THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

THE KINETICS OF POLYMERIZATION AND DEGRADATION OF VINYL COMPOUNDS.

BY

ERIC VANCE B.Sc.(Glas.)A.R.I.C.

CHEMISTRY DEPARTMENT,
GLASGOW UNIVERSITY,
SEPTEMBER 1954.

SUPERVISOR:
Dr. N. GRASSIE.

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PREFACE

This work was carried out at the University of Glasgow during the sessions 1951-1954. Some of the results have been published and copies of reprints of these papers are added as a supplement to this thesis. (Trans. Faraday Soc. 49, 184, 1953 and J. Chem. Soc. 2122, 1954).

I would like to express my thanks to my supervisor Dr Norman Grassie for his constant help and encouragement and to the Department of Scientific and Industrial Research for the award of a maintenance grant. I would also like to thank the University of Glasgow for the apparatus and facilities available and Professor J.M. Robertson and the staff of the department for their general interest.

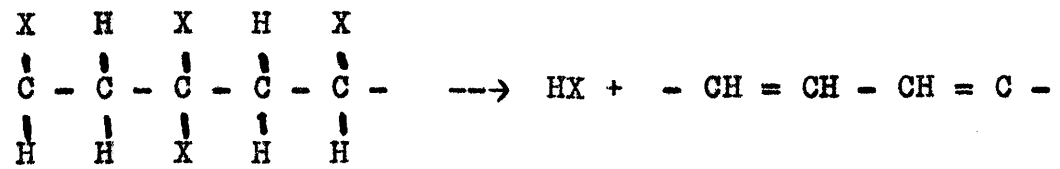
Chapter 1.

General Introduction

Almost since the commercial introduction of synthetic high polymers there has naturally been considerable interest in their stability and in their general degradation properties. Now that the polymerization process is well understood and the structure of the resulting polymers appreciated in a fairly detailed way it has become profitable to proceed to a fundamental investigation of some of their degradation reactions. From a purely academic point of view these investigations have been of interest because of the chemistry of the processes involved and also because degradation results have been used to give information about the structure of the polymer molecules, from which conclusions can in turn be drawn about the polymerization process itself.

Two general types of thermal degradation reaction have been reported. Firstly, there is the type in which the volatile material evolved is more or less monomer, together with dimer, trimer and other low polymeric material. Polythene, for example, gives a small

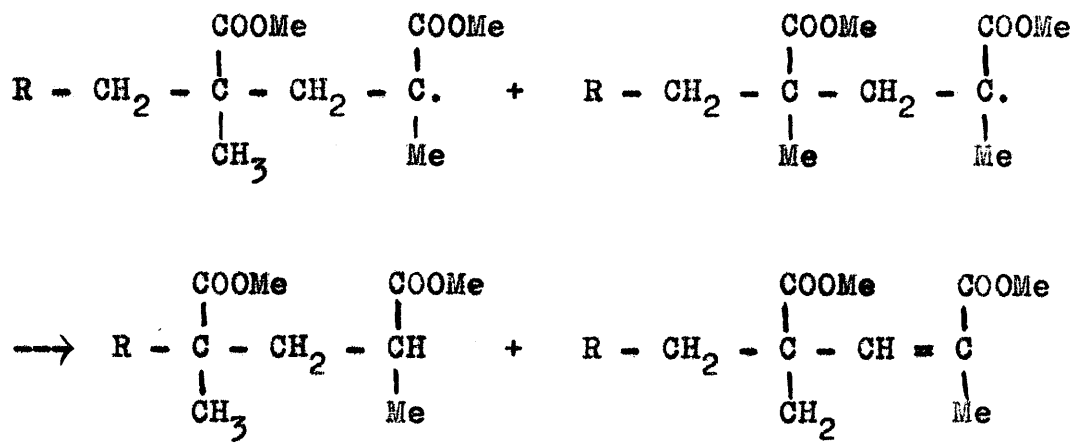
percentage of ethylene (I). Polystyrene gives approximately 50% styrene (II, III, IV, V) and polymethylmethacrylate gives monomer in quantiative yield (VI). Secondly there is the type of reaction which occurs in the case of polyvinyl acetate and polyvinyl chloride where acetic acid and hydrogen chloride respectively are produced (VII, VIII, IX, X) leaving a conjugated poly-acetylenic chain.



The kinetics of the above types of reaction have been worked out and the mechanism defined.

The depolymerization reaction of polymethylmethacrylate consists of radical formation at the chain ends, followed by the unravelling of the chain by a reverse polymerization mechanism. In this work, (VI) it was clearly shown that there existed in a benzoyl peroxide catalyzed polymer two distinct types of molecule having different rates of degradation. These two types of molecule were shown to be present in equal amounts

and, since the unravelling process must be the same for all molecules, it was postulated that these two species were the types containing respectively the saturated and unsaturated ends which are produced when the growth of two polymer radicals is terminated by disproportionation. For example such a reaction in methyl methacrylate is represented as follows -



The implications of this suggestion were not fully discussed in the original papers because the experimental data could provide no further information and the first part of the present work, which is contained in chapter three of this thesis, aimed at proving or disproving this theory and also at deciding which type of molecule was breaking down at the faster rate. This could be done

by using polymers transferred with benzene so that the proportion of each type of end is changed from the original 50%. Such data would also be a final check on the postulated termination and transfer reactions which have been in dispute among polymer chemists.

In addition to the polymers mentioned above, which give high yields of monomer, it has been reported (XI) that polymethacrylo-nitrile gave 80% monomer when heated at 250°C. From this fact, and also because the structure of this polymer, (which contains a CN group instead of a COOMe) is similar to polymethyl methacrylate, it might be expected that the degradation characteristics of these two polymers are closely related and in an investigation the same standard techniques and methods might apply. It was however noted that no details of the polymerization process were available in the literature. The work which is reported in chapter 5 of this thesis aimed at the measurement of the kinetic constants of the various steps of this polymerization process. Such data would provide information about the structure of the polymer and particularly the nature and properties of the chain ends formed by termination and transfer which has been shown to be of supreme importance when the degradation reaction

of methyl methacrylate was considered.

In the measurement of the rate constants mentioned above it is necessary to be able to obtain reliable measurements of number average molecular weights. These can be most readily obtained from osmotic pressure measurements. From the literature and by trial it was discovered that the number of solvents, especially solvents which could be successfully used in osmometry, was extremely limited, hence it was desirable that some experiments should be carried out in order to discover which solvent would be most suitable for such determinations. The work which is contained in chapter four aimed at showing under which conditions reliable osmotic measurements could be made. The results made available by this work were used in the investigation of both the polymerization and the degradation reaction.

During the course of this phase of the work, some interesting anomalies were found in the osmotic behaviour of the polymer and these are discussed in a qualitative way in the above chapter.

When the above information was successfully obtained the work proceeded to an investigation of the thermal degradation reaction itself and preliminary results are discussed in the last chapter of the thesis.

Chapter II

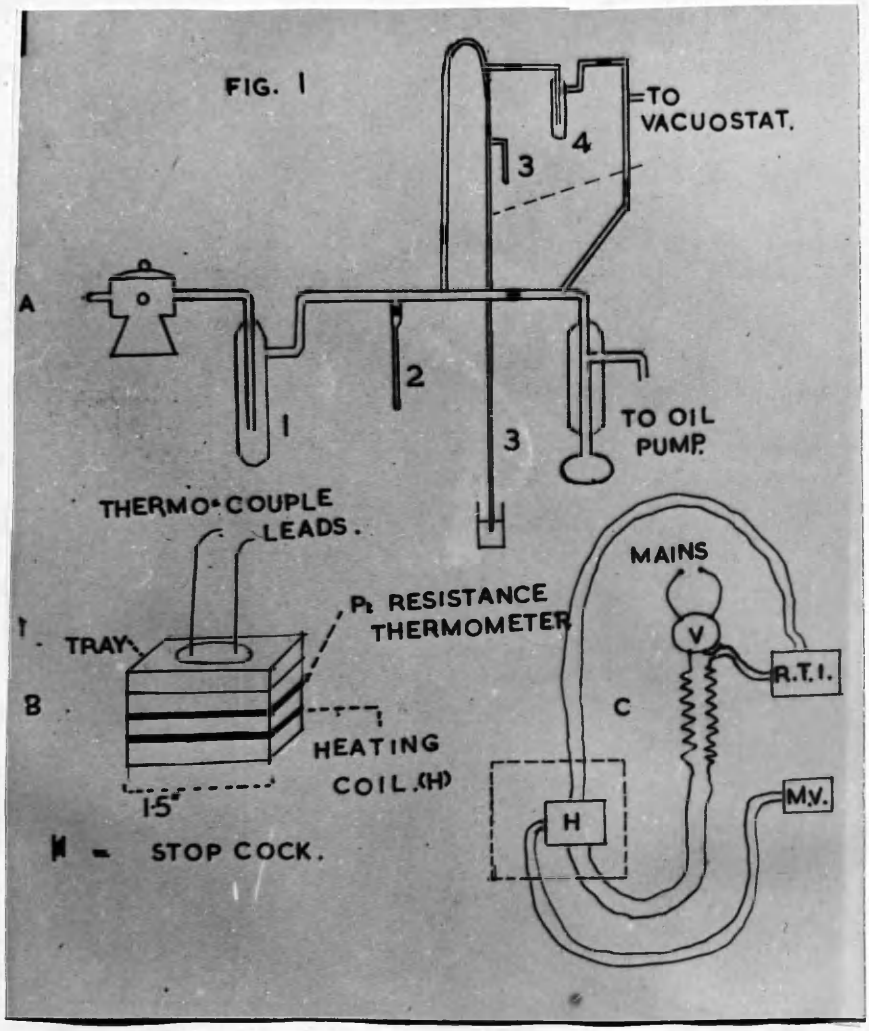
General Experimental Techniques and Methods.

In this work it was necessary to construct and adapt apparatus for the particular problem in hand and it is convenient that the general techniques and experimental method used should be reported at this stage.

Molecular Still.

The apparatus used for degradation experiments was the dynamic molecular still first described by Grassie and Melville (VI), and later modified by Cowley and Melville (XII). It consists essentially of a glass envelope which can be evacuated, using a mercury vapour and an oil pump, to a pressure of 10^{-6} mms Hg. Under these low pressure conditions the possibility of oxidation reactions taking place is eliminated, while the products of the reaction are removed rapidly and effectively - so that no complicated side reactions may take place. At the same time very small rates of reaction can be measured through the minute pressure changes which occur in the still.

Fig. 1 - Glass Work and Circuit of Degradation Apparatus



The degradations were carried out in a copper tray, fitted with thermo-couple leads, which could be screwed to an electrically heated copper block. The temperature was controlled by means of a 'sunvic' temperature resistance controller, type RT.I., using a platinum resistance thermometer of 10 ohms. Diagrams of the general structure of the still and of the heating block are shown in Fig. I. The wires connecting the controller, heater, and thermo-couple to the appropriate instruments were sealed through the glass of the apparatus by means of borated copper wire.

In previous work it has been shown that the even heating required for accurate kinetic measurements is difficult to obtain. This difficulty is obviated by the use of a covering of metallic powder, in this case copper. The copper powder was prepared by the reduction of copper oxide in a current of coal gas. In some experiments, which will be discussed later, the use of copper is impracticable but in these cases, at the temperature used, the polymer was in the form of a mobile liquid and hence reasonable uniformity in heating might be expected. During most of the runs, however copper was used if possible.

As the monomer or volatile material diffused to the liquid air trap (I in Fig. I) a small pressure is set up inside the still which, in the case of the production of a single product, as for poly methyl methacrylate and poly vinyl acetate, has been shown, at low pressures such that there is free diffusion from the hot surface to the liquid air trap, to be proportional to the rate of production of volatiles. This pressure is measured using a pirani gauge and the rate is given by the expression-

$$\frac{V^2 - V_o^2}{V_o^2}$$

Where V is the voltage across the pirani bridge at the rate being considered, and Vo is the voltage at zero rate.

The volume of the products was determined by the distillation of these into a calibrated capillary tube (2, in Fig. I) from the large liquid air trap (I) where they had collected during the course of the reaction. The vapour pressure of the products, which was sometimes of use in identification, was found by distilling them into another tube fitted with a manometer. (3)

Preparation of Polymers.

The Polymers used were prepared in vacuo using, in general, benzoyl peroxide as catalyst. The catalyst was purified by dissolving the crude material in chloroform, removing the water layer, and precipitating by pouring into a large excess of methyl alcohol. It was then filtered and dried at the pump and stored in a dessiccator. When a benzoyl peroxide catalyzed polymer was being prepared it was convenient to introduce the catalyst into the reaction tube as a standard solution in benzene. The benzene was then removed at the water pump leaving behind the solid catalyst.

The monomeric material used for polymerization, rate measurements, or for the preparation of experimental polymeric samples was degassed three times on a vacuum line using liquid air & distilled twice in vacuo before being sealed off in the reaction tube under vacuum. When rate measurements were required the polymerizations were carried out dilatometrically in an electronically controlled thermostat. The type of reaction tube used in these experiments is shown in Fig. 3. Typical dimensions are given. The thermostat tank had a capacity of twenty litres and the temperature was

Fig. 2.- The Osmometer.

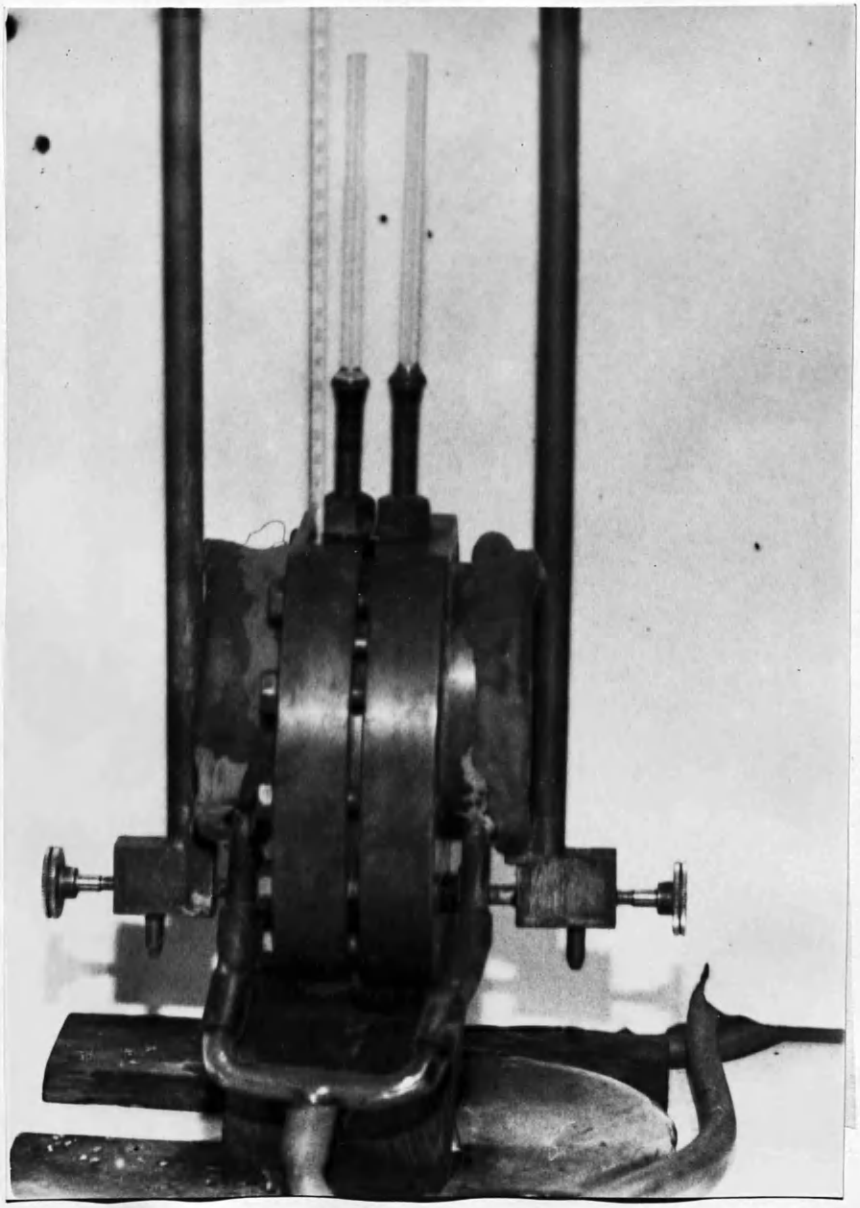


FIG. 3.

4 cms
CONTRACTION

= 10 %

POLYMER-
IZATION.

$r^2 = 0.02$ cms

V - 6.4 c.c.

controlled to ± 0.1C°.

When bulk polymers were prepared polymerization was carried out to 15% conversion since at higher conversions cross linking, chain branching and other side effects may become important. In all cases where the polymer was isolated the monomer-polymer mixture was dissolved in acetone and poured into a large excess of methyl alcohol. The polymers were dried in air for twenty four hours and then in an oven at 80°C.

Measurement of Molecular Weights

The molecular weights were measured on the modified Fuoss Mead Osmometer described by Masson and Melville (XIII). A Bacterial Cellulose membrance was used. The solvents were dried using calcium chloride and purified by distillation through a spiral column. The osmometer was fitted with a water jacket through which water from an accurately controlled thermostat was circulated (± .1C°). The temperature was recorded on a thermometer placed in a socket in the body of the osmometer. No temperature drift was observed. The osmometer and the thermostat were housed in a thermostatically controlled room set a few degrees below the normal working

temperature of the osmometer (Room temperature = 19°C. Osmometer temperatures 20°C - 30°C).

The concentrations were found for the volatile solvents by evaporation of a weighed quantity of solution, from the cell face of the osmometer, to dryness and weighing the resulting polymer. When less volatile solvents were used, solutions were prepared directly by weight.

In the operation of the osmometer the general techniques of Masson and Melville were found to be satisfactory. The two sides of the osmometer were washed six times with solvent and solution respectively. The osmometer was then filled with the sample of solution and fresh solvent. The valve on the solvent side was then closed and the equilibrium pressure allowed to develop. When the final reading had been taken the osmometer was again washed on either side six times with fresh solvent, filled with solvent, and allowed to settle over-night. Constant check was kept on the value of the cell constant which was usually in the region of 0.01 cms solvent. A photograph of the instrument is shown in Fig. 3.

Photochemical Techniques.

For photochemical experiments the source of light was an Osram Mercury Vapour lamp (125W), from which the jacket had been removed. The thermostat in these instances was fitted with a silica window. Since it was desirable in many cases to investigate the effect of light intensity on various reactions, several standard screens were used, which were calibrated on a uranyl oxalate actinometer (XIV, XV, XVI). This procedure can be used reproducibly when the wave length of light used is not less than 2,500A. The transmission of the Osram Lamp is given below in Table I.

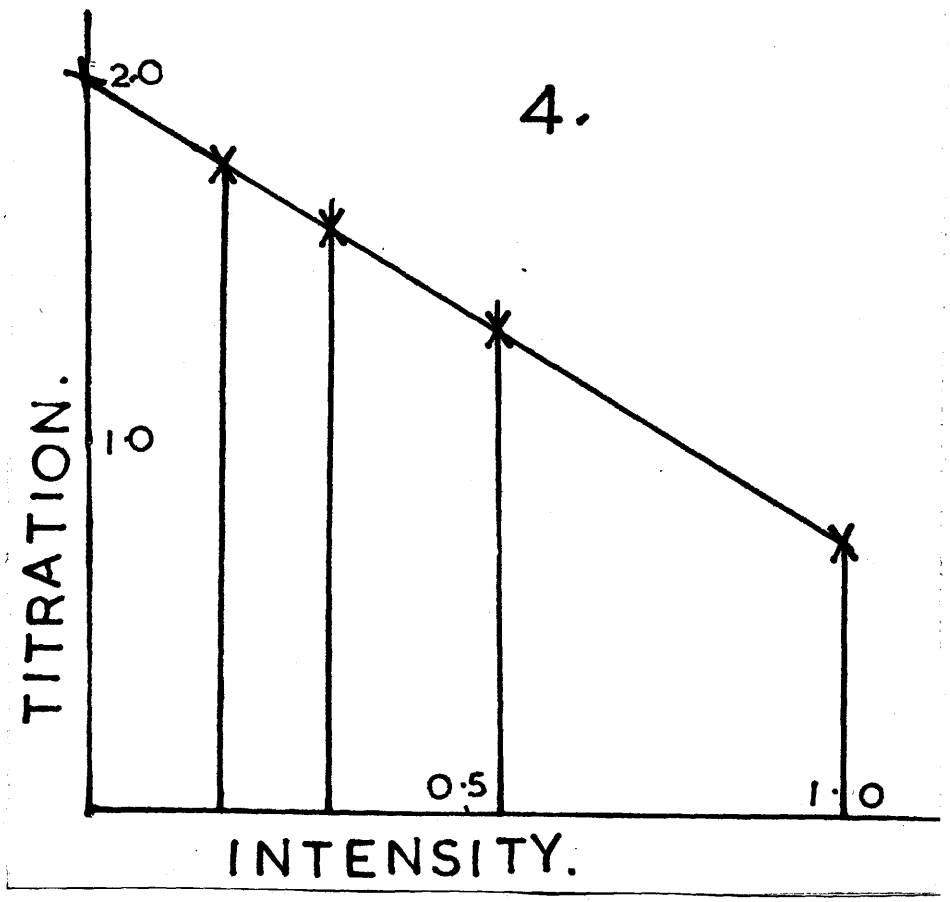
Table I.

Transmission of Osram Lamp (125W.).

Hg line. A°	Approximate Relative energy.	% Transmission of Glass jacket.
5790/5770	75	greater than 95
5461	65	" " 95
4358	50	" " 95
4078/47	30	" " 95
3663/50	100	" " 90
3342	8	60
3132/26	70	5
3022	30	1
2967	20	0.2
2897	8	-
2804	13	-
2760	4	-
2699	5	-
2652	20	-
2650	50	-

The principle of the Uranyl oxalate actinometer depends upon the fact that the UO_2^{++} ion photosensitizes

Fig. 4. - Calibration Curve for Screens.



the decomposition of oxalate ion into CO, CO_2 and HCOOH. The change in oxalate concentration can be conveniently and accurately determined by titration against potassium permanganate, and this type of actinometer is especially useful as the quantum yield does not vary much with changing wave length.

Uranyl oxalate was prepared by mixing hot solutions of oxalic acid (recrystallized) and uranyl nitrate. The uranyl nitrate was purified by igniting on a platinum crucible, 30% sulphuric acid was then added and the whole evaporated until fumes of SO_3 appear. This was repeated three times and then an aqueous extraction performed. This extract was evaporated and the crystals washed. These were again recrystallized.

The oxalate was filtered off, washed, and dried in a vacuum dessiccator.

9.84c.c. of 0.01136 N. Uranyl oxalate were exposed for 1 hour in a glass cell to light from the Hg lamp. The experiment was repeated with various screens interposed between the light and the cell. After exposure the oxalate was titrated against standard potassium permanganate at 80°C. from a micro burette. These results are summarized in table 2. By taking the

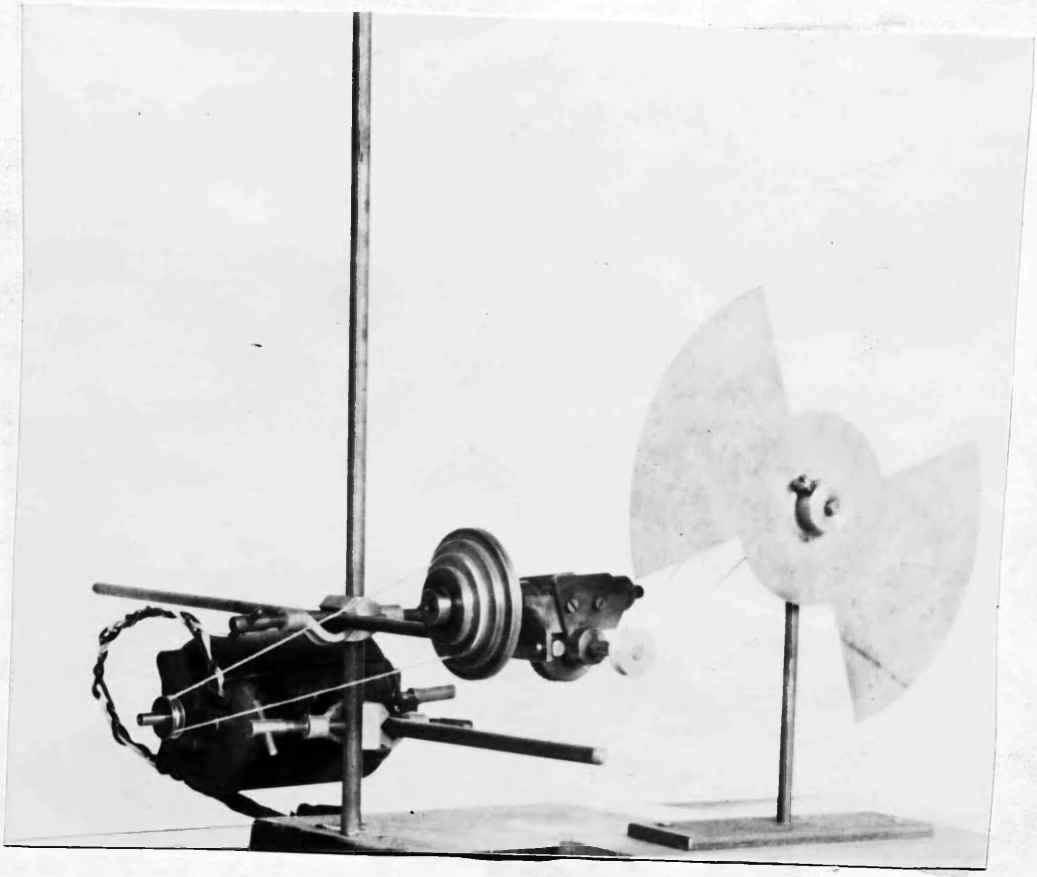
intensity when no screen was used to represent an arbritary value of unity, and the blank to represent a value of zero intensity, and constructing a graph ; (Fig. 4) the intensities produced when various screens were used could be interpolated from the appropriate titration.

