THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

THE THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND METHYL ACRYLATE AND SOME RELATED TOPICS.

BY

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PREFACE.

The work described in this thesis was carried out in the period October 1963 to September 1966, at the University of Glasgow in the Department of Physical Chemistry, which is under the general supervision of Professor J. M. Robertson, C.B.E., F.R.S.

My thanks are due to the U.S. Rubber Company and to the U.S. Air Force (Department of Aerospace Research) for the awards of Research Scholarships for the academic years 1963-65 and 1965-66 respectively, and during the tenure of which this work was carried out.

Thanks are also due to members of the Technical staff of this department for providing general technical assistance, particularly Messrs. R. Smith and G. Perrit who carried out most of the molecular weight measurements.

I am also grateful to the other members of the Macromolecular Chemistry Section for discussions and assistance and particularly to Messrs. J. Colford and L. Davidson who provided some of the material for Chapter 6.

Finally I wish to thank most sincerely Dr. N. Grassie for suggesting the problem and for his general supervision and great help with this work.

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CHAPTER 1.

INTRODUCTION

(1) INTRODUCTION

Synthetic polymers have become commercially important in the past thirty years and, particularly in recent years, their commercial growth has been closely associated with the development of the petroleum industry. Commercial application of polymeric materials required their stabilisation towards physical and chemical factors such as heat, light, mechanical stress, oxidation and hydrolysis some or all of which are encountered during their manufacture and use. Initially empirical methods of stabilisation were developed, however, it soon became apparent that more efficient stabilisation would be achieved if the reaction mechanisms of breakdown or degradation of the polymers were more completely understood. It was factors of this kind which led to intensive studies of polymer degradation being made. Interest in the subject in recent years has been emphasised by the publication of several monographs$^{1-6}$.

The overall deteriorative ageing or weathering of a polymer is usually very complex chemically due to the numerous factors involved and ultimate interest is naturally a consideration of the simultaneous operation of all the factors. Fundamental information, both of industrial and academic interest, can more easily be obtained, however, from the consideration of each factor independently. Thus a great deal of work has been carried out on the thermal and photochemical degradation of polymers under high vacuum so that there is no interference from oxidative processes.

The bulk of these degradation studies have been carried out on vinyl addition polymers, due to their commercial importance and their degradation characteristics are in general well understood, and can be classified into two main groups. This classification has been dealt with in detail[6]. Thus it is convenient to give only a brief outline at this point.

(2) CLASSIFICATION OF DEGRADATION REACTIONS OF VINYL POLYMERS.

The classification of a polymer into one of the groups below, is usually accomplished from a study of molecular weight changes, changes in the structure of the polymer residue and the products formed, during the degradation of the polymer.

(i) Chain Scission or Depolymerisation Reactions.

Depolymerisation reactions are characterised by the breaking of the main polymer chain backbone with the production of various chain fragments such as monomer, dimer, trimer etc., and usually with an accompanying decrease in molecular weight. Apparent distinct types of behaviour occur within this group. Thus poly(methylmethacrylate), thermally degraded at 220°C[7] and photochemically degraded by 2537 Å radiation at 160-180°C[8], gives quantitative yields of monomer, the molecular weight decreasing gradually throughout the reaction. However, when poly(styrene) is thermally degraded at temperatures above 300°C[9], a mixture of monomers (42%) and decreasing amounts of dimer, trimer and tetramer are produced whilst a rapid decrease in molecular weight occurs early in the reaction. Poly-(ethylene), thermally degraded at temperatures above 290°C[10], gives long chain olefin fragments, and the molecular weight drops rapidly early in the reaction. In contrast to poly(styrene), however, little monomer is formed.

All of those reactions can be accounted for by a single free radical mechanism which is somewhat similar to the reverse of the vinyl monomer polymerisation reaction. This depolymerisation reaction can be represented as follows[11-13],

Random Initiation,	$M_n \xrightarrow{k_i} P^\circ_j + P^\circ_{n-j}$,
Terminal Initiation,	$M_n \xrightarrow{k_i} P^\circ_{n-1} + P^\circ_1$,
Depropagation,	$P^\circ_i \xrightarrow{k_d} P^\circ_{i-1} + M_1$,
Intermolecular Transfer,	$P^\circ_i + M_n \xrightarrow{k_f} M_i + P^\circ_n$,
Intramolecular Transfer,	$P^\circ_n \longrightarrow P^\circ_j + M_{n-j}$,
Termination,	$P^\circ_i + P^\circ_j \xrightarrow{k_t} M_i + M_j$ or M_{i+j} ,

in which n is the chain length of the starting material and M_i M_j etc., and P°_i P°_j etc., represent dead polymer molecules and long chain radicals i j etc., monomer units in length. The different behaviours described above depend essentially upon the interplay of depropagation and transfer.

Thus poly(methylmethacrylate) thermally degrading at 220°C has been shown to undergo initiation at unsaturated chain ends[7] and depropagation predominates over transfer, resulting in a gradual decrease in molecular weight and the production of quantitative yields of monomer. Poly(styrene) on the other hand has been shown to undergo random chain scission at weak links in the chain[9], giving the rapid drop in molecular weight, depropagation and transfer both occuring from chain ends resulting in a mixture of products. In the case of poly(ethylene) random chain scission occurs as the result of intermolecular transfer reactions[10] which are predominant, producing chain fragments and little monomer.

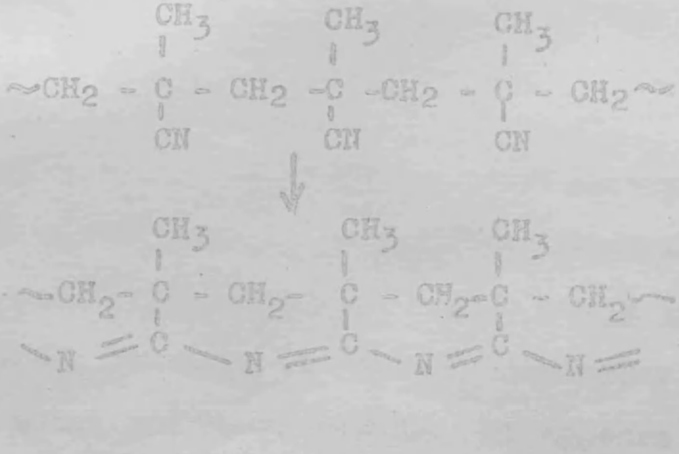
In general the predominance of depropagation or transfer can be related to the structure of the polymers. Where the polymer is made from a disubstituted monomer, such as methyl methacrylate, the intermediate radicals are sufficiently stable to allow depropagation to predominate. However, where the monomer is monosubstituted the polymer will contain labile tertiary hydrogen atoms and the intermediate polymer radicals will be very much more reactive. Both of these factors clearly favour transfer. Poly(styrene) is an exceptional case since the intermediate radical is highly stabilised by resonance with the aromatic nucleus and transfer and depropagation are finely balanced.

(ii) Non Chain Scission or Substituent Reactions.

In these type of reactions the substituent groups in the polymer are modified either by rearrangement, or decomposition. Thus the volatile products of degradation, if any, comprise substances other than monomer. If these reactions are going to occur, clearly they must take place at temperatures below those at which depolymerisation usually proceeds ($>200^{\circ}C$).

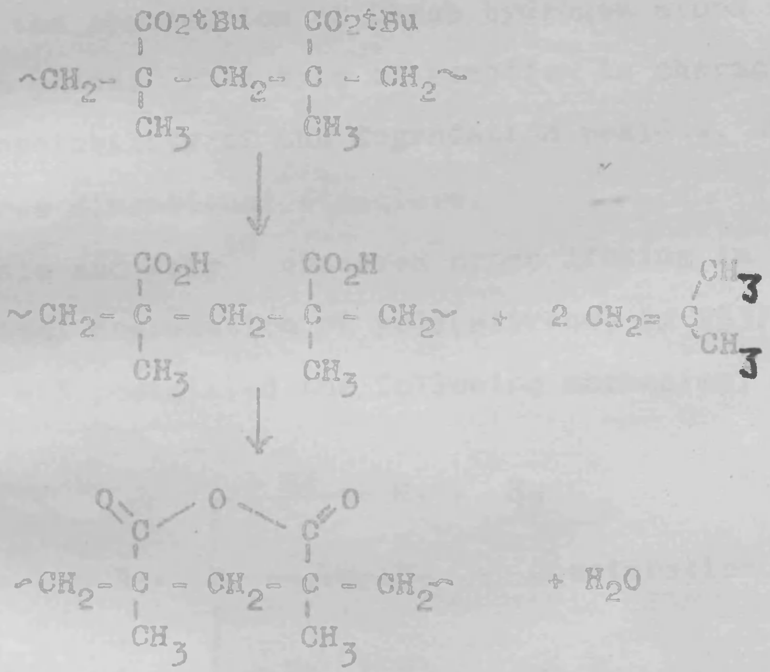
(a) Rearrangement Reactions.

A typical rearrangement reaction occurs on heating poly(methacrylonitrile) at about $200^{\circ}C$[14,15]. At temperatures greater than $220^{\circ}C$ depolymerisation occurs. The rearrangement reaction shown below is completely seperable from the depolymerisation reaction and is characterised by the formation of colour in the degradation residue due to the conjugated -C=N- linkages.



(b) Elimination Reactions.

Many ethylenic type polymers contain ester groups and like short chain esters decompose thermally to acid and olefine Poly(tert-butylmethacrylate), for example, gives quantitative yields of isobutene at 200°C[16]. The methacrylic acid units also formed react in pairs to eliminate water so that poly(methacrylic anhydride) is the final involatile product.

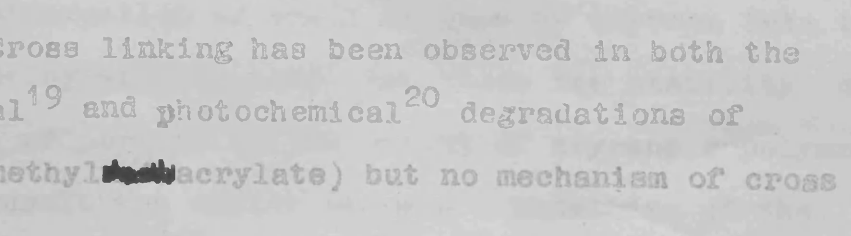


Although depolymerisation and ester decomposition occur almost quantitatively in poly(methylmethacrylate) and poly(tert-butylmethacrylate) respectively they are much more finely balanced in other polymethacrylates such as the ethyl and butyl esters. It appears that, in general, the yield of monomer is smaller the more readily ester decomposition occurs since the anhydride structures which are the ultimate products of ester decomposition block the chains to the passage of the depolymerisation process[17].

(c) Cross Linking Reactions.

Cross linking is a special kind of substituent reaction. It frequently occurs in vinyl polymers which have labile tertiary hydrogen atoms since radicals formed by the abstraction of these hydrogen atoms can combine in pairs. This type of reaction is characterised by insolubility of the degradation residue, due to its three dimensional structure.

Grassie and Weir[18] observed cross linking in the photochemical degradation of poly(styrene) by 2537 Å radiation and postulated the following mechanism,



Cross links.

Cross linking has been observed in both the thermal[19] and photochemical[20] degradations of poly(methyl[redacted]acrylate) but no mechanism of cross linking has been proposed.

(3) DEGRADATION OF COPOLYMERS.

Copolymers are industrially important materials since the useful properties of a polymer such as thermal or photochemical stability, adhesion, solubility, and physical properties in general, can often be favourably influenced by the addition of a monomer. However Farish and Grassie[21] pointed out that no detailed study of copolymer degradation behaviour had been carried out, in contrast to the large amount of work carried out on homopolymers. These authors began a systematic study of copolymer degradation behaviour, choosing comonomers whose individual homopolymer degradation had been well characterised. They studied the two systems, methyl methacrylate/styrene and methyl methacrylate/acrylonitrile.

It was revealed by these studies that it is unwise to assume that the degradation properties of the copolymer can be readily predicted from the behaviour of the two corresponding homopolymers. For example, the introduction of small amounts of styrene into the poly(methylmethacrylate) increases its stability out of all proportion to the amount of styrene copolymerised. This result was explained from a knowledge of the termination reactions during the copolymerisation and homopolymerisation. Bevington and co-workers[22] found that in the copolymerisation of methyl methacrylate and styrene termination is mostly by combination of radicals, leading to saturated chain ends, whilst Grassie and Vance[23] showed that disproportionation is predominant in the termination of poly(methylmethacrylate) forming unsaturated chain ends. Since depropagation occurs from these unsaturated ends in poly(methylmethacrylate) then obviously the copolymer will be more stable, depropagation occuring only from points of random chain scission at higher temperatures.

The study of the methyl methacrylate/acrylonitrile copolymer systems showed that the copolymers degraded in a manner totally different than for the individual homopolymers. Thus the introduction of acrylonitrile into the poly(methylmethacrylate) caused the chains to undergo random chain scission. However an increase in the concentration of the acrylonitrile units decreased the rate of chain scission. Farish and Grassie suggested that the acrylonitrile units may not be directly associated with these apparent weak links but may simply inhibit the end-initiated depolymerisation, thus accentuating the random chain scission which can occur in poly(methylmethacrylate) . Acrylonitrile monomer was found among the products of degradation so that depropagation reactions from these points of chain scission can pass through acrylonitrile units, which is surprising, since poly(acrylonitrile) produces only negligible amounts of monomer[24].

In the photochemical degradation of these copolymers random chain scission occurs, the rate of chain scission increasing with increasing acrylonitrile content, thus Farish and Grassie concluded that in this case the acrylonitrile units are directly responsible for chain scission in contrast with the thermal reaction. However the precise nature of the chain scission is not understood.

(4) AIM OF THE PRESENT WORK.

From the degradation results for these two copolymer systems it can be seen that the systematic study of copolymer degradation as well as being of interest for its own sake, can give information in some cases, which is helpful in elucidating the degradation reactions occuring in the individual homopolymers. The present work is therefore a continuation of these studies of copolymers, retaining methyl methacrylate as one component, and copolymerising it with acrylates, which have quite different degradation characteristics because of their tertiary hydrogen atom. These systems are of especial interest since acrylates are used industrially in this way as stabilisers for poly(methylmethacrylate).

The main part of the work is devoted to the investigation of the thermal degradation of the methyl methacrylate/methyl acrylate copolymer system over a wide range of composition. Poly(methylmethacrylate) degrades at 220°C by depropagation from unsaturated chain ends resulting in quantitative yields of monomer[7]. At higher temperatures (>300°C) it has been proposed by M^cCallum[25] that random chain scission occurs, but since depropagation is predominant and the "zipp length" is very long, the molecular weight does not drop as sharply as might be expected for a random scission process. However the molecular weight of poly(methylacrylate) being degraded at 280-300°C decreases rapidly due to transfer[19]. Since transfer is predominant chain fragments (>75%) and very little monomer (≤1%) are produced[26]. However methanol(15%) and carbon dioxide (7%) are found among the products and must be formed in some sort of substituent reactions[26]. Cross linking also occurs since an insoluble gel is formed during the reaction[19].

It is hoped that a study of the degradation characteristics of copolymers of a range of compositions will help to determine the form of the substituent reactions producing methanol and carbon dioxide.

A smaller amount of work has been devoted to the study of the photochemical degradation of the system by 2537 Å radiation. Poly(methylmethacrylate) degrades photochemically by the same mechanism as the reaction at 220°C[7]. However in poly(methylacrylate) cross linking becomes more significant, chain scission still occurs and products derived from the ester substituent, such as formaldehyde, methyl formate, methanol and carbon dioxide are formed[20]. Thus it is of interest to study the copolymers to find which influence predominates.

A start has also been made to study the thermal degradation of methyl methacrylate/ ethyl acrylate copolymers. The thermal degradation of poly(ethylacrylate) has not been studied. It should be expected to be typical of acrylate degradation, however, except that ester decomposition reactions are possible in this case in contrast to poly(methylacrylate).

CHAPTER 2

APPARATUS AND EXPERIMENTAL TECHNIQUES.

SECTION 1

(1) PREPARATION OF COPOLYMERS.

(i) Introduction.

It is necessary to prepare copolymers for degradation studies in a high state of purity in order to eliminate the possibility of incorporation of impurities in the copolymer chain, since abnormal degradation reactions could conceivably occur at such points.

The sections below (ii)-(iv) detail the experimental methods of achieving this high state of purity. Analar reagents were used wherever possible, otherwise the reagents were purified as described.

(ii) Monomer feed Composition.

(a) Copolymer Equation.

The copolymer equation[27-30]

$$\frac{dA}{dB} = \frac{A\,(\,r_aA + B\,)}{B\,(\,r_bB + A\,)}$$

relates the ratio $\frac{dA}{dB}$ of the moles of monomers A and B entering a copolymer at any instant, to the molar composition of the monomers in the starting mixture. r_a and r_b are the reactivity ratios of monomer A and monomer B respectively.

Provided the copolymerisation is restricted to a low percentage conversion where the monomer feed concentrations are assumed not to change significantly, then $\frac{dA}{dB}$ is equivalent to the molar concentrations of the two monomers in the copolymer.

Thus by copolymerising monomer mixture of known molar composition to a low percentage conversion copolymers of a given composition can be prepared, provided the reactivity ratios of the monomers are known.

For the systems methyl methacrylate/methyl acrylate and methyl methacrylate/ ethyl acrylate at the time when this work was started no values of the reactivity ratios for the radical polymerisation had been reported due principally to the difficulty of analysis of the copolymers.

We found it possible to determine reactivity ratios from proton magnetic resonance (P.M.R.) spectroscopic analysis of the copolymers. Thus the monomer feed necessary to produce a polymer of any required composition could be calculated. The values found for the reactivity ratios are shown in Table 1.

Table 1.

Reactivity Ratios Determined by P.M.R. analysis.

MONOMER SYSTEM.	TEMPERATURE OF POLYMERISATION.	r_a	r_b
Methyl methacrylate (A) Methyl acrylate(B)	65°C	1·8 ± 0·4	0·35 ± 0·1
Methyl methacrylate(A) Methyl acrylate(B)	60°C	2.03 ± 0.12	0.24 ± 0.12

(b) Use of P.M.R. to Obtain Reactivity Ratios.

P.M.R. spectra were obtained on a Perkin-Elmer R 10 60Mc/s spectrometer with integrator, using 20mg. copolymer samples dissolved in 1ml. of deuterated chloroform. The copolymer samples were prepared from monomer mixtures of known composition (Section 1-(i)-(iv)). Ten integrals were obtained for each sample and the average integral used to determine copolymer composition and thus reactivity ratios, by use of the copolymer equation.

(iii) Purification of Materials.

Methyl methacrylate (I.C.I.Ltd.) methyl acrylate and ethyl acrylate (B. D.H. Ltd.) monomers were washed with dilute caustic soda solution to remove inhibitors, subsequently with distilled water to remove residual alkali, and dried over calcium chloride. The monomers were then vacuum distilled, the middle fraction of the distillate being retained, and stored at -18°C till used.

The polymerisation initiator 2:2'azo-iso-butyronitrile was purified by recrystallisation from methanol.

(iv) Polymerisation Technique.

The copolymers were prepared by bulk polymerisation under high vacuum in pyrex dilatometers with stems graduated to 0·01ml.

The apparatus used for filling the dilatometers is shown in figure 1. A pressure of the order of 10^{-5} mm. of mercury was obtained by the use of a rotary oil pump backed by a mercury diffusion pump (both by Edwards High Vacuum Co.)

0·075% w/v initiator was introduced into the dilatometer in benzene solution, the solvent being subsequently removed under vacuum. The purified monomers were degassed in their respective reservoirs by alternate freezing in liquid nitrogen and thawing under vacuum.

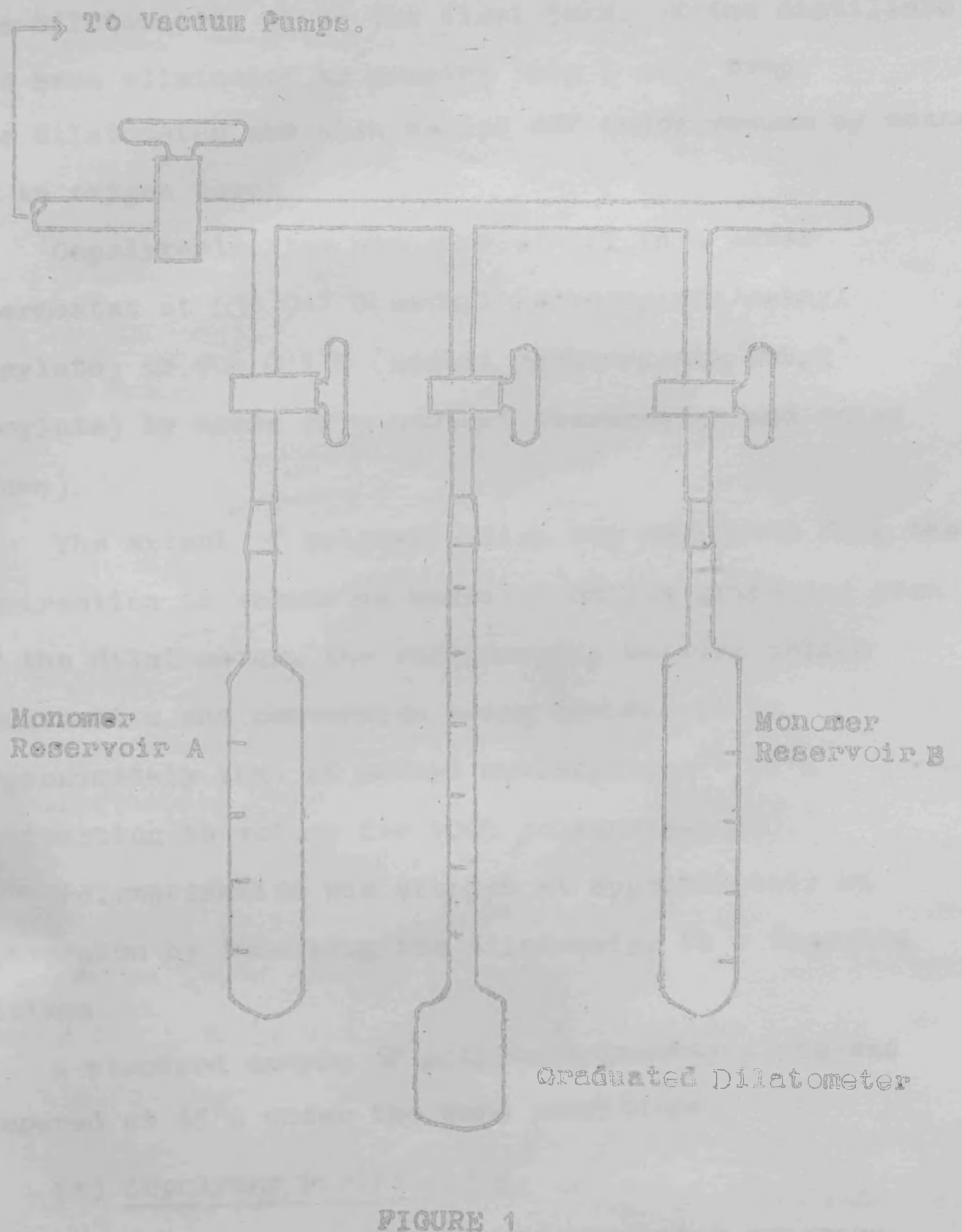


FIGURE 1

Apparatus for Filling the Dilatometers

Calculated amounts of the monomers were distilled into the dilatometer, after the first 5mls. of the distillate had been eliminated by pumping into a cold trap. The dilatometer was then sealed off under vacuum by means of an oxygen torch.

Copolymerisation was carried out in a water thermostat at 65± 0·1°C(methyl methacrylate/methyl acrylate) or 60± 0·1°C (methyl methacrylate/ethyl acrylate) by means of a contact thermometer and relay (Jumo).

The extent of polymerisation was estimated from the contraction in volume as measured on the graduated stem of the dilatometer, the relationship between volume contraction and conversion being assumed to be approximately that of methyl methacrylate[31] (21% contraction in volume for 100% polymerisation).

Polymerisation was stopped at approximately 8% conversion by immersing the dilatometer in a freezing mixture.

A standard sample of poly(methylmethacrylate)was prepared at 65°C under the same conditions.

(v) Copolymer Purification.

The mixture of copolymer and unreacted monomers was dissolved in chloroform and the copolymer precipitated by dropwise addition of this solution to about three times its volume of methanol. This process was repeated three times to remove all the unreacted monomers.

The copolymers were finally dried in a vacuum oven at 50°C for 24 hours and ground to a fine powder (120 mesh). The copolymer powder was then further dried in the vacuum oven, to remove all volatiles used in the precipitation.

(2) PREPARATION OF COPOLYMER FILMS.

(i) Introduction.

The copolymer can be degraded in the solid state as a powder or film. The degradation of a powdered polymer below or near its melting point can lead to irreproducible experimental data, arising from diffusion effects of the products of degradation due to variables such as surface area, particle size and layer thickness. The use of films usually gives more reproducible results since the surface area and thickness of the sample can be standardised.

(ii) Casting of Films From Chloroform Solution.

15-20mg. of the copolymer powder was dissolved in 5ml. chloroform and the solution filtered on to purfied mercury in a 30ml. beaker. The beaker was left for 18 hours at room temperature and the film of polymer formed by evaporation of the chloroform removed by cutting round its edge with a scalpel. The film was later dried in the vacuum oven at 50°C for 24 hours.

(iii) Pressing of Films.

1-20mg. of copolymer powder (120 mesh) was pressed in a 1·3cm. diameter die by means of a 30 ton hydraulic press (Research and Industrial Instrument Co.) with a pressure of approximately 8 tons per square inch applied.

The main advantage of this method is that the film is not contaminated with solvent.

SECTION 2 - DEGRADATION METHODS.

(1) INTRODUCTION.

Thermal and photochemical degradation reactions are usually studied under high vacuum to eliminate the possibility of oxidation of the sample. Further reaction of the products in the degradation zone is also minimised since they are swept quickly away. The kinetics of the degradation reaction can be followed from rate measurements either in an open or a closed flow system.

The former method was applied by Grassie and Melville in their dynamic molecular still[7] a modified form of which was used in the present work[32].

The latter method has been applied by Murphy[33] but there are limitations in that the pressure build up of products in the closed system may influence the degradation behaviour of the polymer. It was, however, necessary to use this method in conjunction with the d.m.s. due to the possibility of catalysis of ester group breakdown since it has been observed[34] that copper catalyses abnormal ester group decomposition in the thermal degradation(260-300°C) of poly(methyl-acrylate).

(2) DYNAMIC MOLECULAR STILL.

(i) Introduction.

The glassware of this apparatus is illustrated in figure 2. The copolymer in the form of a powder or film can be degraded thermally or photochemically under vacuum. If the rate of removal of volatile products is constant, that is, if a uniform pumping rate is maintained, then the rate of production of volatiles is measured by the small transient pressure developed and is measured by a Pirani gauge.

(ii) Measurement of Rate of Volatilisation.

The Pirani gauge in figure 2 consisted of a stretched tungsten filament (50ohm), suspended by cold pressing between the ends of a 18 gauge copper wire supports. The gauge formed one arm of a Wheatstone Bridge circuit as shown in figure3.

The d.m.s. was evacuated to a pressure of about 10^{-5} mm. mercury, and the Pirani bridge balanced by applying a voltage V_0. The measurement of the pressure by the Pirani gauge depends on the fact that if the pressure of a gas in thermal equilibrium with the hot wire is increased, the temperature and thus the resistance of the wire falls, due to the thermal conductivity of heat from the wire by the gas. A higher voltage V at pressure p is thus required to balance the bridge.

At low pressures the term $\frac{V^2 - V_o^2}{V_o^2}$ is proportional to the pressure in the system. It is clearly important that the temperature of the pirani jacket is maintained constant and this was achieved by immersion in melting ice. The constant rate of removal of volatiles was achieved by condensation of the volatiles in liquid nitrogen, and thus the transient pressure $\frac{V^2 - V_o^2}{V_o^2}$ is a measure of the relative rate of volatilisation of the polymer.

For absolute rate measurements it is necessary to calibrate the gauge with the material being measured. This was not possible in this case, however, since these copolymers gave a complex mixture of degradation

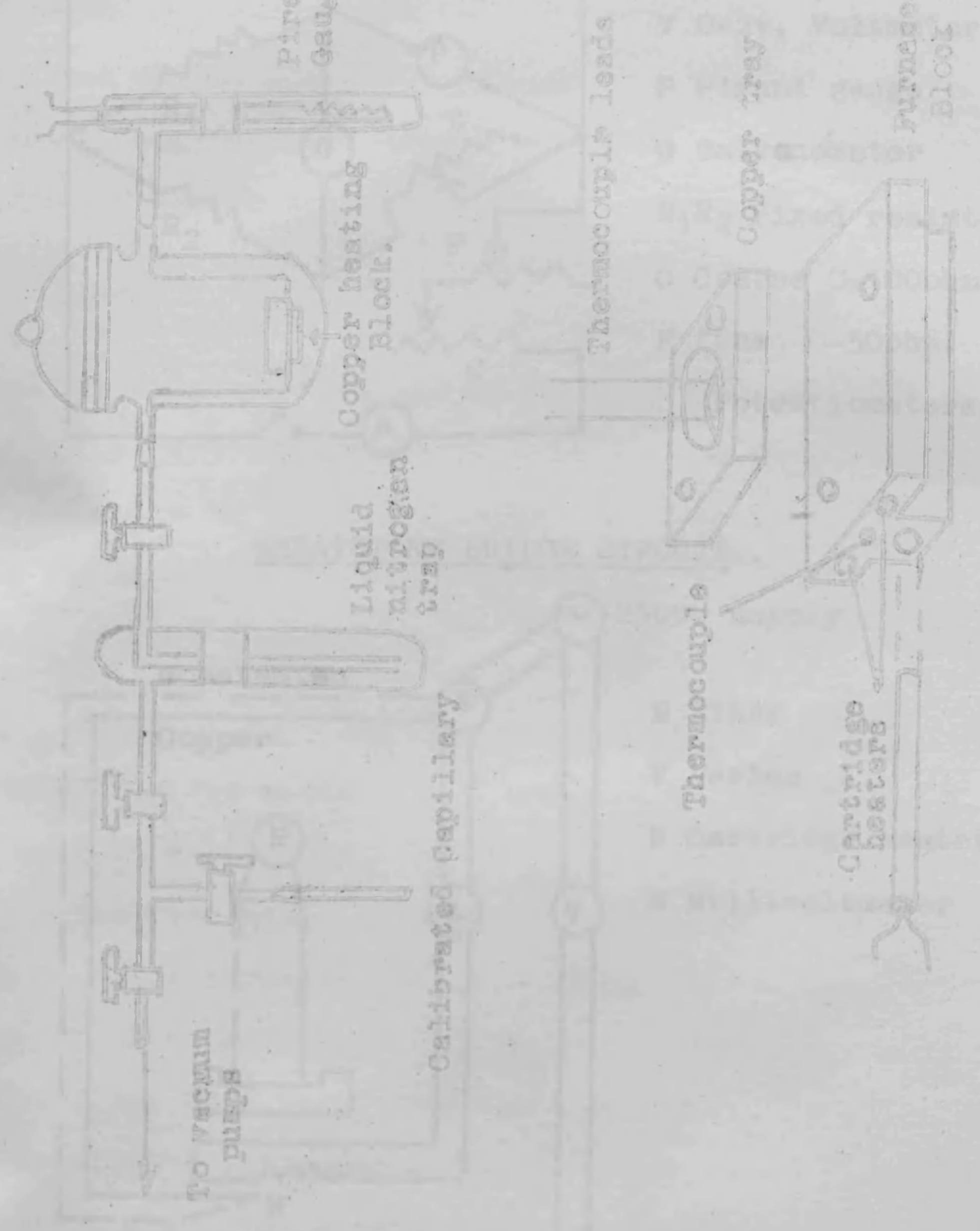
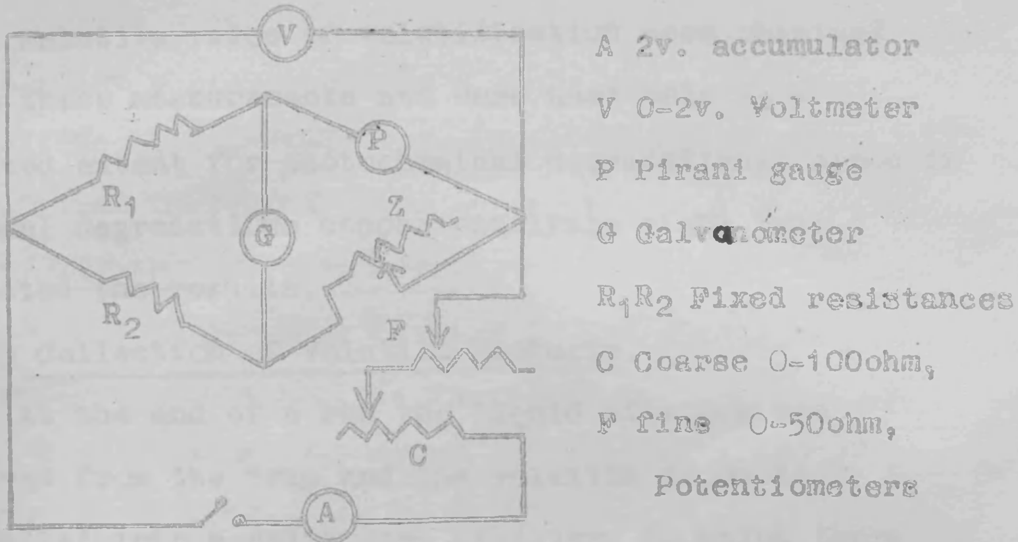


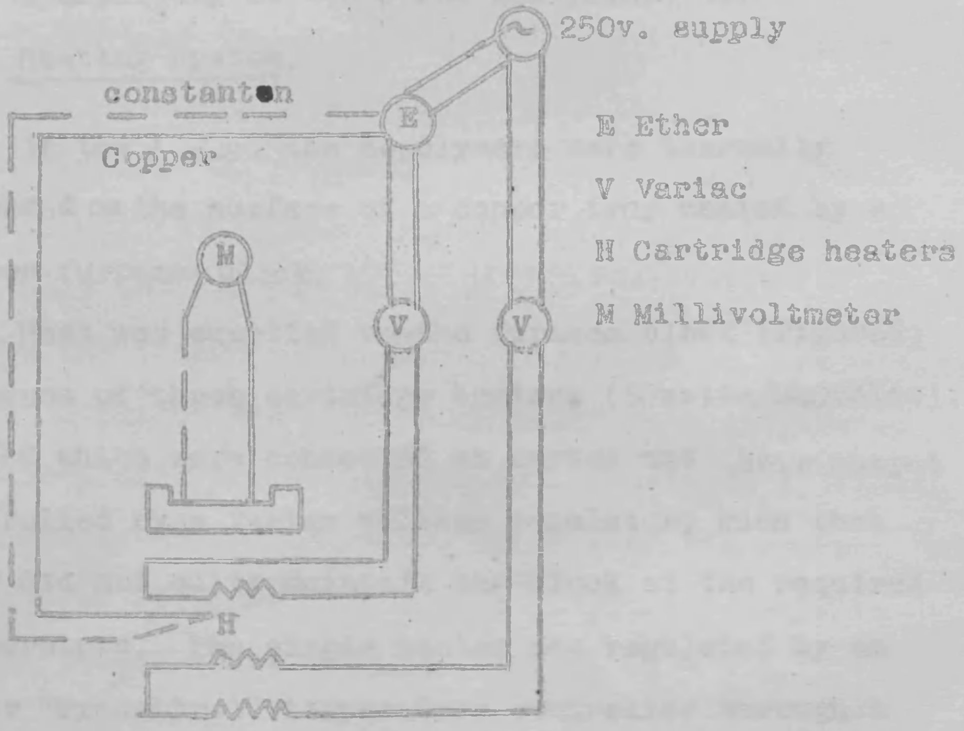
FIGURE 2

Dynamic Molecular Still. Glassware and Copper

Furnace Block.



