagation and termination reactions in going from the distyrl radical to the tristyrl. Furthermore, it appeared that the radical reactivity must increase again when it became still larger. Eaves has shown that the reactivity of small polystyryl radicals is influenced by the nature of the end initiator fragment and clearly it is of interest to obtain more information about this. If the initiator fragment structurally resembles the monomer, radicals will be almost identical with those occurring in bulk polymerisation and the effect of the size of such radicals on their reactivity should be particularly interesting. It is of further interest to study systems involving monomers other than styrene, in order to see if similar reactivity changes take place. With these points in view the work described in this thesis has been performed. An unsuccessful attempt has been made to obtain information on radical activities in, effectively, bulk styrene polymerisation (described in Chapter 8). Quantitative data has been obtained on reactivity changes in growing small polymethyl methacrylate type radicals, and it is on this work that the bulk of the thesis is based.

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CHAPTER 2

APPARATUS, MATERIALS AND GENERAL EXPERIMENTAL PROCEDURE

The Reaction Vessel

Reactions were carried out in pyrex dilatometers of approximately 14 ml capacity. The capillary was of 'Veridia' precision bore with an internal diameter of 1.5 mms. Dilatometer capacities and capillary diameters were determined in the conventional manner using clean mercury, a cathetometer for measuring mercury capillary lengths, and accurate weighings. A side arm was sealed to the dilatometer and before use this complete vessel (see Figure I), like every other

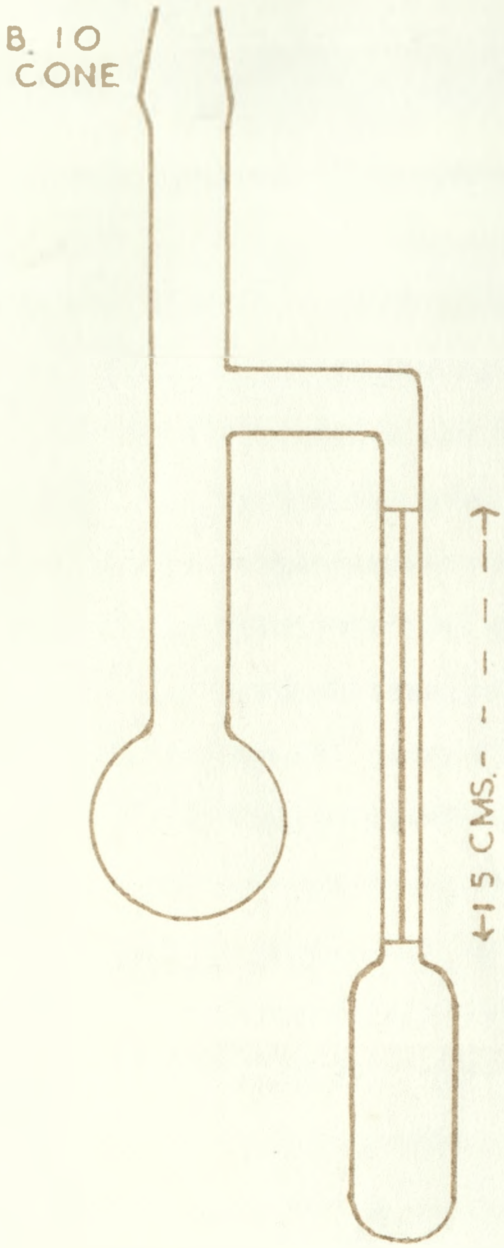

FIG. 1

glass vessel, was subjected to a vigorous cleaning with chromic acid, followed by repeated washing with distilled water and drying.

The Vacuum Apparatus and Reaction Vessel Filling Technique

Since oxygen interferes with polymerisation systems it is important that all reactions must be studied in its absence. An all pyrex glass vacuum apparatus, illustrated in Figure 2, was therefore constructed to remove oxygen and other gases. It was mounted on a rectangular grid. The line was evacuated by a two stage mercury diffusion pump backed by a 'Speedivac' rotary oil pump. These, together with the liquid air trap, reduced the pressure in the system to about 10^{-4} mms of mercury, as measured by a 'sticking vacuum' on the vacustat (V). Reservoirs of pure reactants (R_1 and R_2) were attached to the vacuum line and, after freezing in liquid air, were evacuated in turn and then allowed to warm to room temperature. This procedure was then repeated until the liquids evolved no further gas bubbles. Liquid transfer could now be carried out by high vacuum distillation, the receiver being cooled in liquid air. Taps A, B, C, and D allow isolation of the individual

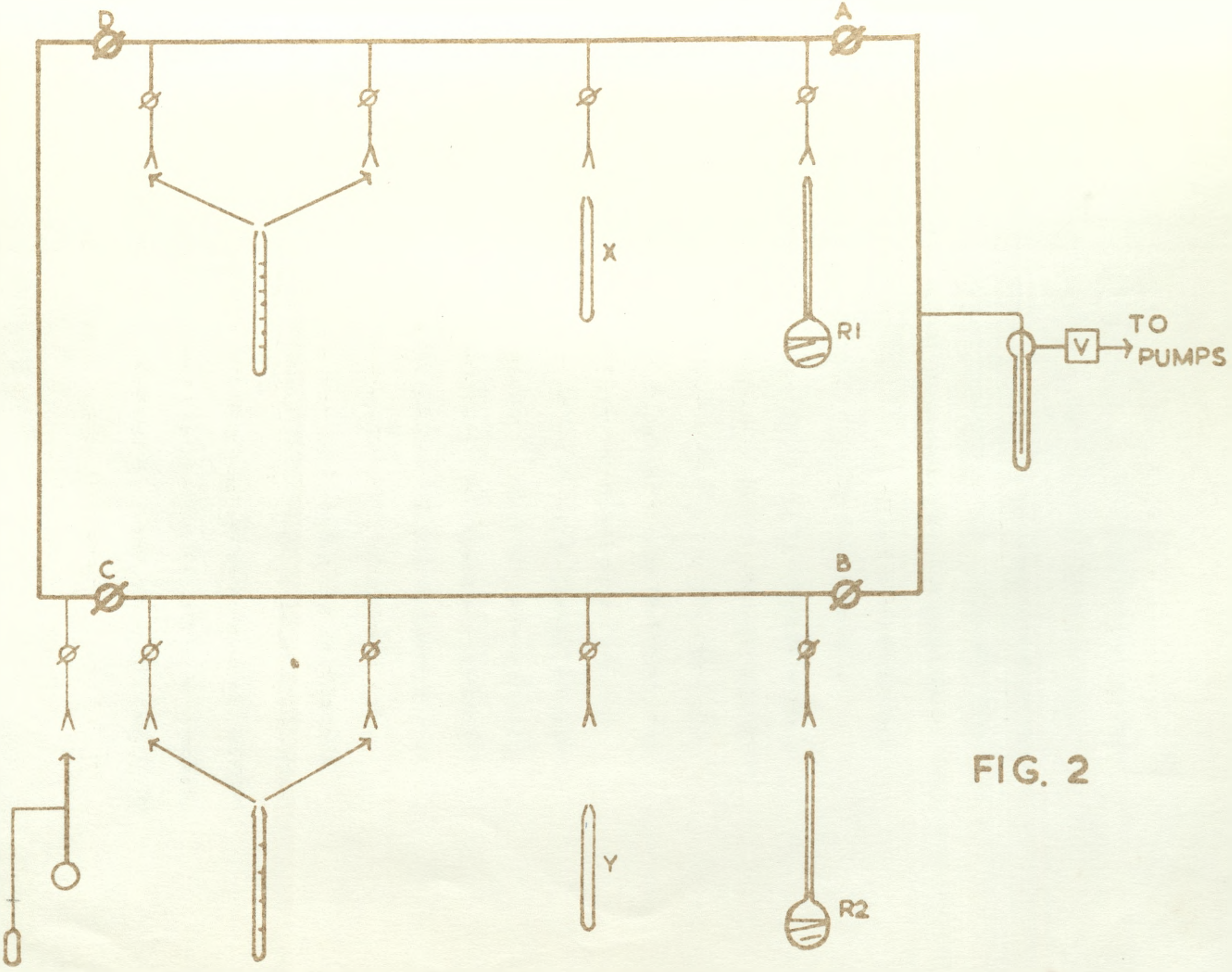

FIG. 2

reactant distillations. (Taps and joints beyond the liquid air trap were greased with silicone grease thickened with talc. On the pumping section of the line Apiezon M grease was used). After distilling first fractions into vessels X and Y, liquid was transferred from the reservoirs to graduated tubes. From the latter the two liquids were distilled separately into the side arm of the reaction vessel, which was then sealed off from the vacuum apparatus and the liquids allowed to thaw. In this way liquid mixtures of known composition were obtained. The complete reaction vessel with side arm was then placed in a thermostat at 30°C and allowed to reach temperature equilibrium. When this was attained, the dilatometer was filled to a convenient capillary height by tipping the shaken mixture of reactants into it. It was then sealed off from the side arm just above the capillary, and stored in a refrigerator until required.

Reactants which distil slowly under high vacuum were added directly into the side arm, using a modified graduated burette (Figure 3). This was drawn out at the

FIG. 3

bottom into a tube $1\frac{1}{2}$ mms in internal diameter and the normal tap, with capillary, was attached at the top. Liquids were introduced into the burette from the bottom by suction through the capillary. Thus the liquid never passed through a tap and therefore never became contaminated with grease.

When bromoethylbenzene was used as a reactant the normal degassing technique failed to remove all dissolved gases. The liquid was therefore added directly into a modified side arm (see Figure 4) and oxygen free nitrogen, previously dried, bubbled very slowly through it for approximately thirty minutes. This technique replaces all dissolved oxygen with inert nitrogen. After freezing the liquid the complete vessel was then evacuated. A water pump was used to remove trapped nitrogen in the supply tube, the latter then being sealed off at X. The normal degassing procedure was then carried out four times. Later it was found that normal degassing completely removed all gases, if the liquid on each melting was thoroughly stirred. Thus a small piece of iron, embedded in glass, was initially introduced into the bromoethylbenzene, and after thawing the latter, an

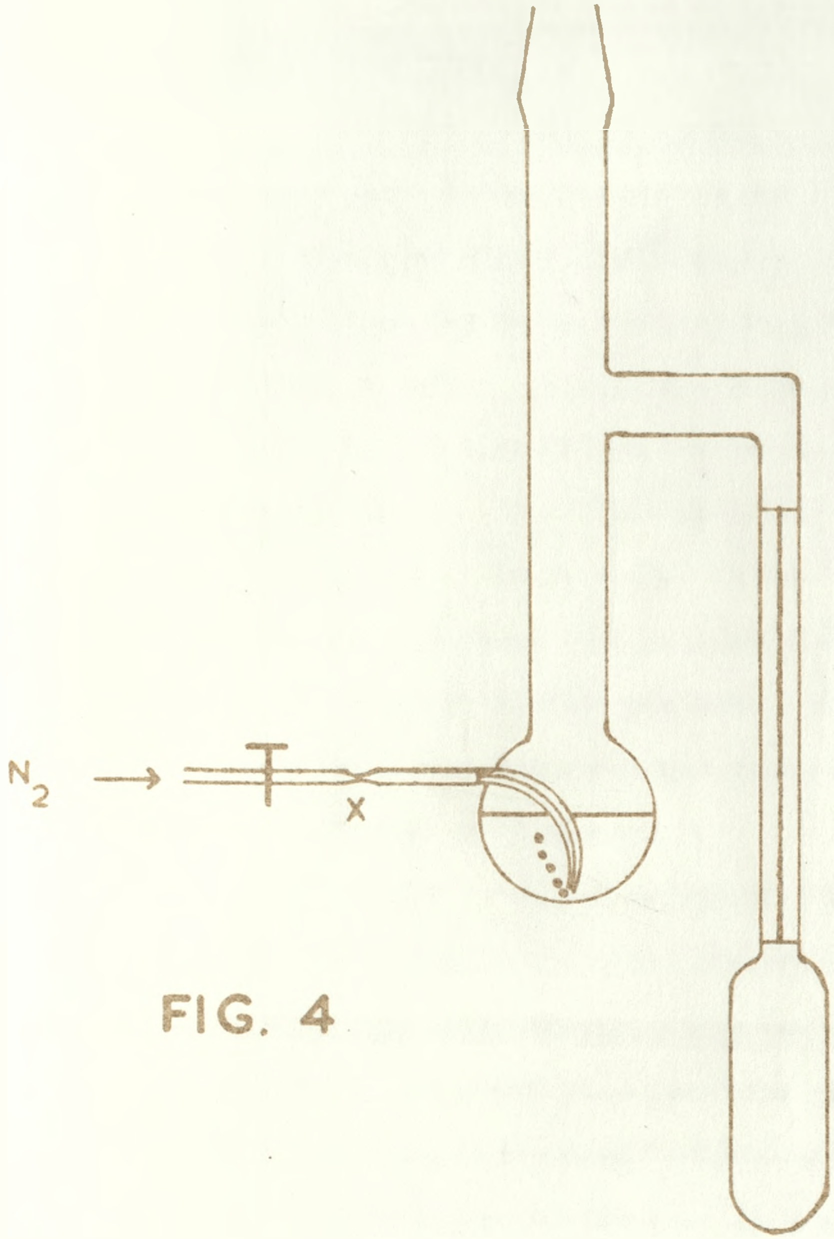

FIG. 4

electrically driven rotating magnet was placed below the side arm bulb.

The Reaction System

A thermostatically controlled distilled water bath was used. It was made of copper sheet with glass windows for light irradiation and for viewing the dilatometer capillary, and was lagged with $^{3}/4''$ of expanded ebonite. Temperature control of the order of ± 0.01°C was obtained by the usual mercury-toluene regulator. The dilatometer was supported in the thermostat on a brass rod fitted with Terry clips. Clamping arrangements ensured that it was placed each time in a reproducible position. Changes in meniscus level were followed by means of a cathetometer reading to 10^{-2} mms.

The source of reaction initiating irradiation was a 125 W Osira mercury arc stabilised with a constant voltage transformer. The lamp was enclosed in an asbestos lined box fitted with a shutter, and was switched on for about half an hour prior to use so as to obtain steady conditions. In preliminary experiments unfiltered light was used, but later a suitable optical filter (Chance 0X1) was chosen to give a practically monochromatic light beam of wavelength 3650 Å. When the dilatometer had reached thermal equilibrium it was exposed to U.V. radiation. Reaction causes volume contraction and the rate was determined by observation of the meniscus level at regular time intervals.

Materials

Bromotrichloromethane was supplied by Eastman Kodak. It was subjected to fractionation in a 4½' column packed with Fenske helices under a vacuum of 80 mms and under nitrogen. The middle fraction was collected (b.pt. 43°C) and was stored in the dark at -20°C. The purity was checked using vapour phase chromatography, mass spectrometry, and infra red analysis.

Commercial methyl methacrylate was freed from the phenolic inhibitor by repeated washing with a 10% solution of sodium hydroxide, followed by repeated washing with distilled water to remove the alkali. The methyl methacrylate was then dried with calcium chloride and distilled under reduced pressure under nitrogen. (B.pt. 39°C at 80 mms). It was stored at -20°C.

Commercial styrene was purified in the same way as methyl methacrylate as it too contained a phenolic inhibitor. It was distilled under 80 mms pressure and the middle fraction collected and stored in the refrigerator.

α-Bromoethylbenzene was prepared by two different methods:

1. Purified styrene was saturated with gaseous hydrogen bromide, allowed to stand overnight, and then poured into water. The resulting oil was separated off and washed in turn with 2N NaOH, 2N HCl, a saturated solution of sodium bicarbonate, and finally with distilled water. After drying over anhydrous sodium carbonate, the liquid was distilled, the fraction boiling at 95°C under 15 mms pressure being collected.[1]

2. Ethyl benzene (120 mls) was kept at 140°C and a slight excess of bromine (56 mls) added dropwise. The resulting mixture was washed with distilled water and dried. It was then cooled in a bath of ice and water when any dibromide present crystallised out. After filtration the liquid was distilled and the fraction boiling at 95°C under 15 mms pressure collected.[2]

Method 2 was found the most convenient. The pure compound tends to decompose under normal conditions and therefore was stored in sealed ampoules under nitrogen at -20°C.

Cyclohexene was obtained commercially and refluxed over copper stearate for an hour in order to remove cyclohexene hydroperoxide formed on standing in air. It was then stored in an evacuated reservoir.

Diethyl maleate and diethyl fumarate were obtained commercially and distilled, middle fractions being retained.

Benzene (cryoscopic grade) and cyclohexane (spectroscopic grade) were used in dilution experiments without further treatment.

Commercial chloroform was freshly distilled before use as a solvent for inhibitors.

Inhibitors

Pure samples of benzoquinone, tetrachloro-o-benzoquinone, and diphenyl-picryl-hydrazyl were kindly supplied by other members of this department.

The Ultra-Violet Spectra of the Reactants

In photochemical reactions it is necessary to know accurately the values of the extinction coefficients of the reactants for all the various wavelengths of light used. These are determined by the use of a Hilger spectrophotometer, an instrument which gives direct readings of $\log_{10}\frac{Io}{I}$ at the required wavelengths (where Io and I are the incident and transmitted light intensities respectively).

Now $$\varepsilon = \frac{1}{c.d.} \log_{10}\frac{Io}{I}$$

(where c is the concentration of the compound in moles/litre; d is the thickness of the cell in cms; ε is the molar decadic extinction coefficient).

Knowing every value in this expression except ε, it is possible to draw up a series of values for this constant at various wavelengths.

The extinction coefficients of bromoethylbenzene (Figure 5), tetrachloro-o-benzoquinone (Figure 6), and diphenyl-picryl-hydrazyl (Figure 6), were therefore measured at various wavelengths. Measurements were made using 1 cm cells and either spectroscopic cyclohexane

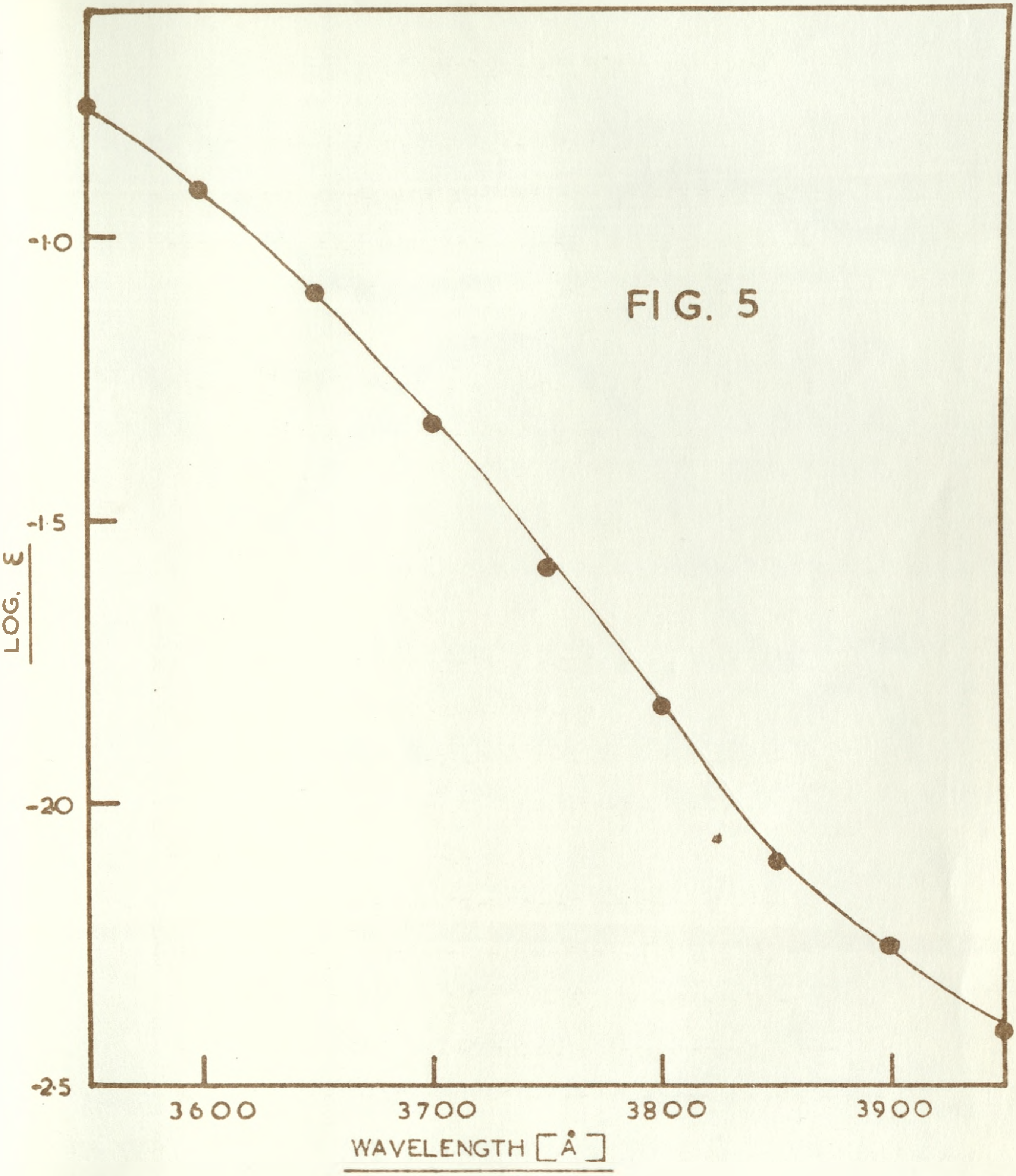

FIG. 5

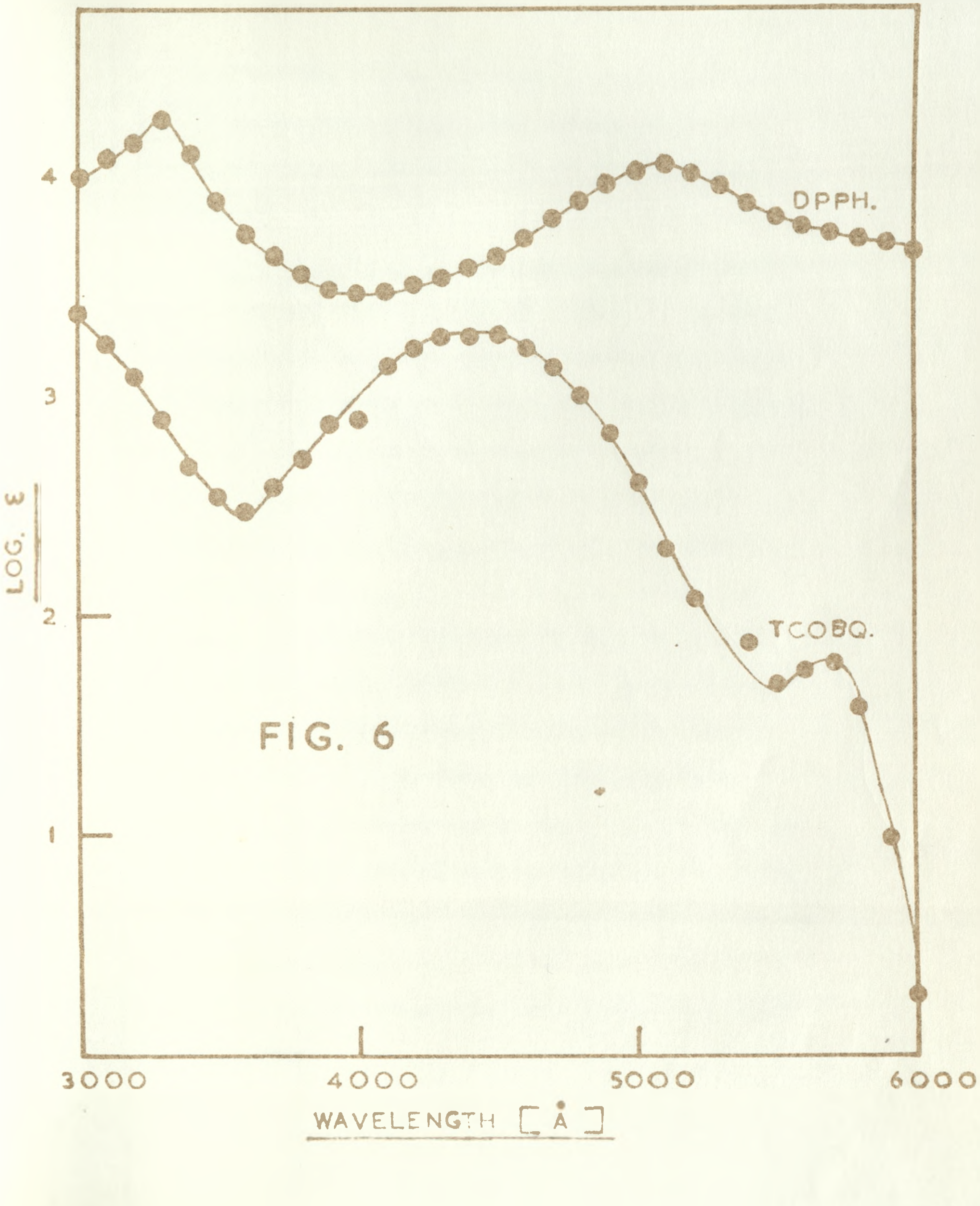

FIG. 6

or spectroscopic carbon tetrachloride as a solvent. Values for methyl methacrylate, styrene and bromotrichloromethane were obtained in a similar manner by Tutton.[3]

Under experimental conditions the light reaching the dilatometer was of wavelength 3650 Å. Knowing the values of the various extinction coefficients at this wavelength, it is possible to determine the light absorption in the dilatometer of any reaction mixture. The principal reaction mixtures studied were those of methyl methacrylate ($\mathcal{E}_{3650\,\text{Å}} = .0011$) and bromotrichloromethane ($\mathcal{E}_{3650\,\text{Å}} = 5.0 \times 10^{-3}$) in varying proportions. Calculation indicates that light absorption in the reaction vessel (width = 1.7 cms approx.) never exceeded 20% with any mixture of the two reactants, and therefore it was concluded that photochemical initiation occurred uniformly throughout the dilatometer. Reaction mixtures containing bromoethylbenzene in high concentration (see Chapter 8) absorbed a high percentage of light (approaching 90%) and it was deduced that with these systems light absorption might disturb the kinetic measurements.