Table 2.

Calibration of Screens.

Condition.		Titration.	Intensity.
No Screen	-	0.735	1
		0.740	
Screen No. 1	-	1.305	0.541
		1.290	
Screen No. 2	-	1.560	0.320
		1.580	
Screen No. 3	-	1.745	0.180
		1.750	
No light, Blank		1.965	0
		1.965	-

Fig. 5. - The Rotating Sector.



Rotating Sector.

Life times of the growing polymer radicals were measured by means of the rotating sector, the theory of which is described by Burnett and Melville (XVII). This consisted of a 'Fracmo' motor which was used to drive a 30:1 reduction gearing through a pulley system. The sector was driven from this gearing system directly by another pulley. A photograph of the apparatus is shown in Fig. 5. The speed of the motor was controlled by a variable resistance and it was found that constant slow speeds could be obtained over long periods by allowing the motor to run fast and using it to drive the gearing arrangement. Rates of polymerization could be quite conveniently chosen where the life time of the radical was in a region suitable to the speeds of rotation.

Absorption Spectra.

Absorption spectra where required were measured on a 'Unicam' spectrophotometer. When the colour reaction which takes place when polymethacrylo-nitrile is heated at low temperatures (150-200°C) the depth of colour and the corresponding extinction coefficient were determined using the 'Spekker' absorptiometer.

The blue green filters No. 603 were used to isolate the required wave length range.

Ammonia estimations.

Ammonia estimations were carried out by collecting the degradation product in a standard amount of water contained in a liquid air trap attached to the vacuum system. 0.3 c.c. Nesslers solution prepared in the manner described below were added to 7 c.c. of this solution and the colour produced compared visually, or using the 'Spekker', with the colour produced in a standard solution of ammonium chloride.

Preparation of Nessler's Solution.

50 gms. of potassium iodide were dissolved in the smallest possible amount of cold water. To this a saturated solution of mercuric chloride was added until a faint excess was indicated, 400 c.c. of a 50% solution of potassium hydroxide were then added and after this solution had clarified by sedimentation it was made up to 1 litre and decanted.

The methods mentioned above are the types of experimental technique employed and particular reference will be made individually to each operation as required in the succeeding chapters.

Chapter III.

Degradation of transferred polymethyl-methacrylates.

This work on the degradation of transferred polymethyl-methacrylates was undertaken primarily as an attempt at the elucidation of the termination and transfer processes which occur in the polymerization of methyl methacrylate, and as a further investigation of the depolymerization reaction.

Although there has been agreement in recent years about the general mechanism of the polymerization reaction and the published values of the kinetic coefficients are fairly consistent, there exist differences of opinion on the exact nature of the chain termination reaction. It is widely accepted that combination or disproportionation of pairs of growing radicals occurs although these possibilities cannot be distinguished kinetically. It has also been suggested by Haward (XVIII) that, at least in the diradical polymerization of styrene, self termination by interaction of two ends of the same chain can be a highly probable process.

Baxendale, Bywater and Evans present strong evidence for combination in their work on methyl

methacrylate polymerization by hydroxyl ions (XIX, XX) and Matheson, Auer, Bevilaqua and Hart (XXXII) support this contention by comparison with radicals like $CH_3 - C - C_6H_4 - \underset{\bullet}{CH} - CH_2 - CH_3$ which exclusively combine. Comparable amounts of both types of termination reaction is suggested by Bickel and Waters (XXI) from studies on methyl isobutyl and benzyl radicals which resemble the active ends of the methacrylate radicals.

It has been shown by Marvel (XXII, XXIII) that polyvinyl-acetate is predominantly composed of head to tail linkages. This might be expected from steric considerations but mainly from the fact that the radical $CH_2 - \underset{X}{\underset{|}{CH}}.$ will be resonance stabilized to a greater extent by the substituent X than the radical $\underset{X}{\underset{|}{CH}} - CH_2.$ so that in the termination process, the configuration of two radicals coming together in an act of termination would nearly always be -

$$- CH_2 - \overset{X}{\overset{|}{\underset{Y}{\underset{|}{C}}}}. \quad + \quad .\overset{X}{\overset{|}{\underset{Y}{\underset{|}{C}}}} - CH_2 -$$

and it might be expected that such a linkage might not be very stable and termination by combination therefore an unlikely process.

Termination by disproportionation is also strongly supported by many workers in this field. Bamford and Dewar (XXIV, XXV) and Valentine and Melville, in reviewing the evidence (XXVI), have decided that the balance lies in favour of disproportionation. In a recent paper further evidence is provided by Valentine Bonsall & Melville (XXVII) for disproportionation in the case of the polymerization of methyl-methacrylate at 30°C, and Bonsall, Valentine and Melville (XXIX) support this contention for styrene at 60°C. However in a very recent paper by Bradbury and Melville (XXVIII) it is quoted that combination occurs as the termination reaction in the polymerization of styrene at 60°C.

In a series of degradation papers by Grassie and Melville (VI) evidence is presented which strongly supports disproportionation although the implications of this aspect of their work was not fully discussed and it is this preliminary evidence which forms the basis for the present investigation. Grassie and Melville have shown that in a benzoyl peroxide catalyzed polymer two

distinct species of molecule exists. If such a polymer is degraded in vacuo at 220°C and the rate of degradation plotted against the % degradation to monomer, a curve of the type shown in Fig. 9 is obtained, showing that the rate decreases to zero at 50% degradation. If the temperature is now increased to 280°C, 100% degradation can be achieved. These two phases of the reaction have energies of activation of 32 & 42 k.cals. respectively.

If the structure of a benzoyl peroxide catalyzed polymer is considered it is clear that the chains are started by either phenyl or benzoyl groups from the catalyst:

$$PhCOO\ OOCPh \longrightarrow 2Ph. + 2CO_2 \text{ or } 2\ PhCOO.$$

This reaction, according to Barnett and Vaughan (XXX), gives predominantly phenyl radicals at higher temperatures. MacKay and Melville (XXXI) have shown that no transfer to monomer occurs in the polymerization reaction so that the structure of a benzoyl peroxide catalyzed polymer will be -

Ph - - - - - - - - Ph by combination,

or

Ph - - - - - - - - -

and by disproportionation.

Ph - - - - - - - - =

In the first instance the polymer sample would be homogeneous being composed of molecules having phenyl group at both ends while in the second case the polymer would be composed of two types of molecule present in equal amounts, one species having a single bond and the other a double bond end structure.

Grassie and Melville (VI) have shown that depolymerization is initiated exclusively at the chain ends, followed by depropogation, so that any difference in degradation characteristics must be due either to differences in the chain ends or depropogation. There is very little likelihood that a structure would exist in the body of the molecule which would allow exactly and only half of the monomer to be evolved and it has been suggested that this behaviour is due to the presence of the equal proportions of saturated and unsaturated ends due to disproportionation.

If the termination reaction had been combination then stable molecules having phenyl groups at both ends would have been produced. All the molecules would have this structure and no degradation should occur at 220°C. If, as has been suggested, the combination link is weak degradation might occur but would proceed to 100% possibly at a lower temperature.

In degradation experiments where photo polymers were used these assumptions have also been supported. It is found in this case that 75% of the polymer is degradable at 220°C and the initial rate is high.

Now if photo-polymerization is a di-radical process half the ends will be saturated by disproporation and if it is a monoradical process half the molecules will possess double bond ends from the initiation step and the same from the disproportionation termination reaction. In each of the above cases 75% of the molecules, on the average, will contain at least one type of each end structure so that the above results can readily be deduced.

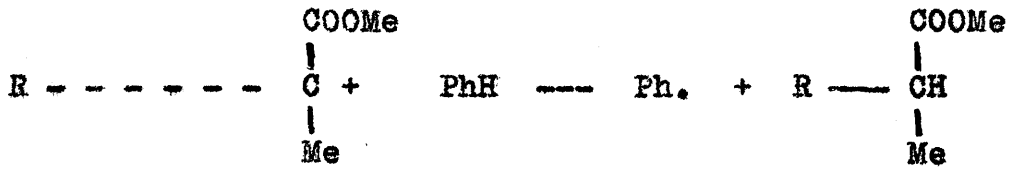
If self termination, as suggested by Haward (XVIII), had occurred there would certainly be no possibility of the existence of two types of molecule and the above results would not fit.

It is also worthy of note in this connection that the existence of two and only two types of molecule present in equal amounts is a good check on the contention of MacKay and Melville (XXXI) that no transfer to monomer is occurring. In this case there would be additional single and double bond ends which would alter the original 50-50 proportion.

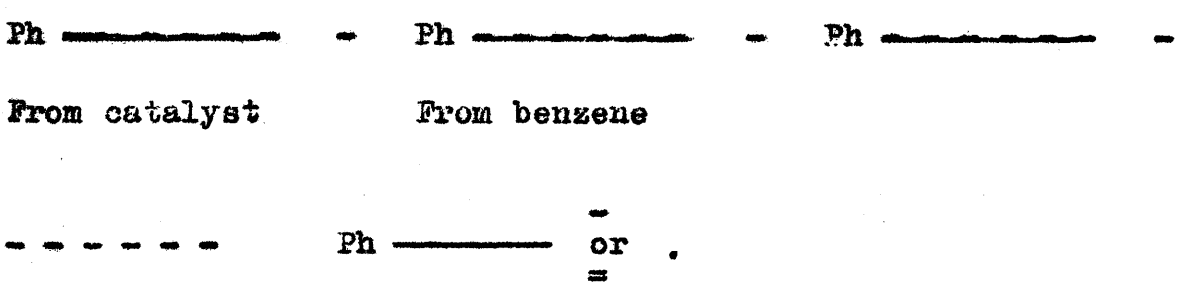
From the above therefore it would appear that termination, in the case of methyl-methacrylate, occurs exclusively by disproportionation producing equal amounts of molecules of the type described above. If the proportions of single and double end structures could be altered and the internal structure of the polymer molecules kept exactly the same it would then be possible, by measuring the initial rates of degradation and the amount of degradable material at 220°C, to decide which type of end group is least stable, (i.e. degradable at 220°C with an energy of activation of 32 k.cals/mol.) and also to provide a final check on the postulated termination reaction.

This is theoretically possible using benzene as a transfer agent. When transfer occurs the growing polymer radical, instead of interacting with another

similar radical, attains stability by the abstraction of a hydrogen atom from a molecule of the transfer agent. Thus if benzene could be used as a transfer agent for methyl methacrylate the reaction would be represented as follows.



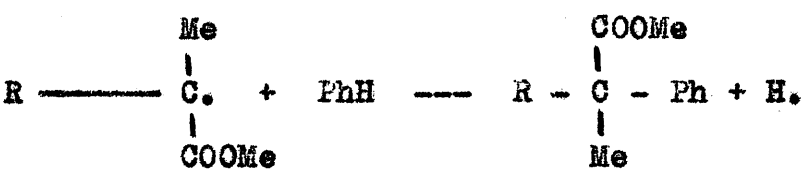
In this case a stable molecule with a saturated end group is produced leaving a phenyl radical which will initiate a new chain. The kinetic chain is shown below-



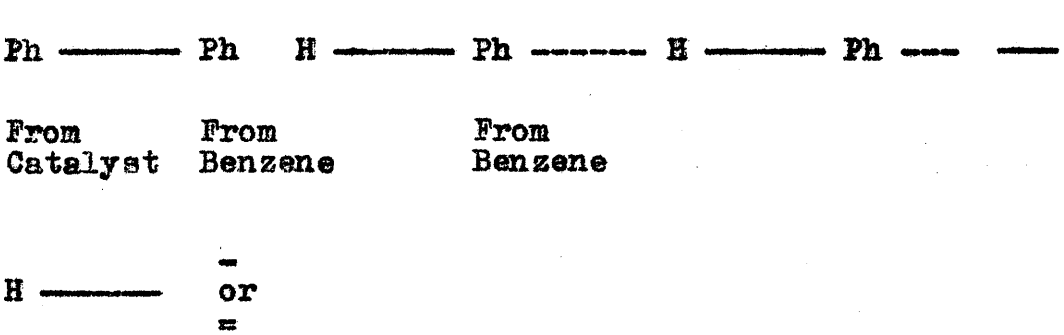
Thus if benzene could be used as a transfer agent for methyl-methacrylate in a benzoyl peroxide catalyzed polymerization, a polymer would be produced which would have the same structure as a normal benzoyl peroxide

catalyzed polymer except that the number of single bond ends would be increased.

It has however been suggested that the mechanism of transfer to benzene, instead of being as described above, is by the abstraction of a phenyl group leaving a hydrogen atom to initiate a new chain.



The kinetic chain would be represented -



This would produce a high proportion of stable molecules terminated by phenyl groups. The implications of this suggestion will be discussed later.

The Problem.

Since the above gives a theoretical method of varying the proportion of single and double bond ends the problem reduces to:-

(1) Showing that benzene acts as a transfer agent in the polymerization of methyl methacrylate.

(2) Using polymers prepared in benzene to investigate the initial rates of degradation and deciding which type of end is unstable at 220°C.

(3) Calculating the relative proportions of the unstable type of end group from measurements on the initial rates of degradation and from kinetic measurements and comparing the results obtained.

(4) Repeating the type of experiment performed by Grassie and Melville, as summarized in figure 9, using a transferred polymer and finding out if the proportion of degradable material at 220°C corresponds to the proportion of the unstable ends.

Kinetics.

If the general scheme of free radical polymerization is considered the polymerization reaction may be represented as follows-

(1) $M + C \longrightarrow P_1$ Initiation, $Vi = Ki\ (C)(M)$.

Where M represents a monomer unit

C " catalyst

P_1 " radical containing one monomer unit

Vi = Velocity of initiation = Ki (C)(M) if catalyst concentration is constant.

(2) $P_1 + M \longrightarrow P_2$

$P_2 + M \longrightarrow P_3$ --- Propogation, $Vp = Kp(P)(M)$.

" " "

$Pn + M \longrightarrow Pn+1$

Where Vp = Rate of Propogation

(x) = Concentration of X.

(3) $Pn + S \longrightarrow Mn + S.$ Transfer to solvent $Vz = Kz\ (P)(S)$

Where S represents a solvent molecule

Mn " dead polymer molecule

S. " solvent radical

Vz = Rate of transfer to ~~monomer~~ SOLVENT

(4) $Pr + Ps \longrightarrow Mr + s$ Termination, $Vt = Kt\ [P]^2$.

or Mr + Ms

Vt = Rate of termination either by disproportionation (Mr + Ms)

or combination (Mr + s.).

Transfer to Monomer is omitted as MacKay and Melville (XXXI) have shown that it does not occur.

If there is no transfer to solvent -

$$\text{chain length}, \overline{P_o} = \frac{\text{Rate of disappearance of monomer}}{\text{Rate of termination of chains}}$$

$$= \frac{K_p(P_o)(M_o)}{Ki(P_o)^2} = \frac{K_p(M_o)}{Kt(P_o)}.$$

Assuming the stationary state -

$$Vi = Vt$$

$$Ki(M) = Kt(P)^2$$

$$\therefore \quad (P)^2 = \frac{Ki(M)}{Kt}.$$

$$\therefore \quad (P) = \left[\frac{Ki(M)}{Kt}\right]^{\frac{1}{2}}.$$

$$\therefore \quad \overline{P_o} = \frac{Kp(M_o)}{Kt} \times \left[\frac{Ki(M_o)}{Kt}\right]^{-\frac{1}{2}}.$$

$$= \text{Constant} \times (M_o)^{\frac{1}{2}}.$$

Hence the molecular weight is proportional to the square root of the monomer concentration. The effect on the molecular weight of the change in concentration due to carrying out the polymerization in solution is therefore given by:

$$\overline{P} = \overline{P_o} \left[{}^{(M)}/_{(M_o)} \right]^{\frac{1}{2}}.$$

so that in A grams of polymer prepared in solution there will be -

$$A/_{\overline{P_o}} \left[{}^{(M)}/_{(M_o)} \right]^{\frac{1}{2}} \quad \text{ends.}$$

Of these there will be -

$$A/_{2\overline{P}_o} \left[{}^{(M)}/_{(M_o)} \right]^{\frac{1}{2}} \quad \text{ends each of single}$$

and double bond ends due to disproportionation.

When transfer to solvent occurs -

$$\text{chain length} = \frac{\text{Rate of disappearance of monomer}}{\text{Rate of termination of chains}}$$

$$\text{chain length} = \frac{Kp(P)(M)}{Kt(P)^2 + K_2(P)(S)} .$$

If the molecular weight is represented by $\overline{P}$, the total number of ends in A gms. of polymer is $A/_{\overline{P}}$ and the proportion of double bond ends in a transferred polymer is -

$$A/_{2\bar{P}_o}\left[(M_o)/_{(M)}\right]^{\frac{1}{2}} \times \bar{P}/_{A}\,.$$

$$= \bar{P}/_{2P_o}\left[(M_o)/_{(M)}\right]^{\frac{1}{2}},$$

(where (M) = concentration of Monomer in Solution,

(M_o) = concentration of monomer in pure monomer,

$\bar{P}_o$ = molecular weight in pure monomer),

and the proportion of single bond ends is -

$$1 - \bar{P}/_{2P_o}\left[(M_o)/_{(M)}\right]^{\frac{1}{2}}$$

From this it is evident that, if monomer concentrations are known, the relative proportions of single and double bond ends can be calculated from molecular weight data in any transferred polymer.

Experimental.

The polymers were prepared and isolated by the general method described in chapter 2. The monomer used in this case was provided by I.C.I. Ltd. The quinone inhibitor was removed by four washings with N. caustic

soda. The monomer was then washed four times with water, dried with calcium chloride, and finally degassed and distilled as described in chapter 2.

The catalyst used was benzoyl peroxide which was purified by the method described above. 'Analar' benzene was purified by distillation through a column and finally degassed and distilled in vacuo.

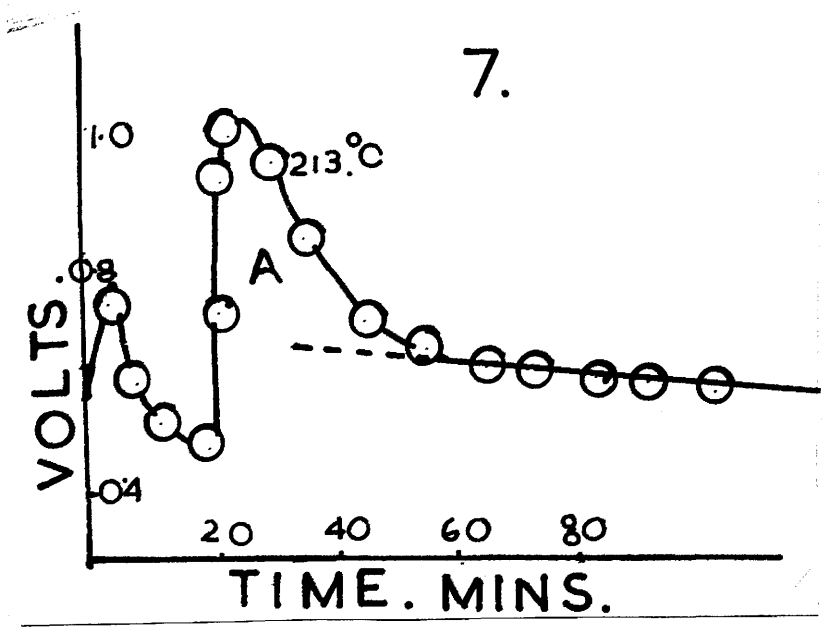
50 c.c. monomer, 50 c.c. monomer + 50 c.c. benzene, 40 c.c. monomer + 360 c.c. benzene were distilled into three reaction tubes, into which the required amount of benzoyl peroxide had previously been introduced so that the overall concentration in each case was 0.025%. These tubes were sealed off under vacuum in the usual manner and the polymerization carried out in a thermostat at 60°C., the polymerization being carried out to 10% conversion.

The polymers were isolated and treated as described in chapter 2 and are denoted I, II and III respectively.

Molecular Weight Measurements.

The molecular weights were measured as described in chapter 2 using benzene as solvent. The values of Π were obtained by measuring several values of osmotic pressure at various concentrations and extrapolating to zero concentration.

Fig. 7. - Degradation Curve for Polymethyl-methacrylate.



Degradation experiments.

The degradation experiments were carried out on the the dynamic molecular still (VI) described in the second chapter. Initial rates of degradation were measured at 213°C.

When polymethyl methacrylate is heated in vacuo and the pressure measured on the pirani gauge plotted against time, a curve of the type shown in Fig. 7 is obtained. The initial peak denoted 'A' is due to the production of volatile material which is absorbed on the polymer. When this volatile material is removed a straight line is obtained which represents degradation to monomer. The initial rate is obtained by producing this line backwards into peak A to the time at which the temperature of degradation (in this case 213°C) was reached. 0.3 gm. of polymer was used in each experiment.

RESULTS.

(a) Molecular Weights.

The molecular weights of polymers I, II and III are shown in Table 3.

Table 3.

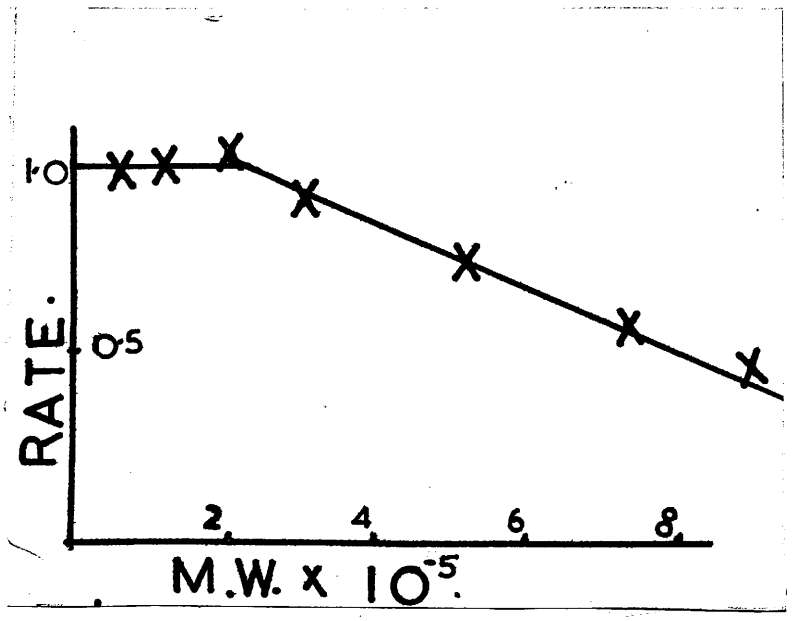
Polymer.	Mol Wt Measured.	Mol Wt calculated from change in conc.
I.	2,000,000 ± 300,000.	-
II.	720,000 ± 50,000.	1,420,000 ± 100,000.
III.	231,000 ± 10,000.	635,000 ± 30,000.

By comparison of the values contained in columns 2 and 3 of the above table, it is clear that the fall in molecular weight is greater than would be expected from the change in monomer concentration, and hence benzene is acting as a transfer agent for methyl methacrylate.

(b) Degradation Results.

Grassie and Melville have shown that the rate of degradation is constant in molecular weights up to 25,000. Above this value the rate falls. This decrease in rate is explained on the grounds of premature termination of the depolymerizing chain. The fall in rate with increasing molecular weight is summarized in figure 8. This shows that only polymer III has a molecular weight which lies in the region where the rate is constant so that direct comparison of the initial rates of degradation

Fig. 8. - Variation of Rate with Molecular Weight.



of the above polymers would be of little value. The appropriate correction could be made using the data shown in Figure 8 but it is more convenient and satisfactory to use a polymer whose molecular weight lies in the region where the rate is constant for comparison with polymer III, and to choose a polymer of similar molecular weight to polymer II for comparison with it. In fact non transferred polymers of molecular weights 94,000 and 725,000 were used in the respective cases.

