THE VACUUM THERMAL DEGRADATION OF POLY (METHYL ACRYLATE) AND POLY (BENZYL ACRYLATE)

David Ross Kane

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews

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THE VACUUM THERMAL DEGRADATION
OF
POLY (METHYL ACRYLATE) AND POLY (BENZYL ACRYLATE)

A thesis presented by David Ross Kane to the University of
St. Andrews in application for the degree of Doctor of
Philosophy.

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DECLARATION

I hereby declare that the following thesis is a record of experimental work carried out by me, that it is my own composition, and that it has not previously been presented in application for a Higher Degree.

The investigation was carried out in the Chemistry Research Laboratories of St. Salvator's College, St. Andrews under the supervision of Dr. G.G. Cameron.

Part of the subject matter of Chapter V has been published in the Journal of Polymer Science, Part B, Polymer Letters.

CERTIFICATE.

I hereby certify that David Ross Kane has spent twelve terms of research work under my supervision, that he has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and that he is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

UNIVERSITY CAREER.

I matriculated in the University of St. Andrews in October 1959, and graduated B.Sc. with Second Class Honours in Chemistry in June 1963.

I was admitted as a Research Student in October 1963.

The work described in this thesis was carried out during the period October 1963 to October 1966.

ACKNOWLEDGEMENTS.

My thanks are due to the Science Research Council for a maintenance grant during the tenure of which the work was performed, and to Professor J.I.G. Cadogan for making available laboratory facilities.

I am also grateful to Dr. G. Woolley for carrying out the mass spectrometric analyses, to Messers T. Norris and J. Rennie for general assistance in the workshop, to Mr. D. McGhee for glassblowing assistance, and to Mrs. J. Galloway and Mrs. P. Pearce of the Geology Department for typing the manuscript.

Finally, I would like to express my sincere appreciation of the guidance and ready encouragement given me by Dr. Cameron, who suggested the problem and supervised the work described in this thesis.

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CHAPTER I

INTRODUCTION

In the field of polymer chemistry the term degradation embraces any process which causes permanent physical or chemical change in the polymer structure. In the more restricted industrial sense, degradation is synonymous with physical deterioration, or any process leading to "failure" of the polymer in the task for which it was designed.

A wide variety of agencies can bring about degradation in polymers. Among the more common are heat, ultra-violet light, all forms of radiative energy, mechanical strain, and attack by oxygen and many other chemicals.

This thesis will be almost solely concerned with the effects of heat on addition polymers under vacuum conditions, and the terms degradation, or thermal degradation will refer to reactions brought about by heat under vacuum.

1. DEVELOPMENT OF DEGRADATION STUDIES

Only in the last forty years has the true nature of macromolecular structure become established. Once this became known, however, there was a ready appreciation of the unique properties that might be conferred on polymeric materials by nature of their structure. This provided the impetus for an immense amount of work in polymer chemistry, and has led to the rapid growth of the plastics industry, and the yearly production and fabrication of huge tonnages of polymers. The retention, by these materials, of manufactured characteristics is obviously of extreme importance, and it was the desire to limit, and if possible to prevent, degradation which led to the initiation of all types of degradation studies. Fundamental investigations of degradations can, above all, be instrumental in bringing about the improvement of existing polymers, and in directing the synthesis and discovery of new materials. They are, however, valuable in many other ways. Originally, degradation studies were employed to establish polymer structures. Staudinger[1,2] showed the head to tail nature of the polystyrene chain by bulk pyrolysis experiments, and Marvel in America directed several investigations of a similar nature[3]. In addition, studies of degradation processes are of considerable intrinsic interest, can often furnish valuable confirmatory, and occasionally new evidence on radical reactivities, and reveal new and interesting reactions.

The thermal degradation reactions of the vinyl polymers have probably been investigated more often, and more thoroughly than those of any other group. The relative ease of obtaining or preparing pure samples of suitable molecular weight and the lack, until recently, of suitable alternative polymer systems, as well as the obvious commercial importance of this group, were all factors responsible. In addition, the purely carbon back-bones of the polymers offered the simplest system for first degradation studies. The effect of polymer preparation variations, of side groups, and of molecular weight on mechanism and stability, could be more easily assessed because of the homogeneous linear back-bone. It was also realised, that a basic knowledge of the degradations of carbon back-bone polymers, provided a background against which the effects of hetero atoms and other structures on polymer stability in general, could be gauged.

Since the first efforts to clarify polymer structures, certain trends in polymer degradation studies are apparent. The first serious attempt at the elucidation of a thermal degradation mechanism, on the basis of rate measurements, was made by Votinov, Kobeko and Marei[4], in 1942. The investigation of the depolymerisation of poly (methylmethacrylate) (PMMA) by Grassie and Melville[5] marked an advance in the design of apparatus, and a better appreciation of the significance of combined molecular weight and volatilization data.

In the 1950's a considerable body of work concerning polymer degradation mechanisms was built up. Most of the common vinyl polymers were studied, and more complex systems like poly (ethylene terephthalate), other fibre forming materials, and synthetic rubbers were more thoroughly investigated. These studies were reinforced by the accumulation of reliable thermal and oxidative data on model compounds, and stimulated by numerous theoretical treatments of polymer degradation reactions.[6-9] The degrading polymer system is suited to mathematical analyses, and with the arrival of electronic computers, solution of the linear differential equations involved became a practical possibility. In fact, the flow of theoretical papers has always kept pace with, and often outstripped, the availability of confirmatory experimental results. Experimental methods generally have improved, as several techniques of following weight loss automatically have evolved. Madorsky's monograph[10] provides a good introduction to the type of apparatus used. In recent years development of more sophisticated equipment, which allows a polymer sample to be raised from room temperature to 500-600°C while weight loss is recorded directly, has created a new method of rapid thermal examination of a polymer sample. In a few hours with this technique of thermogravimetric analysis,[11,12] the stability of the polymer can be assessed, whether or not breakdown occurs in separate stages determined, and the activation energy and order of the reaction with respect to weight obtained.

Nevertheless, for determining breakdown mechanisms, there is still no substitute for the well-tried methods involving detailed qualitative and quantitative examination of products, measurement of molecular weight changes with percentage volatilization, and calculation of volatilization rates, and in the past few years these methods have been increasingly applied to the study of new commercially important polymers such as polyurethanes[13,14] and polycarbonates[15].

Polymer degradation studies will continue to be of the utmost importance as long as polymers and plastic materials are manufactured. The availability of polymers which are stable under extreme conditions, (see Section 3, this chapter), would greatly enhance the capabilities of modern technology.

2. CLASSIFICATION OF DEGRADATION REACTIONS

The thermal decompositions of polymers so far investigated appear in the main to be chain reactions, involving free radical intermediates[16]. There are, however, some exceptions,[17,18] where the presence of moisture and traces of acid polymerisation catalysts can lead to ionic mechanisms. The essential features of the polymer decompositions indicate mechanisms of the Rice-Herzfeld type,[19] which have been used extensively to elucidate organic reactions in the gas phase[20].

The reactions brought about by physical agencies, cause either scissions of the main chain, or involve modifications of its substituents, and this leads to a rough classification of reactions:-

A. Reactions affecting the main polymer chain
  (i) Depolymerisation
  (ii) Crosslinking
B. Reactions involving side groups
  (i) Decomposition
  (ii) Rearrangement

Of all the physical agencies heat probably has the least complicated chemical effects. The reactions above will be explained briefly by reference to thermal degradations where possible.

A.(i) Depolymerisation

Ideally, there are two types of depolymerisation. Which is operative depends on whether radical reactivity and polymer structure favour transfer reactions or not. Once the initiating radicals are produced, depolymerisation may proceed by a process of "unzipping" or stepwise depolymerisation, (in effect, the reverse of the propagation step in polymerisation), with the formation of virtually 100% monomer. The primary radical producing step may occur at the ends of polymer molecules, or at random along the chain. Poly (α -methyl styrene),[21,22] (randomly initiated) and PMMA,[5,23] (chain-end randomly initiated) are the best known "unzipping" polymers. Below 220°C the degradation of low molecular weight ($M_n < 200,000$) PMMA[5,24] is wholly end initiated.

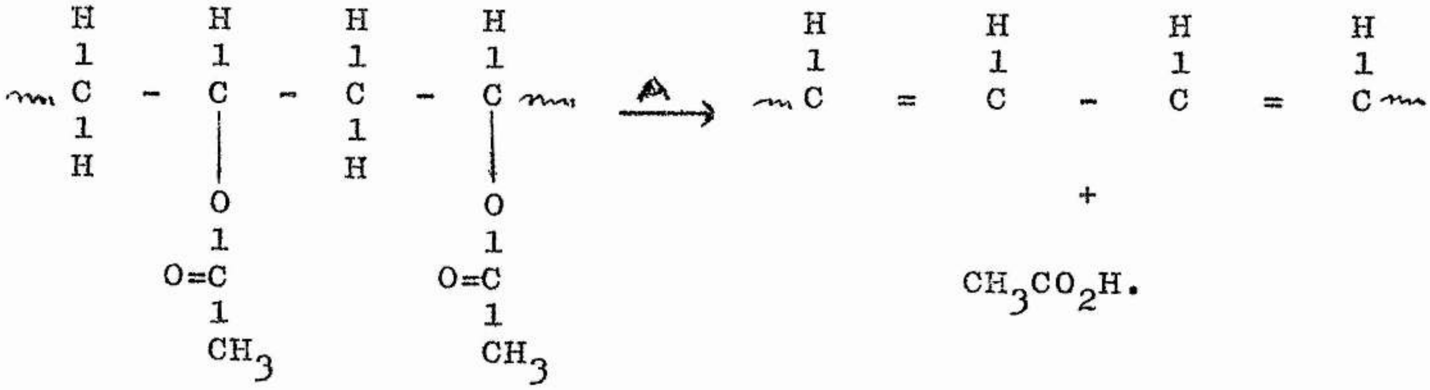
A.(ii) Crosslinking

Crosslinking processes in purely thermal degradations are rare, and are more often found in polymers exposed to light or to high-energy irradiation[25]. Crosslinking is usually associated[26] with the presence of a tertiary hydrogen atom in the back-bone, and the acrylates[27,28] are among the polymers which crosslink most readily on irradiation.

If occurring in concert with chain scission, crosslinking need not be associated with insolubility[29].

B.(i) Side group decomposition

Side group decomposition invariably involves liberation of a volatile product and the formation of a new structure in, or attached to the polymer chain. Thus, if poly (vinyl acetate) is heated above 190° in a vacuum, acetic acid is produced[30] in large yield and polyacetylene chains are formed:-



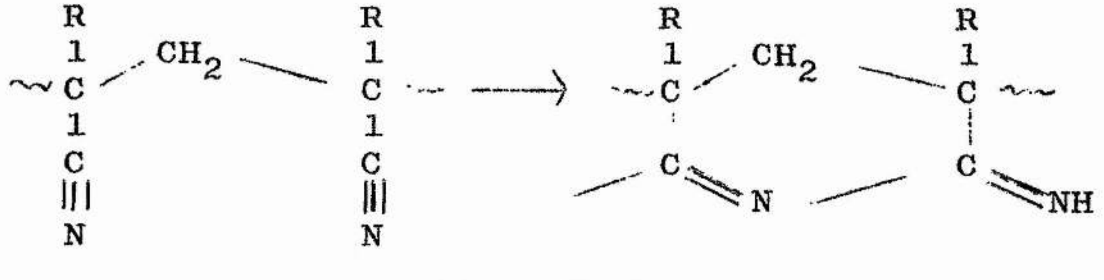
$$\sim CH_2-CH(OCOCH_3)-CH_2-CH(OCOCH_3)\sim \xrightarrow{\Delta} \sim CH=CH-CH=CH\sim + CH_3CO_2H.$$

The acid is produced in a chain reaction initiated by the loss of an acetic acid molecule from the end of a chain, and the formation of an end double bond.

Poly (vinyl chloride) breaks down[31] to a polyene and hydrochloric acid but the mechanism is of a more complex nature. The methacrylate polymers exhibit an interesting series of side group decompositions,[32] which will be discussed in Section 4, of this chapter.

B. (ii). Side group rearrangement

The best known rearrangement reaction in the literature of polymer degradation is associated with the development of colour in the nitrile containing polymers poly (acrylonitrile)[33] and poly (methacrylonitrile)[34]. Grassie and his co-workers have studied the reactions very closely. On heating, initiating centres bring about the formation of six-membered nitrogen containing rings:-



R = H, Me.

Ladder structures may eventually result containing long sequences of conjugated C = N bonds.

3. EFFECTS OF STRUCTURE ON DEGRADATION AND STABILITY

The basic concepts of polymer stability are understood and have been clearly set down in a classical paper by Eirich and Mark[35].

Linear chains of carbon atoms, as in vinyl polymers, are not very resistant to scission and even the more stable vinyl polymers tend to breakdown around 350°C. Decomposition of vinyl polymers is generally complete around 400°C. The pattern of the breakdown is significantly affected by the structure of the repeating unit. Polymers $-(CH_2.CHX)_{\overline{n}}$ give very low monomer yields, (weight percentage of monomer in total weight loss), on pyrolysis, because the main breakdown process involves transfer of the tertiary hydrogen. Polystyrene[36] is an exception to this rule. Polymers $-(CH_2.CXY)_{\overline{n}}$ in which this atom has been replaced by a further substituent group Y decompose at lower temperatures, and often produce almost quantitative yields of monomer. These effects are associated with the weakening of the main chain by α, α di-substitution, with the deactivation of the radical $\sim CH_2-\overset{\circ}{C}XY$, and with the preclusion of transfer reactions. Bamford <u>et al.</u>[37] have used the velocity co-efficient of transfer of a growing polymer chain to toluene at 60°C, (K_{tol} 60°), as a measure of radical reactivity. Radical reactivity and monomer yield on pyrolysis are correlated in Table 1, for some common polymers.

Table 1 illustrates clearly that the high monomer yield from polystyrene is not, in fact, anomalous. A marked degree of resonance in the aromatic nucleus stabilises the radical sufficiently to allow depropagation.

Table 1

Radical reactivity and monomer yield.

Polymer of:-	K_{tol} 60^o	Monomer yield Wt %
methacrylonitrile	0.02	85
α -methyl styrene	-	95
styrene	0.002	42
methyl methacrylate	0.013	95
methyl acrylate	0.56	0.7
acrylonitrile	0.785	1.0
vinyl acetate	7.73	.0

Degradation is usually accompanied by the scission of back-bone links and the volatilization of fragments of polymer. Polymers already having crosslinks, or in which crosslink formation is promoted by heating, can to a certain extent stabilise themselves during pyrolysis by the formation of rigid, infusible networks. Phenol formaldehyde resins,[38] and irradiated vinyl and vinylidene fluoride polymers[39] provide a good example of the former, and poly (vinyl fluoride)[40] of the latter type of stabilisation.

The presence of hydrogen bound to an $\underline{Sp}^3$ hybridised carbon atom is often a source of weakness in a polymer. The stability of polymeric materials is invariably improved by replacement of hydrogen atoms by fluorine; an example of this is poly (tetrafluorethylene) (PTFE).[41] The high thermal stability of PTFE is due to the very close packing of the fluorine atoms, and also to the increase in chain stiffness which results from this.

However, linear chains of carbon atoms are, in general, not resistant to high temperatures. Cyclic structures in the low molecular weight range are much more thermally stable, and the hypothesis that the properties of a polymer which contains repeating aromatic units may mirror the chemical and thermal stability of the parent systems, has received ample experimental support. Koton[42] has reviewed the thermostable ring containing polymers prepared up to 1961. In recent years, several homopolymers containing heterocycles have been found to have outstanding thermal resistance. These include poly (benzimidazole),[43] poly (1, 3, 4 oxadiazole),[44] both with decomposition temperatures above 450°C, and poly (phenyl pyrazoles)[45] which are completely stable up to 400°C. It seems unlikely that purely organic polymers can be produced which are stable much beyond 600°C, and in recent years the search for macro-molecular structures, stable at even higher temperatures, has moved into the field of inorganic polymers with back-bones containing titanium, aluminium, phosphorus and boron atoms.

The incorporation of heavy metal atoms into organic molecules is looked upon as a further method of achieving a combination of polymeric characteristics and extreme thermal stability.

4. DEGRADATION OF ACRYLATES AND METHACRYLATES

To date information on the degradation of acrylates is meagre, but there is sufficient evidence to suggest that more detailed investigations would be worthwhile. The degradations of methacrylate polymers have been better investigated; PMMA in particular has been extensively studied,[23] and the main characteristics of methacrylate decompositions are well understood.

A survey[32] of the common methacrylate polymers has shown that, with the exception of poly (t - butyl methacrylate), all depolymerise to form monomer in high yield. In addition, apart from PMMA and poly (neo - pentyl methacrylate), all exhibit side chain decomposition. The latter two polymers give monomer as their sole degradation product. The side group decomposition liberates an olefin, and reduces the ester to a carboxyl group. The presence of a hydrogen on the carbon atom β to the ester ether oxygen is required for this type of side group decomposition. Competition between depolymerisation and ester decomposition is a general property of methacrylates, PMMA and poly (t - butyl methacrylate) representing opposite extremes of behaviour.

The ester side group decomposition which occurs readil at 180°C is generally followed by elimination of water between adjacent carboxyl groups to give six-membered anhydride rings in the chain. The monomer yield on degradation depends on the ease of side group decomposition, as anhydride rings in the chain block the depropagation reaction. The ester group decompositions have been very fully investigated for poly (n - butyl methacrylate)[46] and poly (t - butyl methacrylate),[47] and their existence in poly (ethyl methacrylate)[48] and poly (iso-propyl methacrylate)[49] degradations has been established beyond doubt.

There has not been a general survey of the acrylate polymers. Poly (methyl acrylate) (PMA) produces virtually no monomer,[50] but appreciable quantities of methanol and carbon dioxide on degradation. As no other polymer with a purely carbon back-bone is known to behave in this way, a novel degradation reaction may occur. In addition, poly (ethyl acrylate) degrades at 230°C producing scarcely any gaseous volatiles.[51] A predominantly random degradation process would appear likely in both these polymers. On the other hand, an ester decomposition reaction occurs in poly (t - butyl acrylate) at 160°C, and has been studied[52] between 180° and 200°C. This reaction is very similar to that in the corresponding member of the methacrylate series, having a non-radical mechanism and being unaccompanied by monomer formation. Ester decomposition without depropagation is also believed to be a feature of the degradation of poly (iso-propyl acrylate).[49] Because of the absence of depropagation reactions the acrylates appear to offer better opportunities for detailed study of the ester decomposition reaction.

PMA was selected as the starting point of the present investigations for two main reasons. Firstly, the corresponding member of the methacrylate series had been closely studied and offered a good background for comparing behaviours. Secondly, the limited data in the literature on PMA indicated that its pyrolytic behaviour was rather unusual. The preliminary aim of the work was, therefore, to elucidate as fully as possible the overall mechanism of the degradation reaction, and at the same time, to determine how the products of degradation are formed.

The structure of poly (benzyl acrylate) (PBA), precludes the conventional ester side group decomposition, and therefore, the study of its degradation, while extending the investigations of the acrylate series, allowed more relevant comparison with the results of PMA degradation, and provided evidence of the effect, on the stability of acrylate polymers, of an aromatic ring in the side group.

CHAPTER II

APPARATUS AND EXPERIMENTAL METHODS

1. PREPARATION OF POLYMERS

1.1. PURIFICATION OF MATERIALS

1.1.1. Methyl acrylate

Laboratory grade methyl acrylate (B.D.H.) was distilled at atmospheric pressure under oxygen-free nitrogen, which was passed through the apparatus for at least two hours before distillation. The first and last thirds of the distillate were rejected, and the middle third was collected, b.p. 77-81^{o} (lit.,[53] b.p. 85^{o}C). Gas chromatography of this product showed only one peak. This was taken as sufficient evidence of purity. The pure monomer was stored in a refrigerator until required, but was always used within 7 days.

1.1.2. Benzyl acrylate

Benzyl acrylate was prepared by the method of Rehberg[54]. Benzyl alcohol (108 g., 1 mole.), methyl acrylate (215 g., 2.5 mole.), <u>para</u>-toluene sulphonic acid (10 g.) and hydroquinone (6 g.), were placed in a round-bottomed flask. The flask was attached to an all-glass 24 in. Vigreux column, and the methanol/methyl acrylate azeotrope rapidly distilled off. The excess methyl acrylate and any unreacted benzyl alcohol were removed under reduced pressure. The final distillate was collected, b.p. 75-80^{o}/$\leq$ 5 mm. Gas chromatography indicated that this contained benzyl acrylate (ca. 85%), and one other component. Infrared analysis of the mixture suggested that the unknown substance was a carboxylic acid. The distillate was therefore shaken up with 2.5% NaOH, and the aqueous layer and the organic layer were allowed to separate. The benzyl acrylate was run off as the organic layer. The benzyl acrylate was washed with distilled water, dried with anhydrous $MgSO_4$, and stored in a refrigerator. Gas chromatography of the purified liquid showed only one component. (Found C, 73.9; H, 6.2; O, 19.9. Calc. for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2; O, 19.7%). Nuclear magnetic resonance spectrum gave proton ratios 3.2:2.0:4.7:, for $CH_2{:}CH.CO_2CH_2C_6H_5$.

Contact between benzyl acrylate and the skin brought about the development of a nettle-like rash. Strict care was therefore necessary when handling benzyl acrylate.

1.1.3. Benzene

"Analar" benzene was used throughout these investigations without further purification.

1.1.4. Methyl acetate

Laboratory grade methyl acetate was dried overnight over anhydrous $MgSO_4$. This $MgSO_4$ was filtered off and the filtrate distilled. The fraction boiling between 52-53° was retained. (Lit.,[53] b.p. 57.5°C). Gas chromatography indicated only one component.

1.1.5. Ethyl benzene.

Laboratory grade ethyl benzene (B.D.H.) was refluxed over sodium for two hours and the fraction boiling between 132-134° was collected. (Lit.,[53] b.p. 135.5°C).

1.1.6. Benzoyl peroxide.

Benzoyl peroxide (B.D.H.), the sole initiator, was recrystallised from chloroform before use.

1.2. POLYMERISATIONS

Polymers of methyl acrylate and benzyl acrylate were prepared in solution under vacuum conditions. Polymerisations were carried out in dilatometers at accurately regulated temperatures (± 0.2°).

1.2.1. Filling of dilatometers and polymerisations

The dilatometer (usually ca. 40 ml volume), was checked for leaks, cleaned and a constriction made in the stem. A weighed amount of benzoyl peroxide was added to the dilatometer followed by a measured volume of monomer from a burette. The dilatometer was attached by cone and socket to the vacuum line, and the monomer degassed by alternately freezing, pumping, and melting. This process was repeated four times. The diluent, in a graduated vessel connected to the same vacuum line, was subjected to the same thorough degassing, and the required volume of diluent then distilled under vacuum to the dilatometer. The dilatometer was sealed off under vacuum and stored in a refrigerator until introduction to the polymerisation bath.

The course of polymerisation was followed by observing the position of the meniscus with a cathetometer at regular time intervals. Monomer and polymer density data,[55] enabled the polymerisation to be stopped at the required conversion (generally $\leqslant$ 20%). Polymerisation was invariably over within 24 hours.

1.2.2. Separation and purification of the polymer

After cooling, the dilatometer was opened and the contents were dissolved in approximately 100 ml. of acetone. The polymer was precipitated by pouring this solution into a large volume of methanol with constant stirring. On removal, the polymer was roughly dried and the precipitation process repeated twice more. Filtrations were carried out if necessary, with the polymer dissolved in acetone. After the third precipitation, the polymer was roughly dried by allowing it to stand in air, was separated into small pieces, and was finally dried either in a vacuum-desiccator, or in a vacuum oven (40-60°), for not less than 48 hours. The polymer was cut into small pieces (ca. 5 mg.), as neither PMA or PBA could be reduced to powder form. Section 5 of this chapter gives full details of polymer preparations.

2. DEGRADATION OF POLYMERS

2.1. APPARATUS

2.1.1. Glassware

Degradations were carried out in the apparatus shown in Figure 1. The molecular still consisted of a cylindrical glass vessel A, approximately 18 cm. deep and 10 cm. in diameter, with four B24 Quickfit sockets sealed on symmetrically. Access to the heating block and tray B within was via a desiccator-type lid C, which fitted to a ground glass flange to give a vacuum tight seal. A glass manifold D, carrying thermocouple and heating leads, was fitted into one of the Quickfit sockets, the wires being sealed to the glass with picein wax. A second Quickfit socket was connected to a cold-trap E, which was linked, (beyond tap T1), through tap T2 to the pumps, through tap T3 to the moveable receiver F, and through tap T4 to the constant volume manometer (Figure 5). The third and fourth B 24 sockets were sealed with stoppers.

The whole apparatus could be pumped down to a vacuum of better than 10^{-4} cm. Hg, by means of a rotary oil pump coupled with a mercury vapour diffusion pump.

2.1.2. Degradation tray

The degradation tray G (Figure 2) was made from a copper tablet 40 mm. square and 9 mm. deep. The central recess 33 mm. in diameter and 7 mm. deep was lined with platinum, (Messers Johnson and Matthey Ltd.), giving a smooth, level, finish. The polymer sample was in contact only with this platinum surface H. The temperature of the

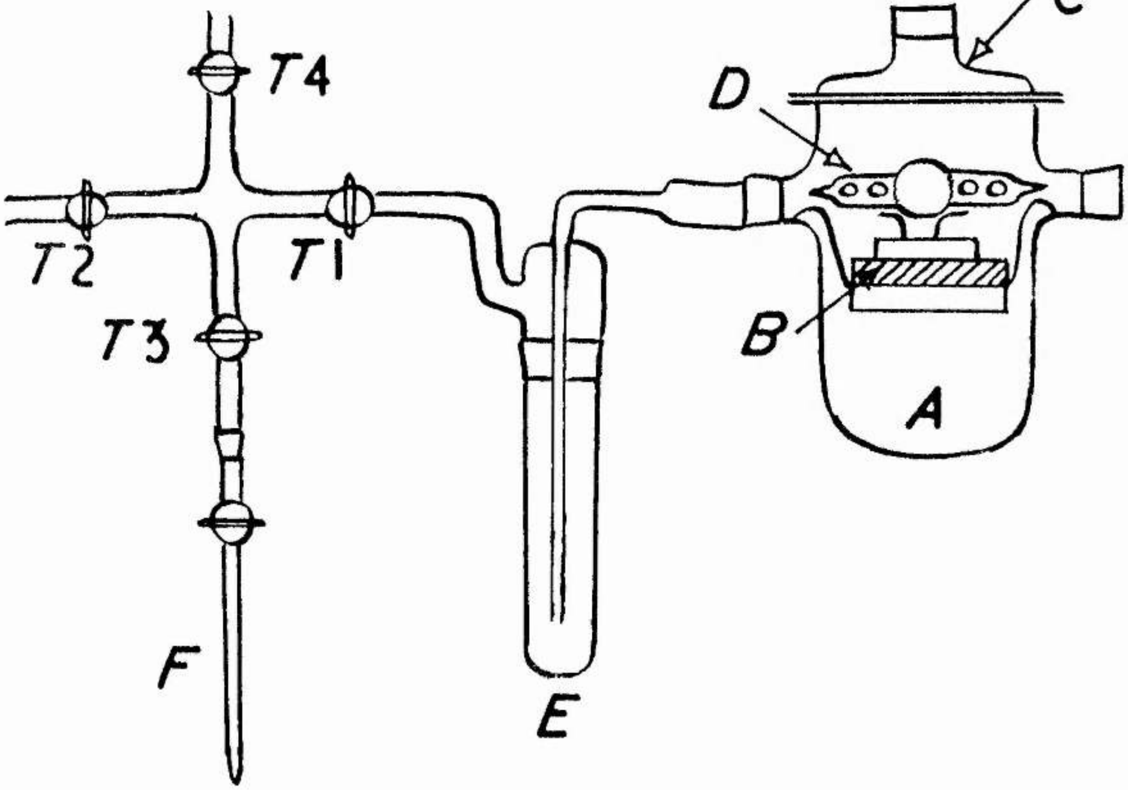


Figure 1 Glasswork of degradation apparatus; molecular still

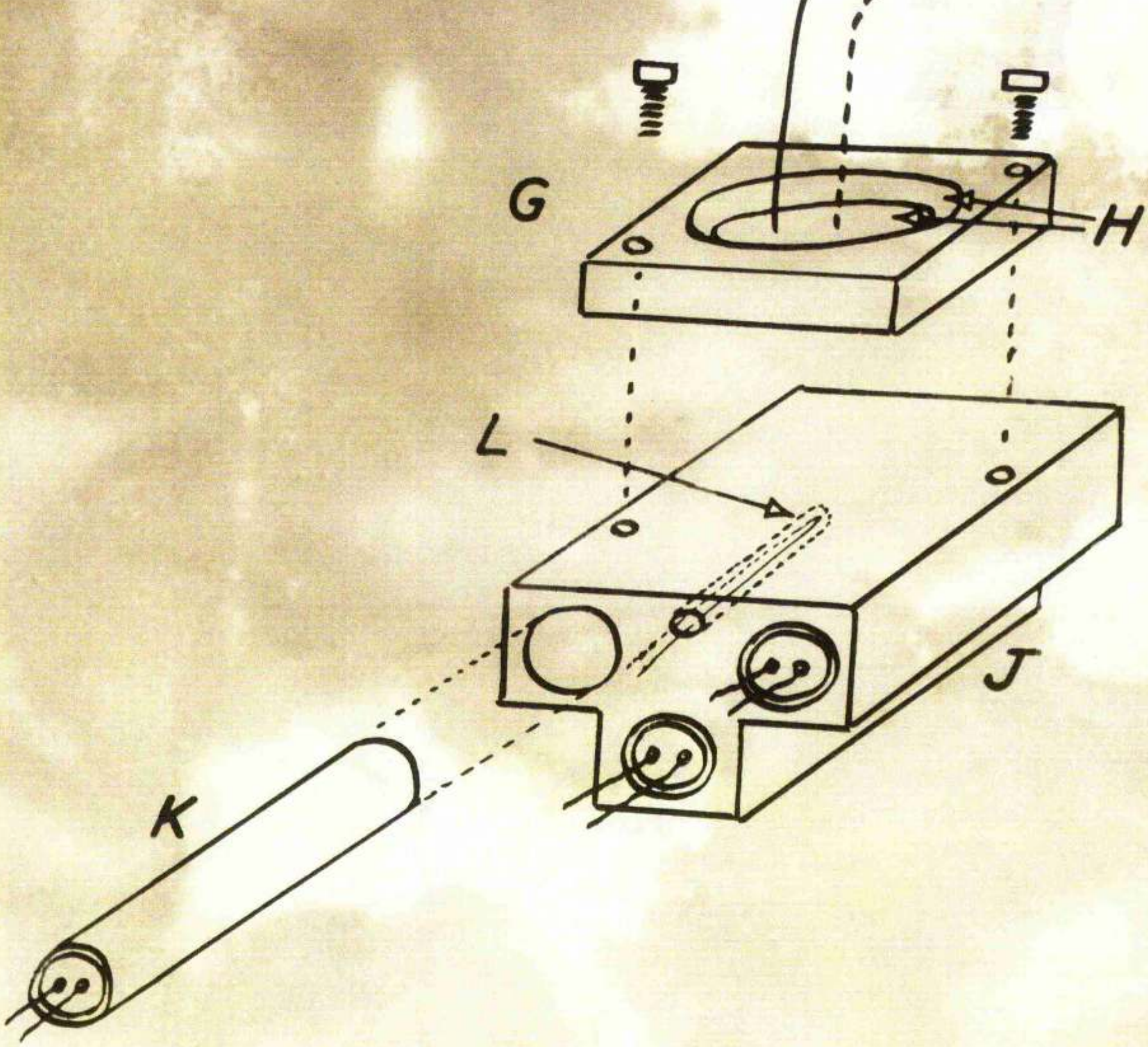


Figure 2 Degradation tray and heating block; "exploded" diagram

tray surface was recorded using a copper/constantan thermocouple lightly soldered to the platinum surface. The output of this thermocouple was measured using an ice/water reference cold junction, and a Pye portable potentiometer. Two holes were drilled at opposite corners of the tray, and good thermal contact between the tray and heating block was obtained by bolting them tightly together. If necessary, the surfaces could be ground to improve contact.