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CHAPTER 3

THE KINETICS OF THE PHOTOCHEMICAL TELOMERISATION OF METHYL METHACRYLATE WITH BROMO TRICHLOROMETHANE

The general kinetic scheme is identical to that first proposed by Kharasch. It consists of the following elementary steps:-

(a) An initiation process brought about by the photochemical breakdown of bromotrichloromethane (BTM) into a free trichloromethyl radical and a free bromine atom, at a rate denoted by R_I.

$$(1) \qquad CCl_3Br \xrightarrow{h\nu} \dot{C}Cl_3 + \dot{B}r \qquad R_I$$

(b) The trichloromethyl radical propagates a polymerisation chain with the methyl methacrylate (M) which terminates by transfer with unchanged BTM. The length of the polymer chain is determined by the relative concentrations of monomer and transfer agent.

(2) $$CCl_3^{\bullet} + M \xrightarrow{k_1} CCl_3M_1^{\bullet}$$

(3) $$CCl_3Mr^{\bullet} + M \xrightarrow{k_p} CCl_3M^{\bullet}_{r+1}$$

(4) $$CCl_3Mr^{\bullet} + CCl_3Br \xrightarrow{k_2} CCl_3MrBr + CCl_3^{\bullet}$$

Equations (3) and (4) are general equations covering polymer radical propagation and transfer respectively. Transfer regenerates a trichloromethyl radical, the polymerisation initiation entity, and so equations (2) (3) and (4) constitute a kinetic chain reaction.

(c) Three chain termination steps are possible, since effectively two types of radicals exist in the system.

(5) $$CCl_3^{\bullet} + CCl_3^{\bullet} \xrightarrow{2kt,1} C_2Cl_6$$

(6) $$CCl_3Mr^{\bullet} + CCl_3Mn^{\bullet} \xrightarrow{2kt,2} \text{Products}$$

(7) $$CCl_3^{\bullet} + CCl_3\,Mr^{\bullet} \xrightarrow{kt,3} \text{Products}$$

Again, the existence of different sized polymer radicals means that general equations must be used for any termination mechanism involving them.

The fate of the bromine atom produced in reaction (1) is not certain but it almost certainly initiates a reaction chain, since no colouration due to free bromine ever occurred. The chain carrier is still, however, the trichloromethyl radical and since chains are long, bromine initiation does not interfere with the postulated kinetic scheme.

(a) $Br^{\bullet} + M \longrightarrow BrM^{\bullet}$

(b) $BrMr^{\bullet} + M \longrightarrow BrM^{\bullet}_{r+1}$

(c) $BrMr^{\bullet} + CCl_3Br \longrightarrow BrMrBr + CCl_3^{\bullet}$

In a similar way the scheme is unaffected by monomer initiation.

In the kinetic analysis of the reaction the following assumptions are made:–

(a) The steady state is established soon after the beginning of the reaction, i.e. the rate of formation of each radical species is equal to the rate of its disappearance.

(b) Termination is bimolecular.

(c) The reactivity of the radicals is dependent at least in the initial stages of the radical growth, on the length of their chain.

In actual fact each discrete step involving the interaction of a growing radical of the polymethyl methacrylate type with either monomer or BTM (i.e. $kp^{(r)}$ or $k2^{(r)}$)in the initial stages of the reaction should have to be assigned a specific constant. This would apply to the termination steps (6,7) as well. In the treatment which follows average apparent quantities $\overline{k}$ will be assigned to these constants.

From the stationary state assumption we have:—

$$\frac{d(\mathrm{CCl}\dot{3})}{dt} = R_I - k_1(\mathrm{CCl}\dot{_3})(\mathrm{M}) + \overline{k_2}(\mathrm{BTM})\sum(\mathrm{CCl_3M\dot{r}}) - 2k_{t,1}(\mathrm{CCl}\dot{_3})^2 - \overline{kt},3(\mathrm{CCl}\dot{3})\sum(\mathrm{CCl3M\dot{r}}) = 0 \tag{1}$$

$$\frac{d(\mathrm{CCl3M\dot{_1}})}{dt} = k_1(\mathrm{CCl}\dot{_3})(\mathrm{M}) - k_2^{(1)}(\mathrm{CCl_3M\dot{_1}})(\mathrm{BTM}) - k_p^{(1)}(\mathrm{CCl3M\dot{_1}})(\mathrm{M}) - 2\,\overline{kt},2(\mathrm{CCl_3M\dot{r}})\sum(\mathrm{CCl_3M\dot{r}}) - kt^{(1)},3(\mathrm{CCl}\dot{_3})(\mathrm{CCl3M\dot{_1}}) = 0 \tag{2}$$

$$\frac{d(\mathrm{CCl_3M\dot{_2}})}{dt} = k_p^{(1)}(\mathrm{CCl3M\dot{_1}})(\mathrm{M}) - k_p^{(2)}(\mathrm{CCl3M\dot{_2}})(\mathrm{M}) - k_2^{(2)}(\mathrm{CCl3M\dot{_2}})(\mathrm{BTM}) - \overline{2kt},2(\mathrm{CCl_3M\dot{_2}})\sum(\mathrm{CCl_3M\dot{r}}) - kt^{(2)},3\,(\mathrm{CCl}\dot{3})(\mathrm{CCl3M\dot{_2}}) = 0 \tag{3}$$

Similar equations can be set up for $\frac{d(\mathrm{CCl3M\dot{3}})}{dt}$, $\frac{d(\mathrm{CCl3M\dot{4}})}{dt}$ etc. up to the final largest radical $\mathrm{CCl_3M\dot{x}}$, which does not undergo propagation. The stationary state equation for this radical is then:—

$$\frac{d(\mathrm{CCl3}\dot{\mathrm{M}}_x)}{dt} = k_p{}^{(x-1)}(\mathrm{CCl3}\dot{\mathrm{M}}_{x-1})(\mathrm{M}) - k_2{}^{(x)}(\mathrm{CCl_3}\dot{\mathrm{M}}_x)(\mathrm{BTM}) - 2\overline{kt,2}(\mathrm{CCl3}\dot{\mathrm{M}}_x)\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r) - kt\overset{(x)}{,}3\ (\mathrm{CC}\dot{\mathrm{l}}_3)(\mathrm{CCl_3}\dot{\mathrm{M}}_x) = 0$$

Summing all these equations up to $\frac{d(\mathrm{CCl3}\dot{\mathrm{M}}_x)}{dt}$ we obtain,

$$R_I - 2\ kt,1(\mathrm{CC}\dot{\mathrm{l}}_3)^2 - 2kt,2[\Sigma(\mathrm{CCl_3}\dot{\mathrm{M}}_r)]^2 - \overline{kt,3}(\mathrm{CC}\dot{\mathrm{l}}_3)\ \Sigma(\mathrm{CCl_3}\dot{\mathrm{M}}_r) = 0 \qquad (4)$$

On subtracting (1) from (4)

$$k_1(\mathrm{CC}\dot{\mathrm{l}}3)(\mathrm{M}) - 2\overline{kt,2}[\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r)]^2 - \overline{k2}(\mathrm{BTM})\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r) - \overline{kt,3}(\mathrm{CC}\dot{\mathrm{l}}3)\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r) = 0$$

$$\therefore\ (\mathrm{CC}\dot{\mathrm{l}}_3) = \frac{\overline{k2}(\mathrm{BTM})\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r) + 2\overline{kt,2}[\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r)]^2}{k_1(\mathrm{M}) - \overline{kt,3}\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r)}$$

Now $2\overline{kt,2}\ [\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r)]^2 \ll \overline{k_2}(\mathrm{BTM})\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r)$,

and $\overline{kt,3}\ (\mathrm{CCl_3}\dot{\mathrm{M}}r) \ll k_1(\mathrm{M})$

Therefore, to a good approximation:

$$(\mathrm{CC}\dot{\mathrm{l}}_3) = \frac{\overline{k2}(\mathrm{BTM})\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r)}{k1(\mathrm{M})} \qquad (5)$$

From (5) and (4) one obtains:

$$R_I - 2kt,1\left\{\frac{\overline{k2}(\mathrm{BTM})\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r)}{k_1(\mathrm{M})}\right\}^2 - 2\overline{kt,2}\ [\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r)]^2 - \overline{kt,3}\ \frac{\overline{k2}(\mathrm{BTM})}{k_1(\mathrm{M})}\ [\Sigma(\mathrm{CCl3}\dot{\mathrm{M}}r)]^2 = 0 \qquad (6)$$

The rate R_B of BTM disappearance is given by

$$R_B = \overline{k_2}(BTM)\sum(CCl_3M\dot{r}) \tag{7}$$

Substituting R_B in (6) we get

$$R_B = k_1(M)\left\{\frac{(\frac{1}{2}R_I)^{\frac{1}{2}}}{\left\{\overline{kt,2}\left[\frac{k_1}{\overline{k_2}}\frac{(M)}{(BTM)}\right]^2 + \frac{\overline{kt,3}}{2}\frac{k1}{\overline{k_2}}\frac{(M)}{(BTM)} + kt,1\right\}^{\frac{1}{2}}}\right\} \tag{8}$$

It can likewise be shown that the rate R_M of monomer disappearance is given by the expression,

$$R_M = \left[\frac{\overline{k_p(M)}}{\overline{k_2}(BTM)} + 1\right] R_B \tag{8a}$$

Equations (8) and (8a) are the general solutions for R_B and R_M. This solution can be considerably simplified if we look into two extreme cases.

When working in a region where $k_1(M) > \overline{k_2}(BTM)$ and assuming that the termination constants $kt,1$, $\overline{kt,2}$ and $\overline{kt,3}$ are of the same order of magnitude, then the second and third terms under the square root may be neglected in comparison with the first and (8) is reduced to

$$R_B = \overline{k_2}(BTM)\sqrt{(R_I/2\overline{kt,2})} \tag{9}$$

In this region termination occurs between polymethyl-methacrylate type radicals. In the opposite region where $\overline{k_2}(BTM) > k_1(M)$ mutual trichloromethyl radical termination takes place and equation (10) will hold:

$$R_B^1 = k_1(M)\sqrt{(R_I/2kt,1)} \tag{10}$$

The expressions for the rate of monomer consumption will be accordingly:—

$$R_M = \left[\frac{\overline{k_p}}{\overline{k_2}}\,\frac{(M)}{(BTM)} + 1\right] \overline{k_2}\,(BTM)\sqrt{\frac{R_I}{2\,\overline{kt,2}}} \tag{9a}$$

$$R_M^1 = \left[\frac{\overline{k_p}}{\overline{k_2}}\,\frac{(M)}{(BTM)} + 1\right] k_1(M)\sqrt{\frac{R_I}{2\ kt,1}} \tag{10a}$$

When high degrees of polymerisation occur $\overline{k_2}(BTM) \ll \overline{k_p}(M)$ and therefore equation (9a) becomes:

$$R_M = \overline{k_p}(M)\sqrt{\frac{R_I}{2\,\overline{kt,2}}} \tag{9a'}$$

With large polymer radicals reactivity is undoubtedly independent of radical size and the propagation and termination constants have no longer to be average.

Thus $R_M = kp(M)\sqrt{\frac{R_I}{2\ kt,2}}$ where kp, kt,2 are the propagation and termination constants for any normal polymer radicals, and the equation becomes identical with that for normal polymerisation.

The adduct composition at any molar ratio of monomer to BTM is given by

$$\frac{R_M}{R_B} = \frac{\overline{k_p}}{\overline{k_2}} \frac{(M)}{(BTM)} + 1 \qquad (11)$$

Thus the quantity $\left[\frac{R_M}{R_B} - 1\right]$ may be considered as the average degree of polymerisation $(\bar{P})$ of these telomers, the 1 : 1 adduct not being regarded as a telomer.

Rewriting (11) we get

$$\frac{1}{\left[\frac{R_M}{R_B} - 1\right]} = \frac{1}{\bar{P}} = \frac{\overline{k_2}(BTM)}{\overline{k_p}\,(M)} , \qquad (12)$$

which expression becomes formally identical with the Mayo transfer equation,

$$\frac{1}{\bar{P}} = \frac{k_2\ (\text{Transfer Agent})}{k_p\ (\text{Monomer})} + \frac{1}{P_o} , \qquad (12a)$$

when $\frac{1}{P_o}$ can be neglected in comparison to the second quantity on the right, i.e. for very low molecular weight polymers.

If telomerisation occurs in the region where $k_1(M) > \overline{k_2}(BTM)$, $R_M > R_B$ and

$$R_M - R_B = \frac{\overline{k_p}(M)}{\sqrt{2\,\overline{k_{t,2}}}}\sqrt{R_I} \qquad (13)$$

In this region the apparent constants $\frac{\overline{k_p}}{k_2}$ and $\frac{\overline{k_p}}{\sqrt{\overline{kt,2}}}$ can be evaluated from (11) and (13), as functions of adduct composition. All three individual constants can be evaluated by independently determining the termination constants. Thus by carrying out lifetime measurements with appropriate reaction mixtures, $\overline{kt,2}$ can be evaluated as a function of adduct composition, and hence also $\overline{kp}$ and $\overline{k2}$.

Telomerisation may take place in the region where $\overline{k_2}(BTM) > k_1(M)$ although this means that the propagation reactivity of the trichloromethyl radical must be very much less than the subsequent polymer type radicals produced. This is unlikely for Robb and Vofsi[1], and also Tutton[2] showed that the trichloromethyl radical is extremely reactive with styrene, which is near methyl methacrylate in monomer reactivity tables. If, however, trichloromethyl radical addition to methyl methacrylate is rate controllingwe have that

$$R_M^1 - R_B^1 = \frac{\overline{k_p}}{k_2} \; \frac{k_1(M)^2}{(BTM)} \sqrt{\frac{R_I}{2\ kt,1}} \qquad (14)$$

Effective termination will take place between trichloromethyl radicals, andthe measured termination constant should therefore be independent of adduct composition. Equations (11) and (14) will enable values to be obtained for k_1, though individual propagation and transfer constants cannot be evaluated as functions of adduct composition.

References

1. Robb and Vofsi - Trans. Faraday Soc., Vol. 55, Part IV, 558 (1959)

2. Tutton - Ph.D. Thesis, Birmingham University (1954)

CHAPTER 4

PRELIMINARY EXPERIMENTS AND THE DETERMINATION OF $\frac{k_p}{k_2}$

In order to evaluate any changes in $\frac{k_p}{k_2}$ with radical size in any polymerisation transfer system it is necessary to determine degrees of polymerisation at various feed compositions [see equations (11) and (12a), Chapter 3]. Furthermore, in this particular work interest was concentrated on reactivity changes in very small polymer type radicals and consequently degrees of polymerisation had to be correspondingly low. Preliminary experiments were therefore designed to find transfer systems which gave these low polymers or telomers at suitable feed compositions from an experimental point of view. It will be appreciated that average degrees of polymerisation were measured in accordance with the average nature of the rate constants to be determined. The following three systems were investigated, reactions being initiated photochemically and followed dilatometrically:—

(a) BTM - Acrylonitrile (AN)
(b) Carbontetrachloride-Vinyl acetate (VA)
(c) BTM - Methyl methacrylate (M)

System (a)

A molar feed composition of approximately $\frac{10(\text{BTM})}{1\ (\text{AN})}$ gave a product which precipitated out of the reaction mixture. This is characteristic of polyacrylonitrile which is insoluble in most polymer solvents, and indicated that the degree of polymerisation obtained was not as low as desired, for very small molecular weight products might be expected to be soluble in the reaction mixture. Even if the average degree of polymerisation was small and the higher molecular weight products were precipitating out, the heterogeneous nature of the system was undesirable.

System (b)

A reaction mixture of molar ratio approximately $\frac{15(CCl_4)}{1(VA)}$ yielded a polymer adduct of about three monomer units per transfer unit (3 : 1). This system, however, required the addition of an initiator since carbon tetrachloride was not photolysed by the ultraviolet light.

System (c)

This particular system was found to be desirable for low molecular weight products were formed in a convenient molar ratio range of the two reactants. In addition the initiation process was unambiguous in the region round 3650 Å and took place mainly by photolysis of the C-Br bond. Reaction mixtures of various feed compositions were studied, the reaction being allowed to proceed until a fall off in the initial rate occurred, indicating approximately 10% conversion of reactants. A typical reaction run is shown in Figure 7, from which the reaction rate can be determined in terms of contraction per unit time. Figure 8 shows a plot of this dilatometric contraction rate against molar fraction of reactants and it will be seen that a maximum rate is observed with a monomer

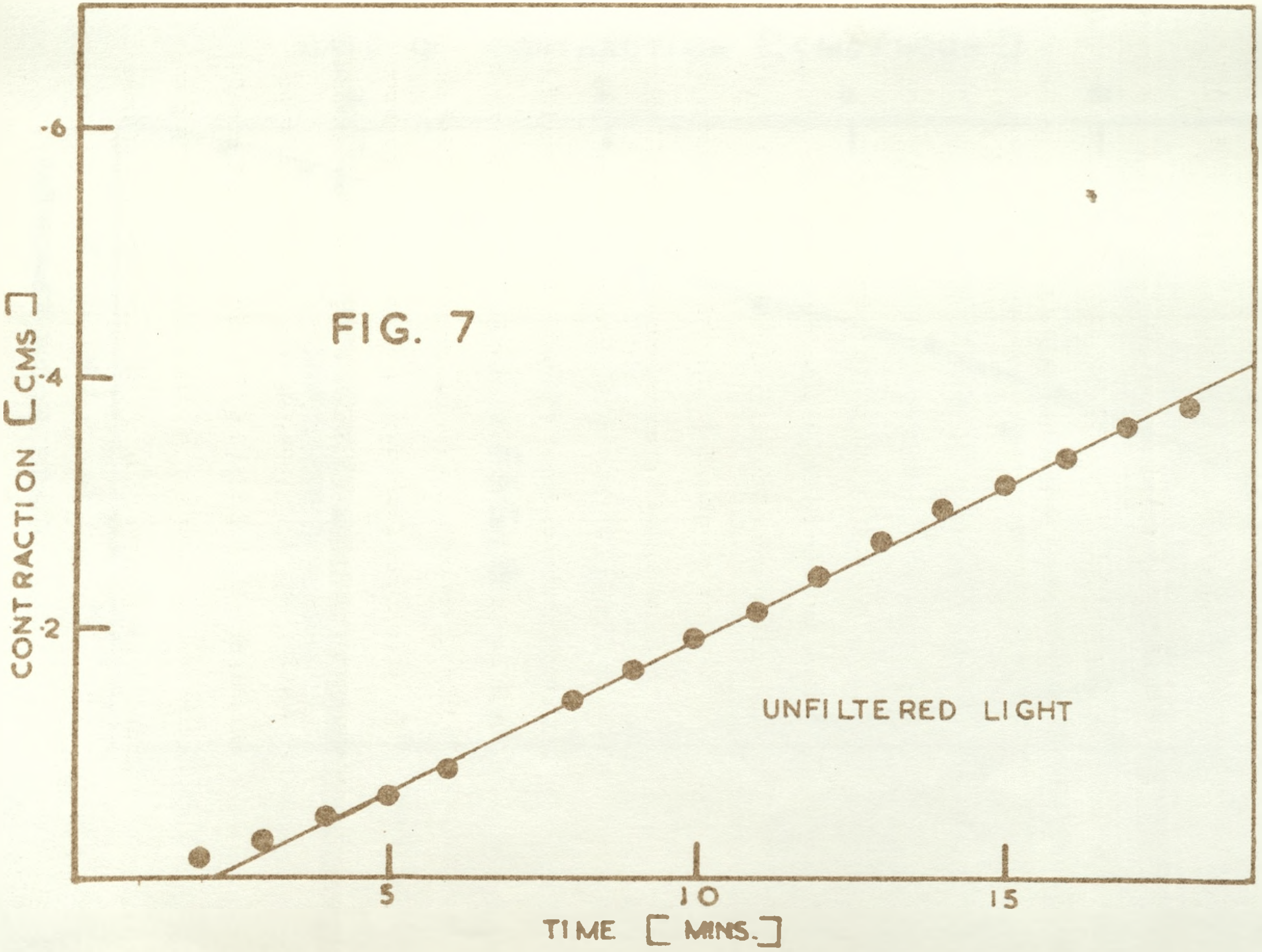
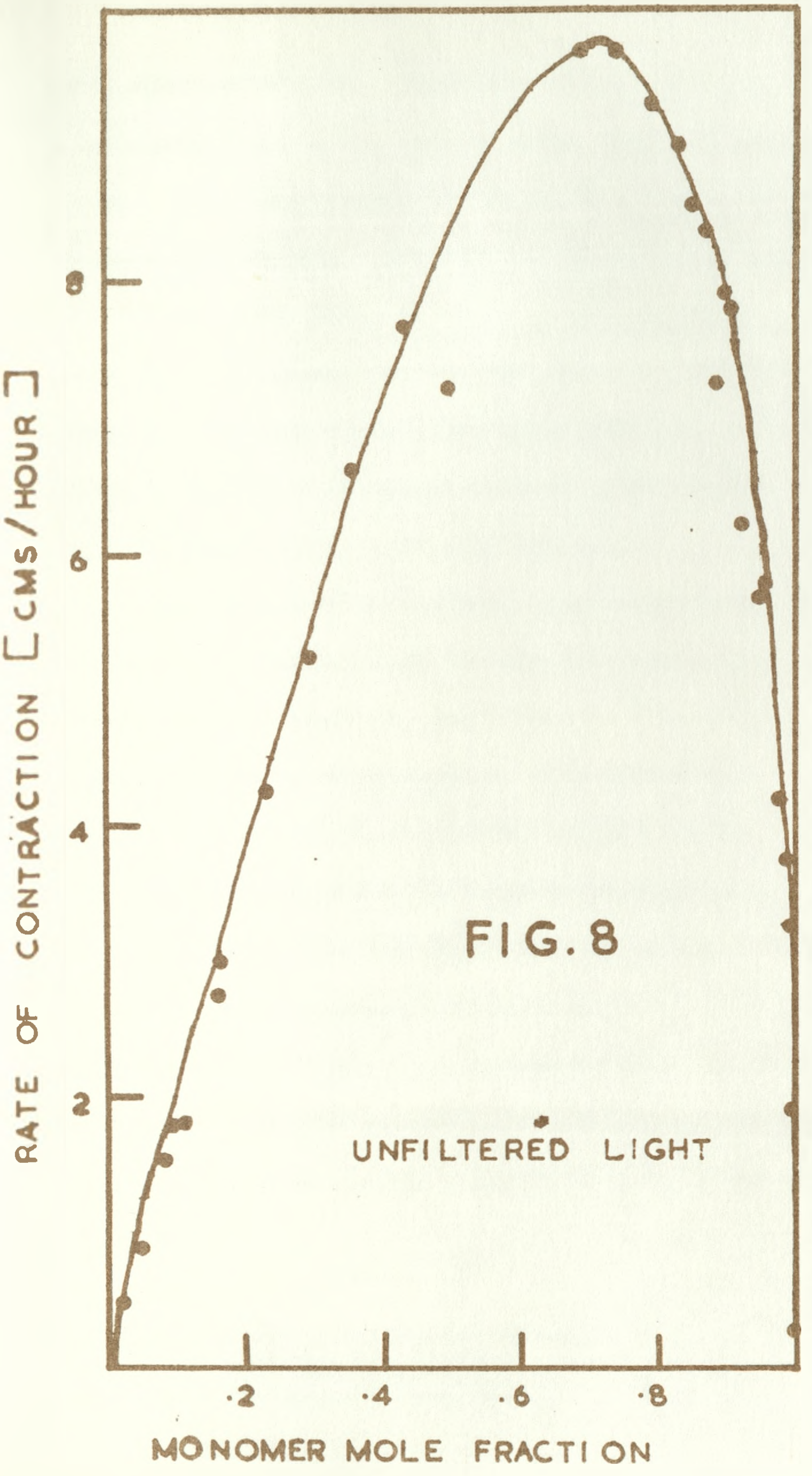


FIG. 7



RATE OF CONTRACTION [CMS/HOUR]
2
4
6
8
·2
·4
·6
·8
MONOMER MOLE FRACTION
UNFILTERED LIGHT

FIG. 8

mole fraction of .72. Equations (8) and (8a) predict a maximum rate in the intermediate range of molar ratios, since reaction initiation in the absence of BTM is negligibly small. Actually a thermal reaction was observed to take place at 30°C, probably due to monomer initiation, but this was always small and about one fortieth of the photochemical rate. Prepolymerisation of the stock methyl methacrylate reduced the thermal rate still further.

The nature of the radical termination step was established by measuring the rate of reaction for various light intensities, the intensity of the light being changed by using screens of known transmission. These screens of fine copper mesh, blackened by immersion in ammonium sulphide, were placed between the light source and the reaction vessel. The transmission factor for each screen was measured on a Hilger Spekker photoelectric absorptiometer. Now, in general, the rate of any photochemical reaction can be expressed in the following manner:-

$$\text{Rate} = kI^N$$

where k = a proportionality constant,
I = the light intensity,
and N = the intensity exponent.

Thus a plot of log reaction rate against log of light intensity (or screen transmission factor) should be linear, with a slope equal to that of the intensity exponent. Table I shows the results of the measured rates of a 1 : 1 molar mixture of methyl methacrylate and BTM for various transmissions at 30°C and Figure 9 shows the plot of log rate against log intensity for reaction systems of varying feed composition, the intensity exponent being determined in each case. It will be seen that in the molar ratio range studied it is approximately .5, indicating that second order radical termination occurred.