WHEATSTONE BRIDGE CIRCUIT..



FURNACE AND THERMOCOUPLE CIRCUITS

FIGURE 3.

products.

Relative rates of volatilisation were obtained from these measurements and were used only to a limited extent for photochemical degradations, since in thermal degradations copper catalysis might have affected the results.

(iii) Collection of Volatile Products.

At the end of a run the liquid nitrogen was removed from the trap and the volatile products distilled into a calibrated capillary in which there yield could be estimated. The volatiles were stored in the capillary at -18°C for analysis.

(iv) Heating System.

In the d.m.s. the copolymers were thermally degraded on the surface of a copper tray heated by a copper furnace block,

Heat was supplied to the furnace block (figure2) by means of three cartridge heaters (50watts/240volts), two of which were connected in series and their output controlled by a Variac voltage regulator, such that they did not quite maintain the block at the required temperature. The single heater was regulated by an Ether "Transitrol" temperature controller through a variable transformer. The electrical circuits associated with the block are shown in figure 3.

By a suitable choice of the voltage through the constant heaters to give a small thermostatting voltage through the "Transitrol" it was possible to maintain the temperature of the furnace to ±0·5°C.

(v) Copper Degradation Tray.

The copper tray (figure 2) had a 32mm. diameter circular recess 4mm. in depth, to the bottom surface of which were silver soldered a copper and a constantan lead. The under side of the tray had been ground with the surface of the furnace block to ensure good contact.

60-80mg. of copolymer powder (120 mesh) covered by a weighed layer of 60-80 mesh copper powder (Hopkins and Williams Ltd.) to ensure good thermal contact, was degraded by screwing the tray firmly to the furnace block, connecting the leads to a thermocouple circuit and heating under vacuum .

The thermocouple circuit is shown in figure 3. The output of the thermocouple had been calibrated by immersion of the tray in an oil bath at different temperatures. Temperature control of the surface of the tray which is that of the polymer if their is good thermal contact, was found to be ± 1°C.

The extent of volatilisation was measured by weighing the tray at the end of a run. The relatively large recess in the tray enabled the polymer sample to be spread thinly over the surface and yet to leave enough residue after degradation for molecular weight measurements to be carried out.

All electrical leads were introduced into the still through capillary tubing sealed with picien wax.

(vi) Adaption for Photochemical Degradation.

For photo-initiated degradation experiments the normal lid of the d.m.s. which was an ordinary 6inch diameter ~~dessicatir~~ desiccator lid, was replaced by a flat topped ~~dessicator~~ desiccator lid in to which a silica window was sealed by "Araldite".

An Osram 125 watt mercury arc lamp with the glass envelope removed was used as an ultraviolet light source. Approximately 5% of the energy emitted from this type of lamp is below 3000 A. The lamp was allowed to stabilise for 1 hour before use. The polymer was photo-degraded in the form of a powder (30mg.) or film (15-20mg.).

Good thermal contact of the film with the heating surface was ensured by covering the film with a silica plate in which holes had been drilled to allow escape of the volatile products. It was found that without this plate the film tended to curl away from the heating surface.

(vii) Adaption for Temperature Programmed Degradation.

The most suitable temperature for isothermal degradation was determined from temperature programmed degradations run on an adaption of the d.m.s. designed by McNeill[35].

The polymer was heated in the form of a powder in a glass degradation tube in an open flow system by a linear temperature programmed oven (Perkin- Elmer F11) with a temperature range from room temperature to 500°C.

The rate of volatilisation was obtained as a recorder trace versus temperature of the sample by means of Pirani gauge (Edwards High Vacuum Model8/2) the output of which was connected to a 10mv. recorder (Leeds and Northrup).

The temperature of the inside surface of the tube had been calibrated against the oven temperature with a copper/constantan thermocouple touching the bottom surface of the tube.

(3) GLASS MOLECULAR STILL.

(i) Introduction.

Some degradations were carried out in the all glass molecular still illustrated in figure 4. This still incorporated a McLeod gauge in a known small volume, thus the absolute production of gaseous materials (carbon monoxide, methane, hydrogen and carbon dioxcde) could be followed directly from pressure measurements. This apparatus eliminated the possibility of abnormal ester breakdown by copper catalysis.

(ii) Heating System.

The copolymer samples were heated in the form of a fine powder (120 mesh) spread over the bottom surface of glass tube A (Quickfit FG35 flange) under vacuum in an open flow system. Heat was supplied by an electrically heated Woods Metal bath, thermostatted at the required temperature by means of an ether "Transitrol" temperature controller actuated by a copper/constantan thermocouple.

The temperature of the inside surface of the glass tube was calibrated against that of the Woods Metal bath by finding the temperature at which small pellets of tin, bismuth and antimony melted(melting points232, 271, and 327°C respectively), while the degradation tube was under vacuum.

The pellets were coated on the surface in contact with the glass with a little Apiezon L grease to simulate the conditions of polymer degradation, where a polymer particle before it had completely melted

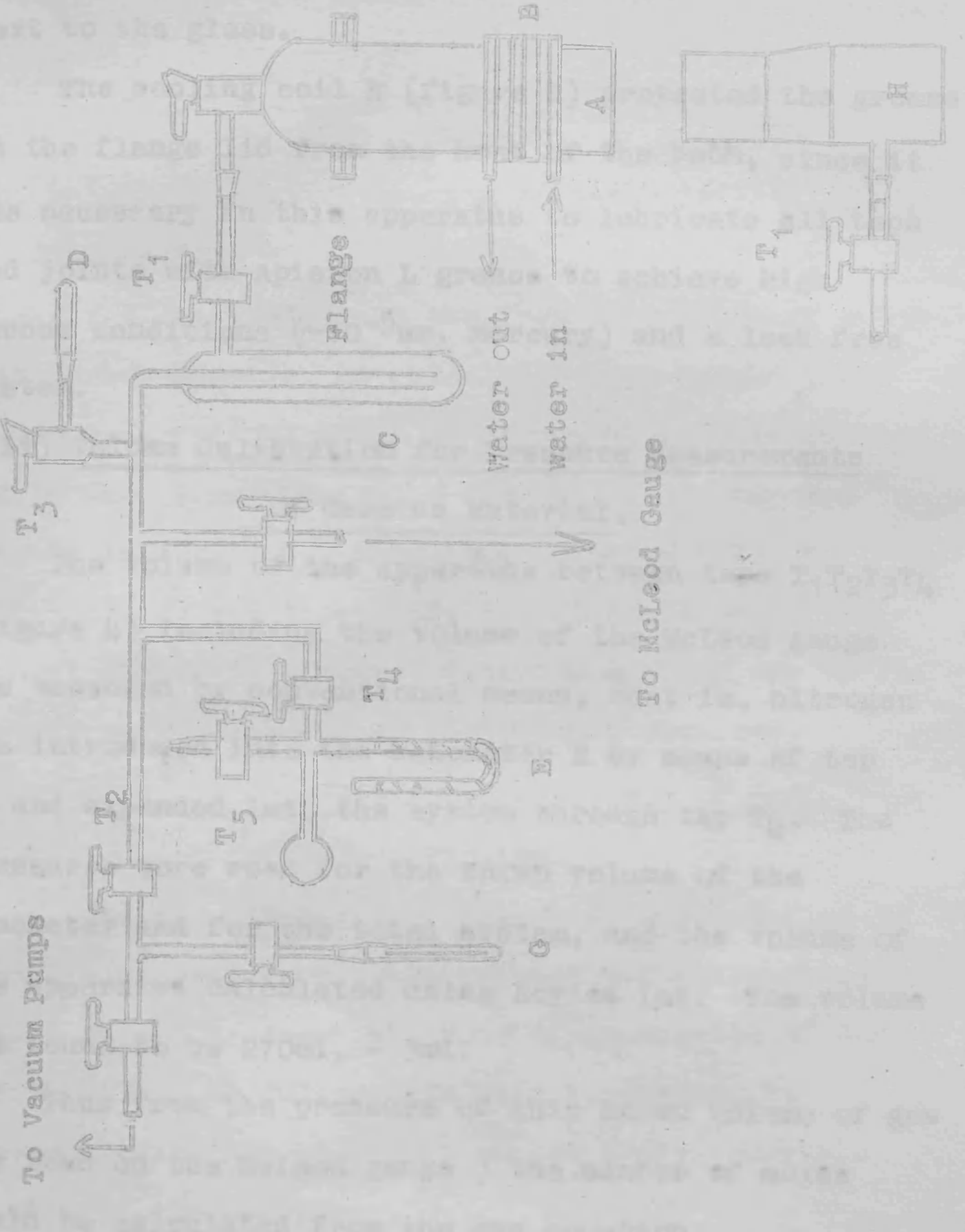


FIGURE 4

Glass Molecular Still.

would be in contact with a layer of molten polymer next to the glass.

The cooling coil B (figure 4) protected the grease on the flange lid from the heat of the bath, since it was necessary in this apparatus to lubricate all taps and joints with Apiezon L grease to achieve high vacuum conditions ($\sim 10^{-5}$mm. mercury) and a leak free system.

(iii) Volume Calibration for Pressure Measurements of Gaseous Material.

The volume of the apparatus between taps $T_1T_2T_3T_4$ (figure 4) including the volume of the McLeod gauge was measured by conventional means, that is, nitrogen was introduced into the manometer E by means of tap T_5 and expanded into the system through tap T_4. The pressures were read for the known volume of the manometer and for the total system, and the volume of the apparatus calculated using Boyles Law. The volume was found to be 270ml. ± 3ml.

Thus from the pressure of this known volume of gas (as read on the McLeod gauge) the number of moles could be calculated from the gas equation.

This calibration was confirmed for carbon dioxode(since this should be the main gaseous product from the decomposition of the methyl acrylate units) by decomposing known weights (0·5-2·5mg.) of sodium bicarbonate at $250^\circ C$, that is,

$$2NaHCO_3 \xrightarrow{250^\circ C} Na_2CO_3 + H_2O + CO_2$$

at which temperature there is no decomposition of sodium carbonate[36].

The calibration in the form of a graph of moles of carbon dioxide, as calculated from McLeod gauge pressure, against moles of carbon dioxode calculated from the weight of sodium bicarbonate decomposed is shown in figure 5. Good agreement was obtained although it was impossible to calibrate below the level of 5×10^{-7} moles of carbon dioxide due to the small weights of sodium bicarbonate required.

(iv) Adaption for Measurements of Rate of Production of Carbon Dioxide.

The glass apparatus (figure 4) was modified to enable degradations to be carried out under vacuum in a closed system. The rate of production of carbon dioxide can be followed in this apparatus, to characterise the breakdown of the methyl acrylate units in the copolymer.

The polymer was degraded in the form of cold pressed films (Section 1 (2)-iii) in a 1·5cm.

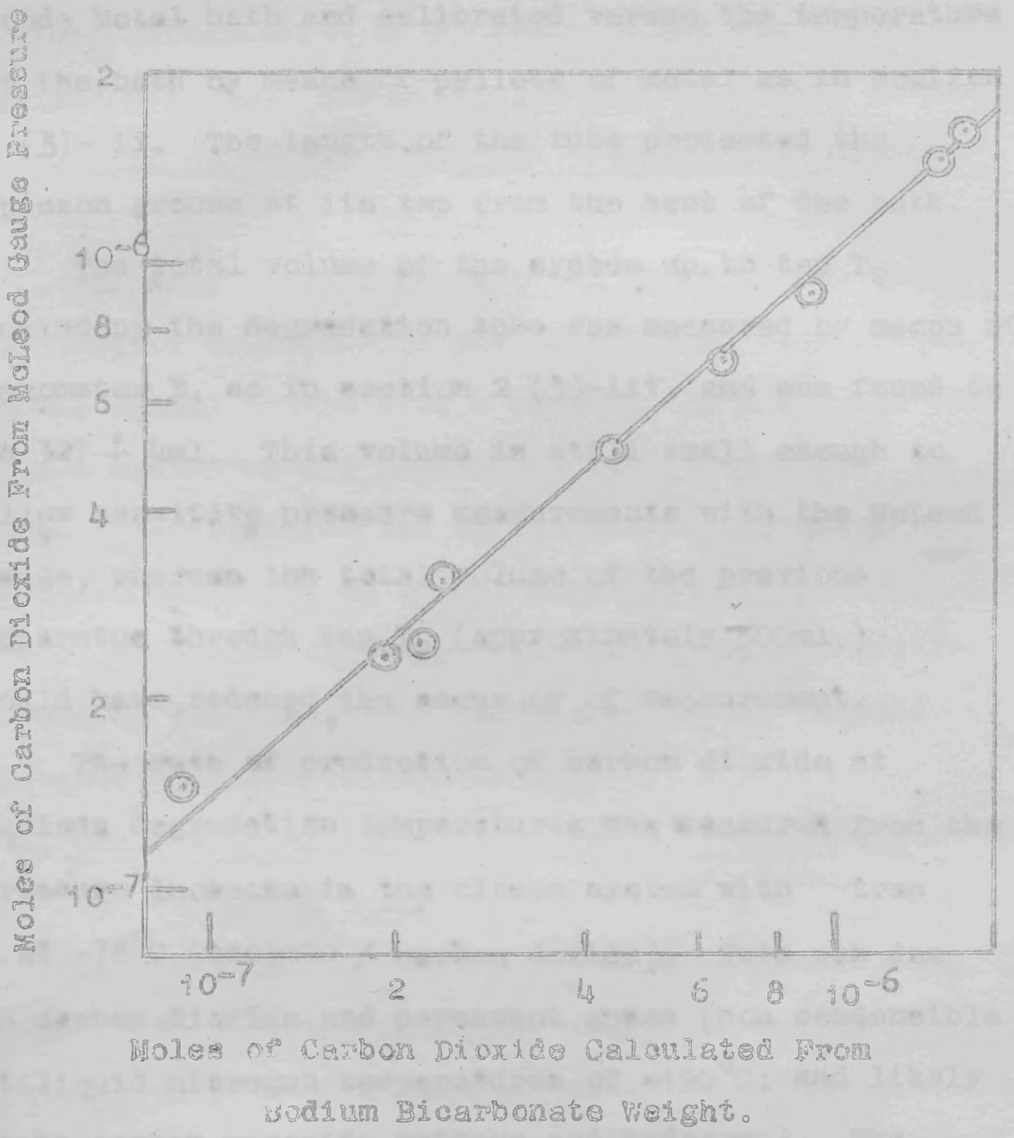


FIGURE 5.

Calibration for Carbon Dioxide Pressure Measurements.

diameter 27cm. long pyrex glass tube heated by the Woods Metal bath and calibrated versus the temperature of the bath by means of pellets of metal as in section 2 (3)- ii. The length of the tube protected the Apiezon grease at its top from the heat of the bath.

The total volume of the system up to tap T_2 including the degradation tube was measured by means of manometer E, as in section 2 (3)-iii, and was found to be 327 ± 4ml. This volume is still small enough to allow sensitive pressure measurements with the McLeod gauge, whereas the total volume of the previous apparatus through tap T_2 (approximately 500ml.) would have reduced the accuracy of measurement.

The rate of production of carbon dioxide at various degradation temperatures was measured from the pressure increase in the closed system with trap C at -78°C (acetone / carbon doxide). This was due to carbon dioxide and "permanent" gases (non condensible at liquid nitrogen temperatures of -190°C, and likely to be carbon monoxide, methane and hydrogen). The permanent gases were estimated in this closed system by the method in section 2 (3)-vi and the pressure increase due to carbon dioxide alone could be determined.

Experimental runs were made for various weights of polymer sample and the carbon dioxide pressure increase per unit weight averaged in order to take account of diffusion of products in the sample and variation in the efficiency of heating of the sample.

(v) Effect of Pressure on the Reaction in a Closed System.

Degradation runs for similar times at constant temperature were carried out in the open flow system, in the closed system with a trap at -78°C and in the closed system with a liquid nitrogen trap. The total volatilisation and carbon dioxide pressure produced was found to be the same within experimental error, thus showing the pressure build up had little effect on the reaction. Table 2 shows the results obtained.

(vi) Collection of Volatile Products of Degradation.

(a) Permanent Gases.

Degradation runs were carried out in the closed system with a liquid nitrogen trap round C, the pressure of permanent gases produced measured by the McLeod gauge, and their amount measured by use of the gas equation. The gas could then be analysed by the methods given in section 3 (i)-ii.

(b) Carbon Dioxide and other Volatiles.

Degradation runs were carried out in the open system. At the end of the degradation taps T_1 and T_2

WEIGHT OF SAMPLE. (mg.)	COPOLYMER COMPOSITION. MMA	MA	% VOLATILIS-ATION.	PRESSURE OF CO_2. X 10 mm.	TYPE OF SYSTEM.
80·6	26	1	85	4·6	open
79·9	26	1	87·5	4·46	closed trap at -78°C.
80	26	1	85	4·07	closed trap at -190°C.
18	2	1	53	4·3	closed trap at -78°C.
19·3	2	1	58	4·0	closed trap at -190°C.

MMA Methyl methacrylate. MA Methyl acrylate.

Table 2.

Effect of Pressyre of the Products on the Reaction.

were closed and the carbon dioxide pressure measured with trap C at -78°C.

Products non volatile at -78°C but volatile at room temperature were distilled into the calibrated capillary G and measured. They were stored at -18°C for analysis.

Products involatile at room temperature, which had condensed on the area of the reaction vessel cooled by coil B, were estimated by weighing the reaction vessel bef [illegible]

vii) Adaption for Photochemical Degradation.

(vii) Adaption for Photochemical Degradation.

For the investigation of the production of carbon dioxide in photochemical degradations the glass apparatus was used because of its small volume. Other aspects of photochemical degradation were studied in the d.m.s. since the temperature of photodegradation (~170°C) is too low to allow copper catalysis.

The glass apparatus was modified by incorporation of degradation tube H (figure 4) , the bottom half of which consisted of a B 40 pyrex cone in which the polymer could be heated by the Woods Metal bath. The top half consisted of a fused silica socket (Thermal Syndicate Ltd.) by which the ultraviolet radiation was transmitted. The joint was lubricated with silicone grease to resist attack from the ultraviolet light.

Carbon dioxide was estimated as in section 2 (3)-vi.

SECTION 3 ANALYSIS OF VOLATILE PRODUCTS OF DEGRADATION.

(i) PERMANENT GASES.

(i) Introduction.

The permanent gases were analysed by oxidation with selective oxidising agents. Iodine pentoxide at 130°C oxidises carbon monoxide to carbon dioxide[37], whilst cupric oxide at 300°C oxidises hydrogen to water, and at 350°C methane to water and carbon dioxide[38].

(ii) Oxidation Methods.

The oxidising agents iodine pentoxide and cupric oxide(both B.D.H. Ltd. micro analytical reagents) were contained in a silica furnace (Jencons B14 silica cone sealed at one end, and in contact with a copper/constantan thermocouple, the whole being covered by a layer of asbestos, in which nichrome heating wire was incorporated). This was substituted for tube E, figure4.

The temperature of the furnace was controlled by the thermocouple in conjunction with an ether Transitrol.

Pressure decreases with iodine pentoxide at 130°C, cupric oxide at 300°C and at 350°C, could be attributed due to the presence of carbon monoxide, hydrogen and methane respectively.

(2) OTHER VOLATILES.

(i) Carbon Dioxide.

The carbon dioxide pressure built up with the trap at -78°C in the system (section 2 (3)- vi) was absorbed by means of soda asbestos tube D,(B.D.H. Ltd. micro analytical reagent), to check that all the pressure build up was due to carbon dioxide.

(ii) Gas Liquid Chromatographic (G.L.C.) Analyses of Other Products.

The volatile products in capillary G (mostly monomers) both from the s.m.s. and the glass apparatus were analysed by means of G.L.C. (Perkin-Elmer Fractometer) using a thermal conductivity detector and helium as carrier gas.

Degradation products from methyl methacrylate/ methyl acrylate copolymers were separated, with sharp peak areas by a column consisting of 10% di-nonyl-phthalate (B.D.H. Ltd.) on chromosorb P type support (80-100 mesh) at 60°C with a gas flow rate of 80cc./ minute.

It was necessary to use a mixed column to separate the isomeric monomers methyl methacrylate and ethyl acrylate, with a low column temperature (50°C) and flow rate (50cc./ minute). The best column for this purpose consisted of a 10% Bentone 34, 10% tris -(tetrahydrofurfuryl)phosphate (Applied Science Labs.) on Embacel (60 mesh, B.D.H. Ltd.). The peaks were not so sharp as in the first case because of those conditions but were very well separated. All reagents used were of gas chromatography grade.

The areas under the monomer peaks were calibrated against monomer mixtures of known molar composition, thus the composition of the volatile products could be measured from their G.L.C. peak areas.

Resolution of small quantities of trace volatiles such as methanol and ethanol was achieved by injecting very large sample sizes (> 3 microlitres) and varying the sensitivity of the detector (from ÷512 to ÷1) to decrease the size of the peaks due to the major components and increase the size of the peaks due to the trace components.

SECTION 4 CHARACTERISATION OF POLYMERS AND DEGRADATION RESIDUES.

(1) MEASUREMENT OF MOLECULAR WEIGHT.

(i) Introduction.

A great deal of information about polymer degradation behaviour has been obtained from a study of number average molecular weight changes during degradation, since the total number of molecules before and after degradation can be counted and thus the number of chain breaks calculated.

Number average molecular weights can be obtained from measurements of the osmotic pressure of polymer solutions; in this work the limitations of older osmometers (eg., time of measurement; diffusion of sample,) have been minimised by the use of a modern automatic osmometer (Mechrolab "High Speed" membrane osmometer).

(ii) Measurement of Osmotic Pressure.

The osmotic pressure of solutions of polymers and degraded samples were obtained from measurements made on a Mechrolab High Speed osmometer, thermostatted at 37°C with toluene as solvent and using cellophane 300 grade (Sylvania) or "aller feinst"(Membranfilter) membranes (the latter membrane was found useful for very low molecular weight material ~ 10,000). A stock solution of polymer with a concentration in the range 0·4-1gm. / 100gm. toluene was prepared. The ~~osmometic~~ osmotic pressure of various known dilutions of this solution were measured.

Measurements of molecular weight can be made on very small samples since 5ml. of solution is sufficient.

This means that only very small polymer samples need be degraded (15-40mg. is sufficient). Previous work[7] required at least 100mg. of polymer to give sufficiently large degradation residues for measurement in traditional osmometers.

Substituting appropriate values in the Van't Hoff equation,[39]

$$\frac{\Pi}{c} = \frac{RT}{M}$$

(c in gm/100gm
π in cm toluene)

at 37°C, $$M = \frac{2{\cdot}63 \times 10^{5}}{\left(\frac{\Pi}{c}\right)_{0}} .$$

Experimental plots of $\frac{\Pi}{c}$ versus concentration are shown for representative samples in figure 6, and the molecular weights of the copolymers prepared for degradation studies are listed in table 3.

(2) SPECTROSCOPIC TECHNIQUE.

(i) Introduction.

Spectroscopic measurements of the copolymers and degraded residues were carried out, since in poly-(methylacrylate) degradation colouration occurs[34]. Thus it was necessary to find whether any changes in structure occured during the degradation of the copolymers. The techniques described below were used only

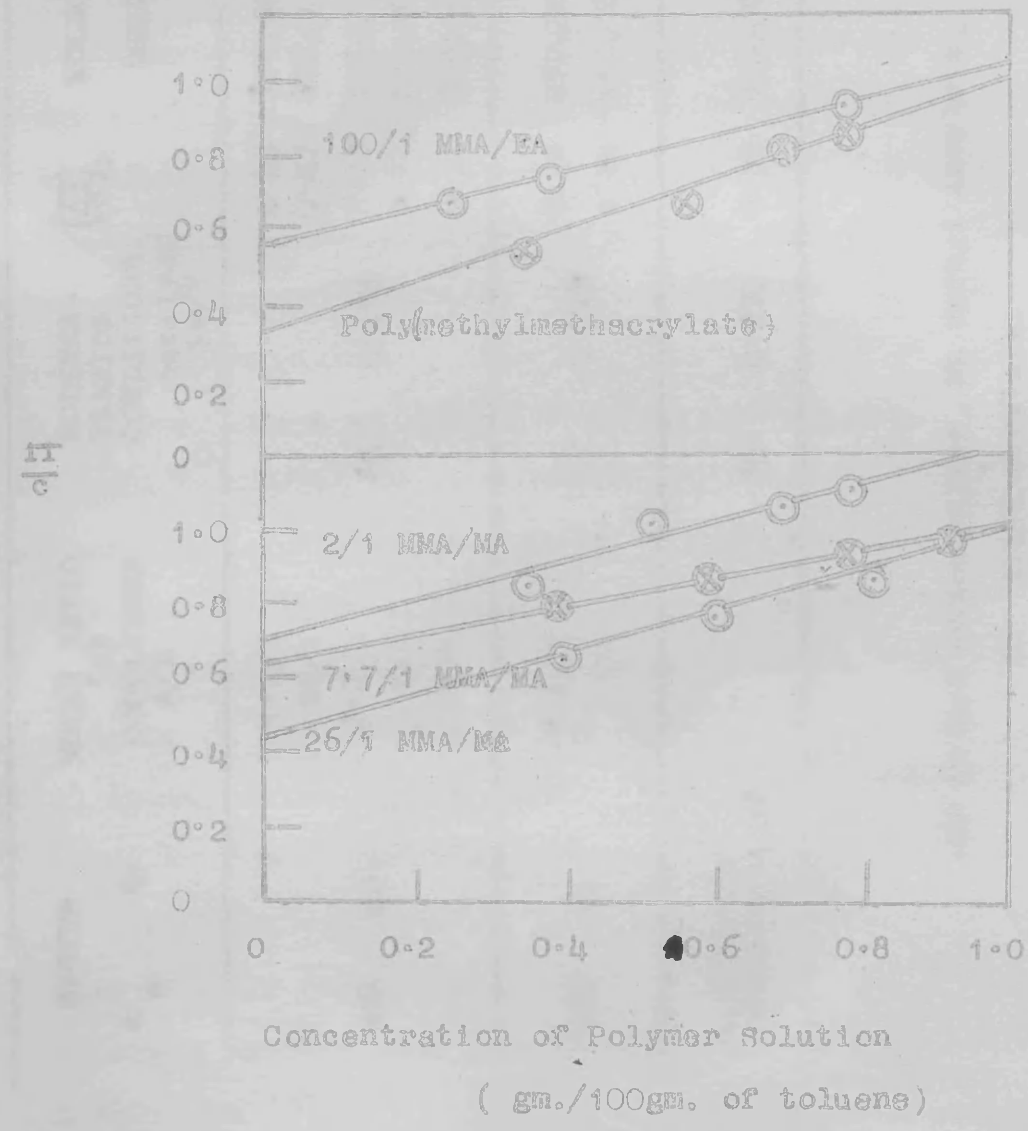


FIGURE 6.

Evaluation of $\left(\frac{\pi}{c}\right)_0$ for Representative Samples.

SYSTEM A	SYSTEM B	MOLAR RATIO IN COPOLYMERS A/B	POLYMERISATION CONDITIONS. °C	POLYMERISATION CONDITIONS. catalyst %w/v	$\left(\frac{\Gamma\Gamma}{c}\right)_{o}$	MOLECULAR WEIGHT.
MMA	MA	112/1	65	0·075	0·43	600,000
		26/1			0·43	600,000
		7·7/1			0·62	425,000
		2/1			0·70	370,000
		0·76/1			0·51	515,000
MMA	EA	100/1	60	0·075	0·56	470,000
		10/1			0·64	410,000
Poly(methyl-methacrylate)			65	0·075	0·32	820,000

MMA methyl methacrylate, MA methyl acrylate,

EA Ethyl acrylate.

Table 3.

Molecular Weights of Polymer Samples.

quantitatively.

(ii) Infra Red Spectroscopy.

Changes in the infra-red (I.R.) absorbtion spectra of the cpolymers and degraded residues were measured on a Perkin- Elmer model 237 spectrophotometer. The copolymer was prepared as a film(section 1 (2)-ii) mounted between two brass rings to prevent warping during measurement.

Copolymers of higher acrylate content and residues from high extents of degradation did not form satisfactory films. For these samples a viscous solution of the polymer in chloroform was dropped on to a salt plate, the chloroform evaporating to form a film of polymer on the surface of the salt plate. The salt plate was dried in the vacuum oven at 50°C for 24 hours to remove residual chloroform.

No solution spectra were run since the residues were usually insoluble in ideal spectroscopic solvents (carbon tetrachloride, methylene chloride and carbon disulphide).

(iii) Ultraviolet and Visible Spectroscopy.

Ultraviolet and visible absorbtion spectra were run on a Unicam model SP 800 spectrophotometer. The copolymer was prepared in the form of a film and mounted between two brass plates to prevent warping.

Since highly degraded samples could not be prepared as a film spectra were run in solutions (15-20% polymer by weight) of chloroform in a 1cm. solution cell. Unfortunately the polymers would not dissolve in the paraffin hydrocarbons , hexane or ethers, which are most suitable due to their low absorbances. Thus the solution spectra of these copolymers was blanked out below about 270 millimicrons, due to the chloroform absorption. However information about conjugated double bonds (absorbing in the region of 275 millimicrons upwards) could still be obtained from these spectra.

CHAPTER 3.

DETERMINATION OF REACTIVITY RATIOS BY PROTON MAGNETIC RESONANCE SPECTROSCOPY.

(1) LIMITATIONS OF COPOLYMER ANALYTICAL METHODS.

The determination of reactivity ratios for the copolymerisation of a pair of monomers, depends on the analysis of their copolymers. Standard analytical methods which have been applied to copolymers include[40], elemental analysis, I.R. and U.V. spectroscopy, radiometric and isotopic methods and copolymer pyrolysis combined with G.L.C. of the pyrolysis products.

In the case of methyl methacrylate/methyl acrylate and methyl methacrylate/ethyl acrylate copolymers the monomer pairs are so similar in structure that most of these methods are inapplicable. Elemental analysis cannot be made accurate enough for the purpose[40], and the application of U.V. and I.R. spectrophotometric methods require the monomers to have significantly different absorbing structures. G.L.C. of the pyrolysis products has been applied but may be of doubtful quantitative validity since copolymer decomposition is subject to minor changes in pyrolysis conditions[41].

Radiometric and isotopic analysis require elaborate and time consuming experimental technique and thus were not considered. Reactivity ratios for the methyl methacrylate/methyl acrylate system were reported in the literature using these above methods[42,43], after the values used in this work had been determined and applied.

Proton magnetic resonance spectroscopy, which has been used for the analysis of vinyl acetate/ethylene copolymers[44,45], can be successfully applied to the methyl methacrylate/methyl acrylate and methyl methacrylate/ethyl acrylate systems since it can detect quantitatively the protons in the different environments of the monomer units.

(2) ANALYSIS OF COPOLYMERS BY PROTON MAGNETIC RESONANCE (P.M.R.) SPECTROSCOPY.

(i) Introduction.

Introducti

The theory behind P.M.R. spectroscopy has been well detailed in the literature[46] and only a very brief summary is given here.

All nucleii have spin properties as well as charge and mass and thus have an associated magnetic moment μ, If a proton is placed in a magnetic field H_o it can occupy two spin energy levels depending on whether ν is applied with or against H_o. The difference in energy between the ~~fields~~ levels is given by,

$$\Delta E = 2\nu H_o$$

and proton shift between the levels is thus proportional to the field strength H_o.

Consider an assembly of equivalent protons in a tube with a radiofrequency coil round the sample, a variable magnetic field is applied perpendicular to the axis of the first coil and its frequency increased till resonance occurs, that is, energy is absorbed from the radiofrequency field to cause proton shift between the two levels. This energy may be detected and recorded to characterise the protons. This is the basic principle of the commercial P.M.R. spectrometer, in this work the Perkin-Elmer 60 Mc/s variable field instrument was used.

The precise value of the resonance field required depends upon the structural environment of the proton because of influence of magnetic fields of adjacent atoms. Thus protons in different environments reveal themselves at different applied field strengths. The abscissa ~~abcissa~~ of the P.M.R. spectrum is expressed in dimensionless units, parts per million change in magnetic field strength and the peak positions recorded automatically in modern spectrometers with reference to the τ scale, where the resonance of tetramethylsilane (τ 10) is + 10.000 parts per million by definition[47].

With proper instrumentation the analysis for protons in different environments can be made quantitative, the integrated spectral intensities being directly proportional to the number of resonating protons in each structural position in the molecule.

(ii) Analysis of Methyl methacrylate/ Methyl acrylate Copolymers.

The P.M.R. spectrum of the standard poly(methylmethacrylate) sample run in $CDCl_3$ is shown in figure 7 The peaks have been assigned as shown in table 4 by Bovey and Tiers[48].

Table 4

τ Values for Characteristic Protons of Poly(methylmethacrylate)

proton type	$-OCH_3$	$-CH_2-$	$-CH_3$
τ value	6·4	8·2	9·1

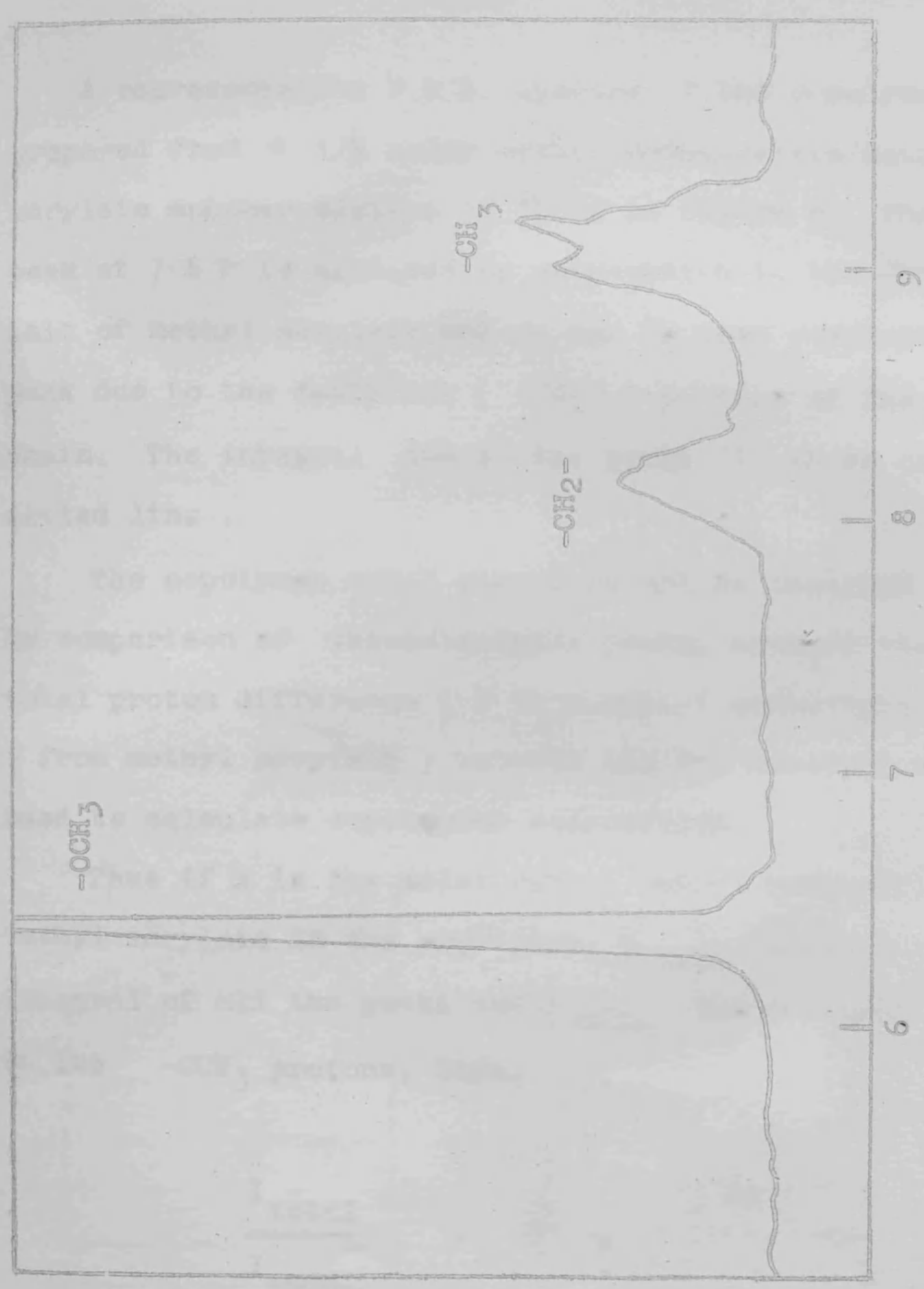


FIGURE 7.