2.1.3. Heating block

The copper heating block J, (ca. 300 g.) is illustrated in Figure 2. The block, which occupied a central position in the molecular still, was supported on a rigid brass cradle. Three cartridge type heaters K, (50 watts/24 volts, Hedin Ltd.), were fitted into holes drilled through the block, as shown in Figure 2. During degradations the two upper heaters were continuously supplied with predetermined voltages, while the lower intermittent heater was switched on and off by the "Ether Transitrol" temperature controller. The "Ether Transitrol" was activated by a chromel/alumel thermocouple, the hot junction L, of which was situated just under the surface of the block, and therefore directly below the centre of the tray. The heat output of the on-off heater was just sufficient to maintain the tray at the required degradation temperature. It is estimated that the tray temperature was controlled to $\pm$ 2^{o}C.

To begin a degradation run the temperature of the tray was raised as rapidly as possible to 25° below the required temperature. Then, by adjusting heater voltages to known settings the tray reached the degradation temperature (in 10-15 min.), with the minimum of over- or under-shoot. Timing of the degradation and collection of volatiles was begun when the tray temperature reached 270°C. Errors introduced by degradation occurring below 270°, and by arbitrary selection of 270° as the starting point, were considered to be insignificant.

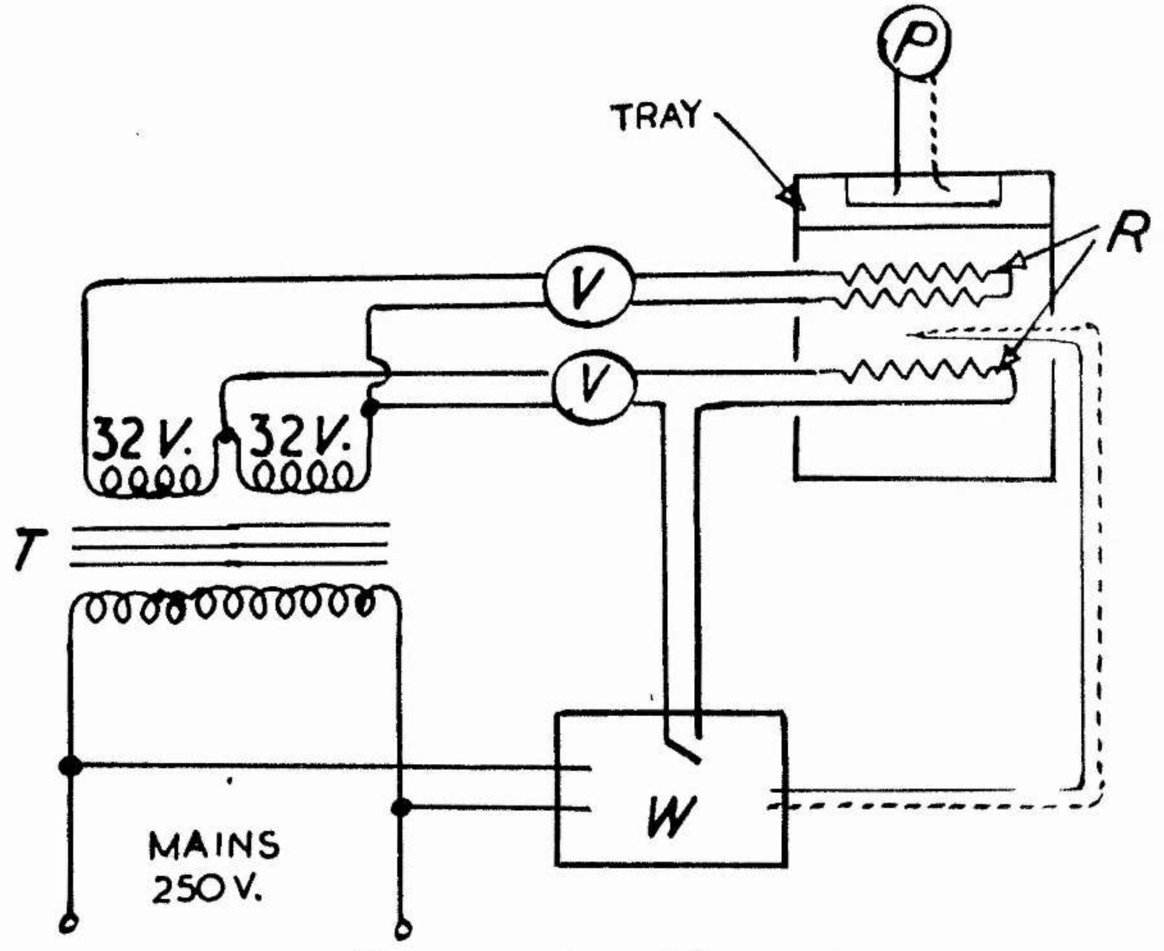
2.1.4. Heating and temperature control circuits

The circuits used are shown in Figure 3. Voltage for the heaters R, was stepped down through a 64/32 volt transformer T, before passing through two variable transformers V, of the heavy current, low voltage type. The "Ether Transitrol" controller W, was modified to operate with a reduced voltage instead of the normal mains supply.

2.2. PROCEDURE.

2.2.1. Sample preparation

Polymer samples (generally 100 mg.) were cast as films on the degradation tray by adding benzene to the weighed sample. These films were sufficiently thin (ca. 0.1 mm.) to virtually eliminate diffusion effects.[56] When the benzene had evaporated in air the tray was bolted to the heating block and the still-lid put in place. The apparatus



P, potentiometer.

Figure 3 Heating and temperature control circuits was then evacuated, the tray temperature raised to 100°C and held there for two hours. This pre-heating removed the last traces of benzene and other solvents, but otherwise had no detectable effect on the polymer. In certain of the earlier experiments, the polymer films were cast on all-copper trays and covered by a layer of copper powder to reduce the possibility of temperature gradients being set up within the sample, and to eliminate sputtering. It was found, however, that the copper layer reduced evolution of volatiles and decomposed[57,58] much of the methanol in the degradation products. For this reason the platinum lining was introduced, and the layer of copper powder omitted.

2.2.2. Pyrolysis

Following the preheating, the tray temperature was raised to the desired degradation temperature, as described previously (Section 2.1.3.). After the required time of pyrolysis, power to the heaters was cut off. Degradation occurring after switching off the heaters was also considered to be negligible as the tray temperature fell within 15 min. to below 255°C. The tray was allowed to cool to room temperature before letting in air to the still. The tray was then removed and weighed to find the amount of polymer volatilized. This quantity was corrected for the small amount of volatiles (ca. 1%) in the original polymer.

3. EXAMINATION OF PRODUCTS OF DEGRADATION

3.1. MOLECULAR-WEIGHT MEASUREMENTS

3.1.1. Pyrolysed Residues

Molecular weights of pyrolysed residues were measured viscometrically.

The limiting viscosity number $[\bar{\eta}]$ of a polymer solution is related to the molecular weight of the polymer by the equation,[59]

$$[\bar{\eta}] = KM_v^{\alpha}$$

K and α are constants dependent on the nature of the polymer and solvent. M_v is the viscosity average molecular weight. The limiting viscosity number is given by,

$$[\bar{\eta}] = \lim_{c \to o} \left[\frac{(t_c - t_o)/t_o}{c} \right]$$

in which t_c and t_o are the times taken for solution of concentration c, in g. per 100 ml. of solution, and of pure solvent respectively, to flow through the viscometer timing marks.

All viscometric measurements were taken with a suspended level instrument at 30° (± 0.05°), using benzene as solvent. The values of K and α for PMA in benzene at 30° are reported[60] as 1.282×10^{-4} and 0.7143 respectively. No values of K and α have been determined for PBA, but limiting viscosity numbers alone were enough to follow the change in molecular size with extent of volatilization.

3.1.2. Fraction II

Molecular weights of short chain fragments (M_n $< 20,000$) were measured using a Mechrolab Vapour Pressure

Osmometer, model 301A, thermostatted at 37°C. This instrument measures (as a temperature difference), the vapour pressure differential set up between comparable solvent and solution systems. An absolute molecular weight M_n was found from the relation,

$$M_n = \frac{K \times c}{\Delta T_{t=o}}$$

in which K is a constant of calibration for the instrument, c is concentration in g. per 100 g. solvent, and $\Delta T_{t=o}$ is the temperature difference between the solution and pure solvent systems at zero time. Benzene was used as solvent, and the constant, K was evaluated using a series of solutions of known concentration of naphthalene in benzene.

The short chain fragments were collected by allowing them to condense on a glass dish, constructed from a cut-down beaker. This dish fitted neatly over the heating block and tray. The still-lid then fitted on as usual. After degradation the dish was removed from the still and the waxy polymer fragments dissolved in benzene and made up to 5 ml. Evaporation of a known volume of this solution gave its concentration. The tray thermocouple could not be used when short chain fragments were being collected but by adjustments of heater voltages to predetermined settings the temperature could be estimated to within 5°C.

3.2. ESTIMATION OF GEL CONTENT IN PYROLYSED RESIDUES

In a large number of degradations the pyrolysed residue was not completely soluble in benzene. After degradation, the tray plus contents were allowed to stand in benzene for two days. The solution was then filtered and made up to a known volume. Soluble polymer was estimated by evaporation of 10 ml. of this solution to constant weight at 100°C. Viscometric measurements were made using a known volume of this solution. This method of gel estimation did not preclude the possibility of microgel fragments passing through the filter, but was sufficiently accurate and reproducible to give good qualitative comparison of results.

3.3. SPECTROSCOPIC EXAMINATION.

3.3.1. Measurements of infrared, ultra-violet and visible spectra.

Extensive use was made of infrared spectroscopy (I.R.). All polymeric samples were measured as films on NaCl plates. Films of polymers from PMA degradations were produced by allowing the benzene of the polymer solution to evaporate at room temperature from the reservoir compartment D of a plate holder, drawn almost to scale in Figure 4. The NaCl plate P, was held between the bottom inward-projecting flange of the base part B, (which has an inner thread), and the reservoir tube C. Parts B and C, which were made of brass , screwed together, and cork washers at plate/brass interfaces

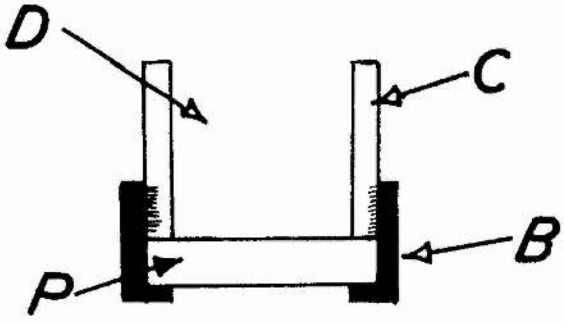


Figure 4 Plate holder for production of PMA films from benzene; sectional diagram

ensured an effective solvent-tight reservoir D, (volume ca. 6 ml.). Approximately 5 ml. of 1% polymer solution gave a film of suitable thickness on evaporation of benzene. The last traces of benzene were removed by oven-drying (ca. 50°). Then the plate and holder together were placed directly in the sample beam of the spectrophotometer. Spectra were measured on a Grubb Parsons G.S.2A spectrophotometer. Certain PMA spectra were repeated on a Perkin Elmer 621 grating spectrophotometer and this machine recorded all spectra of degraded PBA samples. Films of degraded PBA were prepared by smearing polymer over the plate with chloroform, and allowing a few minutes for chloroform to evaporate off. Final traces of chloroform were removed when necessary, in a vacuum-oven at 100°C.

Ultra-violet spectra of PMA films were measured with a Unicam U.P. 700 recording spectrophotometer. Films were prepared again by evaporation of benzene from polymer solutions in a plate holder. A quartz plate was used.

Visible spectra of polymer residues were measured in benzene solution (conc. ca. 0.1 g/dl.) with a Unicam S.P. 600 manually operated spectrophotometer.

3.3.2. Nuclear magnetic resonance measurements

Nuclear magnetic resonance (N.M.R.) spectra were measured at 33.5°C in deuterochloroform (ca. 5% solution) with a Perkin Elmer R 10 60 Mc/s. spectrometer. Tetramethyl silane was used in every case as the internal reference standard.

3.3.3. Mass spectrometric measurements

Mass spectrometric data of products volatile below -76°C were obtained on a 60° Nier (single focussing) type instrument, which had been built within the department.

3.4. GAS CHROMATOGRAPHIC ANALYSIS OF PRODUCTS.

A Griffin D 6 chromatograph was used to investigate degradation products which were liquid at room temperature. Columns and operating conditions employed will be mentioned in the relevant chapters.

3.4.1. Qualitative Analysis

Products were identified by comparison of retention times with those of known compounds. Identification was verified, if necessary, by running samples of product plus the suspected compound. Comparison of traces then provided conclusive evidence.

3.4.2. Quantitative Analysis

In quantitative work, a precise weight of a marker compound was added to the mixture to be analysed. Relevant mixtures of known composition were frequently run between loadings of the required sample, to check reproducibility and operating accuracy of the instrument. Weighing of cut-out peaks gave relative amounts of components.

3.5. PRESSURE MEASUREMENTS FOR CARBON DIOXIDE AND METHANOL ESTIMATIONS.

Pressures of carbon dioxide and methanol were measured at 18°C using a constant volume mercury manometer, (Figure 5).

With tap T5 closed and the mercury level in the barrel N adjusted to Q (constant volume conditions), the gas pressure was given by the height QQ' of the mercury column in limb Y. Readings (cm. Hg) were taken directly from graduated scale X. The flow of mercury to and from the manometer was determined by the pressure on the mercury in reservoir W, and controlled simply by tap T6. The limbs N and Y were wide enough (ca. 20 mm.) to make capillary effects negligible.

3.5.1. Measurement procedure

Before making any pressure measurements the manometer system was pumped out to sticking vacuum and the mercury level brought up to Q. The condensable products in the cold trap E (Figure 1) were distilled under vacuum to stem Z by cooling Z to liquid air temperatures and allowing E to warm to room temperature. During this operation for which 35 min. was allowed the taps T1, T4 (Figure 1), and T5 (Figure 5) were kept open, and taps T2 and T3 (Figure 1) kept closed. The total pressure of carbon dioxide and of methanol at 18°C was measured by closing tap T5 and allowing the stem Z to

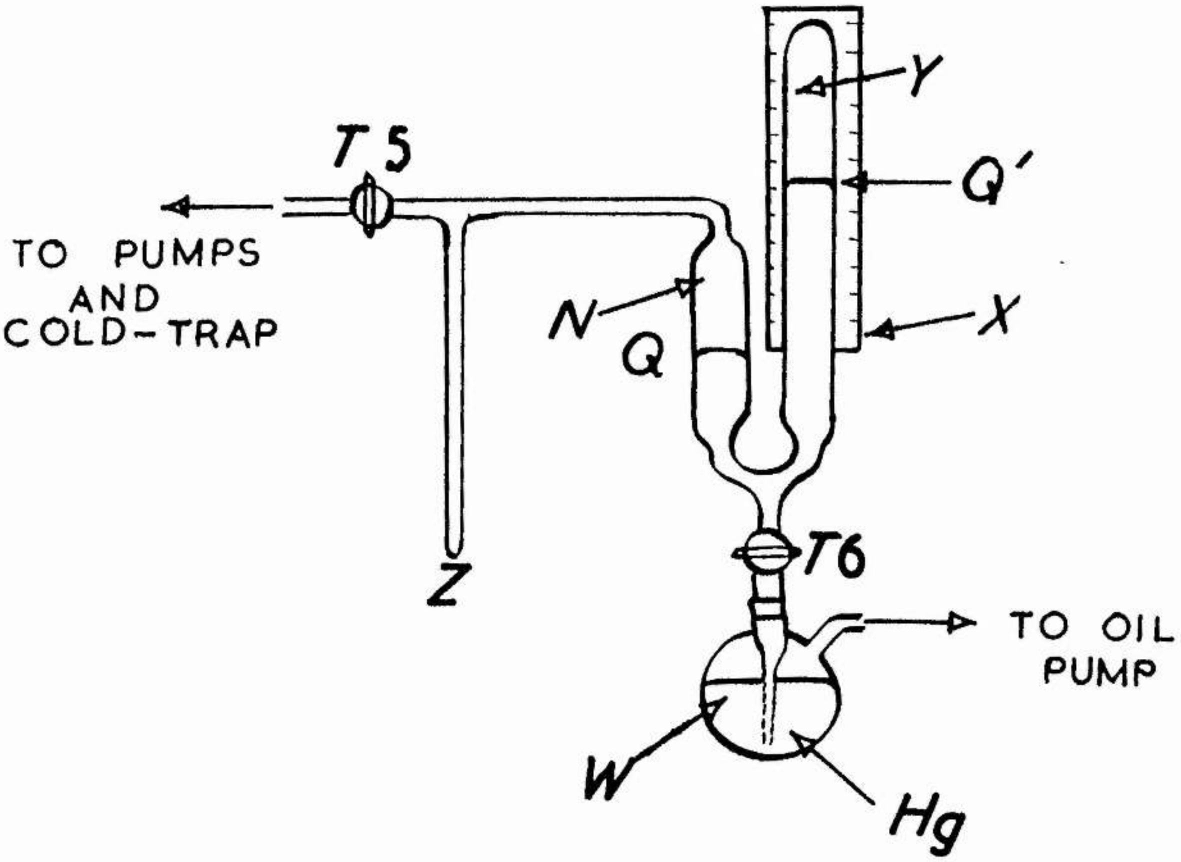


Figure 5 Constant volume manometer

come to room temperature. The mercury level in the left hand limb was then raised to Q and the mercury level Q' in the right hand limb noted. The gas pressure was given by Q' minus Q. In all runs care was taken to see that the methanol pressure was less than the saturated vapour pressure of methanol, (8.6 cm Hg. at 18°C[61]). The pressure of carbon dioxide alone was measured in the same way, but with stem Z cooled to -76°C by a cardice/methanol bath.

Preliminary tests with known mixtures of methanol and carbon dioxide established that this technique gave accurate and reproducible separation of the two substances. Experiments conducted with another cold trap between trap E and tap T1 (Figure 1), showed that condensable volatiles were completely trapped by E.

The pressure measurements from each degradation experiment were corrected for a small blank attributed to physical adsorption of condensable gases, such as water, inside the system. These blank readings were consistent and independent both of time and extent of degradation.

To permit determination of absolute quantities of methanol and carbon dioxide the constant volume V_o, of the constant volume manometer was measured as follows. The manometer system was evacuated to sticking vacuum and the mercury in both limbs brought up to Q. Tap T5 was opened and a small amount of air allowed to enter the manometer before T5 was closed again. A series of pressure/volume readings (Table 2) was taken at $18^{\circ}C$ on the sample of air. It was ensured that the mercury meniscus remained on the undistorted section of the barrel N for each reading. The barrel section N was then removed and the internal radius r, of the undistorted section was found by adding weighed portions of clean mercury and measuring the changes in level of the mercury meniscus with a cathetometer. The internal radius was found to be 0.884 ± 0.015 cm.

The volume V occupied by the sample of air in N is given by the relation,

$$V = V_o + V_A$$

where V_A is any volume additional to the constant volume and is expressed initially (Table 2) in terms of the distance (h cm.) of the meniscus below the constant volume mark Q, i.e. $V_A = \pi r^2 h$.

The pressure p (cm. Hg) of the air sample was given by the difference between the heights of the mercury levels in N and Y.

Boyle's Law holds under the conditions used and hence,

$$pV = \text{const.}$$

$$\therefore \; V_A = \frac{\text{const.}}{p} - V_o$$

This is an equation of the form $y = mx + c$. In Figure 6 V_A is plotted against $^1/_p$. From the plot V_o can be found using the relation,

$$V_o = \frac{\text{gradient}}{p_{V_A} = 0}$$

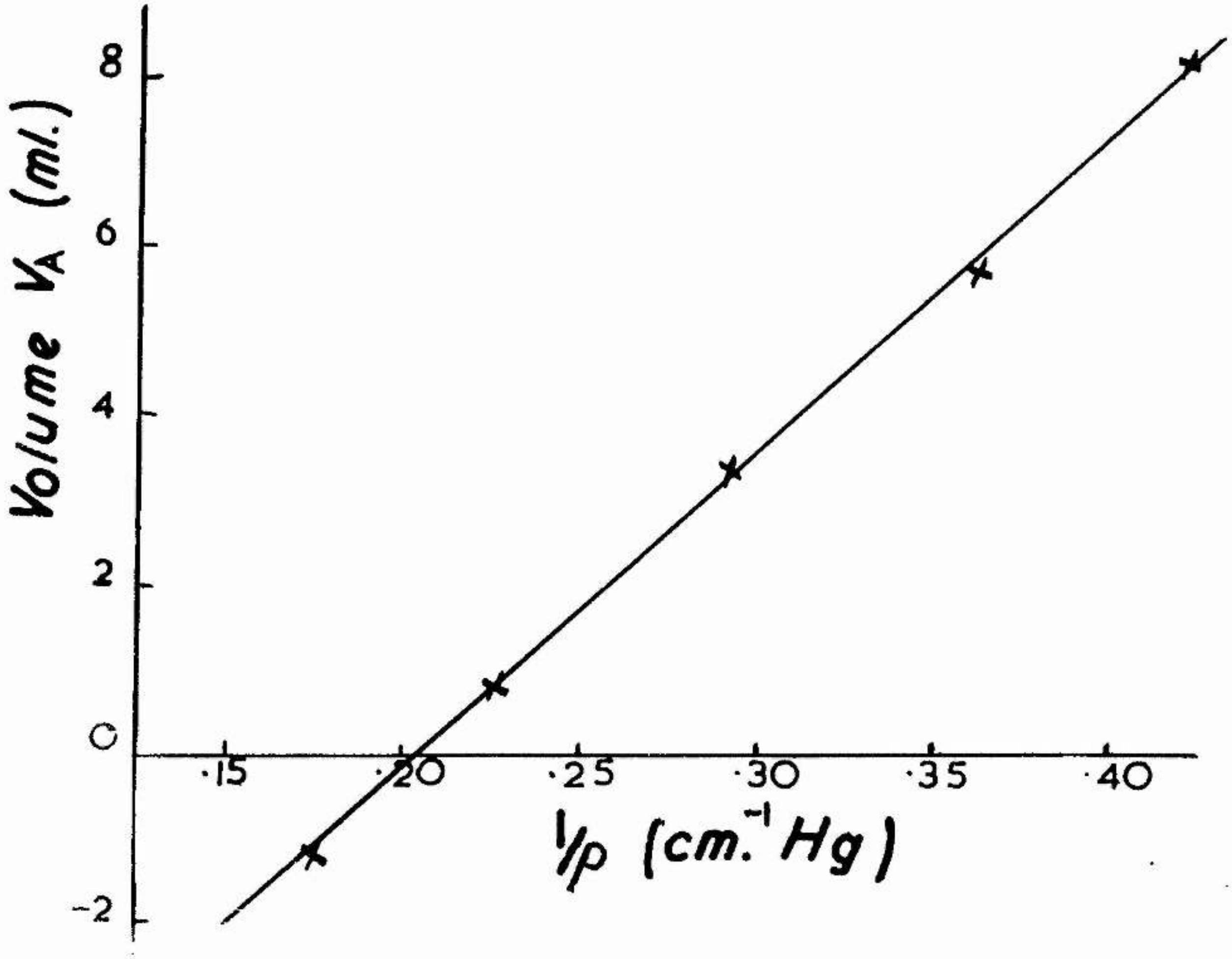


Figure 6 Plot of V_A against $1/p$ for evaluation of manometer constant volume V_0

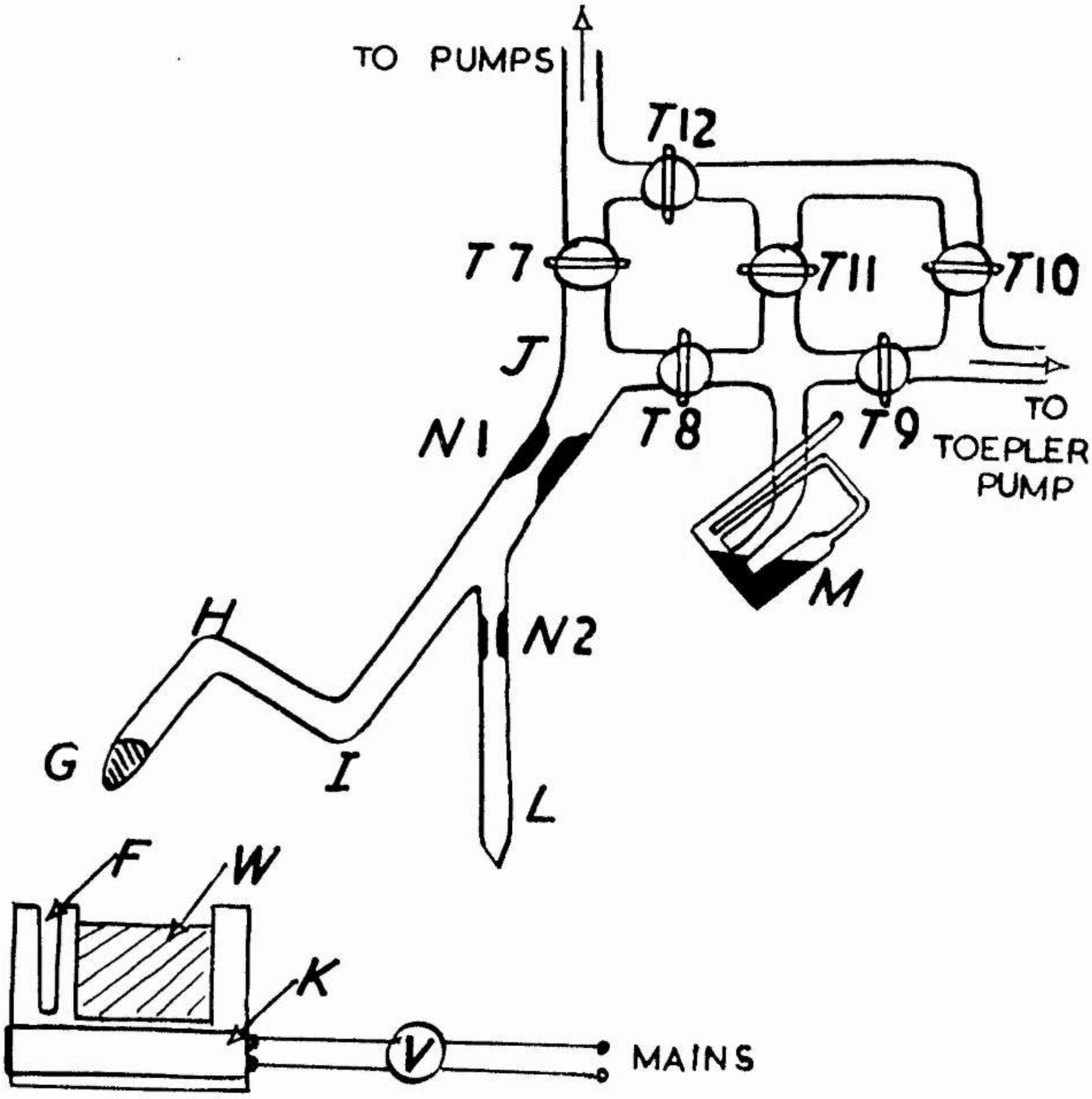


Figure 7 An alternative degradatio apparatus

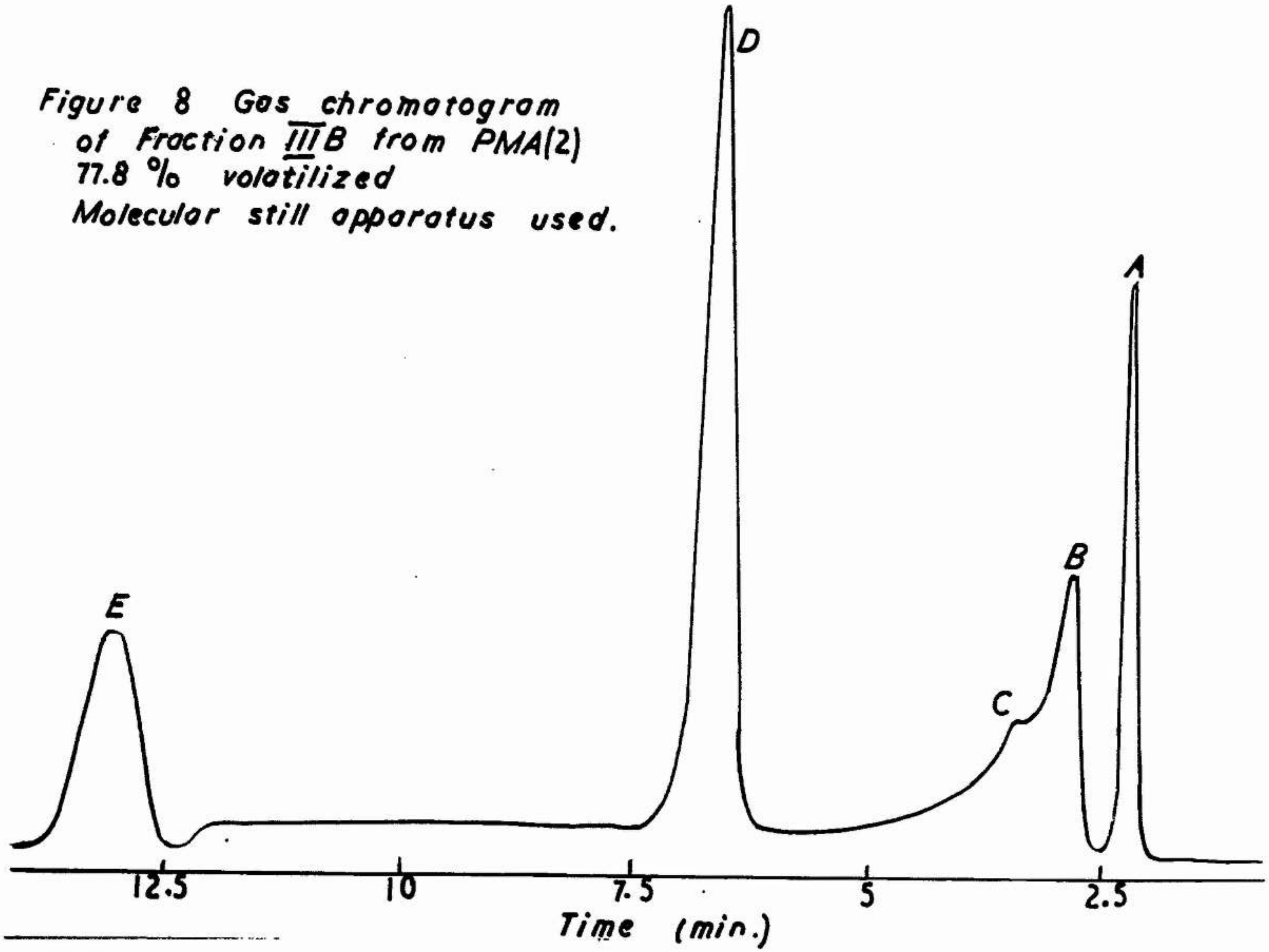


Figure 8 Gas chromatogram of Fraction IIIB from PMA(2)
77.8 % volatilized
Molecular still apparatus used.