Table 1

Light transmission	Rate (cms/hr)	Light transmission	Rate (cms/hr)
100%	7.2	46.5%	4.59
51%	4.95	32.5%	3.9

After each reaction mixture had reached about 10% conversion the reaction was stopped and a sample of about 6 grms withdrawn from the dilatometer and placed in a weighed glass tube. After re-weighing the tube it was

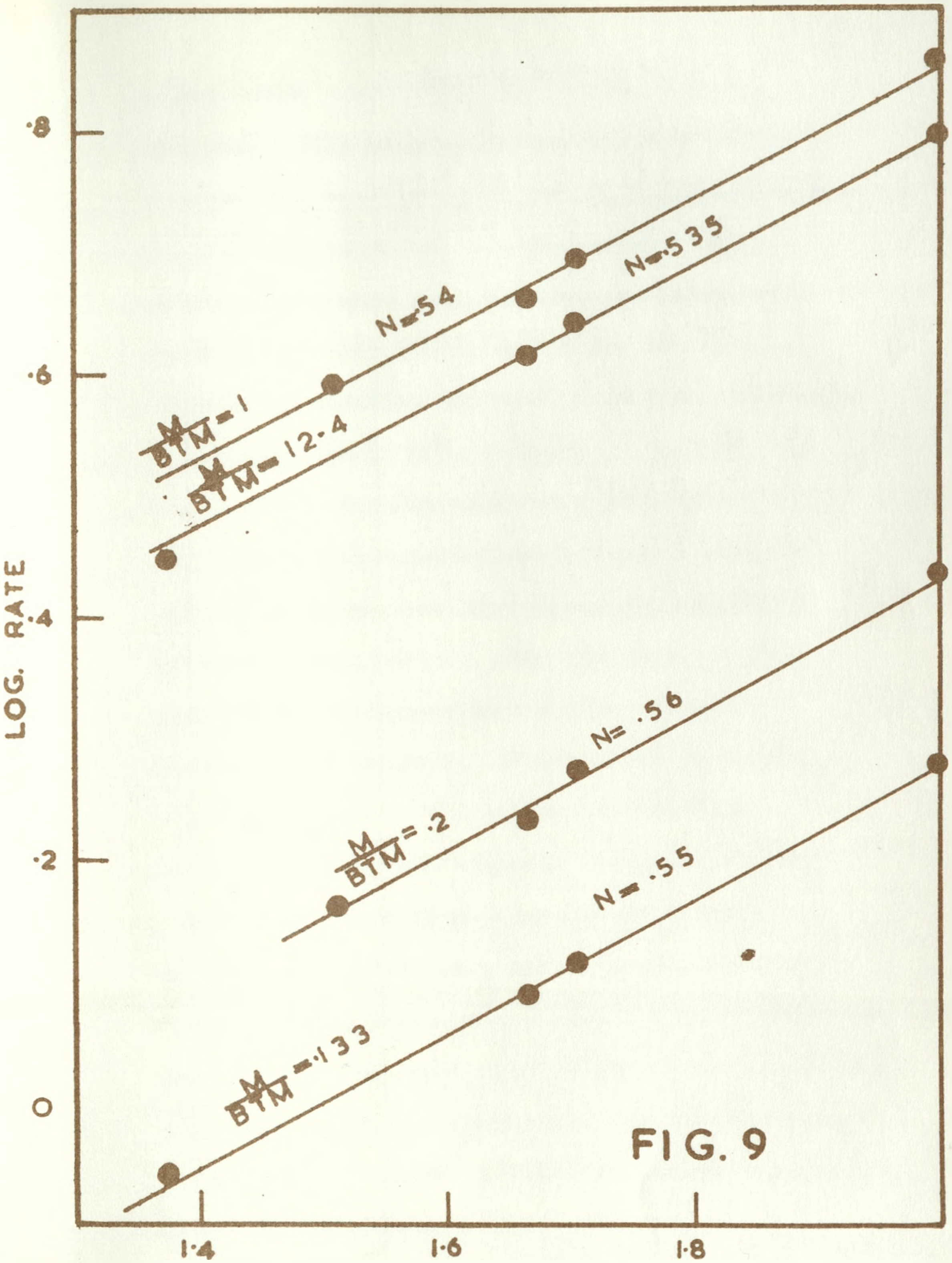

·8
·6
·4
·2
0
LOG. RATE
1·4
1·6
1·8
LOG. INTENSITY
N=·54
N=·535
$\frac{M}{BTM}=1$
$\frac{M}{BTM}=12\cdot4$
N= ·56
$\frac{M}{BTM}=\cdot2$
N= ·55
$\frac{M}{BTM}=\cdot133$

FIG. 9

placed inside a vessel to which a side arm was attached. This vessel was then connected to the vacuum line, see Figure 10, surrounded by a liquid air bath and evacuated. At this point, a tap, isolating the vessel from the line was closed and the liquid air bath transferred to the side arm, whereby the volatiles contained in the glass tube began to condense slowly in the side arm. When all but traces of the volatiles were removed in this way, the sidearm was removed and the vessel connected directly to the vacuum line and pumping continued for about fifteen hours. After this time pumping was discontinued every hour and the glass tube withdrawn and weighed. When the loss in weight did not exceed 0.1 - 0.2 mg per 50-100 mg of residue, pumping was stopped. A sample of this residue was then analysed for carbon, hydrogen, and total halogen content, and from the results the average adduct composition of the reaction product determined. Compositions, as determined by carbon and total halogen analysis agreed well when the adducts were small, but tended to differ for adducts greater than 8:1. For example:-

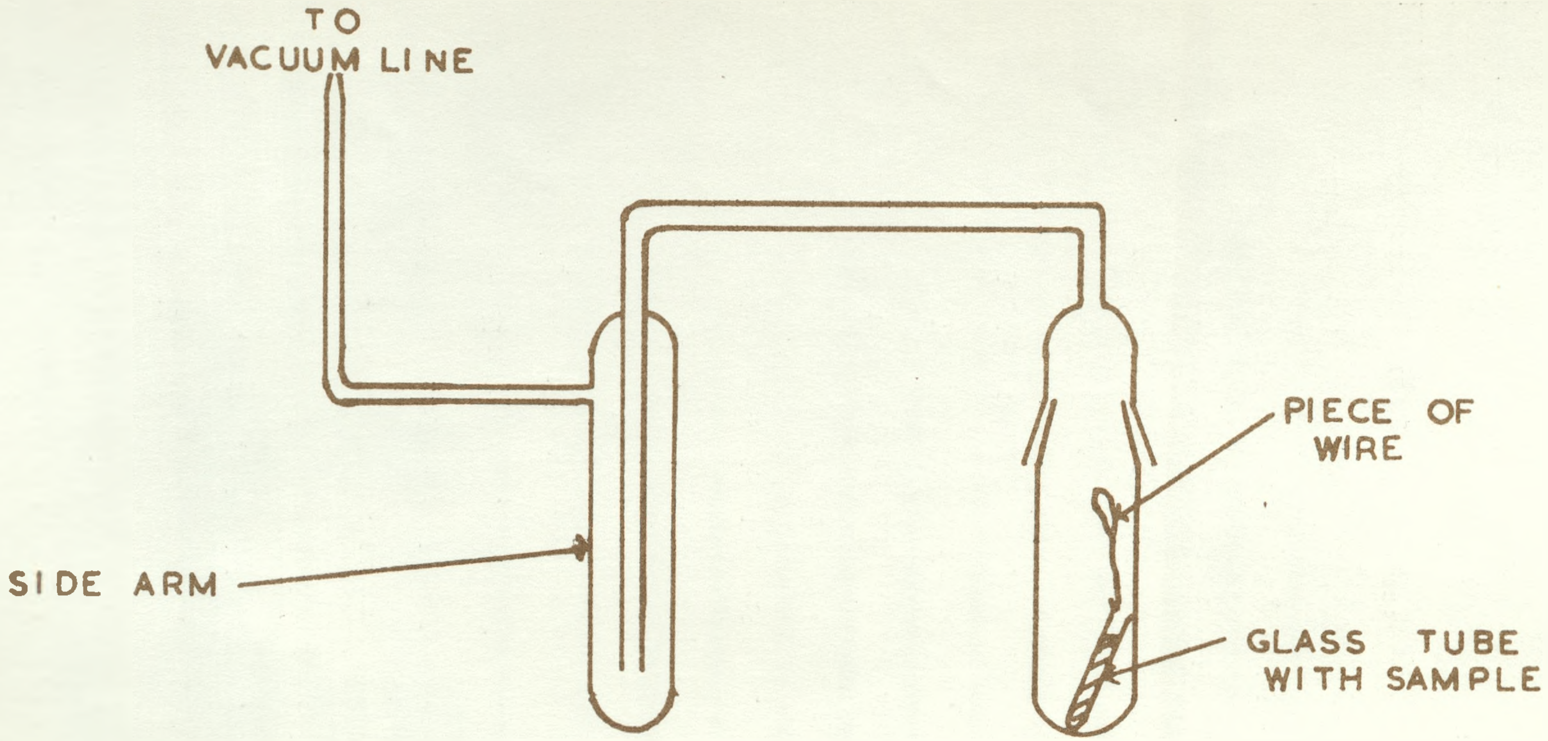


FIG. 10

Table 2

Run number	Adduct composition	
	Based on % carbon	Based on % halogen
8	2.35	2.50
26	5.65	5.60
32	6.80	6.65
29	11.2	12.9
13	20.5	16.4

This was because with high adducts the differences in carbon and halogen content of successive adducts are small. In the same way hydrogen determinations, even for small adducts, tended in general to give different compositions than carbon and halogen determinations. Thus all degrees of polymerisation were determined by carbon and total halogen content, these values being averaged. With adducts greater than 8 : 1, the average values obtained were less reliable and the reliability decreased with increasing degree of polymerisation. In this manner product compositions were determined for different feed compositions and the results are expressed in Table 3.

Table 3

Feed composition [(M)/(BTM)]	Adduct composition [X:1]	F.C.	A.C.	F.C.	A.C.
.054	2.425	.768	4.0	5.90	7.9
.114	2.85	1.0	3.95	6.82	7.6
.133	3.5	2.0	5.15	7.76	11.8
.199	3.9	2.22	5.5	9.15	8.3
.303	3.95	2.90	5.625	10.9	12.05
.421	3.9	3.88	6.5	18.6	18.45
.562	3.95	5.07	6.725	22.1	20.0

Adducts of about 2.5:1 were very viscous liquids, the viscosity increasing with adduct size. From 4:1 - 6:1 they tended to resemble white crystalline solids and above 6:1 they began to have a (cellophane flake-like) appearance. Smooth transitions took place between the different physical appearances. Very large adducts, greater than 20:1, were solid 'polymer-like' materials. Kirkham[1] has found that with BTM and styrene adducts up to 4:1 are viscous liquids, and this is undoubtedly because styrene is much less polar than methyl methacrylate. If a portion of the dilatometer contents was poured into excess methanol, it was found that for all adduct sizes turbidity occurred. When average adduct compositions were greater than approximately 3 : 1, precipitation also took place. This is to be expected for normal polymethyl methacrylate precipitates when its solution is poured into excess methanol. Very low polymers, about 2 : 1 and 3 : 1, might be expected to resemble pure monomer and be soluble in methanol.

In Figure 11 adduct composition is plotted against feed composition, using the data from Table 3. It will be observed that sharp changes in the slope to this curve take place when the adduct composition is about 3.5 : 1 and 4.5 : 1, splitting the graph into three sections. Figure 12 is a plot of the first two sections on a larger scale. According to equation (11), Chapter 3, the slopes to the three sections of the curve (Figure 11) can be identified with the values of $\frac{\bar{k}_p}{\bar{k}_2}$ for the trimeric, tetrameric and pentameric polymethyl methacrylate radicals. Since adduct compositions above 4 : 1 all seem to lie within reason on the same straight line, it seems probable that the value of $\frac{\bar{k}_p}{\bar{k}_2}$ for the pentameric radical can

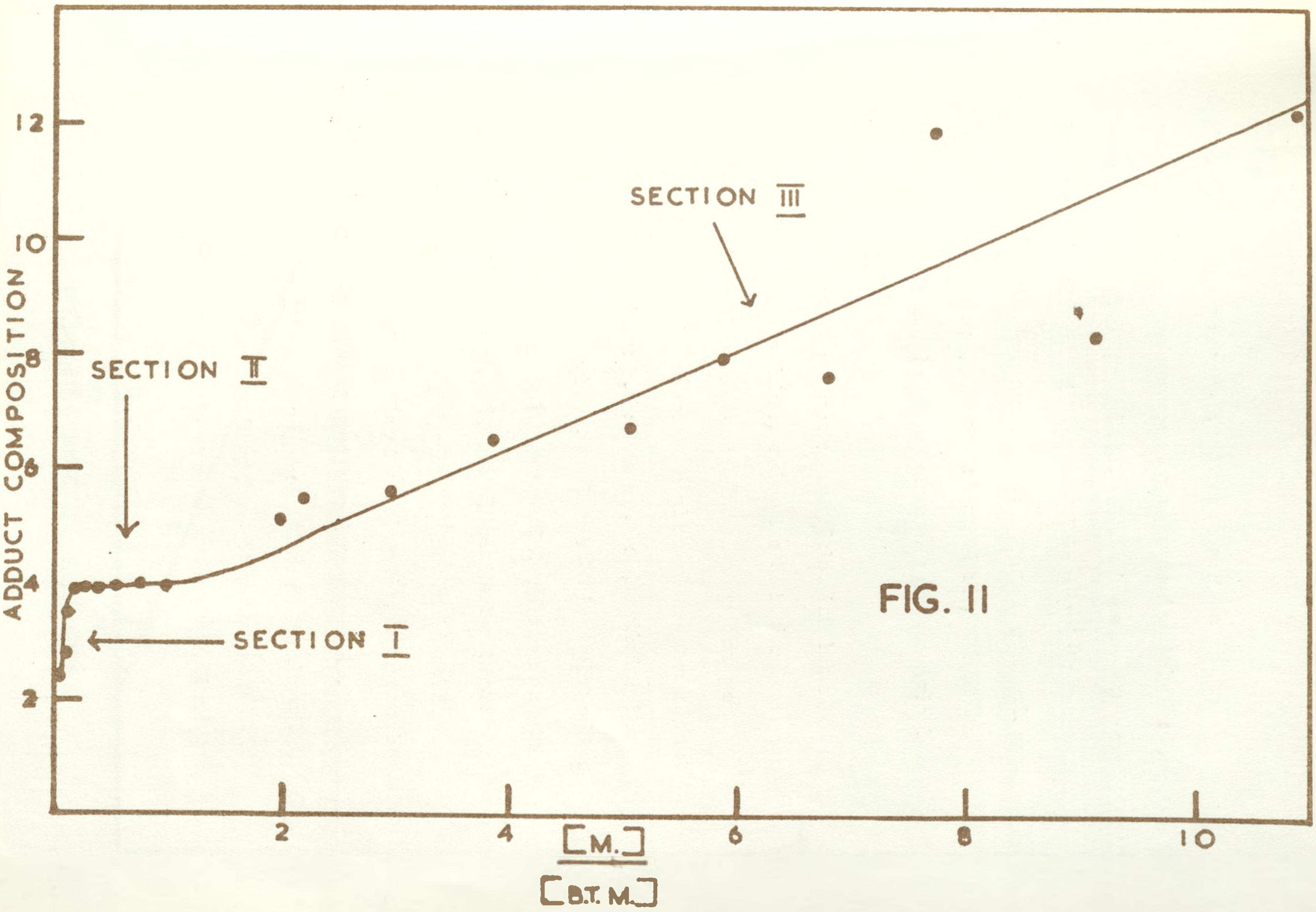

ADDUCT COMPOSITION
12
10
8
6
4
2
2
4
6
8
10
[M.] / [B.T. M.]
SECTION I
SECTION II
SECTION III

FIG. II

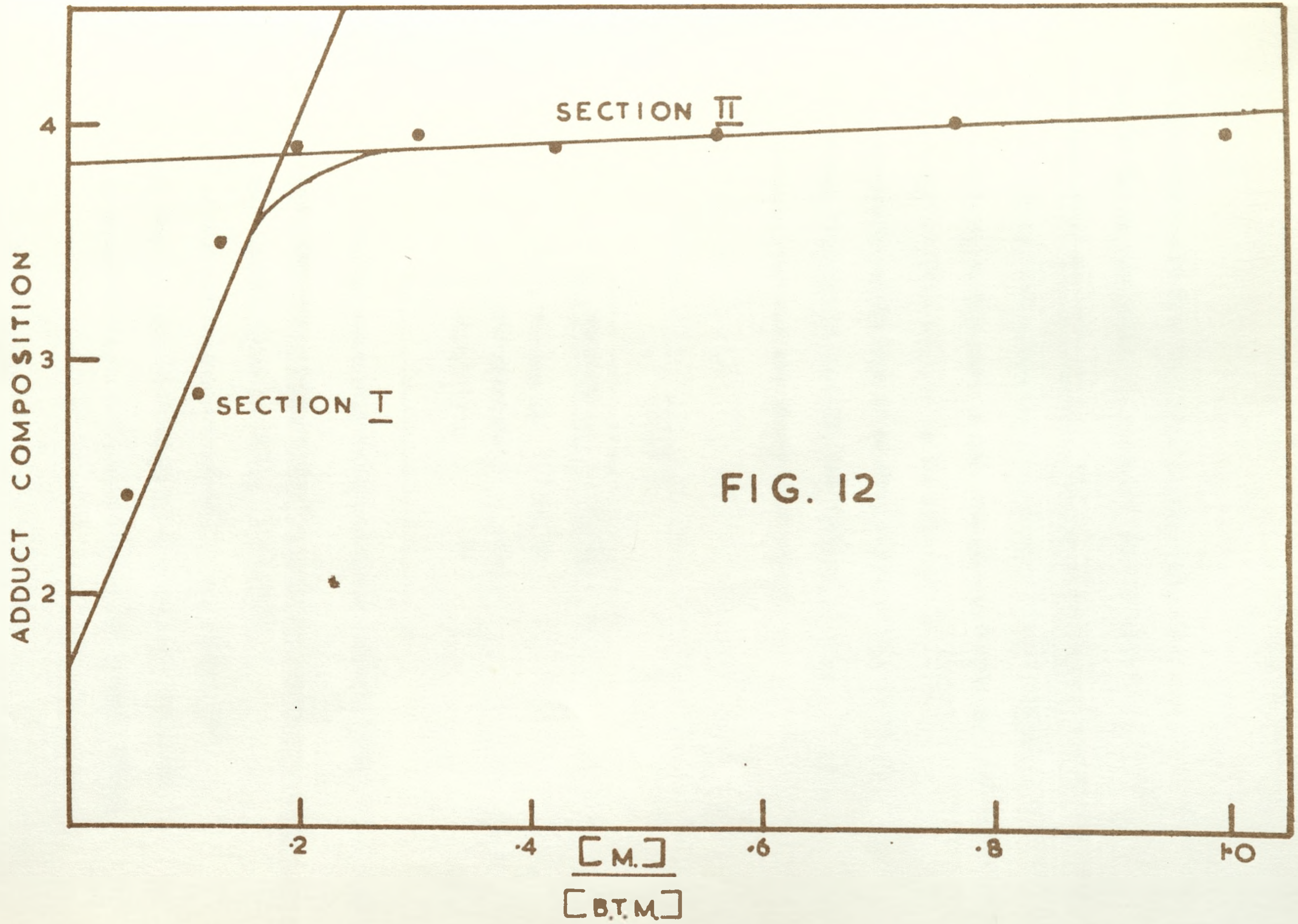


FIG. 12

be identified with that obtained in normal polymerisation for large radicals. In support of this adduct compositions of about 18.5 : 1 and 20 : 1 were obtained from suitable initial feed mixtures and although composition determination in this case is not completely reliable, these large adducts seemed to lie approximately on the extended straight line of section three of figure 11. Thus from Figures 11 and 12, the following values of $\frac{\overline{k_p}}{\overline{k_2}}$ were obtained for various sized radicals:—

Table 4

Radical	$\overline{k_p}/\overline{k_2}$
Trimeric	11.75
Tetrameric	.225
Polymeric	.85

It will be seen that as the average radical size increases from the trimeric to the tetrameric, $\frac{\overline{k_p}}{\overline{k_2}}$ drops by a factor of about fifty. Robb and Vofsi[2] measured a similar fall off in increasing the average dimeric styryl radical by one styrene unit, all radicals again having a trichloromethyl end group. They subsequently showed that the changes in $\frac{\overline{k_p}}{\overline{k_2}}$ were due to changes in $\overline{k_p}$, $\overline{k_2}$ remaining constant. Furthermore, since the value of $\overline{k_p}$ associated with the average trimeric radical was less than that of normal polymerisation, they predicted it would increase again with radical growth. If $\overline{k_2}$ still remained the same this would mean a consequent increase in $\frac{\overline{k_p}}{\overline{k_2}}$. In this light, in the present work with methyl methacrylate, the observed increase in $\frac{\overline{k_p}}{\overline{k_2}}$, after an initial decrease, is interesting. Although $\frac{\overline{k_p}}{\overline{k_2}}$ is less for average trimeric polymethyl methacrylate radicals than for average smaller ones, for the curve of adduct composition against $\frac{(M)}{(BTM)}$ must pass though 1 (see Figure 12), the pronounced fall off occurs with an average tetrameric radical. With styryl-type radicals this pronounced fall off is at a radical size less by one monomer unit, and this difference must undoubtedly be correlated with the different monomer molecule structures. However, before comparing reactivities of radicals of different sizes and types, it is necessary to determine the individual constants, $\overline{k_2}$ and $\overline{k_p}$, for the different radicals. This work is described in the following three chapters.

Characterisation of Adducts by Vapour Phase Chromatography

Robb and Vofsi[3] determined adduct compositions by VPC. In principle, the rates of consumption of both transfer agent and monomer are evaluated and the ratio of the latter to the former is clearly the adduct composition. This technique was therefore investigated in detail and the method eventually developed to a stage where adduct compositions could be found. Unfortunately lack of time prevented complete duplication of the adduct compositions determined by element analysis, but nevertheless the development of the general techniques employed is of interest.

Preliminary Qualitative Work

(1) Apparatus

Robb and Vofsi achieved a good quantitative analysis of mixtures containing BTM and vinyl acetate by using VPC to separate the constituents of the mixture which were then frozen out from the exit gas stream in a trap and weighed. The quantities of material used were of the order of 500 mg. They used a column 140 cms long, packed with kieselguhr impregnated (to 45% of its weight) with dinonyl phthalate and kept at a constant temperature of 78°C. A similar type of column, 80 cms long, was therefore set up (see Figure 13), and the separation of BTM and methyl methacrylate mixtures investigated.

The column E had an internal diameter of 10 mms and was surrounded by a vapour jacket, in which a constant temperature of 78°C was maintained by refluxing carbon tetrachloride. The column packing mixture was prepared by taking crude kieselguhr and stirring it with a large volume of water. After allowing a few minutes for sedimentation, the water and suspended kieselguhr was decanted off leaving the less fine particles behind. This process was then twice repeated with the sedimented kieselguhr, to give a final graded material which was free from the finer particles. This was then washed three times with concentrated hydrochloric acid, three times with distilled water, and finally dried overnight in an oven. A weighed amount of the dry kieselguhr was then mixed with an etheral solution of the appropriate amount of dinonyl phthalate and the mixture continually stirred until the bulk of the ether had evaporated. Final traces were removed by allowing the mixture to stand overnight.

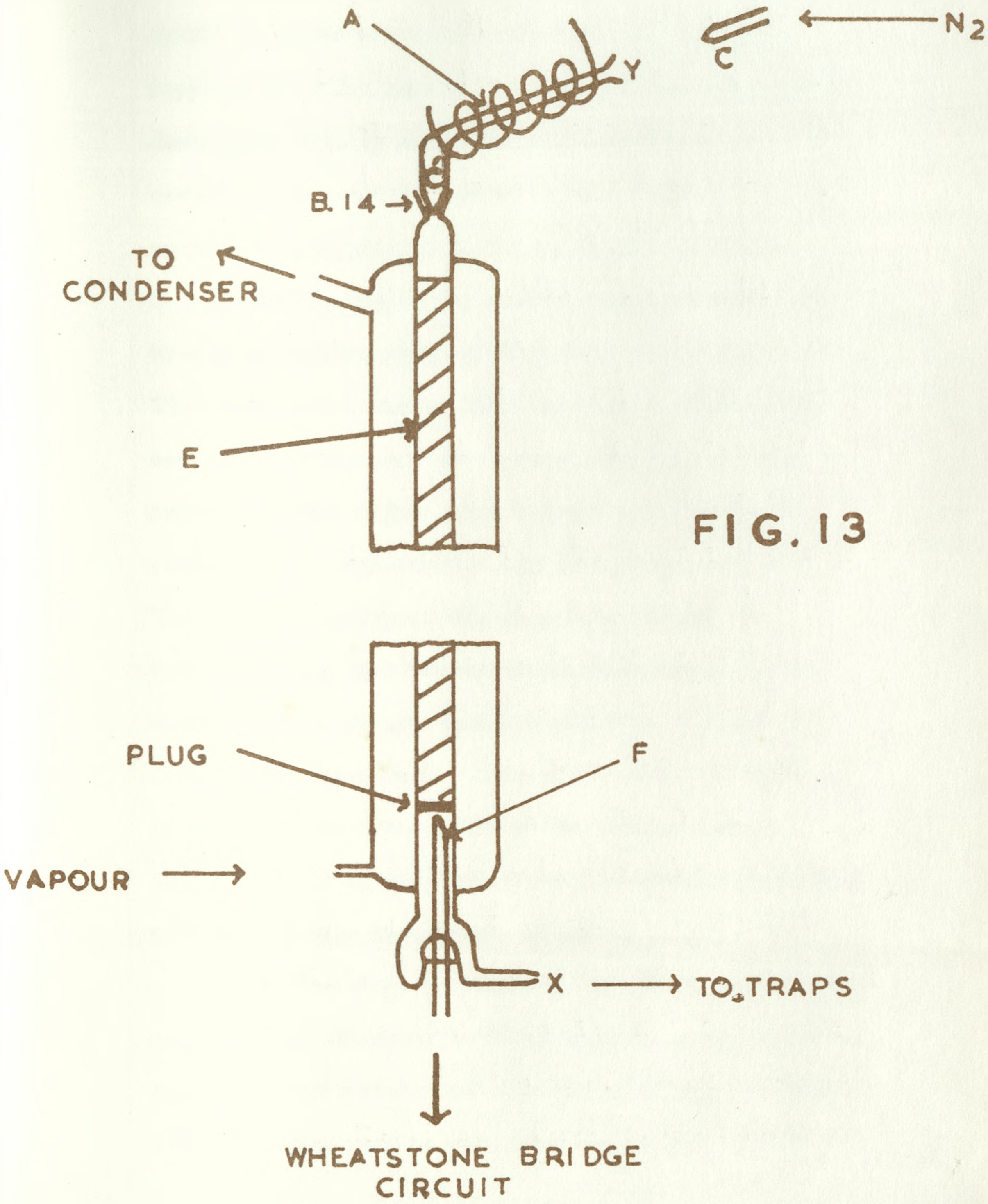

A
N2
Y
C
B.14
TO CONDENSER
E
PLUG
F
VAPOUR
X
TO TRAPS
WHEATSTONE BRIDGE CIRCUIT

FIG. 13

The column was packed by introducing successive small amounts of mixture through the top and tapping the sides gently, so that the material settled down quite firmly on a plug of glass wool fixed in a constriction near the bottom of the column. Gentle suction was applied at X throughout the filling.