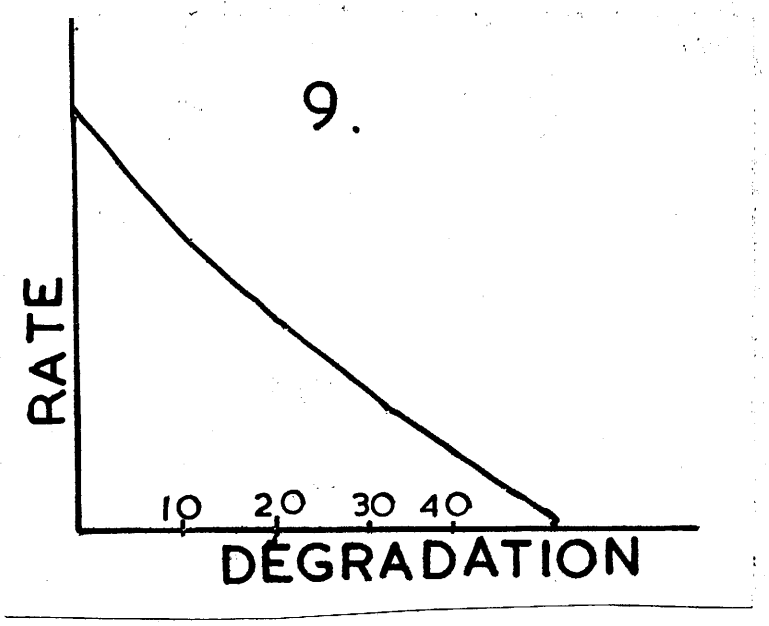
The results obtained in the measurement of initial rates of degradation are shown in table 4.

Table 4.

Polymer.	Initial Rate of Degradation.		Rate Ratio, 'R'. Rtf/Rntf.
	Transferred	Nontransferred	
II.	0.234.	0.404.	0.58.
III.	0.347.	0.608.	0.43.

The first thing which should be noted from the above table is that the initial rate of degradation has fallen in the case of the transferred polymer. This shows

Fig. 9. - Rate: % Degradation for Normal Polymer.



that the species of molecule having the double bond end structure, of which there are fewer in a transferred polymer, is least stable and that it is this type of molecule which degrades at 213°C with an Energy of Activation of 32 k.cals./Mol.

It has been shown above that the relative amounts of single and double bond ends can be calculated from molecular weight data by the formula

$$Ndb. = {}^{P}/_{2\overline{P}_o} \left[{}^{(M)}/_{(M_o)} \right]^{\frac{1}{2}} .$$

This proportion can also be calculated from the values of the rate ratio given in table 4, since the rate ratio is given by:

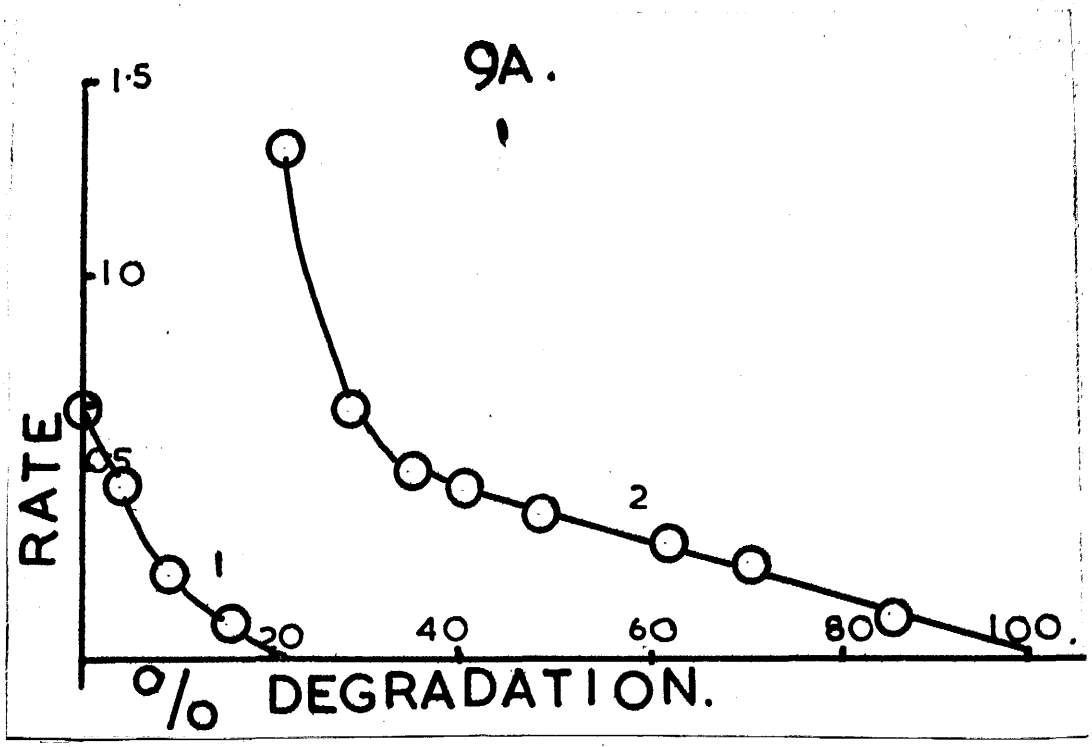
$$\frac{\text{No of double bond ends, transfer occurring}}{\text{No of double bond ends without transfer}} = R.$$

Now $R = \frac{Ndb}{\frac{1}{2}} = 2\ Ndb$.

$\therefore\ Ndb = \frac{R}{2}$.

A further method of determining the proportion of double bond ends is to repeat the type of experiment of

Fig. 9A.- Rate: % Degradation for Transferred Polymer.



Grassie and Melville which is summarized in Figure 9 using a transferred polymer and find the % degradation material at 220°C. Energies of activation could be measured and compared with values obtained in non transferred polymers.

An experiment, where the rate of degradation was plotted against the % degradation to monomer, was carried out using polymer III. The temperature used was 213°C. The results are shown in figure 9A which shows that the rate of degradation decreases to zero at just over 20% degradation. (Curve 1).

The various values of the proportion of double bond ends in the transferred polymer (Ndb) are summarized in Table 5.

Table 5.

Polymer.	Ndb from Mol. Wt. data.	Ndb. from rate Ratio.	Ndb from Fig. 9A.
II	0.26	0.29	-
III	0.18	0.215	0.20+

The values shown in the second third and fourth columns are in good agreement the differences probably

being due to the wide margin of error which must invariably be encountered in measuring a molecular weight of the order of that of polymer I (2,000,000, ± 300,000).

Figure 9A also shows the effect of raising the temperature to 260°C after the 20% double bond end portion has degraded. At this temperature the degradation proceeds, without any marked discontinuity, to 100%, showing that the remaining polymer is homogeneous. (Curve 2 Fig. 9A). The initial steep slope of curve 2 is due to the small amounts of double bond end still remaining, and also, to a much greater extent, to the marked degassing effect which a rise of 50C° will have on the inside of the still.

Approximate measurements of energies of activation give values of 35 k.cal./mol. at 20% degradation increasing to 42 k.cal./mol. from 20% onwards. The consistency of this energy of activation shows that there can be no doubt that the material remaining after 20% degradation is completely homogeneous.

As mentioned it has been suggested that the mechanism of transfer to benzene is by abstraction of a phenyl group leaving a hydrogen atom to initiate a new chain. The kinetic chain is represented as follows

Ph ——— Ph ---- H ——— Ph --- H ——— Ph ——— H ——— or

From peroxide. From benzene.

If this were the case there would be a large proportion of stable molecules terminated at both ends by phenyl groups. The presence of such molecules would be clearly shown as a discontinuity of curve 2 (Figure 9A). The fact that curve 2 proceeds linearly to 100% shows that the above suggested mechanism cannot apply and it must therefore be assumed that transfer to benzene occurs by abstraction of a hydrogen atom leaving a phenyl radical to initiate a new chain.

REVIEW.

Work which has been carried out on the problem of the exact nature of the chain termination reaction has produced many different opinions. The present work supports disproportionation in the case of methyl methacrylate at 60°C. This is in agreement with the majority of results already discussed (XXIV, XXVII) and also with some recent results of Bevington, Melville and Taylor (XLII) which support disproportionation in methyl methacrylate at 25°C. The opposite view is

supported by Matheson et al., Baxendale et al and Arnett (XX, XXXII, LXXI) but the work of Matheson et al was carried out on model substances and their results might not apply. In the polymerization of methyl methacrylate by hydroxyl ions discussed by Baxendale, Bywater, and Evans, termination by hydroxyl or by transfer to water which was used as a solvent might have occurred. In each case molecules containing two hydroxyl group would be produced and the original assumption that such molecules were produced by combination of two radicals might not apply. The work of Arnett (LXXI) is also doubtful since the values of catalyst efficiency used is in marked disagreement* with that of Baysal and Tobolsky ( ). Therefore it appears that termination by disproportionation occurs exclusively for methyl methacrylate between the temperatures of 25°C and 60°C.

The differences of opinion are more marked in the case of styrene. Earlier work (XXVI, XXIV, XXVII) quotes disproportionation as the mechanism but more recent work by Bevington, Melville and Taylor (XLII) using radio active tracer methods strongly supports combination at 25°C. Combination at 60°C is also supported by some unpublished data quoted in XXVIII.

* LXXIII

From the variety of results it appears that no unique mechanism for the termination step in polymerization reactions exists but that each system should be considered separately with the temperature and condition of reaction borne in mind.

Chapter IV.

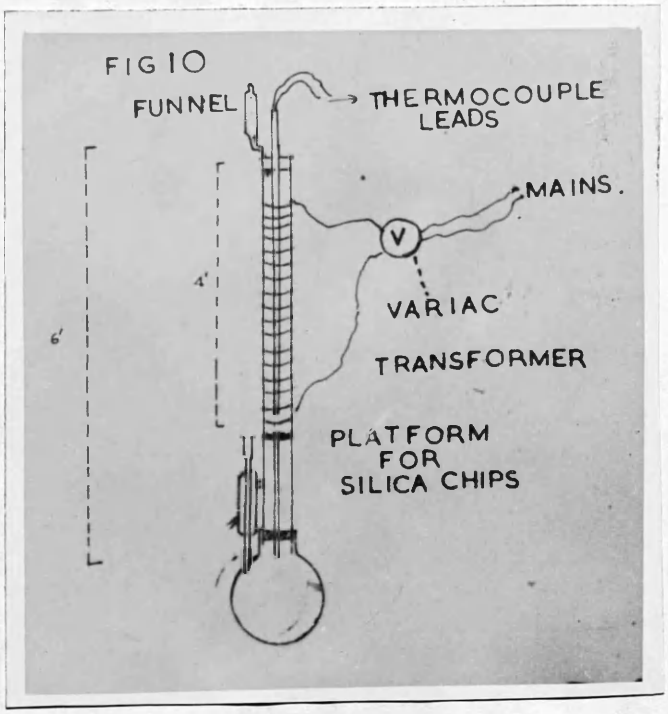
The Preparation and Properties of Methacrylo-nitrile.

Investigation of the polymerization of methacrylo-nitrile and the degradation of its polymer involves the consumption of large quantities of monomer. Commercial monomer is not conveniently obtainable and so it became necessary to investigate the possible methods of kilo-gram. scale preparation.

The methods used required acetone cyanhydrin as starting material.

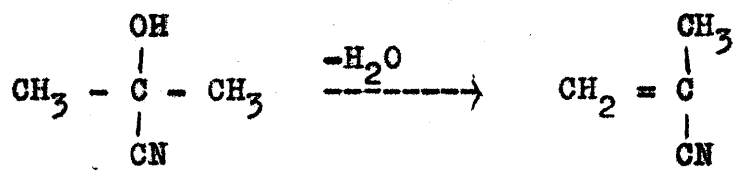
The first supplies of acetone cyanhydrin were prepared by the method of Welsh and Clemo (XXXIII) from acetone and potassium cyanide. In this preparation 290 gms. of acetone were added to a solution of KCN (310 gms. in 1 litre of water); sulphuric acid (1,670 gms., 30% H_2SO_4) was added slowly with constant stirring. The temperature was kept below 0°C by addition of ice. The acetone cyanhydrin formed was extracted from the large bulk of solution by means of a continuous ether extraction apparatus. The ether extract was dried with sodium sulphate, the ether removed on a water bath and the acetone cyanhydrin finally purified by distillation under reduced pressure.

Fig. 10.- Apparatus for Pyrolysis Experiments.



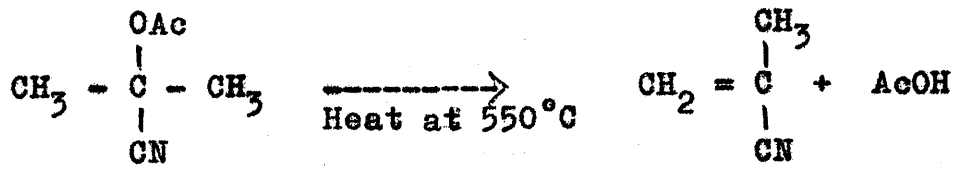
(B.P. 81°C at 15mm. pressure). Later, acetone cyanhydrin became available through I.C.I. Billingham.

In the first method used, (XI) acetone cyanhydrin was converted into meth-acrylo nitrile by dehydration using thionyl chloride-



1 mol of acetone cyanhydrin was placed with 1.1 mols dry thionyl chloride in a flask under reflux with moisture excluded. The flask was heated at 90°C - 100°C until the escape of HCl and SO_2 was complete. The product was removed by distillation (63%) and purified by further distillation through a spiral column. The overall yield was 55% Boiling point of methacrylo-nitrile is 92-93°C.

Although this method yields a satisfactory product it is laborious and time consuming and was replaced by a more convenient method involving the pyralysis of acetone cyanhydrin acetate.



Acetone cyanhydrin acetate was prepared quantitatively by allowing acetone cyanhydrin (1 mol.) and acetic anhydride (1.5 mols.) to stand at room temperature for twenty four hours. The excess acetic anhydride was removed by distillation and the acetate fraction B.P. 180-185°C collected.

The pyrolysis was carried out in an electrically heated silica tube. This was six feet long, set vertically and packed with silica chips. The tube was heated over four feet of its length and an exploring thermocouple fitted so that the temperature in all parts of the interior could be measured. The current supply was controlled by means of a 'Variac' transformer and the required voltage chosen so that a temperature of 550°C could be maintained. The acetone cyanhydrin acetate was run in dropwise at the top from a dropping funnel and the methacrylo-nitrile and acetic acid collected in the three necked flask at the bottom. A diagram of the apparatus is shown in Fig. 10.

The monomer was separated from acetic acid by pouring the mixture into water and extracting with ether, the ether extract being washed with water and subsequently dried with sodium sulphate. The ether was removed on a water bath and the monomer purified by distillation through a spiral column (BP 92-93°C).

The preparation was carried out using 2 kgm. batches of acetone cyanhydrin and the overall yield after extensive purification was 55-60%

Samples of monomer prepared by the above methods were found, on comparison with commercial monomer supplied by Light's Ltd., to have the same rate of polymerization in vacuo.

The bulk of the monomer used in succeeding experiments was prepared by the pyrolysis method.

Preliminary experiments.

Before the main investigation certain preliminary experiments were carried out.

(1) Ultra Violet Absorption Spectrum.

The ultra violet absorption spectrum was measured on the 'Unicam' ultraviolet spectrophotomer as described in chapter 2. This curve is shown in Figure 11. This curve was used as a check on the absorption for the photochemical reaction.

Fig. 11. - Ultra Violet Absorption Spectrum for Meth-acrylo-nitrile.

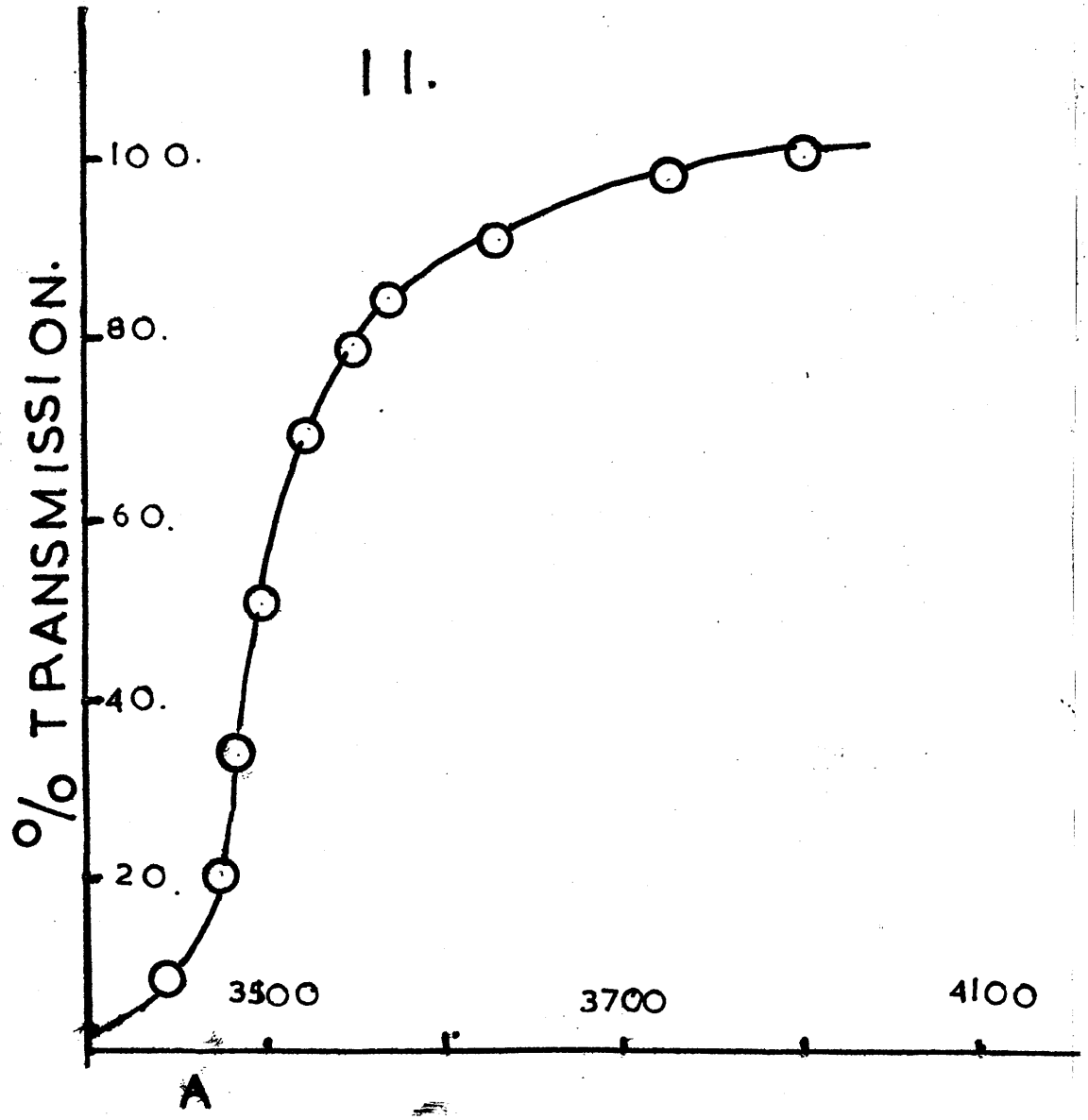
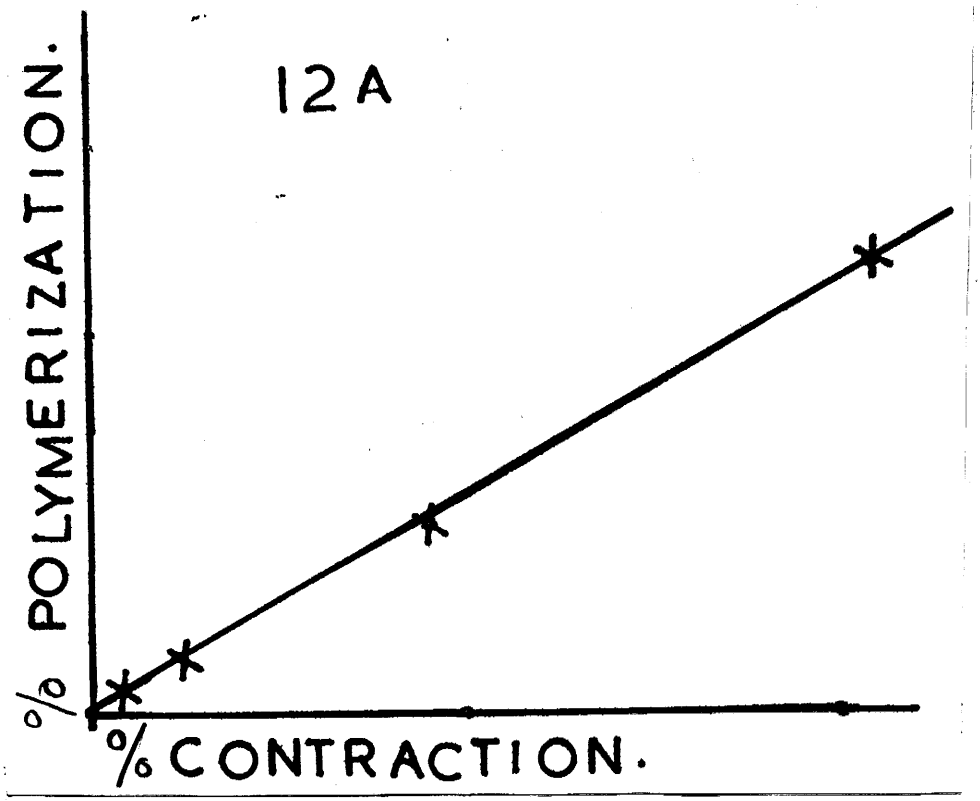


Fig. 12A.- Dilatometric Relationship at 60°C.



(2) Coefficient of Expansion of Monomer.

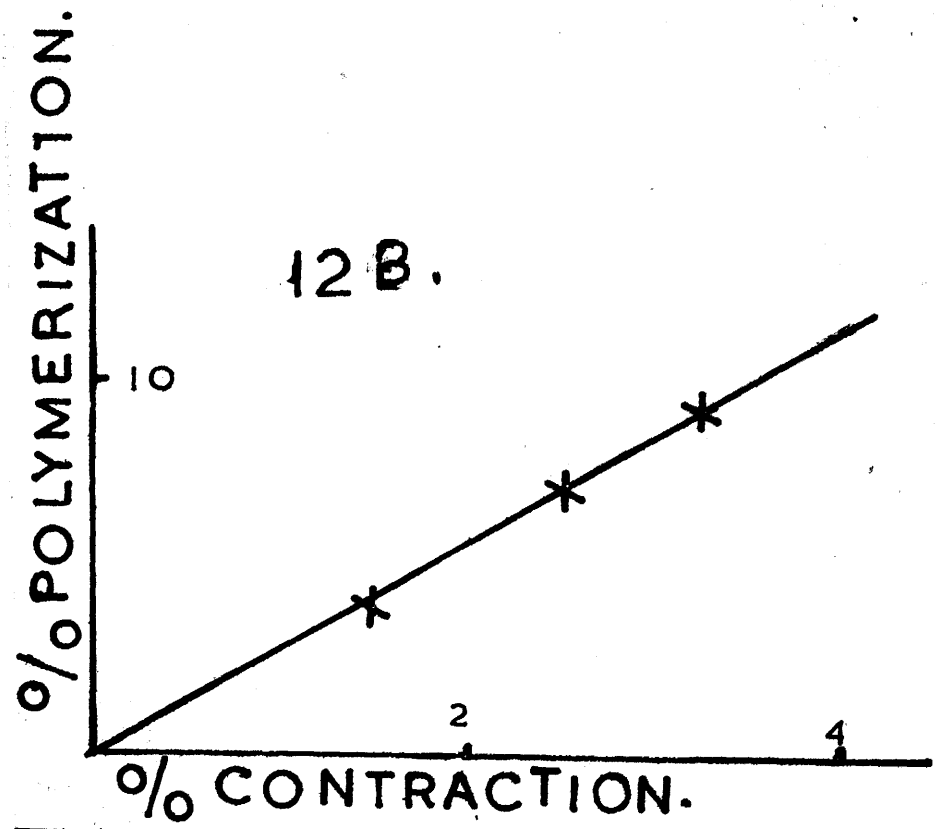
For general use in reactions involving change in volume and in order to calculate changes in density and concentration of pure monomer the coefficient of expansion of monomer was determined. This was done by observing the fall in level of the surface of a known volume (at 23°C) of monomer with change in temperature contained in a calibrated dilatometer tube immersed in a thermostat. The change in level was measured by means of a cathetometer. From these measurements the average coefficient of apparent expansion of methacrylo-nitrile in pyrex was found to be 0.001435 between 90°C and 20°C.

(3) Dilatometric Relationship.

The most convenient way of estimating rates of polymerization is by observing the change in volume which occurs when the monomer is converted to the more dense polymer. An empirical relationship can be drawn up between this contraction and the extent of polymerization and this value can be used in evaluating absolute rates of polymerization.