Table 2

Pressure/volume readings for air sample in constant volume manometer at $18^{o}C$

Reading	Pressure cm. Hg	Volume Vml., Vo + VA ml.	$1/p$ (cm. Hg)$^{-1}$
1	2.3	Vo + 8.10	0.435
2	2.75	Vo + 5.65	0.364
3	3.4	Vo + 3.30	0.295
4	4.5	Vo + 0.75	0.227
5	5.7	Vo − 1.25	0.175

From Figure 6, V_o has a value of 7.6 ml. The possible error is estimated as ± 0.2 ml.

In the experiments on PBA a second manometer of constant volume 8.15 ± 0.2 ml. was used.

4. AN ALTERNATIVE DEGRADATION APPARATUS

4.1. PURPOSE

For certain purposes the molecular still apparatus was not suitable. Quantitative estimation of non-condensable gases was impossible and very involatile products from the PBA degradation could not be collected efficiently. In those cases, the apparatus shown in Figure 7 was used.

4.2. DESCRIPTION.

For each run new glass tubing (ca. 10-12 mm. in diameter) was fashioned into shape GHIJ. An elementary cold-trap L was attached near junction J and constrictions

N1 and N2 made in the tubing. The apparatus was linked at J to the main vacuum line and pumps, and to a calibrated vacustat pressure gauge M through tap T8. Tap T9 then gave access to a Toepler pump. The whole apparatus could be pumped down to a vacuum better than 10^{-4} cm. Hg. The arrangement of taps T7, T10, T11, and T12, made it possible for each section to be kept under high vacuum if necessary, even when the adjacent section was not.

The polymer sample was placed at the foot of stem G (ca. 5-7 cm.) which could then be immersed almost to the bend H in a Woods metal bath W. The bend H prevented (as far as possible) involatile liquids from returning to the heating zone, while bend I provided a convenient preliminary collecting point for involatile liquids.

A band heater K was bolted round the base of the Woods metal bath. By altering the voltage to K with a variable transformer V, the bath temperature was regulated within ± 5°C and read with an ordinary mercury thermometer inserted in pocket F.

4.3. PROCEDURE

The apparatus was evacuated and the sample preheated for two hours at 130°C. During this time any volatile materials adsorbed on the tubing walls were driven off by flaming. The bath temperature took about 20 min. to raise to the degradation temperature ($\geqslant 270^{\circ}$). The sample was isolated by sealing off (at N1) under vacuum as the temperature passed 250°C. In a few experiments in which the pressure of non-condensable gases was to be measured taps T7 and T8 were kept closed from the start of the degradation until pyrolysis was over. The manometer system meanwhile was pumped to sticking vacuum until just before the volatiles were let in for pressure measurements.

4.4. COLLECTION OF PRODUCTS

Condensable volatile products were trapped in stem L and held there at liquid air temperature. Distillation of products to L was assisted, and complete collection for analysis ensured by flaming the tubing thoroughly before sealing off (at N2) under vacuum.

The pressure of non-condensable volatiles was measured by the manometer M, by closing taps T9 and T11, and opening tap T8 after pyrolysis. The volume then available to the non-condensable volatiles was 250 ± 25 ml. The non-condensable volatiles could then be collected for analysis by pumping them into an evacuated vessel by means of a Toepler pump.

5. EXPERIMENTAL DETAILS OF POLYMERISATIONS; MOLECULAR WEIGHTS OF POLYMER SAMPLES

The experimental details of polymerisations and molecular weights of polymer samples are listed in Table 3. The number average molecular weights (M_n) quoted were measured at 37°C in benzene, using a Mechrolab Membrane Osmometer, model 501, with an Allerfeinst membrane. These six were the only molecular weights obtained in this way. The monomer/diluent ratio M/D, is a volume to volume ratio at 20°C. Initiator concentration $[I]$, is given in g. mole./1.

Polymer density data were not available for PBA. The percentage molar volume contraction data for n- butyl acrylate polymerisation were used to estimate the extents of conversion in the polymerisation of benzyl acrylate.

Table 3

Details of polymer sample preparations

Sample	Diluent	Polym. Temp. °C	M/D	$10^4\ [I]$	Conversion %	$10^{-5}M$
PMA						M_v
2	MeAc	55	0.6	2.2	23	31.0
3	Benzene	60	1.0	2.8	22	28.0
7	PhEt	45	1.5	3.0	12	3.24
						M_n
11	MeAc	40	1.0	3.3	20	22.0
12	"	55	1.0	3.3	20	15.5
13	"	70	1.0	3.3	20	4.6
17	PhEt	40	1.0	3.3	20	1.56
18	"	55	1.0	3.3	20	1.37
19	"	70	1.0	3.3	20	1.20
						M_v
21	MeAc	40	1.0	6.5	10	19.5
22	"	50	1.0	6.5	10	19.5
23	"	70	1.0	6.5	10	11.1
24	"	40	1.0	6.5	70	43.0
25	"	50	1.0	6.5	70	30.2
26	"	70	1.0	6.5	70	7.5
PBA						$[\eta]$
1	MeAc	60	0.5	5.6	~25	1.12
2	PhEt	60	0.5	4.8	~25	–

CHAPTER III

THERMAL DEGRADATION OF PMA. PART I.

NATURE OF PRODUCTS, RATES OF OVERALL VOLATILIZATION, AND MOLECULAR WEIGHT CHANGES

1. INTRODUCTION

Poly (methyl acrylate) is the simplest member of the acrylate polymer series, and has a chain built up of $(\text{-}CH_2.CHCO_2Me)\text{-}$ units.

There has been a wide range of studies on the degradation of PMA, including investigation of the effects of ultrasonic waves,[63] of high energy irradiation,[27,64] of chemical attack,[65] and of ultra-violet light.[26] The vacuum bulk pyrolysis of the polymer, however, has received relatively little attention, and no exhaustive studies with a view to clarifying the mode of degradation have been reported. Two investigations[50,66] to date have been concerned with the nature of the volatile products of pyrolysis, the evolution of which distinguishes thermal from the other types of degradation mentioned above. Most of the latter take place with negligible weight loss, and are often studied in solution.

Madorsky has published[50] a detailed analysis, both qualitative and quantitative, of the products of pyrolysis of PMA, and he has also studied[22] the rates and activation energy of the process. Other investigators[66] have made a more cursory examination of the gaseous products of reaction.

This aspect of the degradation has been fairly well established, and the emphasis of the present work is on other more general features, rather than on a minute re-examination of these pyrolysis products. Nevertheless, some qualitative and quantitative data on the degradation products were accumulated, and this chapter begins with a brief comparison of the present and previous results.

In the experiments described in this chapter, a covering of copper powder was used in runs in which molecular weights of residues and percentage volatilizations were being measured, since it was found to have practically no effect on the former, and only a slight retarding effect on the latter. However, for experiments in which Fraction III volatiles were measured quantitatively, the platinum-lined tray was used without the covering of copper, since it was found that the proportions of these volatile products, particularly methanol, were considerably reduced when copper powder was present. Unfortunately, the omission of copper powder increased the scatter of experimental results, probably due to less uniform heating of the polymer melt. This is well illustrated in Figure 9.

2. PRODUCTS OF DEGRADATION

The products of bulk pyrolysis of PMA were fractionated neatly into four types according to volatility, if the reaction was carried out in a molecular still. These fractions and their loci of collection are listed in Table 4.

Table 4

Products of degradation of PMA between 250-400°C

Fraction	Nature	Location	% Wt. loss[+]
I	long chain PMA	tray	residue
II	fragments PMA. MW 633	surface above tray	~ 73
III	condensable volatiles	cold trap	26.7 ± 3.2
IV	non-condensable gases	beyond cold trap	< 0.1

Madorsky's method[50] of numbering the fractions is employed throughout the present work.

2.1. PREVIOUS WORK

The proportions of the various fractions according to Madorsky[50] are shown in Table 4, and results of mass spectrometric analyses of gaseous volatiles are given in Table 5.

2.2. PRESENT WORK

2.2.1. Fraction I

It was quickly established by molecular weight and infrared measurements, (Chapters III and IV), that Fraction I is long chain PMA. It was also noted that a yellow colouration developed in this fraction, (deepening as percentage volatilization increased), and that the fraction was not always completely soluble in benzene. The colouration and gel formation will be discussed in Chapter V.

[+] Weight percentages are quoted throughout unless otherwise stated.

Table 5.

Analysis of gaseous volatiles from PMA. Pyrolyses below 400°

Ref.	Main components	% of total wt. loss	Trace components
50	MeOH	14.6	CH_2:$CMeCO_2Me$,
	CO_2	7.4	C_2H_4,
	Oxygenated cpds. C_4-C_6	3.9	C_2H_6,
	CH_2:$CHCO_2Me$	0.7	CO, CH_4.
66	MeOH	16.2	–
	CH_2:$CHCO_2Me$	6.7	
	CO_2	4.5	

2.2.2. Fraction II

Molecular weight measurements (Table 6), and infrared measurements, (see Chapter IV), confirmed that Fraction II is short chain PMA. A number average molecular weight of 704 was found for these fragments. Quantitative collection of this fraction was impossible, and by difference Fraction II was found to comprise ca. 90% of the weight loss in the degradation. The results of M_n are scattered. Either or both of two factors could be responsible. The size of the fragments evaporating from the polymer melt may increase with percentage volatilization.[67] A more likely explanation is that there is a concentration dependent association between the Fraction II molecules in benzene solution. The vapour pressure osmometer

Table 6

Molecular weight of Fraction II

Run	Temp ^{o}C	% volat.	M_n
222	305	43.1	670
224	320	58.9	585
226	320	78.7	805
228	320	63.5	754
Mean			704

is very sensitive to such association, and experimental readings for the polymer solutions indicated that some association could be present. Nevertheless, the present value of 704 is in reasonable agreement with Madorsky's value of 633.

2.3.3. Fraction III

Fraction III was further divided when necessary into Fraction IIIA, volatile above $-76^{o}C$, and IIIB involatile at $-76^{o}C$, as described in Chapter II.

(a). Qualitative and semi-quantitative analysis

Fraction IIIA was collected from the degradation of PMA(26) at $300^{o}C$ and analysed by mass spectrometry. The cracking pattern, (obtained with an electron accelerating potential of 60 eV.), was corrected for background and compared, (Table 7), with the cracking pattern for pure

Table 7

Comparison of mass spectrometer cracking patterns of Fraction IIIA and carbon dioxide

Mass/Charge ratio, m/e	Fraction IIIA	CO_2
12	-	6.7
13	-	0.9
16	6.7	9.4
22	1.2	-
28	6.7	8.2
29	.0	.1
44	100	100

carbon dioxide[68] at 70 eV. The comparison shows clearly that Fraction IIIA consists entirely of carbon dioxide.

Samples of Fraction IIIB from degradations of PMA(2) and PMA(3) were analysed by gas chromatography. A column of 10% di-nonyl phthalate on silocel was employed with nitrogen as carrier gas at 60°C. Ether was invariably added to the fraction to allow more loadings from the one sample. Figure 8 shows a typical chromatogram of Fraction IIIB from PMA(2). Peaks were identified as follows: peak A, ether which was added; B, methanol; C, methyl acetate; D, methyl acrylate (MA); and E, methyl methacrylate (MMA). Only methanol, methyl acrylate, and methyl methacrylate are produced by the degradation process. PMA(2) was prepared in methyl acetate, and shoulder C was attributed to solvent remaining in the polymer, as no counterpart could be found in the chromatogram of Fraction IIIB from PMA(3), which showed only peaks for methanol, methyl acrylate, and methyl methacrylate.

Results of chromatographic analyses on three, IIIB samples are shown below (Table 8). These analyses were not done under strictly quantitative conditions, but the intention was only to identify the main components and obtain an idea of their relative proportions. Allowance was made for the methyl acetate shoulder when calculating weight percentages of components in Fraction IIIB.

Table 8

Percentage composition of Fraction IIIB

PMA sample	Run	% volat.	Loading no.	% MeOH	%MA	% MMA	Molar ratio MA/MMA
2	75	38.8	89	87.0	9.6	3.5	3.2
			90	-	-	-	3.0
			91	-	-	-	3.0
2	76	77.8	102	73.2	19.8	7.1	3.3
			103	70.7	21.5	7.9	3.2
3	86	63.8	146	93.4	3.3	3.3	1.2
			147	93.4	3.1	3.4	1.05

Even making allowances for the semi-quantitative nature of these results the following tentative conclusions are possible.

(i). Up to 80% volatilization, methanol constitutes at least 70% of Fraction IIIB. As percentage volatilization increases the percentage of methanol in Fraction IIIB may decrease.

(ii). For a given polymer the molar ratio MA/MMA remains constant throughout the course of the volatilization. Different polymers may have different MA/MMA ratios.

(b). Quantitative Analysis

Quantitative measurements were made on Fraction IIIB from PMA(7) using the constant volume manometer ($V_o = 7.6 \pm 0.2$ ml.). Pressures of Fraction III (A + B) and of Fraction IIIA alone, (see Table 10+), are plotted against weight loss in Figure 9. Each run was carried out at 290°C using approximately 50 mg. samples. The plots are essentially linear and the pressure of Fraction IIIB (methanol) may be obtained by difference. As mentioned earlier, (this chapter, Section 1), the experimental points are rather scattered compared with those from runs with copper powder, (see Figure 9 and Table 11). In estimating the amount of methanol from Figure 9 the combined pressure of methyl acrylate and methyl methacrylate was assumed to be negligible. Knowing the manometer volume, the line drawn through the experimental

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+Tables not in the main text are included at the end of chapters.

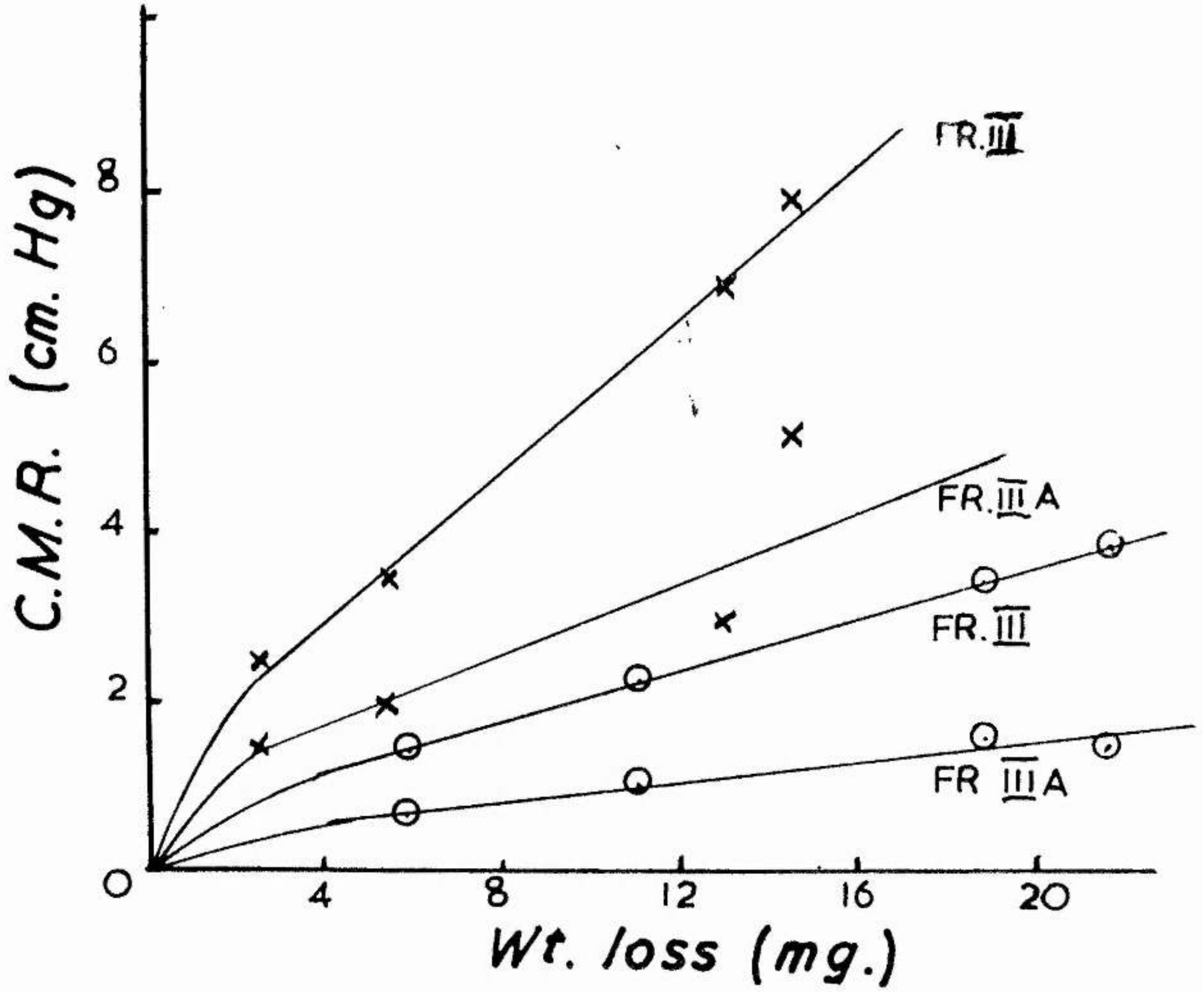


Figure 9 Corrected manometer readings (C.M.R.) against weight loss for degradations of PMA(7) with and without copper powder
Cu powder present, ⊙ ; absent, ×.

points in Figure 9 gives carbon dioxide 4.8%, and methanol 3.4% of the total polymer volatilized. (Calculations made for a conversion of approx. 50%). From the results in Table 8, the weight of methyl acrylate produced may be up to two-sevenths of that of methanol. This estimate, together with the weight percentage of methanol, (3.4% as found above), indicates that methyl acrylate accounts for $\angle$ 1% of the total weight loss.

2.2.4. Fraction IV

Using the alternative degradation apparatus (Figure 7), incorporating the vacustat manometer, the amount of Fraction IV from samples PMA(2) and PMA(26) was measured. Assuming that Fraction IV was entirely of carbon monoxide, which, of possible components, has the highest molecular weight, then the pressure readings together with the volume, showed that this fraction comprises $\angle$ 0.5% of the total weight loss.

2.2.5. Summary

Results obtained concerning the nature and composition of the degradation products are collected below in Table 9. It should be clearly understood that the values in this table are approximate, and are not based on the detailed examination of the products from a single sample.

2.2.6. Discussion

The present work has largely confirmed what was known about the products of degradation.

Table 9

Products of degradation of PMA - present study

Fraction	Nature	% of total wt. loss	Components	% of total wt. loss
I	long chain PMA.	residue	-	
II	short chain PMA. M_n 704	~ 90	low polymer	
III	condensable volatiles	9.2	MeOH	3.4
			CO_2	4.8
			$CH_2:CHCO_2Me$	<1.0
IV	non-condensable gases	<0.5		

The value for carbon dioxide (4.8%) is in reasonable agreement with other results (Table 5), and the estimate of methyl acrylate obtained ($<$ 1%), agrees with Madorsky's value but is rather less than the value from reference 66. The most marked difference between the present and previous results lies in the proportion of methanol evolved. It is quite possible that although the thermal degradation of PMA always follows the same basic pattern, differences in method of polymer preparation (see Table 8), in sample size, in degradation range chosen, and in the type of apparatus employed may be responsible for small but distinctive variations in the composition of the gaseous volatile products. In particular, in the present case the copper heating block may have decomposed some of the methanol gas before it was trapped out, although it is difficult to accept such a large loss in this way. As mentioned in Chapter II, (Section 2.2.1.), copper is a good catalyst[57] for decomposing methanol, the breakdown taking place in two stages,[58]

$$CH_3OH \longrightarrow CH_2O + H_2 \longrightarrow H_2+CO+H_2.$$

One point against this explanation for the low yield of methanol is that no formaldehyde was detected in Fraction III volatiles. The discrepancy is, however, relatively minor and in no way affects the results obtained in later chapters. A further effect of any loss of methanol is to increase the apparent proportion of Fraction II, the amount of which was found by difference.

The very low percentage of monomer produced shows that the "unzipping" reaction, which results in extensive monomer formation from polymers such as PMMA[5] and poly (α-methyl styrene),[50] does not occur in the degradation of PMA. However, the appearance of large amounts of low polymer residue indicates similarities to other polymers undergoing random degradation, notably polyethylene[69] and polyisobutylene.[69,70].

3. RATES OF VOLATILIZATION

3.1. VOLATILIZATION CURVES

Four series of degradations were carried out on

PMA(7) at temperatures of 286, 290, 300 and 310°C. Time of heating, loss in weight, and molecular weight of polymer residues were examined. The results are presented graphically in Figures 10, 14, 15, and 16, and are tabulated in Tables 10-16 at the end of this chapter.

3.2. RATES OF VOLATILIZATION

For a degrading polymer two different rates of volatilization can be calculated.

3.2.1. Rate R_1

The rate of weight loss R_1 is given in percentage of the sample initial weight per unit of time. For a degradation first order with respect to weight of polymer the plot of R_1 against percentage volatilization is linear. Rates of volatilization R_1 were found by differentiation of the volatilization curves with respect to time. The numerical method of differentiation used was found to be more satisfactory than graphical differentiation. Using the numerical method the instantaneous rates of volatilization at unit time intervals were found from the relation,[71]

$$f'_t = \left[\Delta' f_t - \tfrac{1}{2}\Delta^2 f_t + \tfrac{1}{3}\Delta^3 f_t - \tfrac{1}{4}\Delta^4 f_t \ldots \frac{(-1)^m \Delta^m f_t}{m}\right]$$

in which f_t is the percentage volatilization at time t; f'_t, the rate of volatilization at t, and Δ^n, the nth difference from f_t.

Plots of R_1 versus percentage volatilization are shown for PMA(7) at the four temperatures used (Figure 11).

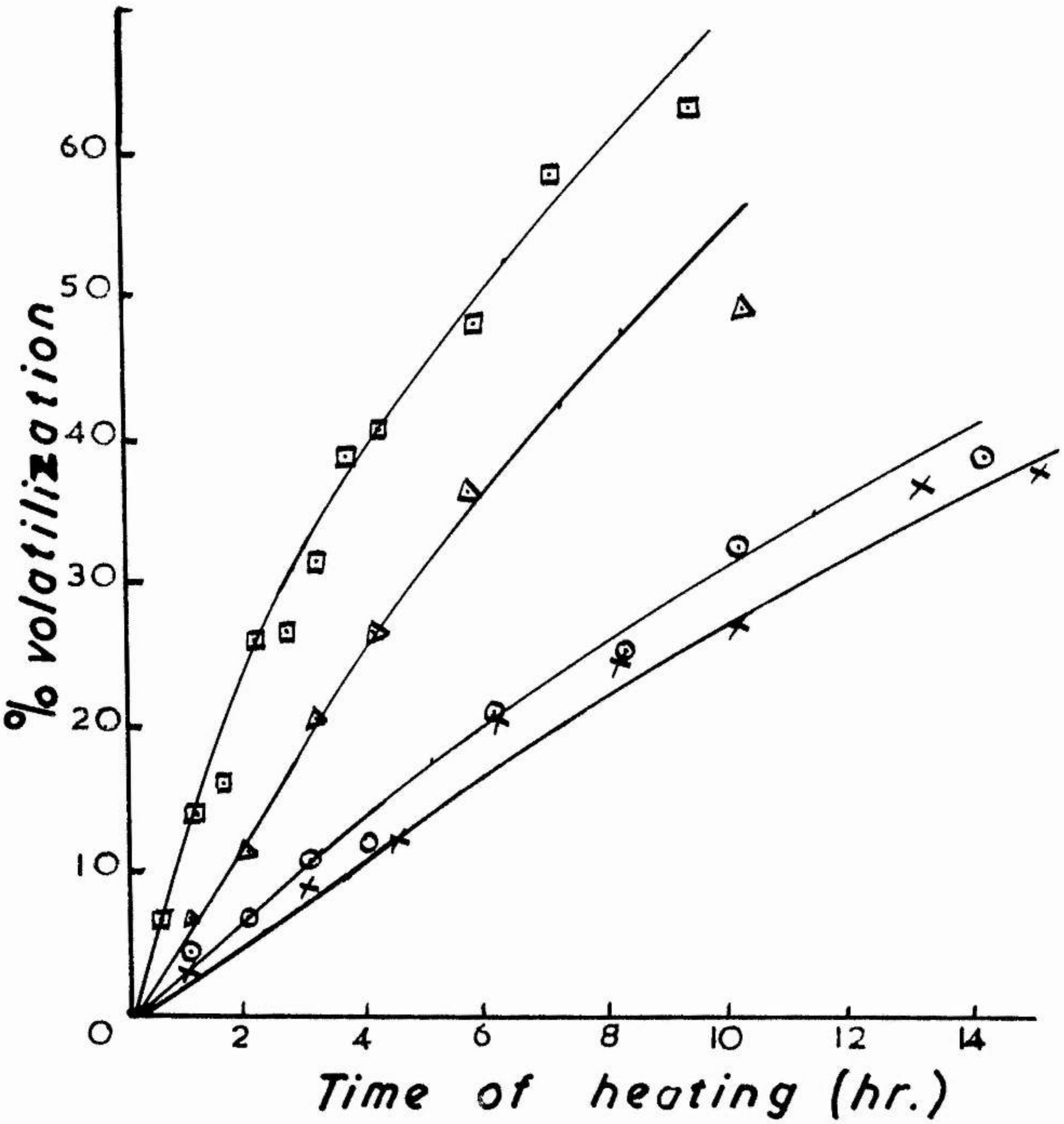


Figure 10 Percentage volatilization against time of heating for PMA(7)
×, 286° ; ⊙, 290° ; △, 300° ; ⊡, 310°C.