To the top of the packed column a preheater tube A of 8 mms internal diameter was connected. This was kept at about 80°C by means of a heating coil in circuit with a few accumulators. At the column bottom a fine tungsten wire, F, having a resistance of about 150w at 78°C, was sealed in. This wire constituted one arm in a wheatstone bridge circuit and served as an indicator. As its counterpart a simple radio resistance of about the same value was used. Two 470 - 520w resistances constituted the other arms of the bridge, their variability being used to obtain a balance as indicated by a Cambridge Instrument Company galvanometer.

Before use, the column, at 78°C, was flushed out with dry nitrogen for about four hours to remove any traces of moisture etc on the packing. A 'white spot' nitrogen source was used and before it was introduced into the top of the column it was bubbled through a spiral containing conc H_2S0_4. The use of a vessel of large capacity in the nitrogen flow circuit buffered any significant pressure changes and thus kept the flow rate as constant as possible. A mercury 'blow-off' prevented the build up of very high pressures. The complete nitrogen circuit is shown in Figure 14, the flow meter being quite simple in design. In principle the build up of nitrogen pressure due to passage through a capillary is compared with the build up due to passage through the column. Clearly the difference in these pressures is a measure of the flow rate, and by the use of an oil manometer, pressure differences could be identified with flow rates after an initial calibration had been performed.

2. Procedure and Results

The preheater tube at 80°C was attached to the top of the heated column and a continuous stream of nitrogen passed through the whole apparatus. With a steady flow rate the wheatstone bridge system was adjusted to give a convenient steady galvanometer reading.

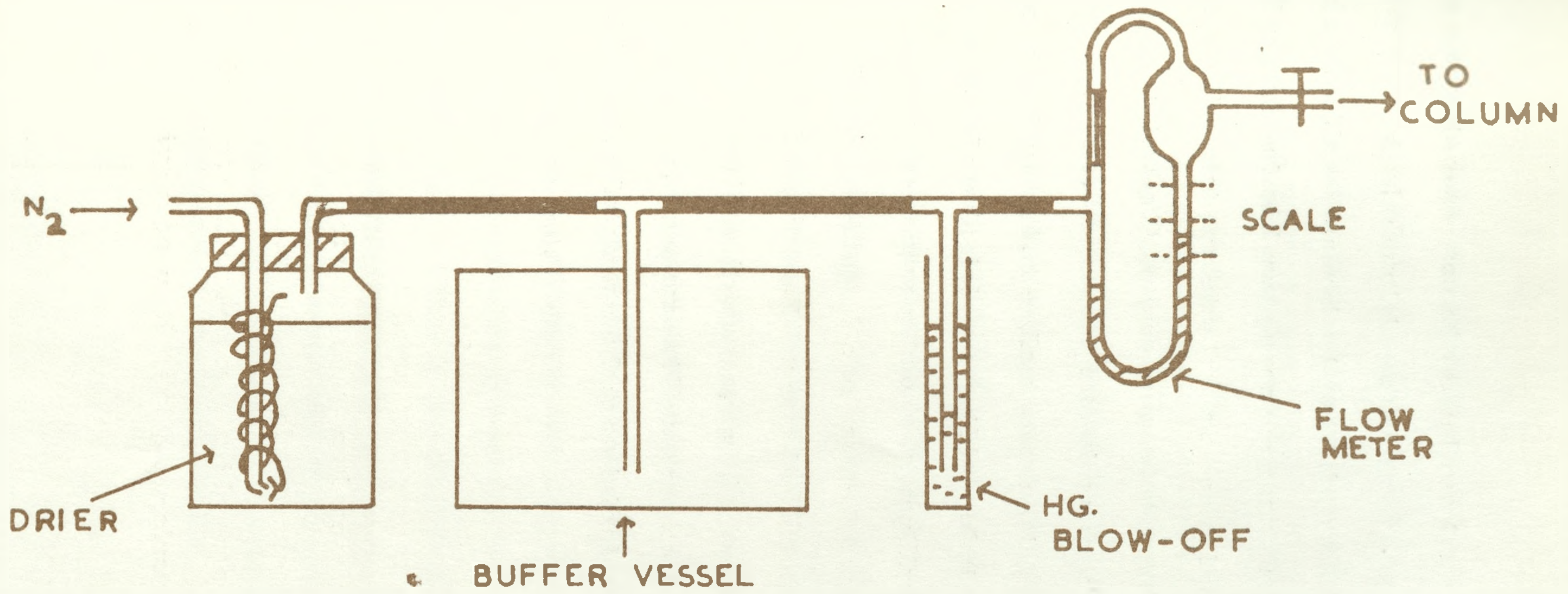
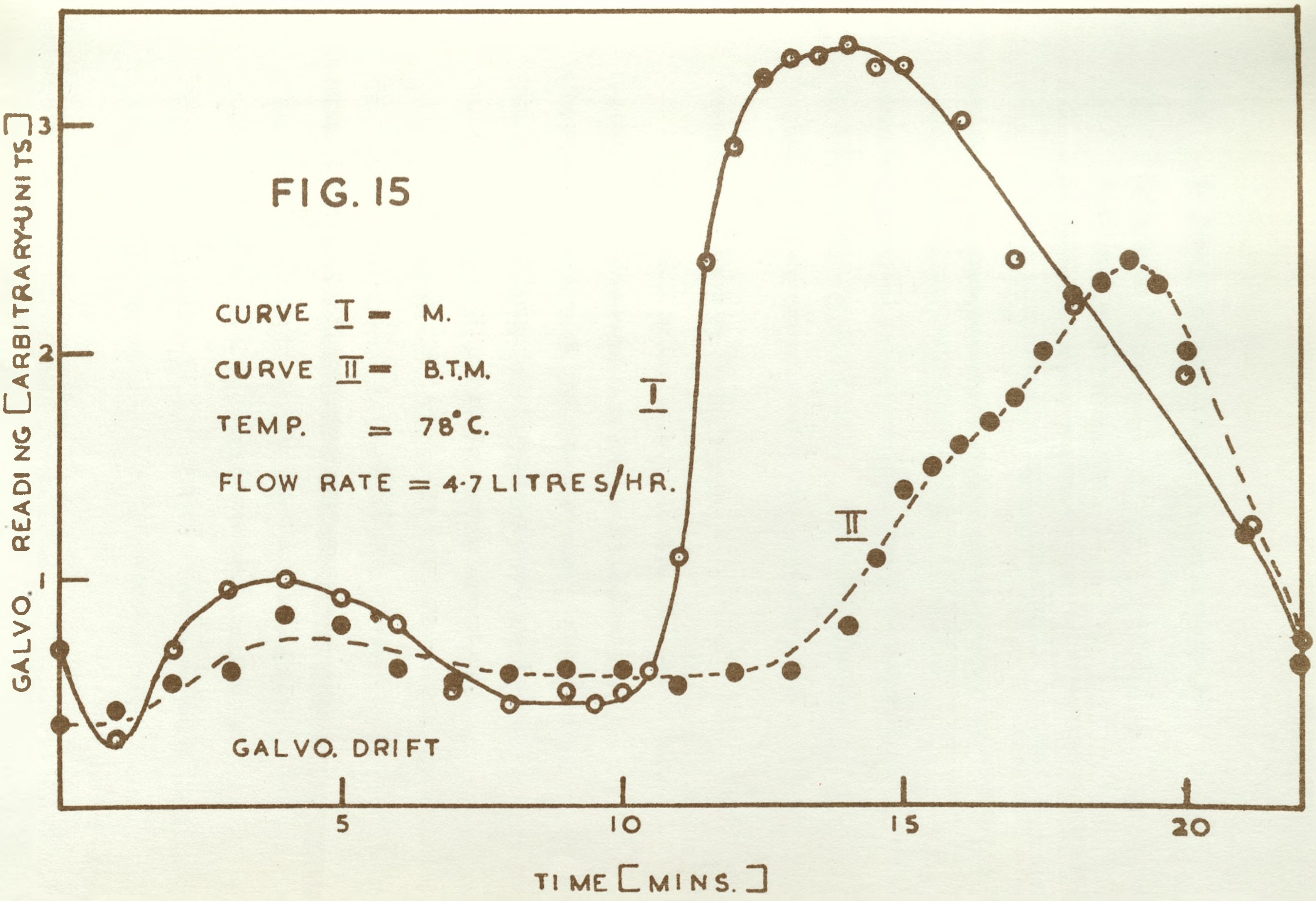

N_2
TO COLUMN
SCALE
FLOW METER
DRIER
BUFFER VESSEL
HG. BLOW-OFF

FIG. 14

The nitrogen flow was then interrupted by means of the tap T causing a slight change in galvanometer reading, and a sample of methyl methacrylate of not more than 500 mg introduced quickly into the preheater tube at Y by means of a syringe. The steady nitrogen flow was then quickly reintroduced, causing the galvanometer to return eventually to its initial steady reading. As soon as methacrylate vapour reached the filament a change in thermal conductivity took place, effectively altering the resistance of the wire and modifying the galvanometer reading. The latter was therefore noted at constant time intervals and in this way the monomer evolution studied under the conditions employed. The experiment was then repeated using a sample of pure BTM instead of methacrylate under the same conditions of flow and temperature. From the two experiments curves I and II, Figure 15, were constructed. Clearly the overlapping in these curves indicated that a quantitative separation of BTM/M mixtures under these conditions was impossible. In order to increase the resolution of the mixtures the following modifications could be tried:-

FIG. 15


CURVE I = M.
CURVE II = B.T.M.
TEMP. = 78° C.
FLOW RATE = 4·7 LITRES/HR.
I
II
GALVO. DRIFT
GALVO. READING [ARBITRARY-UNITS]
1
2
3
5
10
15
20
TIME [MINS.]

(a) Reduction of stationary phase concentration on the kieselguhr

(b) Reduction of sample size

(c) Reduction of temperature

(d) Increase in column length

(e) Change of stationary phase material.

Modification (a) meant that smaller sample sizes would have to be employed and unfortunately the accuracy required in determining adduct compositions by VPC made this undesirable. Thus modifications (a) and (b) could not be used in this particular work.

Reduction of Column Temperature

The effect of decreasing the column temperature to 65°C was to increase the effective separation. However this was still far from complete. Decreasing the column temperature also increased the time spent by the reactants on the column and the deliverance peaks were broadened. These effects were undesirable for longer experiments resulted and the galvanometer detector became less sensitive due to the increased take-off times. Thus on reducing the temperature to 56°C and then to 35°C peak widths were increased so much that any galvanometer changes could not be distinguished from the normal slight oscillations under steady pure nitrogen flow. Therefore an optimum temperature had to be employed and this was too high to give complete resolution of the reactants.

Increase of Column Length

By using a similar column of length 130 cms the separation was increased but was still incomplete. Also the flow rate automatically decreased and therefore a larger retention time resulted. The flow rate could be increased by using higher nitrogen pressures but this was found unsuitable for cones C and C' were often displaced by nitrogen blow off.

Change of Stationary Phase

The choice of the stationary phase was semi-empirical for separation depends on the relative solubilities in it of the two materials to be separated. The following materials, impregnated on graded kieselguhr, were tried in turn:-

1. Apiezon M (10%)
2. Silicone oil (10%)
3. Tricresyl phosphate (45%)
4. Polyethylene glycol (20%)
5. 'Araldite' D resin (10%).

With Apiezon M the resolution obtained was the best and all the other systems gave no better separation than dinonylphthalate. Figure 16 shows the separation achieved with a column 130 cms long, a temperature of 65°C, and a flow rate of 1.1 litres per hour. It was therefore decided to investigate the quantitative recovery of BTM and methacrylate from mixtures of the two, using this column.

Quantitative Work

(1) Experimental Procedure

It will be seen from Figures 15 and 16 that the BTM delivery peaks were not symmetrical and fell more sharply than they rose. Usually the opposite occurs due to absorption of materials on the column carrier causing 'tailing'. The most obvious explanation for this anomaly is that, because the sample size was much greater than in normal VPC work, the time of sample addition became significant in affecting the peak shape and hence the separation achieved. The fact that better separation resulted when the sample was added very quickly supported this explanation. (Considerable time was therefore spent in modifying the method of sample addition). The preheater tube was dispersed with and nitrogen introduced directly into the

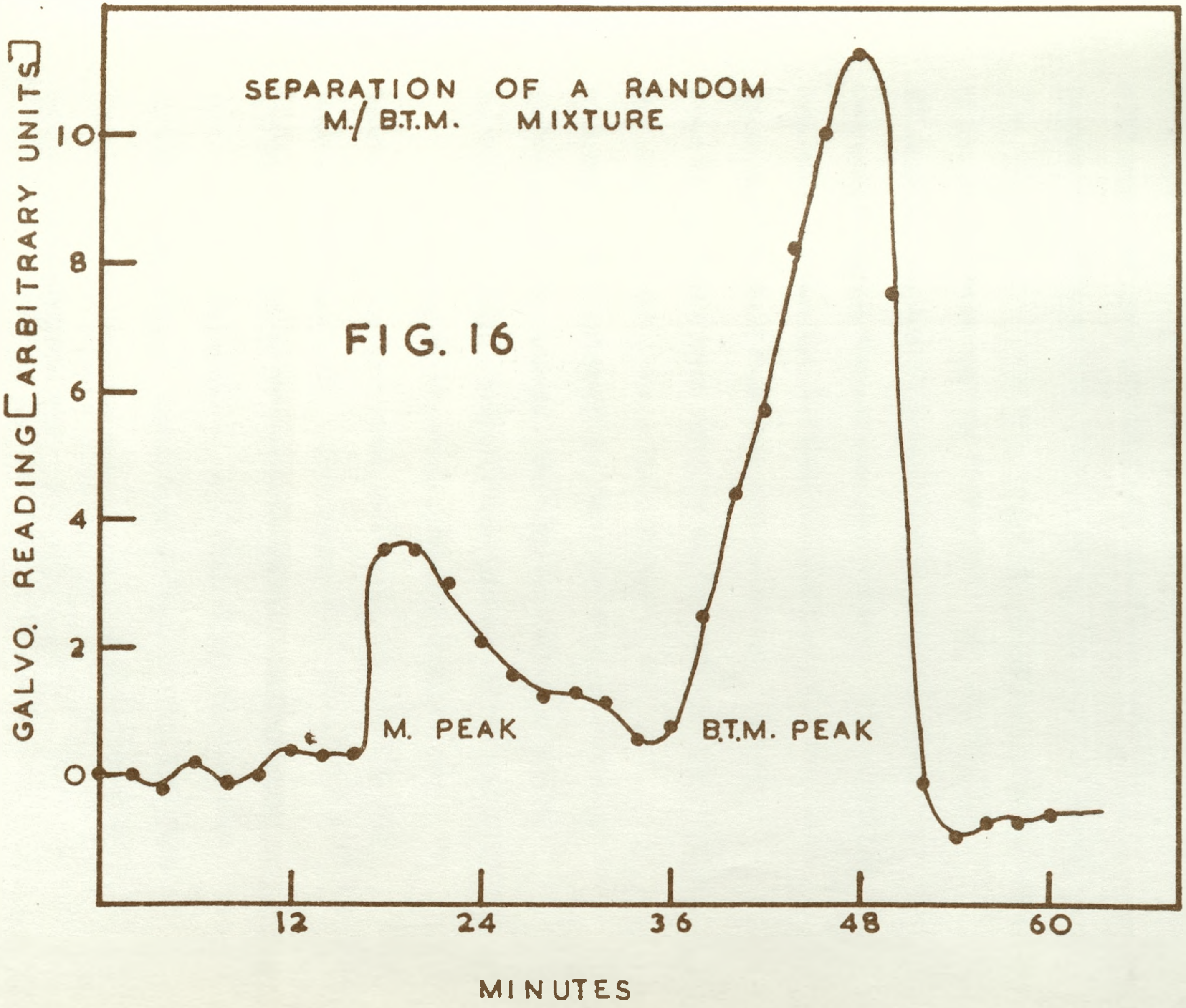


FIG. 16

SEPARATION OF A RANDOM M./B.T.M. MIXTURE column top. When conditions were steady, the nitrogen supply was interrupted and a sample tube, consisting of a B7 standard cone extended to a capillary tip at the bottom end (Figure 17), fitted into the top of the column. The nitrogen inlet tube was then attached to the top end of the sample tube and tap T opened. On rotating the B7 cone the capillary tip was broken and a weighed amount of sample forced onto the column. The capillary had not to be too fine for then the addition time was too great and the final flow rate often affected. In some runs liquid drops were sprayed on the column sides above the heating jacket, where they remained for a few seconds. This affected the subsequent separation and consequently the sample tube was increased in length, so that the capillary broke in the hot zone of the column.

The components were collected in two traps, filled with loose glass wool, and having the dimensions indicated in Figure 18. The traps were connected in series by means of B7 standard joints. Spring clips held the traps in position, no grease being used on any quickfit connection. Initially a horizontal trap feed (see Figure 13) was used but later it was found that vertical delivery of reactants was more satisfactory. The

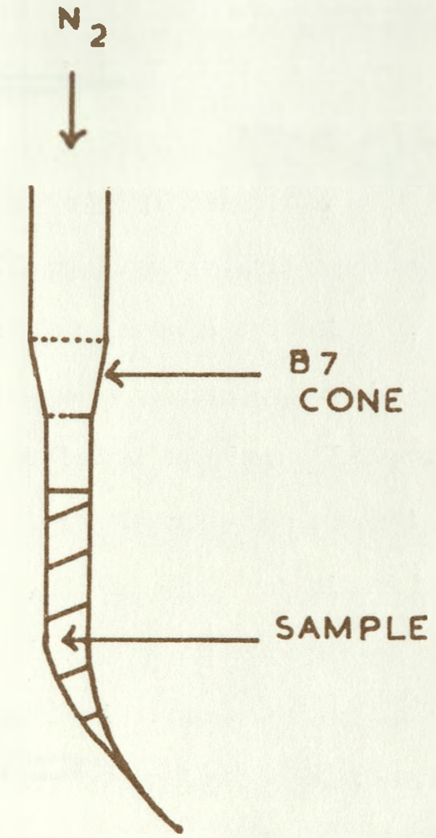
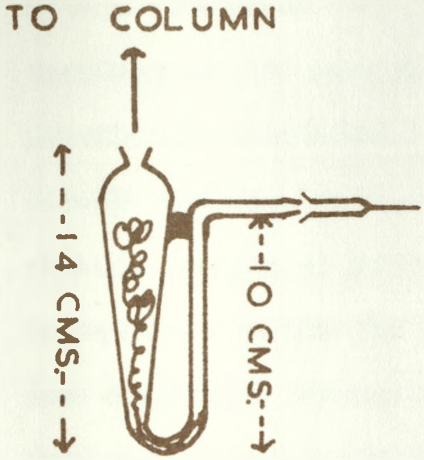
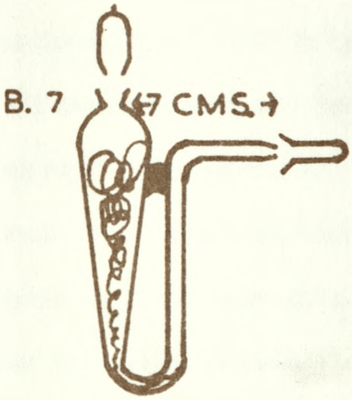


FIG. 17



TRAP ATTACHED
TO COLUMN



TRAP READY
FOR WEIGHING

FIG. 18

nitrogen emerged from the end trap via a drawn out capillary so that back diffusion of moisture was practically eliminated. Immediately after the sample addition the second trap, in which the more volatile component (M) was to be collected, was immersed in liquid air so that the portion filled with glass wool was just covered. Under the stated conditions of nitrogen flow and column temperature this component appeared at the column outlet about 15 minutes after the introduction of the sample, and the BTM appeared some 20 minutes later. Thus 35 minutes after zero time the first trap was submerged in liquid air. One hour after the sample introduction both traps were quickly disconnected and a B7 cone drawn out into a short capillary placed in the B7 socket of each trap. The other trap opening was plugged and the traps allowed to warm up. In warming to room temperature any slight pressure build up was avoided by the loss of volatiles through the short capillaries and this loss for each reactant should remain sensibly constant from run to run. The traps were then carefully dried and weighed. The identical traps had previously been weighed empty and so the amount of each reactant in the mixture could be determined providing the VPC separation and recovery were complete. In practice this was checked by using samples of known pure M and BTM content. It was found that with the conditions employed incomplete capture of monomer occurred in the second trap, the deficient amount appearing in the first trap. The separation was incomplete for undoubtedly 'tailing' of reactants took place. By using separate samples of pure M and BTM in turn it was realised that with the conditions employed, complete quantitative separation could never be realised.

A much larger column, illustrated in Figure 19, was therefore used and carefully packed with a kieselguhr-apiezon M mixture. This column had an effective length of 400 cms and had an internal diameter of 8 mms. With a column temperature of 100°C and a flow rate of $\frac{1}{2}$ litre/hour a complete separation could be achieved. One trap only was attached to the column, and this was immersed in liquid air 20 minutes after the sample addition. Methacrylate came off after 27 minutes and at 45 minutes the trap was replaced by another. BTM appeared $60\frac{1}{2}$ minutes after zero time

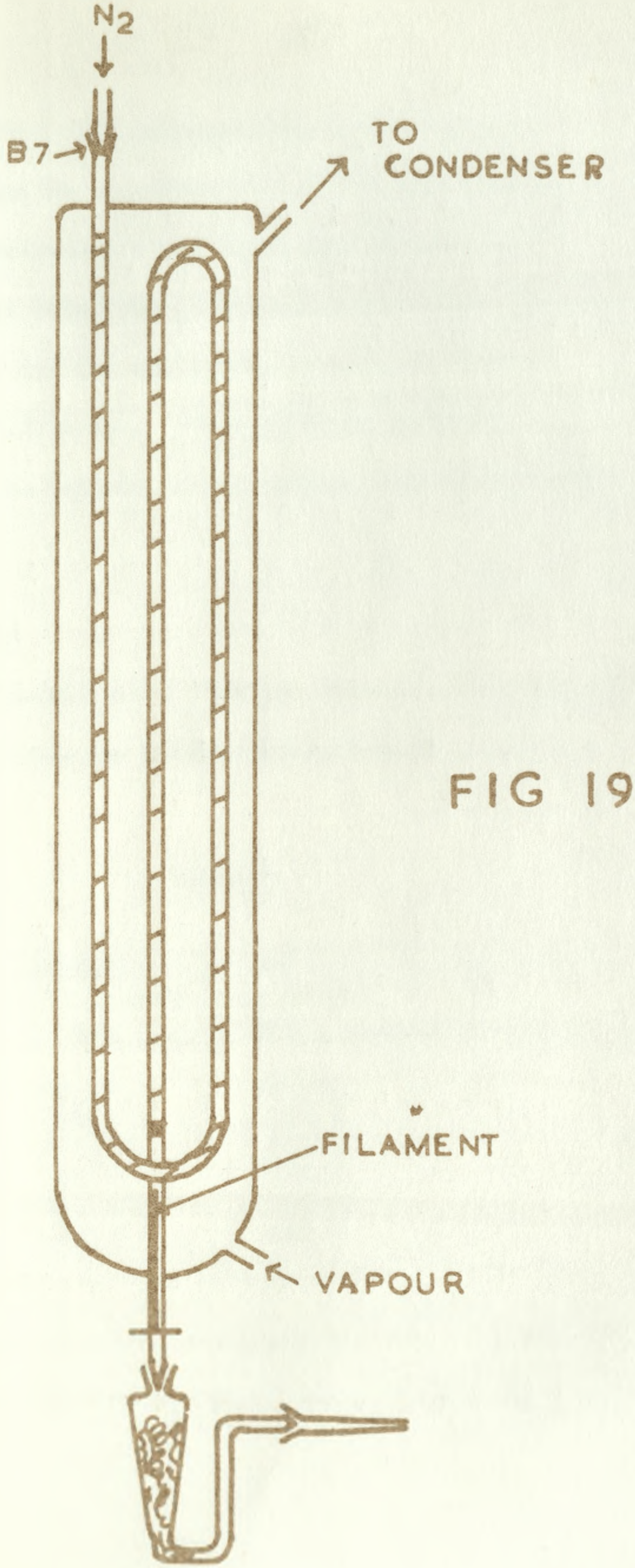


FIG 19

and after a further 24½ minutes the second trap was removed. Once the appearance and disappearance times of the components had been established under fixed conditions using the galvanometer, the latter was dispensed with and the collecting traps switched in using a clock indicator. Five minutes before a trap was removed the bottom of the column was heated with a hair drier.