P.M.R. Spectrum of Poly(methylmethacrylate) Standard.

A representative P.M.R. spectra of the copolymer prepared from a 1/5 molar methyl methacrylate/methyl acrylate monomer mixture is shown in figure 8. The peak at $7{\cdot}6\,\tau$ is assigned by comparision to the $>$CH unit of methyl acrylate and as can be seen overlaps the peak due to the methylene ($-CH_2-$) protons of the chain. The integral due to the peaks is shown as a dotted line .

The copolymer could therefore not be analysed by comparison of characteristic peaks, however the total proton difference (8 from methyl methacrylate, 6 from methyl acrylate) between the two monomers was used to calculate copolymer composition.

Thus if x is the molar ratio, methyl methacrylate/methyl acrylate in the copolymer, I_{total} is the total integral of all the peaks and I_{-OCH_3} the integral due to the $-OCH_3$ protons, then,

$$\frac{I_{total}}{I_{-OCH_3}} = Y = \frac{(8x + 6)}{3(x + 1)} .$$

Therefore $$x = \frac{(3Y - 6)}{(8 - 3Y)}$$

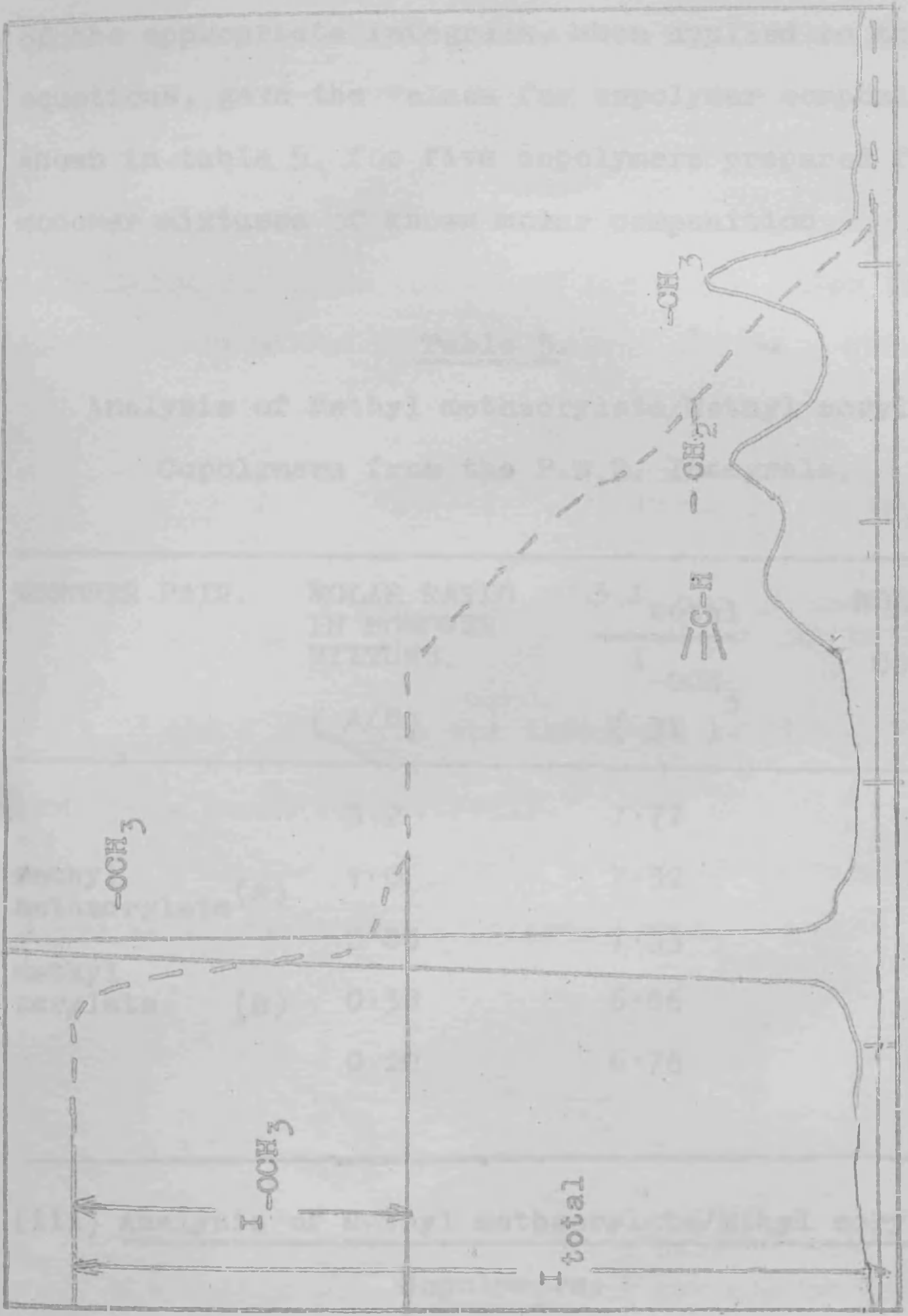


FIGURE 8.

P.M.R. Spectrum of Copolymer from 1/5 Methyl methacrylate/Methyl acrylate Monomer Mixture.

The ratios obtained by averaging ten determinations of the appropriate integrals, when applied to the above equations, gave the values for copolymer composition shown in table 5, for five copolymers prepared from monomer mixtures of known molar composition.

Table 5.

Analysis of Methyl methacrylate/Methyl acrylate Copolymers from the P.M.R. Integrals.

MONOMER PAIR.	MOLAR RATIO IN MONOMER MIXTURE. (A/B)	$\frac{3\,I_{total}}{I_{-OCH_3}}$ (3Y)		MOLAR RATIO IN COPOLYMER. (x)
	5·2	7·77		7·7
methyl methacrylate (A)	1·0	7·32		1·94
	0·85	7·33		2·0
methyl acrylate (B)	0·38	6·86		0·76
	0·20	6·78		0·64

(iii) Analysis of Methyl methacrylate/Ethyl acrylate Copolymers.

In conjunction with Grassie, Fortune and Gemmel[49], P.M.R. spectra were obtained for the methyl methacrylate/ ethyl acrylate copolymers. A representative spectrum is shown in figure 9, where it can be seen that the peak due to the $-OCH_3$ protons (methyl methacrylate) was resolved from those due to the $-OCH_2-$ protons (ethyl acrylate).

The monomer compositions of five copolymers were calculated from the ratios of the areas under those peaks, as measured by the integral curves. Thus,

$$I_{-OCH_2-} \propto 2 \text{ (number of ethyl acrylate units in chain)}$$

$$I_{-OCH_3} \propto 3 \text{ (number of methyl methacrylate units in chain).}$$

I_{-OCH_2-} and I_{-OCH_3} are the integrals of the $-OCH_2-$ and $-OCH_3$ peaks respectively.

If x is the molar ratio of methyl methacrylate/ethyl acrylate in the copolymer, then,

$$\frac{I_{-OCH_2-}}{I_{-OCH_3}} = \frac{2}{3x} .$$

The ratios obtained from the average of ten integrals gave the values of copolymer composition shown in table 6.

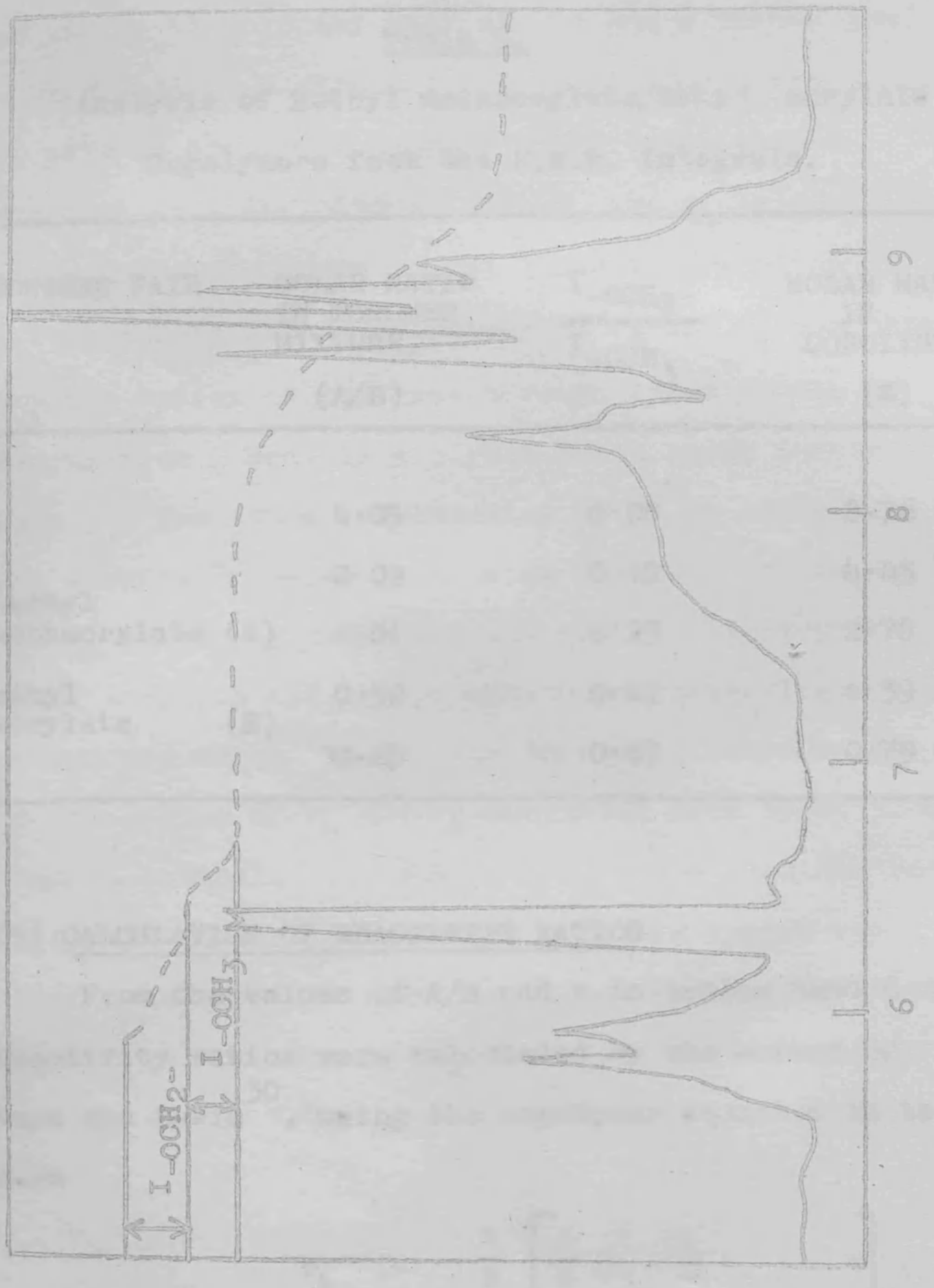


FIGURE 9

P.M.R. Spectrum of Copolymer From the 1/4 Methyl methacrylate/Methyl acrylate Monomer Mixture.

Table 6.

Analysis of Methyl methacrylate/Ethyl acrylate Copolymers from the P.M.R. Integrals.

MONOMER PAIR.	MOLAR RATIO IN MONOMER MIXTURE. (A/B)	$\frac{I_{-OCH_2-}}{I_{-OCH_3}}$	MOLAR RATIO IN COPOLYMER. (x)
methyl methacrylate (A) ethyl acrylate (B)	4·05	0·08	8·76
	2·02	0·15	4·45
	1·01	0·23	2·78
	0·52	0·47	1·39
	0·25	0·67	0·79

(3) CALCULATION OF REACTIVITY RATIOS.

From the values of A/B and x in tables 5and 6 reactivity ratios were calculated by the method of Mayo and Lewis[30], using the copolymer equation in the form

$$r_b = \frac{A}{B}\left[\frac{1}{x}\left(1 + \frac{A}{B}r_a\right) - 1\right].$$

r_b is expressed as a linear function of r_a in terms of

A/B and x, that is, any pair of A/B and x values can be expressed as a straight line plot of r_a versus r_b. For several copolymer samples those lines should intersect at a definite point (r_a and r_b values). Analytical error leads to the lines intersecting at different points and the values of r_a and r_b are obtained from the median of the area through these points of intersection (usually a circle for a large number of lines). The lines intersecting at large angles are more heavily weighted than those at small angles.

r_b versus r_a plots for the methyl methacrylate/methyl acrylate and methyl methacrylate/ethyl acrylate systems are shown in figures 10 and 11 respectively and the values of r_a and r_b estimated from these plots shown in table 7. The reactivity ratios obtained for the methyl methacrylate/methyl acrylate system are rather less accurate than the methyl methacrylate/ethyl acrylate values, due to the more insensitive methods of analysis by the total proton count.

(4) COMPARISON WITH OTHER METHODS OF ANALYSIS.

The last column in table 7 shows the values reported for the methyl methacrylate/methyl acrylate system by radiometric[42] ($r_a = 1{\cdot}69$, $r_b = 0{\cdot}34$)

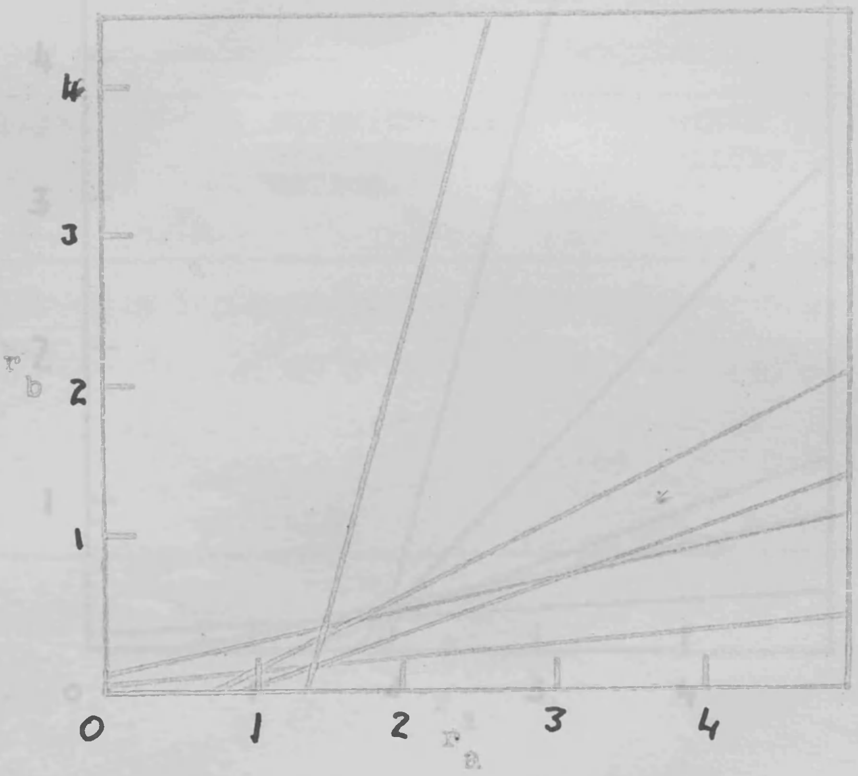


FIGURE 10.

r_b versus r_a plot for the Methyl methacrylate/Methyl acrylate System.

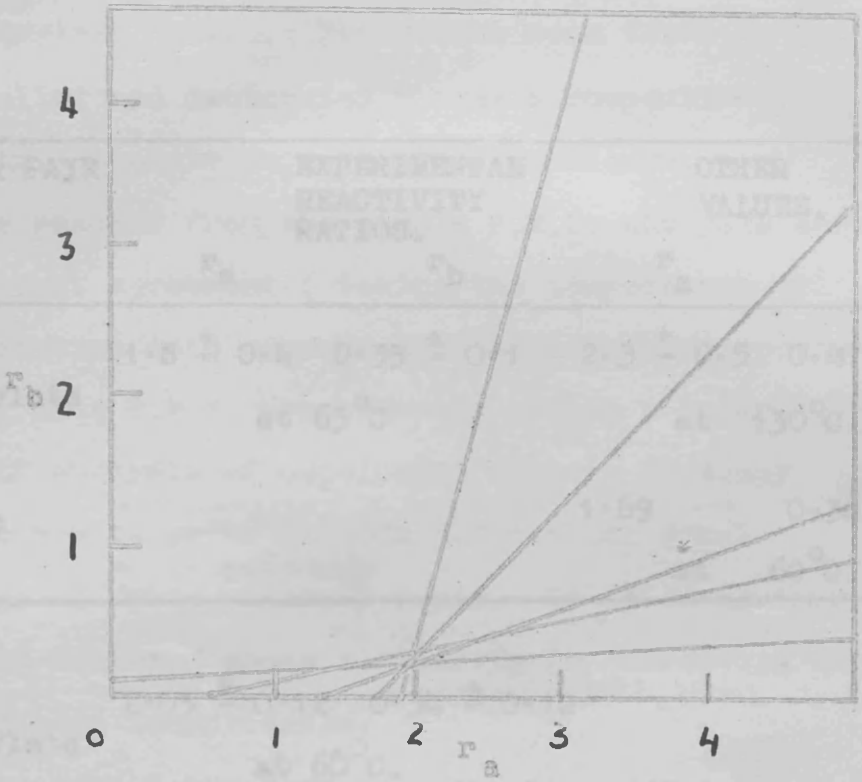


FIGURE 11.

r_b versus r_a plot for the Methyl methacrylate/Ethyl acrylate System.

MONOMER PAIR.	EXPERIMENTAL REACTIVITY RATIOS.		OTHER VALUES.	
	r_a	r_b	r_a	r_b
methyl methacrylate (A)	1·8 ± 0·4	0·35 ± 0·1	2·3 ± 0·5	0·47 ± 0·1
	at 65°C		at 130°C.	
methyl acrylate (B)			1·69	0·34
			at 60°C.	
methyl methacrylate (A) ethyl acrylate (B)	2·03 ± 0·12	0·34 ± 0·12		
	at 60°C.			

Table 7

Experimental Reactivity Ratios and Other Reported Values.

and isotopic[43] ($r_a = 2{\cdot}3$, $r_b = 0{\cdot}47$) analyses. No values have been reported for the methyl methacrylate/ethyl acrylate system. The values were found by use of C^{14} labelled and deuterated monomers respectively, involving elaborate experimental techniques.

The results from the simple P.M.R. analysis are in excellent agreement (taking the temperature of polymerisation into account) with the other reported values. Thus P.M.R. spectroscopy offers a general method of analysis of copolymers with an accuracy comparable with other methods and has the great advantage of being extremely ~~extremely~~ rapid. It is of maximum use among monomers whose similarity in structure make other methods inapplicable.

This method has been extended to cover a range of methacrylate/acrylate copolymers which could not have been analysed by more conventional methods. Excellent results were obtained and a copy of a paper published on the subject[49] is included in the thesis.

CHAPTER 4.

THE THERMAL DEGRADATION OF METHYL METHACRYLATE/ METHYL ACRYLATE COPOLYMERS. (1) GENERAL DEGRADATION CHARACTERISTICS.

(1) PRELIMINARY STUDIES OF TEMPERATURE PROGRAMMED DEGRADATION.

(i) Choice of Temperature for Isothermal Studies.

The results obtained for the temperature programmed degradation of the 112/1, 26/1, 7·7/1 and 2/1 methyl methacrylate/methyl acrylate copolymers are shown in figures 12-15 ,put in the form of rate of volatilisation (pirani pressure trace on 10mv. recorder) of 25mg. samples versus the temperature of the sample.

It can be seen that in all cases appreciable volatilisation of the sample occurs in the temperature region of 260– 300°C and thus isothermal studies can be carried out in this temperature range.

(ii) Comparison of Degradation Behaviour With That of Poly(methylmethacrylate).

The temperature programmed degradation of the poly(methylmethacrylate) standard is shown in figure 16,

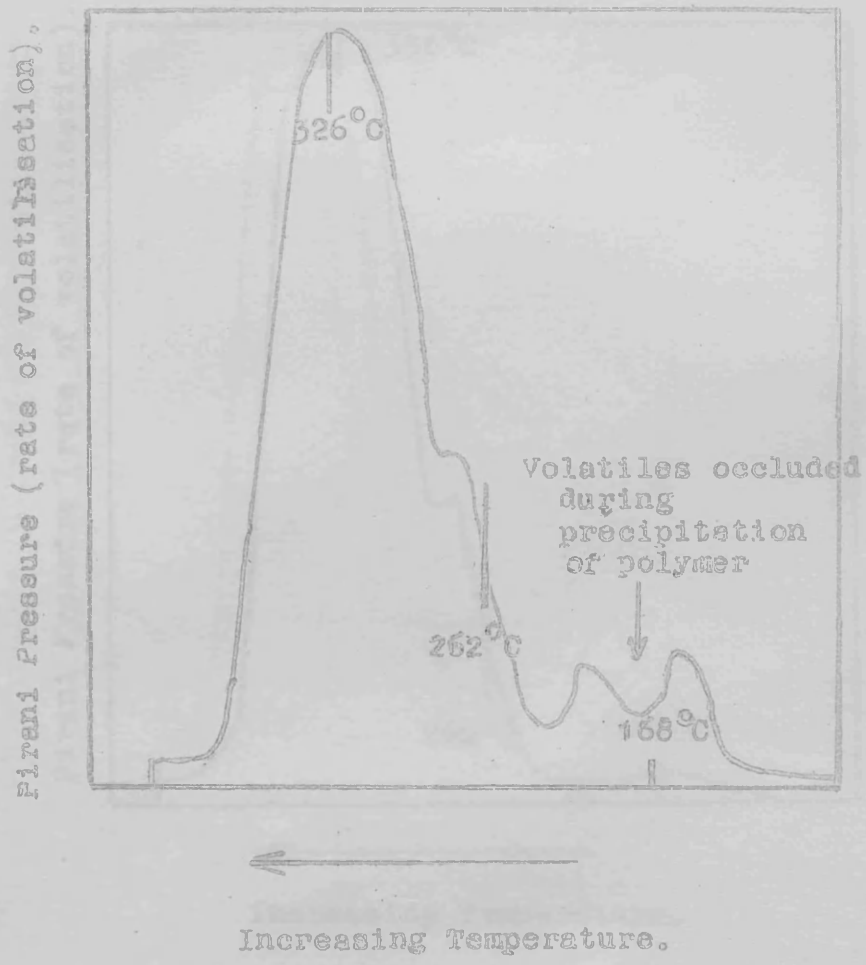


FIGURE 12.

Temperature Programmed Degradation of 112/1 Methyl methacrylate/Methyl acrylate Copolymer.

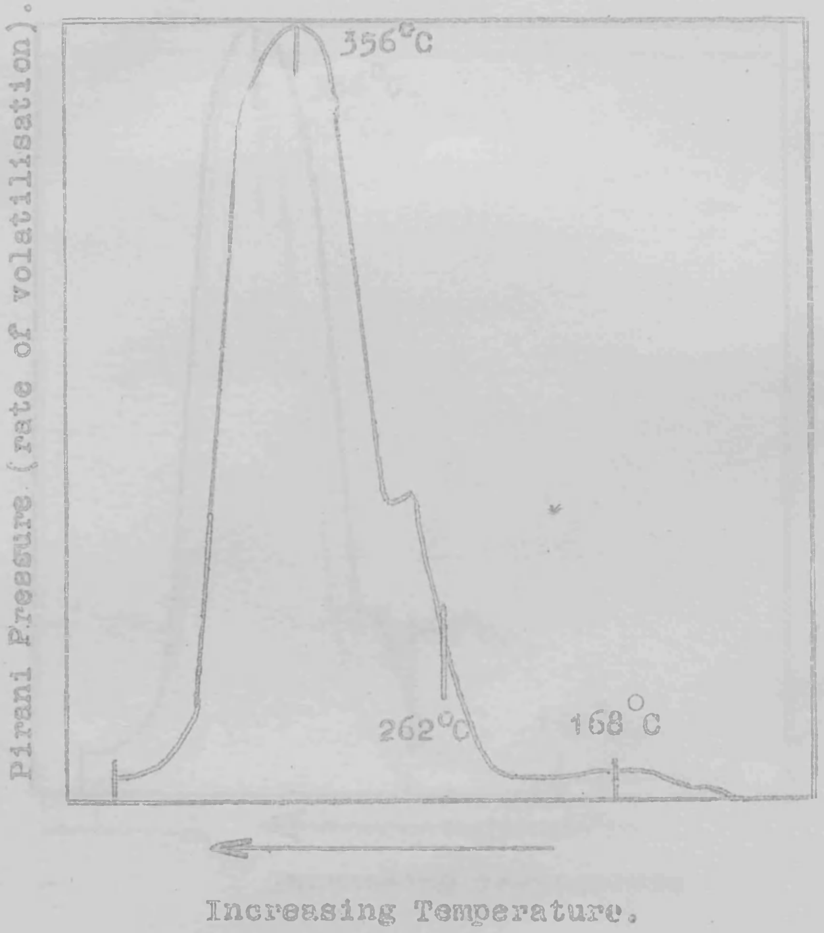


FIGURE 13.

Temperature Programmed Degradation of 26/4 Methyl methacrylate/Methyl acrylate Copolymer.

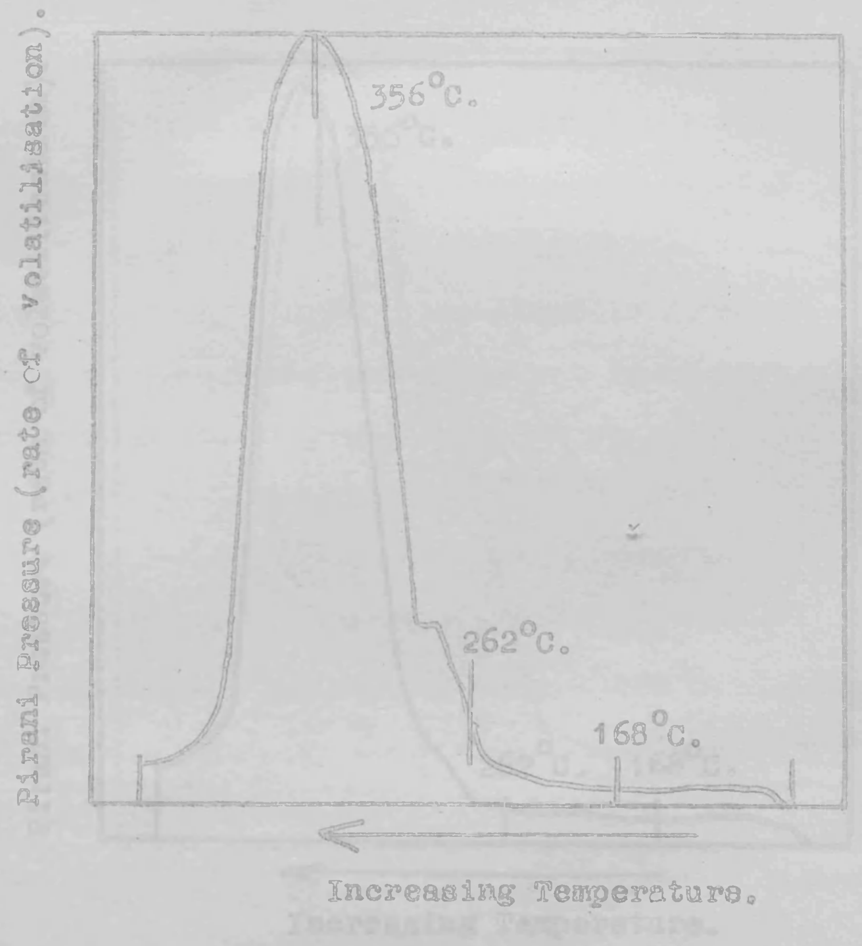


FIGURE 14.

Temperature Programmed Degradation of 7·7/1 Methyl methacrylate/Methyl acrylate Copolymer.

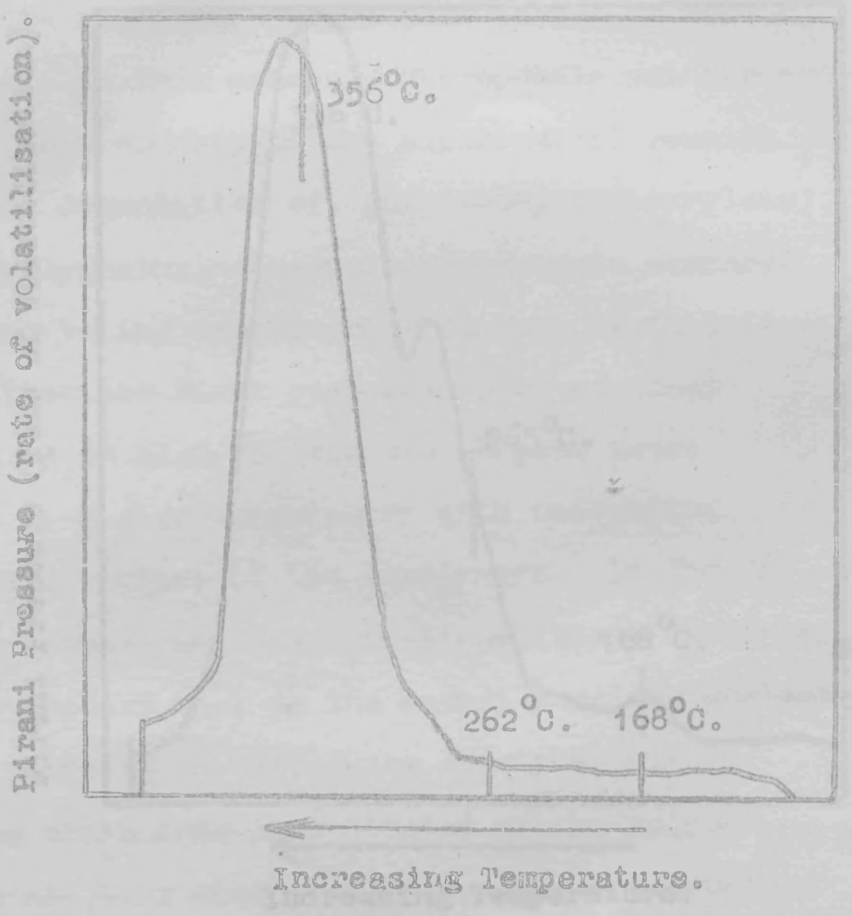


FIGURE 15.

Temperature Programmed Degradation of 2/1 Methyl methacrylate/Methyl acrylate Copolymer.

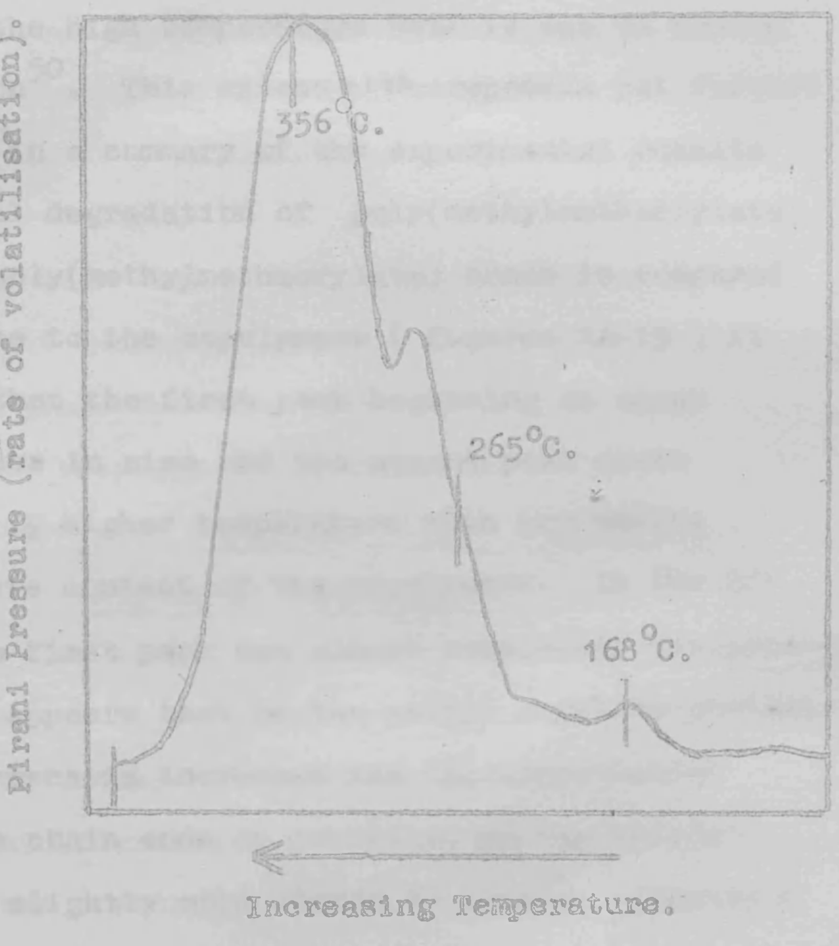


FIGURE 16.

Temperature Programmed Degradation of Standard Poly(methylmethacrylate).

and it can be seen that there are two peaks due to the volatilisation of the polymer sample. The low temperature peak is due to depolymerisation from unsaturated chain ends, while the high temperature peak is due to random chain scission[50]. This agrees with proposals put forward by McCallum[25] in a summary of the experimental results on the thermal degradation of poly(methylmethacrylate).

If the poly(methylmethacrylate) trace is compared with those due to the copolymers (figures 12-15) it can be seen that the first peak beginning at about 200°C decreases in size and the second peak moves gradually to a higher temperature with increasing methyl acrylate content of the copolymers. In the 2/1 copolymer the first peak has almost completely disappeared.

Thus it appears that as the methyl acrylate content of the copolymers is increased the depolymerisation reaction from chain ends is inhibited and the polymer also becomes slightly more stable to monomer production by random chain scission.

(2) ISOTHERMAL DEGRADATION.

(i) Molecular Weight Changes on Degradation.

(a) Comparison of Changes in Copper and Glass Degradation Vessels.

The molecular weight changes which occur in the

the region 260- 300°C, expressed in the form of percentage of original molecular weight, versus percentage volatilisation of the sample, are shown for the 26/1 copolymer in figure 17. These molecular weight changes are characteristic of random chain scission, that is, a rapid drop in molecular weight for a small percentage degradation.

It can be seen that within experimental error in molecular weight measurements, similar changes occur. in copper and glass vessels. Thus it appears that copper does not catalyse chain scission.

(b) Dependence of Molecular Weight Changes upon Copolymer Composition.