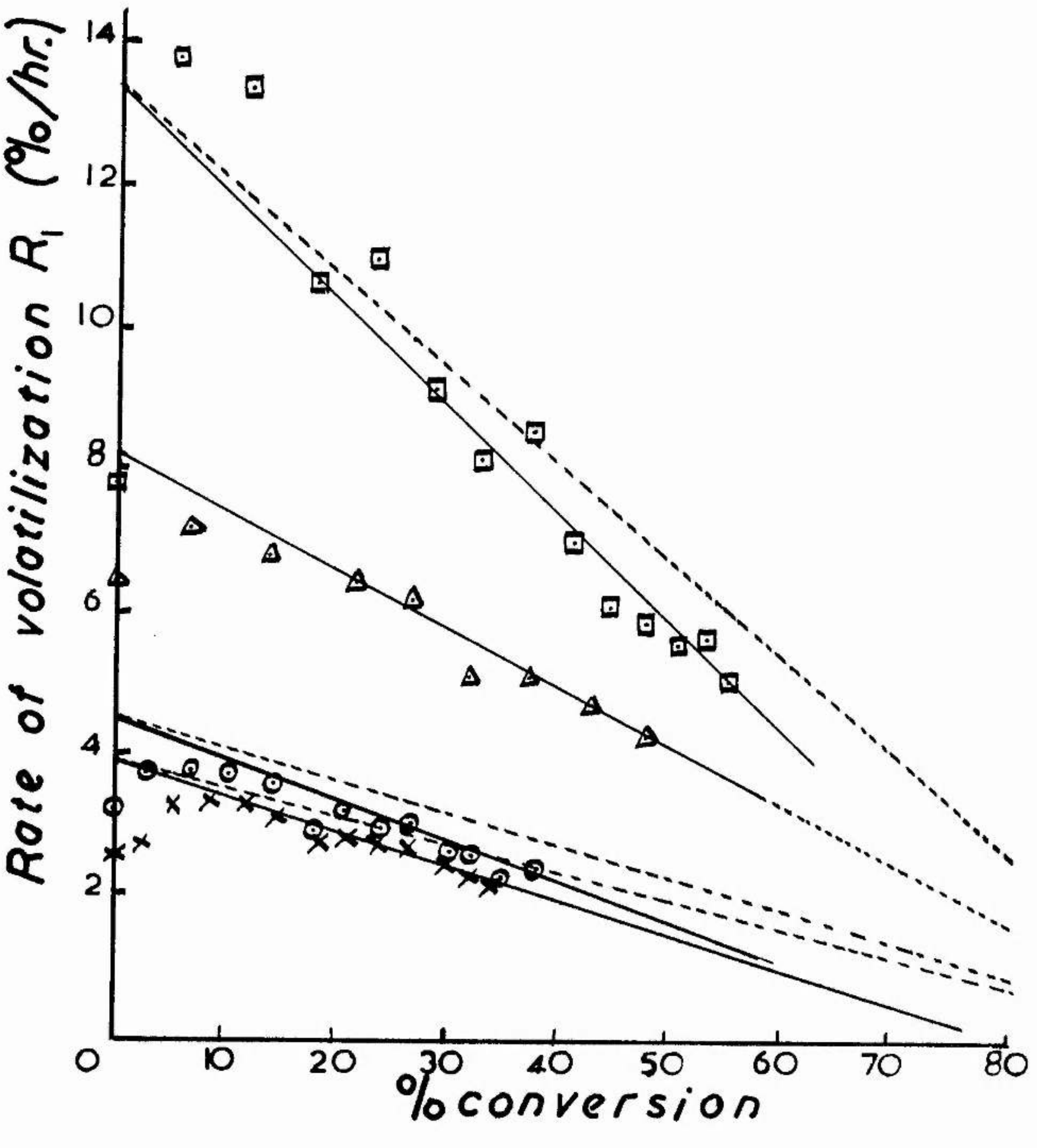


Figure 11 Rate of volatilization R_1 against percentage conversion for PMA(7)

×, 286° ; ⊙ 290° ; △, 300° ; ⊡, 310°C

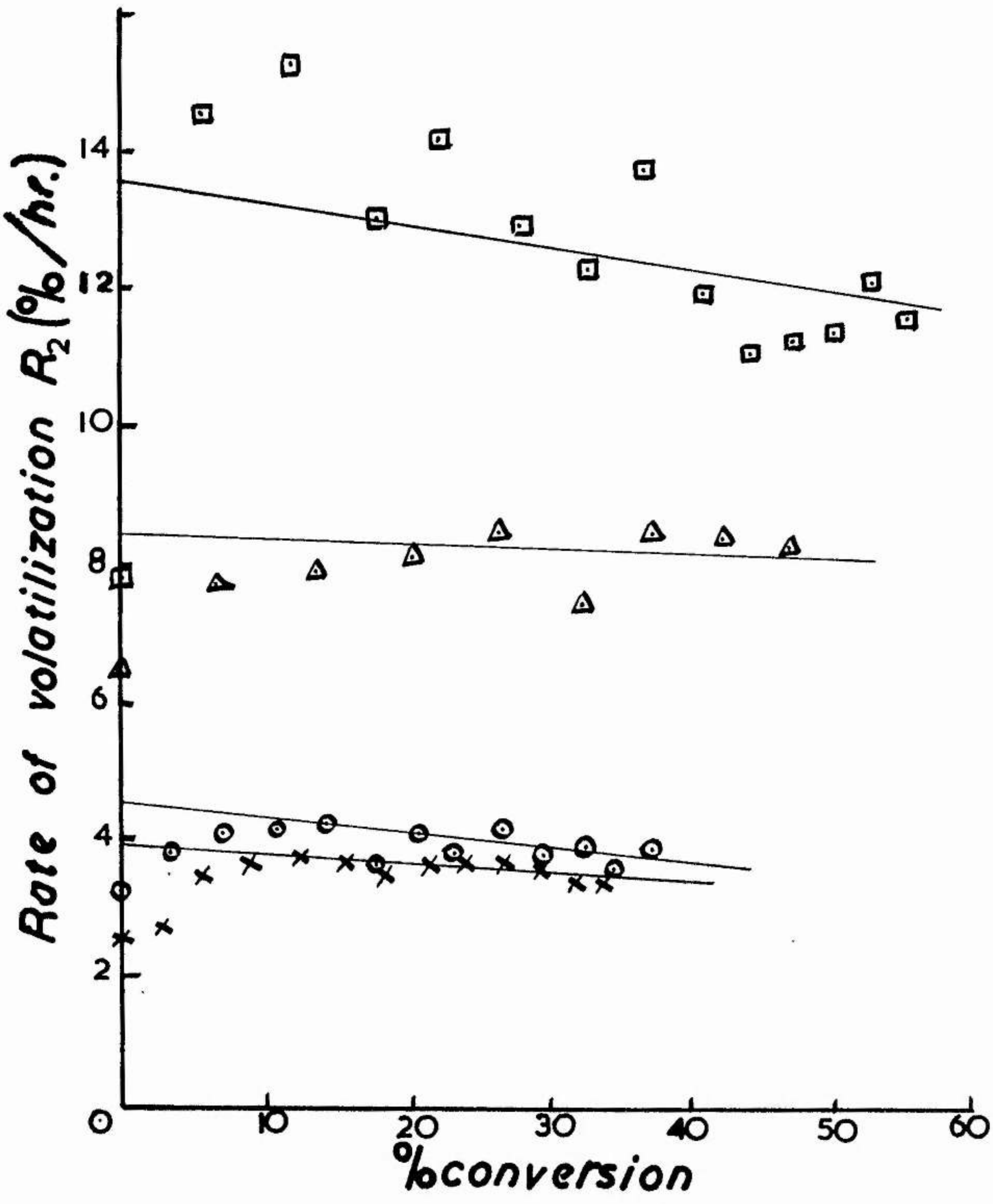


Figure 12 Rate of volatilization R_2
against percentage conversion for PMA(7)
×, 286°; ⊙, 290°; △, 300°; ⊡, 310°C.

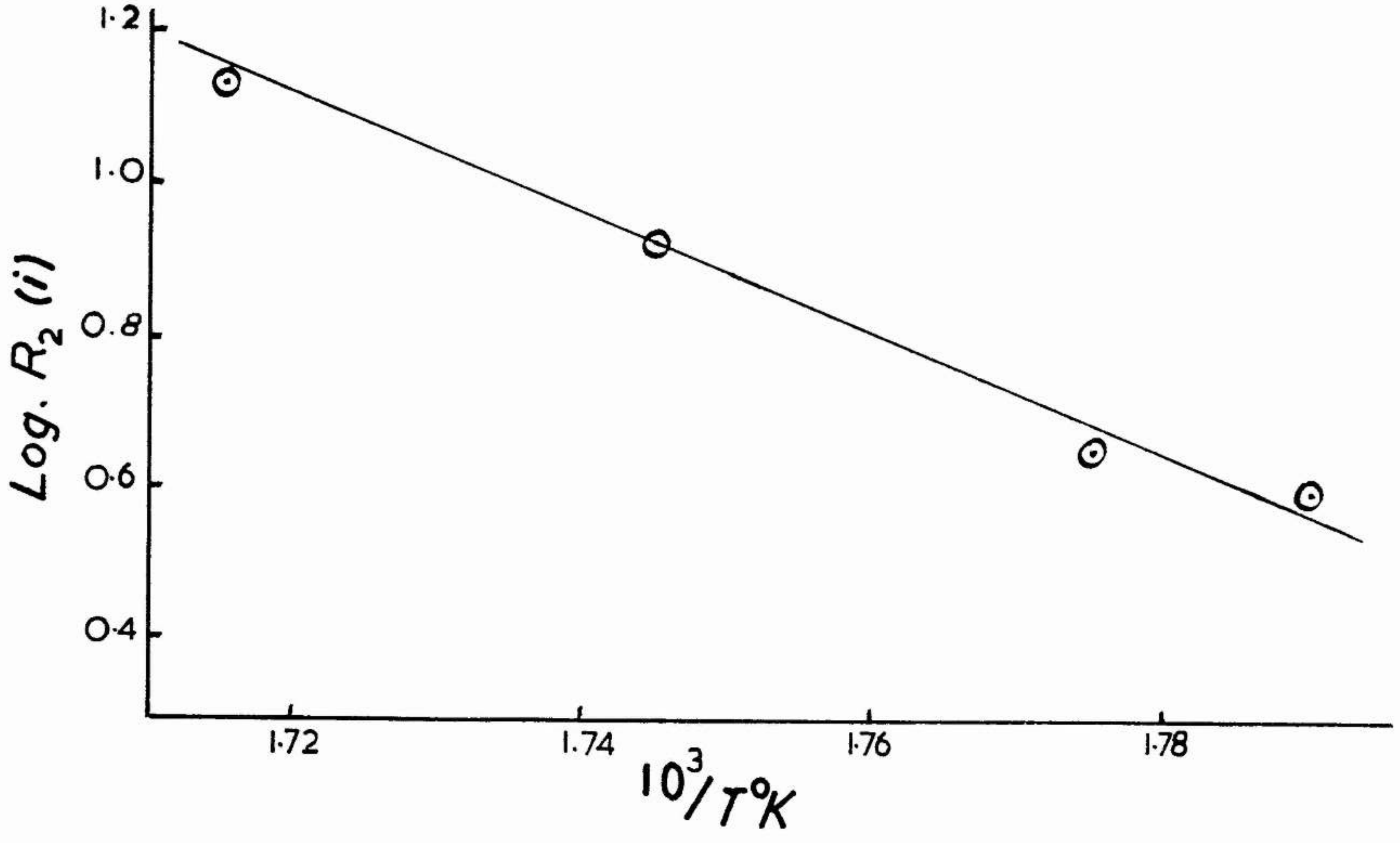


Figure 13 Arrhenius plot of initial rates of volatilization $R_2(i)$ for PMA(7)
$R_2(i)$ in %/hr.

Initial rates $R_1(i)$ at zero volatilization are found by back extrapolation of the linear parts of the experimental curves. The dashed lines in Figure 11 which are drawn from the initial rates to 100% conversion represent the course of a volatilization process which is first order with respect to sample weight.

3.2.2. Rate R_2

Rate of weight loss R_2 is given in percentage of the weight of polymer remaining per unit of time. Rate R_2 is a constant for a reaction first order with respect to weight. Rate R_2 values were calculated from R_1 values from the relation,

$$R_2 = \frac{R_1}{\text{fraction of sample initial wt. remaining}}$$

Plots of values of R_2, found from experimental results, are shown in Figure 12. These are virtually horizontal straight lines, i.e. R_2 is very nearly constant. Initial rates $R_2(i)$ are also obtained by back extrapolation. Corresponding $R_1(i)$ and $R_2(i)$ values (at $t = 0$) are almost identical. (Table 15).

3.2.3. Activation Energy.

The only strictly comparable rates of volatilization for samples heated at different temperatures are the initial rates, for which similarity of molecular weight and molecular weight distributions are assured. An Arrhenius plot (Figure 13) of the initial rates $R_2(i)$, (Table 15), gives 37 ± 2 k. cal./mole. for the activation energy of degradation of PMA(7) which agrees well with Madorsky's value[10] of 34 k. cal./mole. This is the activation energy for the overall breakdown, and cannot be related to any specific process. The initial rate of volatilization of the polymer at 350°C may be more useful in reflecting the stability of the polymer. For PMA(7), R(i) 350°C has a value of 1.9%/min.

The pre-exponential factor A, involved in the Arrhenius equation has a value of 7×10^{11} sec.^{-1}

4. MOLECULAR WEIGHTS OF PYROLYSED RESIDUES

Data on the change in molecular weight as pyrolysis proceeds, and on how the change is related to temperature, time of heating and percentage volatilization, are always of value in clarifying the breakdown mechanism.

The results of molecular weight measurements on samples of PMA(7) pyrolysed at 286, 290, and 300°C are presented in Figures 14, 15, and 16.

4.1. MOLECULAR WEIGHT VERSUS TIME

The plot of molecular weight against time for the three temperatures is shown in Figure 14. The experimental points for each temperature fall on a well defined curve. The higher the temperature of heating the lower the molecular weight of the residue, for equal heating times. Therefore Figure 14 makes it clear that the rate of bond breaking increases with temperature. (This is also well illustrated in Figure 16).

4.2. MOLECULAR WEIGHT VERSUS PERCENTAGE VOLATILIZATION

In the plot of molecular weight against percentage volatilization (Figure 15) which includes results for the three temperatures, the points all lie on one smooth curve. There is a sharp initial drop in molecular weight. Obviously the quantity which determines the length of the pyrolysed chains is the percentage volatilization. Similar behaviour to this is exhibited by polystyrene.[72,73].

4.3. $(^1/M_t - ^1/M_o)$ VERSUS TIME

For a polymer system undergoing random degradation the fraction of backbone bonds broken, α , (often referred to as the degree of degradation), is given by,

$$\alpha = {}^1/DP_t - {}^1/DP_o$$

Where DP_t is the number average degree of polymerisation after time t, and DP_o is the initial number average degree of polymerisation. Also, provided α is $\ll 1$,

$$\alpha = kt$$

where k is the rate constant for bond breaking. Therefore, the plot of $^1/M_t - ^1/M_o$ versus time of degradation should be linear for a simple random degradation, where M denotes an average molecular weight.

Figure 16 shows data for PMA(7) plotted in this manner. In this case, the molecular weights are viscosity averages. Figure 16 shows that in the early stages of reaction the above relationship is obeyed, but it appears that as the reaction proceeds the rate at which back-bone bonds break diminishes. For PMA under these conditions, however, such an interpretation is almost certainly over simplified for the following reasons.

(i). The above theory only applies when no molecules are lost from the reaction system either by evaporation or by complete unravelling. In the system under discussion these conditions are only approached at the beginning of the reaction, and as Table 16 shows considerable amounts of polymer are lost by evaporation in the later stages.

(ii). In addition to chain breaking there is a competing cross linking reaction during pyrolysis of PMA (see Chapter V), and there is no guarantee that these processes show parallel rates throughout the reaction.

(iii). It is assumed that the equation $[\eta] = 1.282 \times 10^{-4} M^{0.7143}$ applies to the polymer residue at all stages of degradation, but the chemical nature of the polymer is changing with time, due to side chain decomposition, and possibly due to crosslinking, and this relation can only be approximately true.

(iv). Where an average molecular weight other than a number average is used in this type of plot, a straight line can only be expected if the molecular weight distribution remains unchanged. In the present work no data on molecular weight distributions were collected.

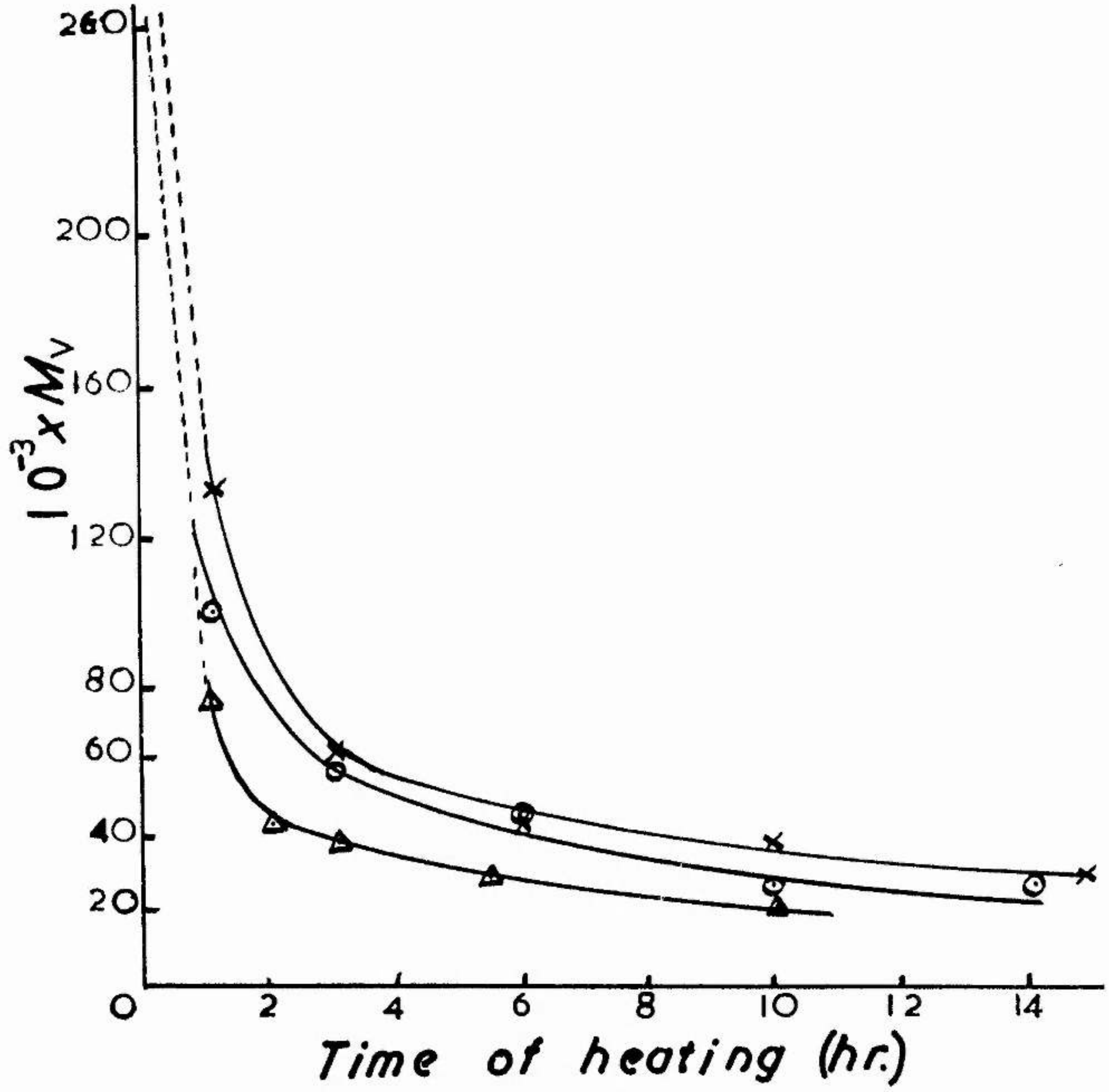


Figure 14 Molecular weight of pyrolysed residues against time of heating for PMA(7)
×, 286° ; ⊙, 290° ; △, 300°C.

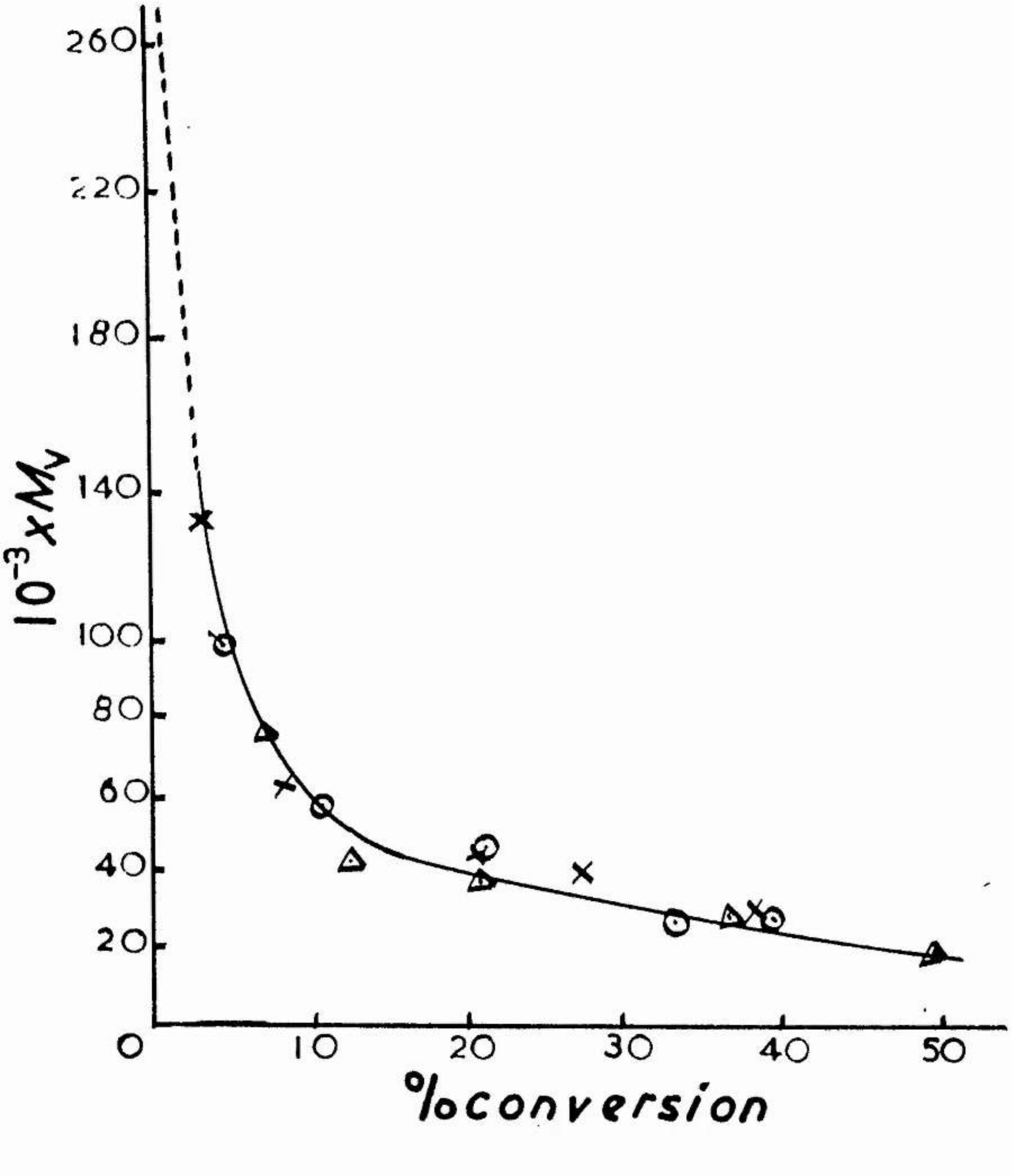


Figure 15 Molecular weight of pyrolysed residues against percentage conversion for PMA(7)
×, 286°; ⊙, 290°; ▵, 300°C.

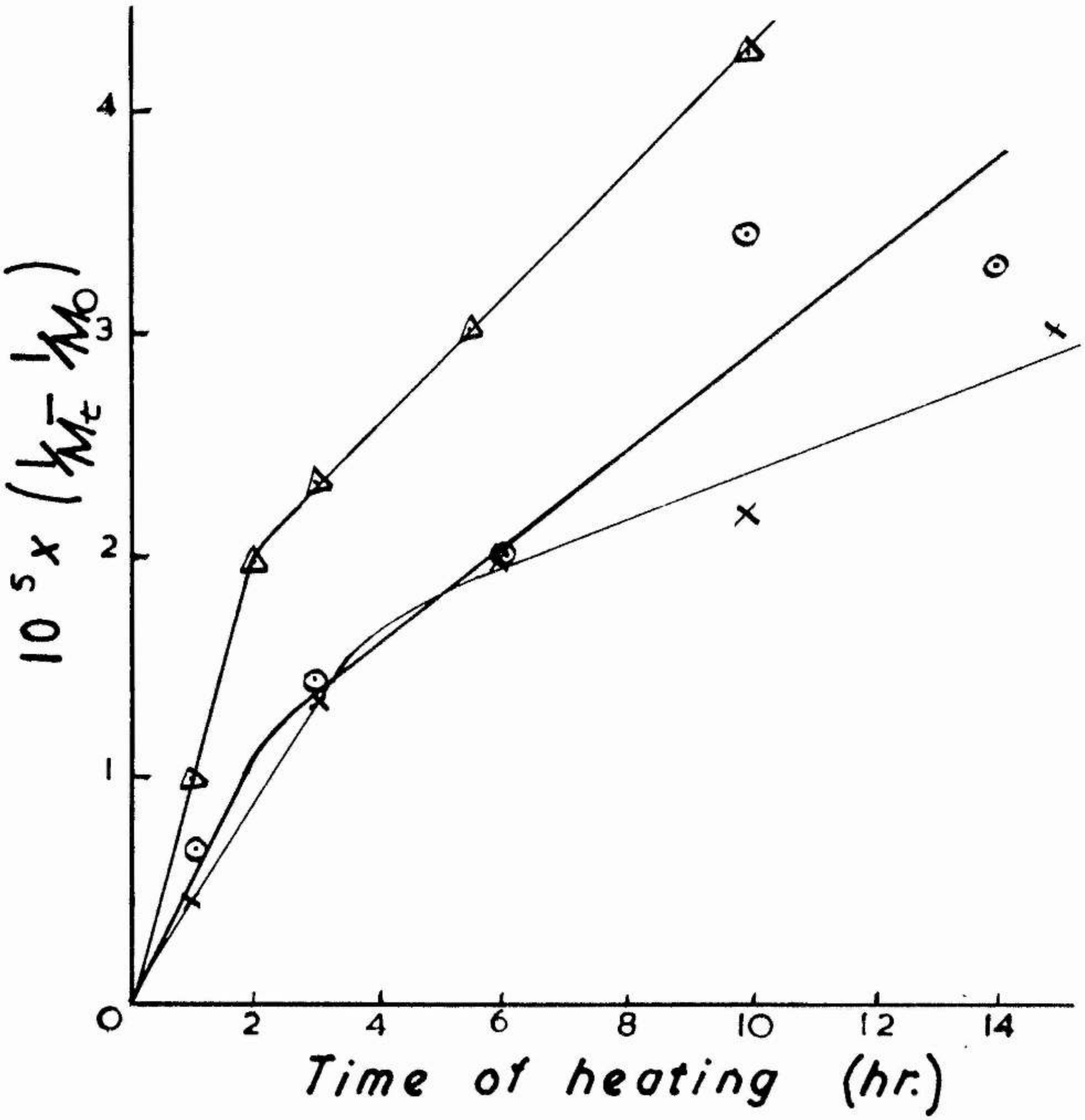


Figure 16 $1/M_t - 1/M_0$ against time of heating for PMA(7)
×, 286°; ⊙, 290°; △, 300°C.

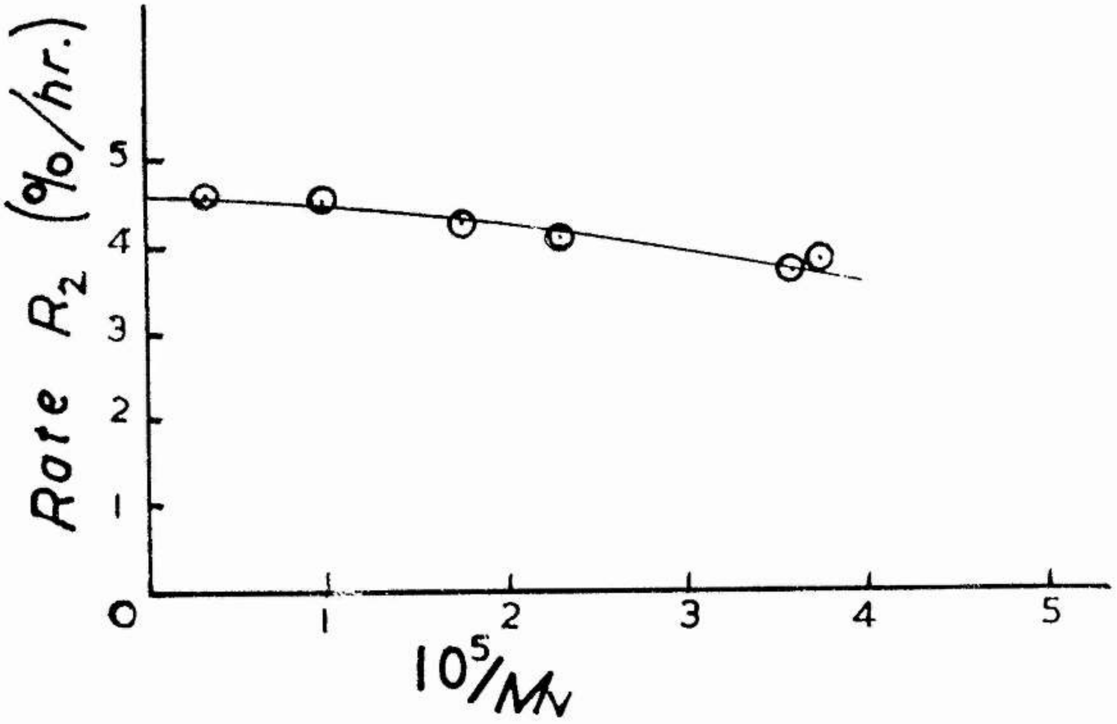


Figure 17 Rate of volatilization R_2 against reciprocal viscosity molecular weight for PMA(7) at 290°C

For these reasons speculation on variation in rates of bond breaking during the pyrolysis of PMA is highly uncertain. In the early stages of the reaction, however, the relationship $1/DP_t - 1/DP_o = kt$ appears to be obeyed, indicating a random scission of chains.

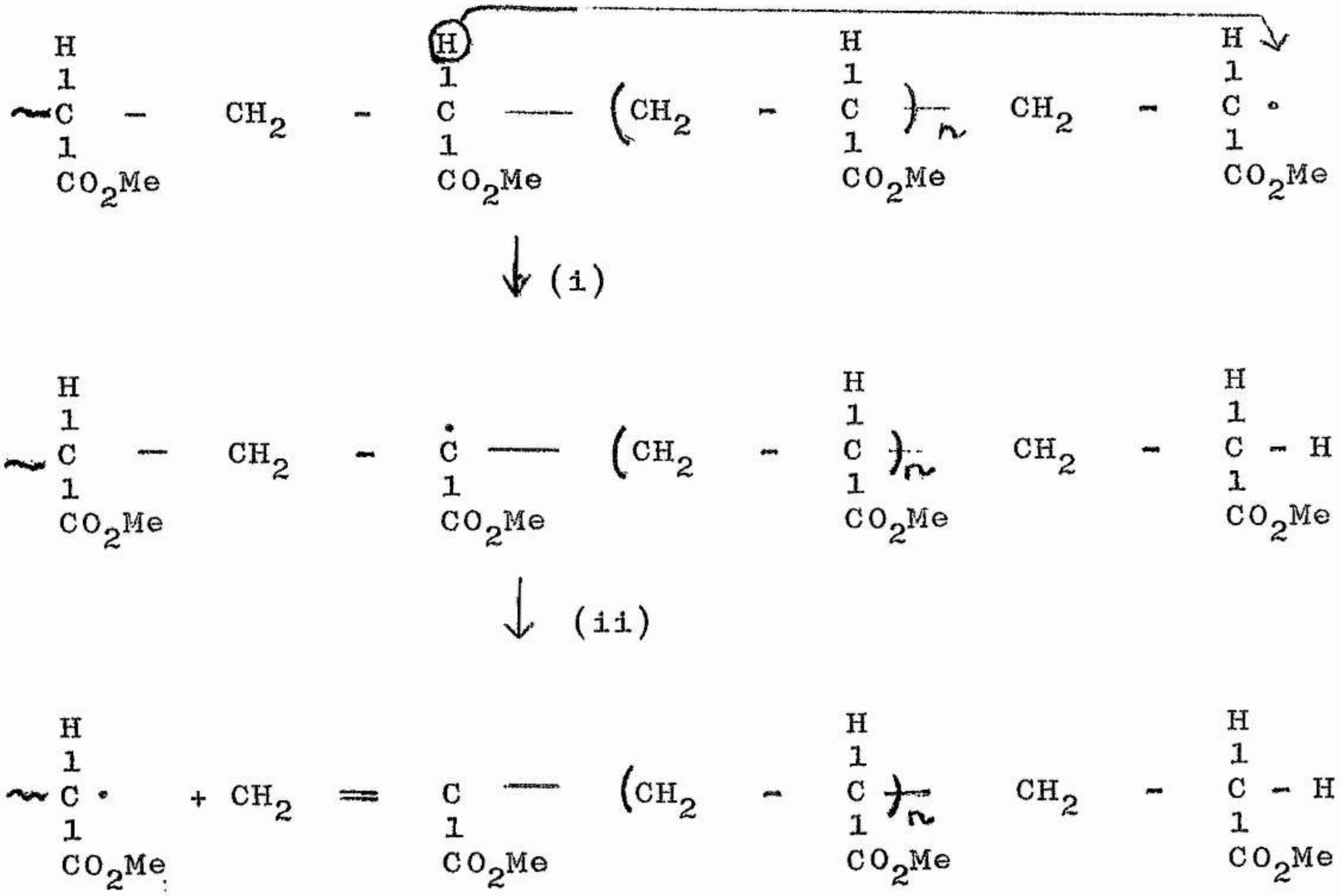
4.4. RECIPROCAL MOLECULAR WEIGHT VERSUS RATE OF VOLATILIZATION

For any polymer the reciprocal of the number average molecular weight is proportional to the number of chain ends present in a given weight. A plot of rate of volatilization R_2 against $1/M_v$ is shown in Figure 17. This shows that the rate of volatilization (% residue / hr.) does not increase with the number of chain ends in the system. In fact it drops slightly. Therefore, it is very probable that chain-end initiation is not important in the degradation of PMA.