(2) Results

Experiments were first performed using samples of pure M only and the following are typical results:—

Table 5

Run No.	Methyl methacrylate mg	M recovered mg	Δ mg
15	69.20	69.05	.15
11	168.5	168.2	.3
14	203.55	203.25	.3
10	335.4	335.4	0
12	393.65	393.25	.4
13	446.3	446.0	.3

It will be seen that recovery was almost complete, an average loss of .24 mg occurring, presumably due to vapour expansion on warming the traps to room temperature.

Experiments using pure BTM were then performed:-

Table 6

Run No.	BTM mg	BTM recovered mg	Δ mg	% loss
17	389.30	384.05	5.25	1.35
19	393.65	388.40	5.25	1.333
18	425.95	420.30	5.65	1.326
16	427.25	421.0	6.25	1.46

In this case a much larger loss occurred, the percentage loss being sensibly constant. This loss was not due to 'tailing' for it was not decreased by increasing the take-off time considerably. Furthermore it did not decrease in successive runs indicating that possible impurities in the column were not the cause, for with time these impurities would be completely 'scavenged' by the BTM. Whatever the cause of the BTM loss, the constancy of the loss made the BTM recovery quantitative and within the accuracy required.

Finally the column was used to separate known BTM/M mixtures:–

Table 7

Run No.	M mg	M recovered mg	Δ mg	BTM mg	BTM recovered mg	Δ mg	% BTM loss
20	144.1	143.7	.4	408.95	403.20	5.75	1.406
24	195.55	195.15	.4	263.0	259.55	3.45	1.31
28	227.65	227.55	.1	260.7	256.95	3.75	1.44
27	275.5	275.2	.3	317.4	313.3	4.1	1.29

Thus the method was developed to a stage where unknown mixtures of BTM and M could be analysed. Experiments were performed to investigate any water blank obtained from the nitrogen supply and a positive result was obtained. The water deposit varied with the nitrogen cylinder source and could not be reduced much by use of a liquid air trap in addition to the concentrated sulphuric acid drier. Use of two sulphuric acid bubblers might well remove all the water, but in any case the small water blank could be allowed for, the BTM and M losses being slightly modified.

References

1. Kirkham - Private communication

2. Robb and Vofsi - Trans. Farad. Soc., Vol. 55, Part IV, 558, (1959)

3. Robb and Vofsi - Vapour Phase Chromatography, Butterworths, p. 428

CHAPTER 5

THE MEASUREMENT OF INITIATION RATES

The evaluation of the rate of initiation, R_I, is an essential step in the determination of the velocity constants of the different steps involved in the kinetic scheme. The usual method of measuring R_I is to inhibit or retard the reaction by the addition of a suitable radical scavenger, which prevents normal chain propagation. The dependence of R_I on the inhibitor concentration is defined by the equation,

$$R_I = -n\frac{d(I_n)}{dt} ,$$

n being the number of chains terminated by one molecule of the inhibitor I_n. Therefore, if the rate of inhibitor disappearance is measured and the value of n is known,

R_I can be calculated as long as $\frac{-d(I_n)}{dt}$ is independent of the initial inhibitor concentration.

The choice of a suitable inhibitor is empirical but tetrachloro-o-benzoquinone was used successfully by Melville, Robb and Tutton[1] when working with systems similar to those experience in the present work. It was decided, therefore, to try this inhibitor and a solution in analar benzene of known concentration was prepared. Various amounts of the quinone were then introduced into the dilatometer side arm by means of the graduated burette described in Chapter 2, and the solvent drawn off by means of a water pump prior to the introduction of the reactants. With quinone concentrations of about 10^{-4} mols/litre complete inhibition virtually occurred, a very slow rate being present before the final rate was obtained. This final rate differed little from the normal uninhibited rate (Table 8), and the straight line portion of it was extrapolated backwards to the time axis and the intercept taken as the apparent induction period. True induction periods were found by subtracting from the apparent values the inhibition time observed in the corresponding uninhibited run. (In all uninhibited runs the reaction started immediately the light shutter was removed but an initial expansion due to the heat of reaction was observed, before the meniscus began to drop at a constant rate. This resulted in a small induction period which varied slightly, between 1.3 and 1.8 minutes with filtered light, with the feed composition). With any feed composition it was found that induction periods were not proportional to the initial inhibitor concentration. With unfiltered light the rate of inhibitor disappearance increased with initial inhibitor concentration (Table 8), but with filtered light the opposite effect took place (Table 9). This clearly indicated that the quinone did not function in the system as a simple radical scavenger.

Table 8

un-
(filtered light)

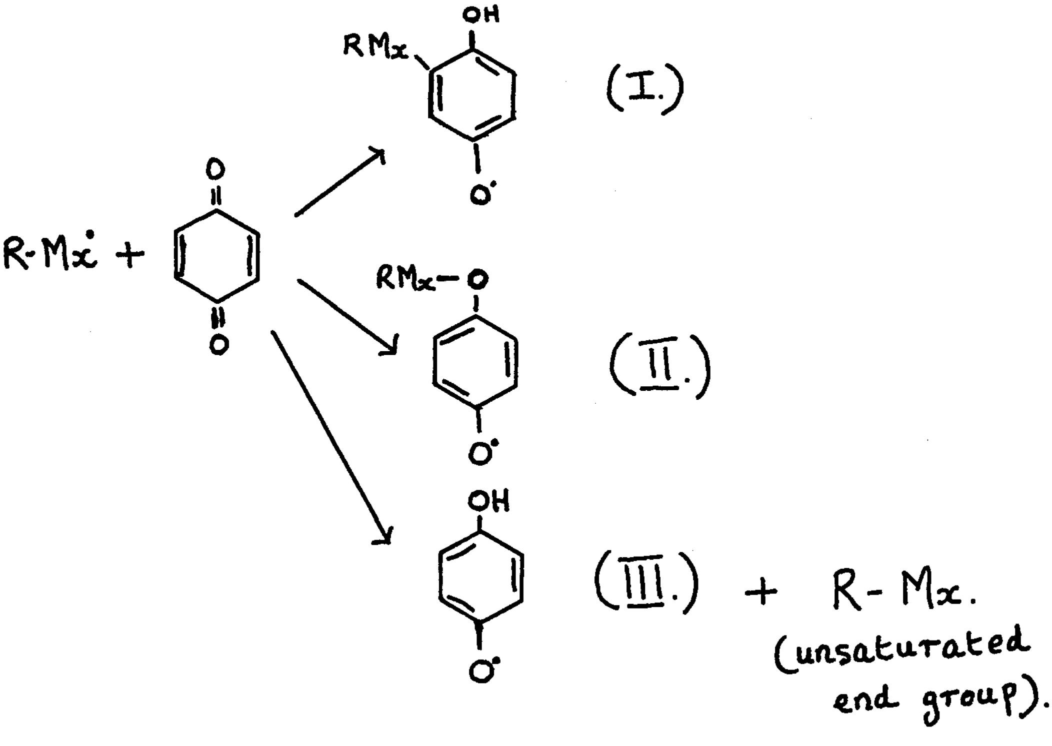
Run No.	(BTM) m./ℓ.	(Quinone) m./ℓ.	Inhibition period (mins.)	$-\frac{d(In)}{dt}$ m./ℓ./s.	Final rate cms./hr.	Uninhibited rate cms./hr.
44	3.03	1.345×10^{-4}	12.6	1.78×10^{-7}	9.32	9.7
43	3.03	2.485×10^{-4}	22.3	1.86×10^{-7}	9.18	9.7
42	3.03	3.62×10^{-4}	29.8	2.02×10^{-7}	9.24	9.7
41	3.03	7.5×10^{-4}	54.8	2.28×10^{-7}	8.79	9.7
47	.703	$.6785 \times 10^{-4}$	14.2	$.795 \times 10^{-7}$	7.2	7.25
48	.703	1.26×10^{-4}	22.8	$.92 \times 10^{-7}$	7.1	7.25

Table 9

(filtered light)

Run No.	BTM m./ℓ.	(Quinone) m./ℓ.	Inhibition period (mins.)	$-\frac{d(In)}{dt}$ m./ℓ./sec.
62	.703	$.388 \times 10^{-4}$	15.9	4.06×10^{-8}
61	.703	$.776 \times 10^{-4}$	44.0	2.94×10^{-8}
58	1.406	$.48 \times 10^{-4}$	6.4	12.5×10^{-8}
57	1.406	$.848 \times 10^{-4}$	21.1	6.7×10^{-8}
60	1.406	1.107×10^{-4}	32.1	5.75×10^{-8}
56	1.406	1.690×10^{-4}	63.4	4.45×10^{-8}
68	5.905	1.337×10^{-4}	16.7	13.3×10^{-8}
69	5.905	1.96×10^{-4}	31.9	10.2×10^{-8}

Much speculation has taken place on the problem of radical scavenging by quinone type molecules and the fact that the mechanism is not fully understood reflects the unreliability of initiation rates determined with these compounds. In thermally initiated polymerisations it is generally considered that benzoquinone stops the growth of polymer type radicals, rather than initiator fragments, giving radicals of the following type[2,3]:—



These resonance stabilised radicals then terminate mutually either by disproportionation which regenerates another quinone type molecule, itself capable of terminating a polymer radical, or by combination. If they disappear exclusively by the most likely process of disproportionation, the ratio of chains terminated to quinone molecules consumed should equal two. In the case of duroquinone in vinyl acetate,[4] however, one molecule of inhibitor is consumed for each chain radical, suggesting that the radicals formed in this case (believed to be type II) disappear by combination. Thus even if the mechanism of quinone inhibition is the comparatively simple process illustrated above, the value of n for the particular molecule used must be ascertained before rates of initiation can be evaluated. However Gregg and Mayo[5] showed that in the unsensitised polymerisation of styrene, at least one of the radicals I, II or III was capable of monomer addition, thereby regenerating the kinetic chain. Thus under certain conditions quinones may act as transfer agents. Also the products of inhibition may to a certain extent inhibit or retard the reaction, further complicating the issue. In photochemical reactions an additional function of the quinone molecule may take place. Using flash photolysis techniques Bridge and Porter[6] showed that the excited singlet state of duroquinone was capable of extracting a hydrogen atom from a suitable molecule (solvent), generating radicals:–

$$ {}^{1}Qo + h\nu \longrightarrow {}^{1}Q^{*} $$

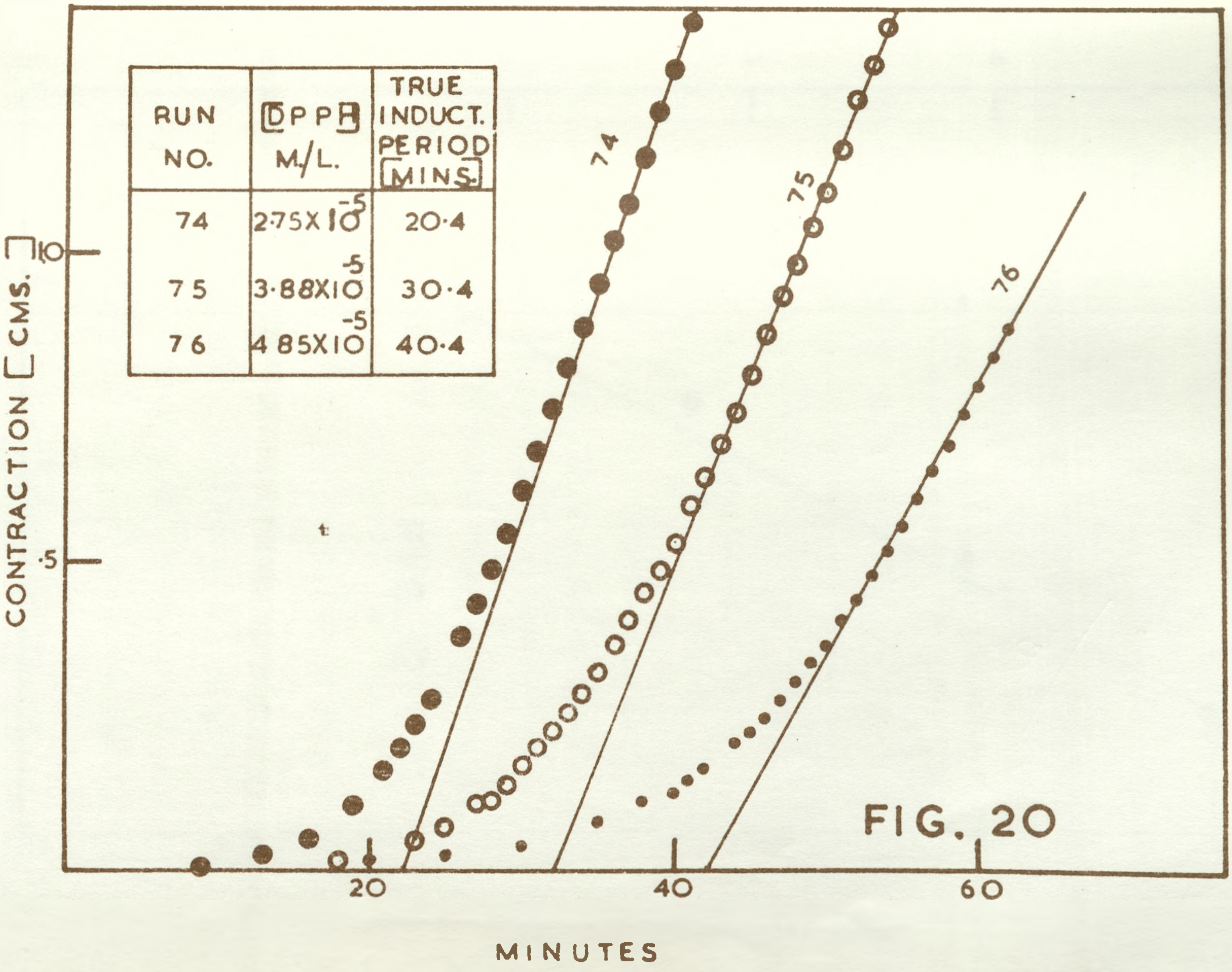
$$ {}^{1}Q^{*} + RH \longrightarrow QH^{\bullet} + R^{\bullet} $$

$$ 2QH^{\bullet} \longrightarrow Q + QH_2 $$

The semiquinone radicals disappear by combination and the radical $R^{\bullet}$ is capable of further reaction such as initiation of polymerisation. In the present work this reaction of excited quinone molecules probably occurred, hydrogen abstraction taking place with methyl methacrylate molecules. This would effectively increase the rate of initiation.

The results obtained with tetrachloro-o-benzoquinone can be qualitatively explained by the type of reactions illustrated above. If the 'final stable' products of inhibition have some inhibitory action, then the rate of inhibitor disappearance might be expected to decrease with increasing inhibitor concentration. This occurred with filtered light. Now with unfiltered light, the light absorption was very much increased (see Figure 6, Chapter 2) and this would result in a much higher concentration of excited singlet states. It is suggested that the effective initiation due to these excited singlet states swamped the 'increased' inhibition caused by the products of the primary scavenging. In this case the rate of inhibitor disappearance would be expected to increase with increasing initial inhibitor concentration and this is in agreement with the experimental results. However, it must be pointed out that these suggestions are put forward very tentatively, for numerous side reactions probably do occur and these may explain the observations, rather than the above reactions. The system is very complex indeed and before any reliable mechanisms can be postulated, further detailed studies should really be made.

The stable free radical α-α'-di-phenyl-β-picryl-hydrazyl (DPPH) is an extremely effective inhibitor of polymerisation which gives no evidence of initiation, and has been successfully used to measure rates of initiation, each hydrazyl radical consuming one chain radical.[4,7] Initiation rates were therefore measured at 30°C using DPPH and assuming n = 1. In Figure 20 three typical inhibitor runs are shown for a constant BTM concentration of .703 m./litre. It will be seen that the final uninhibited rate fell off progressively with increasing initial inhibitor concentration. This behaviour has been observed by other workers[4,7] and is attributed to the retardation caused by the nitro groups of the inhibitor molecule. With low concentrations of DPPH induction periods were within experimental error proportional to inhibitor concentration (Figure 21), but with higher concentrations this was not so, the calculated R_I decreasing with increasing (In_O). This was most certainly due to light absorption by the inhibitor for an examination of the U.V. spectrum of DPPH (Figure 6, Chapter 2) indicated that this was very high. Nevertheless still higher concentrations of DPPH have been used by other workers in determining reliable rates of



RUN NO.	[DPPH] M/L.	TRUE INDUCT. PERIOD [MINS]
74	$2{\cdot}75 \times 10^{-5}$	20·4
75	$3{\cdot}88 \times 10^{-5}$	30·4
76	$4{\cdot}85 \times 10^{-5}$	40·4

FIG. 20

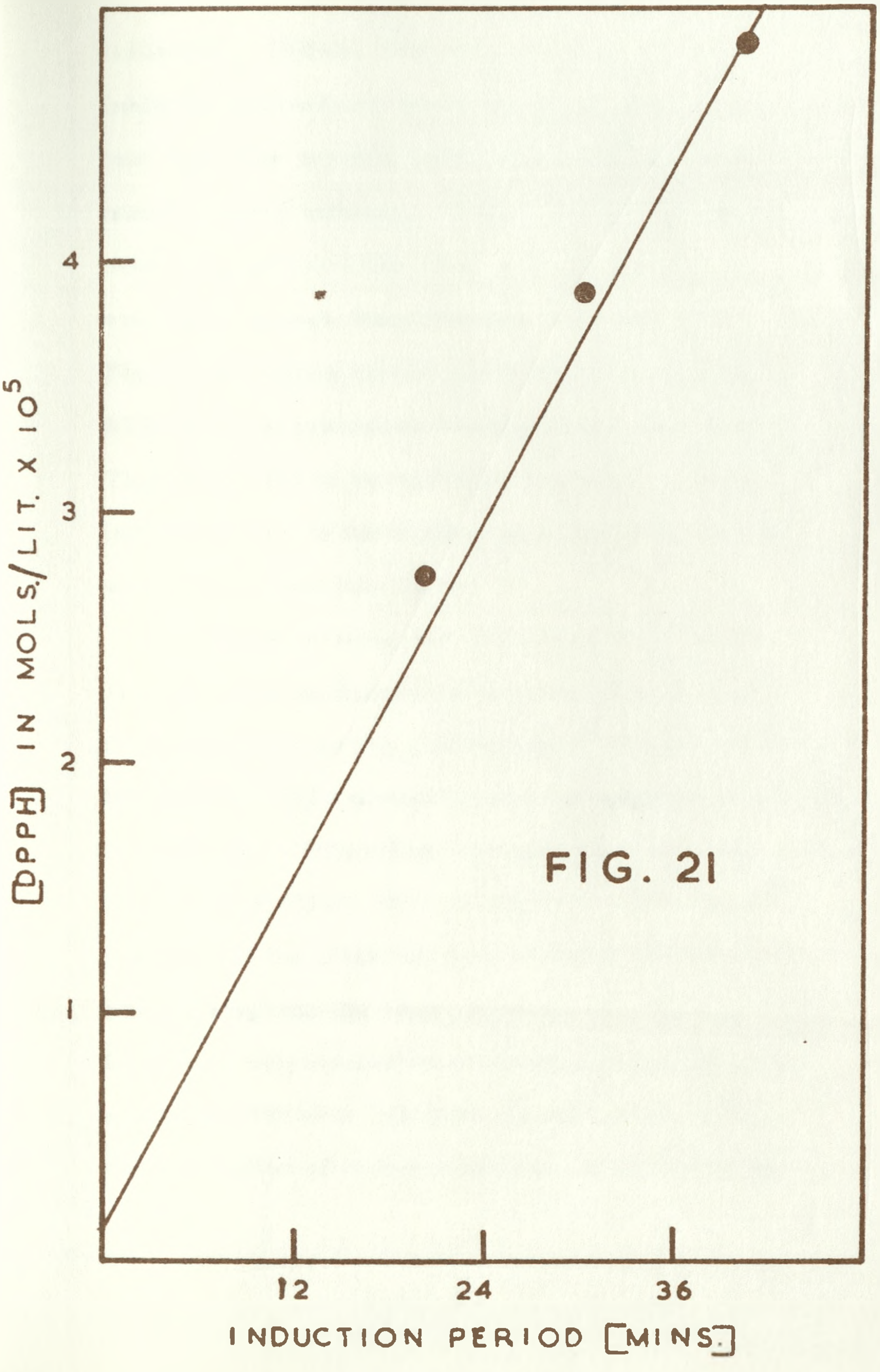


FIG. 21

initiation. It was, however, decided to keep inhibitor concentrations as low as possible, so that induction periods were no more than approximately twenty minutes. Under these conditions scattering of initiation rates with (In_0) still occurred, though discrepancies were not great. Figure 22 (closed circles) is a plot of R_I against BTM feed concentration showing these discrepancies. The graph data is recorded in Table 10. Rates of initiation used in the evaluation of velocity constants were taken from this curve.

It will be observed from Figure 22 that the rate of initiation increased to a maximum and then dropped again, as the dilatometer BTM concentration increased. (The monomer concentration automatically decreased). This effect was real and not due to errors caused by inhibitor light absorption. (The fall off occurred if the inhibitor concentration was kept constant throughout the range of feed composition studied). In normal polymerisation processes initiation rates are proportional to initiator concentrations unless recombination of radicals in their initial molecular

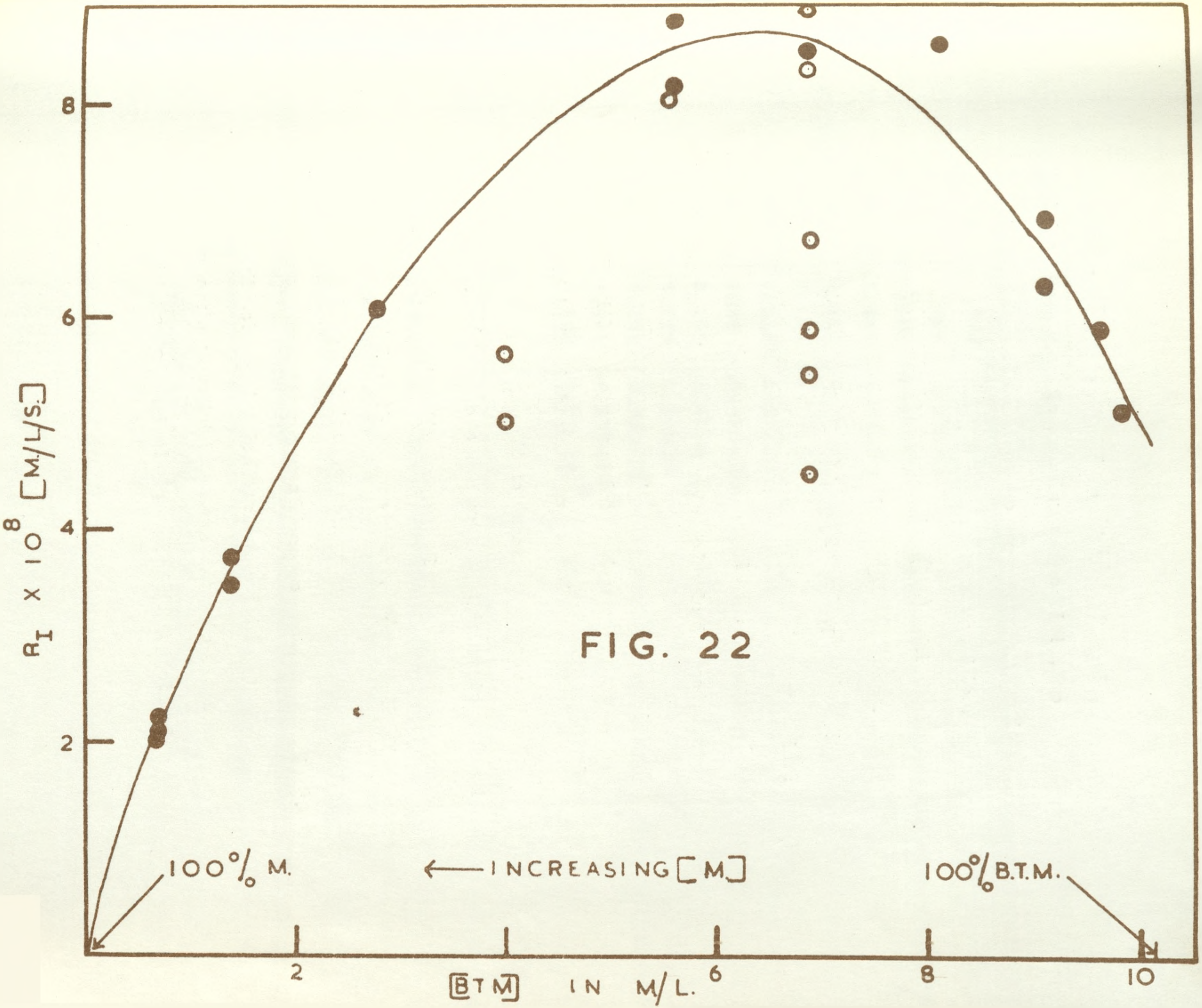

$R_I \times 10^8$ [M/L/S.]
8
6
4
2
100% M.
← INCREASING [M]
100% B.T.M.
2
6
8
10
[BTM] IN M/L.