The molecular weight changes for the 112/1, 7 7/1 and 2/1 copolymers degraded in the region 260- 300°C in the glass molecular still are given in table 12 (Chapter 5) and illustrated in figure 18. Again in all cases the curves are typical of random chain scission. This type of curve reflects the behaviour of (polymethylacrylate) rather than poly(methylmethacrylate) even when only 1% methyl acrylate is incorporated in the copolymer chain. Although it has been suggested that at higher temperatures poly(methylmethacrylate) degrades by random chain scission there are no known cases of the molecular weight falling below the diagonal

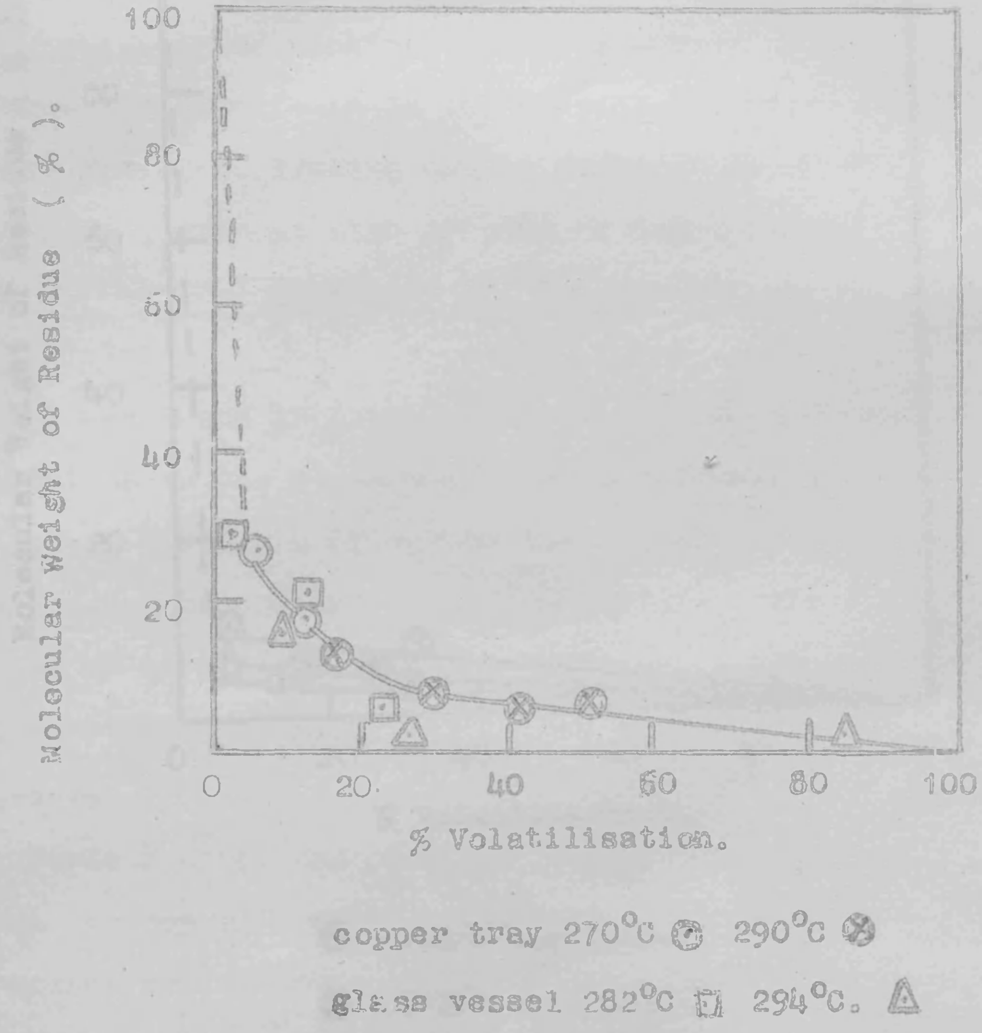


FIGURE 17.

Molecular Weight Changes for 26/1 Copolymer in Copper and Glass Vessels.

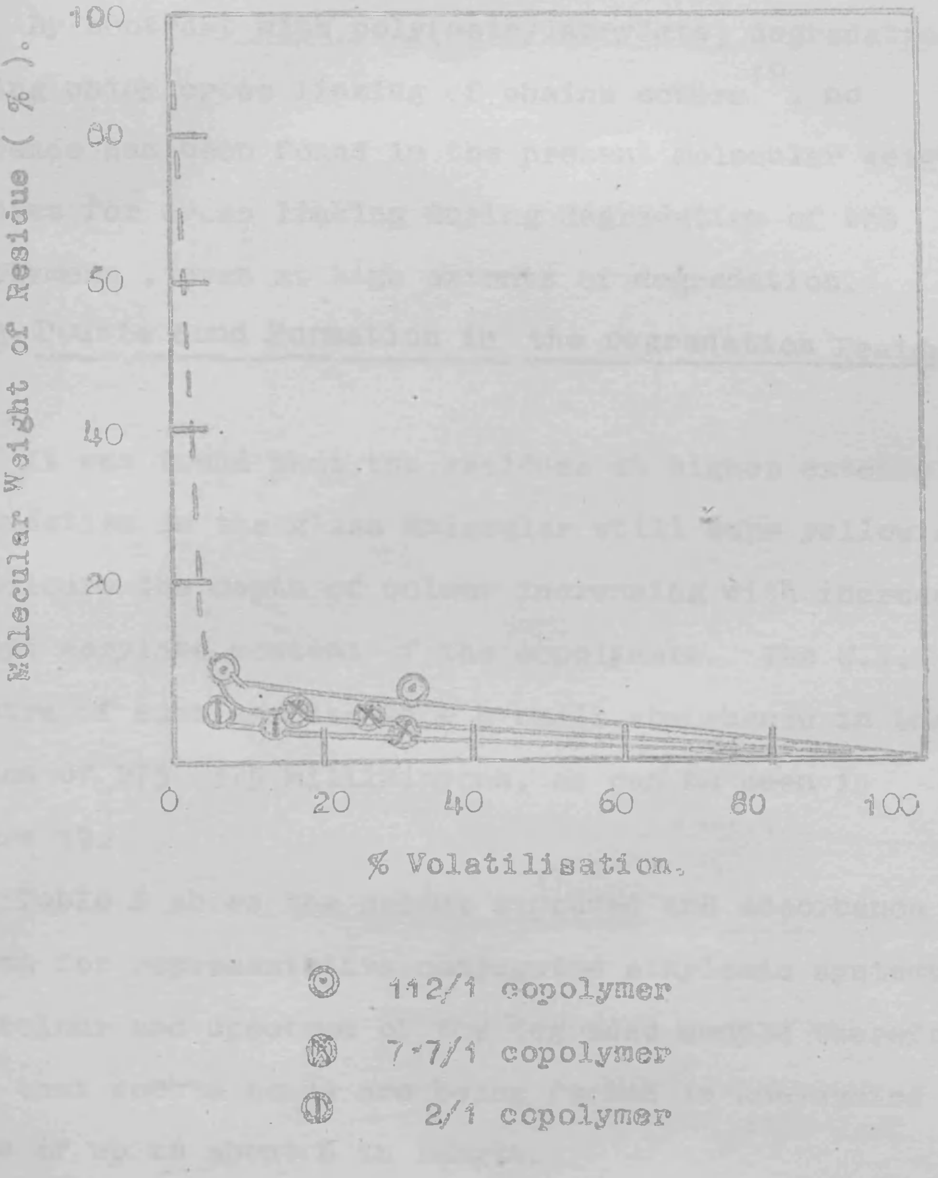


FIGURE 18.

Molecular Weight Changes for 112/1 7·7/1 and 2/1 Copolymers in Glass Vessel.

of the molecular weight / %degradation diagram for polymers within the molecular weight range presently being studied (370,000 - 600,000)[25].

By contrast with poly(methylacrylate) degradation during which cross linking of chains occurs[19], no evidence has been found in the present molecular weight studies for cross linking during degradation of the copolymers , even at high extents of degradation.

(ii) Double Bond Formation in the Degradation Residue.

It was found that the residues at higher extents of degradation in the glass molecular still were yellowish in colour, the depth of colour increasing with increasing methyl acrylate content of the copolymers. The U.V. spectra of such samples show a small absorbance in the region of 275 -375 millimicrons, as can be seen in figure 19.

Table 8 shows the colour expected and absorbance maxima for representative conjugated ethylenic systems[51]. The colour and spectrum of the degraded sample therefore show that double bonds are being formed in conjugated units of up to about 6 in length.

The I.R. spectra of these degraded residues shown for a representative sample in figure 20, also support double bond formation, since the characteristic -C = C-

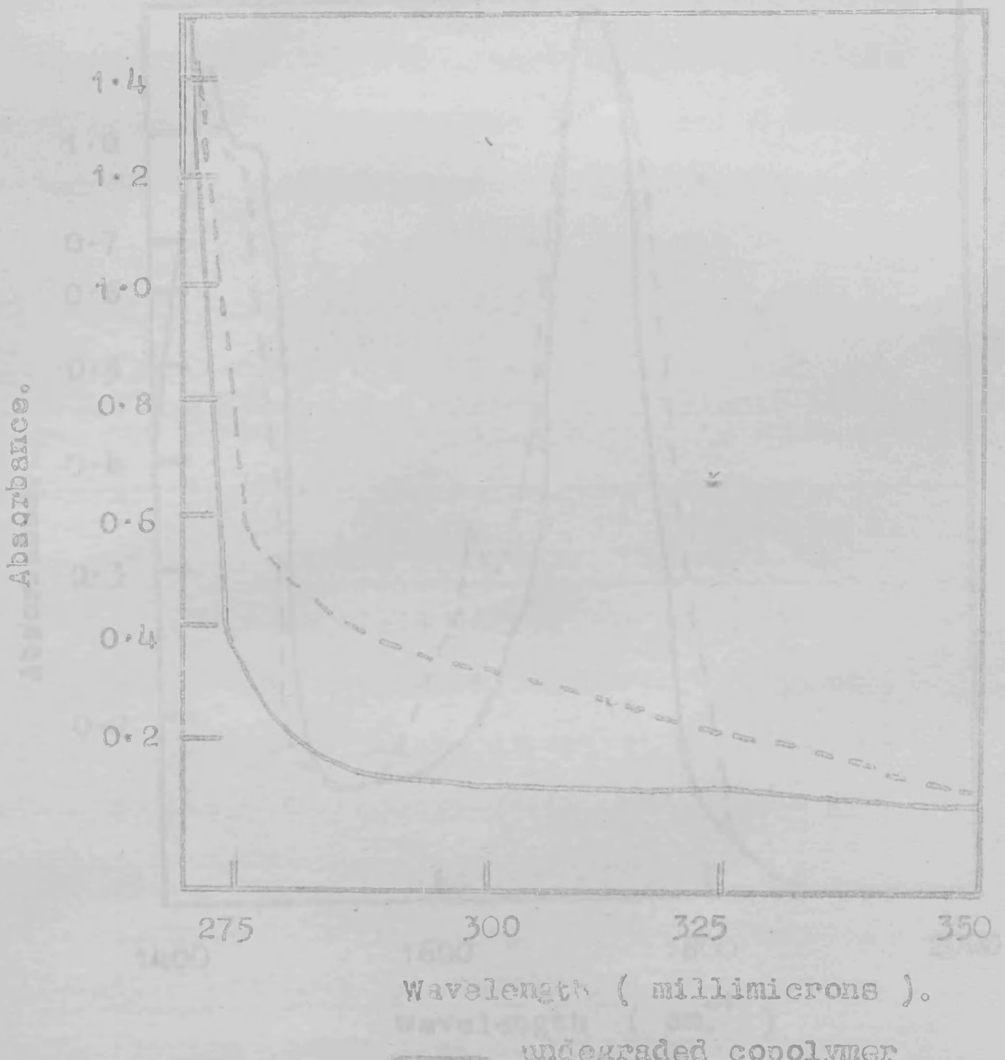


FIGURE 19.

Ultraviolet Spectra of 2/1 Copolymer run in Chloroform.

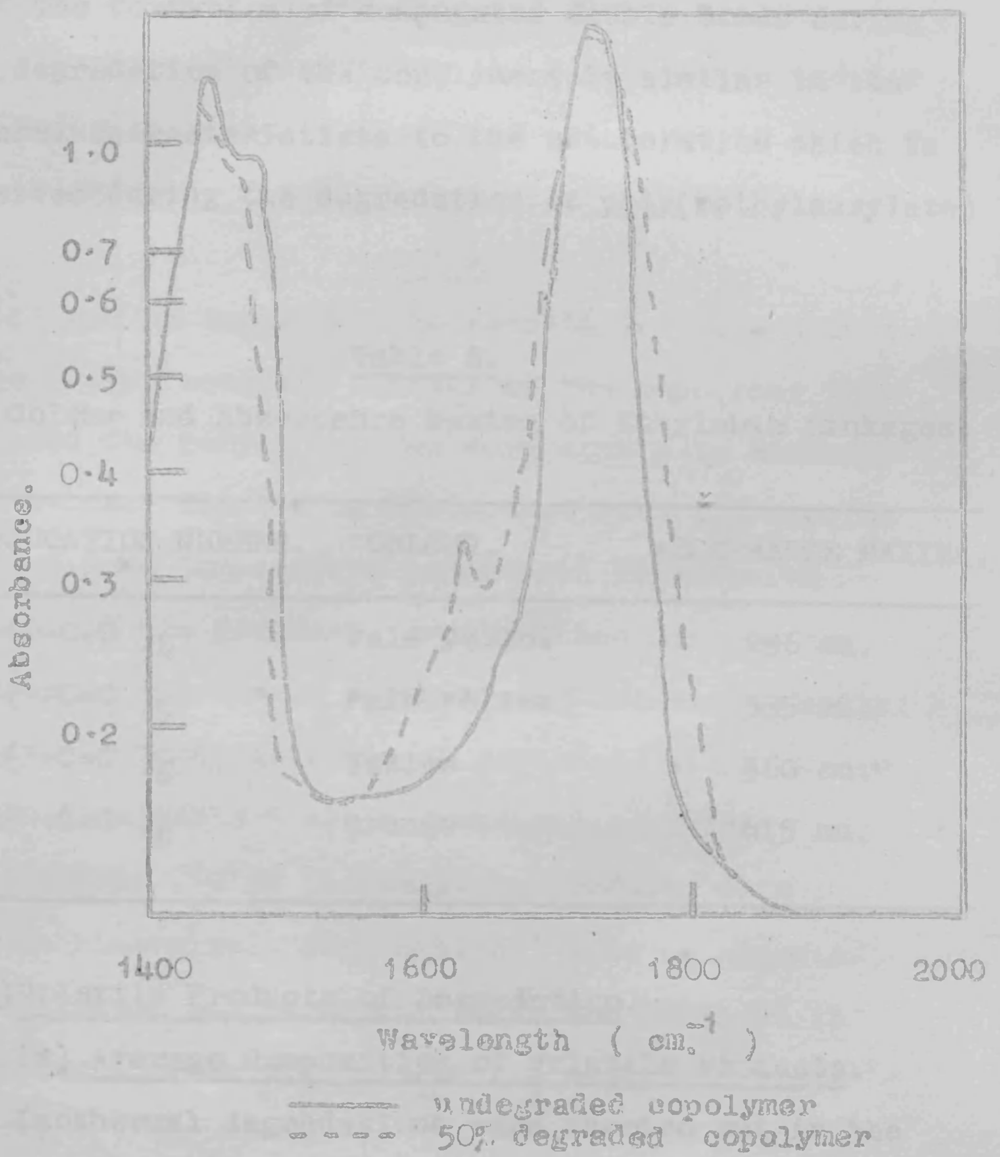


FIGURE 20.

Infra Red Spectra of 2/1 Copolymer as Film on Salt Plate.

absorbance appears at $1630cm^{-1}$. However this peak is much smaller than expected for conjugation which should enhance the absorbance.

The formation of conjugated double bonds during the degradation of the copolymers is similar in its general characteristicts to the unsaturation which is observed during the degradation of poly(methylacrylate)[34].

Table 8.

Colour and Absorbance Maxima of Ethylenic Linkages.

CONJUGATION NUMBER.	COLOUR.	ABSORBANCE MAXIMA.
$(-C=C)_4$	Pale yellow	296 mu.
$(-C=C)_5$	Pale yellow	335 mu.
$(-C=C)_6$	Yellow	360 mu.
$(-C=C)_8$	Orange	415 mu.

(iii) Volatile Products of Degradation.

(a) Average Composition of Volatile Products.

Isothermal degradations were carried out in the glass molecular still in the temperature range 260-300°C until little further reaction occured (measured by weight loss of sample). The composition of the volatile products and the extent of degradation at which further reaction was retarded are given in table 9. These results are based on the average of 3-5 experimental degradations both in the open and closed systems.

For comparison purposes the results reported for poly(methylacrylate) degradation[26] are given in table 9.

(b) Effect of Copolymer Composition on Production of Volatiles.

It can be seen from the results in table 9 that as the methyl acrylate content of the copolymer is increased the sample becomes more stable to thermal degradation. This is in accordance with the results obtained from temperature programmed degradation studies. Chain fragments greater than monomer are produced in increasing amounts with increasing methyl acrylate content, as would be expected, since as can be seen from table 9 chain fragments comprise approximately 75% of the volatile products from poly(methylacrylate) degradation. Also as expected, carbon dioxode and permanent gases are produced in increasing amounts with increasing methyl acrylate content.

There are, however, several significant differences in the production of volatile products than would be expected from a comparison with the degradation behaviour

COMPOSITION OF COPOLYMER.		AVERAGE COMPOSITION OF VOLATILE PRODUCTS (% BY WEIGHT OF TOTAL).						EXTENT OF DEGRADATION.
MMA	MA	Carbon dioxide.	permanent gases. (*)	Methanol.	MMA	MA	Chain fragments	(%)
poly(methyl-methacrylate)					≥96%		trace	95%
112	1	trace			≥96 %		trace	93%
26	1	≤1%	trace		93%	0·8%	5%	84%
7·7	1	≥1%	0·1%		87%	2·5%	10%	80%
2	1	3%	0·4%		64%	7·0%	25%	52%
poly(methyl-acrylate)		7·5%	1%	15%		0·76%	75%	Stabilisation at 45-55% loss[52]

* Permanent gases were found to consist mainly of hydrogen and traces of methane and carbon monoxide.

Table 9.

Composition of Volatile Products of Thermal Degradation of the Copolymers.

of poly(methylacrylate).

For example, no methanol was detected even during the degradation of the copolymer containing 33% methyl acrylate. Methanol is produced in about twice the amount of carbon dioxide in poly(methylacrylate) degradation and yet although carbon dioxide is produced here the methanol production is suppressed. This is a somewhat surprising result and obviously the two reactions which yield those products must be completely separable, although they both undoubtably arise from ester group decomposition.

Methyl acrylate monomer was liberated from the copolymers in much greater amounts than expected by comparison with poly(methylacrylate). In all cases about 1 in 4 of the calculated methyl acrylate monomer units in the copolymer was found as monomer, except for the 112/1 copolymer where no methyl acrylate monomer was detected. This is illustrated in table 10.

The production of greater amounts of methyl acrylate monomer in methyl methacrylate/methyl acrylate copolymers than in poly(methylacrylate) homopolymer agrees with the findings of Strassburger who studied pyrolysis-G.L.C. of the copolymers.[53]

Table 10.

G.L.C. Analysis of Volatile Products.

COPOLYMER COMPOSITION.		G.L.C. ANALYSIS. OF PRODUCTS.	
MMA	MA	MMA	MA
26	1	100	1
7·7	1	35	1
2	1	8	1

(3) DISCUSSION.

(i) Sequence Distribution of Copolymers. *

Copolymerisation of methyl methacrylate with methyl acrylate can lead to block, random or alternating incorporation of methyl acrylate units in the methyl methacrylate chain. The degradation characteristics of the copolymer will obviously depend on the sequence distribution of the monomer units since, for example, in a block of methyl acrylate units degradation similar to poly(methylacrylate) could occur, whilst in a random or alternate arrangement the influence of methyl methacrylate neighbours could possibly interfere with the poly(methylacrylate) degradation characteristics.

The sequence distribution of the copolymers can be predicted from the concept of run numbers introduced by Harwood[54], provided the reactivity ratios, copolymer composition and monomer mixture composition of the system are known. An outline of this method is given below.

The run number R of a system is defined as the number of uninterrupted monomer sequences per 100 monomer units. For example,

$$\sim\underline{A}-\underline{B}-\underline{AA}-\underline{B}-\underline{A}-\underline{B}-\underline{AAA}-\underline{BB}-\underline{A}-\underline{BBBB}-\underline{AA}-\underline{B}\sim .$$

The section of copolymer chain contains 20monomer units arranged in 12 alternating runs, therefore the run number is 60 for this sequence. The polymer is considered to be cyclic to remove end group effects and initially linkages to the right or left of a given monomer unit are considered. The %A-B linkages (number of A-B links per 100monomer units is calculated from

$$\%A-B = \frac{R}{2}$$

since every run of A units is followed by an A-B link and there are as many A runs as B runs in the copolymer. Similarly,

$$\%B-A = \frac{R}{2} .$$

The number of B units which have B neighbours on their right equals the total number of B units minus the number with A neighbours. That is,

$$\%B\text{-}B = \%B - \frac{R}{2}\ ;$$

Similarly, $\%A\text{-}A = \%A - \frac{R}{2}$ where %A and %B refer to the molar percentage of monomer units in the copolymer.

The probability that a given B unit has a B unit on its right, equals the total number of B units which satisfy this condition, divided by the total number of B units present, that is,

$$P_{B-B} = \frac{\%B - R/2}{\%B}\ .$$

Thus the probability that a given B unit has B units on both left and right is the product of the separate probabilities and therefore,

$$P_{B-B-B} = \frac{(\%B - R/2\ )^2}{\%B^2}\ .$$

Similarly for P_{A-A-A} .

Thus the sequence distribution can be calculated provided the copolymer composition and run numbers for the system are known. Other distributions such as P_{A-B-A} P_{B-A-B} etc. can be readily calculated as required.

The run numbers for vinyl copolymerisation are calculated from a knowledge of the polymerisation propagation steps,

$$\begin{array}{llll} \sim A\cdot + A \longrightarrow \sim AA\cdot & k_{11} & & r_a = \dfrac{k_{11}}{k_{12}} \\ \sim A\cdot + B \longrightarrow \sim AB\cdot & k_{12} & & \\ \sim B\cdot + B \longrightarrow \sim BB\cdot & k_{22} & & r_b = \dfrac{k_{22}}{k_{21}} . \\ \sim B\cdot + A \longrightarrow \sim BA\cdot & k_{21} & & \end{array}$$

The rate of monomer unit incorporation into the copolymer is given by,

$$\frac{d(A + B)}{dt} = \begin{array}{l} k_{11}(A\cdot)(A) + k_{12}(A\cdot)(B) + \\ k_{21}(B\cdot)(A) + k_{22}(B\cdot)(B) \end{array}$$

and the rate of sequence generation is given by,

$$\frac{dS}{dt} = k_{12}(A\cdot)(B) + k_{21}(B\cdot)(A) .$$

Thus if the first equation is divided by the second and the stationary state consideration

$$k_{12}(A\cdot)(B) = k_{21}(B\cdot)(A)$$

is applied, then,

$$\frac{d(\ A + B\ )}{dS} \quad = \ 1 + \frac{r_a\%A_f}{2\ \%B_f} \ + \ \frac{r_b\%B_f}{2\ \%A_f} \ ,$$

where %A and %B are the molar percentages of A and B in the monomer feed.

By definition,

$$R = 100\ \frac{dS}{d(\ A + B\ )}$$

therefore,

$$R = \frac{200}{2 + r_aA_f/B_f + r_bB_f/A_f}.$$

Thus R can be calculated from a knowledge of monomer feed composition and reactivity ratios for the copolymerising system.

This method of characterising sequence distribution in copolymers was proposed by Harwood since no uniform way of expressing sequence distribution had previously been applied and thus experimental results from different sources were difficult to correlate.

The sequence distribution of the copolymers calculated by this approach from the reactivity ratios and monomer mixture/copolymer compositions are shown in table 11.

COPOLYMER COMPOSITION. MMA	MA	%MMA-MA BONDS. (R/2)	%MMA-MMA BONDS.	%MA-MA BONDS.	%MMA-MMA-MMA BONDS.	%MA-MA-MA BONDS.
112	1	1·77	98·45	0·015	98·0	
26	1	6·9	92·85	0·25	92·4	0·00625
7·7	1	17·5	79·75	2·75	79·75	0·0443
2	1	50·7	41·31	7·988	0·384	0·0516

Table 11.

Sequence Distribution in Methyl methacrylate/Methyl acrylate Copolymers.

It is clear that the methyl acrylate units are seldom adjacent to each other, for example, there are only 2·75% methyl acrylate-methyl acrylate bonds in a 7·7/1 copolymer. Even for a 2/1 copolymer, whilst their is a greater chance of adjacent units (7·98%), their is a very limited chance of a block of three methyl acrylate units (0·0516%), thus each methyl acrylate unit will be influenced by at least one methyl methacrylate neighbour even for this high methyl acrylate content.

Therefore in all those copolymers it would appear that there are no long sequences of methyl acrylate units which would be expected to have degradation properties reflecting closely those of poly(methylacrylate). Thus any differences in degradation behaviour of the methyl acrylate units in the copolymers from those in poly(methylacrylate) will be attributable to their isolation from each other.

(ii) Conditions for Methanol Production Based on Sequence Distribution.

It could be concluded from these results that the production of methanol requires a number of adjacent methyl acrylate units in the chain since even for the 2/1 copolymer with 8% chance of adjacent methyl acrylate units, no methanol was detected as a volatile degradation product.

Unfortunately it was found difficult to prepare reasonable samples of high acrylate content for degradation studies to confirm this. Due to the rubbery nature of the sample volatiles from the precipitation technique were occluded, thus confusing analysis of the volatile products of degradation.

However this conclusion agrees with results from work carried out on the thermal degradation of ethylene-methyl acrylate copolymers where it was found[55] that block copolymers produced comparable quantities of methanol as poly(methylacrylate) homopolymer, whilst random copolymers produced less methanol than expected for the calculated methyl acrylate content.

Results apparently in conflict with these have been reported for pyrolysis-G.L.C. studies of methyl methacrylate/methyl acrylate copolymers[53], where it was found that a 4/1 molar methyl methacrylate/methyl acrylate copolymer yielded methanol on thermal degradation. However the copolymer for these investigations was polymerised to about 100% conversion and thus would have long blocks of methyl acrylate units in some of the chains. However it was also found that a molar mixture of poly(methylmethacrylate)/poly(methylacrylate) homopolymers gave much greater amounts of methanol than a copolymer of the same composition, so that our conclusions would seem to be correct.

Thus the inhibition of the formation of methanol from the copolymers is clearly due to the absence of blocks of methyl acrylate units in the copolymer molecule and conversely for methanol to be produced it seems that for either steric or chemical reasons blocks of methyl acrylate units must exist in the copolymer.

(iii) Molecular Weight Changes and Sequence Distribution.

It has been shown that the incorporation of methyl acrylate units in the methyl methacrylate chain hinders depolymerisation from the chain ends and promotes the random scission of chains, with the result that the molecular weight curve resembles that for total random scission.

The points of chain scission would therefore appear to be associates with the methyl acrylate units, which from sequence distribution calculations occur at random in the chain for all copolymers studied. Thus the magnitude of the decrease in molecular weight would be expected to be dependent on the methyl acrylate content of the copolymers.

The results in figures 17-18 do not conform to this; the molecular weight decrease for the 2/1 copolymer, for example, is certainly greater than for the others, but not in proportion to the methyl acrylate content. This is so even if a generous allowance is made for values of molecular weights in this region ($\sim$8,000) being only approximate and for methyl acrylate disappearing as monomer or as chain fragments.

Thus the decrease in molecular weight in the copolymers caused by the introduction of the methyl acrylate units does not seem to be a straightforward process dependent simply upon chain scission at acrylate units in the copolymer chain. This will be discussed in Chapter 5.

(iv) Methyl Acrylate Monomer Production

The fact that methyl acrylate units inhibit monomer production from chain ends suggests that a methyl acrylate unit in the chain can act as a stopper for the chain depropagation process in which monomer is liberated. However this process is not 100% efficient since methyl acrylate monomer does appear among the volatile degradation products. The fact that the proportion of methyl acrylate in the monomer mixture of the degradation products is always less than the proportion of methyl acrylate units in the copolymer, is an indication, and may even be a quantitative measure of the efficiency with which methyl acrylate units may be liberated from a depropagating radical.

CHAPTER 5.

THE THERMAL DEGRADATION OF METHYL METHACRYLATE/ METHYL ACRYLATE COPOLYMERS. (2) THE CHAIN SCISSION REACTION.

(1) CARBON DIOXODE PRODUCTION AND CHAIN SCISSION.

(i) Pressure Measurements for Carbon Dioxide.

The production of carbon dioxide during the thermal degradation of the copolymers was followed by the development of pressure in the closed glass system. The results obtained for degradations of similar weights of the 26/1 and 7·7/1 copolymers, in the temperature range 260 - 326°C, are shown in figures 21 and 22 respectively.

The initial retardation in the development of pressure at lower degradation temperatures (260-280°C) is due to the melting of the copolymer samples, which have a much higher melting point (approximately 240°C) than poly(methylmethacrylate). Once the sample is molten and its temperature is thus uniform throughout, it can be seen that there is a sudden rapid increase in the rate of production of carbon dioxide. At a

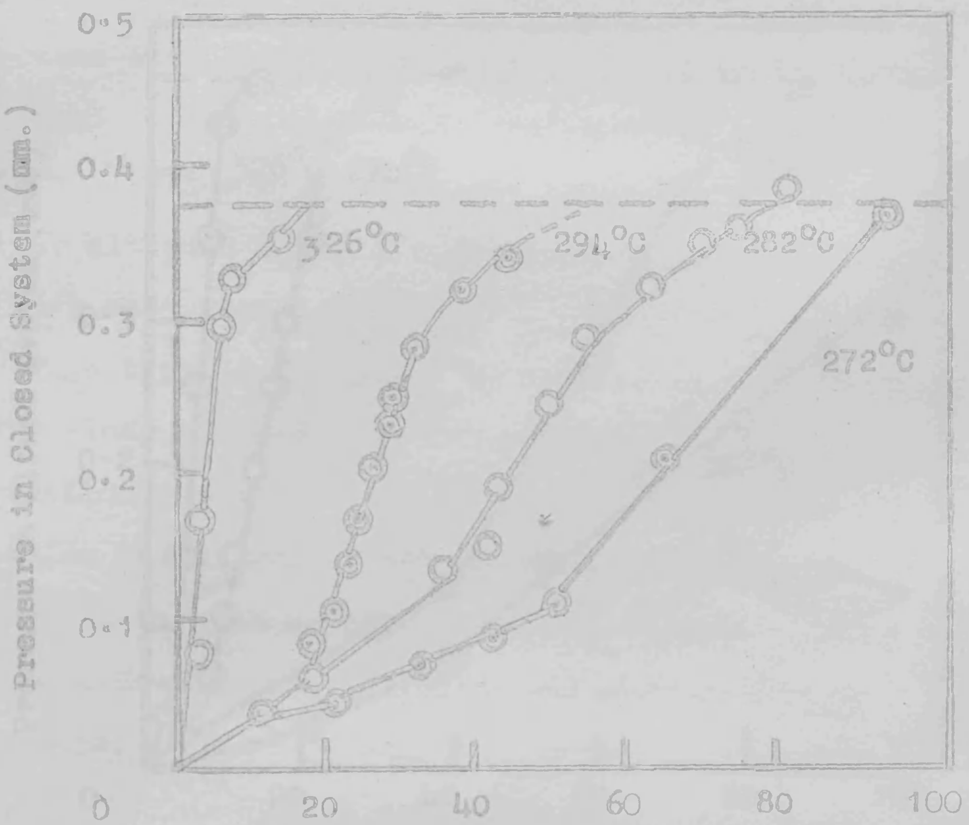


FIGURE 21.

Production of Carbon Dioxide During Degradation of 26/1 Copolymer.

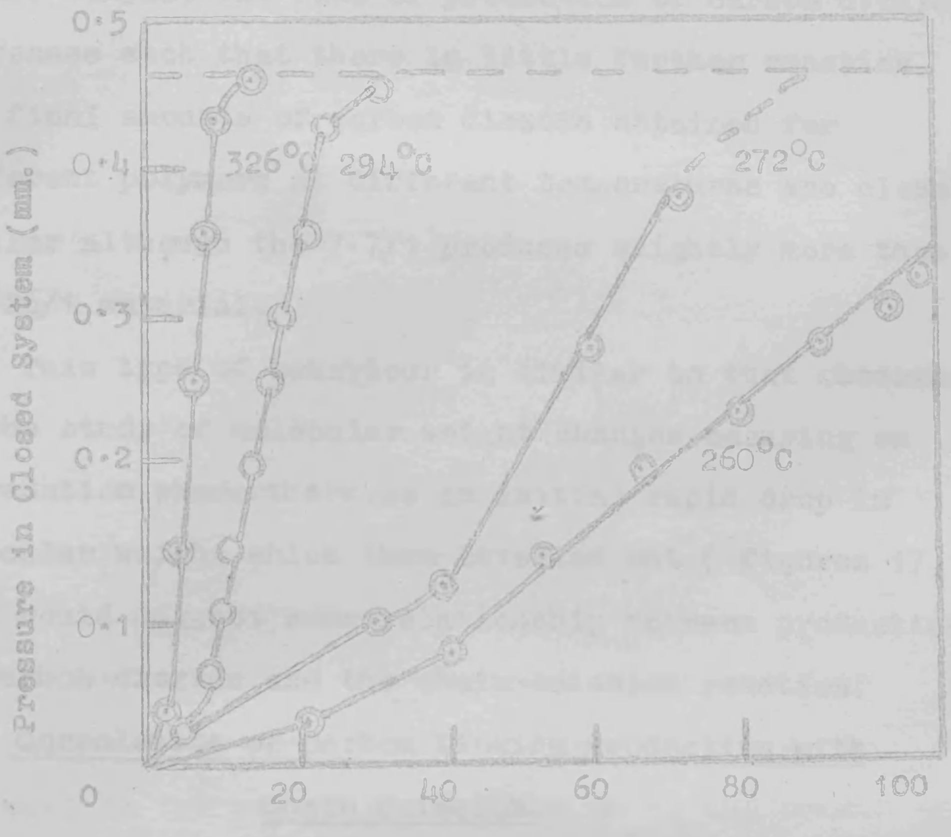


FIGURE 22.

Production of Carbon Dioxide During Degradation of 7·7/1 Copolymer.

certain extent of degradation, which corresponds to the values given in table 9, Chapter 4, for the stabilisation of the sample, the rate of production of carbon dioxide decreases such that there is little further reaction. The final amounts of carbon dioxide obtained for different polymers at different temperatures are closely similar although the 7·7/1 produces slightly more than the 26/1 material.

This type of behaviour is similar to that observed in the study of molecular weight changes occuring on degradation where there was an initial rapid drop in molecular weight which then levelled out (figures 17,18). This would suggest some relationship between production of carbon dioxide and the chain scission reaction.

(ii) Correlation of Carbon Dioxide Production with Chain Scission.

From the molecular weight changes occuring in the polymer during degradation, it is possible to calculate the number of chain scissions N occuring per molecule of polymer.

If it is assumed that no molecules are lost to the system by complete volatilisation (or unzipping) of chain fragments, then the chain length, CL, after volatilisation of a fraction x of the polymer is given by,

$$CL = \frac{CL_o(1-x)}{N + 1} ,$$

in which CL_o is the original chain length.

Thus

$$N = \frac{CL_o}{CL} (1-x) - 1 ,$$

which is equivalent to

$$N = \frac{MW_o}{MW}(1-x) - 1 ,$$

in which MW_o and MW are the original molecular weight and molecular weight at extent of degradation x respectively.

Degradation runs were carried out in the open flow glass system and the carbon dioxide pressure measured at the end of a run, from which the number of moles of carbon dioxide produced per mole of the polymer was calculated. From the degree of volatilisation of the sample and the molecular weight of the residue the value of N was calculated.