5. DISCUSSION

This discussion amplifies the brief comments made at the end of each of the preceding sections.

A noteworthy feature of the reaction is the minute amount of monomer and the large amount of low polymer evolved by PMA. This feature immediately distinguishes the process from that occurring in PMMA,[5] which "unzips" to produce monomer exclusively. Such a profound difference in behaviour between those two structurally similar polymers may at first seem surprising, but clearly the presence of the more labile tertiary hydrogen atoms in PMA permits far more transfer reactions than occur in PMMA. The ready occurrence of transfer in PMA can account for the differences in behaviour of the two polymers. Thus, it is possible that the low polymer is evolved by intra-molecular transfer as in Scheme 1.

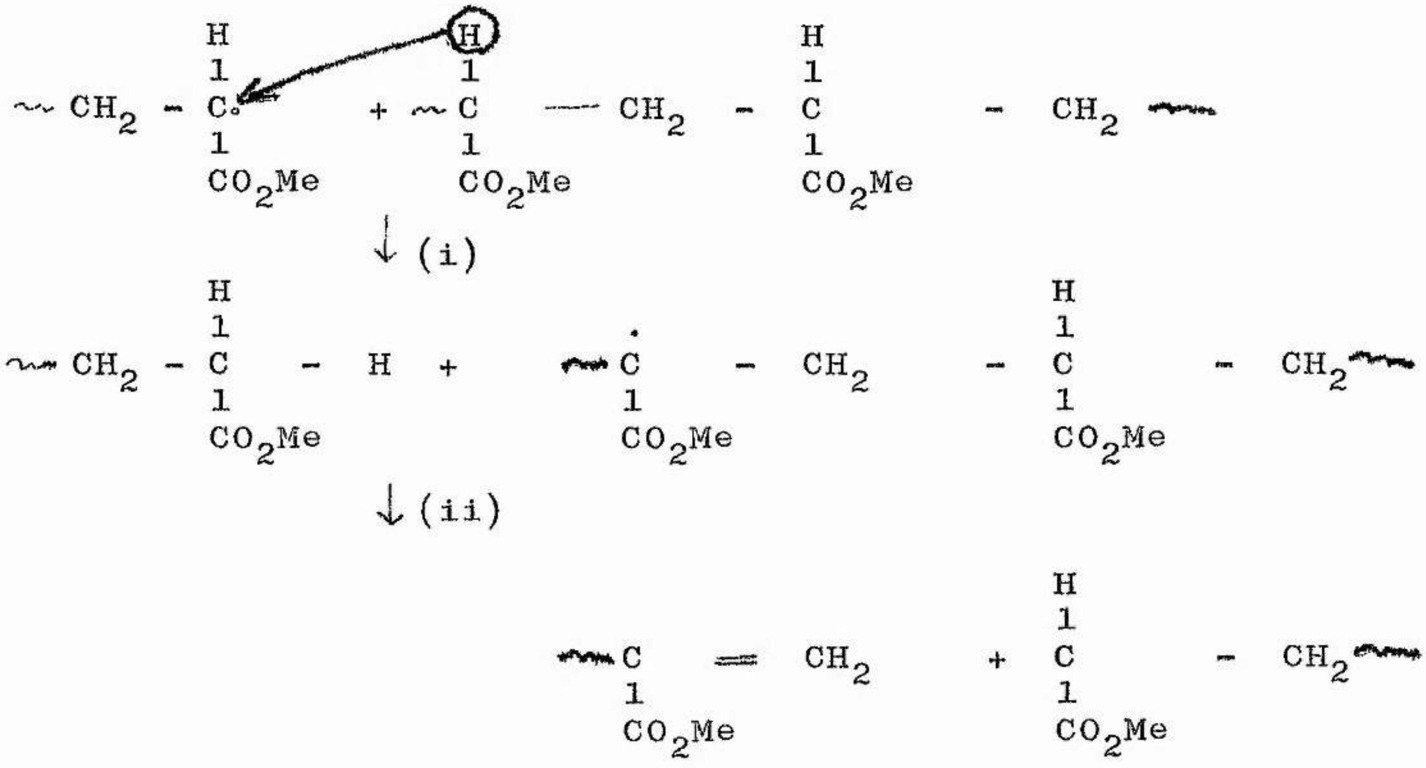


Scheme 1; intramolecular transfer

Scheme 1 is the simplest mechanism involving production of short chain fragments by transfer. Scission step (ii) may occur simultaneously with the transfer step and the scheme is often written as a one step reaction.

Similar chain mechanisms have been previously put forward to explain the breakdown of paraffinic hydrocarbons,[74] and have also been invoked to account for the thermal degradation of a variety of polymers including polystyrene,[73] and polyisobutylene.[75] This radical chain process might be called "unbuttoning", as opposed to "unzipping" which occurs in PMMA.

The above transfer step is an intramolecular one, but there is no reason to exclude intermolecular transfer, (illustrated in Scheme 2), from the picture.



Scheme 2; intermolecular transfer

Intermolecular transfer would probably produce a higher proportion of involatile chains than the intramolecular process and would result in a random fragmentation of the polymer backbone.

According to the theoretical calculations of Simha and Wall[6,8] random breakdown of polymer molecules should produce maxima in the rate of volatilization (R_1) versus percent conversion curves, around 26% conversion. The maximum arises because of the build up of chain fragments sufficiently small to produce a volatile fragment from an internal scission. The position of the maximum is, however, influenced by various factors in individual polymer samples, such as molecular weight distributions[73,76] and precise mode of degradation including degree of intramolecular transfer.[75] Thus, most polystyrene samples show a rate maximum around 40% conversion,[36] while several polyisobutylene fractions showed maxima around 5% conversion.[75] In both of these systems the occurrence of random degradation with transfer is fairly well established. Figure 11 from the present work shows well defined maxima in the rate curves for 286 and 290°C between 5 and 10% conversion. This evidence further supports the case for a random breakdown mechanism with transfer.

For simple random degradation simplified theory predicts, that beyond the maximum the rate curve should follow the line between the extrapolated initial rate and 100% conversion on the conversion axis. This theory is based on the assumption that beyond the maximum the probability that an internal scission produces a volatile fragment remains constant, and that the rate at which bonds break is proportional to the number of bonds in the system. In other words, the rate of loss of weight of polymer is proportional to the weight remaining. This picture is oversimplified but many polymers undergoing random degradation approximate quite closely to it, a good example being linear polyethylene.[21] As can be seen from Figure 11, PMA also comes close to this behaviour. Only an approximate fit could be expected in this case since the reaction involves more than simple random degradation as later results will show.

The molecular weight changes with conversion (Figure 15) are also consistent with a random mechanism, the main characteristic of which is a very rapid drop in relative degree of polymerisation at low conversions.[5,6] Figure 18 shows that the degradation behaviour of PMA lies between that of polystyrene and that of polymethylene.

Polymethylene shows almost ideal behaviour[67] for a linear polymer undergoing random degradation with negligible "unzipping". Polystyrene[72] shows features in accord with random degradation, but the relatively high values at which the relative molecular weight curve levels off may be due to considerable loss of small chains by complete depropagation, "unbuttoning" as well as "unzipping". It seems likely that the intermediate behaviour of PMA is partly explicable in terms of molecules lost by "unbuttoning".

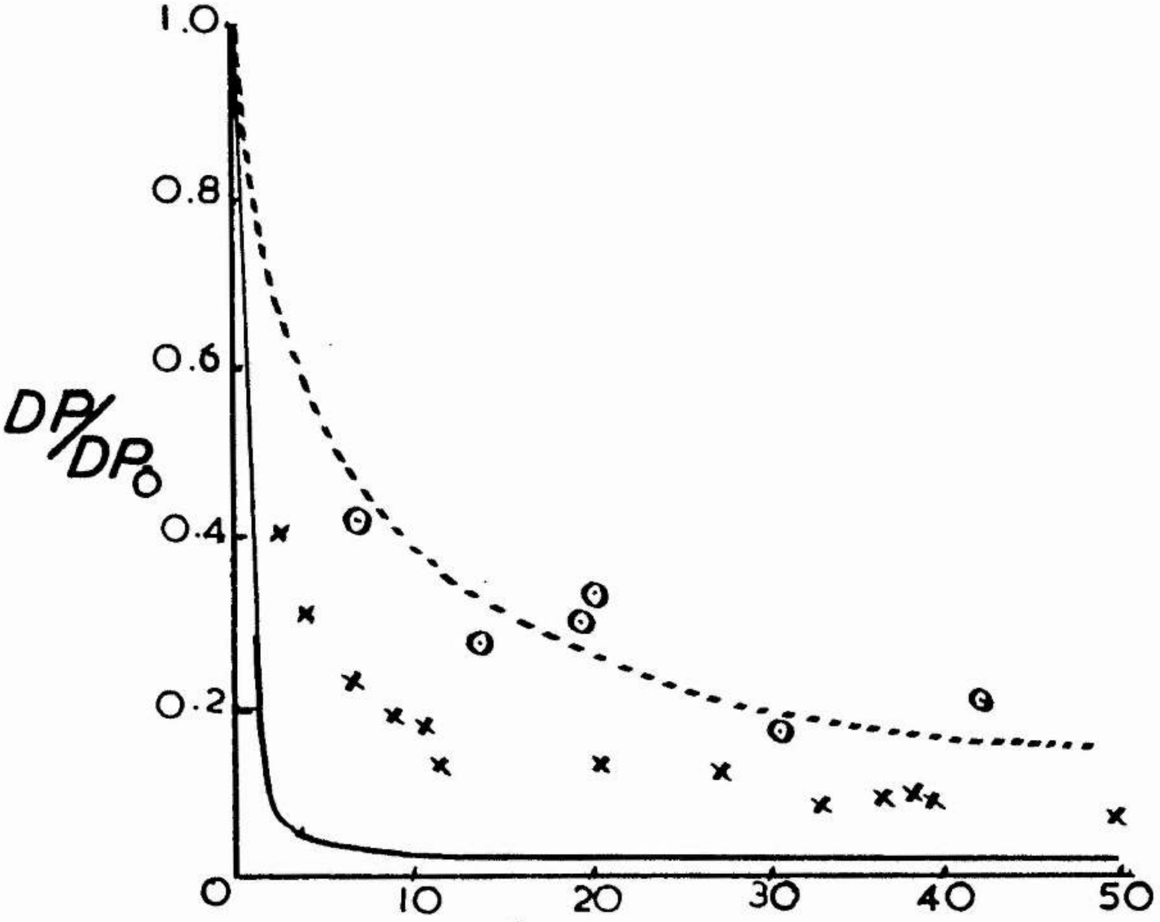


Figure 18 Relative molecular weight against percentage conversion for polymethylene,[67] PMA(7) and polystyrene[72] Polymethylene, —— ; PMA(7), × × × ; polystyrene, --o---o-- .

Figure 16 also supports the random degradation mechanism, at least in the early stages of the reaction. The apparent slowing down of bond scission later in the process is readily explained, as earlier in this chapter, (Section 4.3.), and there is no need to consider on present evidence the existence or otherwise of "weak links".

All of the foregoing evidence strongly supports the view that random breakdown of chains with considerable amounts of transfer occurs on pyrolysis of PMA. There is no direct evidence of the mechanism of the breakdown so far, but the free radical chain processes outlined in Schemes 1 and 2 may well prevail. The initiation step has not yet been given any consideration. The initial formation of a radical, or radicals, could arise from random homolytic scission of the back-bone, from side chain breakdown, or from breaks at chain ends. In the latter two cases the immediate onset of intermolecular transfer could still give a picture consistent with random degradation. On present evidence chain-end initiation is unlikely. As degradation proceeds the number of chain ends per unit weight of polymer increases rapidly, but the rate of volatilization per unit weight of polymer hardly changes, and in fact as Figure 17 shows diminishes slightly. In systems where chain-end initiation of volatile production is important, for example polystyrene, R_2 shows[77] a marked rise as 1/M, and hence concentration of chain-ends, increases. In view of the well-known thermal stability of methyl esters[78] random cleavage of back-bone bonds would seem to be the most probable initiation step.

This discussion has centred around what appears to be the dominating feature in the thermal degradation of PMA —— the inter- and intramolecular transfer reactions which produce random fragmentation of the polymer chains. The other volatile products of the pyrolysis reveal, however, that the overall reaction is more complicated. In particular, the production of methanol and carbon dioxide indicates that some side chain decomposition occurs. Any attempt to explain the presence of these products would be premature at this stage and the following chapter deals with those and other questions of the mechanism in more detail.

6. TABLES OF EXPERIMENTAL RESULTS

Tables 10 and 11

Pressures of gaseous volatiles for degradations of PMA(7). Values plotted in Figure 9.

Table 10

Copper powder absent; degradations at 290°

Run	Time hr.	S.I.W. mg.	Wt. loss mg.	C.M.R. cm. Hg	
				Fr.IIIA	Fr.IIIA + B
90	2.0	47.6	2.5	1.4	2.5
91	3.0	47.0	5.4	1.9	3.4
101	7.5	48.0	13.0	2.9	6.85
107	8.0	48.5	14.5	5.05	7.85

Abbreviations: C.M.R., corrected manometer readings;
S.I.W., sample initial weight.

Table 11

Copper powder present

Run	Temp °C	S.I.W. mg.	Wt. loss mg.	C.M.R. cm. Hg	
				Fr.IIIA	Fr.IIIA + B
29	300	92.8	5.9	0.6	1.4
38	310	81.1	11.1	1.0	2.25
19	290	90.6	18.8	1.5	3.35
22	290	85.5	21.6	1.4	3.75

The results in the above Table 11, and those listed in the other tables 12, 13, 14, 15, and 16 in this chapter were all obtained with a "blanket" layer of copper powder above the film of PMA(7).

Table 12

Extents of volatilization of PMA(7) with time. Degradations at 286, 290°C. Values plotted in Figure 10

Run	T.O.H. hr.	S.I.W. mg.	Wt. loss mg.	% volat.
At 286°C				
8	1.0	100.0	2.6	2.6
9	3.0	91.4	8.0	8.75
17A	4.5	88.0	10.6	12.05
10	6.0	83.5	17.0	20.4
16A	8.0	100.5	25.0	24.8
14	10.0	102.2	27.8	27.2
16C	13.0	100.5	37.3	37.1
17C	15.0	88.0	33.6	38.2
At 290°C				
18	1.0	98.7	3.9	4.0
59	2.0	82.3	5.3	6.4
15	3.0	86.0	9.0	10.5
60	4.0	91.9	10.9	11.9
19	6.0	90.6	18.8	20.8
22	8.0	85.3	21.6	25.4
23	10.0	91.1	30.1	33.0
21	14.0	82.3	32.4	39.3

Abbreviation; T.O.H., time of heating.

Table 13

Extents of volatilization of PMA(7) with time. Degradations at 300, 310°C. Values plotted in Figure 10.

Run	T.O.H. hr.	S.I.W. mg.	Wt. loss mg.	% volat.
At 300°C				
29	1.0	92.8	5.9	6.4
31	2.0	102.5	11.5	11.2
33	3.0	87.8	18.0	20.5
32	4.0	96.2	25.5	26.6
25	5.5	94.6	34.6	36.6
24	10.0	85.4	42.2	49.6
At 310°C				
41	0.5	93.0	5.8	6.2
38	1.0	81.1	11.1	13.7
40	1.5	93.5	15.0	16.1
39	2.0	82.2	21.1	25.7
43	2.5	94.7	25.2	26.6
37	3.0	92.2	29.9	31.3
42	3.5	96.8	37.5	38.8
45	4.0	102.2	41.5	40.6
49	5.5	84.4	40.6	48.2
48	6.75	95.9	56.5	58.9
50	9.0	83.3	53.2	63.9

Table 14

Initial rates of volatilization of PMA(7), R_1(i) and R_2(i) obtained from Figures 11 and 12. Values for Arrhenius plot Figure 13.

Temp. °C	R_1(i) %/hr.	R_2(i) %/hr.	Temp. °K	10^3 T°K	log R_2(i)
286	3.9	3.9	559	1.79	0.59
290	4.5	4.5	563	1.775	0.65
300	8.2	8.4	573	1.745	0.92
310	13.4	13.5	583	1.715	1.13

Table 15

Values for plot of rate R_2 against reciprocal molecular weight (Figure 17). Percentage volatilization and rate values are those for degradations of PMA(7) at 290°C

Run	% volat.	R_2	$10^{-3} \times M_v$	$10^{+5}/M_v$
-	0.0	4.5	324	0.31
18	4.0	4.4	100	1.0
15	10.5	4.3	57.5	1.74
19	20.8	4.1	43.2	2.31
23	33.0	3.85	26.6	3.76
21	39.3	3.7	27.8	3.60

Table 16

Molecular weight changes with time and temperature for PMA(7). Results plotted in Figures 14, 15, 16, and 18.

Run	T.O.H. hr.	% volat.	$[\eta]$	10^{-3} M_v	$10^5/M_v$	$\frac{10^5}{M_v}-\frac{10^5}{M_o}$	$\frac{D.P.}{D.P._o}$
		0.0	1.10	3.24	0.31	–	1.0
At 286°C							
8	1.0	2.6	0.577	133	0.75	0.44	0.41
9	3.0	8.75	0.326	60.9	1.64	1.33	0.19
10	6.0	20.4	0.265	43.6	2.29	1.98	0.13
14	10.0	27.2	0.247	38.9	2.51	2.20	0.12
17C	15.0	38.2	0.200	30.0	3.34	3.03	0.09
At 290°C							
18	1.0	4.0	0.476	100	1.0	0.69	0.31
15	3.0	10.5	0.322	57.5	1.74	1.43	0.18
19	6.0	20.8	0.262	43.2	2.31	2.00	0.13
23	10.0	33.0	0.185	26.6	3.76	3.45	0.08
21	14.0	39.3	0.190	27.8	3.60	3.29	0.085
At 300°C							
29	1.0	6.4	0.390	76.0	1.32	1.01	0.23
31	2.0	11.2	0.265	43.6	2.29	1.98	0.13
33	3.0	20.5	0.240	38.0	2.63	2.32	0.12
25	5.5	36.6	0.195	29.9	3.34	3.03	0.09
24	10.0	49.6	0.158	21.8	4.58	4.27	0.065

CHAPTER IV

THERMAL DEGRADATION OF PMA. PART II
MECHANISMS OF DECOMPOSITION

1. INTRODUCTION

It was suggested in the ~~preceeding~~ preceding chapter that free radical transfer reactions play a major role in the thermal degradation of PMA. These suggestions, however, were based on analogy and speculation and no direct evidence was produced in their support.

Also, no attempt was made to account mechanistically for the production of carbon dioxide and methanol.

A study of the effects of a free radical "catcher" on the degradation, and spectroscopic examination of the polymeric products of degradation offered promising ways of obtaining more information about the component reactions. These experiments are reported and considered in this chapter.

2. EXPERIMENTS WITH 1,4 DIAMINOANTHRAQUINONE

The compound 1,4 diaminoanthraquinone (DAA) reacts with free radicals in the temperature range 286 - 320°C. The precise way in which this reaction takes place is not known,[5] but the DAA molecule probably adds to a free radical. A sample of DAA, a deep-purple coloured powder, was gifted by the Yorkshire Dyeware and Chemical Co.Ltd. While the polymer film was being formed on the degradation tray DAA,(2 mg.) was added in benzene solution. This ensured effective mixing of DAA throughout the polymer. A series of degradations at 290°C was carried out with DAA incorporated into films of PMA(7).

2.1. EFFECT ON VOLATILIZATION CURVES

The effect of DAA on a volatilization curve is clearly shown in Figure 19. Curve 1 represents the retarded volatilization curve (DAA present), while Curve 2 is the volatilization curve for PMA(7) alone at 290°C. Curve 3 is a theoretical curve for volatilization due to Fraction II fragments alone, and is calculated assuming that this fraction constitutes 90% by weight of all the volatiles. In fact, Curve 3 represents a volatilization curve for PMA at 290° assuming that Fraction III production is completely inhibited and that of Fraction II totally unaffected. Comparison of Curves 1, 2, and 3 indicates that DAA strongly retards the volatilization of PMA and in particular that of the lower polymer fraction of the volatiles.

2.2. EFFECT ON MOLECULAR WEIGHT OF PYROLYSED RESIDUES

A plot of molecular weight of the pyrolysed residues against percentage volatilization is shown in Figure 20. The curve obtained from unretarded runs is also included. Figure 20 indicates that percentage volatilization is still the factor determining the residue molecular weight. The plot of molecular weight against time, Figure 21, gives a better idea of how DAA affects the molecular weight changes during degradation, and in fact, DAA is seen to have a fairly small effect,

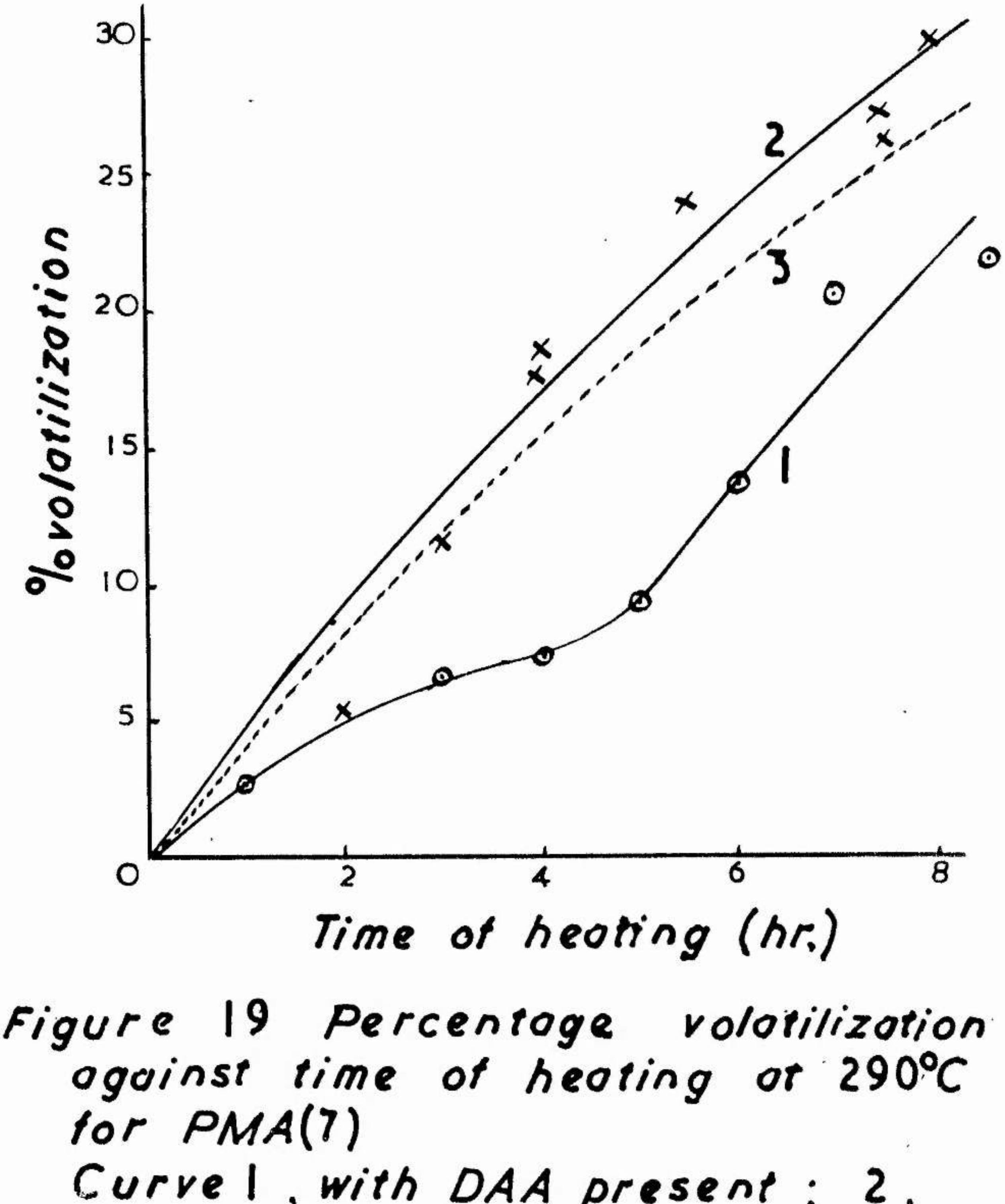


Figure 19 Percentage volatilization against time of heating at 290°C for PMA(7)
Curve 1, with DAA present; 2, without DAA; 3, Fraction II evolution without DAA.

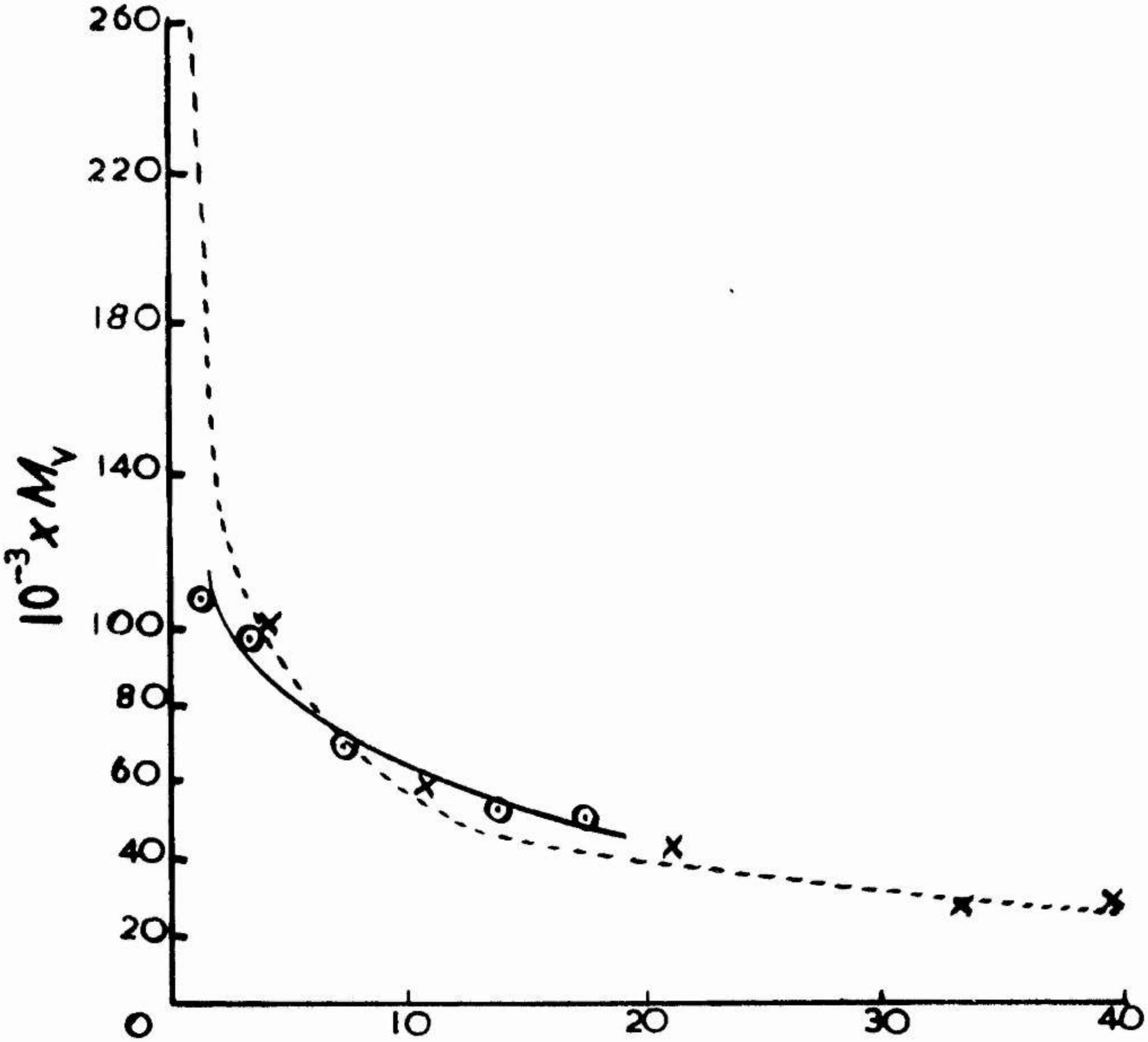


Figure 20 Molecular weight of pyrolysed residues against percentage volatilization at 290°C for PMA(7) incorporating DAA
DAA present, —⊙—⊙— ; absent, --×--×--.