FIG. 22

Table 10

(filtered light)

Run No.	(BTM) m./ℓ.	(DPPH) m./ℓ.	Inhibition period (mins.)	R_I m./ℓ./sec.
74	.703	2.745×10^{-5}	20.4	2.24×10^{-8}
75	.703	3.88×10^{-5}	30.4	2.13×10^{-8}
76	.703	4.85×10^{-5}	40.4	2.0×10^{-8}
72	1.406	4.52×10^{-5}	21.6	3.49×10^{-8}
78	2.812	6.455×10^{-5}	17.7	6.08×10^{-8}
81	5.624	6.5×10^{-5}	12.3	8.81×10^{-8}
80	5.624	8.645×10^{-5}	17.7	8.14×10^{-8}
87	6.89	9.015×10^{-5}	17.8	8.44×10^{-8}
84	8.155	7.065×10^{-5}	13.7	8.60×10^{-8}
83	9.139	5.65×10^{-5}	13.7	6.88×10^{-8}
82	9.139	8.95×10^{-5}	23.8	6.26×10^{-8}
85	9.631	4.255×10^{-5}	12.1	5.86×10^{-8}
86	9.842	4.5×10^{-5}	16.4	4.58×10^{-8}

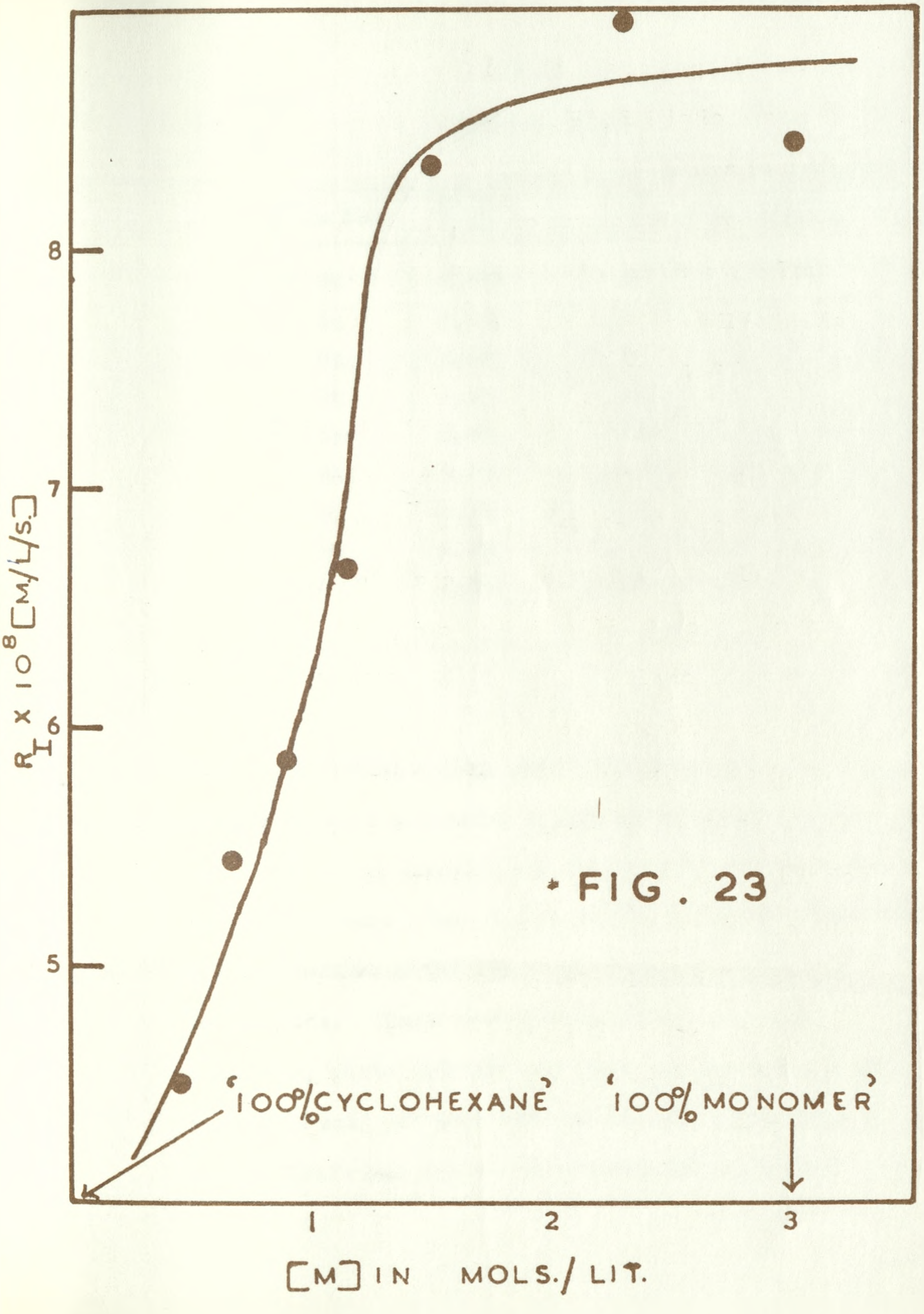
'cages' is effective. In the systems studied very high initiator concentrations were employed and thus any recombination of initiator fragments due to 'caging' effects, might well be enhanced. Thus initiator decomposition may be represented by the following simple scheme:

$$\mathrm{CCl_3Br} \underset{b}{\overset{a}{\rightleftarrows}} [\mathrm{CCl_3^{\bullet}} + \mathrm{Br^{\bullet}}] \xrightarrow{c} \mathrm{CCl_3^{\bullet}} + \mathrm{Br^{\bullet}}$$

From theoretical considerations it can be shown that radical pairs may execute many oscillations in their respective 'cages', consisting of surrounding molecules, before they diffuse apart. This recombination of radicals within the cage is possible[8] (b) especially when one of the radicals is a free atom, for then steric recombination factors must be less. These caged radicals can react with monomer molecules in the walls of the cage, or they can diffuse out and react with monomer in the main body of the solution. With high initiator concentrations, primary radical concentrations within the cage are correspondingly high and furthermore initiator molecules are considerable in the cage wall. This favours radical recombination within the cage and it is suggested that this explains the fall off in initiation rate observed in Figure 22. When radical cage recombination approaches a minimum, initiation rates should tend to a straight line relationship with BTM concentration. With high monomer and small initiator concentrations, conditions which prevail in normal polymerisation, this was so.

With a constant (BTM), corresponding to about the maximum of Figure 22, initiation rates were measured using decreasing concentrations of methyl methacrylate, cyclohexane being used as an inert solvent. The final reaction rates were less than with undiluted monomer and the small induction periods of uninhibited runs were slightly increased with dilution. Figure 23 shows the effect of monomer concentration on the measured R_I. The latter falls off on monomer dilution due to the replacement of monomer molecules by cyclohexane in the cage wall, though it is difficult to understand why the fall off is not gradual. Dilution runs were performed with other BTM concentrations and the complete results are illustrated in Figure 22 (open circles), the data being recorded in Table 11.

Other explanations for the observed initiation rates can no doubt be advanced and it is not claimed that the caging theory is completely satisfactory. However, the simple physical picture of this theory qualitatively explains the observations made and in the absence of more detailed studies on the problem, the



$R_I \times 10^8$ [M/L/s.]
8
7
6
5
'100% CYCLOHEXANE'
'100% MONOMER'
1
2
3
[M] IN MOLS./LIT.

FIG. 23

Table 11

(filtered light)

Run No.	(BTM) m./ℓ.	(M) m./ℓ.	R_I m./ℓ./sec.
106	4.007	1.85	5.01×10^{-8}
94	4.007	3.0	5.66×10^{-8}
98	5.582	3.0	8.03×10^{-8}
100	6.89	.456	4.5×10^{-8}
104	6.89	.685	5.45×10^{-8}
103	6.89	.912	5.86×10^{-8}
105	6.89	1.15	6.69×10^{-8}
89	6.89	1.50	8.35×10^{-8}
90	6.89	2.28	8.96×10^{-8}

theory of radical caging seems reasonable. If the initiation rates measured by inhibitor disappearance are those which actually occurred in the corresponding uninhibited runs, then in determining velocity constants the explanation of the observed results is of no direct importance. Since complete inhibition virtually occurred, chain radicals could not disappear mutually and could only combine with the inhibitor, and thus it seems likely that the observed initiation rates are correct. Furthermore the inhibitor will not distinguish between types of primary radicals or their mode of production. Therefore if bromine atoms or methacrylate molecules contributed to the initiation process, this is included in the measured value.

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CHAPTER 6

DILUTION EXPERIMENTS AND THE DETERMINATION OF $k_p/\sqrt{2k_{t,2}}$

In Chapter 3 kinetic equations were developed for the photochemical telomerisation of any monomer, in this particular work methyl methacrylate, with bromotrichloromethane. It is necessary at this stage to verify some of these equations.

When only 1 : 1 adducts are formed, the rates of monomer and BTM disappearance are equal and three termination reactions may apply. According to equation (10), Chapter 3, which will hold only if the interaction of the trichloromethyl radical with monomer is rate-determining and termination occurs by combination of trichloromethyl radicals,

$$R'_M = R'_B = k_1(M)\sqrt{(R_I/2k_{t,1})} \qquad (10)$$

When the transfer step is rate controlling, termination involves polymer type radicals only and,

$$R_M = R_B = k_2^{(1)}(BTM)\sqrt{(R_I/2k_{t,2}^{(1)})} \qquad (9)$$

For olefins incapable of polymerisation the above two equations are valid and Melville, Robb and Tutton[1] showed that with both cyclohexene and vinyl acetate and feed compositions containing excess BTM, reaction rates were proportional to olefin concentration and also $(BTM)^{\frac{1}{2}}$. However, when working with excess olefin, rates were independent of olefin concentration and proportional to $(BTM)^{3/2}$. This fits the above kinetics, since the rates of initiation were in all cases $\propto (BTM)$. Robb and Vofsi[2] repeated the work using styrene and found that the rate was less than first order with regard to monomer concentration even when the molar ratio of BTM to styrene was greater than 300. This means that trichloromethyl radicals behave almost like a scavenger towards styrene, the interaction constant (k_1) being large.

In the present work with methyl methacrylate, 1 : 1 adducts were not isolated and the operative termination process could not be demonstrated clearly by dilution experiments, since propagation introduced a further monomer dependency term. However, termination almost certainly involved polymer type radicals, for the interaction constant between trichloromethyl radicals and methyl methacrylate must be very high. This follows from the results of Robb and Vofsi (with styrene monomer) and data available in monomer reactivity tables. Also, since telomerisation takes place $\overline{k_p}(M) > \overline{k_2}(BTM)$ and since primary radicals are usually considerably more reactive than chain radicals, $k_1(M)$ must be far greater than $\overline{k_2}(BTM)$. This effectively means termination is between polymer type radicals. Thus the rate of reaction is given by equation (9a),

$$R_M = \left[\frac{\overline{k_p}}{\overline{k_2}} \frac{(M)}{(BTM)} + 1 \right] \overline{k_2}(BTM) \sqrt{\frac{R_I}{2\overline{k_{t,2}}}} ,$$

which reduces to,

$$R_M = \overline{k_p}(M) \sqrt{\frac{R_I}{2\overline{k_{t,2}}}} \qquad (9a')$$

when the degree of telomerisation is comparatively high. Reaction rates were therefore measured with high $\frac{(M)}{(BTM)}$ feed compositions (such that adducts produced were not less than 30 : 1), constant (BTM), and variable monomer concentrations.

Cryoscopic benzene was used as a solvent for with cyclohexane the comparatively large adducts produced precipitated out. Table 12 and Figure 24 summarise these results, and it will be seen that the contraction rate, or the rate of monomer disappearance, was proportional to the monomer concentration.

Table 12

(unfiltered light)

Run No.	(BTM) m./ℓ.	(M) m./ℓ.	Rate cms./hour
108	.07	9.35	2.76
111	.07	4.64	1.63
112	.07	2.285	.735

In a similar manner it was shown that the contraction rate, at constant (M) was proportional to $(BTM)^{\frac{1}{2}}$ or $R_I^{\frac{1}{2}}$, radical caging effects being negligible in the presence of excess monomer. These results are expressed in Table 13 and Figure 25.

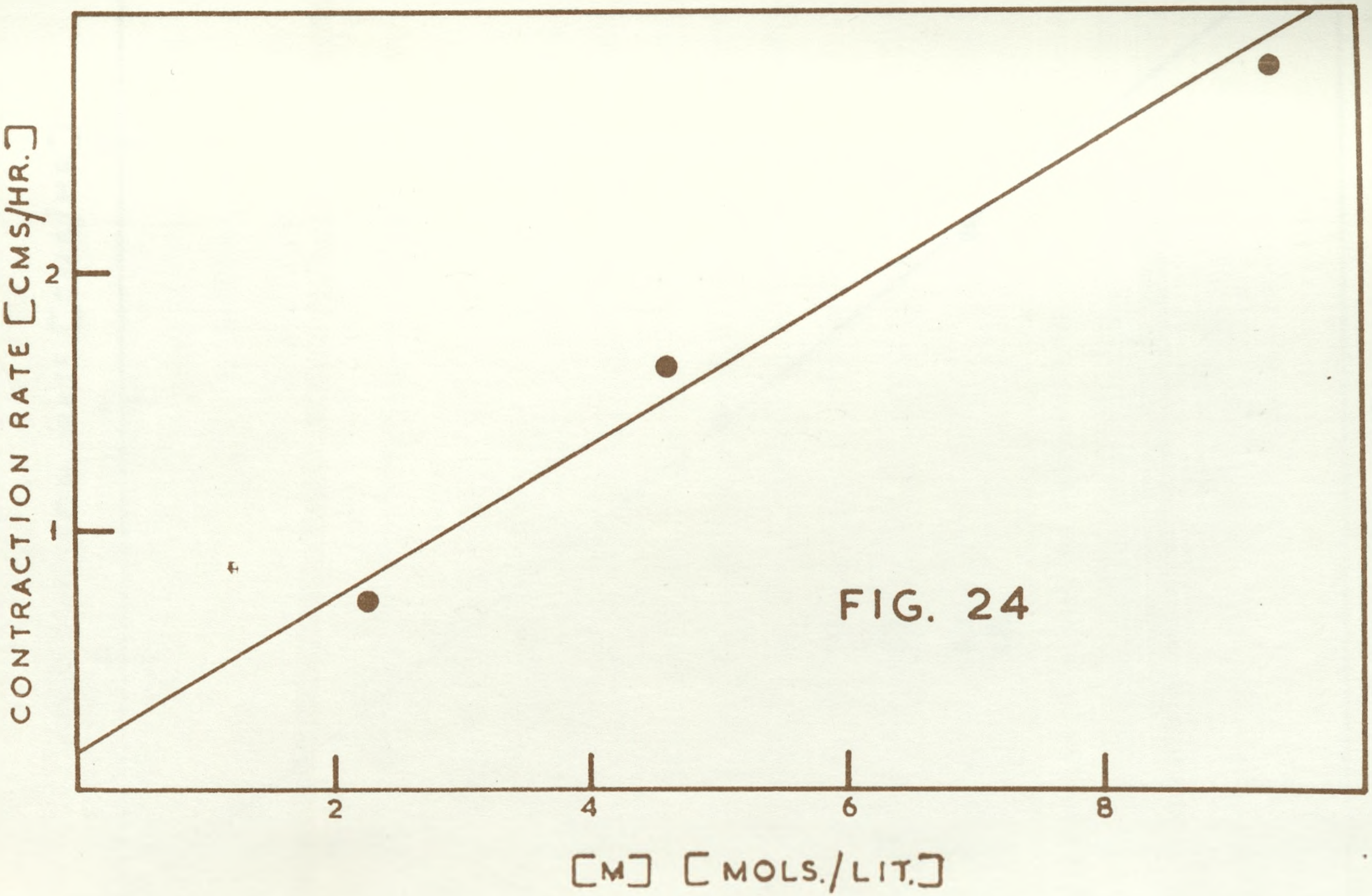

FIG. 24

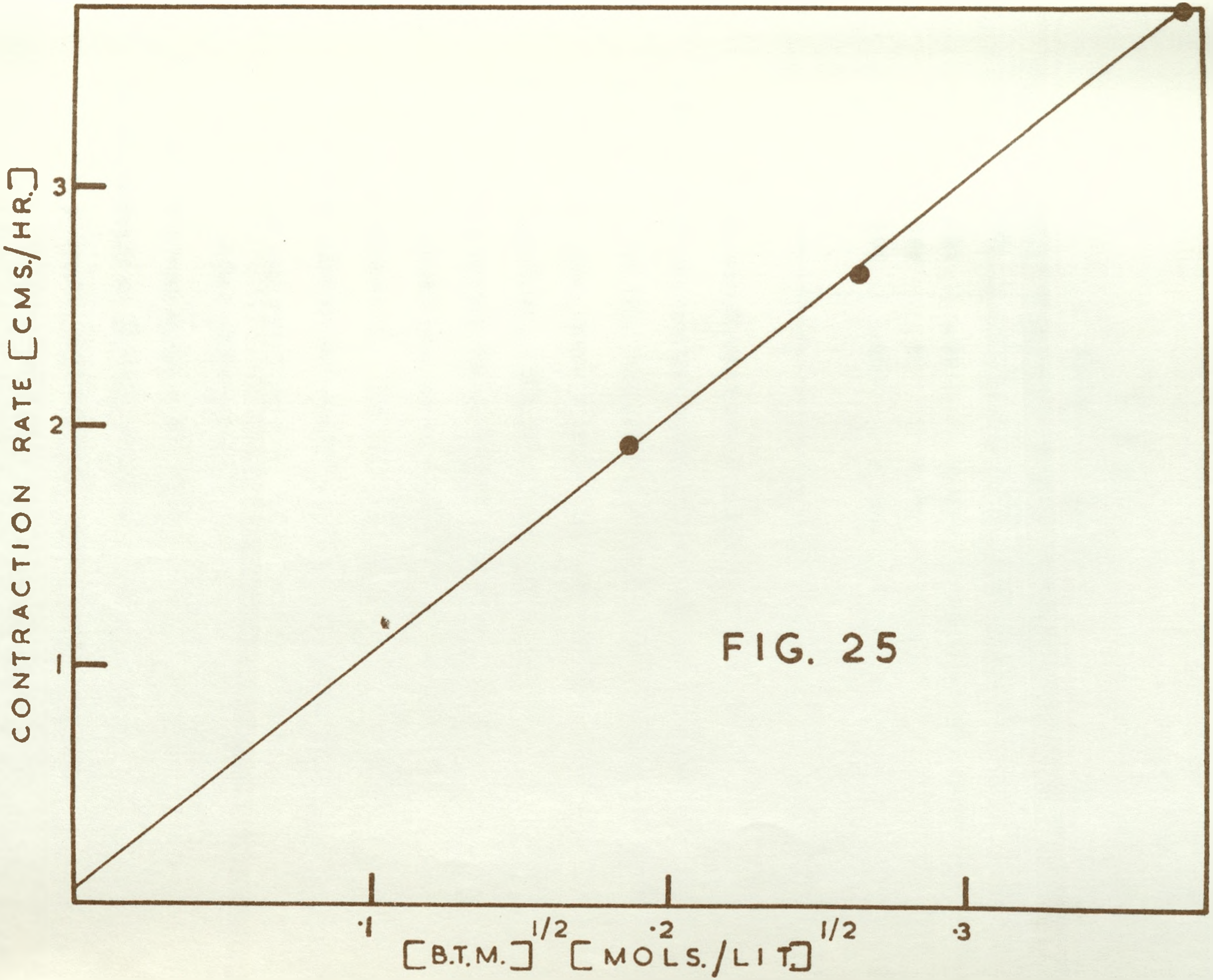

FIG. 25

Table 13

(unfiltered light)

Run No.	(BTM) m./ℓ.	(M) m./ℓ.	Rate cms./hour
107	.14	9.35	3.75
108	.07	9.35	2.76
109	.035	9.35	1.92

When small telomers are produced similar dilution experiments are difficult, for all runs must be performed with feed compositions which yield adducts of the same size, since velocity constants changed with adduct composition. (Figure 11, Chapter 4). In practice this meant small ranges of dilution, for the feed compositions had to correspond to the horizontal section of Figure 11. Furthermore, rate of initiation changes on dilution had to be measured because with the reactant concentrations employed caging effects occurred. After allowing for these changes, the contraction rate was again $\propto$ (M) (Figure 26) and $\propto R_I^{\frac{1}{2}}$. No dependency on (BTM), other than that due to the initiation process, was noticed. The results suggest

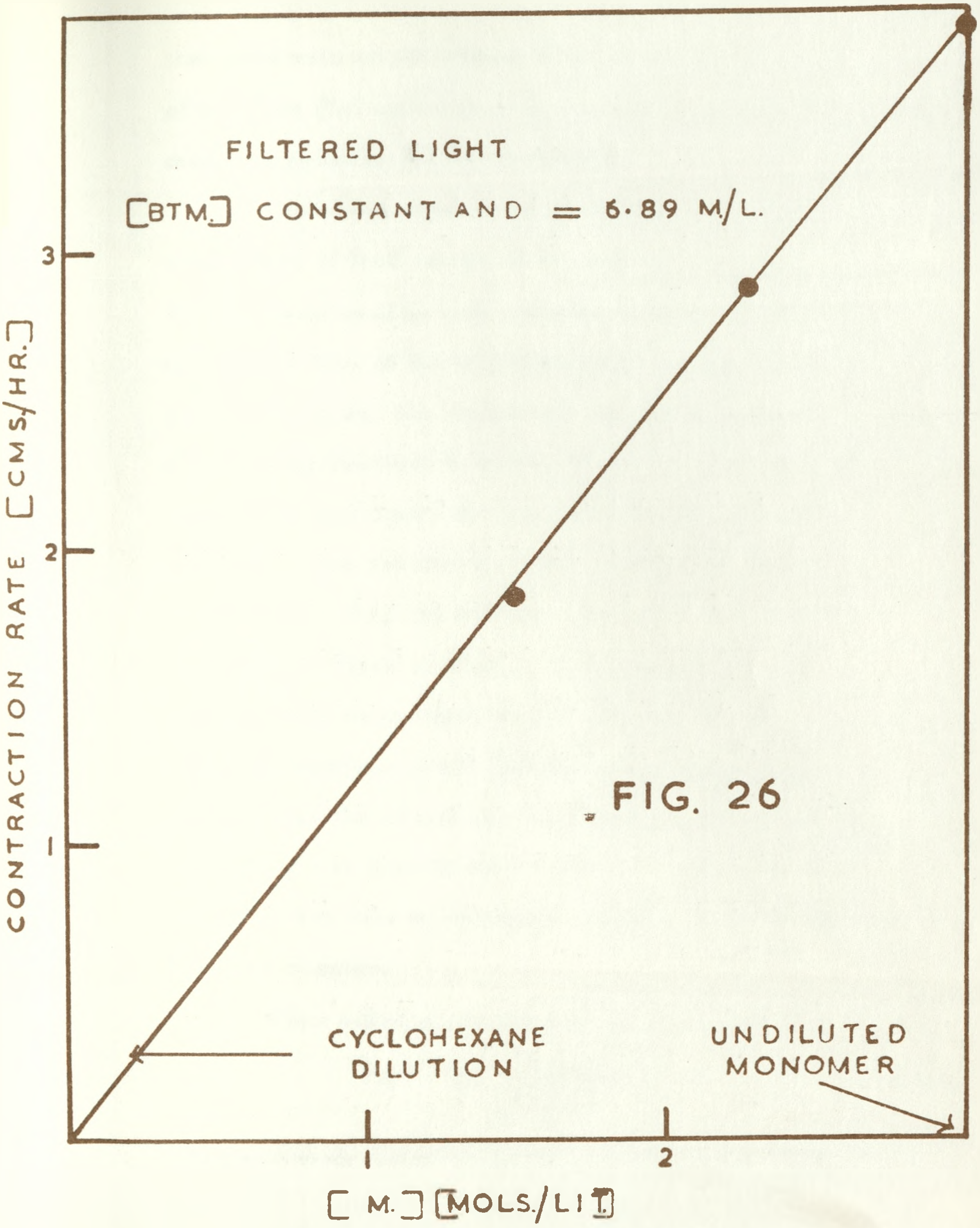

FIG. 26

FILTERED LIGHT
[BTM.] CONSTANT AND = 6.89 M/L.
CONTRACTION RATE [CMS/HR.]
3
2
1
CYCLOHEXANE DILUTION
UNDILUTED MONOMER
1
2
[M.] [MOLS./LIT.]

that even with small telomers the propagation term of equation (9a) outweighs the transfer term and the modified equation (9a') is applicable.

The above experiments indicated that over a wide range of feed composition, contraction rates were proportional to both monomer concentration and the square root of the initiation rate. Using these relationships and the measured contraction rate of a particular reactant mixture, theoretical contraction rates were calculated for runs of different feed composition. The results agreed reasonably well with the corresponding experimental rates and are shown in Figure 27 (open circles). However, if the calculated rates were based on the contraction rate being $\propto$ (Monomer) and $(\mathrm{BTM})^{\frac{1}{2}}$, they were always greater than the experimental values and the general agreement was less (closed circles). This supported the measured rate of initiation values recorded in the previous chapter.