In this experiment a series of benzoyl peroxide catalyzed polymerizations were carried out in vacuo at 60°C, 70°C, and 80°C. the volume contraction noted

Fig. 12B.- Dilatometric Relationship at 70°C.



and the extent of polymerization determined by precipitating the polymer using methyl alcohol-water (75-25), filtering through a sintered glass crucible and drying to constant weight at 100°C. The % contraction was plotted against the % polymerization at the three temperatures and, by constructing a straight line graph of conversion factor: temperature, the conversion factor at any temperature could be calculated. The curves are shown in Fig. 12 (A-60°C 12 B-70°C 12 C-80°C 12 D - conversion factor temperature).

The conversion factors at different temperatures are shown below and compared with values obtained for methyl methacrylate obtained by MacKay and Melville.

Table 6.

Temp. °C	Conversion Factor M.A.N.	Conversion Factor M.M.
20	3.72	3.6
30	3.12	3.48
40	3.04	3.38
50	2.98	3.25
60	2.88	3.1
70	2.78	2.98
80	2.68	2.8

12C.- Dilatometric Relationship at 80°C.

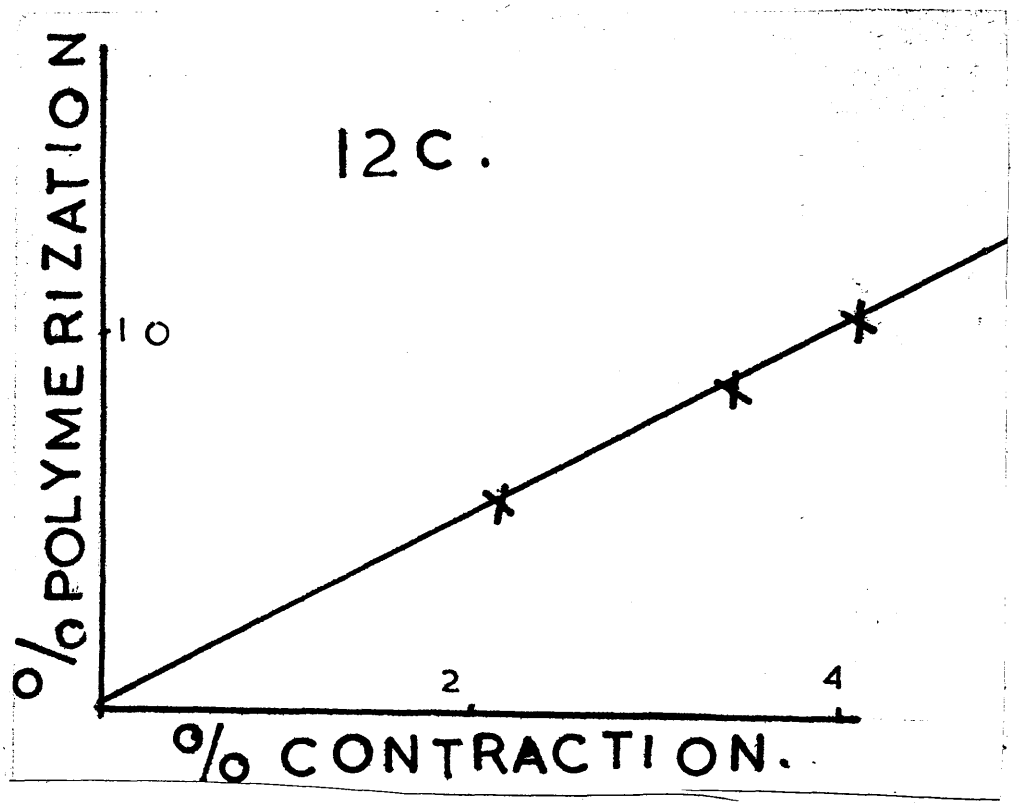


Fig. 12D.- Conversion Factor: Temp. for Methacrylonitrile.

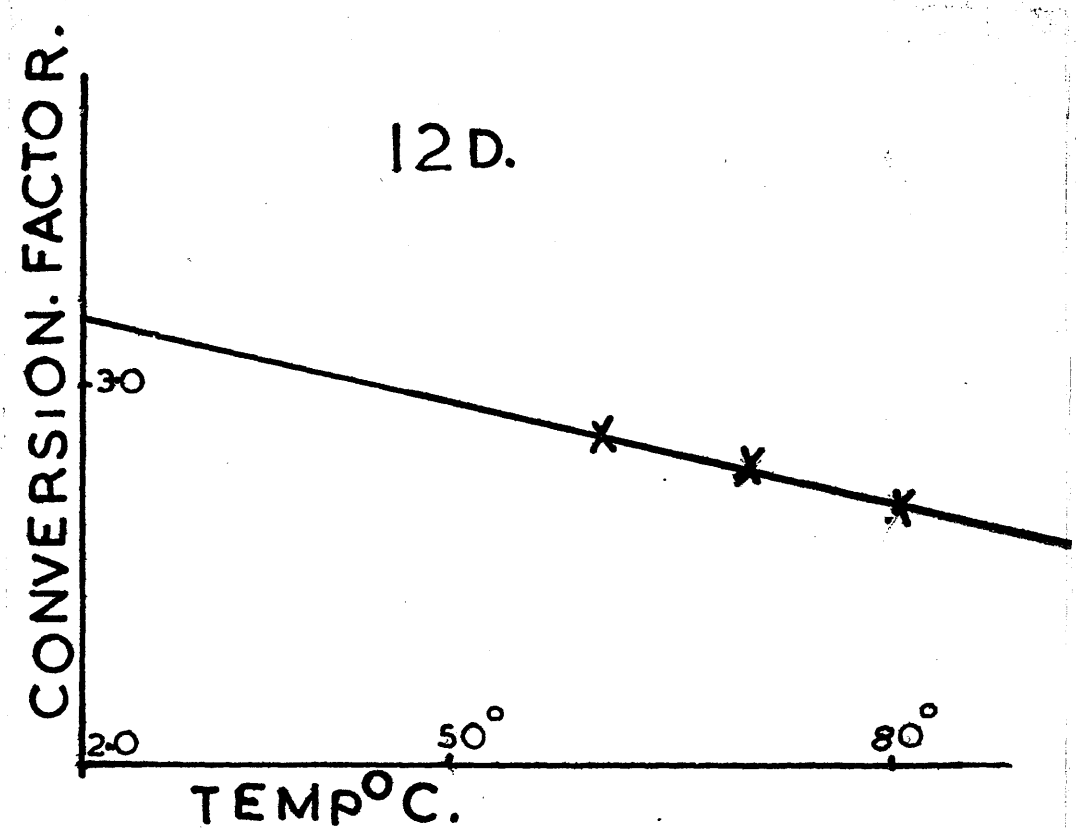
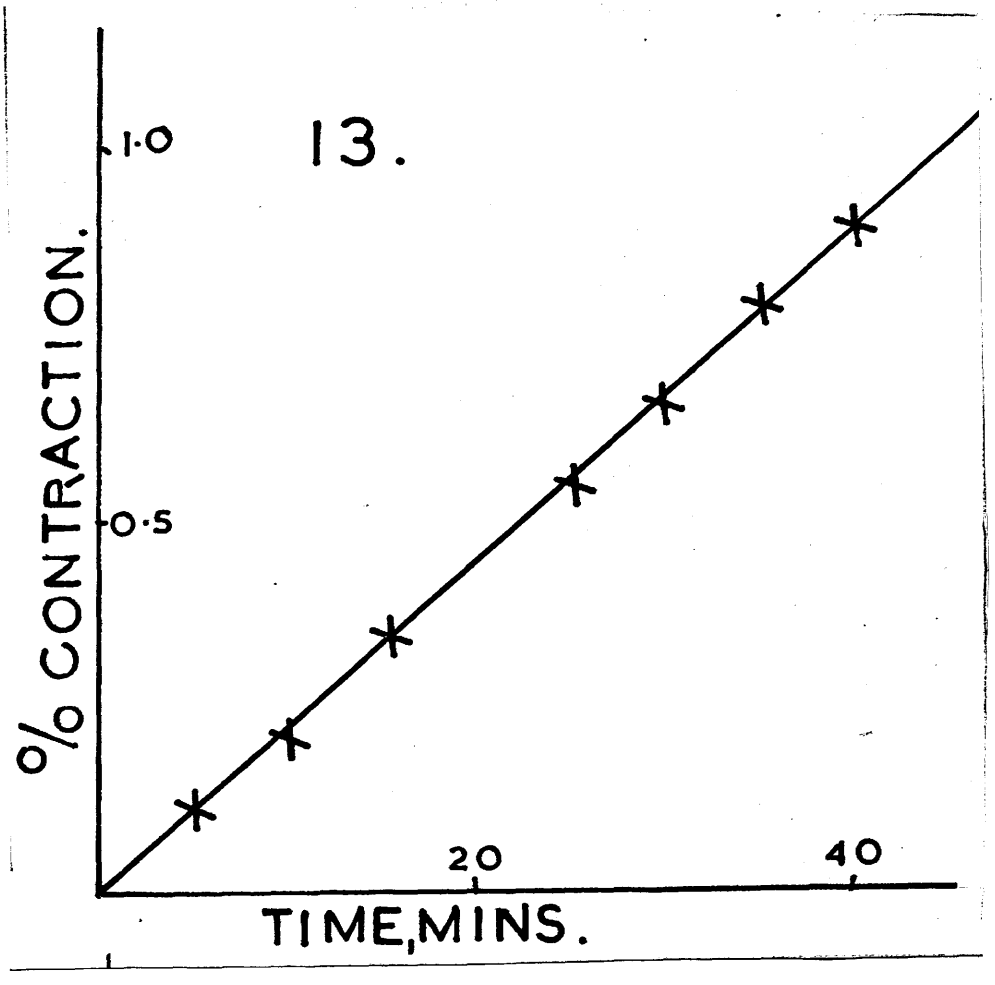


Fig. 13. - Polymerization Curve.



From these results the values of the absolute rates of polymerization can be calculated.

(4) General Polymerization Characteristics.

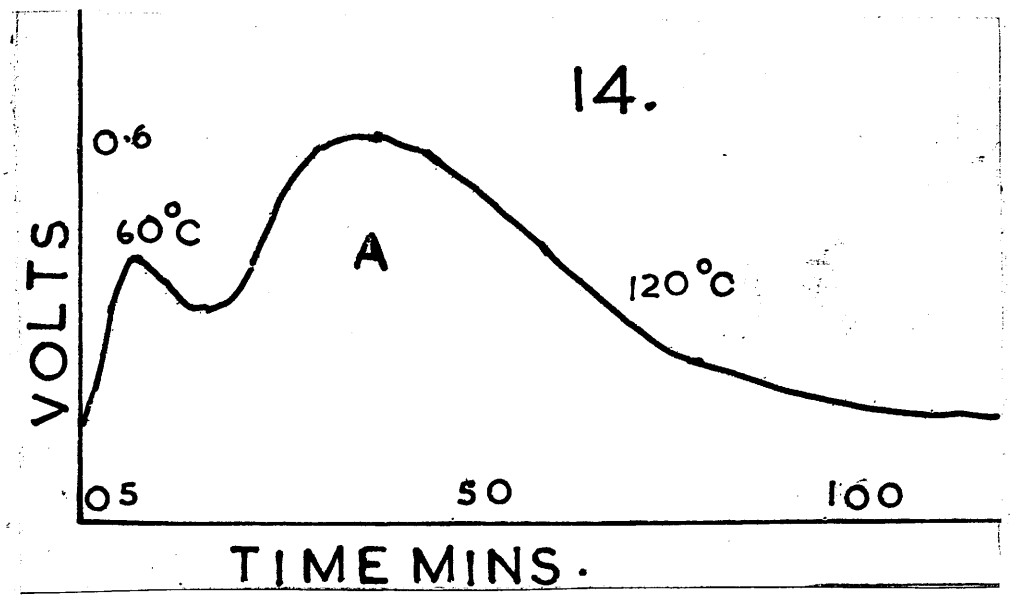
Polymerization occurs where benzoyl peroxide or azo bis-iso-butyro-nitrile is decomposed either thermally or photo chemically. Direct photo-polymerization using the radiation produced by the osram lamp given in table I occurs only very slowly when the monomer is contained in silica tubes. Catalytic polymerization is linear with time in the initial stages and no marked gel effect (XXXIV) is evident. A typical polymerization curve is shown in Fig. 13.

The Polymer.

When polymethacrylo nitrile is precipitated and treated as described in chapter 2, it can be very easily ground into a fine powder. The solvents are limited being acetone, cyclohexanone, methylene chloride, nitrobenzene and methyl ethyl ketone. The polymer swells in chloroform (XXXVI).

When the polymer is heated in vacuo, in the molecular, still a curve of the type shown in Fig. 14 is obtained. The small initial peak produced

Fig. 14.- Volatile Production at Low Temperatures.



when the polymer melts shows that in the finely powdered form, in which this polymer is readily available, there is not much volatile material present.

If Fig. 14 is compared with the similar curve obtained with polymethyl methacrylate shown in Fig. 7 and the relative sizes of the initial peaks obtained this fact can readily be appreciated. This means that in cases where concentrations must be found by direct weighing the error involved due to the presence of these volatile materials will be quite small (XXXV).

The polymer is only moderately soluble in monomer and in some cases precipitation occurs during the polymerization process. This depends on the temperature of the reaction and on the molecular weight produced. For example a polymer prepared at 60°C., 0.025% catalyst concentration, molecular weight 122,000, is insoluble while a polymer prepared at 80°C, 0.8% catalyst concentration, molecular weight 36,500 is completely soluble.

Chapter V.

Osmotic Phenomena and Molecular Weight Measurements in Polymethacrylo-nitrile.

The most reliable methods for the measurement of rate constants in polymerization processes involve, in addition to route measurements, the determination of number average molecular weights. These can be most readily deduced from osmotic pressure data. If ideal osmotic behaviour is encountered π, the osmotic pressure, is proportional to the concentration so that if $\frac{\Pi}{C}$ is plotted against C (the concentration) a straight line, parallel to the concentration axis, would be obtained. With high polymers non ideal behaviour is invariably encountered although in most polymer solvent systems the curve obtained can be described by the expression -

$$\frac{\Pi}{C} = P + Qc. \quad \text{- - - - - - - - - -} \quad (1)$$

or

$$\frac{\Pi}{C} = P + Qc + Rc^2. \quad \text{- - - - - -} \quad (2)$$

For example the equation (1) describes the curve obtained with polystyrene in benzene and (2) holds

for polymethyl-methacrylate in benzene.

These expressions have been given ample theoretical consideration by Huggins (XXXVII) who gives as a value of Q -

$$Q = \frac{RT}{m_c} \frac{d_1}{d_2^2} \left(\tfrac{1}{2} - \mu\right)$$

where m_c = molecular weight of solvent

d_1 = density of solvent

d_2 = density of polymer

u is a constant for the system and in the ideal case when Q = 0 u = 0.5.

If the $\frac{\Pi}{C}$: C curve is represented by either of the above equations it is either linear or gently curved so that extrapolation to zero concentration is easy; whence the molecular weight can be calculated by the classical formula -

$$\frac{RT}{M} = \Pi/_{CO}$$

Where M is the molecular weight of the polymer.

Experimental.

The solvents available for polymethacrylo-nitrile are limited since the interaction between chains, which causes the complete insolubility of polyacrylo-nitrile, is only slightly eased by the introduction of the methyl group; and of those mentioned earlier in chapter 4 the only ones of possible use in osmometry are methyl ethyl ketone, acetone, methylene chloride and cyclo-hexanone. Acetone and methylene chloride are rather too volatile for successful use in osmometry while methylene chloride, in addition to its volatility is a poor solvent. It was evident therefore that the most suitable solvent for routine measurements was methyl ethyl ketone, because of its low boiling point and the convenience of measuring concentrations by evaporation, but some early experiments indicated anomalous behaviour and so an extensive investigation of the osmotic properties of the polymer in this solvent and in cyclo hexanone was undertaken in order to determine conditions under which reliable molecular weight measurements could be obtained.

The osmotic experiments were carried out on the modified Fuoss Mead osmometer of Masson and Melville

using the general method of operation, treatment of solvents and methods of determination of concentrations described in chapter 2.

The polymers were benzoyl peroxide catalyzed prepared in vacuo at 70°C, 80°C and 85°C and are denoted I, II and III respectively. The polymerizations were carried to approximately 15% conversion and the polymers isolated and dried by the process already described in the second chapter.

Results.

In methyl ethyl ketone at 23°C the $\frac{\pi}{C}$: C curve assumes a completely novel shape. This is shown in figure 15 curve I. This curve can be drawn satisfactorily on a much wider vertical scale so that there can be no doubt about the principal details of its shape. Figure 15 also shows the effect of temperature on the curves. Osmotic measurements in cyclohexanone give curves which are normal in shape and examples are shown in figure 15.

Fig. 15.- Osmotic Curves for Polymer 1.

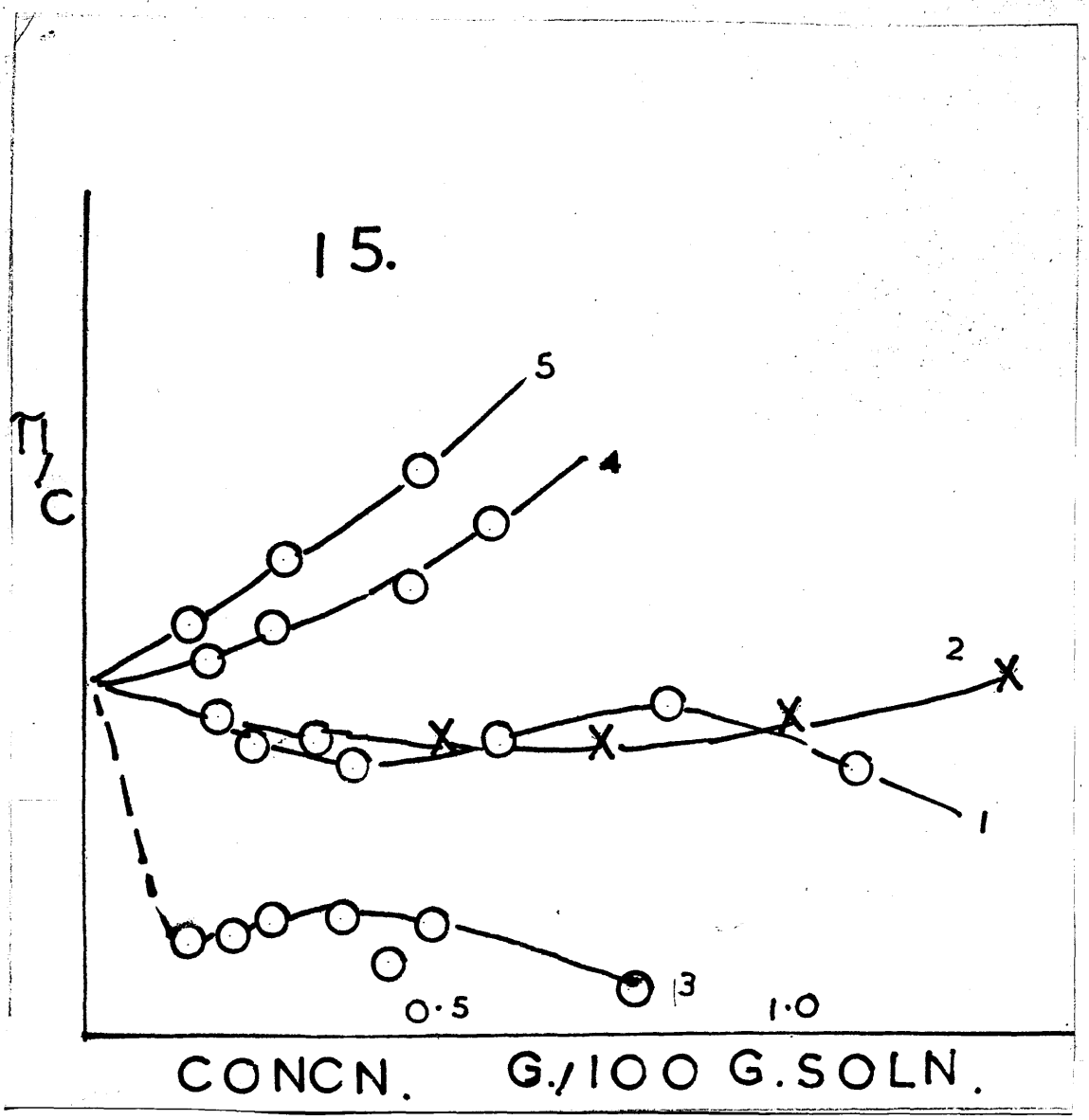


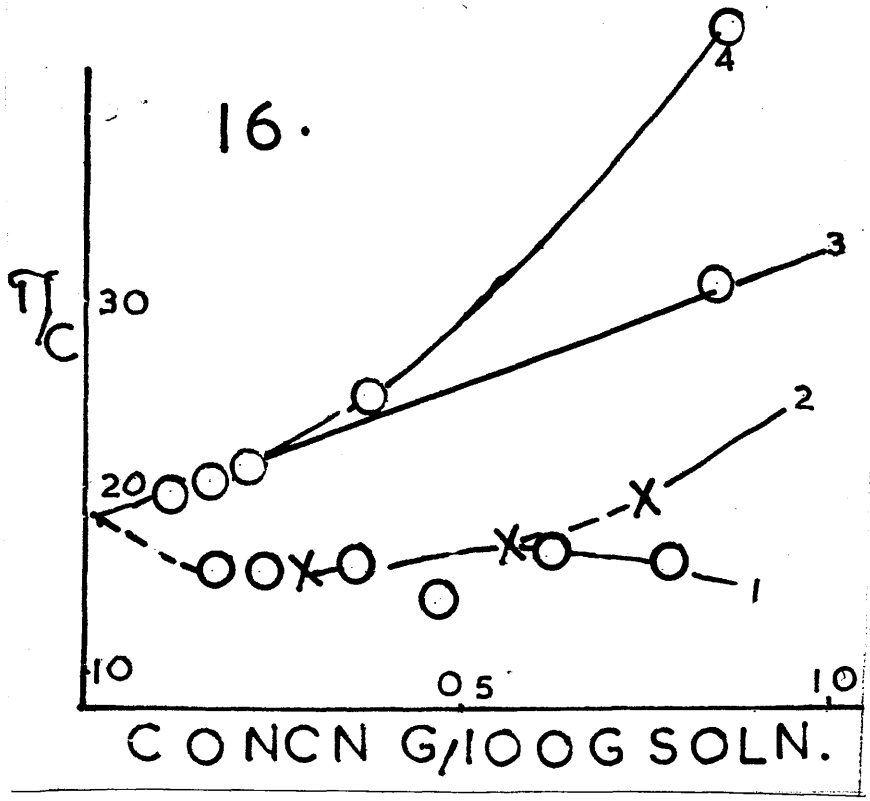
Table 7. - Fig. 15 - Osmotic curves for Polymer I.

Curve No.	Solvent.	Temp.	μ.
1.	Methyl ethyl ketone	23°C	-
2.	" " "	4°C	-
3.	" " "	30°C	-
4.	Cyclohexanone	30°C	0.435
5.	"	35°C	0.376

In methyl ethyl ketone it is clear that at the convenient temperatures for osmotic measurements namely 20-30°C an accurate extrapolation to zero concentration would be impossible, while even at lower temperatures the fact that the gradient is increasing with decreasing concentration would make such an extrapolation doubtful.

The curves obtained in cyclohexanone have intercepts within experimental error and this intercept is also a reasonable one for the methyl ethyl ketone curves at 4°C and 23°C. It must be assumed that the curve at 30°C will bend upwards at some lower value of concentration. The intercept represents a molecular weight of 63,000 ± 2,000. The values of the Huggins μ calculated at the different temperatures in the ~~methyl~~ cyclohexanone ethyl ketone curves shows that at higher temperatures there is increasing

Fig. 16.- Osmotic Curves for Polymer 2.



interaction between polymer and solvent.

Similarly shaped curves were obtained for polymers 2 and 3 and these are shown in Figs. 16 and 17. These polymers have molecular weights of 137,000 ± 5,000 and 34,800 ± 1,000.

Table 8. - Fig. 16 - Osmotic curves for Polymer II.

Curve.	Solvent.	Temp.
1.	Methyl ethyl ketone	24.5°C
2.	" " "	4°C
3.	Cyclohexanone	25
4.	"	30

Table 9. - Fig. 17 - Osmotic curves for Polymer III.

Curve.	Solvent.	Temp.
1.	Methyl ethyl ketone	27°C
2.	Cyclohexanone	27°C

The data used in constructing the above curves is given in full below in Table 10.

Fig. 17. - Osmotic Curves for Polymer 3.