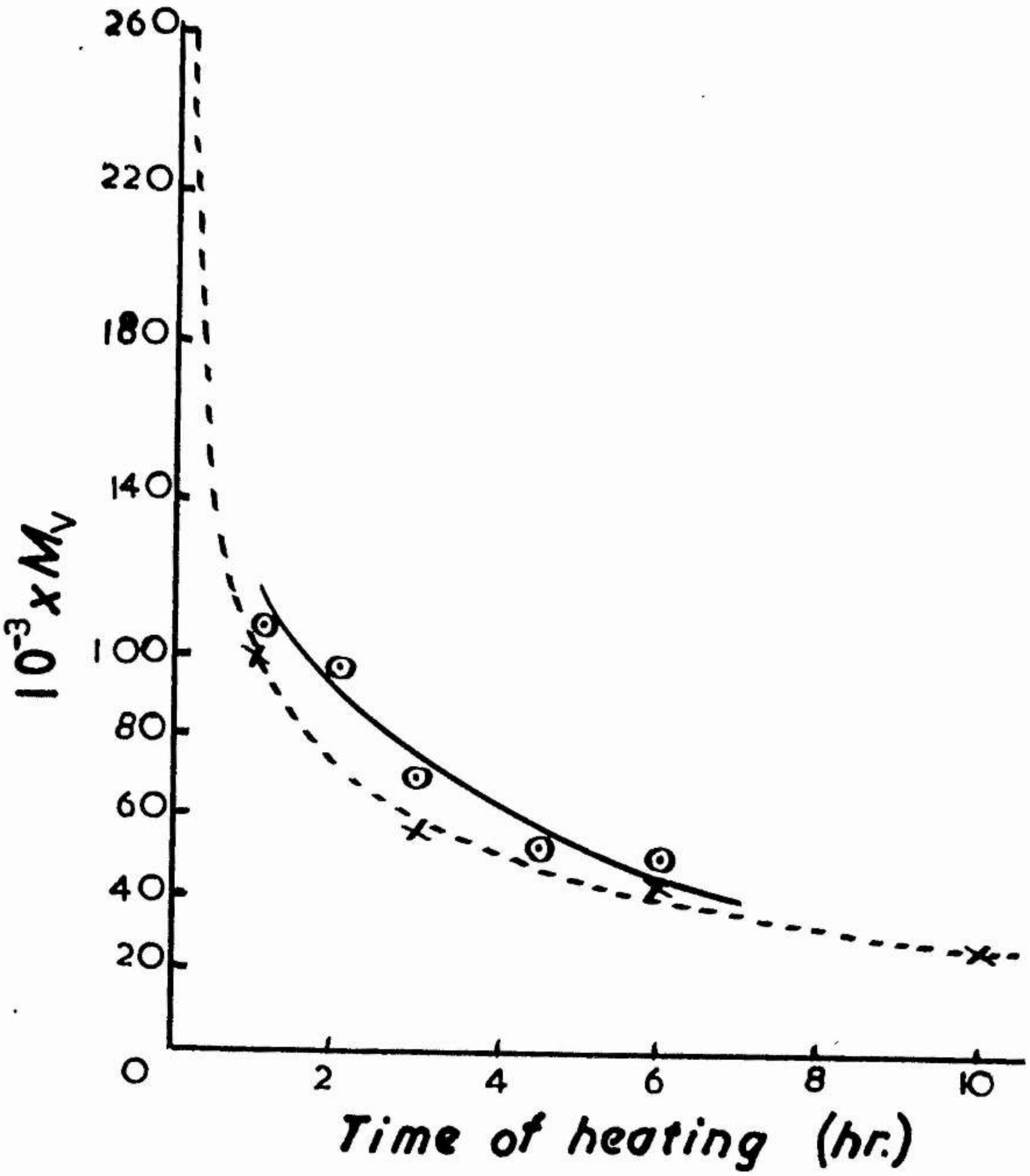


Figure 21 Molecular weight of pyrolysed residues against time of heating at 290°C for PMA(7) incorporating DAA
DAA present, —⊙—⊙— ; absent, -×--×-.

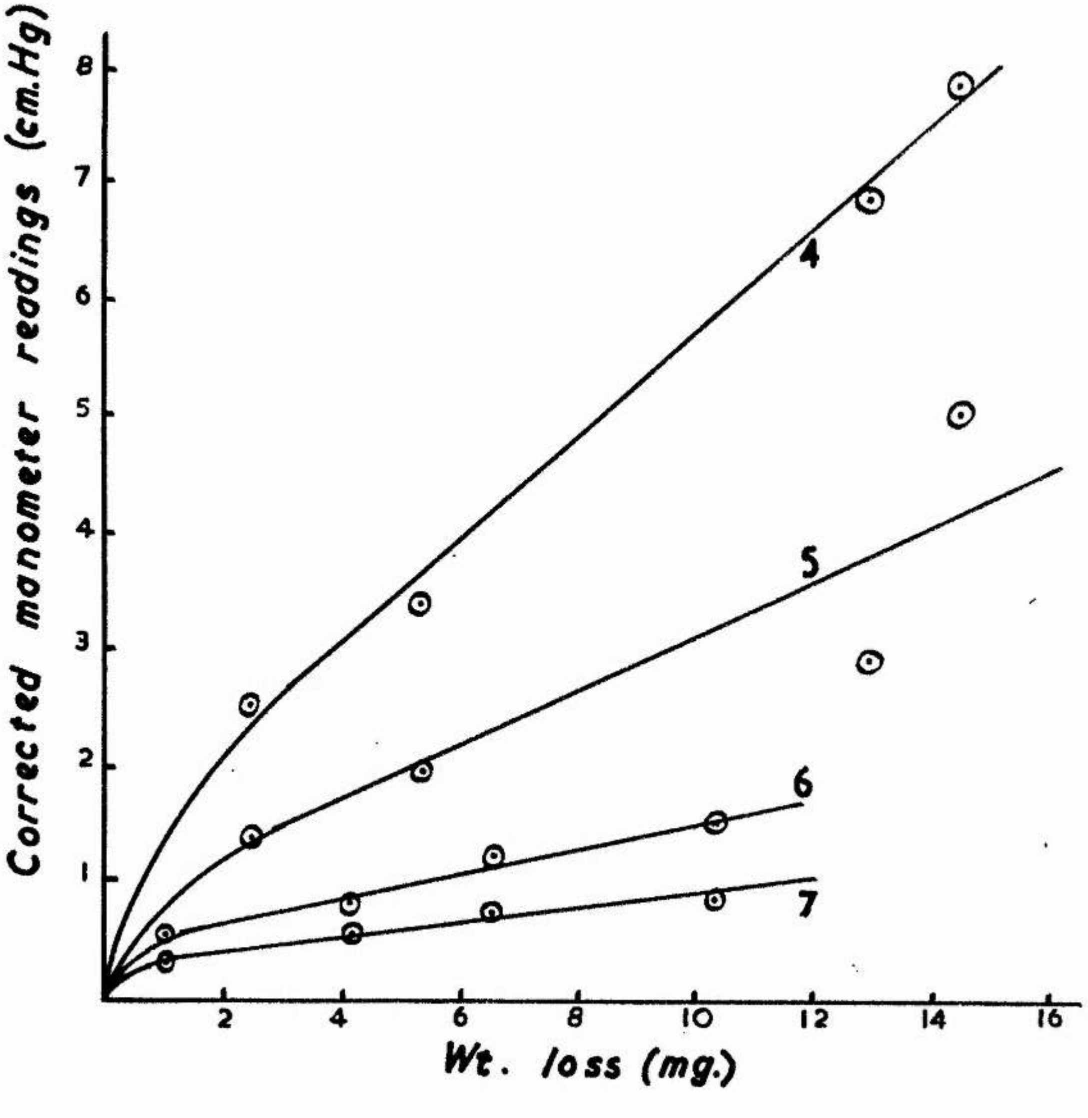


Figure 22 Corrected manometer readings against weight loss for degradations of PMA(7) at 290°C

Curve 4, total volatiles; 5, Fraction $\overline{\underline{III}}$A; 6, total volatiles with DAA; 7, Fraction $\overline{\underline{III}}$A with DAA.

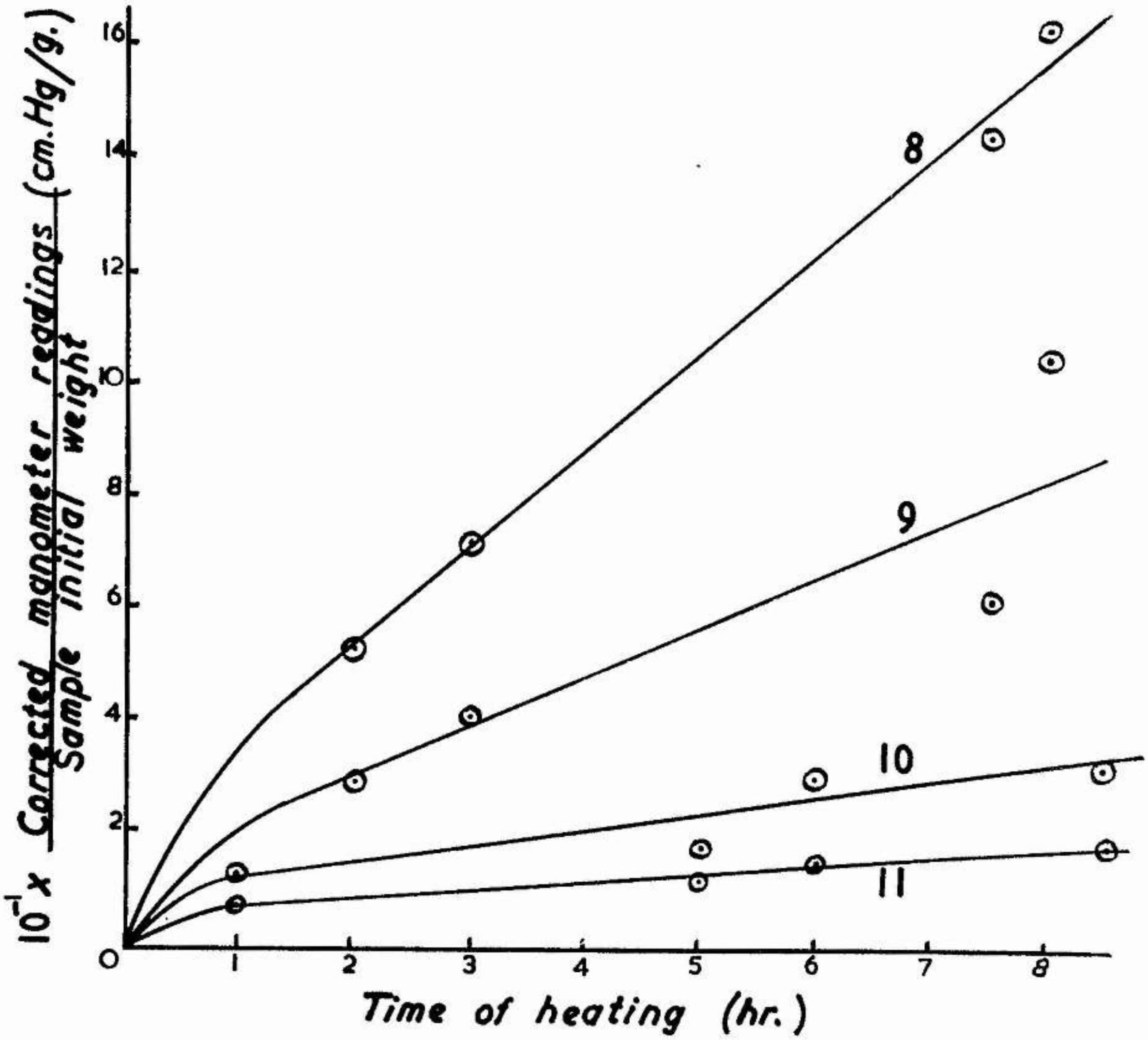


Figure 23 Corrected manometer readings per unit sample initial weight against time of heating for degradation of PMA(7) at 290°C Curve 8, total volatiles; 9, Fraction $\overline{III}$ A; 10, total volatiles with DAA; 11, Fraction $\overline{III}$A with DAA.

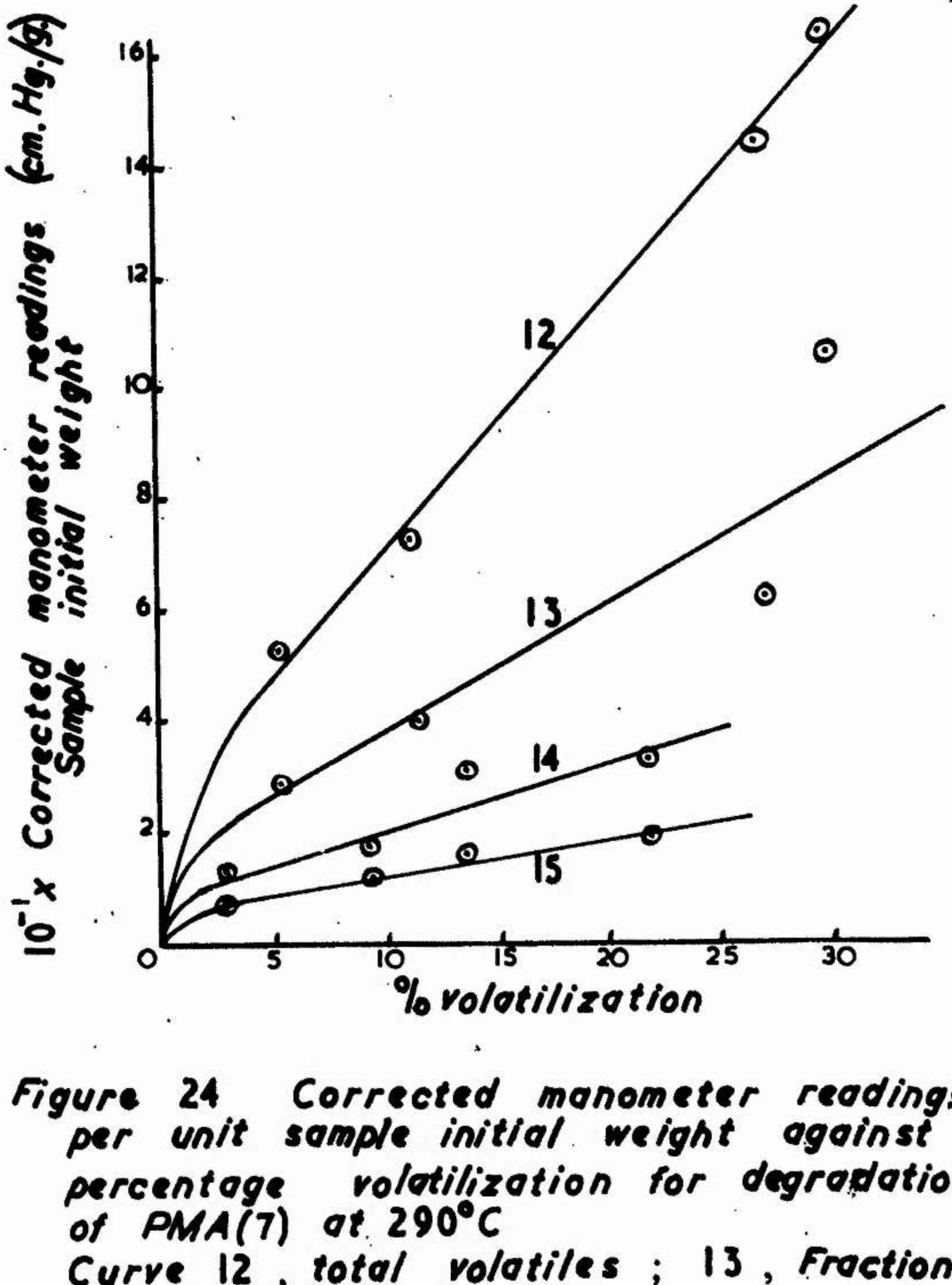


Figure 24 Corrected manometer readings per unit sample initial weight against percentage volatilization for degradation of PMA(7) at 290°C
Curve 12, total volatiles; 13, Fraction IIIA; 14, total volatiles with DAA; 15, Fraction IIIA with DAA.

2.3. EFFECT ON PRODUCTION OF CONDENSABLE VOLATILES

Figure 22 shows the effects of DAA on the proportions of Fractions III and IIIA from the pyrolysis of PMA(7). Figures 23 and 24 present the same results in a rather different way by plotting the pressure of Fraction III volatiles per unit initial weight of polymer against time and percentage volatilization respectively. From Figure 23 it can be deduced that DAA reduces the rate of production of carbon dioxide and methanol by a factor of ca. 7. It is not possible to say whether DAA has a greater effect on the rate of carbon dioxide formation or on that of methanol. Calculations based on Figure 23, however, show that assuming 0.1 mg. DAA remains in the polymer melt after 2 hr. of heating at 290°C, each mole of retarder prevents the formation of about twenty times as many moles of methanol and carbon dioxide in the succeeding 6 hr. Colourimetric measurements showed that less than 0.1 mg. DAA remains in the polymer melt after 1 hr. at 290°C, and the effect of DAA is therefore much more profound than the above conservative estimate suggests. This very marked retardation of methanol and carbon dioxide evolution leaves no doubt that radical chains are involved in the sequence of reactions leading to their formation. Figure 24 illustrates that DAA is more effective in retarding Fraction III production than Fraction II production, since the amount of methanol and carbon dioxide evolved per unit weight of polymer lost is less in the presence of DAA.

2.4. EFFECT ON COLOURATION AND GEL FORMATION

As has been previously stated (Section 2.2.1., Chapter III) many PMA samples showed considerable gel formation and yellow discolouration after degradation. In experiments with DAA however, these side effects were found to be completely eliminated. Even after the last traces of colour due to DAA itself had disappeared, the polymer residue remained clear and translucent, and was always totally soluble in benzene. These observations indicate that colouration and gel formation also involve free radicals. It seems quite possible that there is a connection between colouration and gel formation. Both processes will be dealt with at greater length in Chapter V.

2.5. DISCUSSION

The following statements summarise the salient features of the experiments using the free radical inhibitor DAA.

(i). The evolution of low polymer (Fraction II) is strongly retarded by DAA. (See Figure 19).

(ii). The molecular weight changes with time and percentage volatilization are virtually unaffected by DAA. (See Figures 20 and 21).

(iii). The evolution of both carbon dioxide and methanol (Fraction III) is strongly retarded by DAA. (See Figures 22 and 23).

(iv). DAA retards Fraction III evolution more effectively than Fraction II evolution. (See Figure 24).

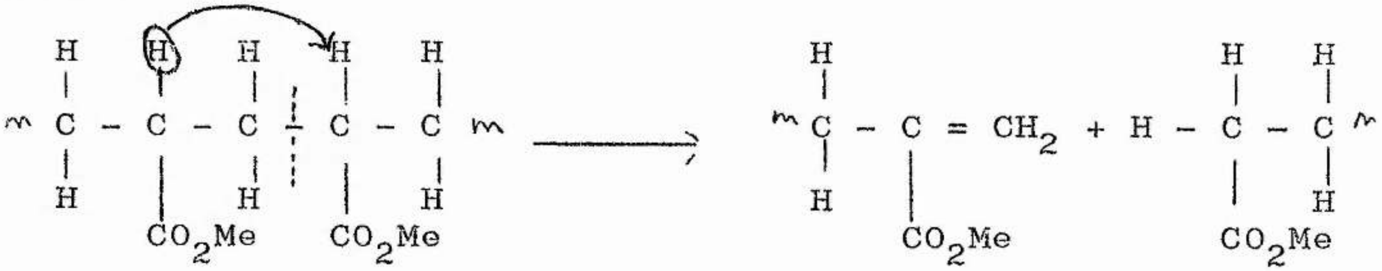
In postulating various mechanisms for the component reactions these points must be borne in mind.

Reactions in which long free radical chains are involved are frequently sensitive to trace amounts of inhibitors [79,80] which have a strong affinity for free radical centres and quickly deactivate them before appreciable reaction occurs. Under some conditions these substances retard [81,82] rather than completely inhibit free radical chain reactions. DAA is known to deactivate free radicals even at fairly elevated temperatures,[5] and the substantial effects of small amounts of this substance on the evolution of Fraction II volatiles in the present work, is a sure sign that these are produced by a free radical chain process. Therefore, the intramolecular transfer process shown in Scheme 2, (Chapter III, Section 5), provides a plausible route for the production of low polymer. Intermolecular transfer can also contribute to the formation of volatiles, but if present, would also play a considerable part in lowering the molecular weight. Any reduction in intermolecular transfer such as by DAA, would be reflected in the molecular weight versus time plot. It has been established, however, that DAA has virtually no effect on the molecular weight changes with time, and consequently intermolecular transfer must be a very infrequent process, and intramolecular transfer must be the main source of low polymer.

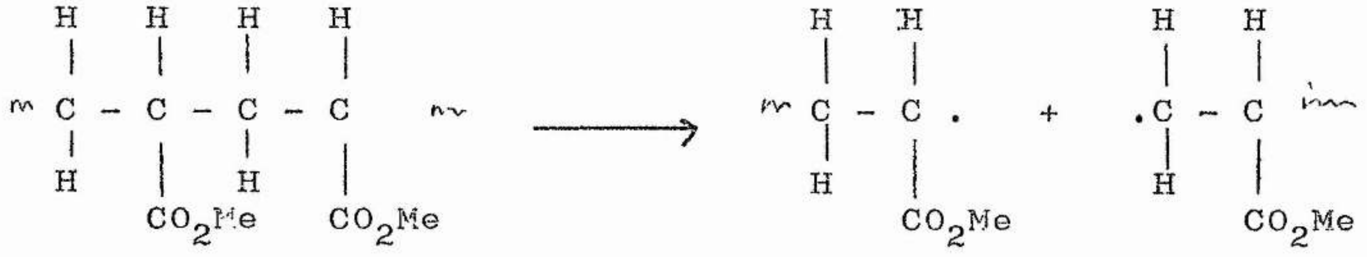
The occurrence of a crosslinking process in the degradation of PMA concurrent with chain scission and transfer will be discussed in Chapter V. It might be argued that the presence of such a combination process weakens the above conclusion in favour of predominantly intramolecular transfer processes. Since crosslinking and intermolecular transfer exert opposite influences on the molecular weight of the degrading polymer it is possible that the effects of intermolecular transfer are obscured by the crosslinking reaction in the absence of DAA. But Figures 20 and 21 show that the combined effects of crosslinking and intermolecular transfer must be virtually the same whether or not DAA is present. It seems extremely unlikely that this should be the case. Crosslinking as a radical combination reaction should be the more strongly retarded by DAA. It is obvious, however, from Figures 20 and 21 that generally the retarded molecular weight values lie <u>above</u> those obtained in the absence of DAA, showing that any crosslinking reaction has been less affected than any competing intermolecular transfer process. This effect can, in fact be most easily explained in terms of a decrease in the frequency of intramolecular processes in the absence of any significant contributions from either intermolecular transfer or crosslinking.

It is felt that these arguments indicate that neither crosslinking nor intermolecular transfer can have very important effects on the molecular weights of pyrolysed residues, and further that the present results are in fact most satisfactorily interpreted in terms of intramolecular transfer predominating after scission.

In the absence of intermolecular transfer, two mechanisms suggest themselves for the random scission of the polymer back-bone. The first is a molecular rearrangement in which a back-bone bond breaks and a hydrogen atom transfers simultaneously.



The second mechanism is a single homolytic break in the polymer back-bone giving the primary radicals (I) and (II).



(I) (II)

Neither of these reactions involves a chain of free radicals and in concordance with experimental results would occur at the same rate whether or not a radical inhibitor was present. The second process seems the more likely of the two and has the added attraction that it provides a plausible initiation step for intramolecular transfer and other free radical reactions. Indeed, this is the most reasonable initiation step as a previous discussion (Chapter III, Section 5) indicates.

Madorsky has recently suggested[10] that the rearrangement process above is probably the only one breaking the chains during the pyrolysis of PMA. The experiments with DAA definitely invalidate such a suggestion, particularly in relation to the formation of low polymer.

The picture which emerges from these considerations is one in which the molecular weight drop is due predominantly to random back-bone scission, and the weight loss to a chain of intramolecular transfer reactions. It is very probable, however, that some of the low polymer comes from random scissions, especially after extensive fragmentation of the original chains, since at that stage a random scission is more likely to occur near a chain end. The effect of DAA on the production of low polymer should therefore be less marked than on reactions which occur exclusively in a free radical chain process. In accordance with this conclusion it is observed that the evolution of Fraction III volatiles is more sensitive to DAA than the production of Fraction II.

The conclusion that the bulk of Fraction II results from intramolecular transfer also supports the suggestion made earlier, that the levelling out of the relative molecular weight versus conversion plot at a relatively early stage could be attributed to the loss of some molecules by complete "unbuttoning."

2.6. SUMMARY

It has been clearly demonstrated that DAA has a pronounced effect on the course and rate of volatilization of PMA. The results emphasise that the active species in the degradation are free radicals, and that the main transfer process occurring is an intramolecular one. It is further evident that all processes in the degradation, transfer, formation of gaseous volatiles, colouration and crosslinking can be rationalised as ramifications in an overall free radical chain reaction initiated by random homolytic bond scission of the polymer back-bone.

3. SPECTROSCOPIC EXAMINATION OF POLYMERIC DEGRADATION PRODUCTS

3.1. INFRARED MEASUREMENTS

3.1.1 Fraction I

The spectrum of undegraded PMA from 2000 - 800 $cm.^{-1}$ is shown in Figure 25. The peak positions correspond well with those obtained by Thompson and Torkington.[83] Spectra of residues pyrolysed to less than 50% volatilization barely differ from the spectrum of the undegraded polymer. Spectra of residues pyrolysed to 51.4, 63.5, 79.5, and 92.0% volatilization were taken, and studied. These spectra are essentially similar. The section of the spectrum from 2000 - 800 cm.$^{-1}$ for the 79.5% volatilized residue is shown in Figure 25 where it can be compared directly with that of the undegraded polymer. This spectrum is typical of the four samples studied. At the same time, it is very similar to that of the undegraded polymer, although in general, the peaks are less sharply defined. The only significant difference between this spectrum, and the spectrum of the undegraded polymer occurs between 1667 and 1429 cm.$^{-1}$ In this range the pyrolysed residue shows five small new peaks at 1665, 1634, 1600, 1534, and 1495 cm.$^{-1}$, the most distinctive peak occurring at 1600 cm.$^{-1}$ It is unlikely that aromatic structures could be formed in the pyrolysis of PMA, and there is no evidence of hydroxyl group absorption in the 3530 cm.$^{-1}$ range. The peak at 1600 cm.$^{-1}$ is attributed,[84] therefore, to aliphatic diene conjugation of C = C links. The peak at 1665 cm.$^{-1}$ is also associated[85] with this type of absorption as conjugated carbonyl ethylenic absorptions of esters do not appear in this range.[86] The absorption at

1634 cm.$^{-1}$ is satisfactorily accounted for by either acrylate or methacrylate C = C linkages.[87] It has not been found possible to correlate the peaks at 1530 and 1495 cm.$^{-1}$ with structures likely to be present in the degraded polymer, because of the lack of supplementary peaks in other ranges with which these absorptions might be linked. It is notable that all the new peaks detected in the spectrum of the degraded polymer were found in a range in which the absorption of the degraded polymer is at its lowest. New peaks may be masked in regions where there is general broad absorption and this may be responsible for the failure to detect supplementary peaks in ranges other than that from 1667 - 1495 cm.$^{-1}$ With this in mind, it is emphasised that the assignments already made can only be tentative.

No new absorptions occur in the range 4000 - 2000 cm.$^{-1}$

3.1.2. Fraction II

Spectra of the waxy fraction collecting on the still lid were examined. These spectra were also very similar to that of the undegraded polymer. Two new peaks were, however, obvious; one at 1630 cm.$^{-1}$, as part of a general broadening of the lower wavenumber side of the carbonyl absorption, and the other at 877 cm.$^{-1}$. The vinylic structure R_1R_2 C = CH_2 is held to be responsible for these absorptions.[86] No other new peaks were observed in the spectrum from 4000 - 800 cm.$^{-1}$

Apart from the absorptions which are satisfactorily explained by invoking C = C bonds, there was nothing else in the spectra of Fraction I or Fraction II residues which could be attributed to new structures. Aldehyde and carboxyl absorptions were not detected.

3.2. ULTRA-VIOLET MEASUREMENTS ON FRACTION I AND FRACTION II RESIDUES

Ultra-violet spectra of the undegraded PMA(7) and of a residue 64.1% volatilized are compared in Figure 26. A definite peak appears at 235 mμ in the pyrolysed residue and there is generally increased absorption in the region usually associated with the carbonyl chromophore.[88] The spectrum of the degraded sample is very similar to that of PMA subjected to photo-irradiation under vacuum conditions.[26] The evidence indicates that certain changes involving the carbonyl group must have taken place. The position of the peak maximum (235 mμ) could indicate conjugation between ethylenic and carbonyl chromophores, but since there seemed little hope of being able positively to identify the structure involved, more extensively degraded residues were not examined.

The ultra-violet spectrum of a sample of Fraction II

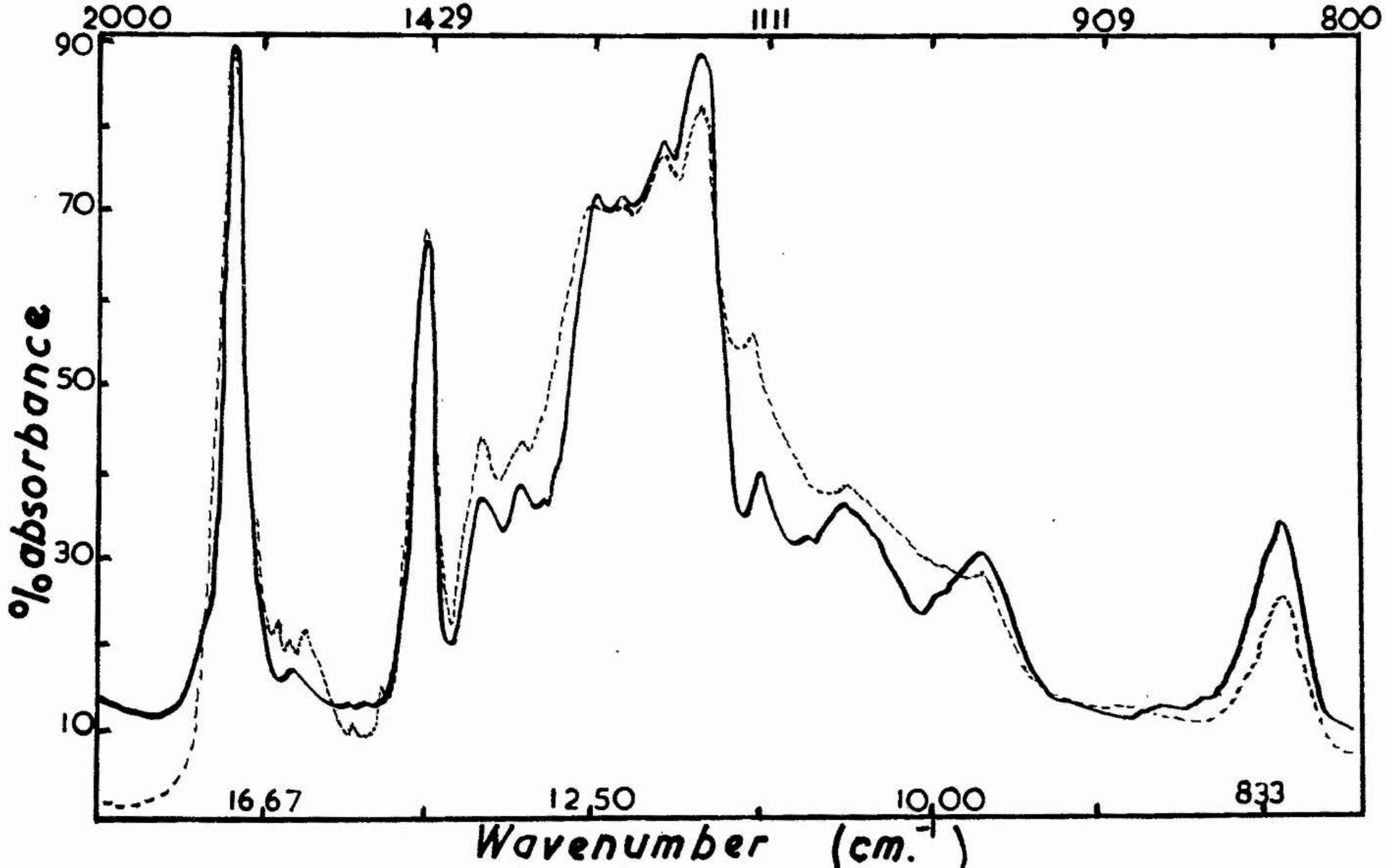


Figure 25 Section of I.R. spectrum from 2000—800 cm.$^{-1}$ of undegraded and degraded PMA (2) Undegraded, ——— ; 79.5 % pyrolysed, - - - - - - .