When adducts greater than 1 : 1 are formed,

$$R_M - R_B = \frac{\overline{k_p}(M)}{\sqrt{2\overline{kt},2}} \sqrt{R_I} \qquad (13)$$

The individual values of R_M and R_B were calculated for any

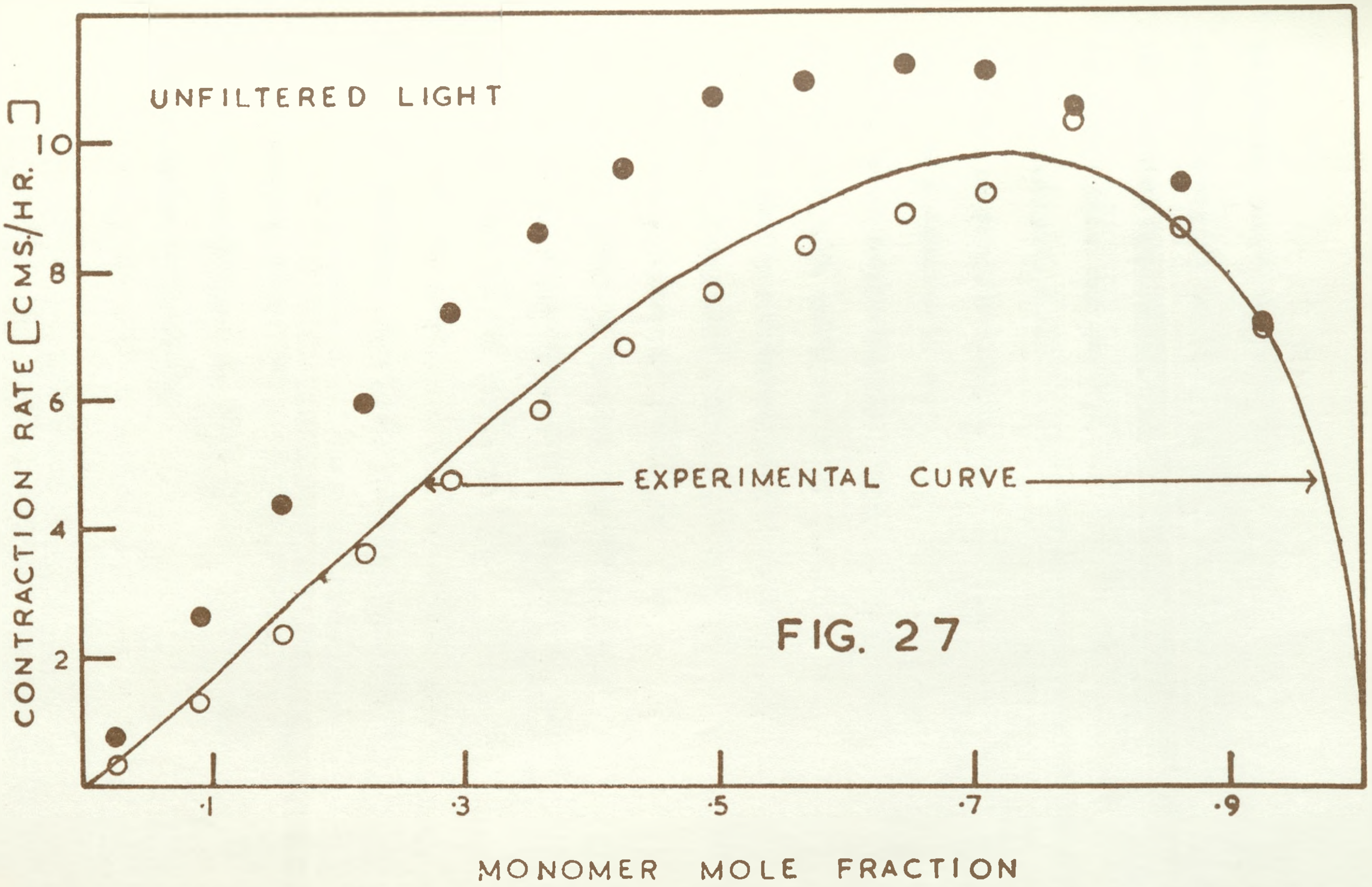UNFILTERED LIGHT
EXPERIMENTAL CURVE
CONTRACTION RATE [CMS./HR.]
10
8
6
4
2
·1
·3
·5
·7
·9
MONOMER MOLE FRACTION

FIG. 27

particular run by determining the total amount of adduct formed in the reaction and also its composition, the reaction time being known. Element analysis gave the adduct composition and complete removal of excess reactants from a weighed reaction mixture sample, as described in Chapter 4, enabled the total weight of product to be found. In this manner R_M and R_B were determined for three series of runs (carried out with unfiltered light), each series corresponding to a different section of Figure 11. Equation (13) was then utilised to determine the corresponding values of $\overline{k_p}/\sqrt{2\,\overline{k_{t,2}}}$. The appropriate values of R_I were calculated from Figure 22 and a knowledge of the relative reaction rates with filtered and unfiltered light. Figure 28 is a plot of the measured R_M and R_B values against feed composition. It will be seen that a maximum must occur in both curves, at a feed composition approximately where the maximum contraction rate was observed (Figure 8, Chapter 4). The results are tabulated in Table 14.

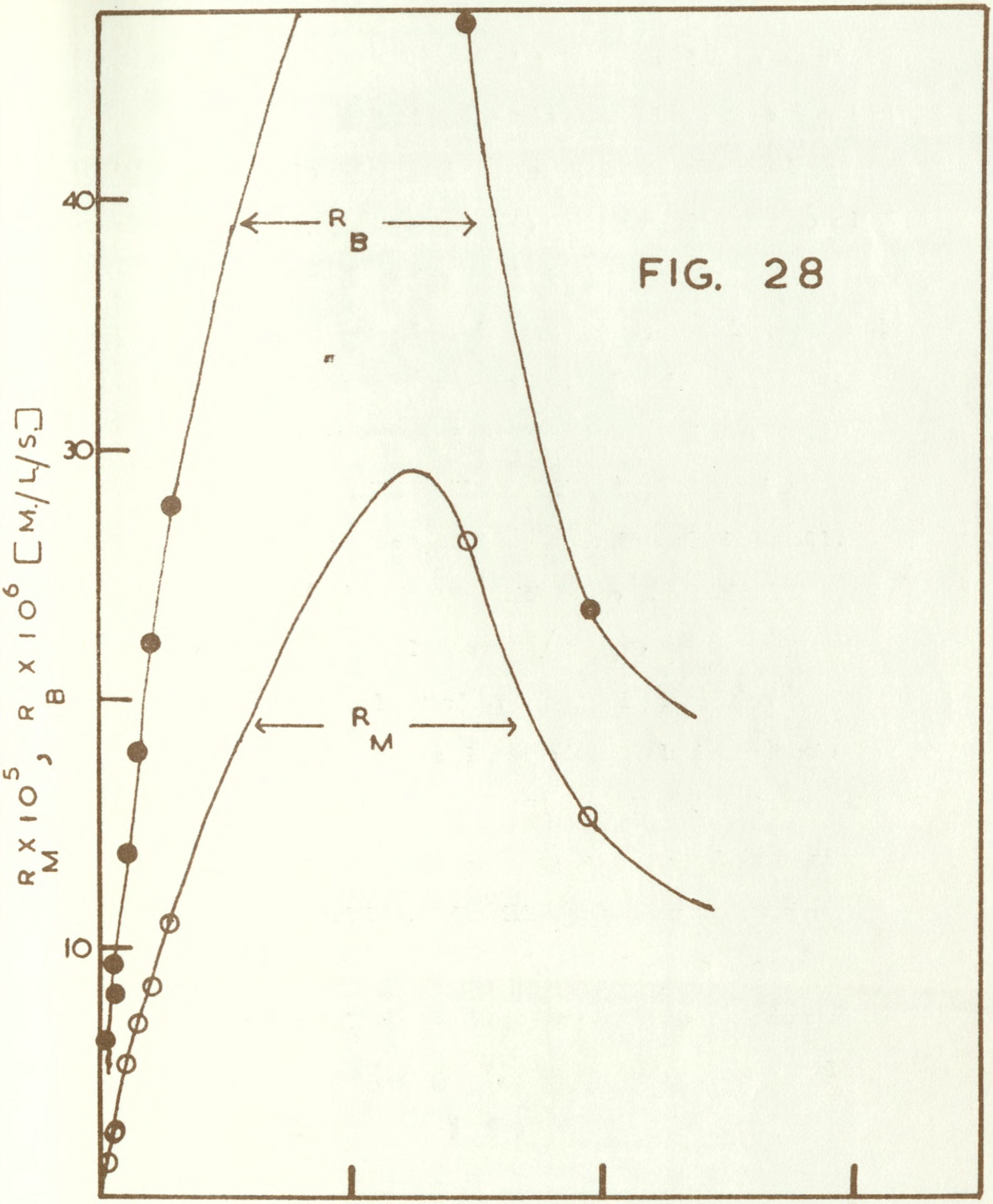

FIG. 28

Table 14

Section of figure 11	R_M m./ℓ./sec.	R_B m./ℓ./sec.	$R_M - R_S$ m./ℓ./sec.	(M) m./ℓ.	$R_I^{\frac{1}{2}}$ $m^{\frac{1}{2}}/\ell^{\frac{1}{2}}/sec^{\frac{1}{2}}$	$\overline{k}_p/\sqrt{2\overline{k}_t}$, 2 $\ell^{\frac{1}{2}}/m^{\frac{1}{2}}/sec^{\frac{1}{2}}$
I	15×10^{-6}	6.2×10^{-6}	8.8×10^{-6}	.518	3.66×10^{-4}	4.65×10^{-2}
I	26.6×10^{-6}	9.34×10^{-6}	17.26×10^{-6}	1.024	3.89×10^{-4}	4.33×10^{-2}
I	28.8×10^{-6}	8.24×10^{-6}	20.56×10^{-6}	1.179	3.96×10^{-4}	4.44×10^{-2}
II	54.4×10^{-6}	13.9×10^{-6}	40.5×10^{-6}	1.658	4.15×10^{-4}	5.89×10^{-2}
II	70.9×10^{-6}	17.9×10^{-6}	53×10^{-6}	2.315	4.31×10^{-4}	5.31×10^{-2}
II	86.9×10^{-6}	22.3×10^{-6}	64.6×10^{-6}	2.927	4.41×10^{-4}	5.01×10^{-2}
II	110×10^{-6}	27.8×10^{-6}	82.2×10^{-6}	3.541	4.43×10^{-4}	5.25×10^{-2}
III	264×10^{-6}	47.0×10^{-6}	217×10^{-6}	7.15	3.52×10^{-4}	8.62×10^{-2}
III	153×10^{-6}	23.5×10^{-6}	129.5×10^{-6}	7.57	3.24×10^{-4}	5.28×10^{-2}
III	133×10^{-6}	7.2×10^{-6}	125.8×10^{-6}	8.95	1.9×10^{-4}	7.39×10^{-2}

While sharp changes in $\frac{\overline{kp}}{\overline{k2}}$ are taking place with feed composition (Figure 11) it will be seen that no such changes are observed in the values of $\overline{kp}/\sqrt{2\overline{kt,2}}$, which remain reasonably constant. The average value of the latter (5.62×10^{-2}) differs little from the corresponding value for very high degrees of polymerisation at 30°C, as calculated from methyl methacrylate polymerisation data. This is commonly accepted as about 4.1×10^{-2}.[3] Similar results were obtained by Mayo[4] and also Robb and Vofsi[2] for the telomerisation of styrene. The former attributed the observed changes in $\frac{\overline{kp}}{\overline{k2}}$ to changes in $\overline{k2}$, but Robb and Vofsi, by determining the individual constants, showed that $\overline{k2}$ for the average dimeric and trimeric radicals was the same. Thus sharp changes occurred in both $\overline{kp}$ and $\overline{kt,2}$, although $\overline{kp}/\sqrt{2\overline{kt,2}}$ was constant. With methyl methacrylate a much larger range of radical sizes can be studied and it is of interest to compare the individual values of $\overline{k2}$, $\overline{kp}$ and $\overline{kt,2}$ for these radicals. The effect of radical structure on transfer can also be studied by comparison of the individual constants ($\overline{k2}$) with those obtained by Robb and Vofsi for styryl radicals. (They also used BTM as the transfer agent). Consequently radical life time measurements were carried out with three feed compositions, each corresponding to a different section of Figure 11. This work is described in the next chapter.

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CHAPTER 7

THE DETERMINATION OF RADICAL LIFETIMES

Radical lifetime determinations in photochemically initiated polymerisation reactions have been achieved by using essentially two distinct, theoretically related, techniques. At the start of any 'pure photochemical' polymerisation the radical concentration is zero, and a finite time must be required (on removing the light shutter) for it to reach the steady state value. Since the rate of polymerisation is proportional to the radical concentration, the interval preceding arrival at the steady state, must be characterised by an acceleration in the polymerisation. This interval is related to the radical lifetime. In a similar way when the light is turned off, the radical concentration, and hence the polymerisation rate, decays to zero. Several methods ('non-stationary state') have been evolved which make possible the direct determination of these natural induction and decay periods.[1,2,3,4,5] The technique of using continuously intermittent illumination has been more widely used in order to determine the lifetime of chain carriers. This technique is essentially a method of integrating a large number of natural induction and decay periods. In the present work both the non-stationary state technique and that of intermittent illumination were used, the former in a semi-quantitative manner only. The relevant theoretical data is given below.

1. The Non-Stationary State Technique

When the stationary state of any radical chain reaction is reached the rates of radical production and disappearance are equal, and the concentration of radicals, $(P)_s$, is given by,

$$(P)_s = \left(\frac{R_I}{2\,k_t}\right)^{\frac{1}{2}} ,$$ [2 kt is the rate constant for the operative termination mechanism]

provided second order radical termination takes place. During the initial stages of the reaction, i.e. when the radical concentration is being built up, the conditions governing the concentration of active centres, (P), is

$$\frac{d(P)}{dt} = R_I - 2\,kt\,(P)^2 \quad ,$$

and integration of this equation gives

$$\tanh^{-1}\left\{(P)/(P)_s\right\} = (2\,kt\,R_I)^{\frac{1}{2}}\,t = \frac{t}{\tau} \quad ,$$

since the integration constant must be zero from the conditions that at t = 0, (P) = 0. τ is the lifetime of the active particle and is defined by

$$\tau \quad = (2\,kt\,R_I)^{-\frac{1}{2}}$$

In polymerisation reactions, the rate of polymerisation at any instant is given by

$$\frac{-d(\text{Monomer})}{dt} = kp\,(P)\,(\text{Mon}),$$

and therefore in the initial stages of the reaction

$$\frac{-d(\text{Mon})}{dt} = kp\,(P)_s\,(\text{Mon})\,\tanh\left(\frac{t}{\tau}\right)$$

Integration of this equation leads to

$$-\ell n\left\{(\text{Mon})/(\text{Mon})_o\right\} = \left(\frac{kp}{2\,kt}\right)\ell n\,\cosh\left(\frac{t}{\tau}\right)$$

If F is the fraction of monomer converted, i.e. 1-F =

(Mon)/$(\mathrm{Mon})_0$, then

$$-\ln(1-F) = \left(\frac{kp}{2\,kt}\right) \ln \cosh \left(\frac{t}{\tau}\right)$$

Under experimental conditions the value of F is small, so that

$$F = \left(\frac{kp}{2kt}\right) \ln \cosh \left(\frac{t}{\tau}\right)$$

When the stationary state is achieved, it is easy to show that the above equation becomes

$$F = \left(\frac{kp}{2kt}\right)\left(\frac{t}{\tau} - \ln 2\right) \qquad (15)$$

It is evident from this equation that if the fraction of monomer is plotted against time, a straight line will eventually result whose intercept on the time axis, t_i, is given by

$$t_i = \tau \ln 2$$

When telomerisation takes place a similar equation can be derived and again $t_i = \tau \ln 2$. Similar treatment can be applied for the case of steady state radical concentration decay, and the whole analysis can be repeated for a first order radical termination mechanism.

2. Intermittent Illumination Technique

The application of intermittent illumination for the determination of radical lifetimes in chain reactions was first shown to be possible by Briers, Chapman and Walters.[6] Melville[7] first used the technique in polymerisation reactions when he studied the vapour phase polymerisation of methyl methacrylate. Burnett and Melville[8] modified the original theory and utilised it to determine the termination constant for polyvinyl acetate radicals. Since then the theory has been considerably extended.[9] In the development below it is assumed that second order radical termination takes place and there is no dark reaction. Furthermore, the propagating centres are assumed to be generated uniformly throughout the reaction system, i.e. the light is weakly absorbed. These conditions were effectively realised in the methyl methacrylate/BTM systems studied.

As before the steady-state concentration of radicals is

$$(P)_s = \left(\frac{R_I}{2kt}\right)^{\frac{1}{2}} \qquad (16)$$

During the light flash, the radical concentration is governed by the differential equation

$$\frac{d(P)}{dt} = R_I - 2\,kt\,(P)^2,$$

which can be integrated to give

$$\left(\frac{2\,kt}{R_I}\right)^{\frac{1}{2}} \tanh^{-1}\left[\,(P)\left(\frac{2\,kt}{R_I}\right)^{\frac{1}{2}}\,\right] = 2\,kt\,t + C,$$

or, using equation (16), $(P) = (P)_s \tanh[\,(2\,kt\,R_I)^{\frac{1}{2}} t + C^1]$

If λ is the duration of the light flash then the average concentration of radicals over the light flash is

$$\overline{(P)}_\ell = (\lambda)^{-1}\int_0^{\lambda}(P)dt = (4\,kt\lambda)^{-1}\,\ln\left\{\frac{1-[(P)1/(P)_s]^2}{1-[(P)2/(P)_s]^2}\right\},$$

where $(P)_1$ and $(P)_2$ are the radical concentrations at the beginning and end of the light flash. During the dark period

$$\frac{d(P)}{dt} = -2\,kt\,(P)^2,$$

whence

$$(P)^{-1} = 2\,kt\,t + C^{11},$$

or using the conditions that $(P) = (P)_2$ at $t = 0$, at $t = r\lambda$, $(P) = (P)_1$, since the duration of the dark period is $r\lambda$ (r being the ratio of the period of darkness to that of light),

$$(P)_1^{-1} - (P)_2^{-1} = 2\,kt.\,r\,\lambda. \qquad (17)$$

Further, the average radical concentration over the dark period is

$$(\bar{P})_d = (r\lambda)^{-1}\int_0^{r\lambda}(P)dt = (4\,r\,kt\lambda)^{-1}\,\ln\,[(P)_2/(P)_1]^2.$$

The average radical concentration over the whole cycle of light and dark is

$$(P)_o = (r+1)^{-1}\,[\,(\bar{P})_\ell + r\,(\bar{P})_d\,],$$

which gives

$$(P)_o = \frac{1}{4(r+1)kt\lambda}\left[\ln\left\{\frac{1-[(P)_1/(P)_s]^2}{1-[(P)_2/(P)_s]^2}\right\} + \ln\left\{\frac{(P)_2}{(P)_1}\right\}^2\right] \tag{18}$$

Here it is convenient to introduce a dimensionless parameter, m, defined by

$$m = \tanh^{-1}(P)_2/(P)_s - \tanh^{-1}(P)_1/(P)_s = 2kt\lambda(P)_s = (R_I\,2\,kt)^{\frac{1}{2}}\lambda \tag{19}$$

Recasting the first equality in equation (19) in logarithmic form

$$2\left\{m + \ln\left[\frac{1+(P)_1/(P)_s}{1+(P)_2/(P)_s}\right]\right\} = \ln\left\{\frac{1-[(P)_1/(P)_s]^2}{1-[(P)_2/(P)_s]^2}\right\} \tag{20}$$

Substituting equation (20) in equation (18) and using the definition of $(P)_1$ from equation (17) gives

$$(P)_o = \frac{m}{2\lambda(r+1)kt}\left\{1 + m^{-1}\ln\left[1 + \frac{rm}{1+(P)_s/(P)_2}\right]\right\},$$

and since $m = 2\,kt\lambda(P)_s$

$$\frac{(P)_o}{(P)_s} = (r+1)^{-1}\left\{1 + m^{-1}\ell n\left[1 + \frac{rm}{1 + (P)_s/(P)_2}\right]\right\} \tag{21}$$

From equations (17) and (19)

$$\tanh^{-1}[(P)_2/(P)_s] - \tanh^{-1}\left[\frac{(P)_2/(P)_s}{rm\{(P)_2/(P)_s\} + 1}\right] = m,$$

from which it can be shown that

$$\frac{(P)_2}{(P)_s} = \frac{r\,m\,\tanh m + \{(r\,m)^2\tanh^2 m + (r\,m + \tanh m)\tanh m\}^{\frac{1}{2}}}{2(r\,m + \tanh m)} \tag{22}$$

Substitution of equation (22) in equation (21) gives a relationship involving $(P)_o/(P)_s$, m and r only.

Now when reaction chains are long the reaction rate is proportional to the concentration of active particles so that the ratio of radical concentrations, $\frac{(P)_o}{(P)_s}$, can be effectively replaced by the ratio of the measured rates under intermittent and steady illumination. Using equation (21), theoretical curves of this latter ratio against log m can be drawn for various values of r. With the use of suitable apparatus experimental values of the ratio can be determined at different flashtimes (λ) using a fixed value of r. If these are then plotted against log $(R_I^{\frac{1}{2}}\lambda)$ the resulting curve should resemble the theoretical curve in shape, and be displaced from it by a numerical value of log $(2\ kt)^{\frac{1}{2}}$. (This follows since m is by definition equal to $R_I^{\frac{1}{2}} (2\ kt)^{\frac{1}{2}} \lambda)$. For the steady state the radical lifetime, τ , is defined by

$$\tau = \frac{\text{No. of radicals per unit volume}}{\text{Rate of disappearance of radicals per unit volume}}$$

$$= \frac{(P)_s}{2\ kt\ (P)_s^{\ 2}} = \frac{1}{2\,kt\ (P)_s} = \frac{1}{(2\,kt\ R_I\ )^{\frac{1}{2}}}$$

Thus having determined the value of kt by the method above, τ can easily be calculated.

Experimental Work and Results

1. Thermocouple Method of Following the Non-Stationary State

Five methods have been employed for following rapidly the non-steady state of liquid phase polymerisation reactions.[1,2,3,4,5] These methods are based on the small change of dielectric constant, refractive index, volume, viscosity, or temperature of the medium. Of these the latter method is in general most useful. In principle, it involves the measurement, as a function of time, of the increase in temperature, while an exothermic reaction proceeds under adiabatic conditions. This method was utilised in the present work.

The reaction vessel and complete apparatus has been described in detail elsewhere.[10] In principle a thermocouple is situated in the centre of a specially designed reaction vessel and is used, in conjunction with a low-impedance D. C. amplifier and a suitable recording system, to measure the temperature in this region as the reaction is photochemically induced. The length of time during which conditions in the vessel remain adiabatic determines the applicability of the method for comparatively long lifetime measurements.

Reactions were carried out in the absence of air with four different M-BTM feed compositions. The filled reaction vessel was placed in a thermostat and after a test signal had been sent to the recording apparatus, the reaction mixture was exposed to U.V. light. When the recorded rate of temperature rise was constant (after about 30 seconds) the reaction was stopped. The procedure of test voltage, then reaction initiation was repeated at least twice. A typical recorder trace is shown in Figure 29. Under adiabatic conditions the rise in temperature is directly proportional to the amount of reaction, and thus Figure 29 can be identified with equation (15). Using

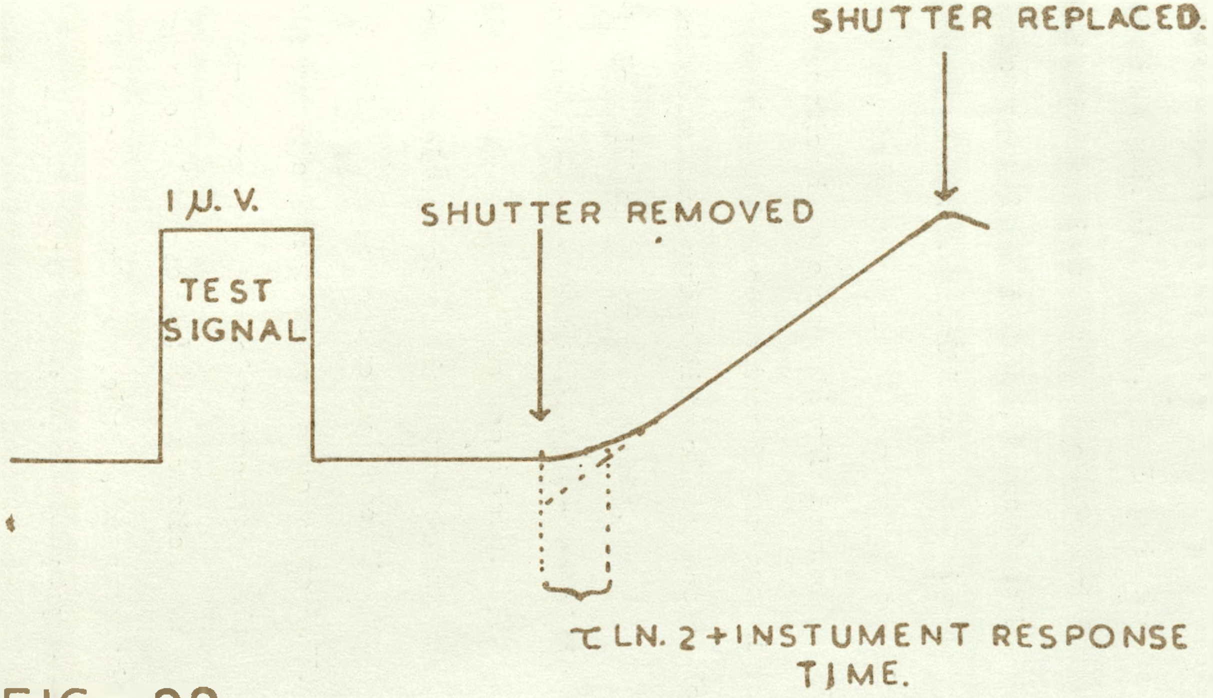
SHUTTER REPLACED.
1 μ. V.
TEST SIGNAL
SHUTTER REMOVED
τ LN. 2 + INSTUMENT RESPONSE TIME.

FIG. 29

the successive traces the average intercept on the time axis was measured and after subtracting the known response time of the instrument (.5 seconds), a value was obtained for the radical lifetime. Reaction rates were also measured and the table below summarises the results.

Table 15

Run No.	(M)/(BTM)	Measured intercept (secs.)	Calculated lifetime (secs.)	Comparison of $2\overline{kt},2$ values	Reaction rate (μvolts/sec.)
1	.066	<1	-	-	5.14×10^{-3}
2	1.34	2.28	2.6	1 (Standard)	33.7×10^{-3}
3	4.5	2.03	2.2	2.45	37.2×10^{-3}
4	9.15	2.94	3.5	1.66	35.9×10^{-3}

Because of the small intercept obtained in Run 1, the corresponding calculated lifetime was subject to a large error.

The above work was performed in the early stages of the research topic investigation, before any rate of initiation determinations had been made and the detailed slope of Figure 11 evaluated. The runs were thus of random feed composition and termination constants could not be calculated from the lifetime measurements. When initiation rates relevant to the dilatometric work were later evaluated, termination constants in the thermometric runs could be compared but not separately evaluated (see column 5, Table 15). It will be seen that, within experimental accuracy, the termination constant varied little in the feed composition range studied. Since the latter corresponded to Section III of Figure 11, this conclusion is not unexpected and supports the idea that with methyl methacrylate type radicals, velocity constants are independent of radical size when the radicals are greater than the tetrameric. Unfortunately the experimental limits of the apparatus prevented the termination constant in Run 1 (corresponding to Section I, Figure 11) being compared with the other values.