The results obtained are shown in figure 23 as chain scissions per mole of polymer plotted versus the moles of carbon dioxide produced, for various degradations of the 112/1,26/1,7·7/1 and 2/1 copolymers,degraded in

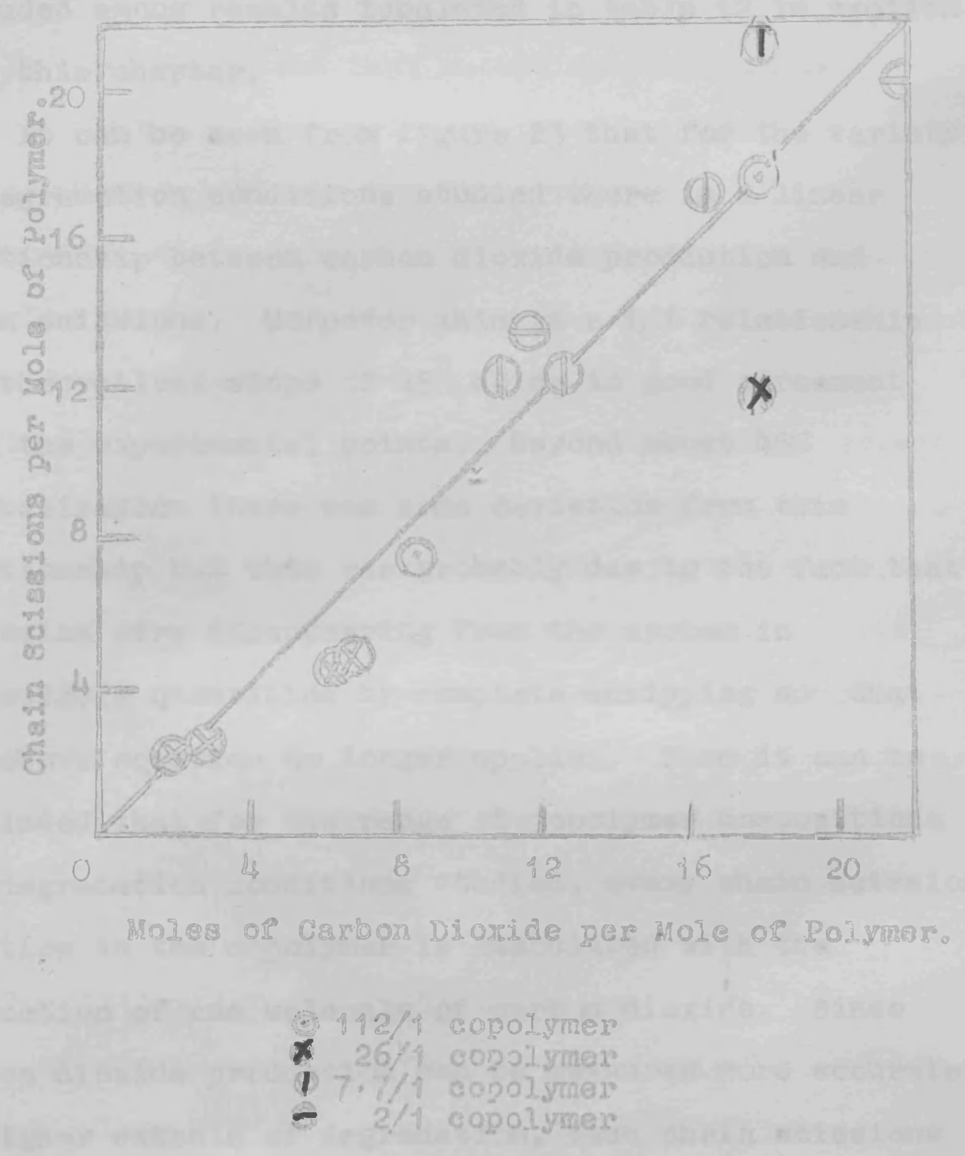


FIGURE 23.

Relationship Between Carbon Dioxide Production and Chain Scission During Degradation.

the form of powder or cold pressed film in the temperature region 270-326°C and from 2-45% volatilisation. The actual experimental results and conditions are included among results tabulated in table 12 in section 2 of this chapter.

It can be seen from figure 23 that for the variety of degradation conditions studied there is a linear relationship between carbon dioxide production and chain scissions. Moreover this is a 1/1 relationship the theoretical slope of 45° being in good agreement with the experimental points. Beyond about 45% volatilisation there was some deviation from this relationship but this was probably due to the fact that molecules were disappearing from the system in appreciable quantities by complete unzipping so that the above equation no longer applies. Thus it can be concluded that for the range of copolymer compositions and degradation conditions studied, every chain scission reaction in the copolymer is associated with the production of one molecule of carbon dioxide. Since carbon dioxide production can be measured more accurately at higher extents of degradation, than chain scissions can, due to the inaccuracy in the measurement of lower molecular weights, all data on chain scission in the following sections were calculated from measurements of carbon dioxide pressure.

(2) VOLATILISATION AND CHAIN SCISSION.

(i) Introduction.

It has been shown that methyl acrylate units effectively block the unzipping reaction which is initiated at relatively low temperatures at the unsaturated chain ends of poly(methylmethacrylate). At higher temperatures, in the copolymers, chain scission and monomer production occurs. It is reasonable to suppose that chain scission is associated with the methyl acrylate units and that the radicals thus produced can unzip, at least to the next methyl acrylate unit in the chain. If this is so then the number of chain scissions occuring at a certain extent of degradation should be directly related to the amount of monomer produced and the number of monomer units produced per chain scission would be a measure of the "zip length" of the depolymerisation reaction for each copolymer sample.

(ii) Volatilisation and Chain Scission.

Copolymers were degraded in the form of powder in the open glass system. The percentage volatilisation was determined by weight loss and chain scissions calculated from carbon dioxide pressure. The results obtained for the 26/1,7·7/1 and 2/1 copolymers are included in table 12

COMPOSITION OF COPOLYMER. MMA	MA	PHYSICAL FORM OF SAMPLE.	TEMPERATURE OF DEGRADATION. °C	%VOLATILISATION.	MOLECULAR WEIGHT OF RESIDUE.	CHAIN SCISSIONS PER MOLE.	CARBON DIOXIDE PER MOLE.
112	1	powder.	294	6·6	66,000	7·46	8·22
		"	282	22·5			7·22
		"	294	31·5	58,000	6·21	11·58
25	1	powder.	282	26	15,000	28·6	24·5
		"	"	62			52·4
		"	"	79·5			66
		"	294	2·3	175,000	2·34	2·77
		"	"	23·6	40,000	11·8	17·6
		film	272		190,000	2·2	1·89
		"	294	12·5	115,000	4·8	6·0
		"	326	11·0	110,000	4·68	6·58
7·7	1	powder	282	16·4	27,000	12·14	10·5
		"	"	25	23,600	12·5	12·4
		"	"	31·4	13,000	21·3	17·85
		"	294	17·3	20,000	17·5	16·06
		"	"	32·2			18
		"	"	50·3			30
		"	326	74·7			35·5
2	1	powder	294	13·9	15,000	20·3	22
		"	310	5·34	24,000	13·6	11·18
		"	"	15·4	16,800	17·7	17·7
		"	"	27·3			35·5
		"	"	45·2			48·3
		"	"	53·4			60·3

Table 12.

Summary of Carbon Dioxide/Chain Scission Results.

and figures 24-26 illustrate that a linear relationship exists between volatilisation and chain scission, in agreement with the proposals made in Section (2)-(i).

(iii) Estimation of the Zip Length.

The slopes of the experimental plots (figures 24-26) which are the percentage of the total monomers in the copolymers lost per chain scission per copolymer molecule are listed in the second column of table 13. The zip length per chain scission for each copolymer can readily be calculated from those values as shown in table 13.

The zip length for the 112/1 copolymer (powder) was estimated from the average value of the total monomers lost per chain scission, per molecule of copolymer (table 13, column 2), calculated from the results in table 12, since for these copolymer samples there were not enough experimental results to give a plot of volatilisation versus chain scission.

(iv) Zip Length and Copolymer Composition.

The zip length of the depropagation reaction from the unsaturated chain ends of pure poly(methylmethacrylate) varies from 500 to 4000 monomer units [7]. The same depropagating radical will be formed by initiation at chain ends, as by chain scission in the copolymers

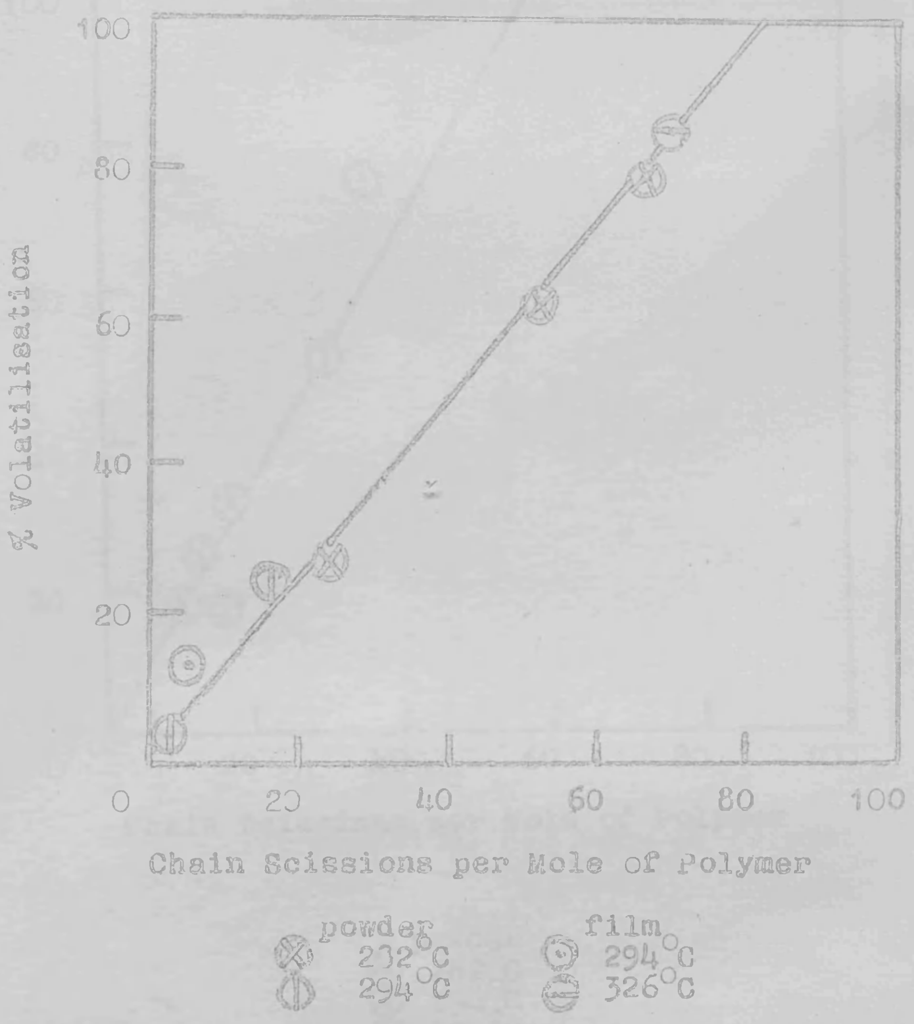


FIGURE 24.

Relationship Between Volatilisation and Chain Scission for Degradation of 26/1 Copolymer.

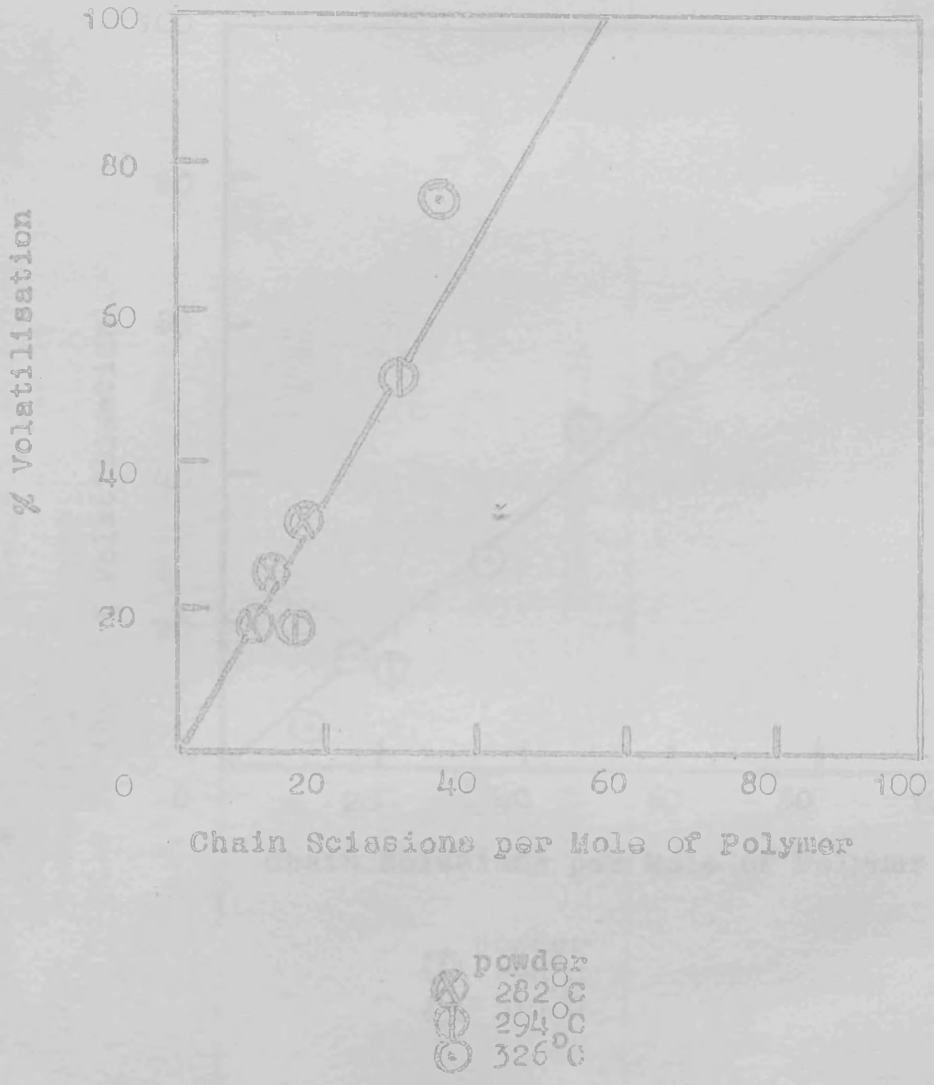


FIGURE 25.

Relationship Between Volatilization and Chain Scission for Degradation of 7·7/1 Copolymer.

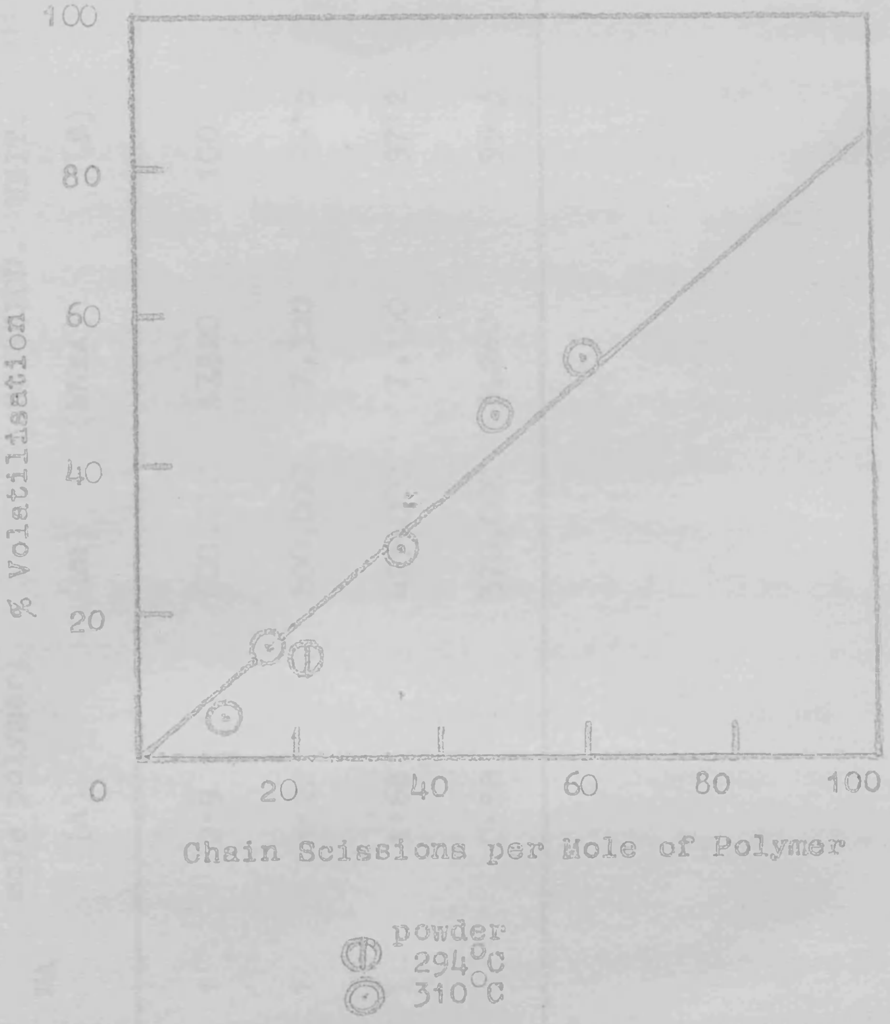


FIGURE 26.

Relationship Between Volatilisation and Chain Scission for Degradation of 2/1 Copolymer.

COMPOSITION OF COPOLYMER		SLOPE (%voln./chain scission/ mole polymer)	MOLECULAR WEIGHT.	FRACTION OF MW LOST/ SCISSION.	AVERAGE WEIGHT OF MONOMER UNIT.	ZIP LENGTH.
MMA	MA	(A)	(MW)	(MW x A)	(B)	$\left(\frac{MW \times A}{B}\right)$
112	1	2·9	600,000	17,320	100	173
26	1	1·22	600,000	7,320	99·5	73·6
7·7	1	1·68	425,000	7,150	97·2	73·5
2	1	0·88	370,000	3,260	95·3	34·2

Table 13.

Calculation of Zip Length from Points of Chain Scission.

(the nature of the chain scission reaction is discussed in Section(6)-(i)). The results in table 13 show that the incorporation of less than 1% of methyl acrylate in the methyl methacrylate chain considerably shortens the zip length of the depropagation reaction and that it is progressively decreased by increasing the methyl acrylate content of the copolymer. This is in agreement with the concept of the blocking of the depropagation reaction by methyl acrylate units as discussed in Chapter 4 Section (3)-(iv).

However, the experimental zip lengths indicate that blocking by methyl acrylate units is not completely efficient as was suggested from the investigation of monomer production (Chapter 4 Section (3)-(iv)) since for example in the 2/1 copolymer a zip length of no more than five would be expected if the reaction were blocked at the first methyl acrylate units beyond the points of chain scission.

The nature of the blocking reaction of the methyl acrylate units in the copolymer will be discussed in Section(6).

(v) Chain Scission and Transfer.

It is evident that transfer reactions become more important with increasing methyl acrylate content of the copolymers, since chain fragments comprise a larger proportion of the volatile products of degradation (Chapter 4 table 9). It has been shown that depolymerisation of the copolymers occurs from the points of chain scission (Section 2). Chain fragments could be produced by transfer reactions occuring in competition with depropagation to monomer. This reaction would be somewhat similar to that observed for poly(styrene)[9] as discussed in Chapter 1. On the other hand, chain fragments could be produced in independent transfer reactions involving chain ends. In the former case the chain fragments would comprise a definite proportion of the volatile products of degradation independent of the extent of degradation, whilst in the latter case there would be a variable relationship between chain fragments and volatilisation. In this section the relationship between volatilisation and chain fragments has been investigated for the 7·7/1 and 2/1 copolymers. The 112/1 and 26/1 copolymers formed only small quantities of chain fragments, which could not be estimated with sufficient accuracy.

The copolymers were degraded in the open glass system and the chain fragments produced compared with the total volatilisation. From the results in table 14 it is clear that within experimental error the chain fragments comprise a constant proportion of the total volatiles, for the various extents of degradation in the two copolymers studied. These results indicate that the chain fragments are produced by transfer reactions involving the depropagating radicals.

Table 14.

Relationship of Chain Fragments with Volatilisation.

COPOLYMER COMPOSITION. MMA	MA	%VOLATILISATION.	CHAIN FRAGMENTS. (% of total volatiles)
7·7	1	25	13·7
		31·4	7·8
		32·2	7·6
		50·3	12·7
		74·7	8·5
2	1	13·9	23·4
		15·4	17
		45·2	25·7
		53·4	25·1

(3) CHAIN SCISSION AND COPOLYMER COMPOSITION.

(i) Introduction.

As discussed previously (Chapter 4 Section (3)-(iii)) there must be some definite relationship between the methyl acrylate content of the copolymers and the number of chain scissions resulting from the presence of this comonomer in the methyl methacrylate chain. It was obvious from these molecular weight studies that this was not a linear relationship although limitations in the accuracy of the measurement of molecular weights did not allow the precise relationship to be determined. It has been shown, however, that rates and total amounts of chain scission can be estimated from measurements of carbon dioxide pressure, so that an alternative method is available for investigating this relationship between chain scission and copolymer composition.

(ii) Rate of Chain Scission.

The rate of chain scission was estimated from the rapid increase in carbon dioxide pressure in the closed glass system, which occurs after the sample has melted. (figures 21 - 22). Various weights of sample were degraded and the pressure increases averaged to take account of side effects (Chapter 2 Section(3)-(iv)). Absolute rates of chain scission, expressed as pressure increase per mg. sample per minute, were thus obtained. The experimental results are included in figures 27,28, Section (4), the horizontal lines through the values indicating the average value of absolute rate. Rates are presented in table 15, from which it can be seen that the rate of chain scission at a particular

COMPOSITION OF COPOLYMER		TEMPERATURE OF DEGRADATION.	RATE OF CHAIN SCISSION.	MA CONTENT OF COPOLYMER	$\sqrt{MA}$ CONTENT	$\frac{RATE}{\sqrt{MA}}$
MMA	MA	°C	(mm./mg./min.) x10^4	(% total monomer)		
26	1	294	5·2	3·7	1·92	2·71
7·7	1	294	7·2	11·5	3·39	2·12
2	1	294	12·38	33	5·75	2·15
26	1	272	2·2	3·7	1·92	1·145
7·7	1	272	3·17	11·5	3·39	0·935

Table 15.

Relationship Between Rate of Chain Scission and Methyl Acrylate Content of Copolymers.

temperature is proportional to the square root of the methyl acrylate content.

No results were obtained for the 112/1 copolymer due to the small amounts of carbon dioxide produced making rate measurements difficult and for the 2/1 copolymer at 272°C, due to the high viscosity of the sample at this low temperature, inhibiting the escape of the carbon dioxide from the polymer.

(iii) Total Chain Scission.

The total amount of chain scission occuring on degradation of the 112/1,26/1,7.7/1 and 2/1 copolymer samples in the temperature region 260-326°C, were estimated from the pressure of carbon dioxide built up in the closed system at the point of low rate of production of carbon dioxide (figures 21,22).

From the results shown in table 16 it can be seen that for different temperatures of degradation the total amount of chain scission in a copolymer sample is the same within experimental error (second last column table 16). The total amount of chain scission appears to be proportional to the square root of the methyl acrylate content of the copolymers as shown by the last column in table 16.

These dependences of total chain scission and rate of chain scission on the square root of the methyl

COMPOSITION OF COPOLYMER. MMA	MA	WEIGHT DEGRADED (mg.)	TEMPERATURE OF DEGRADATION. °C	$\sqrt{MA}$ CONTENT OF COPOLYMER.	TOTAL PRESSURE OF CO_2 (mm.) (A)	$\frac{A}{WEIGHT}$. (B)	$\frac{B}{\sqrt{MA}}$ x10^3
112	1	4·2	294	0·937	0·0094	0·00462	4·92
		20·1	326	"	0·0822	0·0041	4·4
26	1	3·5	326	1·92	0·0334	0·00955	4·97
		9·0	326	"	0·0655	0·00728	3·80
		9·5	294	"	0·0910	0·00959	4·99
7·7	1	2·4	272	3·39	0·036	0·0150	4·4
		2·5	294	"	0·0395	0·0158	4·65
		4·1	326	"	0·0664	0·0162	4·78
		9·3	294	"	0·156	0·01675	4·95
2	1	18·0	310	5·75	0·4382	0·02435	4·23
		20·7	"	"	0·460	0·0222	3·87

Table 16.

Relationship of Total Chain Scission with Methyl Acrylate Content of Copolymers.

acrylate content of the copolymers are rather unsuspected but seem to confirm the inference made from molecular weight measurements that the mechanism of degradation of these copolymers is not simple. This will be discussed further in Section (6) of this chapter.

(4) ACTIVATION ENERGY FOR CHAIN SCISSION.

Further rate measurements were carried out on the 26/1 copolymer at 282 and 326°C and the 7·7/1 copolymer at 260 and 326°C as described in Section (3)-(ii). The results obtained are shown, along with the results previously discussed, in figures 27,28, the horizontal lines indicating the average values of absolute rates of chain scission at the different temperatures.

The activation energy for the overall chain scission reaction was obtained by the use of the Arrhenius Equation[56],

$$\log k = \frac{-E}{2{\cdot}303RT} + \text{constant}$$

in which k is the rate constant, T the absolute temperature, R the gas constant and E the activation energy of the reaction in kilocalories per mole. The logarithms of the absolute rates of chain scission were plotted against the reciprocal of the absolute

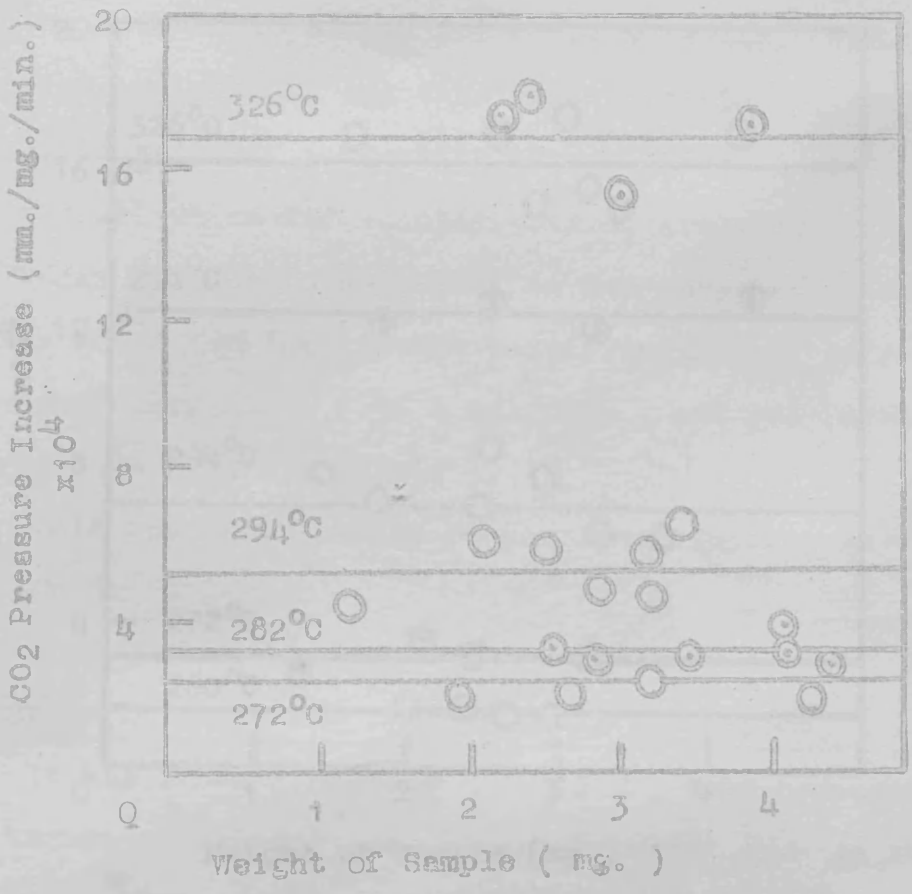


FIGURE 27.

Estimation of Carbon Dioxide Absolute Pressure Increase for Degradation of 26/1 Copolymer.

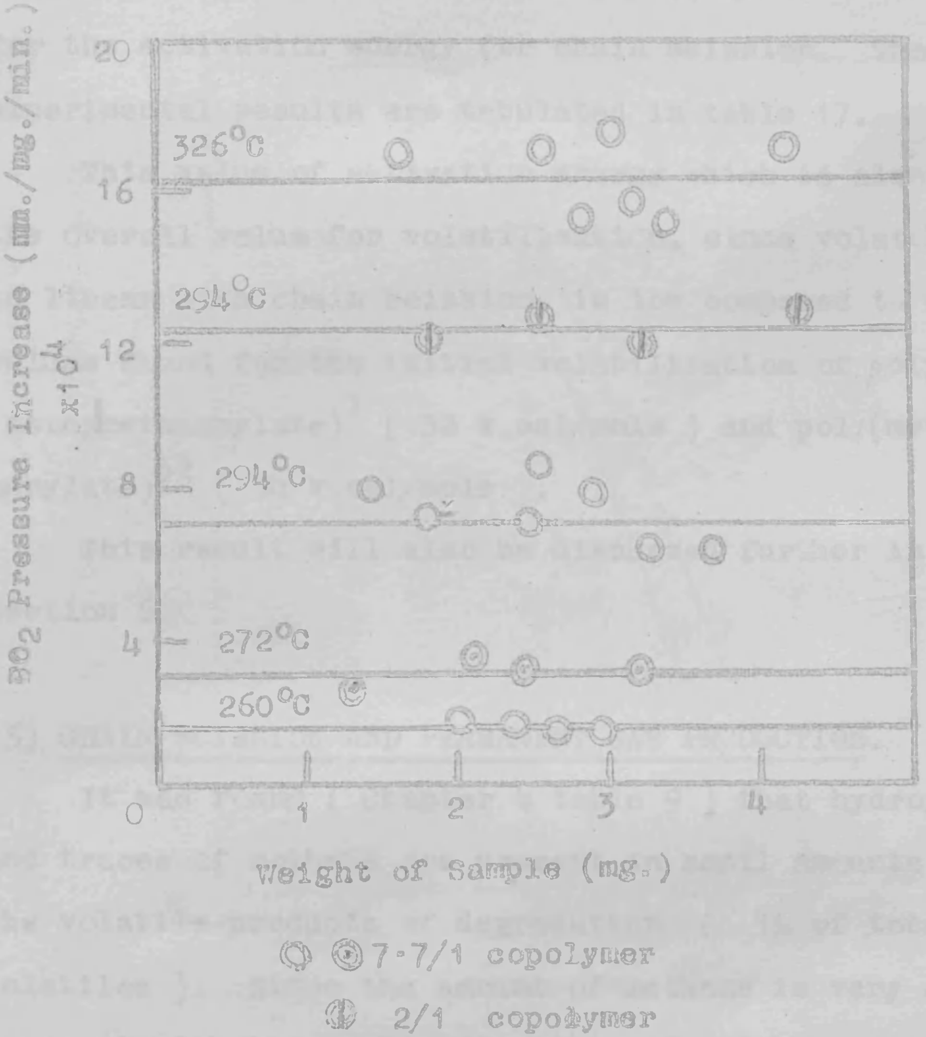


FIGURE 28.

Estimation of Carbon Dioxide Absolute Pressure Increase for Degradation of 7·7/1 and 2/1 Copolymers.

temperatures of degradation and from the slopes of the two experimental plots for the 26/1 and 7·7/1 copolymers (figure 29) a value of 23·5 ± 1 k.cal./mole was found for the activation energy for chain scission. The experimental results are tabulated in table 17.

This value of activation energy which is also the overall value for volatilisation, since volatilisation is linear with chain scission, is low compared to the values found for the initial volatilisation of poly-(methylmethacrylate)[7] (32 k.cal/mole) and poly(methylacrylate)[52] (34 k.cal/mole).

This result will also be discussed further in Section 6.

(5) CHAIN SCISSION AND PERMANENT GAS PRODUCTION.

It was found (Chapter 4 table 9) that hydrogen and traces of methane are present in small amounts in the volatile products of degradation (1% of total volatiles). Since the amount of methane is very small compared with the carbon dioxide production it is clear that the liberation of the carbon dioxide, which must come from the ester group, does not follow the liberation of a methyl group as part of a volatile fragment.

Although the gases are present only in small amounts, it was nevertheless found that for any given

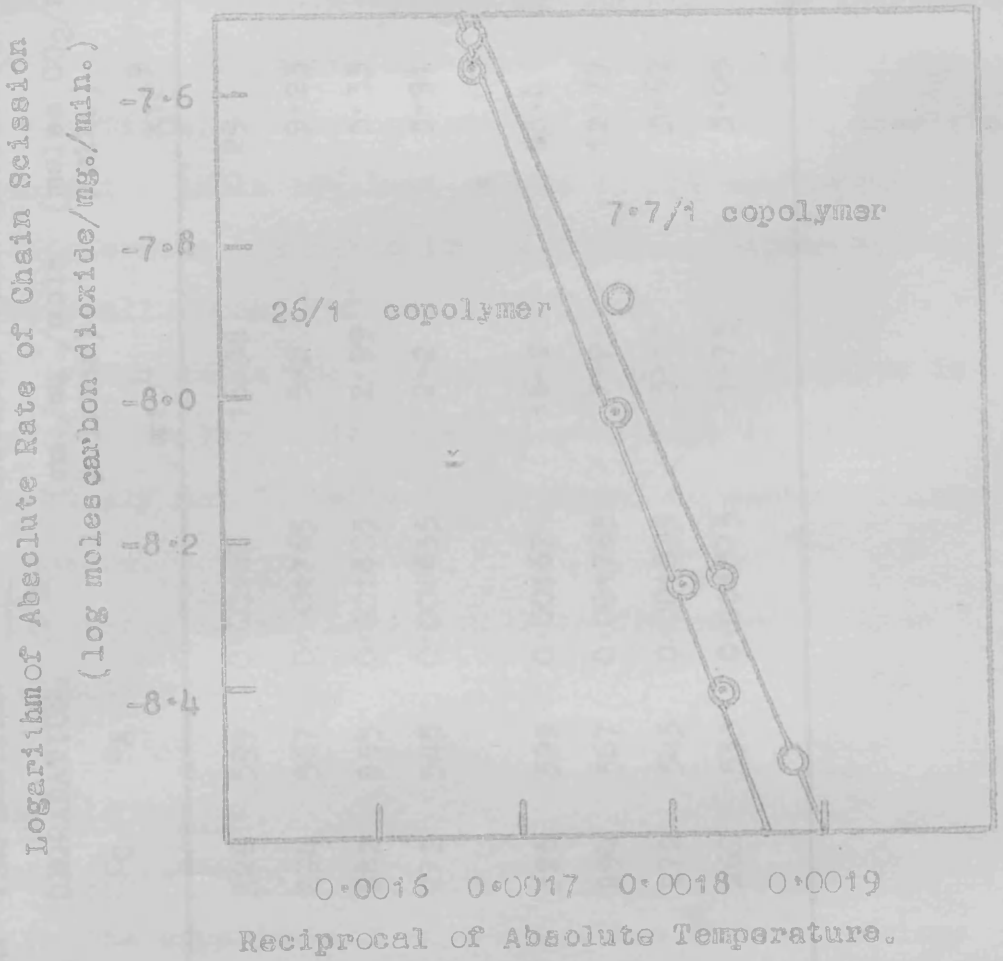


FIGURE 29.

Determination of Activation Energy for Chain Scission.