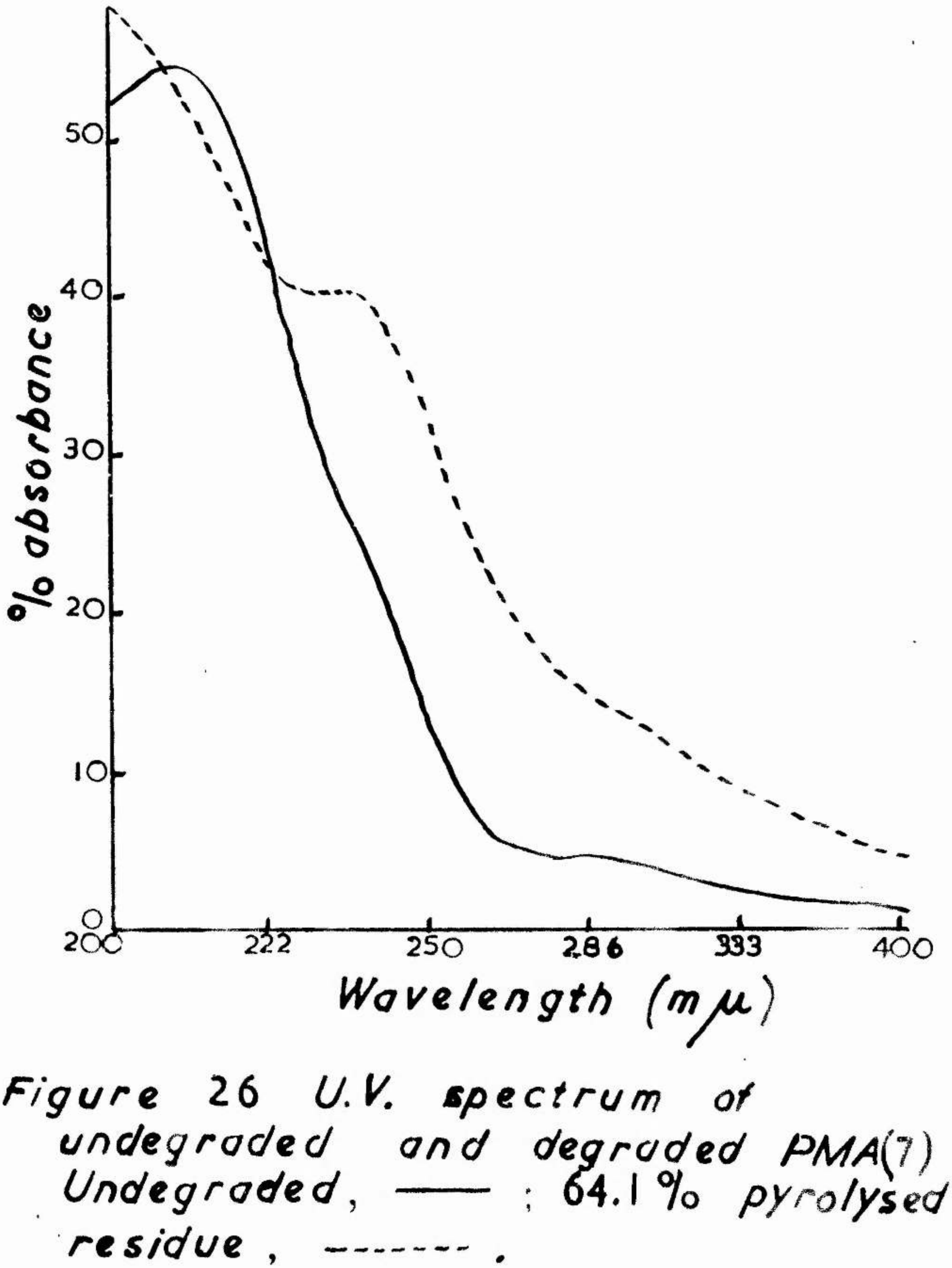


Figure 26 U.V. spectrum of undegraded and degraded PMA(7)
Undegraded, —— ; 64.1 % pyrolysed residue, ------- .

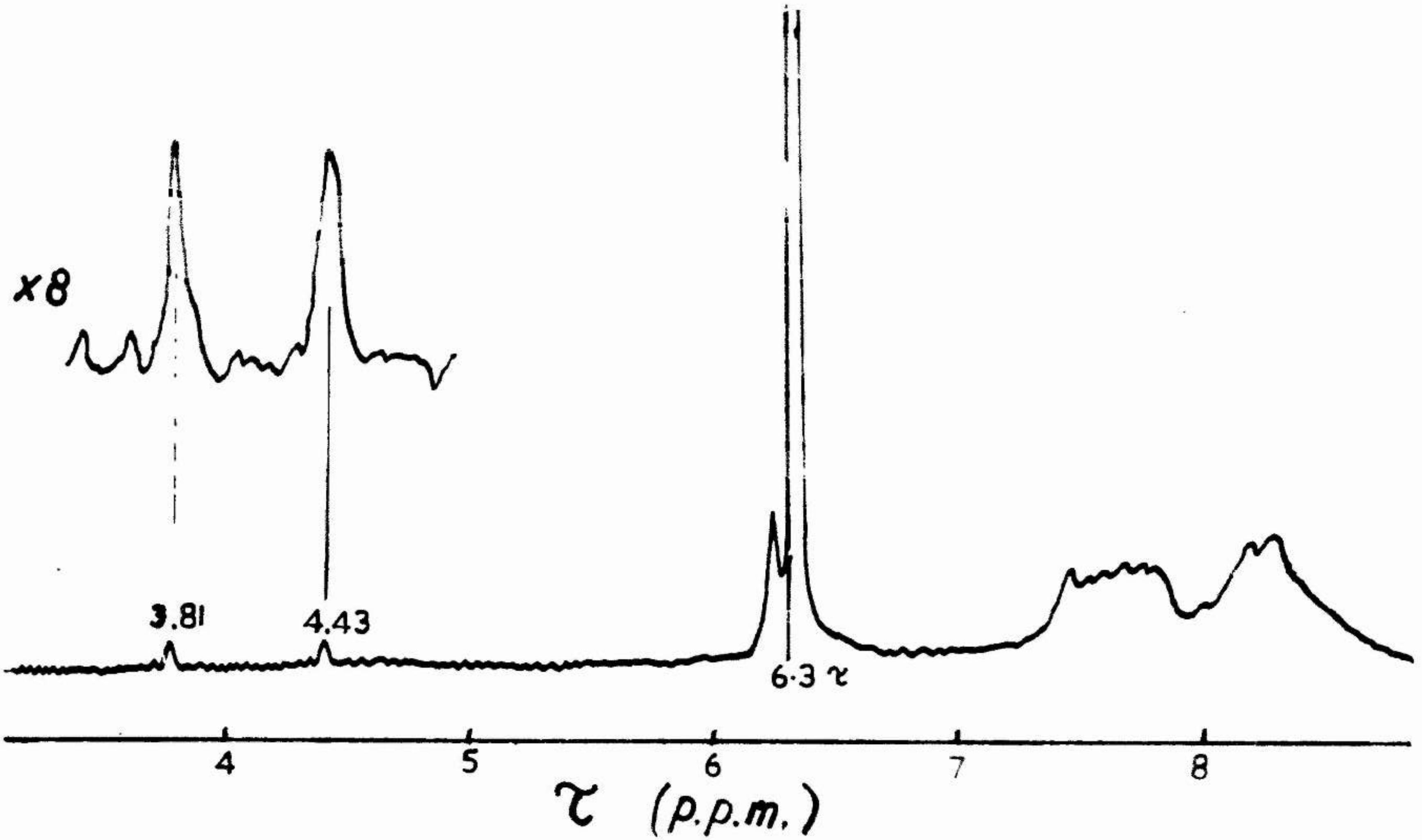


Figure 27 N.M.R. spectrum of a Fraction II residue from PMA(2)

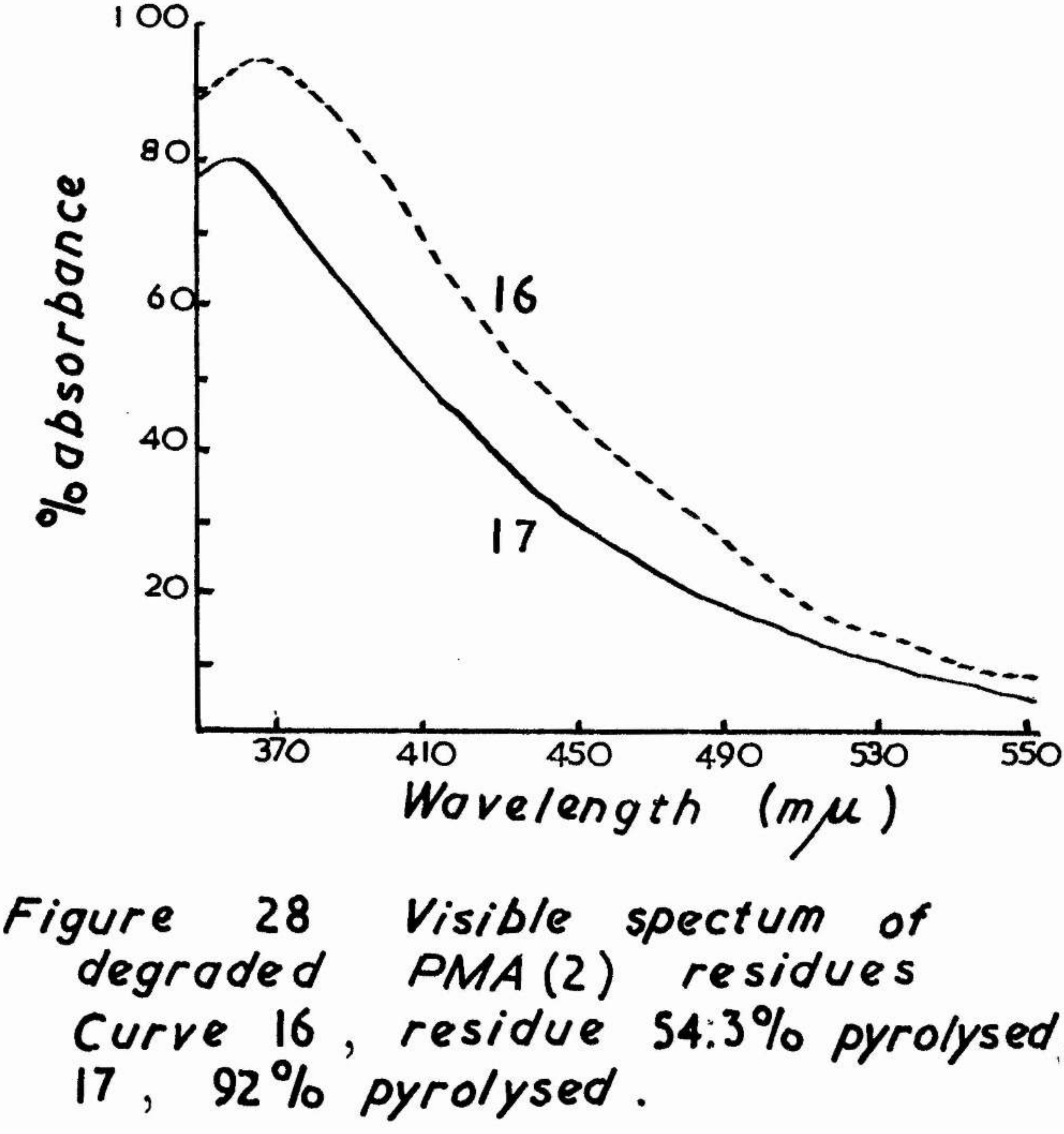


Figure 28 Visible spectum of degraded PMA (2) residues Curve 16, residue 54.3% pyrolysed; 17, 92% pyrolysed.

was virtually identical to that of Fraction I. A maximum also appeared at 235 mμ.

3.3. NUCLEAR MAGNETIC RESONANCE MEASUREMENTS

3.3.1. Fraction I

Undegraded PMA contains three types of protons. Protons of the methoxyl group were located at 6.32 ± 0.02 τ. The peaks for chain protons are very broad, the maximum for methine protons occurring near 7.7 , and that for methylene protons near 8.2 τ. No new peaks were detected from 0 - 10 τ in the spectra of pyrolysed residues which showed peaks only in the three positions discussed above. Residues pyrolysed to 50.0, 64.1, and 79.5% were examined. Semi-quantitative estimates of peak areas obtained either by electronic integration or weighing of cut out peaks are noted in Table 17 below. The results show clearly that the numerical ratio of methoxyl to chain protons decreases as volatilization increases.

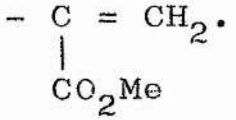
Table 17

Ratio of methoxyl to chain protons in Fraction I residues of PMA(2)

Run	% volat.	Peak Areas (area units)		No. OMe protons
		OMe, 6.32 τ	chain, 7-9 τ	No. chain protons
–	0.0	7.5	7.2	1.04
125	50.0	3.6	3.8	0.95
126	64.1	2.9	3.8	0.76
111	79.5	4.6	7.15	0.64

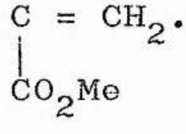
3.3.2. Fraction II

A typical N.M.R. spectrum of a Fraction II sample is shown in Figure 27. In contrast to the spectra of the degraded polymer, and of the pyrolysed Fraction I residues, this spectrum shows two new peaks at 3.81 and 4.43 τ. These peaks are unambiguously characteristic[89] of the terminal methylenic structure



$-\underset{\displaystyle CO_2Me}{\underset{|}{C}} = CH_2$.

The size of each ethylenic proton absorption peak is comparable to that of the peak caused by the absorption of chloroform in the deuterochloroform. Chloroform comprises approximately 1% of commercial deuterochloroform. The molar concentration of the polymer in deuterochloroform was known, and therefore it was possible to estimate that there is about one double bond per Fraction II molecule. This result is confirmed in a more rigorous way as follows. The small peak at 6.25 τ on the side of the main methoxyl proton peak is attributed to absorption by methoxyl protons in an ester group attached to a doubly bound carbon i.e.



$-\underset{\displaystyle CO_2Me}{\underset{|}{C}} = CH_2$.

Horizontal scale expansion and integration indicated that one ester group in seven is like this. As there are, on average, eight methyl acrylate units in the short chain fragments (Mn = 704) there must indeed be about one double bond per Fraction II molecule.

The ratio of methoxyl to chain protons in Fraction II residues obtained from extensively degraded samples was also studied. This ratio is very nearly independent of conversion (Table 18). Certainly the ratio does not decrease so obviously as that for Fraction I residues.

Table 18

Ratio of methoxyl to chain protons in Fraction II residues from PMA(2)

Run	% volat.	Peak Areas (area units)		No. OMe protons / No. chain protons
		OMe 6.32 τ	chain 7-9 τ	
–	0.0	7.5	7.2	1.04
125	50.0	7.3	7.0	1.04
126	64.1	2.2	2.3	.96
112	92	7.1	6.9	1.03

3.4. VISIBLE SPECTRAL MEASUREMENTS

The visible spectra of two Fraction I residues are shown in Figure 28. Spectra of a sample of Fraction II and a polymer sample in which colouration was produced by rapid aging (Chapter V, Section 2.4.2.) were also studied. The colour of the residues and the position of maximum absorptions for the four are listed below (Table 19).

Table 19

Maximum absorption (λ max.) values and colours of degraded PMA(2) samples

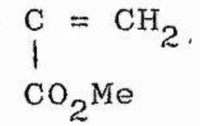
Run	Sample	Colour	λ max. mμ.
144	Fraction I 53.2% volat.	yellow	363
112	Fraction I 92% volat.	dark brown	358
146	Fraction II	pale yellow	362
A	Aged PMA (2)	deep yellow	368

The position of the maximum, λ max., was observed to vary slightly with the concentration of the polymer solution.

The results of experiments 144 and 112 show that there is no bathychromic shift of absorption occurring as volatilization increases. This is clear evidence that long chains of conjugated polyene units do not form in the degradation of PMA. The two other results, taken in conjunction with this conclusion emphasise that it is a change in intensity of absorption rather than a change in fundamental wavelength of absorption that causes the apparent colour changes.

That a maximum is observed at all is rather surprising as no maximum was evident around 360 mμ in the ultra-violet spectra of degraded polymers. (See Section 3.2., this chapter). There is, however, some absorption at 360 mμ in the ultra-violet spectra. It is thought that the very strong absorption around 360 mμ in the visible spectrum allows the detection of a shoulder or small peak, which cannot be distinctly defined at the same position in the ultra-violet spectrum where absorption is much less intense.

3.5. DISCUSSION

The only new structures which these spectrometric measurements clearly identify are the terminal double bonds. Obviously the colouration is due to some other new structures, and although these have not been positively identified it is thought that isolated conjugated $- C = C - C = C -$ structures may be responsible. The stronger absorption of the peaks at 1665 and 1600 cm.$^{-1}$ compared to that of the terminal double bond absorption at 1634 cm.$^{-1}$ is attributed not to a numerical superiority of $- C = C - C = C -$ structures over  $-\underset{\displaystyle CO_2Me}{\underset{|}{C}} = CH_2$ structures, but, in fact, to the very much more intense absorption [86] of the conjugated linkage.

The techniques used in this investigation are apparently not sufficiently sensitive to define, even at advanced stages of degradation, any other new structures produced.

A study of the rate of degradation of poly (ethyl acrylate) [51] supports this conclusion. Conley [51] has examined the degradation of poly (ethyl acrylate) by following the decrease in absorption of peaks in the whole range of the I.R. spectrum. In neither oxygen nor helium could he detect the functionality of new structures produced at 230°C. He concluded that any new groups formed were of insufficient concentration to be detected, or were masked by the vibrational bands due to ester linkages. He noted that all absorption bands decreased at the same rate and postulated, therefore, a completely random degradation. A notable feature of his investigation concerned the production of carbon dioxide and ethanol. These components were easily detected in the oxidative breakdown, but only minute traces could be found when the degradation was carried out in helium. He concluded that the carbon dioxide and ethanol were formed as products of combined thermal and oxidative degradation.

The present and previous [50,66] degradations of PMA, which gave evidence of appreciable amounts of carbon dioxide and methanol, were carried out at temperatures in excess of 270°C. It is likely that the difference in quantity of gaseous volatiles produced in the vacuum pyrolyses of poly (ethyl acrylate) and PMA, is due to the higher temperatures employed in the degradation of the latter bringing about greater fragmentation of new structures formed in radical reactions.

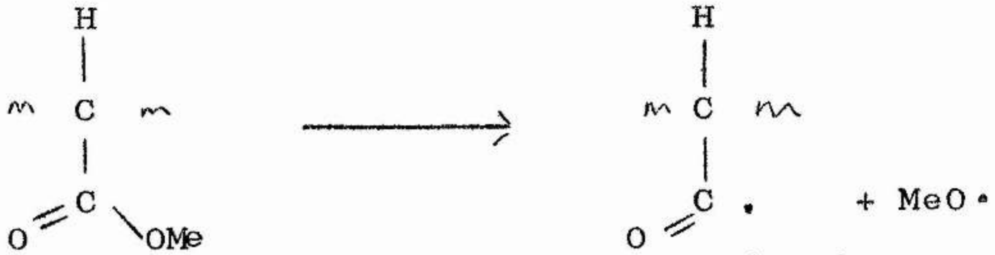
Despite the apparent minor amounts of carbon dioxide and methanol in the products of degradation of PMA, the discussion which follows, in Section 4., has been made fairly extensive, firstly because the quantities of these products are unusually high for a polymer degradation and secondly, because they indicate the occurrence of a rather novel ester decomposition. This unusual type of breakdown might well be a consequence of the polymeric environment of the ester groups.

4. FORMATION OF METHANOL AND CARBON DIOXIDE; POSSIBLE MECHANISMS

The thermal breakdown of methyl esters is complex, studies [90] of decomposition reactions of methyl esters of saturated monobasic and of saturated α, ω dibasic acids containing from four to eight methylene groups in the chain have shown that methylene chain scission is the important primary reaction, and that competing reactions involving radical breakdown of the methyl ester group are relatively minor. Methyl acrylate was the principle product in these pyrolyses which were carried out around 500°C.

In the degradation of PMA, the evidence shows that methanol and carbon dioxide are produced in reactions involving free radicals. The present results suggest that they are produced in entirely different processes, rather than as parts of one particular sequence of steps, since they are not evolved in equimolar proportions.

The most obvious route for the production of methanol is straightforward ether link scission thus :-



(III)

but such a mechanism receives little support from the experimental facts.

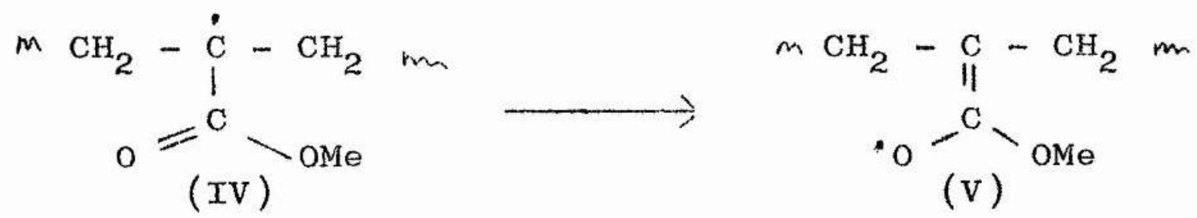
Firstly, DAA could not inhibit the production of methyoxyl radicals by this simple scheme, although by a combination process it could prevent these radicals from extracting hydrogen. However, after 2 hr. of degradation there is insufficient DAA left in the polymer melt to sustain such a process, (see Section 2.4., this chapter), and the rate of evolution of methanol should rapidly return to the unretarded value. Secondly, PMMA might reasonably be expected to undergo a similar process but pyrolysis produces monomer almost exclusively. [5] The final point which strongly supports the arguments against such a mechanism concerns the stability of the carbonyl radical which would be formed, and the relative amounts of methanol and carbon monoxide in the products of degradation. The acetyl radical $CH_3\underset{\bullet}{C} = O$, which is the simplest analogue of the carbonyl radical (III) in the above mechanism, is known to be extremely unstable. [91] In fact, its decomposition is essentially complete in the gas phase at 120°C as follows, [92]

$$CH_3 - \dot{C} = O \xrightarrow{120^{\circ}} CH_3\cdot + CO$$

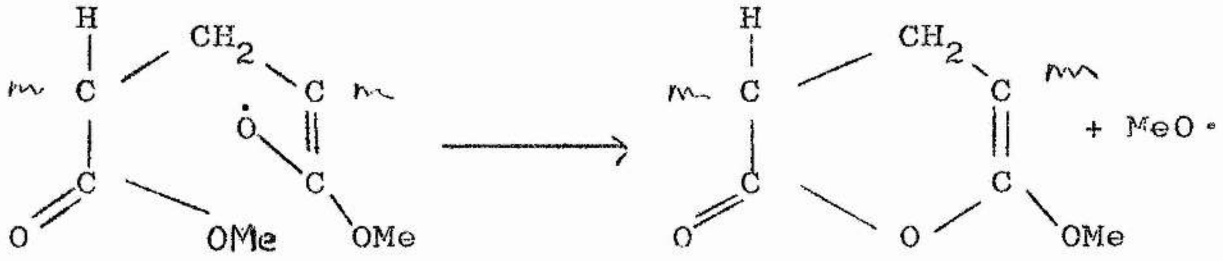
Obviously caution is necessary when correlating this gas phase breakdown with the behaviour of a related carbonyl radical in a polymer melt. Nevertheless, there seems no reason why the carbonyl radical (III) should be stable around 300°C in a polymer system and therefore, if methanol were produced by such a mechanism, then equimolar amounts of carbon monoxide should also be obtained. In the present and previous investigations, the molar ratio of methanol to carbon monoxide in the degradation products is vastly in excess of unity. Thus, there can be little doubt that a methoxyl radical is not produced by straightforward bond scission. This question of stability of carbonyl radicals means that any mechanism of methanol production involving carbonyl radical intermediates must also be regarded sceptically.

The reactivity of the methoxyl radical lies midway between that of a methyl radical and that of a chlorine atom,[93] and there is no reason to suppose that methanol cannot be produced by the formation of a methoxyl radical and then a subsequent abstraction of a hydrogen atom. The experiments of McBay [94,95] have shown that for the methoxyl radical in solution at 130°C abstraction of the most labile hydrogen atom available is the most likely and almost the only course of reaction.

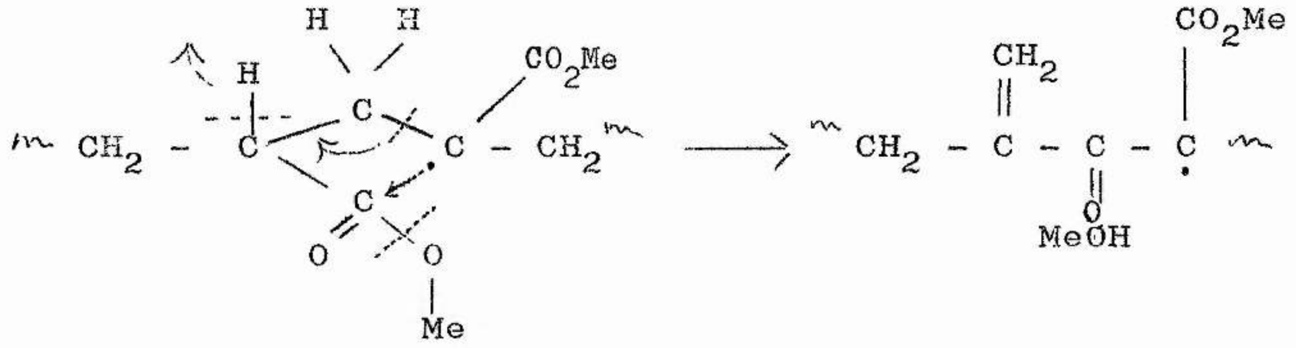
It is obviously not wise to attempt to deduce too much by comparing the depolymerisation process in PMMA with the reactions occurring in the degradation of PMA. The ease of monomer production in PMMA might render any competing process of negligible importance. However, it seems possible that the primary radicals (I) and (II), (see Section 2.6., this chapter), produced by the initiation step in PMA, are not directly responsible for the methanol and carbon dioxide production, and in this case then, that the tertiary radical (IV) and its resonance mesomer (V) are vitally involved in the production of these gaseous volatiles.



Any mechanism suggested for the production of methanol and carbon dioxide must fit in with the observed facts. Among the more plausible explanations for the formation of methanol are Schemes 3 and 4 below.



Scheme 3.

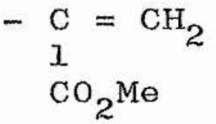


Scheme 4

Scheme 4 involves a bond rearrangement proceeding through a four-membered ring transition state. Radical attack on the carbonyl carbon atom is simultaneous with bond scissions which bring about the elimination of methanol from the structure. The new radical formed may abstract a hydrogen to give a substituted vinyl ketone structure. Both this structure and the vinyl ether structure formed in Scheme 3 would contribute to the general broadening of the I.R. carbonyl absorption. In particular, the vinyl ether structure could cause some of the new increased absorption around 1610 cm.,$^{-1}$ [87] and might be responsible for the peak at 1530 cm.$^{-1}$ [85] The stability of such new structures around 300°C is difficult to assess, but certainly, it would be very difficult to obtain positive evidence for the existence of small numbers of such structures in company with ester linkages.

One promising mechanism for the production of methanol, involving the formation of a ketene and a methoxyl radical (Scheme 5), has been eliminated. The infrared evidence showed that there was definitely none of the characteristic (2160 cm.$^{-1}$) ketene absorption [96] in the degraded residues.