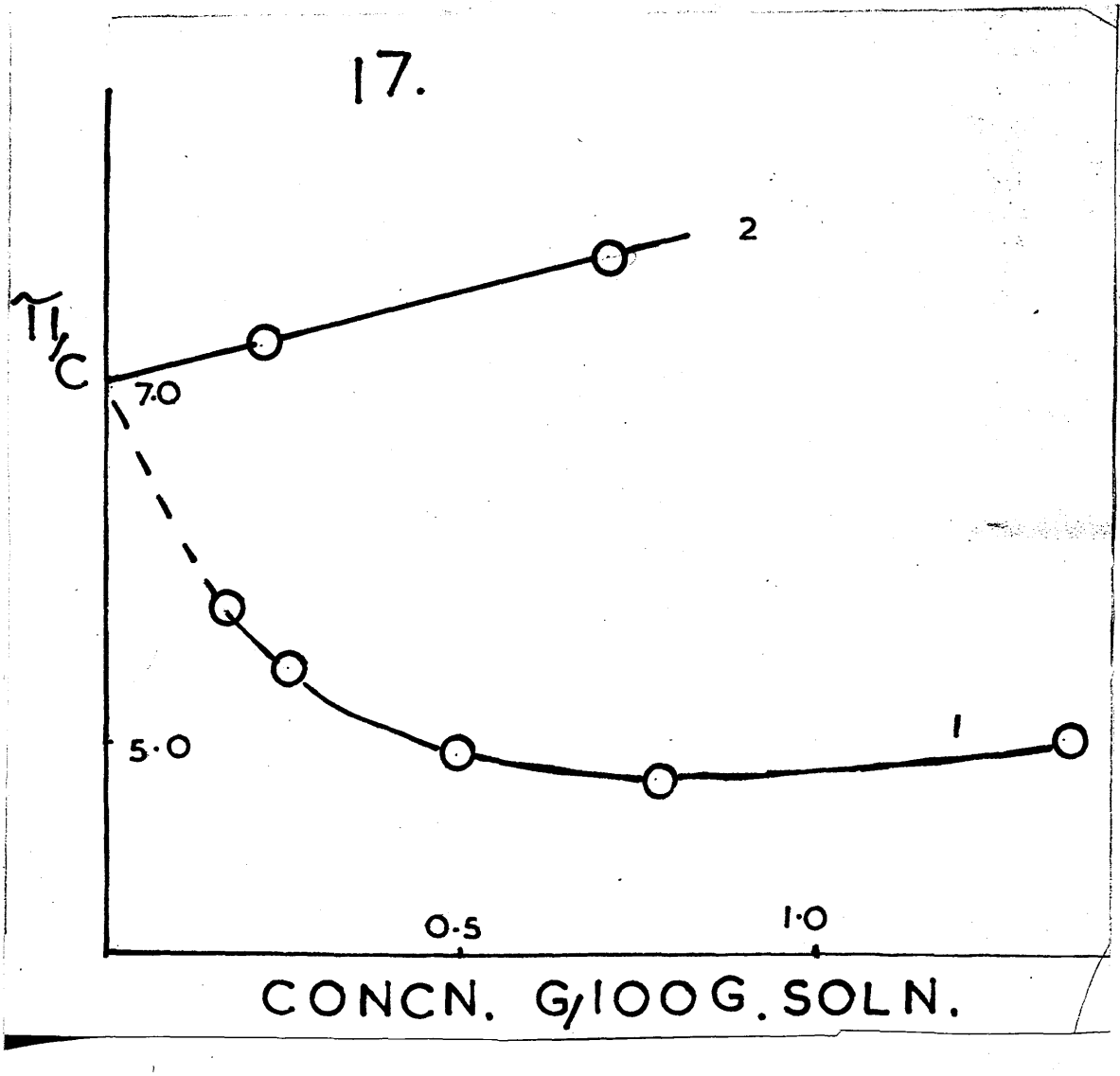


Table 10.- Osmotic Data for Figs. 15, 16 and 17.

Fig.	Solvent.	Temp. °C	π. cms sol^n	C. gms/100g	$\frac{\pi}{C}$	Curve.
15	Methyl ethyl ketone	23°C	4.93	1.425	3.51	1
"	" " "	"	4.00	1.085	3.69	"
"	" " "	"	3.165	0.814	3.89	"
"	" " "	"	2.180	0.590	3.70	"
"	" " "	"	2.120	0.570	3.71	"
"	" " "	"	1.325	0.372	3.56	"
"	" " "	"	1.195	0.326	3.67	"
"	" " "	"	0.985	0.275	3.58	"
"	" " "	"	0.685	0.180	3.71	"
"	" " "	"	0.874	0.241	3.66	"
"	" " "	"	0.740	0.179	4.13	"
"	" " "	"	1.270	0.372	3.43	"
"	" " "	4°C	5.25	1.295	4.05	2
"	" " "	"	3.74	0.980	3.82	"
"	" " "	"	2.60	0.710	3.88	"
"	" " "	"	1.90	0.510	3.73	"
"	" " "	"	1.090	0.285	3.8	"
"	" " "	30°C	1.725	0.752	2.29	3
"	" " "	"	1.240	0.471	2.63	3

Table 10 contd.

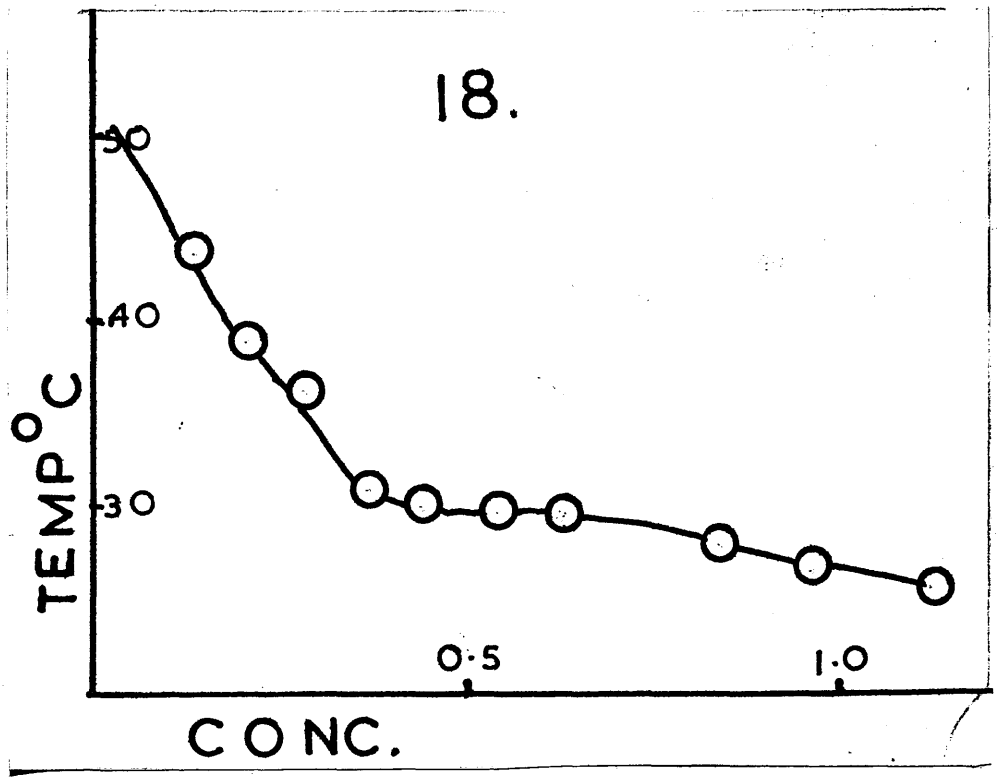
Fig.	Solvent	Temp. °C	π cms sol^n	C gms/100g	$\frac{\pi}{C}$	Curve
15	Methyl ethyl ketone	30°C	0.980	0.368	2.66	3
"	" " "	"	0.675	0.255	2.64	"
"	" " "	"	0.525	0.196	2.58	"
"	" " "	"	0.360	0.142	2.54	"
"	Cyclohexanone	35°C	2.57	0.473	5.44	4
"	"	"	4.42	0.715	6.18	"
"	"	"	1.32	0.276	4.74	"
"	"	"	0.845	0.193	4.37	"
"	"	30°C	2.79	0.563	4.96	5
"	"	"	1.710	0.378	4.52	"
"	"	"	1.18	0.270	4.21	"
"	"	"	0.705	.171	4.1	5
16	Methyl ethyl ketone	24.5°C	1.235	0.774	1.59	1
"	" " "	"	0.990	0.617	1.62	"
"	" " "	"	0.607	0.384	1.58	"
"	" " "	"	0.446	0.291	1.53	"
"	" " "	"	0.251	0.163	1.55	"
"	" " "	4°C	2.58	0.750	1.93	2
"	" " "	"	0.966	0.580	1.65	"

Table 10 contd.

Fig.	Solvent.	Temp. °C	π. cms sol^n	C. gms/100g	$\frac{\pi}{C}$	Curve
16	Methyl ethyl ketone	4°C	0.597	0.370	1.60	2
"	" " "	"	0.352	0.230	1.53	"
"	Cyclohexanone	30°C	3.875	0.861	4.50	4
"	"	"	0.900	0.358	2.50	"
"	"	"	0.485	0.227	2.13	"
"	"	25°C	3.83	0.840	3.21	3
"	"	"	0.400	0.20	2.0	"
17	Methyl ethyl ketone	27°C	6.93	1.375	5.06	1
"	" " "	"	3.65	0.752	4.85	"
"	" " "	"	2.435	0.492	4.95	"
"	" " "	"	1.37	0.254	5.40	"
"	" " "	"	0.816	0.143	5.71	"

Another interesting property of the polymethacrylonitrile-methyl ethyl ketone system, and one which is obviously connected with its osmotic behaviour, is that the solubility decreases with increasing temperature. For example a 1% solution is cloudy at room temperatures but completely clear even at -78°C. This effect is shown in figure 18 and table 11 for polymer I.

Fig. 18.- Solubility Curve for Polymer 1.



Precipitation in these systems takes place by gradual agglomeration of particles so that when precipitation becomes apparent by cloudiness the actual aggregates are quite large. Figure 18 was constructed by noting the temperatures at which visual cloudiness appeared and disappeared ~~were noted~~ (never differing by more than 1C°) and the mean of these were plotted ~~was~~ against the concentrations.

The experiment was carried out in a narrow necked pyrex tube (5 c.c. capacity) immersed in a large flask (500 c.c.) containing methyl ethyl ketone. A wire stirrer was arranged inside the flask and a glass plunger placed inside the 5 c.c. tube. The flask was slowly heated with a micro-burner and the temperatures, described above, noted. The heating flask contained methyl ethyl ketone rather than water to avoid any contamination of the polymer solution with water vapour.

It should be noted in this connection that methyl ethyl ketone gives a mutually closed solubility curve with water (XXXVIII). In this instance however it was impossible to extend the polymethacrylo-nitrile-methyl ethyl ketone curve above 80°C because of the boiling point of the solvent.

Table 11.

Data for Solubility Curve of Polymer I.

Concentration. g/100g sol^{n}.	Temperature where cloudiness appears °C.
5.15	below 20°C
1.54	24.5
0.946	26.5
0.826	28
0.623	29.5
0.528	29.8
0.428	30
0.363	33
0.196	39
0.268	36.5

The fact that visual precipitation is occurring with concentrations of 1% in the temperature region in which osmotic data is obtained gives immediately a reason for the negative slope at high concentrations shown in Figs. 16 and 17. When the agglomerates become large before precipitation the molecular weight tends to infinity and the osmotic pressure falls to zero. By comparison of the curves shown in Figs. 18

and 15 it is clear that there is good agreement between the precipitation point at the temperature considered and the beginning of the negative slope. At low temperatures as in the curves obtained at 4°C the polymer remains in solution and hence this negative portion is eliminated. When a polymer of low molecular weight is used, as in Fig. 17, no precipitation is occurring at 27°C because of the higher solubility of the polymer and hence this final negative portion again disappears. When however a polymer of high molecular weight, such as polymer 2, is used precipitation occurs at a lower concentration value with the corresponding effect on the osmotic curve as shown in Fig. 16. For a fuller appreciation of this phenomenon some further theoretical points should be considered.

Theoretical Considerations.

Considering a state where molecular aggregation is occurring; it is obvious that the amount of aggregation will depend on concentration.

Hence if α = No. of aggregative interaction/mol. of polymer we may write -

$$\alpha = f(c)$$

If CLo. is the average No. of monomer units in unassociated molecules and CL. average No. of monomer units in associated aggregates then -

$$CL = \frac{CLo}{1-a} = \frac{CLo}{1-f(c)} \qquad (3)$$

Now if the normal osmotic curve is governed by the conventional expression of equation (2):-

$$\frac{\pi}{C} = P + Qc + Rc^2 ,$$

and the effect of changing concentration is considered on equations (2) and (3) the following effects become clear.

As C increases from zero CL becomes greater than CLo and π decreases causing a negative slope. As C increases at low concentrations this negative slope continues but is soon cancelled by the Qc and Rc^2 terms of equation 2 and the curve tends to normality. Finally as f(c) --- 1 , $CLo/_{1-a}$ --- infinity and CL tends to infinity. Thus $\frac{\pi}{C}$ tends to zero and the curve again assumes a negative slope.

The effect of temperature on the curves is explained in the same way as the increasing solubility

with decreasing temperature. Polymers are soluble or insoluble depending on whether polymer-solvent or polymer-polymer attraction predominates. In this system both the polymer and the solvent are polar and both types of attraction are strong and apparently finely balanced. At lower temperatures polymer-solvent attraction predominates, agglomeration is prevented and the curves approach normality. When the temperature is raised polymer-solvent attraction is suppressed, the increased temperature allowing the slower polymer molecules to interact and also driving out the solvent molecules from the polymer environs causing agglomeration to occur.

Previous Work.

Although S shaped curves have not previously been reported anomalous behaviour in the cases of certain other systems have been noted.

Firstly Steurer (XL) observed that ethyl cellulose in benzene and toluene solution had normal positive curves down to a value of 0.1-0.2% concentration where they curved upwards to a much higher value of $\frac{\pi}{c_o}$. It is assumed, but not proved, that this value is the same as the value of $\frac{\pi}{c_o}$ obtained in other solvents. A dynamic equilibrium where the associated molecules break

down at low concentrations is postulated.

Secondly Doty noted (XXXIX) that solutions of poly vinyl ~~acetate~~ CHLORIDE in dioxan had negative osmotic slopes and thirdly such slopes are reported in a recent paper by Moranwitz and Gobran (XLI) in work on solutions of acidic and basic polymers. These curves are linear and in the second case have different intercepts at different temperatures. This phenomenon is explained by the postulation of a static association of molecules which even at low concentrations shows no signs of breakdown.

The present work shows a dynamic equilibrium depending on temperature and concentration resembling that quoted by Steurer (XL).

Viscosities.

Viscosity measurements which might be used as a check on the molecular weight measurements are unsatisfactory because the viscosity of the polymer in methyl ethyl ketone is very low. This indicates that the molecules are coiled up as one would expect in a bad solvent.

The viscosities obtained at 24.5°C are shown below in Table 12.

Table 12 - Viscosity of Polymer II in methyl ethyl ketone at 24.5°C.

Concn. C. g/1009. Soln.	Specific Viscosity. η_{SP}.	$\eta_{SP}/C = [\eta]$
0.814	0.214	0.255
0.688	0.160	0.233
0.584	0.148	0.254
0.397	0.122	0.282
0.303	0.0800	0.274
0.250	0.0641	0.251

In conclusion therefore, for the purpose of measuring molecular weights as required in the evaluation of rate constants or in the investigation of degradation reactions cyclohexanone, is a completely satisfactory solvent. Methyl ethyl ketone could be used in a limited temperature range if the peculiar shape is borne in mind and extrapolation made using only points which lie on the low concentration negative slope. Reasonable accuracy should be obtained if the molecular weight is low and a suitably low temperature is chosen. In the work which follows cyclohexanone has been used almost exclusively.

Chapter VI.

Rate Constants in the Polymerization of Methacrylo-nitrile.

In work which has previously been reported on the degradation of high polymers it has been shown that an accurate description of the structure of the polymer molecules is of supreme importance. Abnormalities in structure in small concentration such as end groups and branches have been shown to have a large effect on the degradation characteristics. This fact has been clearly demonstrated in the consideration of the degradation of methyl methacrylate reported in chapter 3. A certain amount of such structure information can readily be obtained from a critical examination of the polymerization reaction and the determination of the kinetic coefficients of the various steps of the process.

The general mechanism of free radical polymerization is shown in the scheme below:-

Initiation,	$M + C \longrightarrow P_1$	...	$Vi = Ki(C)(M)$.
Propogation,	$P_1 + M \longrightarrow P_2$		
	$P_2 + M \longrightarrow P_3$	---	$VPi \quad KP(P)(M)$.
	$Pn + M \longrightarrow Pn+1$		
Transfer to Monomer,	$M + Pn \longrightarrow Mn + P_1$		$Vtr = K_t(P)(M)$.
Termination.	$Pr + Ps \longrightarrow Mr + Ms$ or $Mr + s$		$Vt = Kt(P)^2$,
	combination or disproportionation.		

Where the conventional notation for free radical, catalyst, monomer, and rate coefficients is as already assigned in chapter 3.

Assuming a stationary state -

$$\frac{d(P)}{dt} = Ki(C)(M) - Kt(P)^2 = 0 .$$

$$\therefore (P)^2 = \frac{Ki(C)(M)}{Kt} .$$

$$\therefore (P) = \left[\frac{Ki(C)(M)}{Kt}\right]^{\frac{1}{2}} .$$

The measured Rate R, the rate of disappearance of monomer, which is given by the expression KP(P)(M).

$$\therefore KP(P)(M) = R ,$$

$$\therefore (P) = \frac{R}{KP(M)} ,$$

$$\therefore R = KP(M)^{3/2} \times Ki^{\frac{1}{2}}(C)^{\frac{1}{2}}/Kt^{\frac{1}{2}}$$

$$= \text{constant } X(C)^{\frac{1}{2}}.$$

$$\therefore \log R = \tfrac{1}{2} \log C + \text{constant.} \qquad (1)$$

Thus, if termination is by the mutual interaction of two radicals resulting either in combination or disproportionation, the measured Rate R will be proportional to the square root of the catalyst concentration. Plotting this data as logarithms as shown by equation 1; a straight line slope 0.5 is obtained if termination occurs as described above.

In photo chemical polymerizations the general scheme becomes:-

$$M + h\nu \longrightarrow P_1 \qquad Vi = f(I).$$

$$Pn + M \longrightarrow Pn + 1 \qquad Vp = Kp(P)(M).$$

$$Pr + Ps \longrightarrow Mr + s \text{ or } Mr + Ms \qquad Vt = Kt(P)^2.$$

where I is the light intensity.

and from the stationary state equation -

$$f(I) = Kt(P)^2 \qquad (P) = \left[\frac{f(I)}{Kt}\right]^{\frac{1}{2}}$$

$$\text{and Rate} = \frac{Kp\ f(I)^{\frac{1}{2}}\ (M)}{Kt} = \text{constant} \times f(I)^{\frac{1}{2}} \qquad (2)$$

Thus the Rate is proportional to the square root of light Intensity.

Also if the average chain length of the polymeric material formed is given by the following expression:-

$$\text{chain length} = \bar{P} = \frac{\text{Rate of disappearance of monomer}}{\text{Rate of termination of chains}}$$

$$= \frac{Kp(P)(M)}{Kt(P)^2 + Kf(P)(M)}.$$

$$\therefore \frac{1}{\bar{P}} = \frac{Kt(P)}{Kp(M)} + \frac{Kf}{Kp}.$$

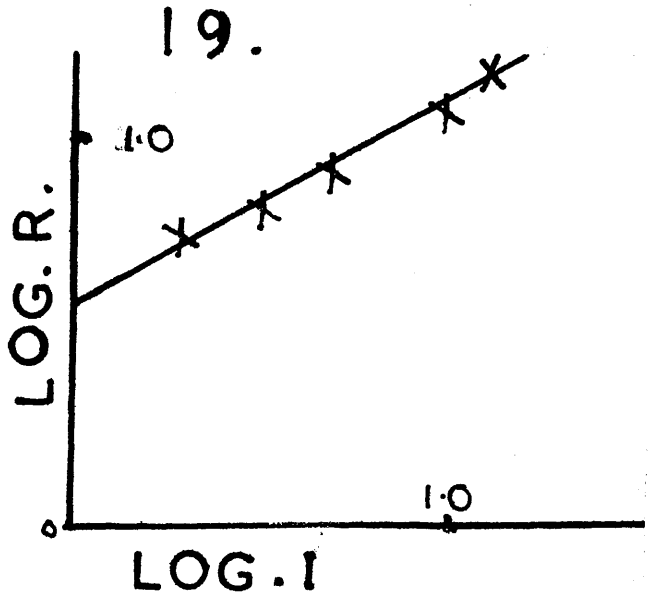
$$\therefore \frac{1}{\bar{P}} = \frac{Kt(R)}{Kp^2(M)^2} + \frac{Kf}{Kp}. \qquad (3)$$

Thus if the measured rate is plotted against the reciprocal of the chain length the slope will give the value of Kt/Kp^2, and the intercept Kf/Kp.

In order to assign absolute values to the kinetic coefficients it is necessary to obtain another relationship between Kp and Kt. This is found be measuring the life time of the growing radical.

$$\tau = \frac{\text{concentration of active centres}}{\text{rate of disappearance of active centres}}$$

Fig. 19.- Effect of Light Intensity on Bzo_2 Polymerization.



$$\therefore \nu = \frac{(P)}{Kt(P)^2} = \frac{1}{Kt(P)}$$

$$\therefore \nu = \frac{Kp(M)}{RKt}$$

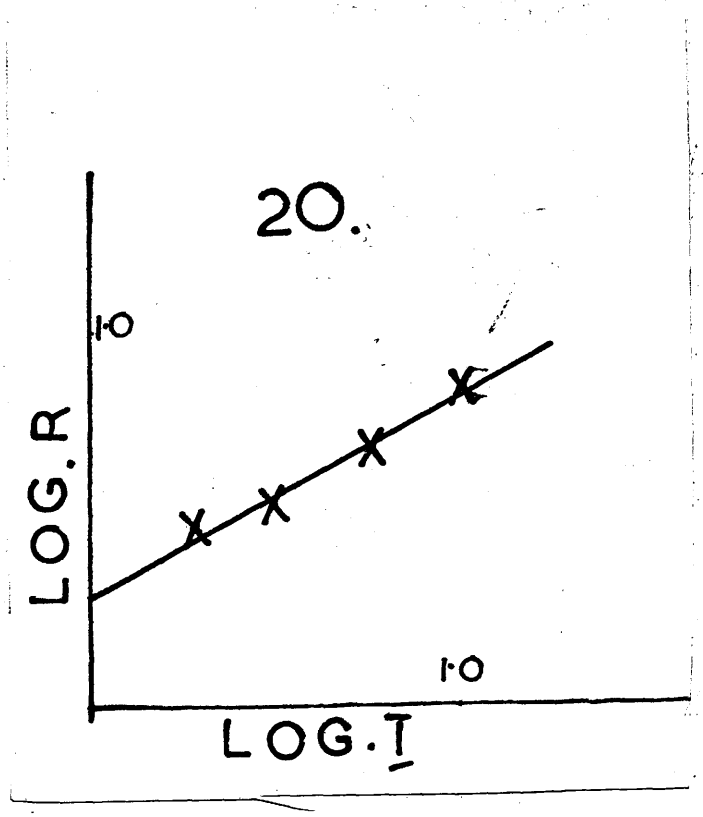
$$\therefore \frac{Kp}{Kt} = \frac{\nu R}{(M)} \qquad (4)$$

Hence by obtaining the data required for equations (3) and (4) values can be assigned to Kp, Kf and Kt.

Results

The general experimental technique for the catalytic preparation of polymers, described in chapter 2, was employed. The chain lengths were calculated from osmotic measurements on the modified Fuoss Mead osmometer in cyclohexanone and methyl ethyl ketone solution as described in chapters 2 and 5. In this connection, since it was suspected that the molecular weight increased at higher conversions, polymerizations were never carried beyond 2-3%. The absolute rates of polymerization were calculated by the dilatometric relationship already given taking the concentration of monomer as 11.91 gm. mol./litre at 30°C.