2. The Measurement of Radical Lifetimes Using a Rotating Sector

In order to carry out these measurements the experimental equipment used in the evaluation of overall rates and rates of initiation, had to be completely changed. An 'Osira' 125 watt mercury arc lamp operated from the D.C. mains via a 130 ohm resistance was used as a light source. The light beam was focussed by means of a quartz lens, and a thin sectored disc (14" diameter) fitted to an aluminium wheel (11" diameter) arranged to cut the light at the focus point. A divergent beam emerged from the focus point, forming an illuminated circular area at the plane of the dilatometer. The latter was situated so that the light completely covered the bulb and it was as close to the sector as possible. This arrangement was achieved by placing the reaction vessel in a small cubic copper tank of about 1 litre capacity. Water at 30°C was circulated through the tank from an ordinary thermostat by means of a pump. The dilatometer bulb was completely immersed in the water, which retained a reasonably constant temperature, and the capillary protruded out of the tank. A special holder was used for the dilatometer to ensure that its position did not vary from experiment to experiment. Sectored discs (giving a 1 : 1, light to dark ratio) made of phenolic laminate, were attached to the aluminium wheel, and the latter carefully balanced by counterweights. Thus on rotating the wheel equal periods of light and darkness were obtained. The wheel was driven by a D. C. motor fitted with reduction gears. A gear box enabled three different speeds to be obtained and a variable 800 ohm resistance in series with the motor extended the number of sector speeds attainable. With this arrangement flash times ranging between 1.3 to 25 seconds were obtained. Shorter flash times were obtained by using a different D. C. motor, the aluminium wheel being driven directly or through a 30 : 1 reducing gear. The sector speed was determined by using a rev counter and a stop watch.

In carrying out a dilatometer run, the unsectored rate was first measured followed by a rate determination at a definite flash time. The unsectored rate was then measured again. This procedure was repeated with different flash times, until the unsectored rate fell below about 85% of its initial value. In this way a complete lifetime curve was evaluated from two or three runs. The corresponding rate of initiation was measured and the ratio of sectored rate to unsectored rate plotted against log $(R_I^{\frac{1}{2}}\lambda)$, λ being the flash time. The best theoretical shaped curve was drawn through these points and the displacement from the corresponding theoretical curve measured. (The latter was constructed using literature data). Figure 30 shows the experimental curve obtained with a reaction mixture corresponding to Section II of Figure 11. Other runs were performed corresponding to the other sections of Figure 11, and the complete results are tabulated in Table 16.

In each case the termination constant was evaluated and hence the radical lifetime. It was found that, within the experimental accuracy of the rotating sector method, the termination constant did not change with initial feed composition, and thus was independent of radical size in the range investigated. This effectively means that

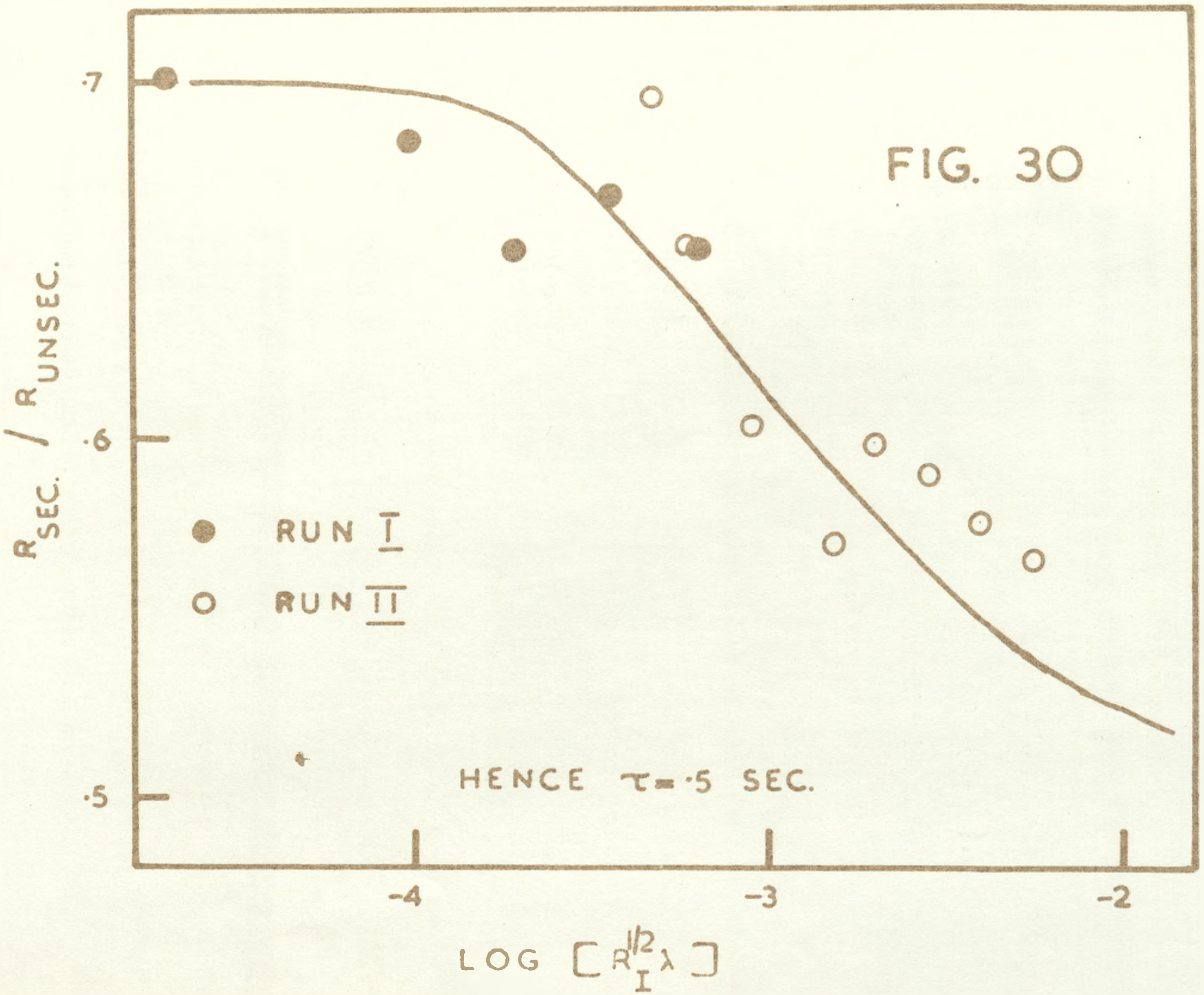
·7
·6
·5
$R_{SEC.} / R_{UNSEC.}$
● RUN I
○ RUN II
HENCE $\tau = \cdot 5$ SEC.
−4
−3
−2
LOG $[R_I^{1/2} \lambda]$

FIG. 30

Table 16

λ secs	$\log (R_I^{\frac{1}{2}}\lambda)$	$\frac{\text{R sec.}}{\text{Run sec.}}$	λ secs.	$\log (R_I^{\frac{1}{2}}\lambda)$	$\frac{\text{R sec.}}{\text{Run sec.}}$
(a) $\frac{(M)}{(BTM)} = .121 : R_I^{\frac{1}{2}} = 3.06 \times 10^{-4}\ m^{\frac{1}{2}}/\ell^{\frac{1}{2}}/sec^{\frac{1}{2}}$					
.0839	-4.5904	.6885	2.2	-3.1710	.6435
.2894	-4.0526	.672	4.435	-2.8675	.6215
.5635	-3.7632	.674	11.7	-2.4461	.5855
.7927	-3.6153	.676	15.53	-2.3224	.576
1.271	-3.4098	.662			
(b) $\frac{(M)}{(BTM)} = .51 : R_I^{\frac{1}{2}} = 3.35 \times 10^{-4}\ m^{\frac{1}{2}}/\ell^{\frac{1}{2}}/sec^{\frac{1}{2}}$					
.059	-4.7038	.702	1.907	-3.1945	.6515
.2862	-4.0177	.6835	2.717	-3.0405	.604
.5715	-3.7179	.653	4.49	-2.8225	.570
1.05	-3.4535	.668	5.925	-2.7020	.598
1.339	-3.3478	.695	8.425	-2.5493	.5885
1.79	-3.2218	.654	11.84	-2.4007	.576
			16.83	-2.2480	.565
(c) $\frac{(M)}{(BTM)} = 3.53 : R_I^{\frac{1}{2}} = 2.54 \times 10^{-4}\ m^{\frac{1}{2}}/\ell^{\frac{1}{2}}/sec^{\frac{1}{2}}$					
.5575	-3.8356	.705	2.675	-3.1675	.628
.620	-3.8033	.667	4.43	-2.9492	.590
.7877	-3.6990	.667	5.996	-2.8176	.6215
.925	-3.6295	.6615	8.837	-2.6488	.5955
1.315	-3.1979	.6615	10	-2.5952	.584
1.68	-3.3703	.6345	11.85	-2.5214	.587
1.915	-3.3130	.670	20	-2.2941	.536

the changes in radical reactivity observed in Figure 11 are due to variations in the radical transfer constant $(\overline{k_2})$ with radical size. This result is very surprising in view of the fact that Robb and Vofsi[11] evaluated similar transfer constants, yet dissimilar propagation and termination constants, for the average dimeric and trimeric styryl radicals. The individual values of $\overline{k_2}$ and $\overline{k_p}$ for different sized methacrylate type radicals were calculated from the measured $2\overline{k_{t,2}}$ values, and the data in Tables 4 and 14. These are shown in Table 17. Discussion of the complete results is left to Chapter 9.

Table 17

Temp. °C	Radical	$\overline{k_2}$ lit/m./sec.	$\overline{k_p}$ lit/m./sec.	$\overline{k_{t,2}}$ lit/m./sec.
30	Trimeric	21.5	253	1.6×10^7
30	Tetrameric	1350	304	1.6×10^7
30	Polymeric	472	401	1.6×10^7

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CHAPTER 8

PHOTOCHEMICAL REACTIONS OF VARIOUS OLEFINS WITH α-BROMOETHYLBENZENE

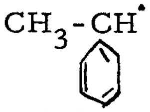
In work described in preceding chapters, information has been obtained of the effect of radical size on radical velocity constants. Telomerisation systems were studied and consequently average velocity constants, for average radical sizes, were evaluated. Clearly if discrete radicals of different sizes can be studied, the corresponding velocity constants are more significant. This chapter describes some preliminary work done with this object in mind.

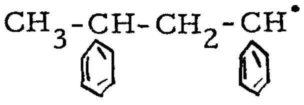
Theory

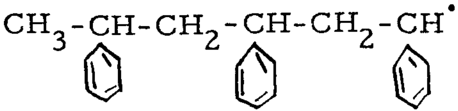
The work of Melville, Robb and Tutton[1] illustrates how the absolute reactivities of olefins towards a discrete radical can be compared. In a similar manner reactivities of different radicals towards a particular olefin can be correlated. If these different radicals resemble successive radicals formed in the early stages of a monomer polymerisation, then information is obtained on the reactivities of discrete polymer-like radicals of different sizes. The operative kinetic mechanism, after Kharash, can be represented as follows:-

$$\begin{array}{llll}
1. & R\,Br \xrightarrow[R_I]{h\nu} R^{\bullet} + Br^{\bullet} & & \text{Initiation} \\
2. & R^{\bullet} + \overset{|}{\underset{|}{C}} = \overset{|}{\underset{|}{C}} \xrightarrow{k_1} R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}^{\bullet} & \left.\begin{array}{l} \\ \\ \end{array}\right\} & \text{Chain} \\
3. & R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}^{\bullet} + R\,Br \xrightarrow{k_2} R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Br + R^{\bullet} & & \\
4. & 2R^{\bullet} \xrightarrow{2k_{t,1}} R-R & & \\
5. & 2R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}^{\bullet} \xrightarrow{2k_{t,2}} \text{Pdt.} & \left.\begin{array}{l} \\ \\ \\ \end{array}\right\} & \text{Termination} \\
6. & R^{\bullet} + R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}^{\bullet} \xrightarrow{2k_{t,3}} \text{Pdt.} & &
\end{array}$$

The radical, R$^{\bullet}$, is varied throughout a radical series, such as

(a)

$CH_3-\underset{C_6H_5}{CH}^{\bullet}$

(b)

$CH_3-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}^{\bullet}$

(c)

$CH_3-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}^{\bullet}$

The olefin must react with R$^{\bullet}$ radicals and be capable of propagating a chain reaction. Kinetic analysis indicates that when reaction (2) is rate controlling

$$\frac{-d(C=C)}{dt} = \frac{k_1 R_I^{\frac{1}{2}}(C=C)}{(2kt,1)^{\frac{1}{2}}} ,$$

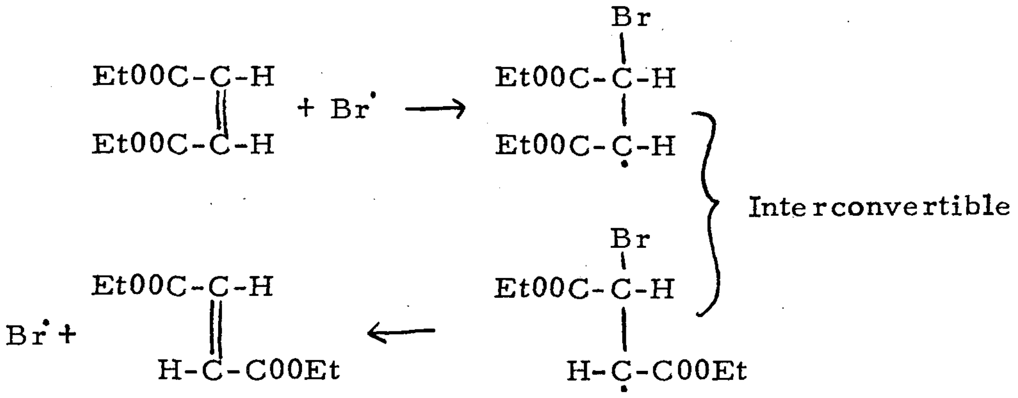
and when reaction (3) is rate controlling

$$\frac{-d(C=C)}{dt} = \frac{k_2 R_I^{\frac{1}{2}} (R\,Br)}{(2\,kt,2)^{\frac{1}{2}}}$$

All the velocity constants in these two expressions can be evaluated experimentally and thus their variation with the nature of R$^{\bullet}$ studied.

Preliminary Experiments

Difficulties obviously occur in the preparation of any series of RBr compounds but these undoubtedly will be least with the benzene ring type compounds illustrated above. Thus it was decided to investigate the growing styryl radical reactivity and various olefins were tried as suitable reactants with α-bromoethylbenzene (BEB). Photochemical reactions were studied in the absence of oxygen by dilatometry. No contraction occurred with cyclohexene, indicating that the chain reaction was unfavourable or no initiator radicals were produced. However BEB was shown to photolyse in the presence of U.V. light by comparing the rate of bulk styrene photopolymerisation with that of a 1 : 1 molar styrene-BEB mixture. The latter was twenty times faster and had an intensity exponent of .5. Thus probably cyclohexene was unreactive towards the radicals produced. The more reactive olefin diethyl maleate yielded a surprising reaction. Expansion was observed in the dilatometer and the product obtained, after pumping all the reactants off and recrystallising the residue from petroleum ether, contained no bromine. Element analysis, melting point determination, and mass spectrometer data indicated the product might well be the half ester of fumaric acid. Undoubtedly isomerisation of the ester had taken place in the presence of bromine atoms[2] causing the increase in volume.



The postulated half ester was explained by slight hydrolysis of the full ester. However, the desired chain reaction did not take place and no detailed investigation of the system was made. Diethylfumarate gave a very slow contraction rate. The product contained bromine but was a mixture, partly soluble in caustic soda solution. This indicated the possibility of a small chain reaction in which the termination product was in comparable amount to that of the chain. Thus a still more reactive olefin had to be tried and unfortunately this meant using styrene, which can polymerise. However, with reactant concentrations adjusted so that a 1 : 1 adduct only is produced, the kinetic scheme is unaltered and clearly the values of k_1 to be measured must closely approach values of the propagation constants relevant to the first few steps of bulk styrene polymerisation.

The Photochemical Reaction Between BEB and Styrene

The product of a 1 : 1 molar reaction was analysed, after purification by precipitation from methanol, and was found to be a polymer with approximately 45 monomer units in the molecule. Runs were therefore performed with higher BEB concentrations and the products analysed, the following results being obtained.

Table 18

Molar ratio $\frac{(BEB)}{Styrene}$	Adduct produced
10	1.3 : 1 (I)
20	1.1 : 1 (II)
40	1 : 1 (III)

The molecular weight of adduct II was determined by the freezing point depression of cryoscopic benzene. Values of 276 and 271 were obtained (the theoretical value for a 1 : 1 adduct is 289) and thus it seems that with BEB to styrene molar ratios of 20 : 1 and greater, no polymerisation takes place. With greater relative styrene concentrations telomerisation takes place and average adducts are isolated.

With feed compositions which eliminated telomerisation, the photochemical contraction rate was very small ($<.018$ cms/hr), and was not significantly increased by the addition of either benzoyl peroxide or 1-1'-azo-bis-cyclohexane carbonitrile. A thermal reaction also took place, probably due to thermal breakdown of BEB. The thermal reaction rate was therefore measured at three different temperatures, enabling the activation energy of the process to be evaluated. This was found to be about 22 kcal/mole and represents the overall activation energy for the initiation, propagation and termination reactions. The intensity exponent of the photochemical reaction was measured and found to be about .65. This indicated that the chain length of the reaction was small, probably due to the relative unreactivity of the radicals concerned. Measurement of the overall reaction rate and the rate of initiation supported this. Clearly the system was both theoretically and experimentally unsuitable for the desired studies and thus this method of approach to the research problem was abandoned in favour of that reported in the bulk of this thesis. However, the investigation of polymer type radicals other than styryl, might yield valuable data using this interesting method of approach.

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CHAPTER 9

DISCUSSION OF RESULTS

The results evaluated in Chapter 7 indicate that a reactivity maximum is associated with the transfer reaction to BTM of the polymethyl methacrylate radical during the initial stages of growth. At the same time termination and propagation reactivities appear, within the accuracy of experimental determination, to be independent of radical size and identical with those reactivities normally associated with large polymethyl methacrylate radicals. ($k_p \sim 300\ \ell/m/sec$ and $k_{t,2} \sim 2 \times 10^7\ \ell/m/sec.$).

These conclusions are entirely different from those obtained by Robb and Vofsi[1] studying reactivity changes in different sized styryl radicals. In this case termination and propagation constants are influenced by radical size, though the debromination reaction is not. Clearly any general theoretical interpretation of the complete results is difficult, since the conclusions formed in the methyl methacrylate work seem completely at variance with the results of Robb and Vofsi. However, many factors influence radical reactivity and much information is still required before accurate predictions on radical behaviour can be made. Thus although the conclusions deduced from the present work are surprising in comparison with the styrene results, there are no theoretical grounds for rejecting these conclusions as unreliable. A theoretical interpretation of the complete results must thus explain the dependency of radical reactivity on both radical size and structure.

It was originally suggested by Walling and Mayo and their collaborators[2,3,4] that the transition states in polymer radical propagation and transfer reactions may contain polar contributions from structures such as $R^+ [>\dot{C} - C<]^-$ or $R^+ Q^- \dot{X}$ (where $R^{\cdot}$ is a polymer radical, $>C = C<$ the monomer, and XQ the transfer agent). More recent work with transfer reactions has substantiated this idea.[5,6] If these polar contributions are significant it would be expected that the electron donating or accepting properties of the reactants would have an important influence on the rate of reaction. The latter is of course influenced by other factors (e.g. steric and resonance) all of which can be regarded as characteristic of the general reactivity of the reactants. Thus the reactivity of a radical can be artificially separated into two components predominantly polar and non-polar in origin. This is the basis of the 'Q-e' scheme originated by Alfrey and Price.[7] In this scheme reactants in polymerisation reactions are assigned separate numerical Q and e values, which are characteristic of the general reactivity and polar nature of the reactants respectively. Rate constants in polymerisation reactions can be more readily correlated and predicted knowing the different Q and e values of the reactants.

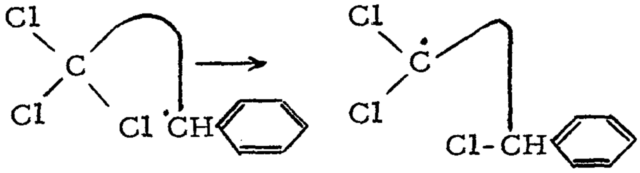
Recently Bamford, Jenkins and Johnston[8] have demonstrated the relative importance of the general reactivity (Q) and polar (e) factors in various polymerisation systems. A quantitative and uniform measure of the general reactivity of various radicals was obtained from the velocity coefficients of the transfer reactions between the radicals and toluene, for reactions of the latter would be expected to be affected by polar factors to a minor extent only. Different reactions of the radical series were then considered and if the appropriate velocity constants could be correlated with the general reactivity of the radicals, evidence was obtained for the absence of polar effects in the reactions studied. Where a series of velocity constants could not be correlated with the general radical reactivity, the presence of polar factors was established.

Using the above approach Bamford showed that reactions involving the addition of various type radicals to styrene were essentially free from polar influences. However, in transfer reactions with carbon tetrabromide the situation was quite different for indirect evidence was obtained of transition states containing contributions from polar structures of the type

$$R^{+}\ Br^{-}\ \dot{C}Br_3\ ,\ R^{+}\ \dot{Br}\ \overset{-}{C}Br_3$$

In this case radicals carrying electron attracting groups react less readily than would be expected from their general reactivity, while electron donating radicals react more readily. These conclusions help the interpretation of Robb and Vofsi's results and also those of this thesis.

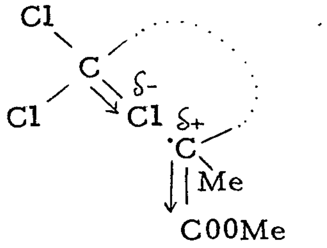
Following Bamford's conclusions it would seem that the different propagation reactivities of the dimeric and trimeric styryl radicals can be correlated with differences in the general reactivity of the radicals, rather than with any polar differences. If this is so it is necessary to explain the large difference in general reactivity of the two radicals, since the free electron environment is essentially the same in both although the trimeric radical is larger by one monomer unit. Furthermore, with these radical sizes it would be expected that the trichloromethyl end group would have little influence on the general radical reactivity. However, by constructing radical models it can be shown that the dimeric and trimeric styryl radicals are sterically very different. With the trimeric radical the free electron approaches so close to an end group chlorine atom that an internal transfer reaction within the radical can probably take place, as illustrated below



This effectively means that the trimeric radical is structurally completely different from the dimeric for the free electron now appears on the 'head' of the radical. Such a radical would be expected to differ greatly in general reactivity from the dimeric. Styryl radicals greater than the trimeric will all be structurally characteristic of the dimeric and therefore have similar general reactivities. This fits the data of Robb and Vofsi, who found that the dimeric radical reactivity in propagating, resembled that associated with the polystyryl radical. In a similar manner the changes in termination constant are explained.

Now the process of styryl radical transfer to BTM will be strongly influenced by the polar properties of the reactants in addition to the general reactivity of the radicals involved. Thus reactivity changes parallel to those observed in propagation will not necessarily be expected. Furthermore, if the transfer process with both the dimeric and the trimeric radical is very efficient, reactivity differences will not be apparent. Now the normal styryl radical, and therefore the dimeric, is an electron donor ($e = -.8$) while bromotrichloromethane is an electrophilic reagent ($e \sim +2$). This would effectively enhance the stability of an activated complex and give a very efficient transfer reaction. In a similar manner the rearranged trimeric radical, if electron donating, might well transfer with BTM very readily. Thus similar polar contributions by different structural radicals may swamp any effects of different general radical reactivity and result in the observed independence of the transfer process on radical size.

With methyl methacrylate radicals propagation and termination reactivities are independent of radical size although transfer to BTM is not. Bamford has shown that methyl methacrylate propagation, unlike that of styrene, is influenced by polar factors in addition to general radical reactivity. The polar influence, however, will be much less effective than in radical transfer to very electrophilic molecules, such as BTM. The methyl methacrylate results thus seem to indicate that the different sized radicals, while having similar general reactivities, possess significant differences in polar properties. Probably, therefore, no internal radical rearrangements take place and the radicals are all structurally similar. However, in the trimeric methyl methacrylate radical the free electron approaches close to the trichloromethyl end group, though not as close as with the corresponding styryl radical. In this position the radical tail may become closely associated with a chlorine atom (although evidence is against any internal rearrangement), especially since the radical is an electron acceptor ($e = +.4$) and the atom probably carries a slight negative charge.



Such an association will undoubtedly influence the availability of the radical to form transition complexes in transfer reactions. A tetrameric methylmethacrylate radical is more sterically free from end group influences and transfer is consequently facilitated. The subsequent decrease in transfer constant on further radical growth may well be due to further modification of the polar influence of the radical, by such as radical coiling. Once again the availability of the radical to form transition complexes will be affected, and a consequent change in transfer reactivity will result.

Although it has long been considered that polymer radical reactivity may well be dependent in the initial stages of radical growth on radical size, no precise data has been obtained on this question until very recently. The lack of information available on this particular research problem is itself a criticism of any theoretical interpretation of the results obtained to date. Clearly further experimental investigations should be carried out before advancing any really valid explanation. The interpretation given above of the available results can of course be criticised, though in the absence of further information speculation on the above lines can only be made and no concrete theories advanced. A logical extension of the work to obtain data on the effects produced by different radical end groups, different transfer agents, and different radical types, is necessary. Only with such data can a proper understanding of the results be made.

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