COMPOSITION OF COPOLYMER.		TEMPERATURE OF DEGRADATION.		$\frac{1}{T^{\circ}A}$	ABSOLUTE RATE (mm./mg./mole polymer)	ABSOLUTE RATE (moles CO_2/mg./min.)	LOG(RATE)
MMA	MA	°C	°A		$\times 10^4$	$\times 10^9$	
26	1	326	599	0·00167	16·38	29	-7·538
		294	567	0·001765	5·2	9·23	-8·035
		282	555	0·001805	2·99	5·33	-8·27
		272	545	0·001835	2·2	3·91	-8·408
7·7	1	326	599	0·00167	16·2	28·4	-7·547
		294	567	0·001765	7·2	12·79	-7·893
		272	545	0·001835	3·17	5·62	-8·25
		260	533	0·001875	1·73	3·05	- 8·516

Table 17.

Experimental Results for Determination of Activation Energy of Chain Scission (figure 29).

polymer there is a constant ratio of chain scissions to molecules of permanent gas produced, which is illustrated by the results in table 18. Moreover as the methyl acrylate content of the copolymer increases, this ratio decreases, and appears to be inversely proportional to the square root of the methyl acrylate content (table 18, last column). It was impossible to determine the ratio in the 112/1 copolymer due to the small amounts of gases involved.

Thus while the production of permanent gases is related to the chain scission reaction, it is certainly not directly proportional to carbon dioxide pressure.

These relationships will be discussed further in Section 6.

(6) DISCUSSION.

(1) Mechanism of the Chain Scission Reaction.

The experimental data described in the previous sections clearly indicate that the reaction mechanism is complicated and certainly involves more than simple cleavage at methyl acrylate units involving carbon dioxide production , followed by unzipping of the methyl methacrylate segments of the chains. In this section several chain scission mechanisms will be

COMPOSITION OF COPOLYMER, MMA	MA	TEMPERATURE OF DEGRADATION. °C	%VOLATILISATION.	RATIO OF CHAIN SCISSIONS/PERMANENT GASES.	AVERAGE RATIO. (A)	$\sqrt{MA}$	$A \times \sqrt{MA}$
26	1	200	1	20	20	1·92	38·4
		220	2	25			
		294	85	18			
		294	85	17			
		326	80 "	20			
7·7	1	326	80	11·95	11·9	3·39	40·3
		326	<1·0	11·9			
2	1	294	50	7·72	7·64	5·75	43·8
		310	52·2	7·2			
		310	60	8			

Table 18.

Permanent Gases and Chain Scissions. Relationship with Methyl Acrylate Content of Copolymers.

considered in order to determine which fits the experimental results most satisfactorily.

The dependence of rate of chain scission on the square root of the methyl acrylate content of the copolymers (Section (3)-(ii)) and the low energy of activation for chain scission (Section (4)) are both consistent with the suggestion that chain scission proceeds by a chain reaction mechanism. The most obvious initiation step in this chain reaction is random scission in the methyl methacrylate sections of the chains which is known to occur in pure poly(methylmethacrylate) at the temperatures used in the present investigations. The methyl acrylate units are of course blocking the normal depropagation reaction which is initiated at the unsaturated methyl methacrylate chain ends.

If M_n represents a polymer molecule and R· a long chain radical, then initiation can be represented by,

$$M_n \xrightarrow{k_i} R\cdot + R\cdot \quad ,$$

and thus,

$$\text{rate of initiation} = k_i(M_n).$$

Propagation of the chain reaction could occur by transfer between these radicals and the tertiary hydrogen atoms of the methyl acrylate units in the polymer chains.

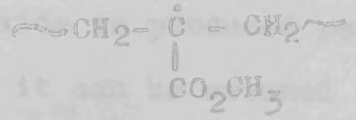
Thus,

$$R\cdot + \sim MA \sim \xrightarrow{k_p} R + \sim \dot{MA} \sim .$$

Therefore,

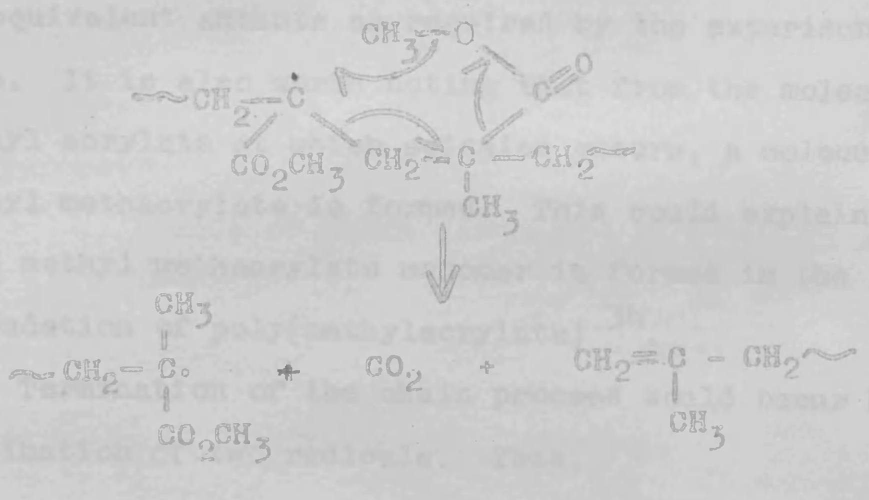
$$\text{rate of propagation} = k_p(R\cdot)(MA).$$

The resulting radical,



$$\sim CH_2-\overset{\cdot}{\underset{CO_2CH_3}{C}}-CH_2\sim$$

could rearrange by the following six-membered ring mechanism,



(A) (B)

which is somewhat similar to one proposed for the production of carbon dioxide during the photochemical degradation of poly(methylacrylate) [20].

The radical A could then either depropagate to monomer or could carry on the propagation reaction of chain scission by abstracting a tertiary hydrogen atom. The unsaturated chain end B could depropagate to monomer by a similar mechanism to poly(methylmethacrylate) [7]. In accordance with experimental findings one molecule of carbon dioxide is produced per chain scission in this mechanism, if it can be assumed that the chain length is appreciable, such that the number of initiation steps which occur without production of carbon dioxide is negligible compared with the number of propagation steps. In addition, carbon dioxide is produced without methane in equivalent amounts as required by the experimental data. It is also worth noting that from the molecule of methyl acrylate at which scission occurs, a molecule of methyl methacrylate is formed. This could explain why some methyl methacrylate monomer is formed in the degradation of poly(methylacrylate) [34].

Termination of the chain process would occur by combination of two radicals. Thus,

$$R\cdot + R\cdot \xrightarrow{k_t} R-R \quad ,$$

and

$$\text{rate of termination} = k_t(R\cdot)^2 .$$

Although this radical chain reaction mechanism could also be consistent with the low energy of activation, the experimentally observed rate relationship does not follow from it. If it is assumed that the chain length of the reaction is long then the rate of chain scission is given by the rate of propagation, that is,

$$\text{rate of chain scission} = k_p(R\cdot)\,(MA).$$

In the stationary state,

$$\text{rate of initiation} = \text{rate of termination},$$

that is,

$$k_i(M_n) = k_t(R\cdot)^2,$$

therefore,

$$R\cdot = \sqrt{\frac{k_i(M_n)}{k_t}}.$$

Therefore,

$$\text{rate of chain scission} = k_p \frac{k_i^{\frac{1}{2}}}{k_t^{\frac{1}{2}}}(M_n)^{\frac{1}{2}}(MA),$$

$$= \text{constant} \times (MA),$$

since k_p, k_i, k_t and M_n are all constant.

Thus it follows from this mechanism that the rate of chain scission should be proportional to the methyl acrylate content of the copolymer. From the experimental data described in Section (3)-(ii), however, it was established that the rate of chain scission is proportional to the square root of the methyl acrylate content of the copolymer.

If it is assumed that initiation occurs only in the vicinity of methyl acrylate units then,

$$\sim MA \sim \xrightarrow{k_i} R\cdot \quad ,$$

and

$$\text{rate of initiation} = k_i(MA).$$

If propagation and termination are assumed to be as before, then in the stationary state,

$$k_i(MA) = k_t(R\cdot)^2 \quad ,$$

therefore,

$$R = \sqrt{\frac{k_i}{k_t}(MA)} \quad .$$

Therefore,

$$\begin{aligned} \text{rate of chain scission} &= k_p(R\cdot)(MA) \quad , \\ &= k_p \frac{k_i^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} (MA)^{\frac{3}{2}} \\ &= \text{constant x } (MA)^{\frac{3}{2}} \end{aligned}$$

Again this relationship is not in accordance with the experimental data. In fact it is clear that the correct relationship will only be obtained if it is assumed that in the propagation step the radical can attack the chains at random and not exclusively at methyl acrylate units. If the initiation and termination steps are as before, then,

$$\text{rate of chain scission} = \text{rate of propagation}$$
$$= k_p(R\cdot)(M_n).$$

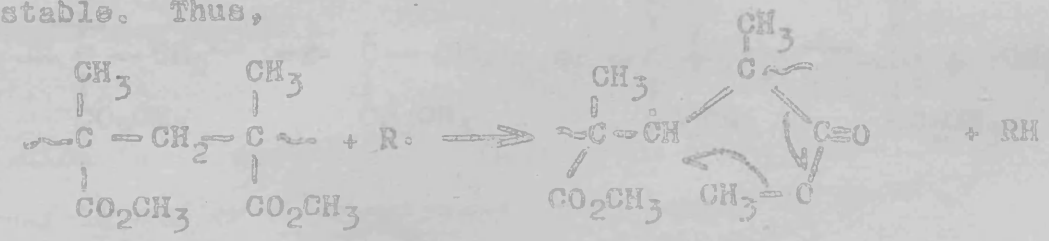
Since as before ,

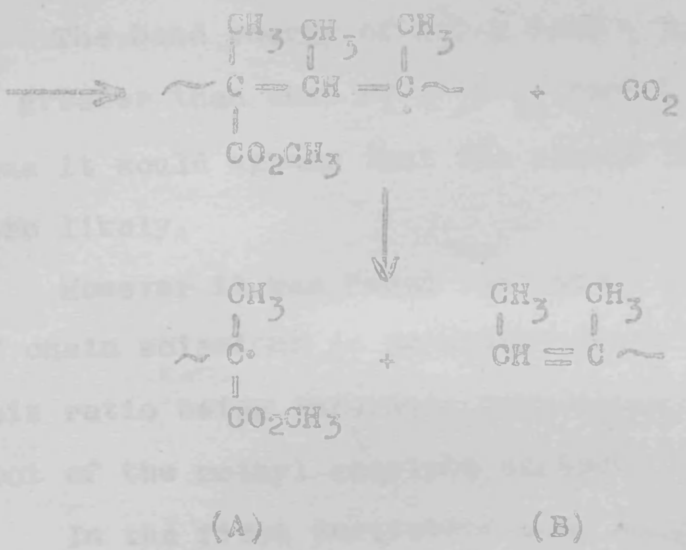
$$R\cdot = \sqrt{\frac{k_i}{k_t}(MA)} \quad ,$$

then,

$$\text{rate of chain scission} = \frac{k_p k_i^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} (M_n)\ (MA)^{\frac{1}{2}},$$
$$= \text{constant} \times (MA)^{\frac{1}{2}}.$$

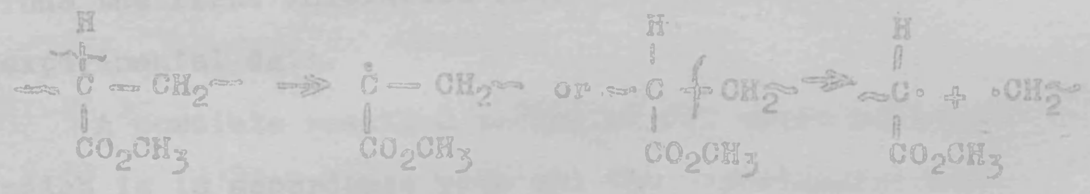
Since methyl methacrylate units do not incorporate tertiary hydrogen atoms it seems that the point of attack of the radicals in the propagation step must be the methylene groups in the chain. A five membered ring mechanism would then be involved. However since this ring contains an oxygen atom the reaction should still be favoured since these furan type rings are particularly stable. Thus,





Again a molecule of carbon dioxide is produced per chain scission and the radical A could either depropagate to monomer or initiate another propagation step. The unsaturated chain end B could also depropagate to monomer by a similar mechanism as for poly(methylmethacrylate). Carbon dioxide is produced without any equivalent methane or other methyl radical products.

The initiation reaction at methyl acrylate units could occur in the following two ways.



The bond energy of a $>$C–H bond (97 k.cal./mole) is greater than that of a $>$C–C$<$ bond (85 k.cal./mole) [57]. Thus it would appear that the second possibility is the more likely.

However it was found that there is constant ratio of chain scissions to permanent gases for each copolymer, this ratio being inversely proportional to the square root of the methyl acrylate content (Section (5)).

In the first initiation step suggested above, hydrogen is produced and propagation is equivalent to the chain scissions. Thus,

$$\frac{\text{rate of propagation}}{\text{rate of initiation}} = \text{(chain length of reaction)}$$

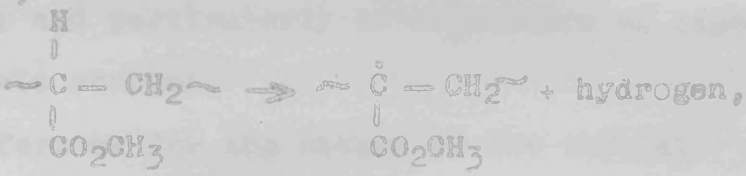
$$= \frac{\text{chain scissions}}{\text{permanent gases}}$$

$$= \frac{k_p k_1^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} (MA)^{\frac{1}{2}} \Big/ k_1 (MA)$$

$$= \text{constant} \times \frac{1}{(MA)^{\frac{1}{2}}}$$

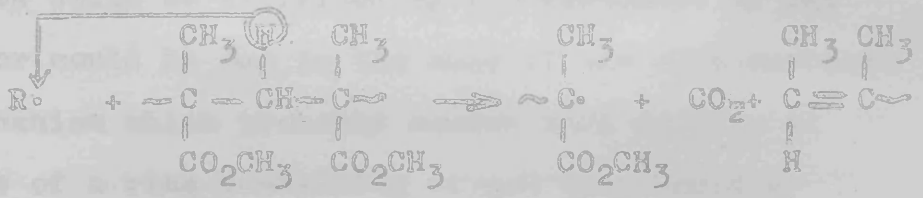
Thus the first initiation reaction suggested fits the experimental data.

A possible reaction mechanism for chain scission which is in accordance with all the experimental data may therefore be summarised as follows, Initiation,



$$\sim\underset{CO_2CH_3}{\overset{H}{C}}-CH_2\sim \;\rightarrow\; \sim\underset{CO_2CH_3}{\overset{\circ}{C}}-CH_2\sim + \text{hydrogen},$$

Propagation,



$$R\cdot + \sim\underset{CO_2CH_3}{\overset{CH_3}{C}}-\overset{\textcircled{H}}{CH}-\underset{CO_2CH_3}{\overset{CH_3}{C}}\sim \;\rightarrow\; \sim\underset{CO_2CH_3}{\overset{CH_3}{C}}\cdot + CO_2 + \underset{H}{\overset{CH_3}{C}}=\overset{CH_3}{C}\sim$$

Termination,

$R\cdot + R\cdot \rightarrow$ dead polymer molecule.

Although the above mechanism is in best agreement with the experimental results there are several points on which its validity could be challenged. Thus there is no obvious reason why the tertiary $\geq$C-H bond should break more readily than the $\geq$C-C$\leq$ bond. Thus resonance effects of the ester group should not significantly stabilise the tertiary radical. As discussed in Chapter 1 Section (2)-(ii)-(c) hydrogen is usually produced during cross linking processes or reactions resulting in unsaturation. Although no cross linking is observed here, unsaturation has been detected (Chapter 4 Section (2)-(ii)) and it may be that hydrogen is produced in this reaction and that the observed relationship with chain scissions is an artifact of the system. This might be clarified by further study and particularly of copolymers of higher methyl acrylate content.

The preference for the attack of the initial radical on the $-CH_2-$ units rather than the more obvious $\geq C-H$ units could be explained by the abundance of the former, or could be due to the ease of the five-membered ring mechanism which probably occurs more readily in the case of a ring containing oxygen than would a process involving a six-membered ring intermediate. This point also could be further clarified by incorporation of more methyl acrylate in the chain.

The very unusual relationship between total chain scission and the square root of the methyl acrylate content cannot be explained on a kinetic basis. However the complicated nature of the chain reaction must in some way be responsible for this result and further study of this copolymer system is clearly necessary for its clarification.

This information about the degradation behaviour of the methyl methacrylate/methyl acrylate copolymers is also of interest in connection with the degradation of poly(methylacrylate), in which cross linking masks the chain scission reaction[19]. Thus the above mechanism may be an indication of the fundamental mode of degradation of poly(methylacrylate) and obviously further study of copolymers of higher methyl acrylate content could be of particular interest in this connection.

(ii) The Depolymerisation Reaction from the Points of Chain Scission.

It has been shown (Section (2)) that the depolymerisation of the copolymers occurs from the points of random chain scission, the normal depolymerisation from unsaturated methyl methacrylate chain ends being blocked by the methyl acrylate units in the chain. The nature of this inhibition of monomer production could either be direct blockage by methyl acrylate units, or as was determined by Farish for styrene/methyl methacrylate copolymers[21], the proportion of unsaturated ends is lowered due to a change in the nature of the termination reaction during polymerisation. For the copolymer system under discussion, no experimental evidence is available as to which of these conditions is operative.

Although the zip length of the depolymerisation reaction is less the greater the methyl acrylate content the blocking process is not complete since the zip lengths of higher methyl acrylate content copolymers indicate that the reaction can proceed through a number of isolated methyl acrylate units (Section (2)-(iv)) and this is substantiated by the detection of methyl acrylate monomer in the degradation products (Chapter 4 Section (2)-(iii)).

It is possible that although the depropagation reaction may pass through single methyl acrylate units, it is blocked by the presence of a pair of adjacent methyl acrylate units, where behaviour similar to that of poly(methylacrylate) is to be expected. The first column in table 19 gives the experimental zip lengths for the copolymers(taken from table 13) and these are compared with the number of monomer units between isolated methyl acrylate units(second column table 19) and the number between pairs of adjacent methyl acrylate units (third column),the values being calculated from the sequence distribution data in table 11.

Table 19.

Correlation of Zip length with Sequence Distribution of the Copolymers.

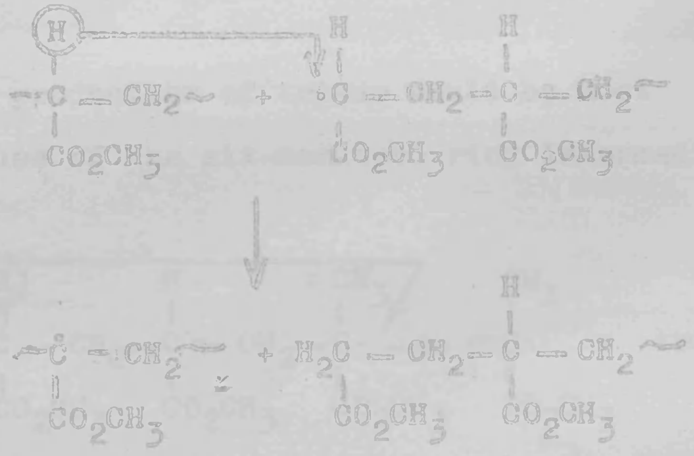
COMPOSITION OF COPOLYMER MMA	MA	EXPERIMENTAL ZIP LENGTH.	NUMBER OF MONOMER UNITS BETWEEN MA UNITS.	NUMBER OF MONOMER UNITS BETWEEN MA PAIRS.
112	1	173	112	
26	1	73·6	26	400
7·7	1	73·5	7·7	36·4
2	1	34·2	2	12·5

It can be seen that the experimental zip length for the 112/1 copolymer is approximately correct for stoppage of the depropagation reaction at the first methyl acrylate units beyond the point of chain scission. 100% methyl methacrylate monomer would be obtained in this case in agreement with the experimental results (Chapter 4 Section (2)-(iii)).

In the case of the 26/1 copolymer stoppage of the depropagation reaction after it had passed through one methyl acrylate unit would give the right order of zip length (~53) and monomer ratios of approximately 52/1 methyl methacrylate/methyl acrylate (compared with the experimental value of 100/1). Allowing for experimental error these calculated values are in reasonable agreement with the experimental results.

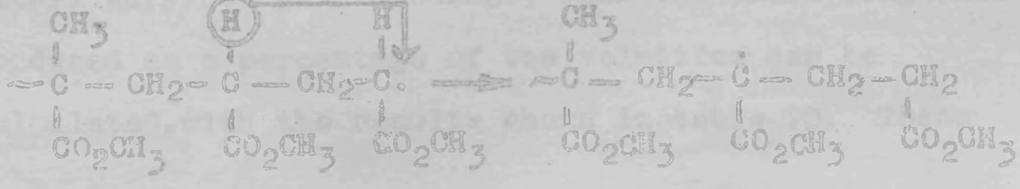
However in the 7·7/1 and 2/1 copolymers the experimental zip lengths are very much longer than for blockage at single methyl acrylate units, but are much nearer blockage at pairs of adjacent methyl acrylate units. It appears, however, that the depropagation reaction can pass through on the average at least one of those pairs of methyl acrylate units. It is difficult to account for the observed monomer yields (Chapter 4 Section (2)-(iii)) for these copolymers.

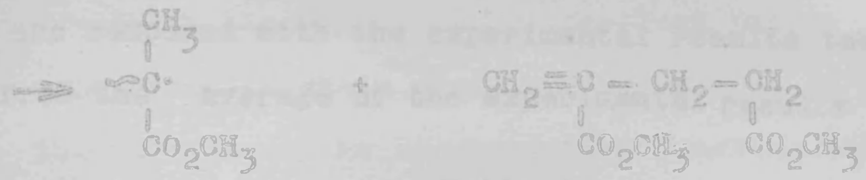
This blocking reaction could occur by intermolecular transfer between a radical at a methyl acrylate pair and the tertiary hydrogen atom of another methyl acrylate unit giving radical A, which could propagate the chain scission reaction and the stable chain end B.



(A) (B)

In certain sterically favourable cases intra-molecular transfer similar to that which occurs in the degradation of poly(styrene)[9] could be possible, leading to chain fragments and a methyl methacrylate radical which would depropagate at least to the next methyl acrylate pair, thus increasing the zip length of the reaction.

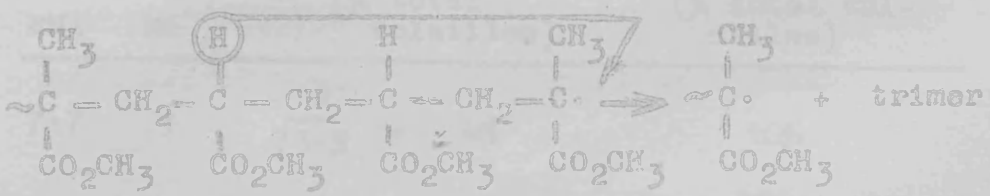




$$\longrightarrow \sim\overset{CH_3}{\underset{CO_2CH_3}{C\cdot}} + CH_2{=}\underset{CO_2CH_3}{C}-CH_2-\underset{CO_2CH_3}{CH_2}$$

(dimer).

Similarly the production of trimer would be most favoured because of the six-membered ring intermediate.



$$\sim\overset{CH_3}{\underset{CO_2CH_3}{C}}-CH_2-\overset{H}{\underset{CO_2CH_3}{C}}-CH_2-\overset{H}{\underset{CO_2CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CO_2CH_3}{C\cdot}} \longrightarrow \sim\overset{CH_3}{\underset{CO_2CH_3}{C\cdot}} + \text{trimer}$$

It is thus possible to account for chain fragments being produced in conjunction with the depolymerisation reaction from the points of chain scission.

It can be seen from table 19 that the depropagation reaction in the 7-7/1 and 2/1 copolymers passes through approximately one and three methyl acrylate pairs respectively. If it is assumed that, on the average, one molecule of trimer is produced for passage through one methyl acrylate pair blockage, then the chain fragments produced as a percentage of the volatiles can be calculated, with the results shown in table 20. These are compared with the experimental results taken from the average of the experimental results in table 14.

Table 20.

Comparison of Calculated and Experimental Amounts of Chain Fragments.

COPOLYMER COMPOSITION. MMA	MA	CALCULATED VALUE (% total volatiles)	EXPERIMENTAL VALUE (% total volatiles)
7·7	1	$\frac{3}{73\cdot5} = \simeq 4\%$	10%
2	1	$\frac{8}{34\cdot2} = 23\cdot3\%$	23%

Excellent agreement is obtained for calculated and experimental results for the 2/1 copolymer, though the results are at variance for the 7·7/1 copolymer. However allowing for experimental error the results for the 7·7/1 copolymer are of the right order.

Thus it can be concluded that in the copolymers of lower methyl acrylate content isolated methyl acrylate units effectively block the depropagation reaction. In the copolymers of higher methyl acrylate content the reaction can pass through methyl acrylate units but is partially blocked at methyl acrylate pairs. The production of chain fragments appears to be related to the passage of the depropagation reaction through these blockage points.

It obviously will be of interest to continue this investigation to determine the nature of this apparent change in blocking ability with changing concentration of methyl acrylate units in the copolymer. Thus again useful information should be obtained from a study of copolymers of higher methyl acrylate content.

CHAPTER 6.

OTHER TOPICS RELATED TO THE THERMAL DEGRADATION OF THE METHYL METHACRYLATE/METHYL ACRYLATE COPOLYMERS.

(1) THE PHOTOCHEMICAL DEGRADATION OF METHYL METHACRYLATE/ METHYL ACRYLATE COPOLYMERS.

(i) General Degradation Characteristics.

(a) Effect of Temperature on Degradation.

Dainton and Ivin[58] have shown that depropagation/ propagation processes are controlled by the equilibrium,

$$P_n^{\circ} \underset{\text{propagation}}{\overset{\text{depropagation}}{\rightleftharpoons}} P_{n-1}^{\circ}N + M_1$$

In thermal degradation studies the polymer sample is usually at such a high temperature that it is in the form of a reasonably mobile liquid so that monomer can diffuse rapidly from the system and depropagation predominates. However in photochemical studies the sample is often degraded in the solid state, thus monomer diffuses slowly from what is effectively a very viscous medium. There is therefore a tendency for the propagation reaction to occur and thus for depropagation to be effectively inhibited.

To counteract this effect Cowley and Melville photodegraded poly(methylmethacrylate) using 2537 Å radiation in the temperature range 160-180°C[8]. The softening point of the polymer lies in this region thus allowing free diffusion of monomer, but the temperature is below that at which thermal initiation takes place (~200°C). In the present investigations it was necessary to work below the softening point of the copolymers (~240°C) since thermal degradation was observed at about 195°C. Thus diffusion effects would be expected, which would decrease with increasing temperature. Preliminary experiments were therefore carried out to determine the overall effect of the temperature on the degradation rate and in particular to try to observe whether diffusion effects were operative.

The 26/1 and 7·7/1 copolymers were photodegraded in the d.m.s., in the temperature range 140-180°C, for a constant time (30min.). The percentage volatilisation of the sample was determined by loss in weight and is plotted against the temperature of degradation in figure 30. The experimental results are given in table 21.

It can be seen that there is a linear increase in

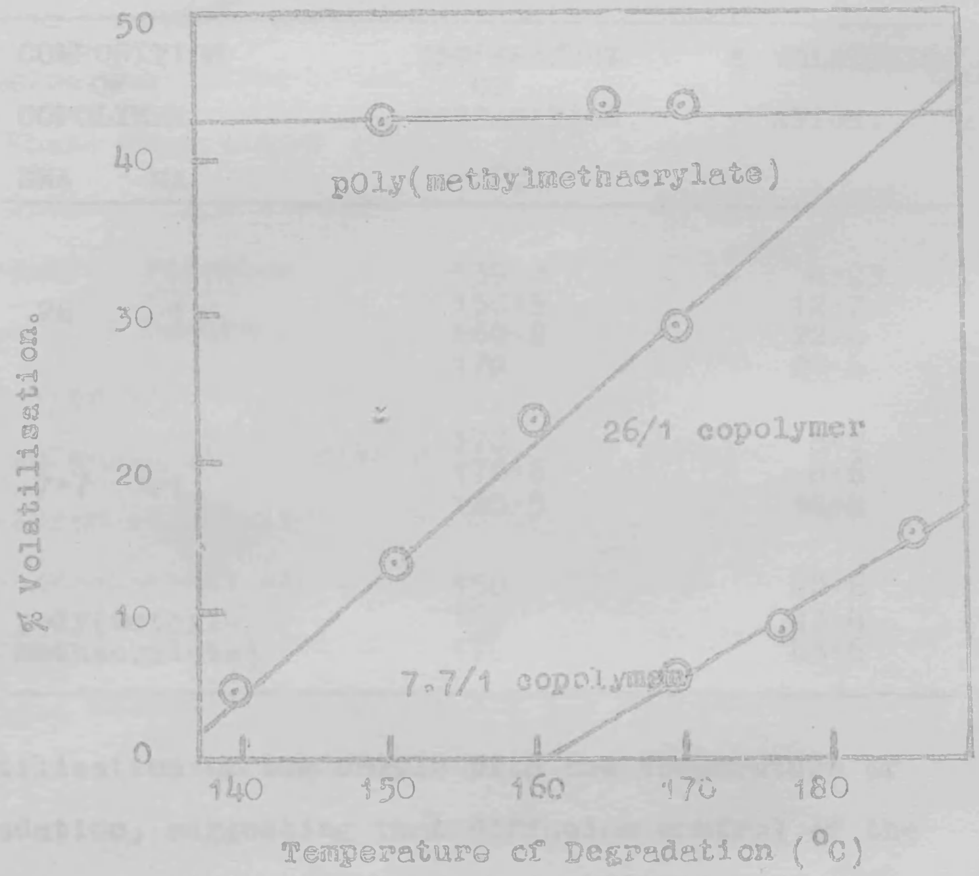


FIGURE 30.

Effect of Temperature on Photodegradation of copolymers for Constant Time (30 min.).

Table 21.

Effect of Temperature on Volatilisation of Sample During Photodegradation for Constant Time (30min.)

COMPOSITION OF COPOLYMER		TEMPERATURE OF DEGRADATION.	% VOLATILISATION.
MMA	MA	°C	
26	1	139·2	4·23
		150·5	12·7
		160·2	22·4
		170	28·4
7·7	1	170	5·2
		176·6	8·6
		185·5	14·4
poly(methylmethacrylate)		150	42·6
		165	43·4
		170	43·6

volatilisation of the sample with the temperature of degradation, suggesting that diffusion control of the rate is occuring in these samples, the higher degradation temperatures resulting in easier escape of the monomer from the system.

However the poly(methylmethacrylate) standard photodegraded in this temperature range did not show any diffusion effect (figure 30 and table 21),although the work was carried out below the softening point of this high molecular weight polymer (820,000). All the samples were degraded in the same form (fine powder). Thus it would be expected that if diffusion effects were present in one polymer, they should be present in them all and it would therefore seem that the reactions are not diffusion controlled after all.

These temperature effects could alternatively be more intimately associated with the mechanism of the degradation reaction occuring in the copolymers. This aspect will be discussed later (Section (1)-(iii)) in greater detail.

As a result of these preliminary experiments, 170°C was chosen as a suitable temperature for the study of the photochemical degradation, appreciable reaction occuring at this temperature without interference from possible thermal degradation and all results described below were obtained at this temperature.

(b) Molecular Weight Changes on Degradation.

The molecular weight changes which occur during photochemical degradation at 170°C of the 112/1,26/1, 7·7/1 and 2/1 copolymers are given in table 22 and illustrated in figure 31. These molecular weight changes are characteristic of random chain scission, reflecting the behaviour of poly(methylacrylate), even for the incorporation of only 1% methyl acrylate

COMPOSITION OF COPOLYMER. MMA	MA	TIME OF DEGRADATION. (minutes)	% VOLATILISATION.	MOLECULAR WEIGHT OF RESIDUE.	CHAIN SCISSIONS PER MOLE OF POLYMER.
112	1	10	5·4	250,000	1·266
		30	20·7		
		60	41·4	237,000	0·47
		90	53·6		
		120	60·8		
25	1	5	1·7	376,000	0·117
		15	4·0	248,000	1·32
		23	13·4	229,000	1·273
		30	30·4	172,000	1·5
		45	34·2	180,000	1·19
		60	36·2	145,000	1·645
		90	46·2	118,000	1·68
		120	54·0	125,000	1·21
7·7	1	5	1·5	411,000	0·022
		15	2·9	321,000	0·27
		23	4·4	181,000	1·25
		30	5·2	263,000	0·528
		45	16·2	168,000	1·12
		65	20·3	144,000	1·35
		75	22·3	157,000	1·10
		90	27·8	150,000	1·05
		120	29·8	140,000	1·13
		300	40	81,000	1·955
2	1	30	1·75	149,000	1·46
		60	5·8	78,000	3·08
		150	13·9	49,000	2·52
		300	28·2	45,000	4·91
		600	39·6	47,000	2·96

Table 22.

Summary of Photodegradation Results at 170°C.

Polymer in Form of Powder.

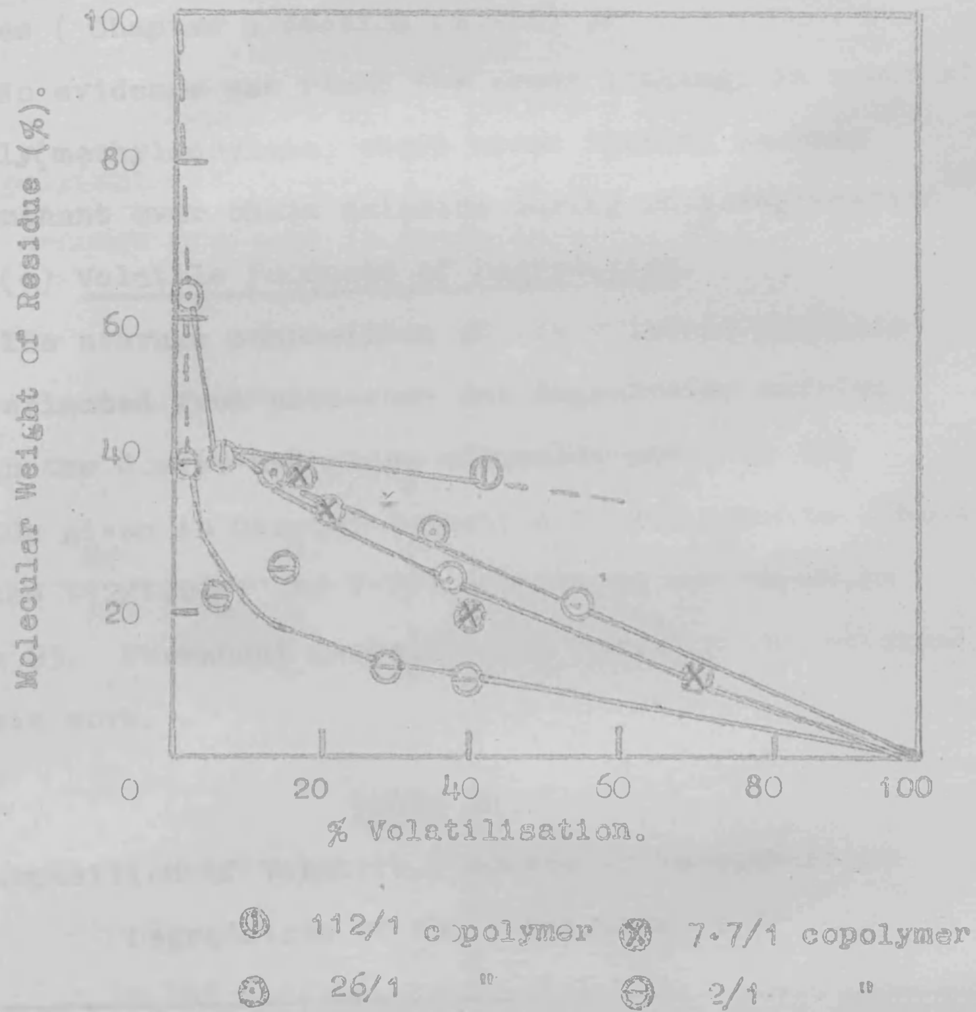


FIGURE 31.