Fig. 20 - Effect of Light Intensity on Azo Polymerization



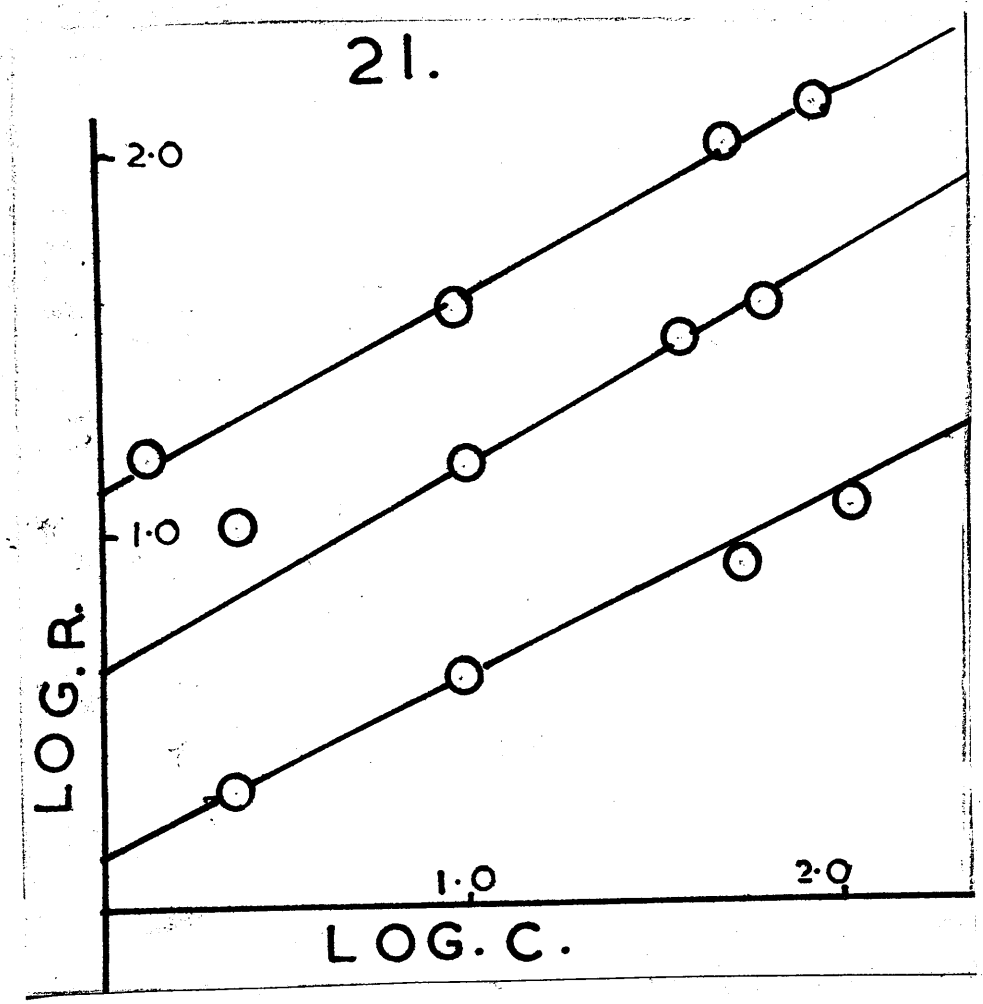
(A) 'Square Root Relationship - data required for the application of equation (1).

A series of experiments was carried out using different measured catalyst concentrations at 59.1°C., 70°C and 80°C. The rates of polymerization were plotted against the value of the catalyst conc. calculated in gms./100 c.c. at the temperature of the experiment and the results obtained are shown in Table 14.

The effect of light intensity on the rate of polymerization was also investigated. As has already been mentioned in chapter 4 photo-chemical experiments in silica tubes with radiation from the osram lamp, given in Table I, showed that the photochemical rate was too slow for convenient photochemical investigations. However, as photosensitized experiments were necessary in later work, the effect of light intensity on benzoyl peroxide and azo-bis-iso-butyro-nitrile photo-sensitized polymerizations were investigated. The temperature chosen (30°C) was such that no thermal catalytic polymerization occurred.

The light intensity was varied using the screens calibrated on the uranyl oxalate actinometer described in chapter 2. The rates of polymerization were plotted

Fig. 21.- Log Rate: Log Catalyst Conc. For Methacrylo Nitrile.



against the light intensity and the results are shown for the catalysts dibenzoyl peroxide and azo-bis-iso-butyro-nitrile in Figs. 19 and 20.

Square root relationships are observed and the exponents are quoted in table 15. This shows that the termination step consists of mutual interaction of polymer radicals.

Table 14.

Temperature °C.	Rate.R. % contract/hr.	log Rx100	Catalyst concn.C. %	Log Cx100.
59.1	0.0200	0.3010	0.025	0.3979
59.1	0.0407	0.6090	0.0961	0.9827
59.1	0.074	0.869	0.563	1.7505
59.1	0.013	1.033	1.051	2.021
70	0.105	1.021	0.025	0.3979
70	0.149	1.173	0.0956	0.980
70	0.319	1.504	0.374	1.573
70	0.411	1.614	0.606	1.783
80	1.060	2.025	0.468	1.670
80	1.361	2.134	0.874	1.928
80	0.395	1.597	0.088	0.945
80	0.119	1.086	0.117	0.682

These results are summarized in Figure 21 and the exponent calculated from the slope as shown in equation (1). The values of the exponents and the corresponding temperatures are shown in Table 16.

Table 15 - Intensity Exponents in photosensitized Polymerizations

Catalyst.	Temp.	Exponent.
Dibenzoyl Peroxide	30°C	0.53
Azo-bis-iso-butyro-nitrile	30°C	0.54

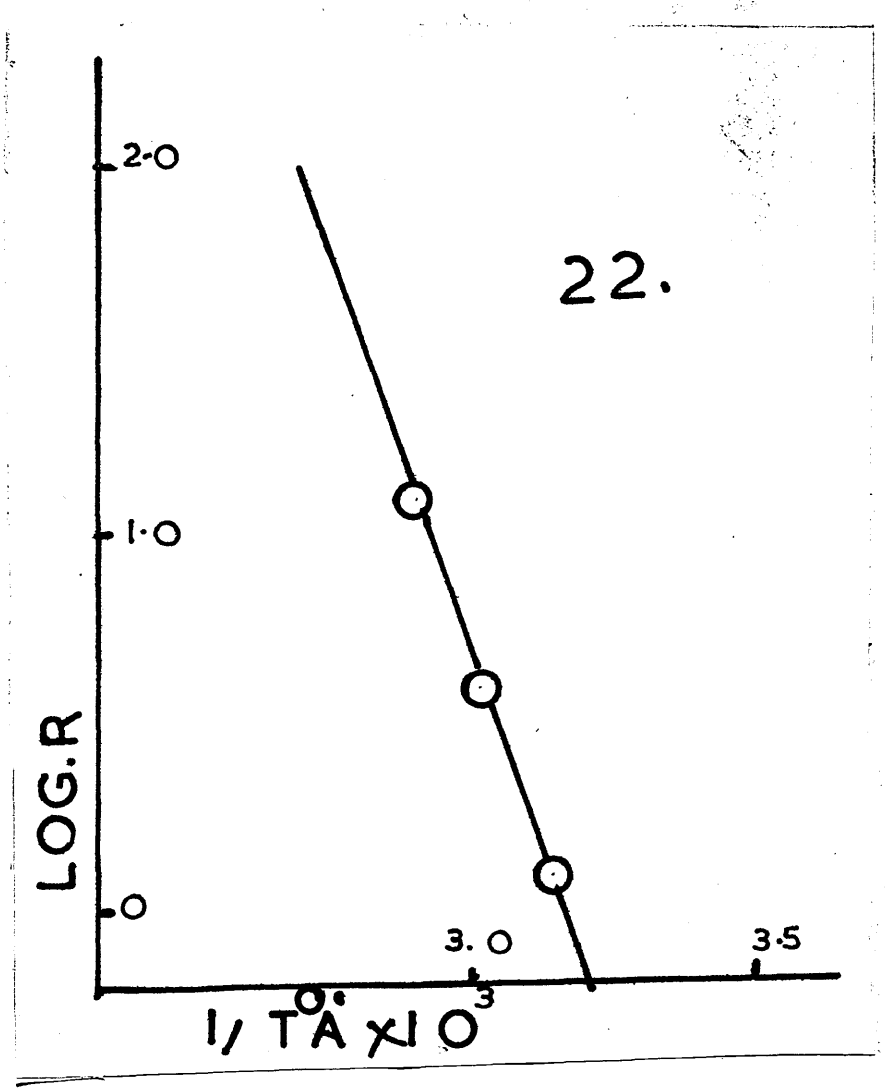
Table 16

Exponents in benzoyl peroxide catalyzed reactions

Temp.	Exponent.
59.1°C	0.49
70°C	0.52
80°C	0.52

The overall energy of activation can be calculated from the above data by taking the relative rates at the three temperatures at some arbritary value of catalyst concentration. These rates are shown in Table 17. and the energy of activation deduced from Fig. 22.

Fig. 22 - Overall Energy of Activation.



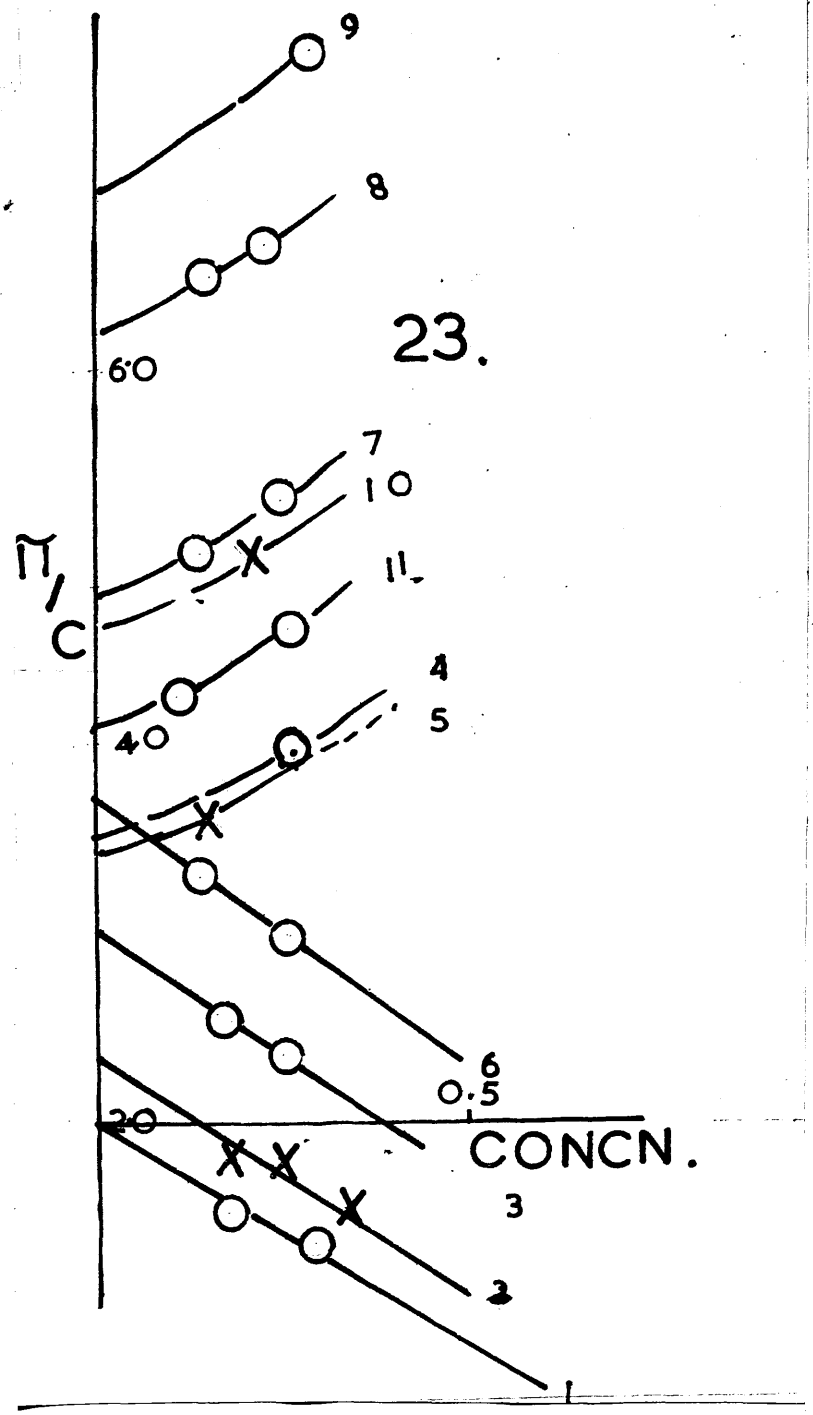

23.
9
8
6·0
7
10
11
π/C
4
5
4·0
6
0·5
2·0
CONCN.
3
2
1

Table 17 - Energy of Activation of Thermal Catalytic Reaction.

Catalyst Concn.	Temp.	log R x 100
0.01%	59.1°C	0.12
"	70°C	0.62
"	80°C	1.11

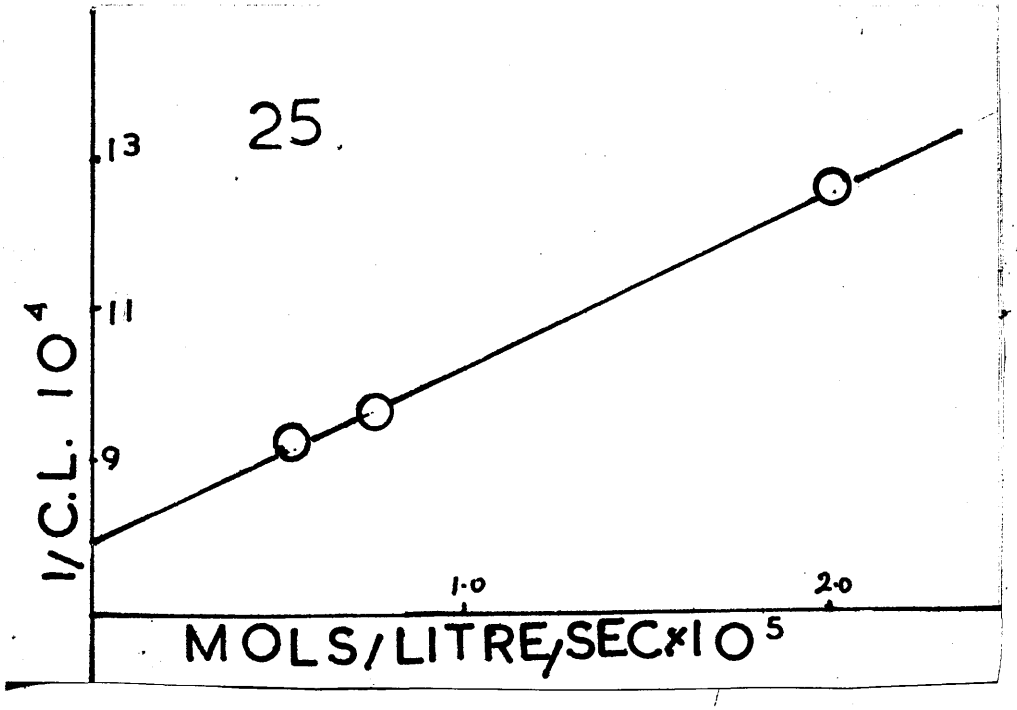
Energy of activation calculated from Fig. 22

= 24.6 k.cal/mol.

(3) Determination of Kt/Kp^2 and Kf/Kp. - evaluation of the data required in (2).

To provide the data for application of equation (2) a series of experiments were carried out at 59.1°C., 70°C. and 80°C. where the rates of the reaction were determined, the polymer isolated and the chain length determined osmotically. The reciprocal of the chain length was plotted against the absolute rate of the reaction (mols./litre/sec.) and the values of $Kt/_{Kp}{}^2$ and $Kf/_{Kt}$ calculated from the slope and intercept respectively . The results are shown in Table 18 and summarized in Figs. 24, 25, 26. The osmotic curves obtained in the molecular weight measurements are shown

Fig. 25 - 1/Chain Length: Rate at 50°C.



in Fig. 23. Polymers 1, 2, 3 and 6 being measured in methyl ethyl ketone at 23°C, and the rest in cyclohexanone at 30°C.

Table 18. - Data for Equation (2).

Polymer. No.	Temp. °C.	Rate. mols/litre/sec.	$\frac{\pi}{C_o}$	Mol.Wt.	1/chain length. x 10^4.
1.	59.1	0.196×10^{-5}	2.0	122,000	5.48
2.	59.1	0.386×10^{-5}	2.45	100,600	6.40
3.	59.1	0.675×10^{-5}	3.06	81,600	8.20
4.	59.1	1.081×10^{-5}	3.55	70,500	9.50
5.	70	1.04×10^{-5}	3.48	73,400	9.15
6.	70	1.42×10^{-5}	3.70	69,100	9.68
7.	70	0.390×10^{-4}	4.8	53,300	12.6
8.	80	$.990 \times 10^{-4}$	6.20	41,100	16.3
9.	80	1.271×10^{-4}	7.00	36,500	17.8
10.	80	0.337×10^{-4}	4.65	54,700	12.3
11.	80	0.110×10^{-4}	4.15	61,300	10.98

The value of the concentration of monomer was calculated from the value of the density at 30 (0.800) and the coefficient of expansion quoted in chapter 4. The densities and concentrations used at each temperature are shown in table 19.

Fig. 24.- 1/Chain Length: Rate at 60°C.

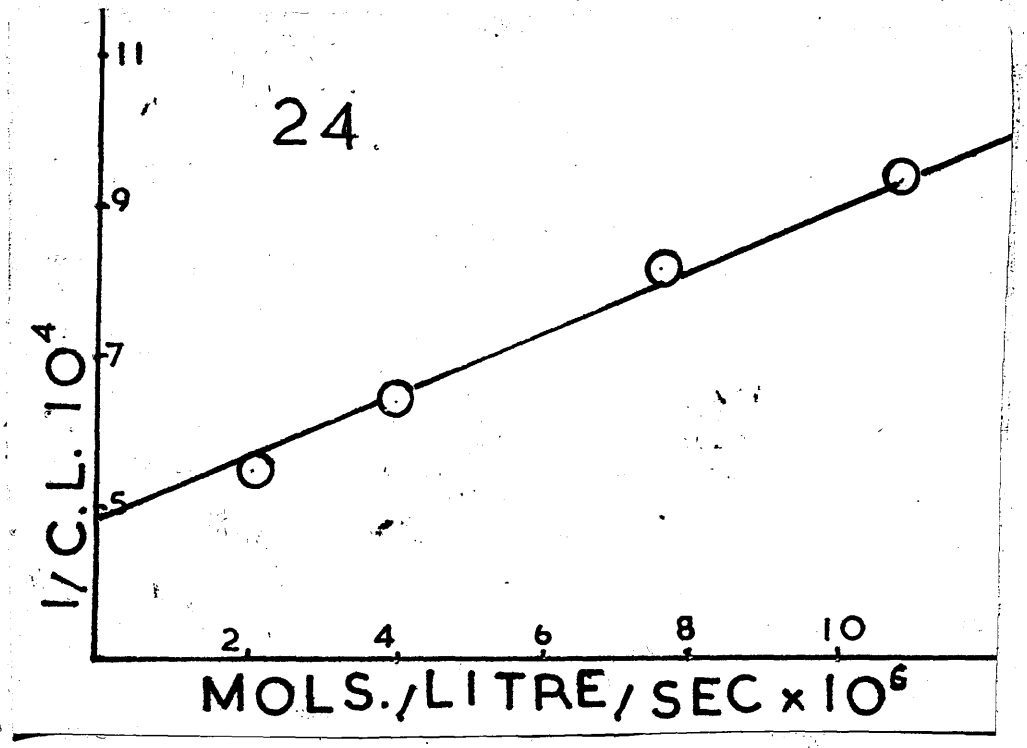


Table 19.

Density and Concentration of Monomer at Various Temperatures.

Temp °C.	Density g/c.c.	(M) g.mol/litre
30	0.799	11.91
60	0.770	11.50
70	0.760	11.35
80	0.747	11.21

The values of the slopes and intercepts obtained from the diagrams shown in Fig. 24, 25, 26 are shown below in Table 20.

Table 20.- Values of Kf/Kp^2 and Kf/Kt at 59.1°C., 70°C., & 80°C.

Temp. °C	Slope.	Intercept.	$Kt/Kp^2 = M^2 \times$ slope mols/litre/sec units	Kf/Kp. mols/litre/sec units
59.1	41.0	4.85×10^{-4}	5.45×10^3	4.85×10^{-4}
70	12.2	7.9×10^{-4}	1.58×10^3	7.9×10^{-4}
80	5.6	10.3×10^{-4}	7.05×10^2	10.3×10^{-4}

From the data given in Table 20, the energies of activation of the Kt/Kp^2 and Kf/Kp terms can be calculated. These are shown in Figures 27 and 28 and the corresponding data in Table 21.

Fig. 26 - 1/Chain Length: Rate at 80°C.

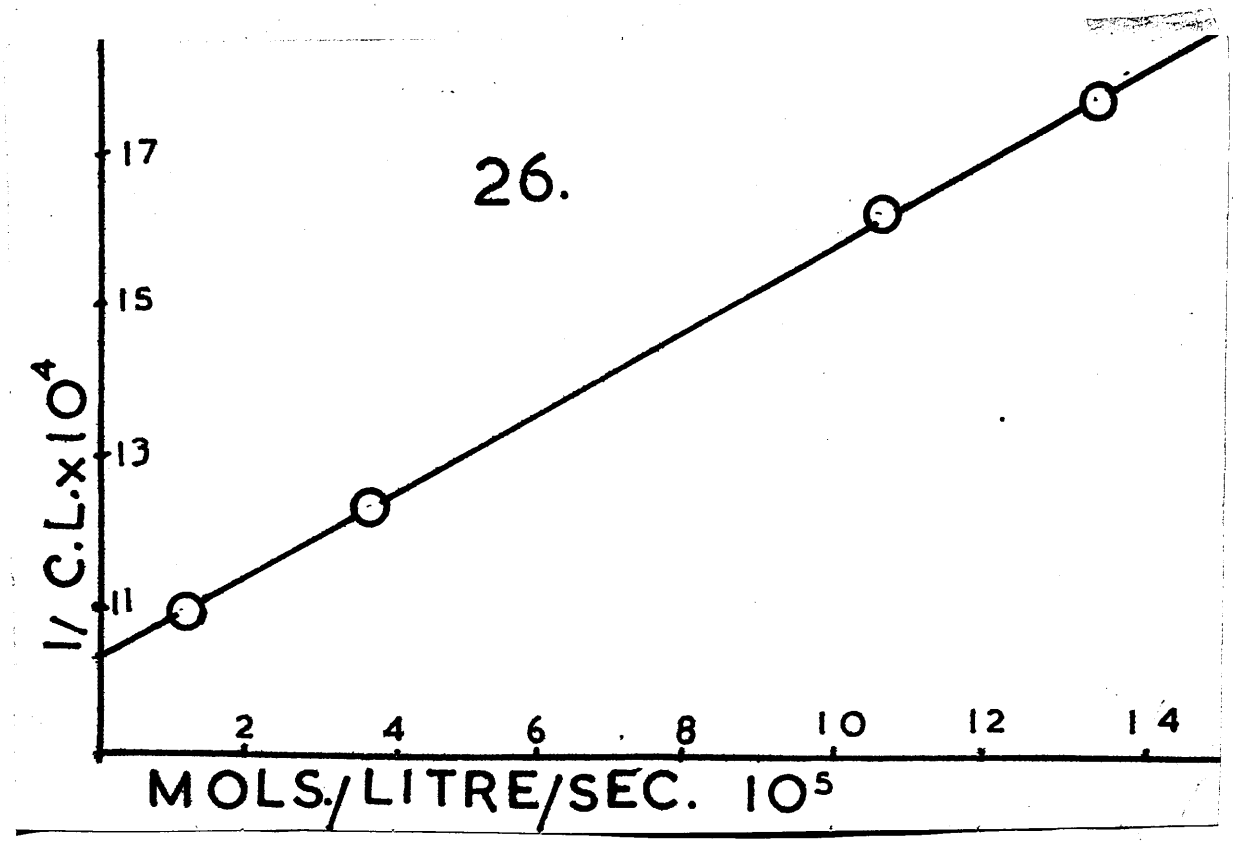


Table 21.

Temp. ° A	$\frac{1}{T}$ °A	log Kt/Kp^2	log $Kf/Kp \times 10^4$
332.1	3.02×10^{-3}	3.736	0.686
343	2.925×10^{-3}	3.198	0.898
353	2.825×10^{-3}	2.848	1.013

The energies of activation of the terms are found to have the following values:-

$$Et/Ep^2 = -18.2 \pm 2 \text{ k.cals/mol.}$$

$$Ef/Ep = 9.1 \text{ k.cals/mol.}$$

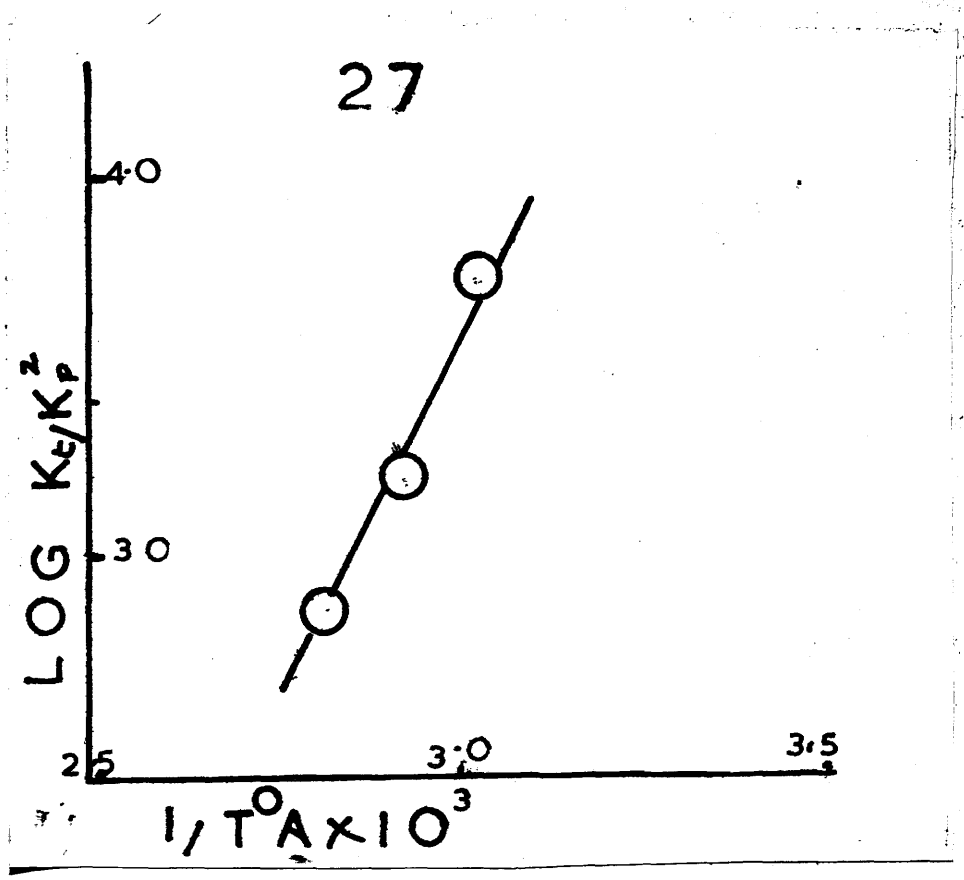
The overall energy of activation quoted in section A of this chapter (24.6 k.cals/mol.) is mainly the energy of activation of the break down of Benzoyl peroxide catalyst. From the standard kinetic scheme and the assumption of the stationary state, Vi = Vt, the measured rate can be shown to be given by the expression -

$$R = \frac{Kp.Ki^{\frac{1}{2}}}{Kt^{\frac{1}{2}}}(C)^{\frac{1}{2}}(M).$$

Thus the Energy of activation of the measured rate is that of the term -

$$\frac{Ki^{\frac{1}{2}}\ Kp}{Kt^{\frac{1}{2}}}$$

Fig. 27 .- Energy of Activation of K_p/K_t^2 .