Molecular Weight Changes on Photodegradation of Copolymers at 170°C.

in the methyl methacrylate chain. This result is somewhat similar to that obtained from thermal degradation studies (Chapter 4 Section (2)-(1)).

No evidence was found for cross linking, in contrast to poly(methylacrylate) where cross linking becomes predominant over chain scission during photodegradation[20].

(c) Volatile Products of Degradation.

The average composition of the volatile products was estimated from photochemical degradation carried out in the d.m.s. and glass molecular still by the methods given in Chapter 2 Section 3. The results obtained for the 112/1, 26/1 and 7·7/1 copolymers are shown in table 23. Permanent gases, if any, were not investigated in this work.

Table 23.

Composition of Volatile Products of Photochemical Degradation of the Copolymers.

COMPOSITION OF COPOLYMER.		AVERAGE COMPOSITION OF VOLATILE PRODUCTS. (% by weight of Total)			
MMA	MA	MMA	MA	Chain Fragments	Carbon Dioxide
112	1	100			
26	1	99	<1	trace	trace
7·7	1	89	>1	10	trace

As expected methyl methacrylate comprises the greater part of the degradation products. However much more methyl acrylate monomer is produced than expected since no monomer at all is obtained on photodegradation of poly(methylacrylate) [20]. The actual composition of the monomer products is shown in table 24.

Table 24.

G.L.C. Analysis of Volatile Products.

COPOLYMER COMPOSITION.		G.L.C. ANALYSIS OF PRODUCTS.	
MMA	MA	MMA	MA
112	1	$\geqslant$1000	1
26	1	320	1
7·7	1	80	1

About one in ten of the methyl acrylate units in the chain appears as monomer, which is again somewhat similar to the thermal degradation results (one in four of the methyl acrylate units appearing as monomer).

(d) Volatilisation as a Function of Time.

Percentage volatilisation versus time of degradation curves are shown in figure 32 (the results being given in table 22) for the 112/1,26/1,7·7/1 and 2/1 copolymers photodegraded at 170°C. A similar curve for the

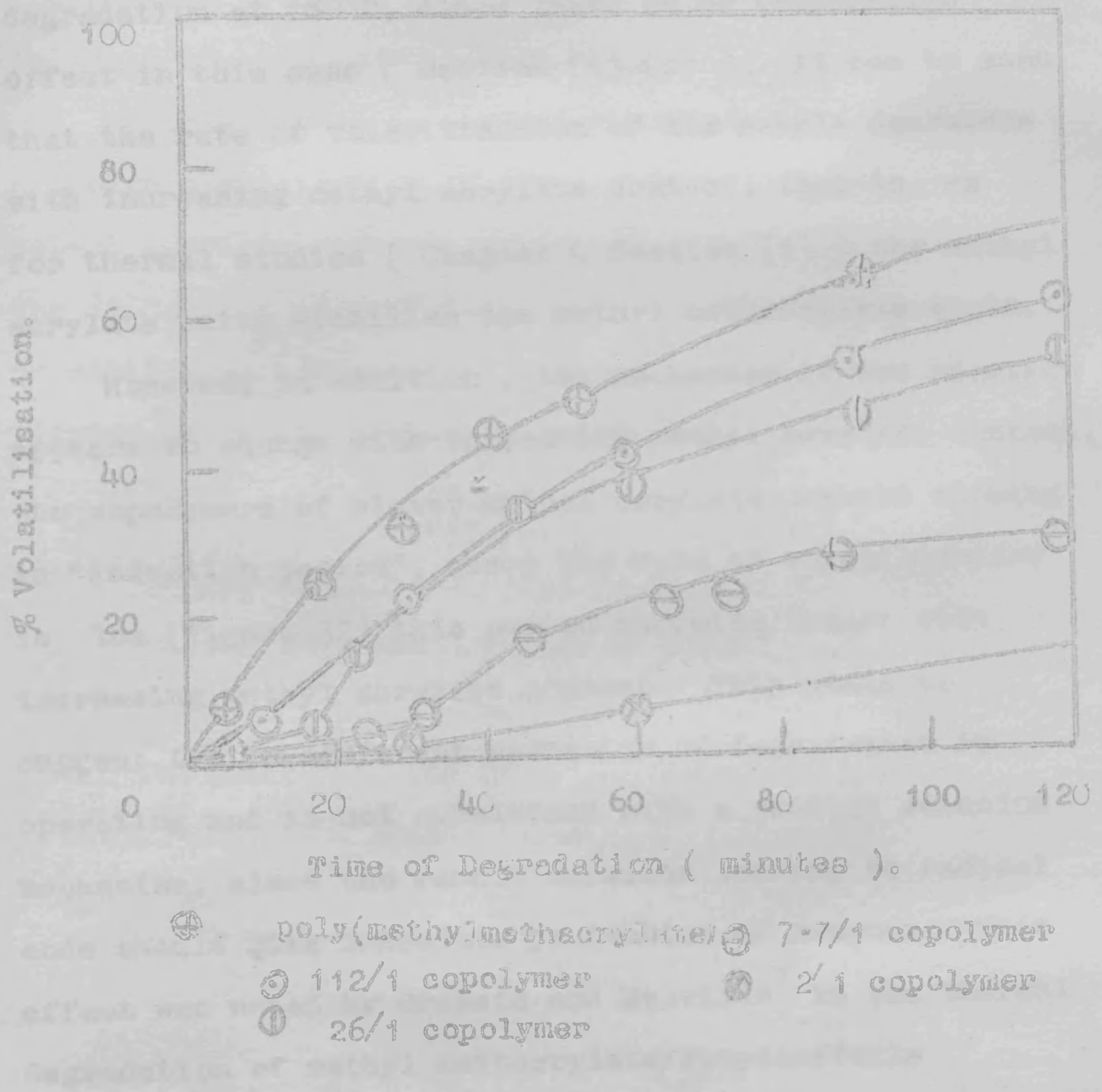


FIGURE 32.

Volatilisation of Copolymers Photodegraded at 170°C in Form of Powder.

poly(methylmethacrylate) standard (figure 32) was extrapolated from the work of Farish[21], for photo-degradation at 180°C, since there is no temperature effect in this case (Section (1)-(a)). It can be seen that the rate of volatilisation of the sample decreases with increasing methyl acrylate content, that is, as for thermal studies (Chapter 4 Section (1)) the methyl acrylate units stabilise the methyl methacrylate chain.

However, in addition , the mechanism of the reaction appears to change with increasing methyl acrylate content, the copolymers of higher methyl acrylate content showing an "induction period", where the rate of volatilisation is low (figure 32) this period becoming longer with increasing methyl acrylate content. This seems to suggest that a different mechanism of degradation is operating and is not consistent with a radical scission mechanism, since the random scission leading to radical ends should give immediate production of monomer. This effect was noted by Grassie and Melville[7] in the thermal degradation of methyl methacrylate/acrylonitrile copolymers.

However it was thought that since the degradations were carried out below the melting point of the copolymers some abnormal effects could be occuring in the powdered form of the sample. Degradations were therefore carried out on the 26/1 and 7·7/1 copolymers in the form of a film, covered with a silica plate and the results obtained are shown in figure 33 and listed in table 25.

In these cases no induction periods are observed, although stabilisation of the sample with increasing methyl acrylate content occurs, thus it is probable that the "induction effect" is associated with some sort of transition occuring in the viscous powdered form of the polymer below its softening point.

Table 25.

Summary of Photodegradation Results at 170°C. Polymer Degraded in form of Film Covered with Silica Plate.

COMPOSITION OF COPOLYMER. MMA	MA	TIME OF DEGRADATION. (minutes)	% VOLATILISATION.
26	1	5	12·2
		15	16·5
		30	16·5
		60	28·0
		120	47·1
7·7	1	5	9·3
		15	12·2
		30	12·4
		60	27·5
		120	39·6

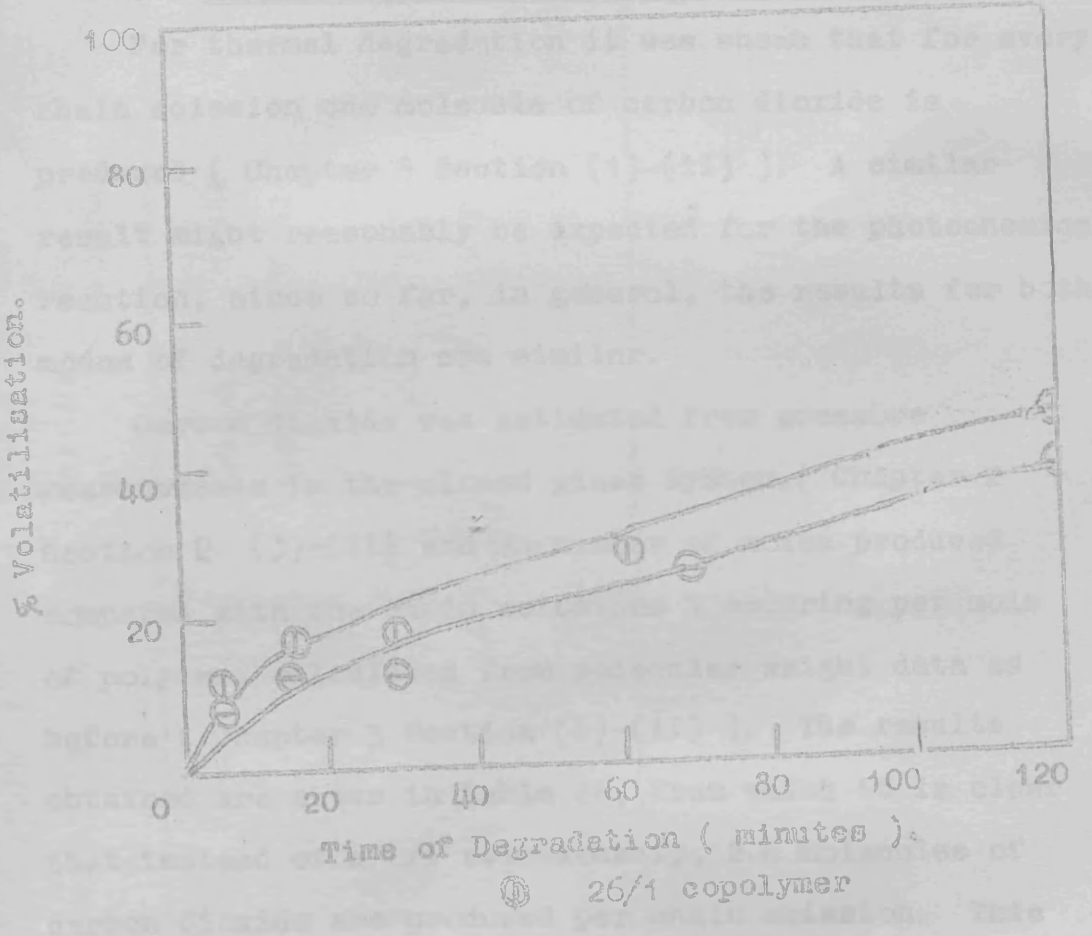


FIGURE 33.

Volatilisation of Copolymers Photodegraded at 170°C in Form of Film.

(ii) The Chain Scission Reaction.

(a) Chain Scission and Carbon Dioxide Production.

For thermal degradation it was shown that for every chain scission one molecule of carbon dioxide is produced (Chapter 5 Section (1)-(ii)). A similar result might reasonably be expected for the photochemical reaction, since so far, in general, the results for both modes of degradation are similar.

Carbon dioxide was estimated from pressure measurements in the closed glass system,(Chapter 2 Section 2- (3)-(iii) and the number of moles produced compared with the chain scissions N occuring per mole of polymer, calculated from molecular weight data as before (Chapter 5 Section (1)-(ii)). The results obtained are shown in table 26, from which it is clear that instead of a 1/1 relationship, 2-4 molecules of carbon dioxide are produced per chain scission. This will be discussed in Section (1)-(iii).

(b) Chain Scission and Volatilisation.

In the thermal degradation of the copolymers it was found that the volatilisation of the sample occurs from the points of chain scission (Chapter 5 Section (2)). It is to be expected that a similar result would be obtained in this case.

The percentage volatilisation of the 26/1,7·7/1 and

COMPOSITION OF COPOLYMER.		TEMPERATURE OF DEGRADATION.	%VOLATILISATION.	MOLECULAR WEIGHT OF RESIDUE.	CHAIN SCISSIONS PER MOLE POLYMER.	CARBON DIOXIDE PER MOLE POLYMER.
MMA	MA	°C				
26	1	160	11·6	244,000	1·062	4·84
		170	11·5	292,000	0·82	4·46
7·7	1	170	24·8	118,000	1·71	5·15
		170	46·2	70,000	2·26	10·6
2	1	170	7·4	75,000	3·57	7·47

Table 25.

Carbon Dioxide/Chain Scissions Results for Photochemical Degradation.

2/1 copolymer samples are plotted against the number of chain scissions per mole (from results in table 22) in figures 34-36. A linear relationship,is obtained, although there is more scatter in the plot in this case, as compared to thermal studies, due to the more inaccurate calculation of chain scissions from molecular weight data, rather than directly from carbon dioxide pressure.

Thus it can be concluded that the volatilisation of the copolymers proceeds from the points of chain scission and the zip lengths can be calculated as shown in table 27 the same way as previously (Chapter 5 table 13). The zip length is much longer than observed in the thermal degradation of these copolymers shown in last column in table 27 (taken from table 13). However,as before, blockage of the depropagation reaction by the methyl acrylate units is clearly occuring, since zip lengths decrease with increasing methyl acrylate content.

The longer zip lengths during photochemical degradation will be discussed in Section (1)-(iii).

(c) Chain Scission and Copolymer Composition.

Chain Scission and Copolymer Composition

It was shown that during the thermal degradation of the copolymers (Chapter 5 Section (5)) the chain scissions in each copolymer sample reached a maximum value, this value being proportional to the square root

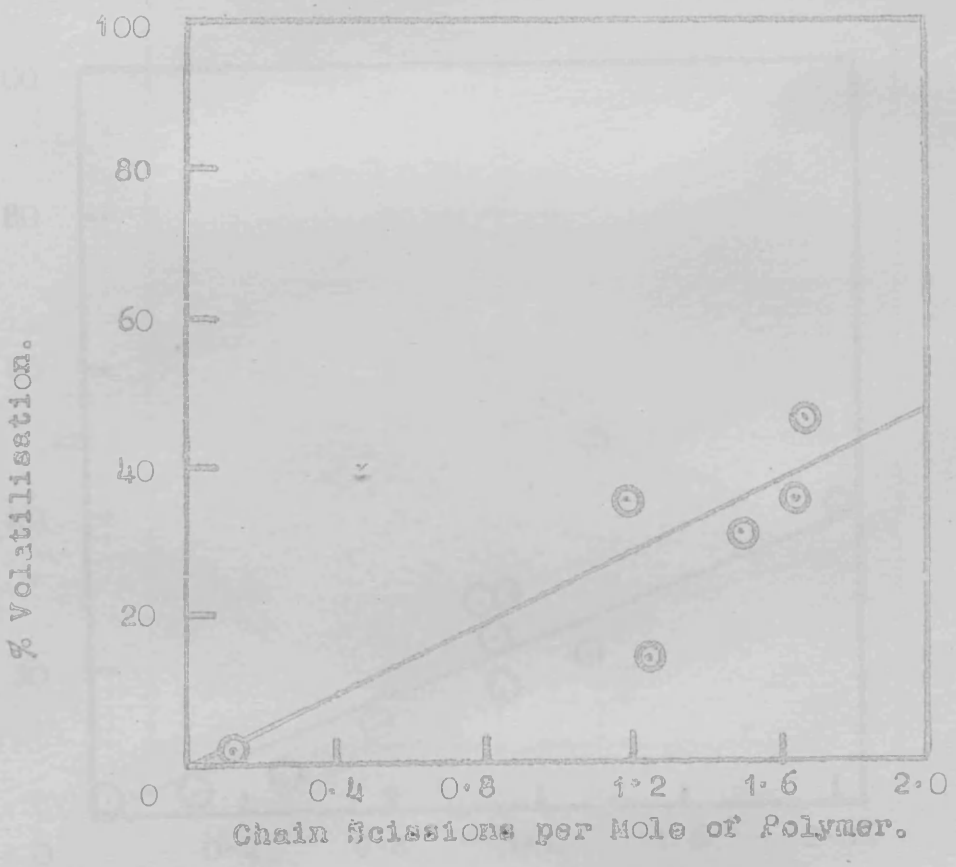


FIGURE 34.

Relationship Between Volatilisation and Chain Scission for Photodegradation of 26/1 Copolymer.

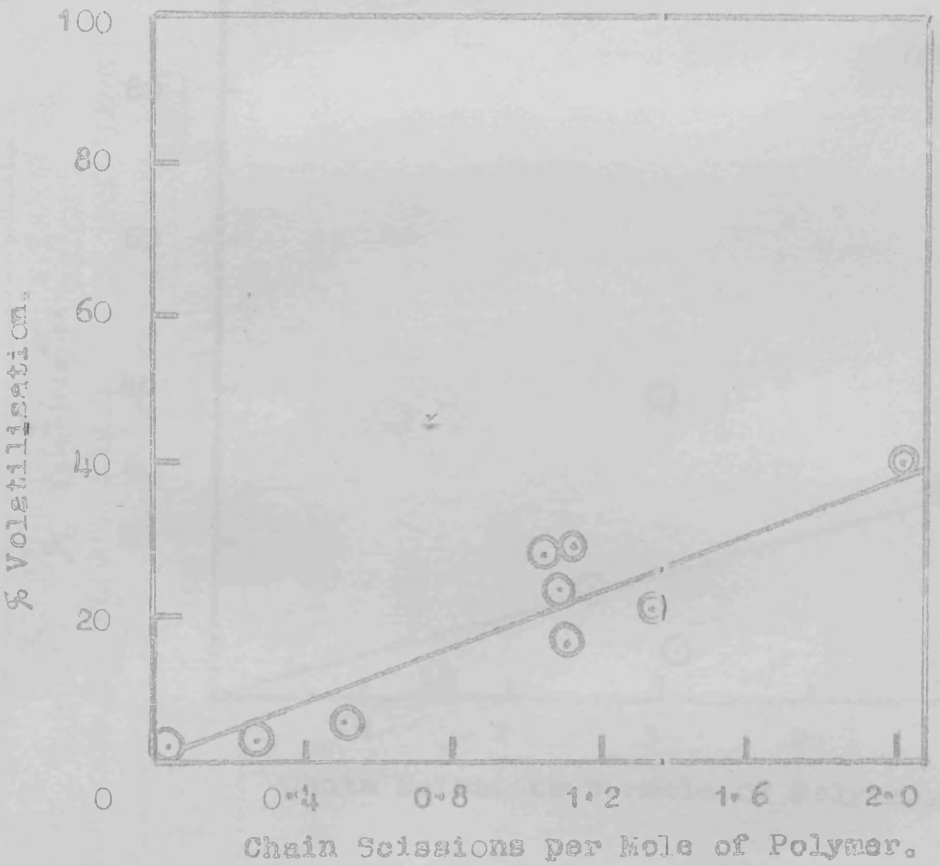


FIGURE 35.

Relationship Between Volatilisation and Chain Scission for Photodegradation of 7·7/1 Copolymer.

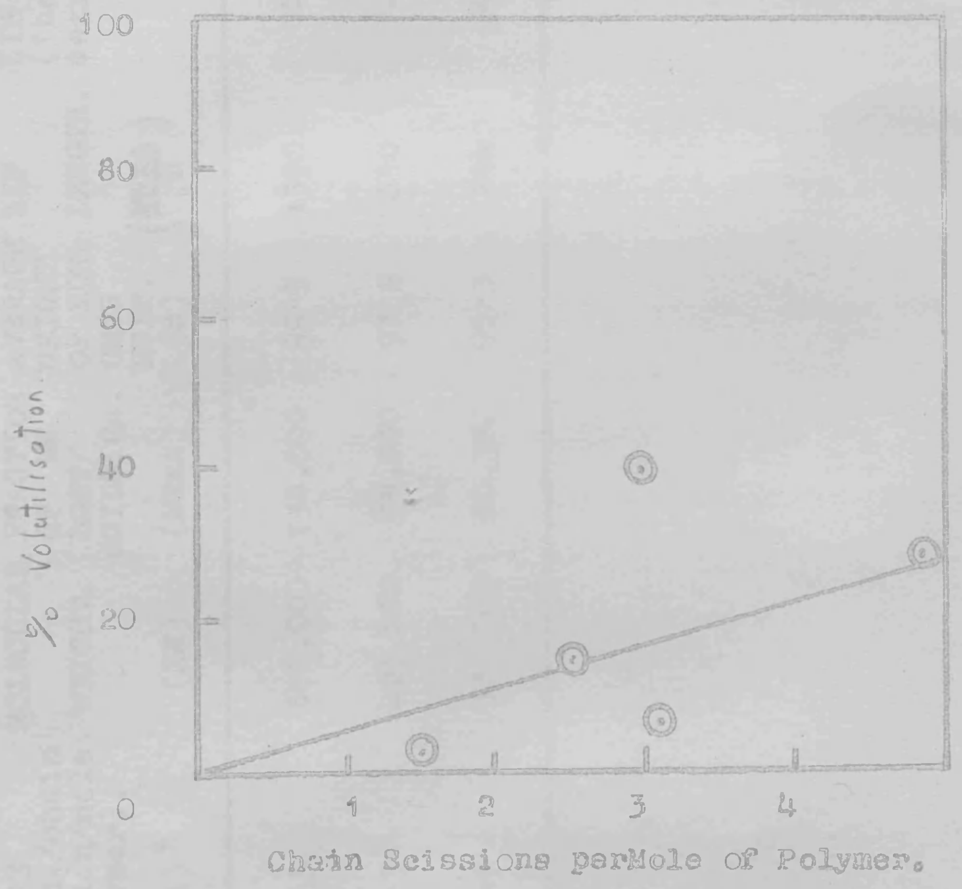


FIGURE 36.

Relationship Between Volatilisation and Chain Scission for Photodegradation of 2/1 Copolymer.

COMPOSITION OF COPOLYMER. MMA	MA	SLOPE (%voln./chain scission/mole polymer). (A)	MOLECULAR WEIGHT. (MW)	FRACTION OF MW LOST/ SCISSION. (MWxA)	AVERAGE WEIGHT OF MONOMER UNIT. (B)	ZIP LENGTH. $\left(\frac{MWxA}{B}\right)$	ZIP LENGTH (thermal degradation)
25	1	2·3	600,000	138,000	99·5	1390	74
7·7	1	18·5	425,000	78,700	97·2	810	74
2	1	5·5	370,000	20,300	95·3	214	34

Table 27.

Calculation of Zip Length from Points of Chain Scission for Photodegradation of Copolymers.

of the methyl acrylate content of the copolymer.

The chain scissions occuring on photochemical degradation of the 26/1,7·7/1 and 2/1 copolymers all reach a maximum value as shown in figure 37 (from results in table 22), greater amounts of chain scission occuring with increasing methyl acrylate content of the copolymers. However it is not possible in this case to determine the relationship with methyl acrylate content, since the molecular weight data are not sufficiently accurate. Nevertheless it is clear from figure 37 that the total chain scission occuring in each copolymer could be, as in the thermal reaction, proportional to the square root of the methyl acrylate content.

(iii) Discussion.

The results reported for photochemical degradation in Sections (1)-(i),(ii) above, show a strong general resemblance to those obtained from thermal degradation of the same copolymers (Chapters 4,5). Thus in the photochemical degradation, the methyl acrylate units appear to block depropagation from methyl methacrylate chain ends, since volatilisation of the sample is retarded with increasing methyl acrylate content of the copolymer. (Section (1)-(ii)-(b)). This blockage is not complete, however, since some methyl acrylate monomer is observed

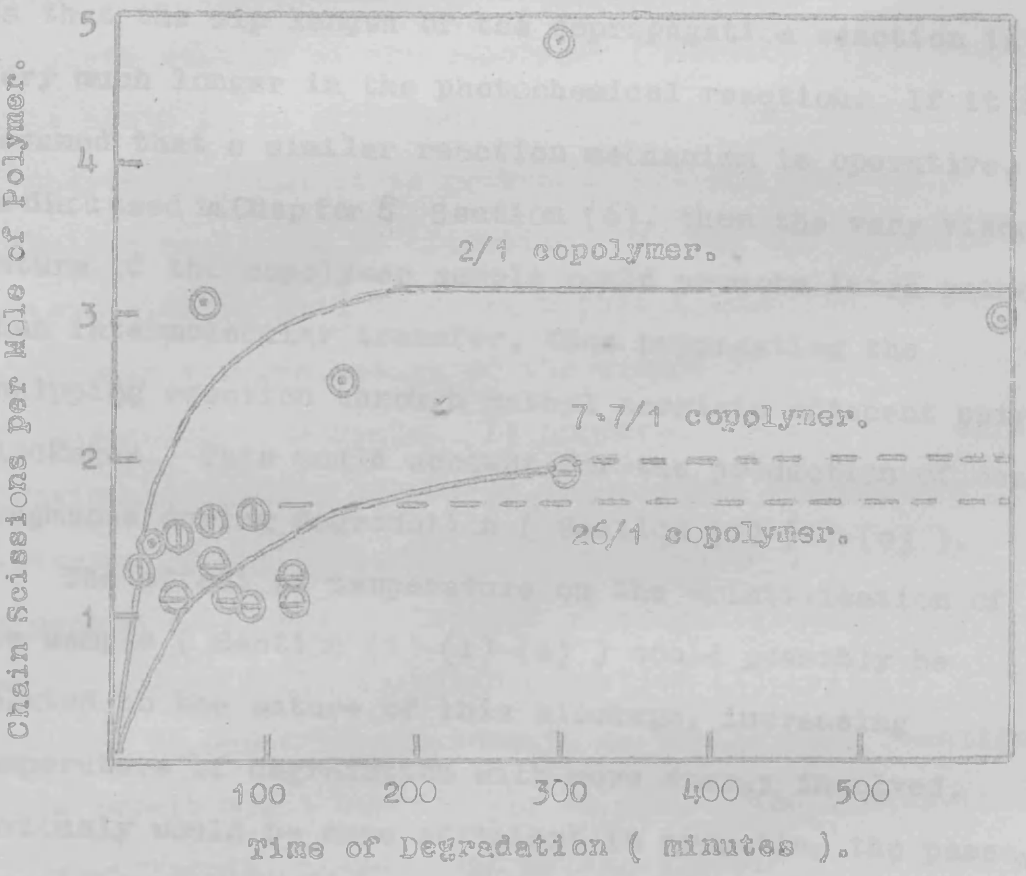


FIGURE 37.

Chain Scissions Occuring During the Photodegradation of the Copolymers.

in the degradation products (Section (1)-(i)-(c)). All these results are exactly as were obtained from thermal studies, as discussed in Chapter 5 Section (6).

An interesting difference between the two processes is that the zip length of the depropagation reaction is very much longer in the photochemical reaction. If it is assumed that a similar reaction mechanism is operative, as discussed in Chapter 5 Section (6), then the very viscous nature of the copolymer sample could promote intra rather than intermolecular transfer, thus propagating the unzipping reaction through methyl acrylate adjacent pair blockages. This would account for the production of chain fragments during degradation (Section (1)-(i)-(c)).

The effect of temperature on the volatilisation of the sample (Section (1)-(i)-(a)) could possibly be related to the nature of this blockage, increasing temperature of degradation with more energy involved, obviously would be more efficient in promoting the passage of the depropagation reaction through the methyl acrylate pair. However Farish found a similar effect of temperature on the volatilisation of styrene/acrylonitrile copolymers[21]; thus this effect may not be so simple as proposed above and is well worthy of investigation in its own right.

It was shown that in the photochemical degradation, chain scission does not proceed by straightforward breakage at methyl acrylate units in the chain, since the total chain scissions occuring in a copolymer are probably proportional to the square root of the methyl acrylate content of the copolymer (Section (i)-(ii)-(c)). This again is in agreement with the thermal results (Chapter 5) and it is probable that the same chain reaction mechanism is operative. It was not possible to obtain kinetic data to confirm this assumption, since the extremely viscous nature of the sample rendered rate measurements inaccurate. It appears, however, that carbon dioxide production is a more complicated function of chain scission in the photochemical degradation , since approximately three molecules of carbon dioxide are produced per chain scission (Section (i)-(ii)-(a)) as opposed to the 1/1 relationship in the thermal reaction. This result might conceivably be due to the limitations of experimental measurement of the extremely low carbon dioxide pressure involved and this will have to be further investigated in greater detail.

This preliminary investigation of the photochemical degradation of the copolymers has indicated that they degrade in a similar fashion as for thermal initiation. Whether this is true in whole or in part will be determined only by a much deeper investigation of the degradation characteristics. The unusual feature of the degradation reaction, namely the apparent induction effect,(Section (1)-(i)-(d)), could be due to the very unfavourable reaction conditions due to the viscous nature of the powdered sample and any further work on this subject would have to investigate more thoroughly the effect of the physical form of the sample on its degradation.

(2) THE THERMAL DEGRADATION OF METHYL METHACRYLATE/ ETHYL ACRYLATE COPOLYMERS.

(i) Introduction.

This work is intended only as an initial investigation of this copolymer system to determine any general differences from the methyl methacrylate/methyl acrylate copolymer degradation behaviour. From results of methyl methacrylate/methyl acrylate copolymer degradation it is apparent that the greatest amount of useful information would be obtained from a study of copolymers in the region of composition 100/1-1/1 molar methyl methacrylate/ethyl acrylate and thus two copolymers were prepared with the compositions 100/1 and 10/1 methyl methacrylate/ethyl acrylate respectively. All degradations were carried out in the glass molecular still using the appropriate experimental methods (Chapter 2 Section 2-(3)) already well illustrated (Chapters 4,5) and temperatures greater than 250°C were chosen for degradation by comparison with the methyl methacrylate/methyl acrylate system.

(ii) General Degradation Characteristics.

(a) Molecular Weight Changes on Degradation.

The molecular weight changes occuring on thermal degradation of the 100/1 and 10/1 copolymers in the temperature range 250-320°C are shown in figure 38 (from the results in table 28). As for the methyl methacrylate/methyl acrylate system (Chapter 4 Section (1)), incorporation of only 1% ethyl acrylate in the poly(methylmethacrylate) chain leads to a molecular weight drop on degradation typical of the random chain scission exhibited by poly(acrylates). It is obvious from figure 38 that the molecular weight drop for the 10/1 copolymer is approximately ten times that for the 100/1, so in this case it appears that chain scission is proportional to the ethyl acrylate content of the copolymer, as opposed to,the square root relationship observed in the methyl methacrylate/methyl acrylate system (Chapter 5 Section (3)-(iii)). This will be discussed in Section 2-(iii)-(c).

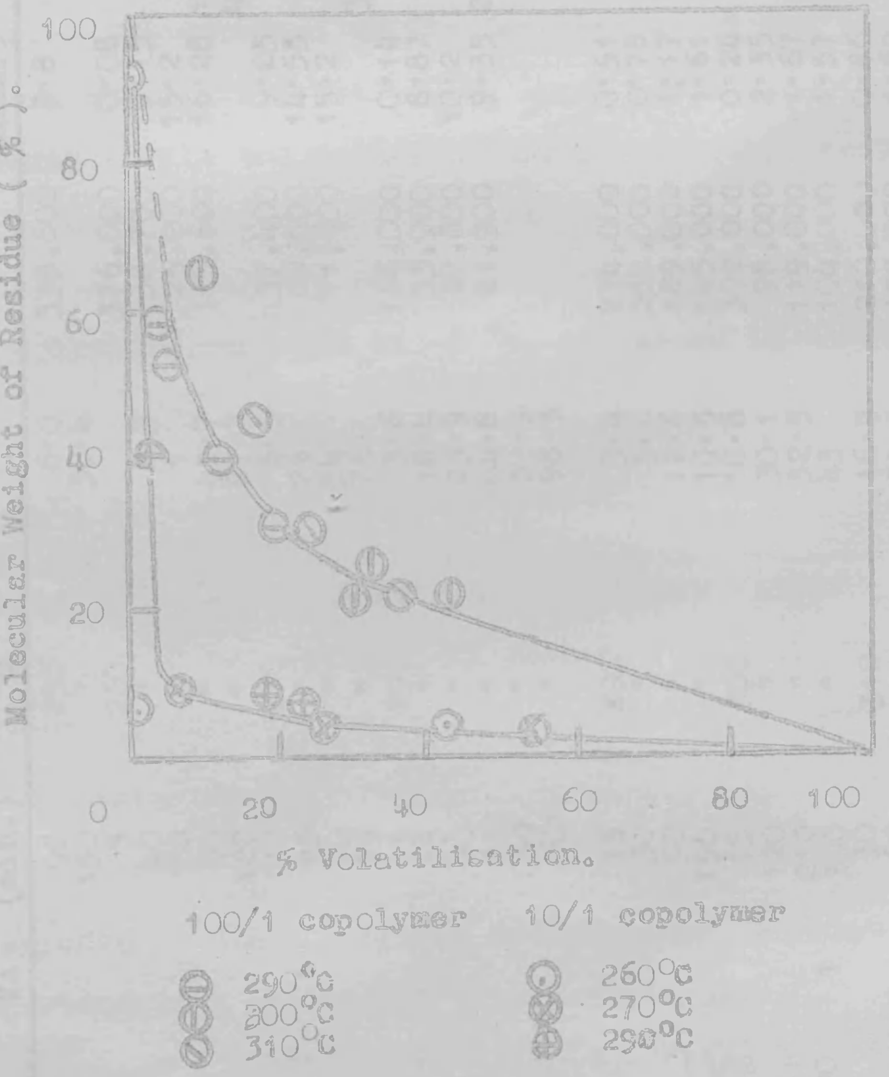


FIGURE 38.

Molecular Weight Changes on Degradation of Methyl methacrylate/Ethyl acrylate Copolymers.

COMPOSITION OF COPOLYMER. MMA	EA	TIME OF DEGRADATION. (min.)	TEMPERATURE OF DEGRADATION. °C	%VOLATILISATION.	MOLECULAR WEIGHT OF RESIDUE.	CHAIN SCISSIONS/ MOLE.	CO_2/ MOLE.	OTHER GASES/ MOLE.
10	1	90	250	6·0	335,600	9·8	5·55	1·65
		150	"	30·4				
		5	260		376,000	0·08	0·62	0·13
		40	"	4·3	38,700	9·15	3·55	1·76
		60	"	1	25,200	15·2	9·44	3·31
		90	"	42·7	13,600	16·28	18·6	3·7
		120	"	87·7			43·5	8·3
		30	270	6·5	37,400	9·25		
		45	"	26	19,500	14·55		
		50	"	54	11,600	15·2	9·43	3·32
		75	"	76			35	8·8
		5	290	3·6	166,000	0·14	0·79	1·6
		15	"	18·4	33,900	8·87		
		20	"	23·9	27,800	10·2		
		25	"	44·8	21,900	9·35	29·2	5·33
		30	"	50·9				
		60	"	98·3				
100	1	15	290	3·4	274,000	0·51		
		30	"	5·6	250,000	0·78		
		90	"	12·6	189,000	1·17		
		150	"	10·5	145,000	1·61		
		15	300	10·8	302,000	0·24	0·68	0·38
		120	"	30·1	98,000	2·35	3·17	2·02
		210	"	32·5	119,000	1·67	3·77	3·73
		300	"	43	104,000	1·57	2·98	4·36
		30	310	16·9	210,000	0·86		
		60	"	23·3	138,000	1·62	0·64	
		120	"	35·7	104,000	1·91	2·46	3·75
		180	"	49·3	113,000	1·11		
		210	320	68·6	57,400	1·57	0·43	1·94

Table 28.