The energy of activation of Ki is that of the breakdown of Benzoyl peroxide and a great many workers have given values for this under various conditions which show great consistency. Table 22 shows these values, the appropriate reference and the conditions under which the measurements were obtained; the values are quoted directly or calculated from data given in the original papers.

Table 22.- Energies of Activation of Decomposition of Benzoyl Peroxide.

Solvent.	E k.cal/mol.	Ref.
Benzene .	32	
Ethyl Benzene .	31	XLIII.
Coumene .	31	&
Benzaldehyde .	31	XLIV .
Benzene + 20% Styrene .	30.5	
Ethyl Benzene + 20% Styrene .	31	
Benzene .	29.6	
Toluene .	29.6	
Carbon Tetrachloride .	29.6	XLV .
Nitrobenzene .	29.6	
Methyl acetate .	29.6	
Ethyl acetate .	29.6	

Table 22.- contd.

Solvent.	E k.cal/mol.	Ref.
tert-Butyl Benzene.	30.4	
Cyclohexane.	28.2	XLVI.
Methyl cyclohexane.	30.7	
N. Octane.	29.0	
Butyl acrylate.	27	XLVIII.
Allyl acetate.	29.5	XLIII.
Maleic anhydride.	29.8	XLII.

Bawn and Mellish (XLV), in reviewing the situation, state that the energy of activation required to break benzoyl peroxide into radicals is independent of the medium and is of the order of the constant value quoted (30 k.cals.).

From this value the energy of activation of the $Kt/_{Kp}{}^2$ term can also be calculated thus:-

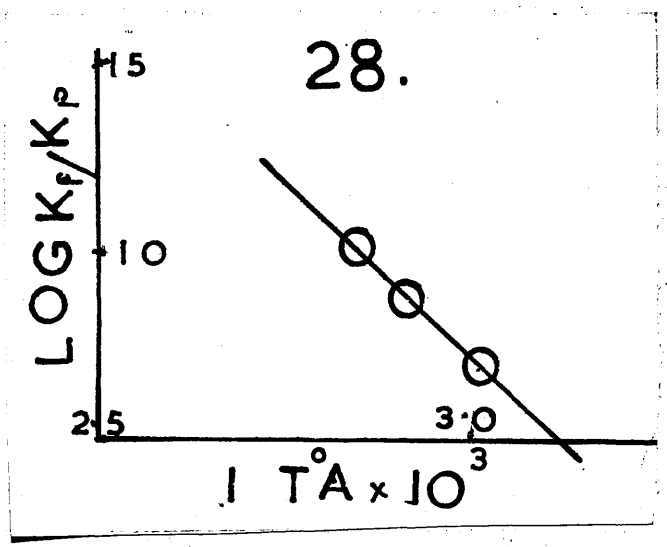
$$E_R = \tfrac{1}{2}E_1 + Ep - \tfrac{1}{2}Et$$

$$24.6 = 15.0 + Ep - \tfrac{1}{2}Et$$

$$\therefore \quad Ep/_{Et}{}^{\frac{1}{2}} = 9.6 \text{ k.cals/mol.}$$

$$\therefore \quad Et/_{Ep}{}^2 = -19.2 \text{ k.cals/mol.}$$

Fig. 28.- Energy of Activation of Kf/Kp.



Alternatively, the activation energy of the break down of benzoyl peroxide in methacrylo-nitrile can be calculated from the value of E $Kp^2/_{Kt}$ quoted from equation (2). Thus the energy of activation of the decomposition of benzoyl peroxide = 32 k.cals/mol. which can be compared with the values in other solvents given in Table 22.

The energy of activation of $Kp/_{Kt^{\frac{1}{2}}}$ can be found directly from photo chemical data. If, as can reasonably be assumed, the photo chemical initiation reaction is temperature independent and since the rate measured (R) is given by the expression R = Kp(P)(M); then if the steady state -

$$dp/_{dt} = f(I) - Kt(P)^2 = 0 \text{ is assumed}$$

$R = Kp(M)\ [f(I)]^{\frac{1}{2}}/Kt^{\frac{1}{2}}$, and hence the energy of activation of the photochemical reaction will be the energy of activation of $Kp/_{Kt^{\frac{1}{2}}}$.

With methacrylo-nitrile the photo-chemical reaction is very slow and there is great difficulty in keeping the silica window of the thermostat reproducibly clean over the long periods which would be required to construct a full energy of activation curve. However,

if small catalyst concentrations are used at a temperature where no thermal catalytic polymerization occurs, the increased rate produced will make the problem easier. The results shown below in Table 23 show values calculated from direct photo chemical and benzoyl peroxide photosensitized polymerization data.

Table 23.

Energies of Activation in Photochemical Polymerizations.

Condition.	Temp.	Rate. cms contn./100 mins.	$E = \frac{\text{Log } R_2 - R_1 \times 2.303}{1/T_1 - 1/T_2} R.$
PhCOOOOCPh	305.5	0.162	8.0
catalyzed	313	0.236	
direct	303	0.058	5.0
photochemical	313	0.076	

The values of the energy of activation calculated by the various methods described above are summarized in Table 24.

Table 24 - Energies of Activation of the $Kp/_{Kt}^{\frac{1}{2}}$ term.

Method of calculation.	Energy of Activation.	No.
Mol. Wt. & Rate Data.	9.0 ±1 k.cals/mol.	1.
Overall E. and Table 22.	9.2 "	2.
Direct photochemical reaction.	5.0 "	3.
Photo-sensitized Bzo_2 " .	8.0 "	4.

From the values of the energy of activation given in Table 24. The average value of $Ep/_{Et}^{\frac{1}{2}}$, calculated from the data given by methods 1 and 4, can be quoted as 8.5 ± 1 k/cals/mol. The value found by method 4 is unreliable because of the error already mentioned, and method 2 depends on the assumption that the energy of activation of the break down of benzoyl peroxide is the same as in other solvents. It is obviously of the same order but should not be used to calculate an accurate value of $Ep/_{Et}^{\frac{1}{2}}$ since the actual value of the energy of activation of the break down of Bzo_2 in this solvent has not been specifically measured.

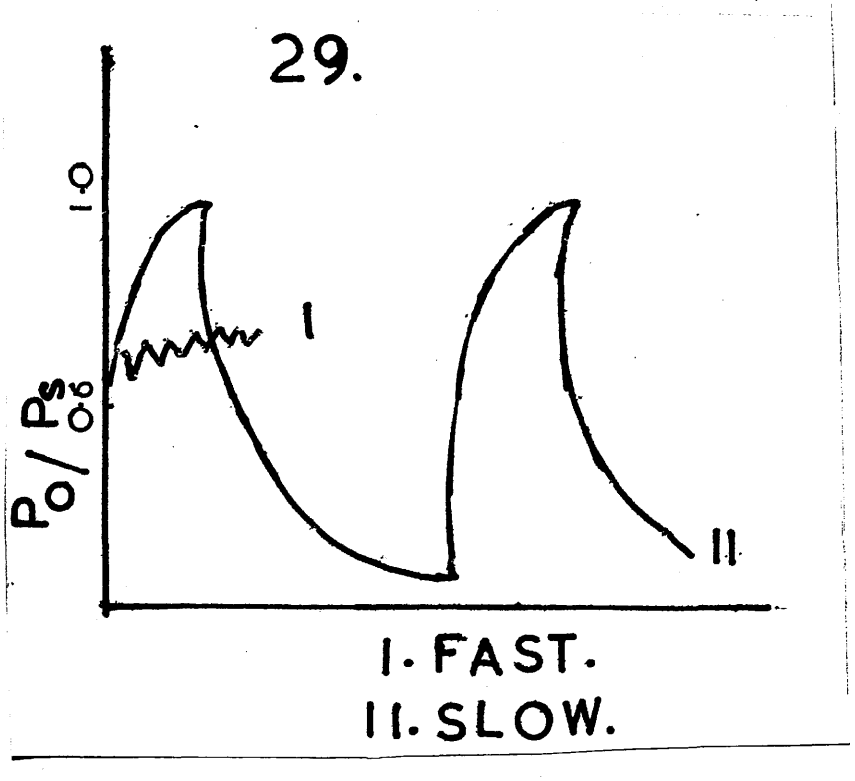
In a series of papers (XLVIII- L) on monoradical and diradical polymerizations the possibility of transfer to catalyst is considered. Assuming monoradical polymerization when monoradical producing catalysts are used, the following expression can be derived by introducing transfer to catalyst into the Reaction scheme.

$$\frac{1}{\bar{P}} = \frac{Kf}{Kp} + Kc/_{Kp} \frac{[Cat.]}{[M]} + \frac{RKt}{Kp^2} \qquad (5)$$

where Kc is the constant for transfer to catalyst

$$Vc = Kc(P)(Cat.).$$

Fig. 29 - (Po)/(Ps) with Intermittent Illumination.



It is evident that if transfer to catalyst is occurring the plot of $1/_{P}$ against R would not be a straight line as shown in Figs. 24, 25 and 26, and it must therefore be assumed that no transfer to catalyst is occurring under these conditions. Under similar conditions with styrene, transfer to catalyst takes place, according to Johnstone and Tobolsky (LVII).

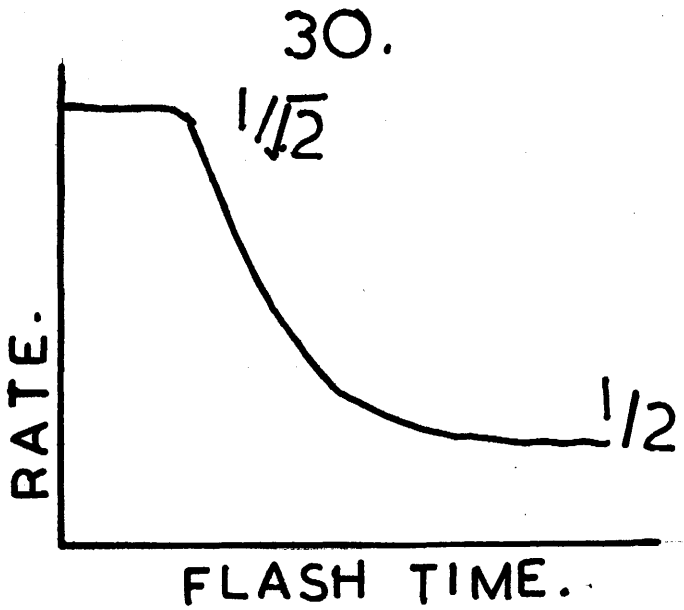
(C) Determination of $Kp/_{Kt}$.

To provide the data required for application of equation (4) a series of experiments were carried out using azo-bis-iso-butyro-nitrile in a photo sensitized reaction. The life times were measured using the rotating sector described in chapter 2.

Briefly the principle of the method is as follows. If (P) is the concentration of radicals under intermittent illumination and $(P)_s$ the concentration of radicals under steady illumination, then for a slow rotation $(P)(P)_s$ will build up to a value of unity during the 'on' period and decrease to a value of almost zero during the 'off' period so that for slow rotations, when the flash time is longer than the life time of the radical, the Rate measured is half the rate at steady illumination.

$$\therefore \quad R_{slow} = \frac{R}{2}.$$

Fig. 30 - Rate: Time of Flash.



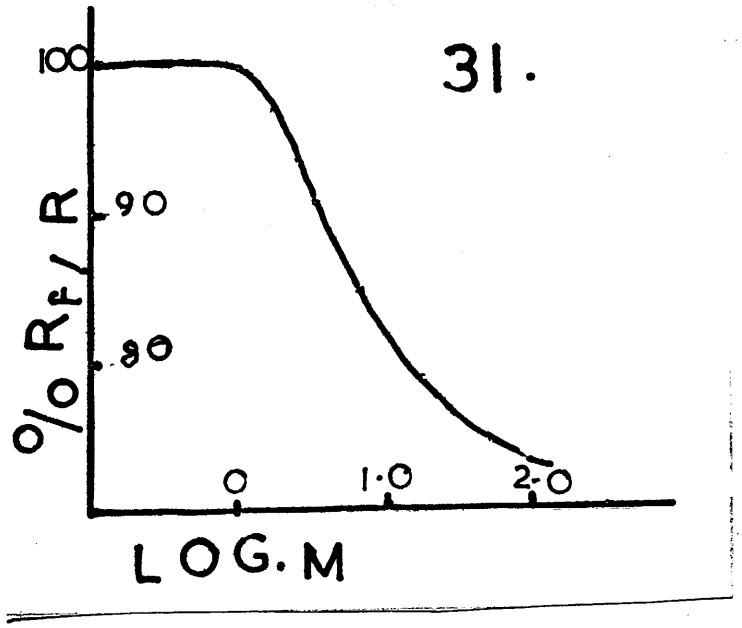
If the rate of rotation is such that the flash time is less than the life time of the radical then at this fast rotation (P)(P)s rises rapidly during the 'on' period and decreases less rapidly during the 'off' period. This results in the establishment of a steady state in which the effective concentration of radical does not change. When the 'off' and 'on' periods are equal (i.e. when the sector is cut at 90°) the effective light intensity is halved when fast rotation is used, and the rate observed will be given by the expression -

$$R_{obs} = R/\sqrt{2}.$$

The change in $(P)/(Ps)_s$ during intermittent illumination is shown in Fig. 29. Curve 1 shows the behaviour at slow rotation and curve 11 shows the attainment of the steady state at fast rotation. The value of (P)(Ps) when the section is cut at 90° = 0.706 ((P)(Ps) x $1/\sqrt{2}$).

When the rate of the reaction is plotted against sector speed a curve of the type shown in Fig. 30 is obtained. At the period when the flash time approximates to the life time of the radical a change of rate will occur. From this change the approximate value of the life time can be found.

Fig. 31.- Theoretical Curve of Burnett & Melville.



Burnett and Melville (XVII) have shown in an extensive theoretical consideration of this method that the value of the life time is the value of the flash time when the curve is beginning to fall away. They define m as the number of times the flash time (t) is greater than the life time (r), and derive mathematically a curve relating m and $\sqrt{2}(Po)/(Ps)$.

(Po = concentration of radicals during the region of change in rate).

$$\frac{\sqrt{2}(Po)}{(Ps)} = \frac{Po}{Ps/\sqrt{2}} = \frac{\text{Rate in region of change}}{\text{Rate at fast rotation}}$$

This theoretical curve is shown in Fig. 21.

Thus it is only necessary to know the rate at some intermediate speed of rotation and the rate at fast rotation. From this ratio the value of m can be found from the theoretical curve and from this r^2 can be evaluated since by definition -

$$r^2 = t/m .$$

In these experiments the appropriate rates were measured and from the ratio m was found. From this value r^2 was calculated and hence Kp/Kt.

A sample of the experimental results are shown below in Table 25 and Table 26.

Table 25.

K_p/K_t at 20°C.

Rfast. cms/100	Rs. mins	% Rs/Rf	m.	t. secs	r^2. secs	RF. mols/ltre/sec.	K_p/K_t.
0.725	0.610	84.0	5.5	1.0	0.183	0.345×10^{-4}	0.75×10^{-6}
0.56	0.52	93.0	2.7	4.0	.37	0.269×10^{-4}	1.11
0.530	0.490	93.4	2.51	1.0	0.39	0.26×10^{-4}	1.21×10^{-6}

Average Value =

1.04×10^{-6} mols/ltr/sec.

Table 26.

K_p/K_t at 30°C.

Rfast. cms/100	Rs. mins	%Rs/Rf.	m.	t. secs	r^2. secs	RF. mols/ltre/sec.	K_p/K_t.
0.8	0.75	93.8	2.4	1	0.417	0.304×10^{-4}	1.75×10^{-6}
0.69	0.65	94.3	2.37	1.05	0.441	0.314×10^{-4}	1.65×10^{-6}
0.72	0.65	90.4	2.7	1.0	0.383	0.320×10^{-4}	$1.41 c10^{-6}$
0.65	0.60	92.3	2.5	1.0	0.40	0.298×10^{-4}	1.40×10^{-6}
0.59	0.53	90	3.16	1.05	0.403	0.270×10^{-4}	1.3×15^{-6}

Average Value =

1.51×10^{-6} mols/ltre/sec.

t was measured by observing the sector speed by means of a stop watch.

There is a wide margin of error involved in this experimental method and it has been suggested that a factor of two should be applied to the results to cover the possible discrepancies.

Melville and Jones (LI) have shown that if r' is small, for conditions of steady illumination the following expression will hold.

$$d(P)/dt = (P)/r \qquad \text{(a)}$$

$$\left(\frac{d(P)}{dt} = \text{Rate of starting of chains}\right)$$

Since the stationary state is represented by the equation -

$$dp/dt = f(I) - Kt(P)^2 = 0 \qquad \text{(b)}$$

and the rate of polymerization by -

$$-d(M)/dt = Kp(P)(M) = R, \qquad \text{(c)}$$

the following expression can be derived.

$$Kp = R/d(P)/dt \;\; r(M) \qquad \text{(d)}$$

Thus if $d(P)/dt$ could be determined by inhibitor methods (LII-LV), Kp could be evaluated directly.

In this case however, since the photo-chemical reaction is slow, extensive photochemical experiments are impossible.

From the average values of the Kp/Kt term given in tables 25 and 26 the value of Ep-Et can be calculated. This will be subject to the error of this method already quoted and the best value will be that obtained from the average values of a large number of experiments at two temperatures. From this value and from the values of $Ep/Et^{\frac{1}{2}}$ already quoted the individual values of Ep and Et can be calculated.

Average value of Ep-Et = 7.2 k.cals/mol.

From this and earlier values the following energies of activation were obtained.

Ep = 9.8 k.cals/mol.

Et = 2.6 "

Ef = 18.8 "

The individual values of the kinetic constants can be worked out from the values of Kt/Kp^2 and Kp/Kt, which can be calculated at any temperature.

Table 28 shows the results obtained at 70°C together with the energies of activation and the temperature independent factors.

Table 28.

Individual Values for Kinetic Coefficients.

Temp.	Kp,	Kf.	Kt,	Ep,	Ef,	Et,	Ap,	Af,	At.
70°C	110	8.7×10^{-2}	19.1×10^{6}	9.8 ± 2	18.8	2.6	10^{4}	8×10^{4}	9×10^{8}

The values of the kinetic constants for other monomers are shown in Table 29.

Table 29 - Kinetic Constants for Various Monomers.

Monomer.	Temp. °C.	Kp.	Kf.	Kt.	Ep.	Ef.	Et.	Ref.
Methyl Methacrylate	0	41.6	6.13×10^{-4}	2.7×10^{6}	-	-	-	
"	24	310	-	6.8×10^{6}	-	-	1	LVI
"	30	286	-	-	4.4	-	-	XXXI
"	25	273	-	-	6.3	-	-	LV
"	22	128	-	8.4×10^{6}	-	-	-	LXI
"	30	273	-	-	-	-	-	LVII
"	25	512	-	46.6×10^{6}	-	-	-	LIX
Styrene	30	110	8.3×10^{-4}	1.01×10^{6}	-	-	2.4	XXXII
"	25	18.7	6.7×10^{-4}	2.79×10^{6}	6.5	14.2	2.4	LXI
"	30	51.9	-	10.5×10^{6}	6.3	-	-	XXXI
"	25	39.5	6.3×10^{-4}	6.0×10^{6}	-	14.4	1.9	XVII
Vinylacetate	15	750	-	3.9×10^{6}	4.4	-	0	XXXII
"	25	1012	-	5.9×10^{6}	7.3	-	-	LX
"	25	977	-	5.9×10^{6}	-	-	5.2	LXII
"	0	28.0	14.0×10^{-4}	220×10^{6}	3.2	6.1	0	LXIII
Butyl Acrylate	30	13	-	10×10^{6}	-	-	0	LXIV
Methyl Acrylate	25	1730	-	9.4×10^{6}	7.1	-	5.3	XXXII
"	25	720	-	4.3×10^{6}	7.1	-	5.3	XXXII
Vinyl Chloride	25	6.2×10^{3}	-	1100×10^{6}	3.7	-	0	LXV
Butyl Methacrylate	30	379×10^{6}	-	4.5×10^{6}	4.5	-	-	LXVI
Propyl Methacrylate	25	467×10^{6}	-	1100×10^{6}	-	-	-	LXVII
Vinylidene Chloride	25	8.6	-	1.75×10^{5}	25	-	40	LXXII

Tables 28 and 29 show the values of the kinetic constants for this monomer compared with those obtained for other monomers. The diverse values obtained for the same monomer by different workers, using different experimental techniques, show the accuracy which is involved. These differences are mainly due to the wide margin of error encountered in the measurement of Kt.

For the purpose of determining structures of polymers for use in degradation experiments the values which are required are the ratios $Kp/Kt^{\frac{1}{2}}$ and Kf/Kp, which are obtainable from rate and molecular weight data and can be quoted with reasonable accuracy.

Chain Branching.

It was noted at an early stage of the investigation that the molecular weight increased with increasing extent of polymerization. If this molecular weight phenomenon had been due to a 'gel' effect (XXXIV) an increase in rate with increasing conversion would have been noted. Since no effect of this type was encountered the molecular weight increase must be due to chain branching. In the measurement of kinetic constants the conversion was never carried out beyond 2-3% where the increase in molecular weight is not apparent but in bulk polymers prepared for degradation purposes this branching

will be more important and might have a considerable effect on the degradation characteristics.

In order to investigate this phenomenon several experiments were carried out in which polymers were prepared under the same conditions of catalyst concentration and temperature with different % conversions. The molecular weights of these polymers were measured at 27°C in cyclohexanone and the results are shown in Table 30.

Table 30 - Mol. Weights at Different Conversions.

Temp. °C.	Conversion %	Catalyst conc. (%)	Mol. Wt.
70	20	0.025	130,000
70	3	0.025	73,400
80	1	0.50	42,000
80	5	0.50	48,000
80	12	0.50	53,500
60	3	0.025	122,000
60	15	0.025	Polymer insoluble.

The results which are contained in this chapter show that the polymer produced in thermal catalytic

polymerization consist of molecules which are terminated by a disproportionation or a combination reaction. A fairly large proportion of molecules will be terminated by double bond ends due to transfer to monomer, and it is likely that branching occurs to a large extent at higher conversions.

Other References - LXVII, LXVIII.

Chapter VII.

The Thermal Degradation of Polymeth-acrylo-nitrile.

In chapter I the types of degradation reaction undergone by polyvinyl compounds have been discussed and these have been classified under two separate headings as regards their degradation characteristics. According to the small amount of information available, poly-meth-acrylo-nitrile appeared to belong to the group typified by polymethyl methacrylate since it was reported (XI) that this polymer gave monomer in virtually quantitative yield. However it soon became obvious that this reaction is very much more complicated than this and the methods of investigation require to be altered.

Degradation reactions were carried out in the dynamic molecular still described in chapter 2. The polymers were benzoyl peroxide catalyzed and prepared in vacuo as already described. The molecular weights were measured on the modified Fuoss-Mead Osmometer of Masson and Melville using cyclohexanone as solvent. The reactions involving extinction coefficients were followed using the 'Spekker' absorptiometer or the 'Unicam' spectrophotometer as required. Ammonia

estimations were carried out by measuring the depth of colour produced in Nessler's solution as described in chapter 2.

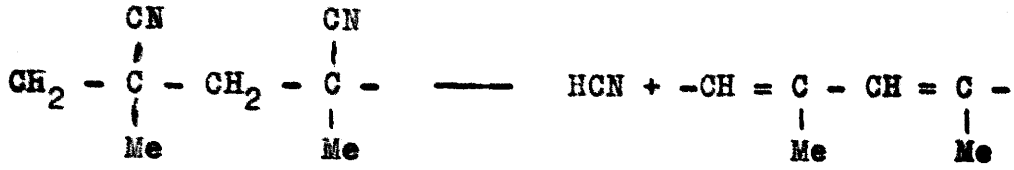
(a) General Degradation Characteristics.

When the polymer is heated in vacuo molting occurs at a temperature of 110-120°C. From this temperature up to 200°C no monomer or other volatile material is produced in large enough quantities to cause a change in pressure inside the still. In this temperature range the polymer becomes deep red. At 210°C monomer production becomes evident and this reaction proceeds quickly to completion at 250-260°C. Above this temperature no further volume of liquid is collected but increased temperature causes a change of pressure inside the still suggesting that more volatile material is being produced. After the monomer is removed a black residue, insoluble in acetone or cyclohexanone, remains.

The effect of ultra violet light on the molten polymer was investigated by directing the radiation from the Osram 125w lamp (Table 1) on to the tray containing polymer at 150°C. No acceleration in monomer production was noted.

(b) Products obtained in the Degradation Process.

The fact that monomer and a black insoluble residue was produced suggested that the reaction might be one in which both types of degradation mechanism, discussed in chapter 1, took place. In this case HCN would be produced leaving a conjugated poly-acetylene chain.



In order to find out if the volatile products contained HCN the yield collected in the liquid air trap 1 was distilled into the side arm 3 of the apparatus and the vapour pressure measured on the monometer. The vapour was expanded into a known volume and the vapour pressure again measured. If the sample is homogeneous no change in vapour pressure will be noted on expansion. If, as discussed in ref. VII, the products consist of several compounds the vapour pressure will remain constant until the liquid of highest vapour pressure evaporates, then change, on successive expansions according to the change in volume, until its vapour

is completely removed. At this point a steady pressure caused by the compound of next highest vapour pressure will be observed.

By observing the number of expansions required for each compound the proportions of each in the product can be determined.

The results obtained by the application of this technique to the volatile products from the degradation of methacrylo-nitrile are shown in Table 31.

Table 31.

Vapour Pressure of Volatile Products from Polymer Degradation.

Temperature,	Vapour Pressure,	Compound.
-70°C	400 mms	CO_2 collected possibly from small leak in still head.
25°C	80 mms	Monomer
Expand into Vi (4.55c.c.)	80 mms	"
"	"	"

The vapour pressure: temperature curve for monomer is shown in Fig. 34.

After a large number of successive expansions the vapour pressure remained constant at the value which would be expected for pure monomer. The initial high pressure is probably due to carbon dioxide collected in the large liquid air trap 1 (Fig. I) from small leaks in the still head. This high pressure does not disappear at solid CO_2 temperatures. HCN under similar conditions at -70°C has a vapour pressure of 1.58 mms.

From this vapour pressure data it is clear that the volatile material produced is totally momomer with no indication of the presence of HCN. When the product is distilled into the liquid air trap 4 in figure I and tested with silver nitrate solution no precipitate is obtained. Thus by chemical as well as vapour pressure methods no HCN can be detected.

Sodium fusion tests on the black insoluble residue indicated the presence of nitrogen and a complete analysis on the micro scale gave results which are shown in Table 29.

Inaccuracies, especially in the nitrogen estimation, are to be expected in the micro analysis of high melting materials and every precaution possible was taken during the experiment. The residue was prepared as a fine powder and the tube tapped during the combustion.

Table 22 - Analysis of Residue.

Polymer.	C %	N %	H %	Insol. Residue %
Heated to 250°C.	67.31	13.32	7.16	3.40
Heated to 300°C.	68.9	19.7	7.26	-
Undegraded Polymer.	71.7	20.9	7.4	

From the analysis of the products it is clear that no reaction involving the production of HCN leaving a conjugated double bond polyacetylene residue is occurring. The residue under these conditions has the same analysis (within experimental error) as the original polymer.

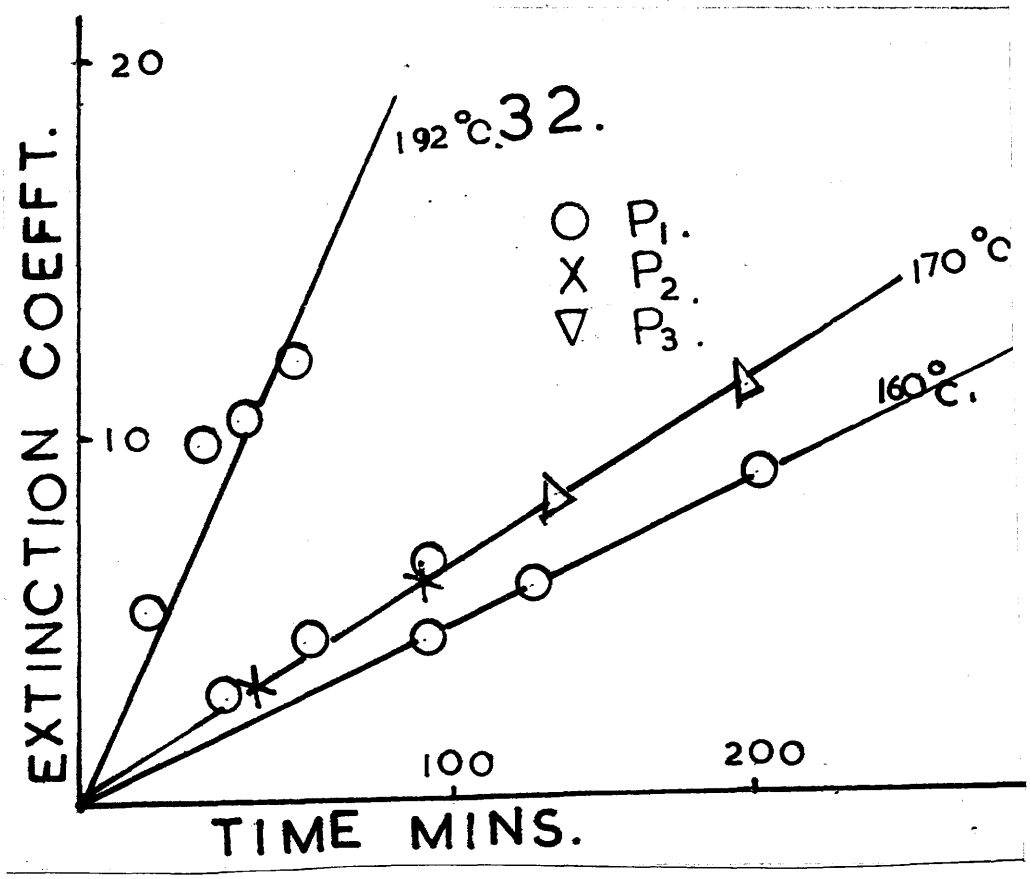
When a polymer sample is heated in air, in a test tube over a bunsen flame, a gas is produced which turns red litmus paper blue suggesting that at higher temperatures ammonia is being produced.

The yield of monomer, measured in the calibrated capillary tube 2 (Fig. I) at 250°C., is 50-55%.

(b) The Colour Reaction.

The colour which is produced when the polymer is heated at low temperatures was investigated quantitatively by determining the extinction coefficient for different times of heating. An initial investigation of the absorption spectrum showed that absorption was occurring

Fig. 32.- Rate of Colour Reaction.



in the region 4,000-5,000 angstroms. Accordingly, in the 'Spekker' measurements of the optical density the blue-green filter No. 603 was used which is transmitting light of this required wave length.

The solvent used for the red polymer was 'analar' acetone which had been distilled through a glass spiral column. The results obtained and the concentrations used are shown below in Table 30 and summarized in Fig. 33. The polymers denoted P_1, P_2 and P_3 were benzoyl peroxide catalyzed prepared at 80°C (1 x 2) and 70°C (3) respectively. They were isolated and treated in the manner described in chapter 2. The molecular weights were measured in cyclohexanone at 27°C.

Table 33.

Polymer.	M.W.	Temp. °C.	Concentration,	Time,	$\log^{I_o}/I$,	Ext. Coefft.
P 1.	54,600	170	0.2728g/100c.c.	60 mins.	1.19	4.36
"	"	170	0.1970 "	90 "	1.23	6.24
"	"	170	0.1852 "	40 "	0.533	2.90
"	"	192	0.0857 "	30 "	0.833	9.71
"	"	192	0.0430 "	60 "	0.492	11.62
"	"	192	0.1766 "	17½ "	0.900	5.70
"	"	192	0.0922 "	45 "	0.950	10.03
"	"	160	0.1159 "	180 "	1.01	8.6
"	"	160	0.1294 "	90 "	0.546	4.24
"	"	160	0.1108 "	120 "	0.736	6.5
P 2.	130,000	170	0.1073 "	90 "	0.625	5.82
"	"	170	0.0961 "	40 "	0.385	2.64
P 3.	36,000	170	0.141 "	45 "	0.352	2.5
"	"	170	0.684 "	180 "	0.750	11.0
"	"	170	0.0828 "	135 "	0.745	9.0

From the above results it is evident that the molecular weight of the polymer has no effect on the rate of the colour reaction. The production of colour depends on the number of monomer units rather than the number of polymer

Fig. 33.- Absorption Spectra of Red Polymers.

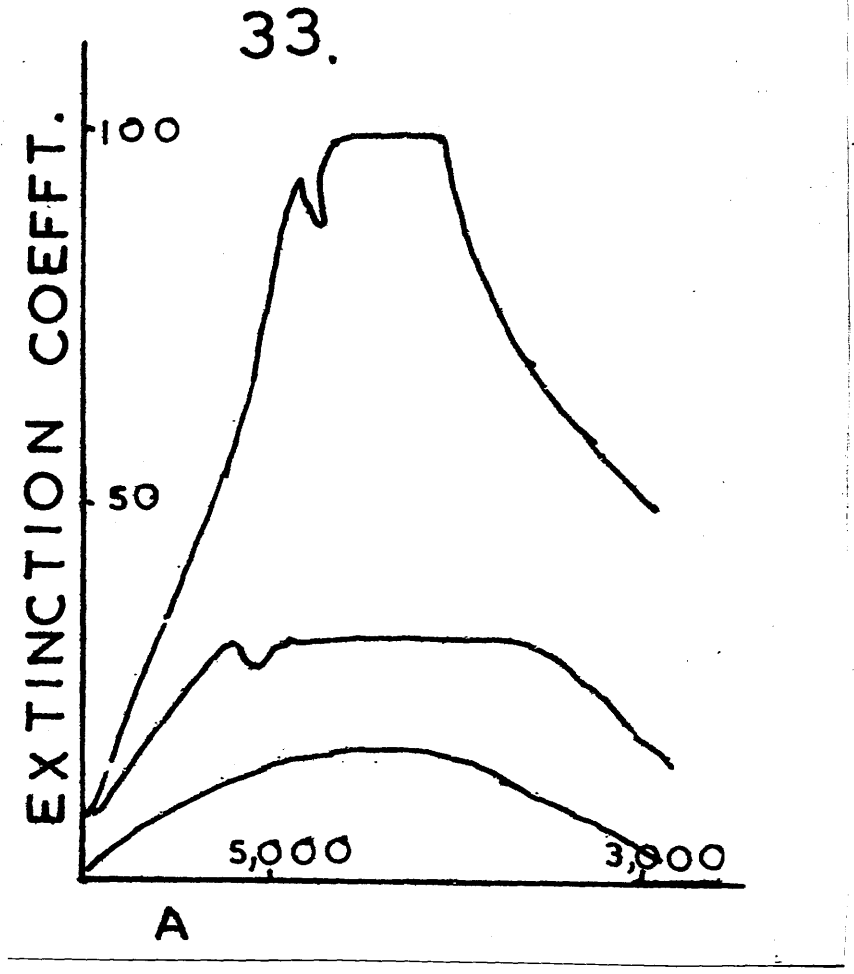
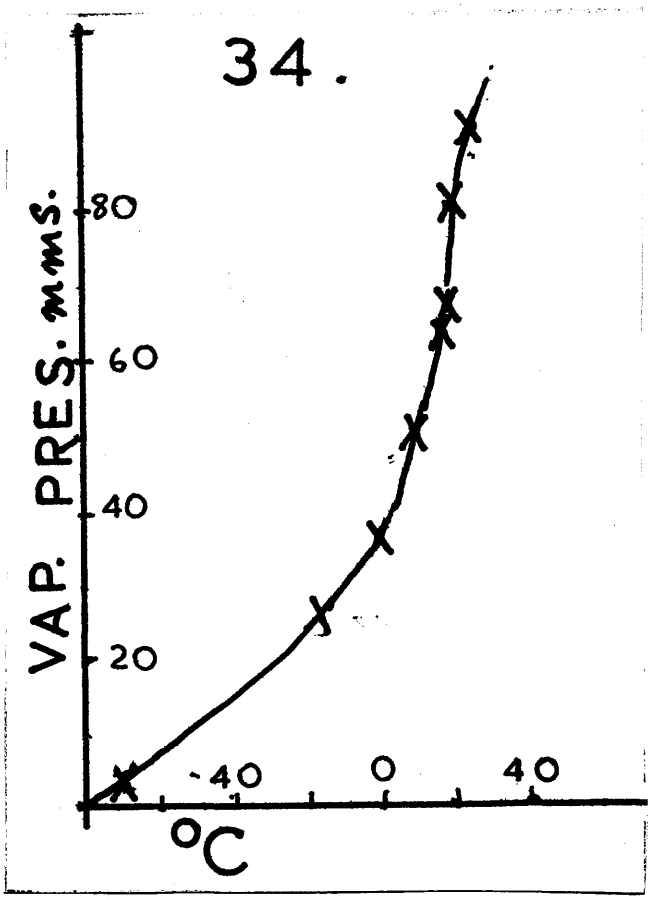


Fig. 34.- Vapour Pressure Curve for Methacrylo Nitrile.



molecules. Any suspicion that the colour is due to a change in structure at the chain ends is therefore eliminated.

The energy of activation of the colour reaction was calculated from the rates at the three temperatures shown above. These results are shown in Table 31 and summarized in Fig. 33.

Table 34.

Rate, E/100 mins.	T°A,	$^1/T°A$,	Log R.
22.0	465	2.14×10^{-3}	1.37
6.8	443	2.26×10^{-3}	0.842
4.6	433	2.313×10^{-3}	0.660

E = 20.0 k.cal/mol.

The complete absorption spectra of three polymer samples heated for different lengths of time at 170°C were measured on the 'Unicam' ultra violet spectrophotometer. The values of the extinction coefficients were calculated from concentration values of base gm. mols./litre. These curves are shown in Fig. 34. Absorption over a wide range occurs so that no conclusion can be drawn about the group responsible for the production of colour.

Effect of Coloration on Molecular Weight.

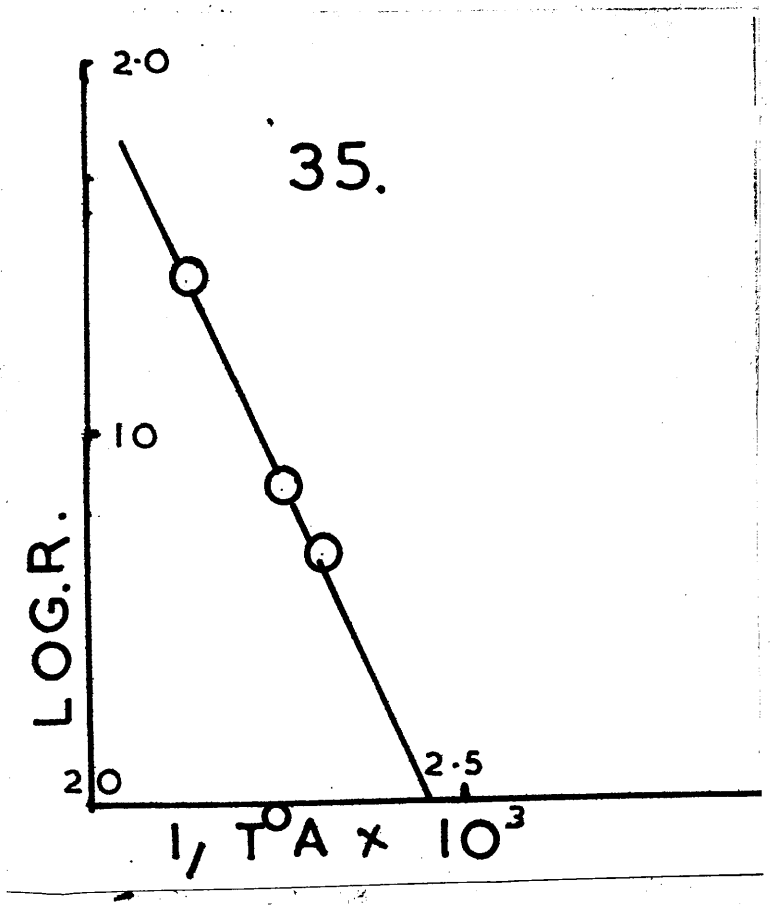
Since the polymer becamse insoluble at higher temperatures it might be expected that the production of colour was connected with a cross linking reaction causing an increase in the molecular weight. In order to check this theory samples of polymer of known molecular weight (37,700) were heated for different lengths of time at 170°C. and the molecular weight of the red polymer measured in cyclohexanone at 27°C. The results are shown in Table 32.

Table 35.

Time Heated.	$\frac{II}{C_o}$.	Mol. Wt.	Temp.
0	6.68	37,700	170°C.
90 mins.	6.41	39,400	170°C.
3½ hours	6.36	39,600	170°C.
6 hours	6.36	39,600	170°C.

From the data shown above it is evident that no marked increase in molecular weight occurs as the colour reaction proceeds. The slight increase which is shown is probably due to a cross-linking reaction occurring independently of the colour reaction.

Fig. 35.- Energy of Activation of Colour Reaction.



(d) Production of Monomer

Kern and Ferow (XI) reported 80% yield of monomer at 250°C. Under the conditions of vacuo and careful temperature control employed in these experimental techniques 50% monomer is recoverable at 250°C. The rate, measured on the pirani, decreases uniformly to zero at 50% degradation at 250°C. As the temperature is raised, more monomer is produced but rate measurements are complicated by the production of a volatile material which does not condense effectively in liquid air.

The temperatures and volumes obtained are shown in Table 36.

Temp.°C	% Monomer.	Polymer.
250	50%	M.W. 53,500
300	53.5%	
310	60%	

The energy of activation of the monomer reaction was measured by finding the rates at various temperatures from the pirani gauge. This data is shown in Table 37 and summarized in Fig. 36.

Fig. 36. - Energy of Activation of Production of Monomer.

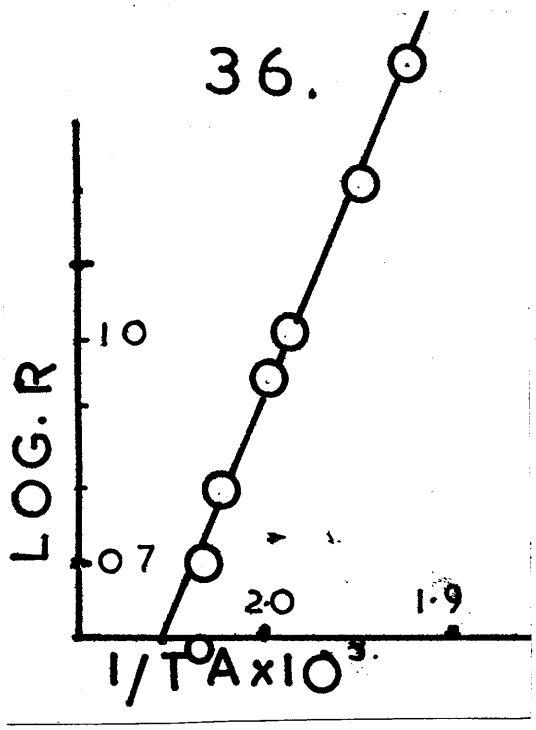


Table 36.- Energy of Activation of Monomer Reaction.

Temperature. T°C.	T°A.	$^1/T \times 10^3$.	Rate. $\frac{V^2 - V_o^2}{V_o^2}$	Log R x 10.
260	533	1.87	1.39	1.143
256	529	1.895	1.24	1.093
251	524	1.916	0.768	0.885
250	523	1.918	0.654	0.816
246	519	1.931	0.493	0.693

Energy of Activation = 24.2 k.cals/mol.

Reaction at High Temperatures.

When the temperature goes above 300°C a pressure registers on the pirani although no further yield of monomer is obtainable. When the products are distilled into liquid air trap 4 containing water and then tested with Nessler's solution, prepared as described in chapter 2, the characteristic brown coloration produced by ammonia appears.

The rate of production of volatile material at high temperatures was measured by observing the change in pressure inside the still and the energy of activation calculated. The data is given in Table 37.

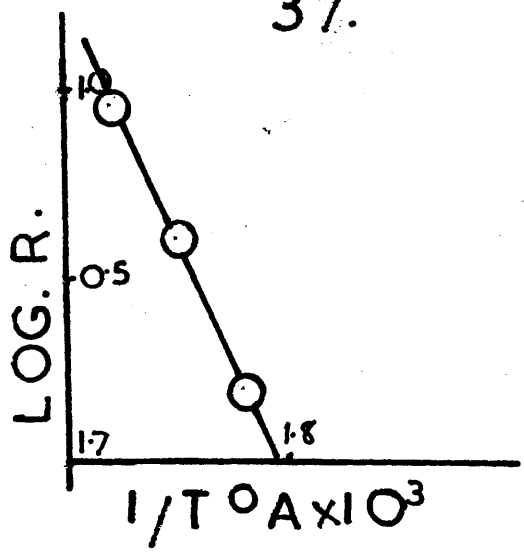

LOG. R.
1·0
0·5
1·7
1·8
1/T °A x 10³

Table 37.

Temperature. T°C.	T°A.	$^1/T \times 10^3$.	Rate $\frac{V^2 - Vo^2}{Vo^2}$.	Log R x 10.
312	581	1.725	.952	9786
283	556	1.795	.164	2148
296	570	1.760	.391	5922

From these results an energy of activation curve was drawn and is shown in Fig. 36.

E = 67 k.cals/mol.

Ammonia estimations were carried out using Nessler's solution as described earlier.

The results are shown in Table 38.

Rate.	Log R x 10^5.	T°A.	$^1/T°A \times 10^3$.
4.20×10^{-5} gms/100 mins.	0.623	573	1.739
1.03×10^{-5} "	0.128	563	1.789
2.1×10^{-5} "	0.322	567	1.765

E = 53 k.cals/mol.

There is some doubt about the absolute validity of these results since it was suspected that ammonia is not being effectively condensed in liquid air in the apparatus used. A modification where the reaction is carried out in a closed system with a series of liquid air traps is probably required.

In conclusion therefore, the thermal degradation of polymethacrylo-nitrile probably consists of a number of apparently quite distinct processes. Monomer is probably produced by a mechanism of a similar type to methyl methacrylate but on the surface the reaction producing colour, monomer and ammonia are not connected. The energies of activation have been determined for each type of reaction but there is no correlation between any pair of them. It is not immediately obvious how any more information about this reaction can be obtained from the pure polymer and one of the most hopeful approaches would appear to be an examination of carefully prepared co-polymers where the number and length of the methacrylo-nitrile unit sequences are accurately known.

Chapter VIII.

Conclusions and Summary of Work.

The work discussed in this thesis may be summarized under two headings-

(A) By an extension of previous degradation work to transferred polymers it has been shown that of the two types of end groups produced by the disproportionation of two growing radicals in the polymerization of methyl methacrylate the species possessing the double bond end structure is least stable.

If termination occurs by disproportionation and transfer by abstraction of a hydrogen atom from a benzene molecule leaving a phenyl group to initiate a new chain it is shown that the relative proportions of single and double bond ends can be calculated from molecular weight and concentration data. These calculated values were found to be in good agreement with values calculated from initial rates of degradation and from the amount of degradable material at different temperatures. These results are a good check on the postulated theories of termination and transfer and the results cannot be explained by any other mechanism.

(E) The work then moved to a consideration of the degradation of polymethacrylo-nitrile but as no details of the polymerization process were available the kinetic constants were first determined. In this work the values of the propogation, transfer and termination constants were evaluated together with the appropriate energies of activation and temperature independent factors.

In these experiments, in which molecular weight measurements were required, some interesting osmotic phenomena were encountered. When methyl ethyl ketone was used as solvent S shaped $^{II}/C$: C curves were obtained. These are explained in terms of polymer solvent and polymer - polymer attraction. Further investigation showed that cyclohexanone is a completely satisfactory solvent for osmotic measurements.

The thermal degradation reaction of polymethacrylo-nitrile was found to be different from the general type of degradation reaction already discussed in the literature. At temperatures below that at which monomer is produced the polymer gradually became red. This colour reaction was investigated quantitatively as was the production of monomer which takes place at higher

temperatures.

Above 300°C ammonia appears in small quantities and this reaction is also discussed. An extension of this work to include copolymers with methyl methacrylate is finally suggested.

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