Summary of Results of Degradation of Methyl methacrylate/ Ethyl acrylate Copolymers

(b) Volatile Products of Degradation.

The volatile products of degradation were analysed only qualitatively. Chain fragments involatile at room temperature are detected in the degradation of the 10/1 copolymer, but not for the 100/1, which is as expected by comparison with the methyl methacrylate/methyl acrylate system (Chapter 4 Section (2)-(iii)).

The G.L.C. analysis of the products volatile at room temperature, but not at -80°C, are shown in table 29.

Table 29.

G.L.C. Analysis of Volatile Products.

COMPOSITION OF COPOLYMER,		G.L.C. ANALYSIS OF VOLATILE PRODUCTS.		
MMA	EA	MMA monomer	EA monomer	Ethanol.
100	1	180	1	
10	1	135	1	2

Small amounts of ethyl acrylate are produced, as expected by comparison with the methyl methacrylate/methyl acrylate system (Chapter 4 Section (2)-(iii)). However the 100/1 copolymer produces much more acrylate than the comparable methyl acrylate copolymer (112/1) from which no methyl acrylate monomer was detected. In the 10/1 copolymer ethanol is produced in twice as great amounts as the amounts of ethyl acrylate, which is a surprising result, since in the comparable methyl acrylate copolymer (7·7/1) no methanol is detected (Chapter 4 Section (2)-(iii)). Although no detailed sequence distribution studies are possible with only two copolymers, it is clear by comparison with the 7·7/1 copolymer , that the 10/1 methyl methacrylate/ethyl acrylate copolymer should contain an insignificant amount of ethyl acrylate blocks.

Carbon dioxide was found in the products of degradation, as well as a gas which is volatile at -80°C but not at -190°C and thus could be ethylene[59]. Permanent gases were not investigated. Further information about the gaseous products is given in Section (2)-(iii)(a).

(c) Volatilisation as a Function of Time.

The percentage volatilisations of the 100/1 and 10/1 copolymers plotted as a function of the time of degradation (from results in table 28) are shown in figure 39. It can be seen that the 100/1 copolymer is much more stable than the 10/1, which is completely the reverse of the results obtained for the methyl methacrylate/methyl acrylate system. This is a surprising result but a greater number of copolymers must be studied before any definite conclusions can be drawn.

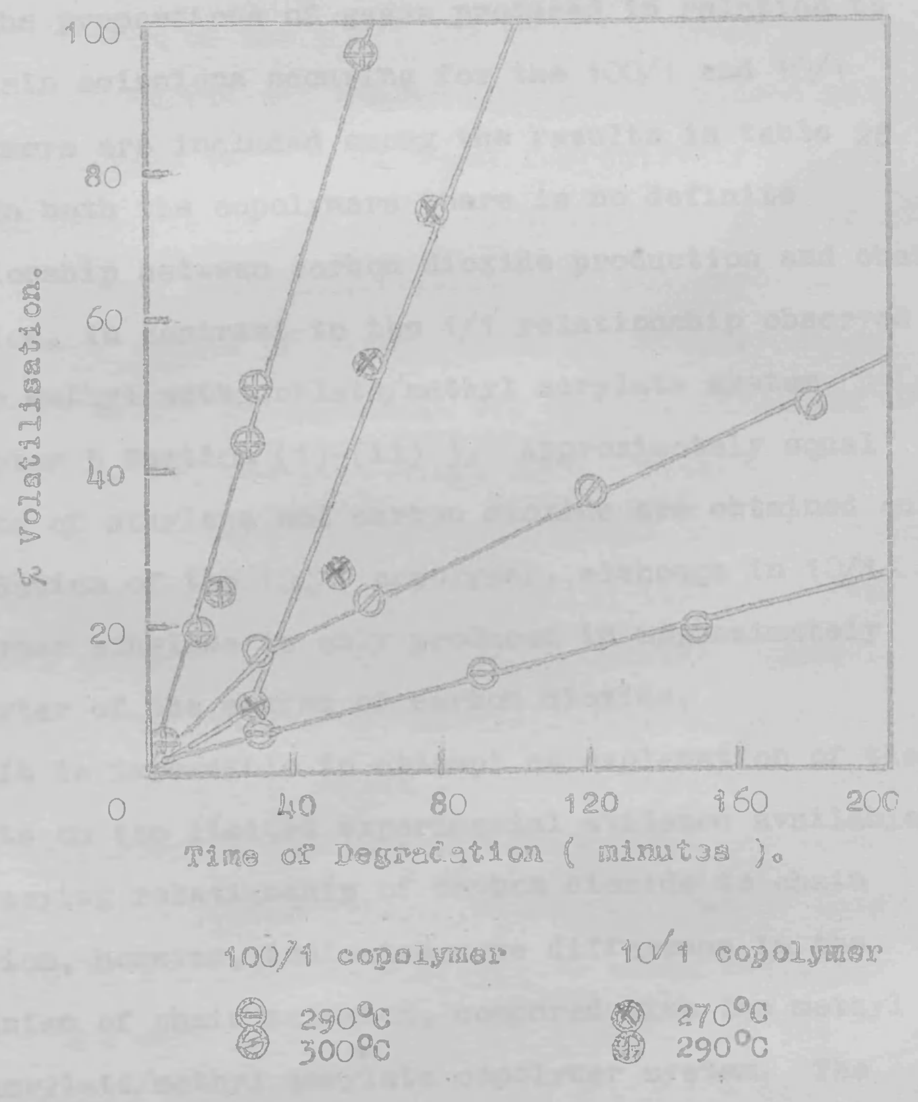


FIGURE 39.

Volatilisation of Methyl methacrylate/Ethyl Acrylate Copolymers.

(iii) The Chain Scission Reaction.

(a) Chain Scission and Gas Formation.

The proportions of gases produced in relation to the chain scissions occuring for the 100/1 and 10/1 copolymers are included among the results in table 28

In both the copolymers there is no definite relationship between carbon dioxide production and chain scission, in contrast to the 1/1 relationship observed in the methyl methacrylate/methyl acrylate system (Chapter 5 Section (i)-(ii)). Approximately equal amounts of ethylene and carbon dioxide are obtained on degradation of the 100/1 copolymer, although in 10/1 copolymer ethylene is only produced in approximately a quarter of the amount of carbon dioxide.

It is impossible to attempt an explanation of these results on the limited experimental evidence available. The varying relationship of carbon dioxide to chain scission, however, indicates some difference in the mechanism of chain scission, compared with the methyl methacrylate/methyl acrylate copolymer system. The ethylene obviously arises from ester decomposition.

(b) Chain Scission and Volatilisation.

It would be expected that, as observed for methyl methacrylate/methyl acrylate copolymers, volatilisation of the sample would proceed from the points of chain scission, the acrylate units blocking the depropagation reaction (Chapter 5 Section (2)-(ii)). The percentage volatilisation of the 100/1 and 10/1 copolymer samples are plotted versus the number of chain scissions per mole of polymer in figures 40,41 respectively (from results in table 28). A linear relationship is obtained which confirms that volatilisation of the copolymer occurs from points of chain scission. However since molecular weight measurements are used to calculate chain scissions, the points are more scattered than the corresponding methyl methacrylate/methyl acrylate data.

As before (Chapter 5 Section (2)-(iii)) it is possible to calculate the zip length of the depropagation reaction. The results of this calculation are shown in table 30. Since zip length decreases with increasing ethyl acrylate content it seems that ethyl acrylate units must block the depropagation reaction. However this blocking is not completely effective since the zip lengths are much greater than for stoppage at the first single ethyl acrylate units in the chain for both copolymers. Thus the reaction must pass through several single ethyl acrylate units and this is confirmed by the observation of ethyl acrylate monomer among the degradation products (Section (2)-(ii)-(b)).

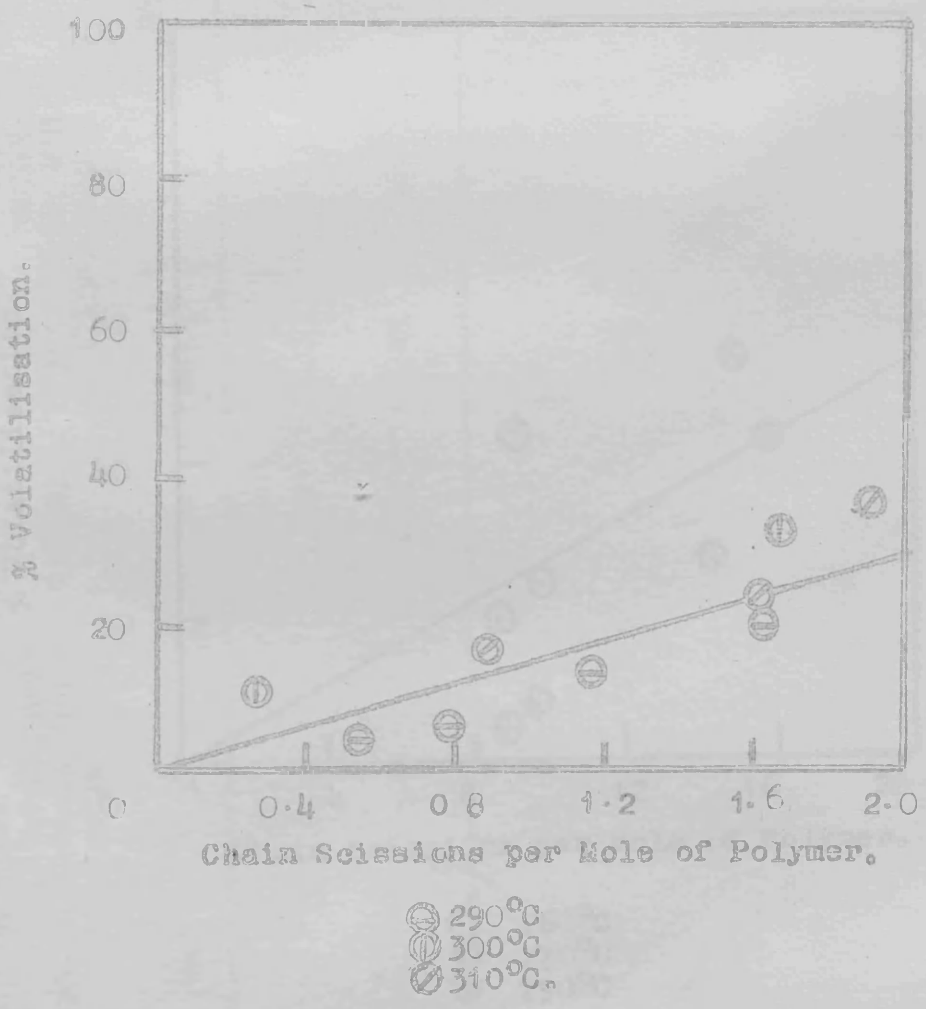


FIGURE 40.

Relationship Between Volatilisation and Chain Scission for Degradation of 100/1 Methyl methacrylate/Ethyl acrylate Copolymer.

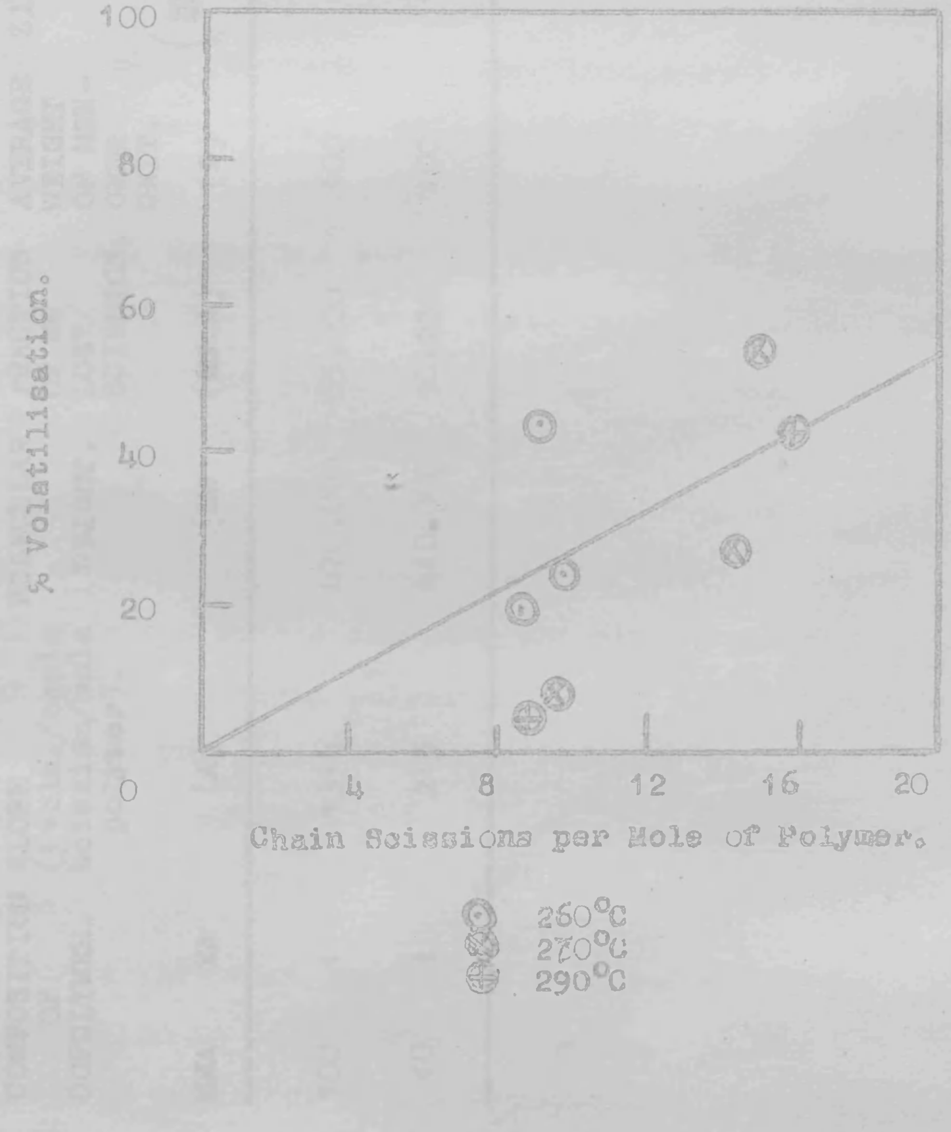


FIGURE 41.

Relationship Between Volatilisation and Chain Scission for Degradation of 10/1 Methyl methacrylate/Ethyl acrylate Copolymer.

COMPOSITION OF COPOLYMER. MMA	EA	SLOPE (g.voln./chain scission/mole polymer). (A)	MOLECULAR WEIGHT. (MW)	FRACTION OF MW LOST/ SCISSION. (MWxA)	AVERAGE WEIGHT OF MONOMER UNIT. (B)	ZIP LENGTH. $\left(\frac{MW \times A}{B}\right)$
100	1	13·4	470,000	63,000	100	630
10	1	2·5	410,000	10,250	100	102

Table 30.

Calculation of Zip Length for Degradation of Methyl methacrylate/Ethyl acrylate Copolymers.

(c) Chain Scission and Copolymer Composition.

Figures 42,43 show chain scissions plotted against the time of degradation for the two copolymers (from the results in table 28). The chain scissions reach a maximum value for each copolymer independent of the extent and temperature of degradation. This value is dependent on the ethyl acrylate content of the copolymers, since the extrapolated value of the maximum for the 10/1 copolymer (~16 chain scissions/mole) is approximately ten times that for the 100/1 copolymer (~1·6 chain scissions /mole).

In this system, therefore, chain scissions appear to occur at ethyl acrylate units in the chain. Not all ethyl acrylate points are attacked since the theoretical total number of chain scissions is not reached in either copolymer. The chain scission reaction will be discussed in Section (2)-(iv).

(iv) Discussion.

Since this work represents only a preliminary investigation it is not possible to account for the degradation behaviour of the copolymer systems in any detail and thus only tentative suggestions about the degradation mechanisms can be made. However it is intended in this section to discuss the results obtained

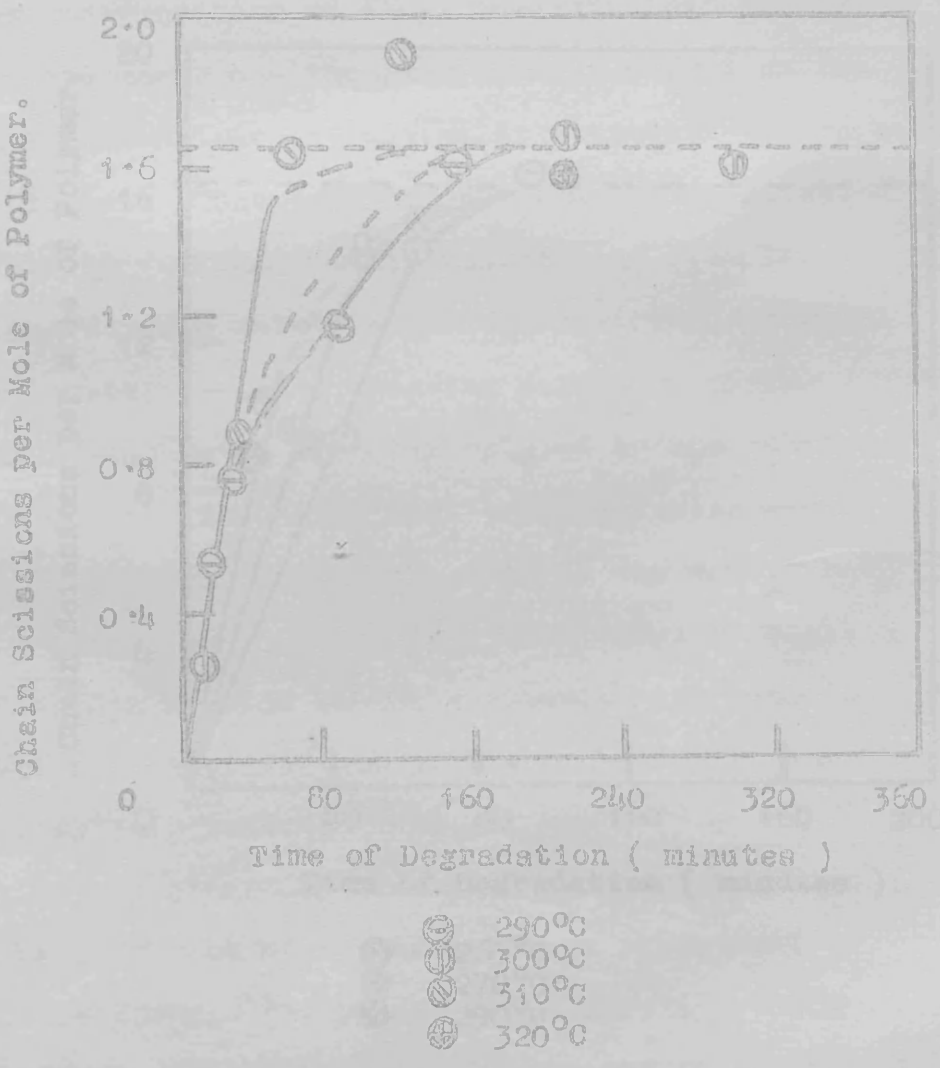


FIGURE 42.

Chain Scissions Occuring on Degradation of 100/1 Methyl methacrylate/Ethyl acrylate Copolymer.

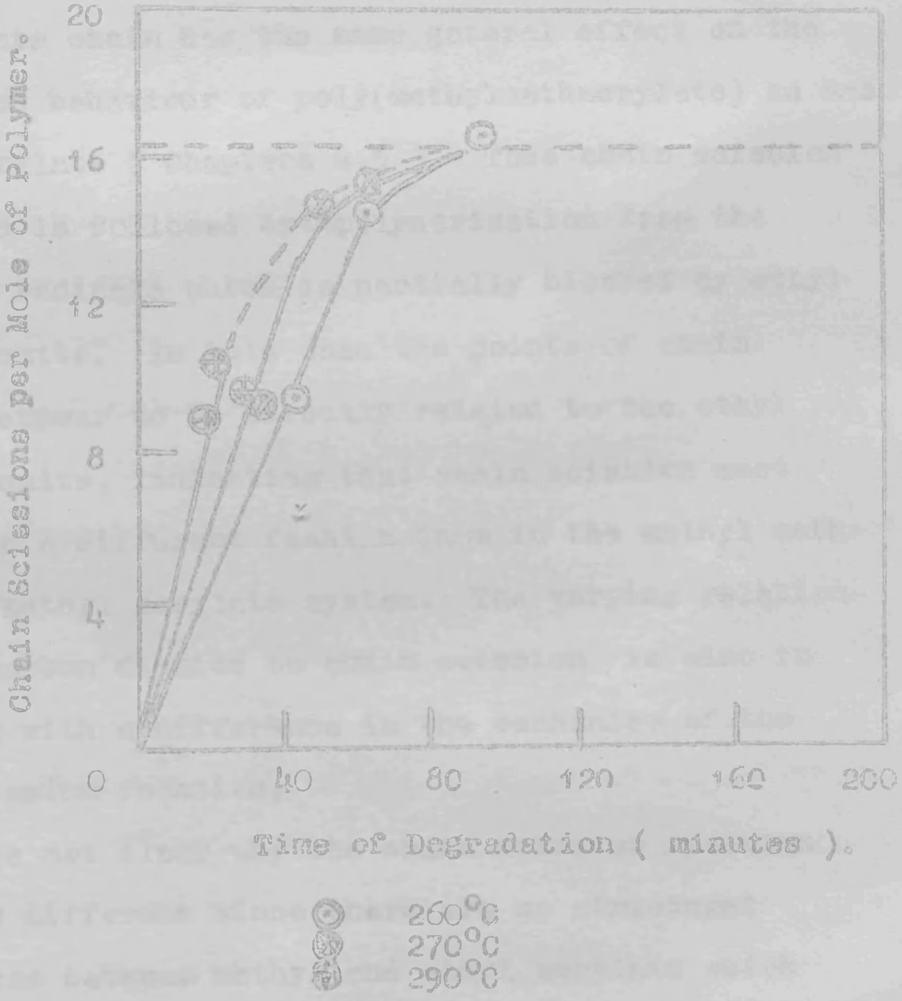


FIGURE 43.

Chain Scissions Occuring on Degradation of 10/1 Methyl methacrylate/Ethyl acrylate Copolymer.

in such a way as to indicate the direction of future experimental work.

The incorporation of ethyl acrylate into the methyl methacrylate chain has the same general effect on the degradation behaviour of poly(methylmethacrylate) as has methyl acrylate (Chapters 4,5). Thus chain scission occurs and is followed by depolymerisation from the resulting radicals which is partially blocked by ethyl acrylate units. In this case the points of chain scission appear to be directly related to the ethyl acrylate units, indicating that chain scission must proceed in a different fashion than in the methyl methacrylate/methyl acrylate system. The varying relationship of carbon dioxide to chain scission is also in agreement with a difference in the mechanism of the chain scission reaction.

It is not clear why the chain scission reaction should be different since there are no structural differences between methyl and ethyl acrylate which should affect the chain reaction proposed to account for chain scission in the methyl methacrylate/methyl acrylate system. One clear difference from the methyl methacrylate/methyl acrylate system is that ester decomposition is now taking place and this may in some way affect the overall degradation characteristics.

At this point it would be unwise to draw further conclusions and this aspect of the work should clearly be followed up.

The experimental zip lengths (table 30) indicate that the depropagation reaction is not completely blocked by the ethyl acrylate units. It is of interest to compare the blocking ability of ethyl acrylate with that of methyl acrylate. Thus in the 10/1 copolymer the depropagation reaction passes through approximately 9 ethyl acrylate units which compares favourably with the 7·7/1 methyl methacrylate /methyl acrylate copolymer where the reaction passes through approximately 9 methyl acrylate units (from table 13). However in the 100/1 copolymer the reaction passes through approximately 6 ethyl acrylate units, which agrees with the large amount of ethyl acrylate in the products of degradation (180/1 methyl methacrylate/ ethyl acrylate), whereas in the 112/1 methyl methacrylate/methyl acrylate copolymer the reaction is blocked at the first methyl acrylate units beyond point of chain scission.

This latter result would tend to indicate that the ethyl acrylate monomer is less efficient in blocking the unzipping reaction and would explain the experimental findings that increasing ethyl acrylate content makes the copolymer much more unstable (Section

(2)-(ii)-(c)), since greater amounts of chain scission would occur, from which the copolymer could readily depolymerise. However the results of 10/1 copolymer degradation do not confirm this as they show that ethyl acrylate has the same blocking ability as methyl acrylate in a copolymer of comparable composition.

Further study of this problem using copolymers of various ethyl acrylate content should help to explain these contradictory results which are of particular interest since ethyl acrylate is used commercially to stabilise poly(methylmethacrylate) in proportions of approximately 30/1 methyl methacrylate/ethyl acrylate. Thus according to the above results this copolymer should be more unstable than one containing smaller amounts of ethyl acrylate.

The volatile products of degradation, such as, chain fragments, monomers, carbon dioxide and ethylene (arising from ester elimination),are as expected by comparison with the methyl acrylate copolymers. However, as noted in Section (2)-(ii)-(b), ethanol would not be expected as a product of degradation of the 10/1 copolymer, if as for the methyl methacrylate/methyl acrylate system, ethanol is only produced in a block of ethyl acrylate units. Further study of copolymers of higher ethyl acrylate content should help to explain this result.

CHAPTER 7.

SURVEY OF RESULTS AND SUGGESTIONS FOR FUTURE WORK.

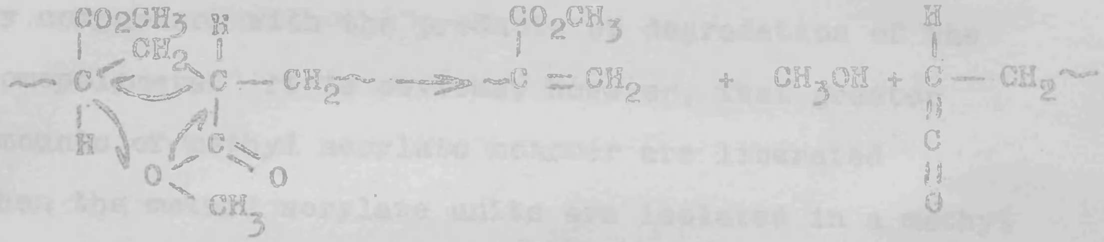
Methyl methacrylate/methyl acrylate and methyl methacrylate/ethyl acrylate copolymer systems have been studied as part of a general investigation of the degradation behaviour of copolymers. As a preliminary it was necessary to estimate the reactivity ratios for these two systems. Values had not previously been reported, probably because the closely similar chemical structures of the two comonomers made analysis extremely difficult. P.M.R. spectroscopy was used to analyse the copolymers since it can distinguish quantitavely between protons in different environments in the two monomer units. The values of reactivity ratios obtained in this way are in good agreement with values published, for the methyl methacrylate/methyl acrylate system, since this work was started. This method has been extended to a wider series of methacrylate /acrylate copolymers with excellent results . P.M.R. spectroscopy clearly offers a general method of analysis of copolymers whose constituent monomers are similar, provided they have protons in different environments.

The methyl methacrylate/methyl acrylate copolymer system was found to degrade in approximately the same fashion thermally and photochemically. It is therefore convenient to discuss the two reactions together. Copolymer degradation may be treated most conveniently from the point of view of the effect of a second monomer on the degradation of a homopolymer. Thus in the case of poly(methyl methacrylate) the incorporation of only 1% methyl acrylate has a profound effect on the thermal and photochemical degradation. The methyl acrylate units block the normal depolymerisation from unsaturated chain ends. After all these unsaturated chain ends have reacted depropagation only occurs from points of random chain scission and of course is blocked by the methyl acrylate units in the chain. Thus the methyl methacrylate/methyl acrylate copolymers are very much more stable thermally than poly(methylmethacrylate) as shown by the temperatures at which reaction occurs at a conveniently measurable rate (260°C for copolymers compared to 220°C for poly(methylmethacrylate)). In the photochemical degradation much less volatilisation occurs in the copolymers, than in poly(methylmethacrylate), at similar temperatures. This again indicates stabilisation by the comonomer methyl acrylate. In both the thermal and photochemical reactions, as expected, stability increases with increasing methyl acrylate content.

Sequence distribution studies show that in the copolymer molecules the large majority of methyl acrylate units are separated from each other by blocks of methyl methacrylate. There are however small amounts of pairs of adjacent methyl acrylate units. The experimental zip lengths from points of chain scission, for the thermal degradation of copolymers of low methyl acrylate content, show that the depropagation reaction is effectively blocked by isolated methyl acrylate units. In copolymers of higher methyl acrylate content the zip length indicates that the reaction can pass through single methyl acrylate units, but very much less readily through adjacent pairs of methyl acrylate units. This blocking reaction at methyl acrylate pairs can be explained in terms of intermolecular transfer reactions occuring at the unstable methyl acrylate radicals to form stable saturated chain ends. Some depropagation through the methyl acrylate pairs does occur during the thermal degradation and this could be explained by intra-molecular transfer to form a chain fragment larger than monomer and a methyl methacrylate radical, which can readily depropagate. In photochemical degradation the zip lengths are much longer than in the thermal reaction showing that depropagation can occur more readily through methyl acrylate pairs. In this case the copolymer samples are very viscous and it is possible that this favours the intramolecular rather than intermolecular transfer reaction.

Much more work is necessary on this aspect of the degradation since it is not clear why the blocking efficiency should alter with increasing methyl acrylate content of the copolymers. This explanation of longer zip lengths in the photochemical degradation is only tentative and this needs further investigation. A study of copolymers with higher methyl acrylate content and also copolymers of methyl methacrylate with other monomers capable of transfer and thus having blocking ability, should produce interesting results.

The degradation behaviour of poly(methylacrylate) is also affected by the addition of a comonomer. Thus the production of methanol which forms approximately 15% of the volatile products of thermal degradation of poly(methylacrylate) is suppressed in the copolymers. This suprising result can be related to the isolation of the methyl acrylate units in the methyl methacrylate chain. It appears that it is necessary to have a block of methyl acrylate units before methanol is liberated. It may be tentatively suggested that a mechanism of the type shown is involved, which depends upon the existence of adjacent methyl acrylate units.



This mechanism could be thoroughly investigated by degrading copolymers with the methyl acrylate labelled in the $-O-\overset{x}{C}H_3$ position with C^{14} thus allowing any methanol produced to be estimated with a high degree of accuracy. By covering a range of copolymer compositions, it should be possible to determine very exactly the conditions required for methanol production.

This work illustrates one of the advantages of copolymer degradation studies. Thus in the thermal degradation of poly(methylacrylate) the various reactions occuring are superimposed and it is difficult to determine the individual degradation mechanisms. In copolymers the methyl acrylate units are "diluted" by isolation in the methyl methacrylate chain, thus removing some of the masking reactions which occur in the homopolymer. This allows the mechanism of methanol production to be investigated in detail.

Apart from methanol, the volatile products of the thermal and photochemical degradations are as expected by comparison with the products of degradation of the homopolymers. It is obvious, however, that greater amounts of methyl acrylate monomer are liberated when the methyl acrylate units are isolated in a methyl methacrylate chain.

The chain scission reaction which occurs during the thermal degradation of the copolymers also illustrates a variation from the expected behaviour. The polymer chains do not break directly at methyl acrylate units as might be expected. A complicated reaction mechanism is operative, which from a study of the kinetics of chain scission, proceeds by means of a radical chain reaction. The initiation step of this chain reaction is the formation of radicals at methyl acrylate units in the chain, hydrogen being liberated. The propagating radical, however, can attack any main chain methylene group, to liberate eventually, as the result of a five-membered ring mechanism, one molecule of carbon dioxide. for every chain scission. This type of chain scission might possibly occur in poly(methylacrylate), accounting for the observed carbon dioxide formation, although no data is yet available, due to the masking cross linking reaction. However it is probable that the mechanism only applies to the copolymer system and occurs because the separation of the methyl acrylate units allows the propagation step of the chain reaction to proceed. This point is worthy of further study and could lead to an understanding of the chain scission mechanism in poly-(methylacrylate).

The chain reaction mechanism is particularly open to criticism in the assumption that hydrogen is produced in the initiation step. Although the experimental results indicate that this is true, unsaturation is observed in the copolymers and as discussed in the Introduction (Section (2)-(ii)-(c)), hydrogen can be liberated in reactions leading to unsaturation and cross linking. Further study of the initial stages of degradation of copolymers containing methyl acrylate with the tertiary hydrogen atom replaced by deuterium could clear up this point. This system would serve a double purpose since at higher extents of degradation methanol production could be investigated.

The molecular weight changes on photodegradation show that the chains do not break initially at methyl acrylate units, therefore it is probable that a radical chain scission mechanism is operative as for thermal degradation. Carbon dioxide production does not appear to bear a simple 1/1 relationship with chain scission, however, so it is possible that the chain scission mechanism is slightly different. However, it is difficult to obtain kinetic data to confirm the mechanism in this case due to the viscous nature of the sample. This aspect of the work requires further investigation.

The copolymers show an apparent induction effect when photodegraded in the form of powder. However when the sample is degraded in the form of a film this effect disappears. It is not possible to explain this interesting result on the limited experimental evidence available, however, it is probably due in some way to the nature of the powdered form of the polymer below its melting point and not to the fundamental nature of the chain scission reaction. This result illustrates the difficulty of interpreting polymer degradation behaviour where the physical form of the sample can affect the degradation characteristics as discussed in Chapter 2 Section 2. Before any further detailed study of the photodegradation of this copolymer system is undertaken therefore, it is obviously important to investigate fully the effect of the physical form of the sample on its degradation behaviour.

The thermal degradation of methyl methacrylate/ethyl acrylate copolymers was studied in a preliminary way. The results are therfore limited and it is not possible to discuss the mechanism in detail. However, the same general degradation behaviour was observed as for the methyl methacrylate/methyl acrylate system, although several important differences were detected. Thus the ethyl acrylate units stabilise the methyl methacrylate chain in a similar way to methyl acrylate, by blocking the normal depropagation reaction from chain ends. After the reactive chain ends have reacted depropagation only occurs from points of chain scission and is also blocked by ethyl acrylate units in the chain, though apparently not as effectively as by methyl acrylate, since the experimental zip lengths are longer for the ethyl acrylate copolymers. However, in contrast to methyl methacrylate/methyl acrylate copolymers, as the ethyl acrylate content is increased the copolymers become more unstable. This surprising result could possibly be due to the less efficient blocking of the depropagation reaction by the ethyl acrylate units in the chain.

The chain scission reaction in this case appears to occur directly at ethyl acrylate units. The mechanism of chain scission must therefore be different from that in the methyl methacrylate/methyl acrylate system. The carbon dioxide/chain scission relationship is not 1/1 and again this is consistent with a difference in the chain scission mechanism.

The volatile products of degradation are as expected by comparison with the degradation behaviour of the homopolymers and the methyl methacrylate/methyl acrylate system except that for the production of ethanol rather less ethyl acrylate appears to be necessary than methyl acrylate for the production of methanol. Ethylene is observed in the products arising from ester decomposition reactions as expected. Since ester decomposition is the degradation characteristic which is different from the methyl methacrylate/methyl acrylate system, it could be that the different degradation behaviour of the two systems is related in some way to this reaction and future work would have to investigate this point more fully.

Thus in agreement with the conclusions drawn by Farish in an earlier investigation of copolymer degradation (discussed in Chapter 1 Section (3)), the copolymer systems studied in this work exhibit unusual and distinctive degradation behaviour not predictable from a knowledge of the reactions of the individual homopolymers. From this unusual behaviour information about the degradations of the homopolymers can be obtained, particularly in the case of poly(methylacrylate) in which cross linking masks the fundamental homopolymer reactions. This illustrates the importance of the study of the degradation of copolymers, which so far has been surprisingly neglected. Study of further copolymer systems should be of great interest.

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