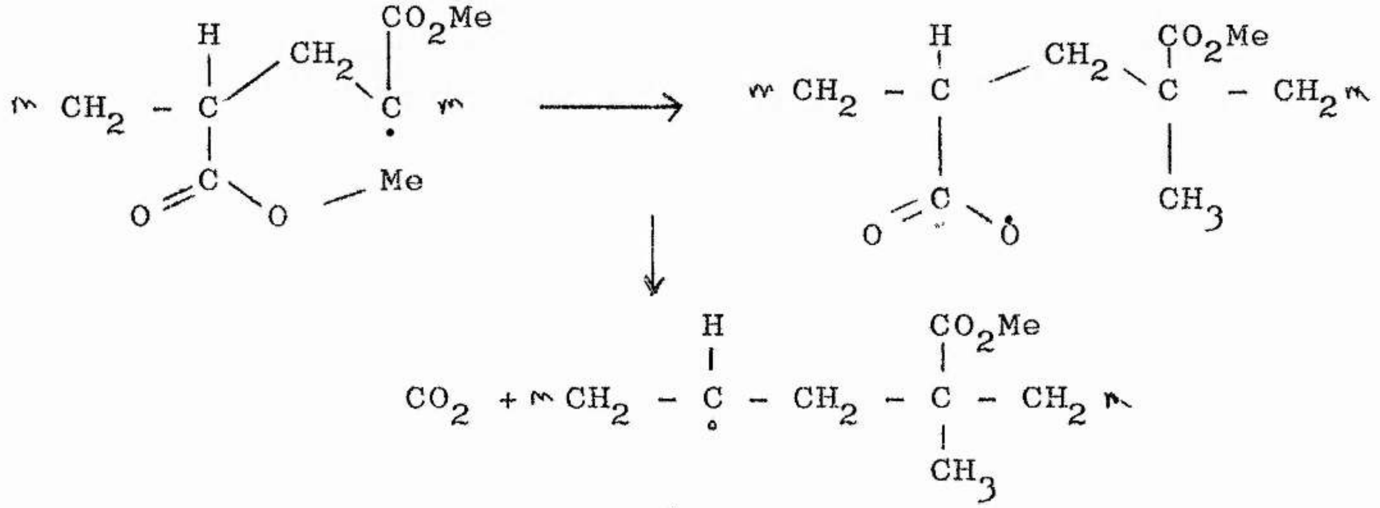
Scheme 5

The effect which either of the possible new structures (in Schemes 3 and 4) would have on the ultra-violet spectrum of the degraded polymer is more difficult to judge, because there is an absence of ultra-violet absorption measurements on structures of this precise nature. The vinyl ether (Scheme 3) which, in addition, is part of a lactone ring can best be compared with related unsatured lactones. [97] The comparison indicates that the vinyl ether would probably not give a peak at 235 mµ, although it could contribute to the generally increased absorption between 230 and 280 mµ. The ketone, as a substituted α, β unsaturated enone would be expected to have a peak maximum around 224 mµ. [88] As methyl methacrylate itself shows no absorption maximum around 235 mµ [98] it is fairly certain that the terminal methylenic structure 

$$-\underset{\substack{|\\ CO_2Me}}{C}=CH_2$$

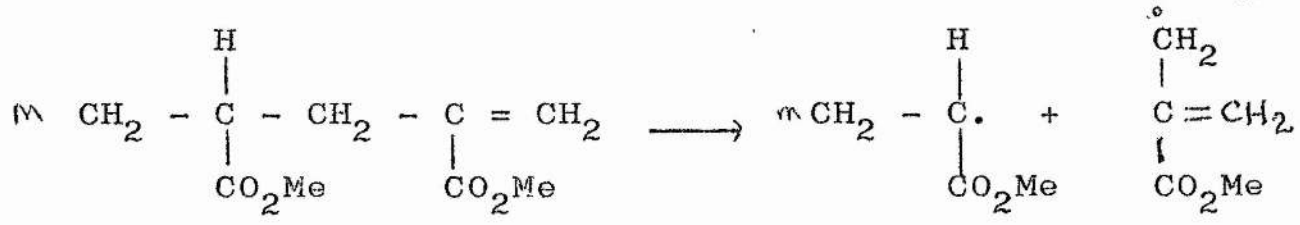
can also be ruled out as the cause of the peak at 235 mμ. A conjugated diene function $- C = C - C = C -$ is thought to be responsible for this absorption maximum.[88]

Carbon dioxide is also produced largely in a free radical chain reaction. It is possible that the mechanism is similar to that suggested by Fox *et al.*[26] for the evolution of carbon dioxide in the photodegradation of PMA, that is :-



Scheme 6

One criticism of Scheme 6 is that there is no known analogue in another system, in which the migration of a methyl radical is involved. It is noteworthy, however, that Scheme 6 introduces the methyl methacrylate unit into the polymer chain, thus accounting for its appearance in small amounts among the reaction products. This monomer may also be formed at chain ends in a reaction of the type :-



$$\sim CH_2-\overset{H}{\underset{CO_2Me}{C}}-CH_2-\underset{CO_2Me}{C}=CH_2 \longrightarrow \sim CH_2-\overset{H}{\underset{CO_2Me}{\dot{C}}} + \underset{CO_2Me}{\overset{\dot{C}H_2}{C}}=CH_2$$

The radical decomposition of esters consists frequently of a number of competing processes [99] rather than a single definitive mode of breakdown. The pyrolysis of PMA is very likely to follow this type of pattern since it has been shown that no single process for the production of either carbon dioxide or methanol appears particularly likely. In the absence of further detailed information, the routes of formation suggested above must be regarded as highly speculative.

5. TABLES OF EXPERIMENTAL RESULTS

Tables 20 and 21

Degradations of PMA(7) at 290°C without copper powder. Values plotted in Figures 19, 22, 23, and 24.

Table 20

Unretarded degradations

Run	T.O.H. hr.	S.I.W. mg.	Wt. loss mg.	% C.	C.M.R. cm.Hg		10^{-1} C.M.R./S.I.W. cm.Hg/g.	
					Fr.IIIA	Fr.III A+B	Fr.IIIA	Fr.III A+B
90	2.0	47.6	2.5	5.3	1.4	2.5	2.9	5.25
91	3.0	47.0	5.4	11.5	1.9	3.4	4.0	7.15
89	4.0	47.9	8.4	17.5	–	–	–	–
106	4.0	46.7	8.7	18.6	–	–	–	–
93	5.5	37.8	9.0	23.8	–	–	–	–
94	7.5	35.6	9.5	26.1	–	–	–	–
101	7.5	48.0	13.0	27.1	2.9	6.85	6.1	14.3
107	8.0	48.5	14.5	29.9	5.05	7.85	10.4	16.2

Abbreviation; C., volatilization.

Table 21

Degradations retarded by 2 mg. DAA

					C.M.R. cm.Hg		10^{-1}C.M.R./S.I.W. cm.Hg/g.	
Run	T.O.H. hr.	S.I.W. mg.	Wt. loss mg.	% C.	Fr. IIIA	Fr.III A+B	Fr.IIIA	Fr.III A+B
96	1.0	41.8	1.1	2.7	0.3	0.55	0.7	1.3
95	3.0	40.1	2.6	6.4	–	–	–	–
108	4.0	46.6	3.3	7.2	–	–	–	–
100	5.0	47.8	4.4	9.2	0.55	0.80	1.15	1.7
109	6.0	48.8	6.6	13.5	0.75	1.45	1.5	3.0
99	7.0	50.5	10.3	20.4	–	–	–	–
98	8.5	48.0	10.4	21.7	0.85	1.55	1.8	3.2

Table 22

Molecular weight changes with time and percentage volatilization for retarded degradations of PMA(7) at 290°
Copper powder present; 2 mg. DAA present.
Results plotted in Figures 20 and 21.

Run	T.O.H. hr.	S.I.W. mg.	Wt. loss mg.	%C.	10^{-3} x M_v
54	1.0	96.9	1.2	1.2	107
57	2.0	92.3	3.0	3.2	97.7
56	3.0	90.8	7.4	8.2	69.3
53	4.5	95.7	13.3	13.9	51.3
55	6.0	90.3	15.8	17.5	50.2

The values of molecular weight against percentage volatilization and time of heating for unretarded degradations of PMA(7) at 290°C, from Table 16, are also plotted in Figures 20 and 21 respectively.

CHAPTER V

THERMAL DEGRADATION OF PMA, PART III. GEL FORMATION AND COLOURATION DURING PYROLYSIS

1. INTRODUCTION

Mention has been made in previous chapters of an insoluble gel which formed in the pyrolysed residues during degradation, and of the development of a yellow colouration which accompanied this.

At the beginning of degradation studies on PMA(7), in order to conserve the sample, preliminary runs to check heater voltages and reproducibility of volatilization were carried out using samples of PMA(2) and PMA(3). Pyrolysed residues from both of these samples became distinctly yellow and had developed insolubility at moderate degrees of volatilization. These pyrolysis effects were initially absent from PMA(7).

The presence of the gel indicated a crosslinking reaction superimposed upon chain scission. Initial investigations of the gel formation have already been described.[100] The results are summarised in Table 23.
The proportion of the gel in the polymer residue increased with the degree of volatilization. The results suggested that the amount of gel formed was not simply related to the initial molecular weight of the sample, nor to the degree of conversion in polymerisation within the range studied, but rather was connected with the temperature of polymerisation.

Table 23

Preliminary investigations of gel formation reaction

PMA Sample	Temp. of polym. °C	Conversion %	Diluent	Initial M.W.	%volat. at286°C	% gel in residue
(3)	60	22	Benzene	2.7×10^6	10.1	17.8
					18.3	37.8
					19.8	38.5
(2)	55	23	MeAc	3.2×10^6	12.9	1.0
					30.6	1.3
					40.8	7.5
(7)	45	12	PhEt	3.2×10^5	8.8	0
					20.4	0
					37.1	0

It was thought that the effect might be caused by subtle differences in structure such as differing degrees of branching.

The most significant aspect, however, of both the colouration and the gel formation is that they indicate quite clearly that reactions other than simple chain scissions, transfers, and side group breakdowns are occurring within the degradation of PMA.

This chapter describes the further investigation of some features of the gel formation and colouration.

2. FACTORS AFFECTING EXTENT OF GELATION

2.1. EXTENT OF VOLATILIZATION

It has already been shown that the extent of gel formation increases with percentage volatilization of the residue.

This effect was demonstrated much more clearly by a series of degradations on PMA(19). The results are plotted in Figure 29, which shows that percentage insolubility is proportional to percentage volatilization, at least as far as 45% conversion. This relationship allows the weight of insoluble material (assuming a sample initial weight of 100 mg.) to be calculated. Weight of insoluble material for degradations of 100 mg. samples is plotted against percentage volatilization in Figure 29.

2.2. TEMPERATURE OF DEGRADATION

The temperature of degradation has a profound effect on the extent of gelation, and this is shown by the results listed in Table 24. The pyrolysed residues of two different samples degraded at 290°C have fair degrees of insolubility. At degradation temperatures of 320 and 330°C, the pyrolysed residues of the same two samples are completely soluble, despite the fact that there has been a higher degree of conversion.

Table 24

Effect of temperature of degradation on percentage insolubility

Run	Sample	Temp. °C	T.O.H. hr.	S.I.W. mg.	Wt. loss mg.	% C.	% insol.
161	22	290	6.0	96.5	18.9	19.6	23.0
163	22	330	0.9	89.6	23.4	26.1	0.0
162	25	290	6.0	98.2	19.6	20.0	41.1
166	25	320	0.8	104.5	32.1	30.9	0.0

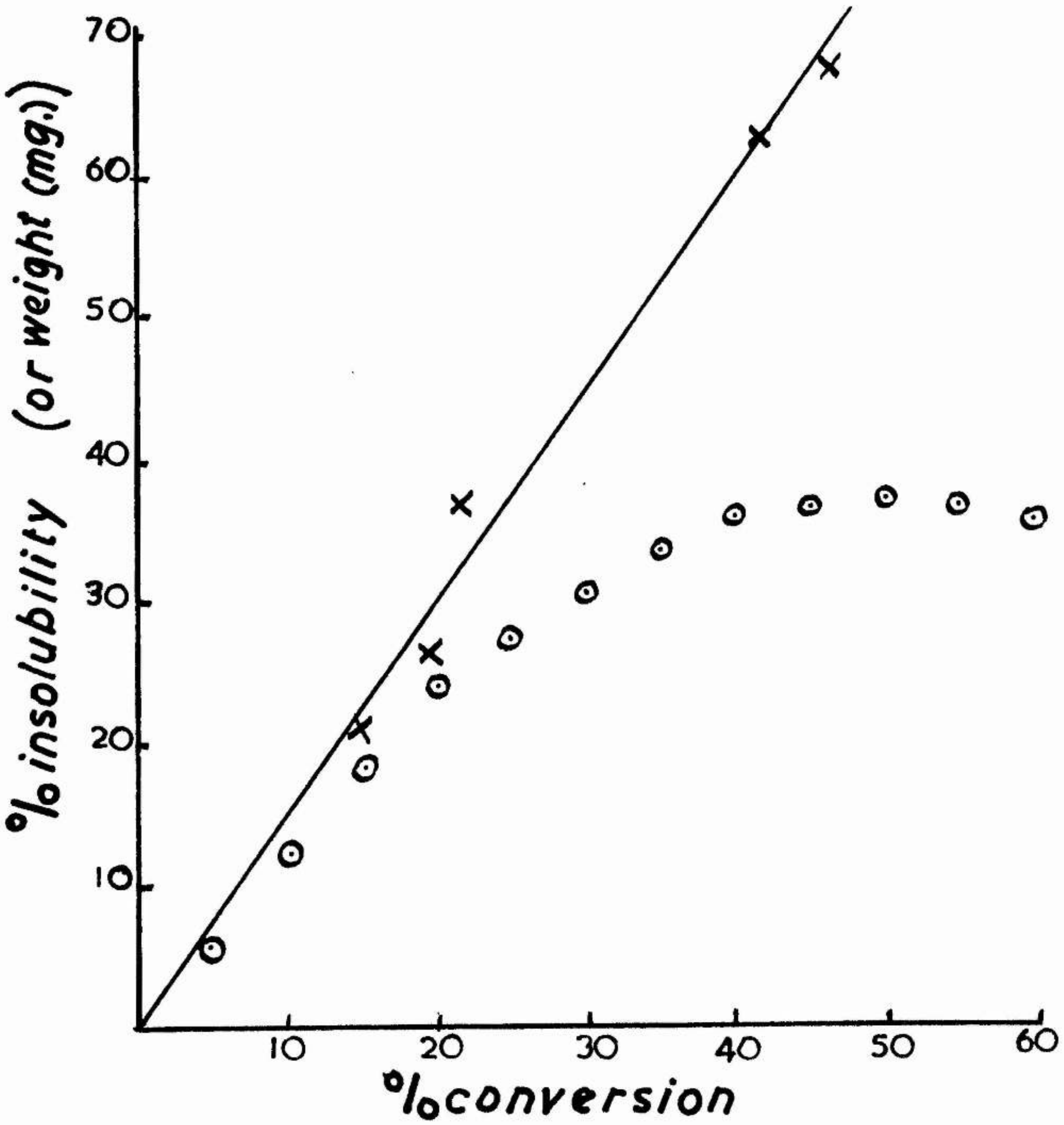


Figure 2.9 Percentage insolubility against percentage volatilization for degradation of PMA (19) at 290°C (The weight of gel which therefore forms from 100 mg. PMA (19) is also plotted against percentage volatilization). ×, percentage insolubility; ⊙, weight of gel from 100 mg. sample.

Although gel formation was absent at higher temperatures the discolouration of residues was still apparent.

2.3. CONDITIONS OF PREPARATION

The preliminary investigations of gel formation had indicated that the temperature of sample preparation might have an effect on the extent of gel formation during pyrolysis, possibly due to differing degrees of branching within the samples. Investigations concerned with the effect of variation in sample preparation conditions on the gel formation during pyrolysis are described below.

2.3.1. Effect of diluent and polymerisation temperature

In a polymerisation process chain transfer of propagating radicals to monomer, diluent, and polymer chains can take place. Transfer to monomer is insignificant in the polymerisation of methyl acrylate,[101] and the main transfer process in the absence of a labile hydrogen atom in the diluent involves abstraction of a tertiary hydrogen atom from the polymer chain, and hence the introduction of branches into the polymer molecule. Compared with methyl acetate, ethyl benzene is a good transfer agent, since it has two relatively labile hydrogen atoms.

Polymer samples were prepared at 40, 55, and 70°C in both methyl acetate and ethyl benzene. Details of preparation of this IF group of polymers are available in Table 3, (Chapter II, Section 5.), but the most relevant data will be included for convenient reference in Table 25. During the preparation of this 1F group of polymers, great care was taken to ensure that within each set of three the temperature of preparation was the only variable. For this reason, all the monomer used in the preparation of the 1F polymers (11), (12), (13), (17), (18), and (19) was from one distillation batch, and each polymerisation was taken to the same degree of conversion (20%). The effect of temperature and of the differing chain transfer constants on the molecular weights of polymer samples is obvious from Table 25, and it is highly probable that the concentration of branches will be greater in the methyl acetate polymers (11), (12), and (13).

Each polymer in the group was pyrolysed to near 20% volatilization at 290°C, and the percentage insolubility determined. By making in each case, a small correction, using the linear relationship between percentage insolubility and percentage volatilization, values of percentage insolubility for 20% volatilization at 290°C (G_{20}) were found. (See Table 25). The gel forming tendency of each polymer at 290°C is reflected in the corrected insolubility (G_{20}) values which are plotted against temperature of preparation in Figure 30. The profiles of these plots were surprising, particularly the minimum in the curve for the three polymers prepared in ethyl benzene, and the high G_{20} values for the sample prepared in methyl acetate at the lowest temperature, 40^{o}.

Table 25

Preparation details and degradation results for 1F group of polymer samples. Samples prepared to 20% conversion; degradations at 290°C

Sample	Temp. of polym °C	$10^{-5} \times M_n$	Run	T.O.H. hr.	% volat.	% insol.	G_{20}
Polymers prepared in methyl acetate							
11	40	22	145	9.0	27.0	30.9	22.9
12	55	15.5	141	1.5	25.0	30.8	24.7
13	70	4.6	140	1.7	24.4	68.7	56.5
Polymers prepared in ethyl benzene							
17	40	1.55	137	6.0	23.4	47.1	42.1
18	55	1.37	133	6.0	20.7	22.1	21.4
19	70	1.20	143	3.0	19.5	26.4	27.1

No correlation between gel forming tendency and molecular weight or rate of volatilization was apparent for this group of polymers. Despite the inconclusive nature of the results in themselves, it was felt that these experiments did indicate, for a second time, that there might be some relation between gel formation and temperature of preparation.

2.3.2. Effect of conversion and polymerisation temperature

To obtain additional information on the effects of sample preparation on degradation characteristics, and if possible either to verify, or invalidate the results which had already been obtained, a new group (2F) of two sets of polymers was

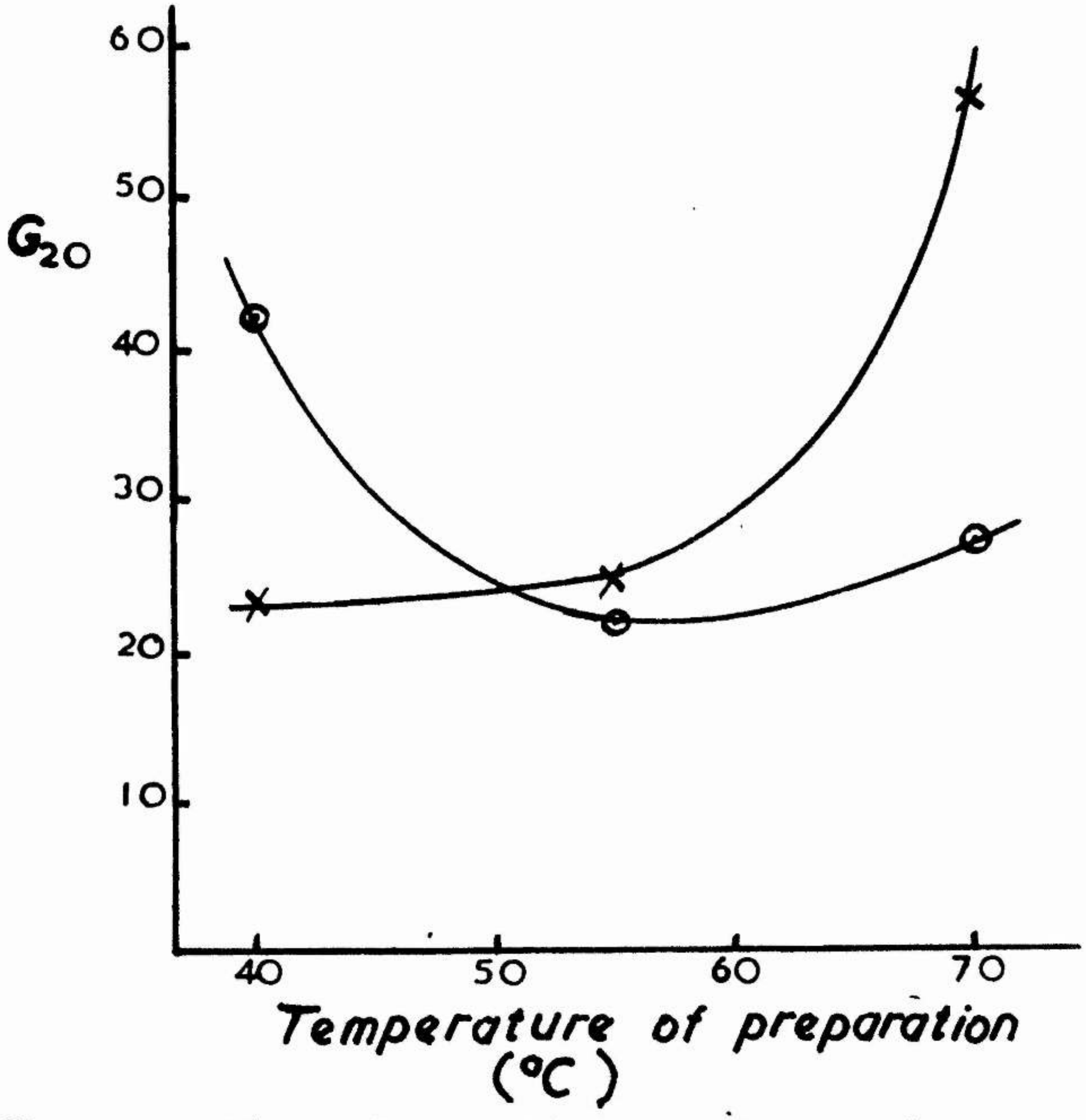


Figure 30 Percentage insolubility for 20% volatilization at 290°C (G_{20}) against temperature of preparation of 1F polymers

×, MeAc as diluent ; ⊙, PhEt as diluent.

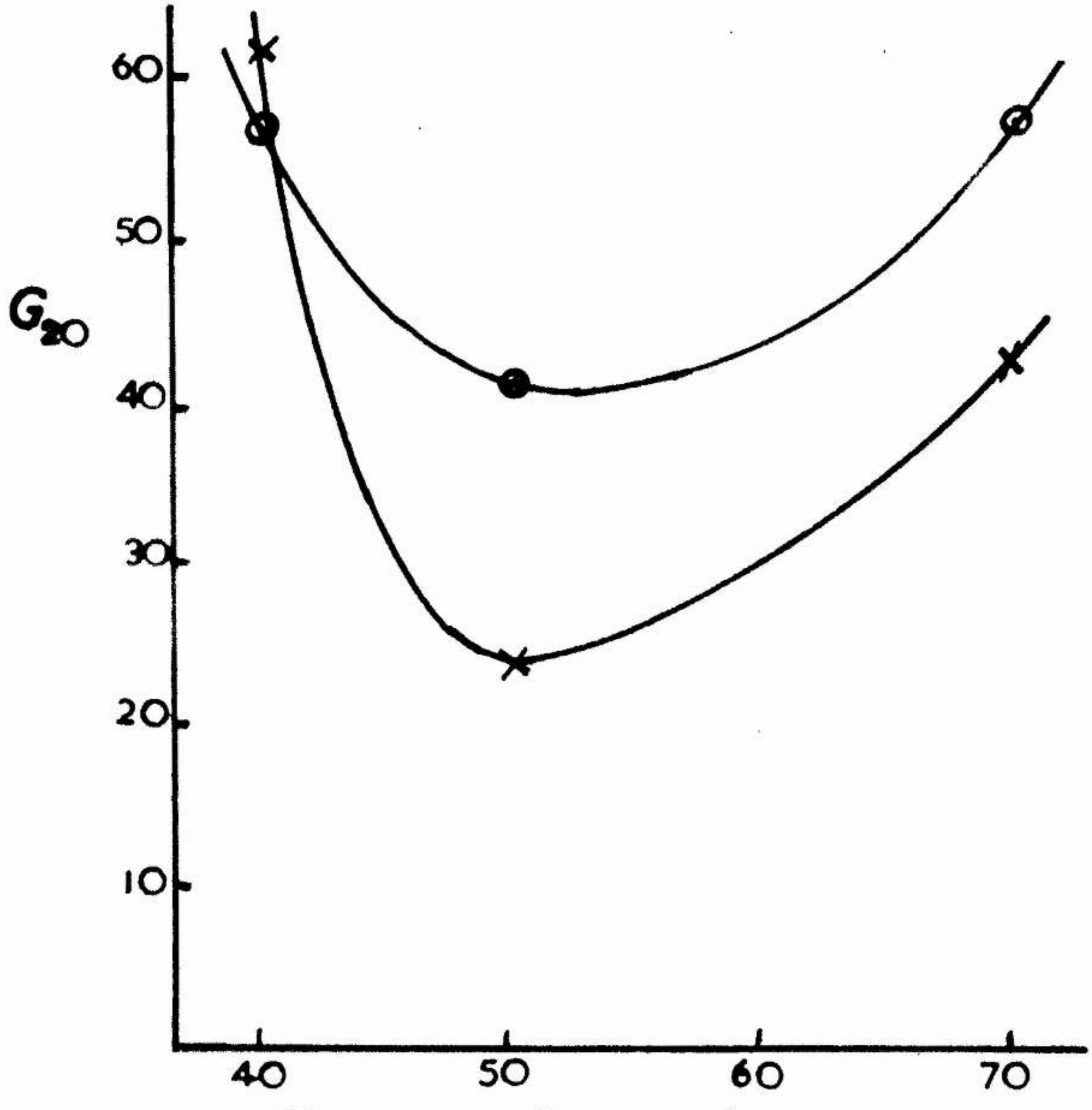


Figure 31 Percentage insolubility for 20% volatilization at 290°C (G_{20}) against temperature of preparation of 2F polymers. ×, samples prepared to 10% conversion; ⊙, to 70% conversion.

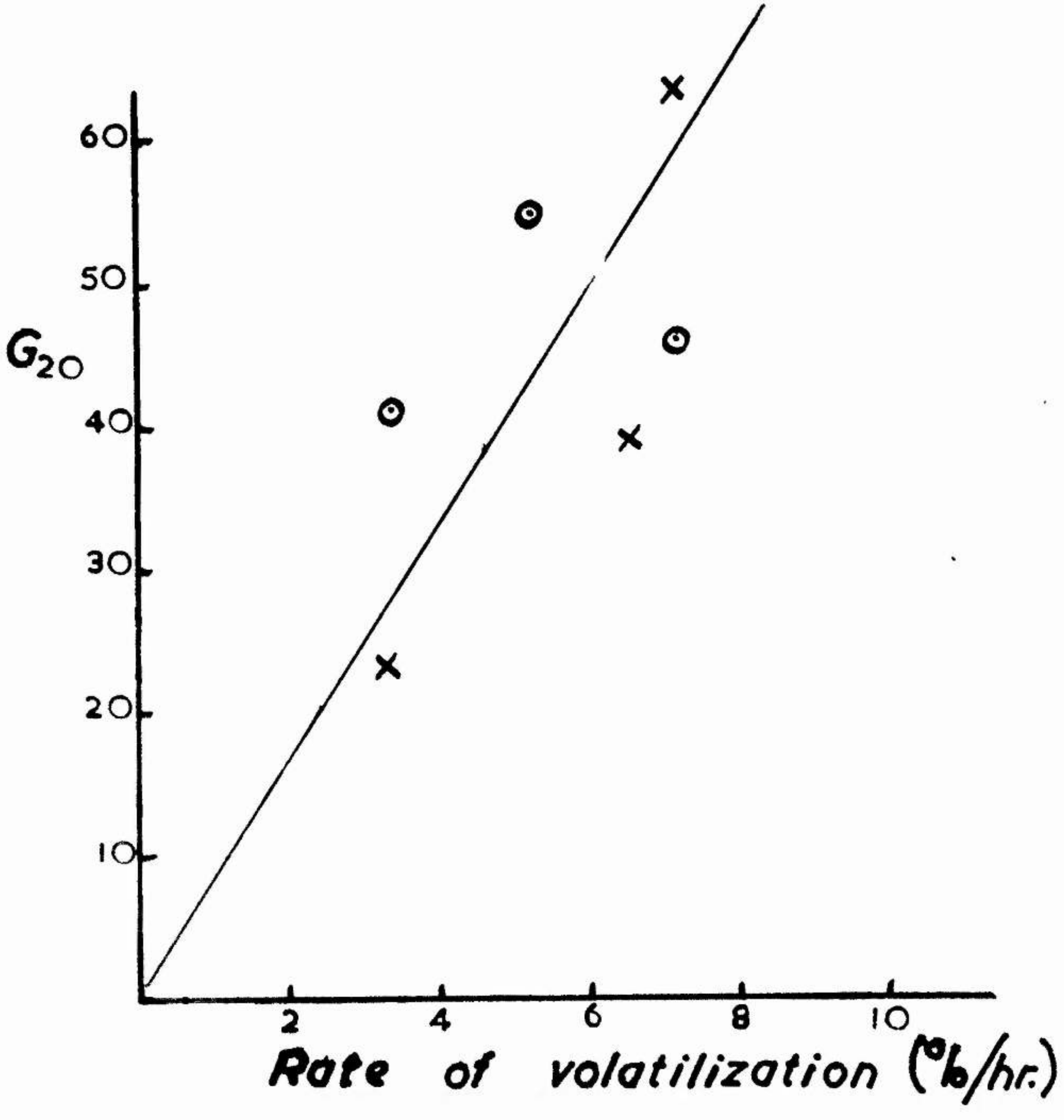


Figure 32 Percentage insolubility for 20% volatilization at 290°C (G_{20}) against rate of volatilization of 2F polymers
×, samples polymerized to 10% conversion; ⊙, to 70% conversion.

prepared in methyl acetate. One set was taken to 10% conversion, the other to 70% conversion. Since the average concentration of polymer segments around a propagating radical increases with increasing conversion, the concentration of branches in polymers taken to 70% conversion will be higher than in polymers taken to 10% conversion. Again monomer samples used came from the same distillation batch, although the batch itself was different from that which provided the previous (1F) group of polymers.

Aging effects (see Section 2.4.1., this chapter) can occur during storage of PMA. To reduce these as far as possible the samples (21) - (26) were stored in a refrigerator.

These polymers were also pyrolysed to near 20% volatilization at 290° and the percentage insolubility found, and corrected to the percentage insolubility for 20% volatilization at 290° (G_{20}). The results are listed in Table 26, and a plot of percentage insolubility at 20% volatilization against temperature of polymerisation is shown in Figure 31. The plots of percentage insolubility for 20% volatilization at 290°C against temperature of preparation of the 2F polymers are both of the same shape, with a pronounced minimum around 50°C. (Figure 31). The polymers prepared at higher conversions show higher G_{20} values than those polymerised to 10%, with the possible exception of those prepared at 40°C where the extent of gel formation seems to be comparable. The most

Table 26

Preparation details and degradation results for 2F group of polymer samples. Samples prepared in methyl acetate; degradations at 290°C.

Sample	Temp. of polym. °C	$10^{-5}M_v$	Run	T.O.H. hr.	%volat.	dC/dt % hr.	%insol.	G_{20}
Samples polymerised to 10% conversion								
21	40	19.5	168	2.5	17.8	7.1	54.9	61.7
22	50	19.5	161	6.0	19.6	3.3	23.0	23.5
23	70	11.0	164	3.0	19.5	6.5	41.5	42.6
Samples polymerised to 70% conversion								
24	40	43.0	170	4.25	21.8	5.1	61.3	56.7
25	50	30.0	162	6.0	20.0	3.3	41.1	41.1
26	70	7.5	165	3.0	21.8	7.3	58.4	57.5

striking feature of the curves, however, is the well defined minimum around 50°C. This behaviour is similar to that of the 1F set prepared in ethyl benzene and may be a general pattern of behaviour for PMA. Of all the twelve samples used in this study only PMA(11) does not fit into this pattern, and it is note-worthy that this was the only polymer of the group which showed an induction period before polymerisation. These two anomalies may be connected.

For the 2F group of polymer samples the approximate rates of volatilization at 290°C were calculated by dividing the extent of volatilization by the time of heating. Figure 32 shows these approximate rates plotted against G_{20} values, and indicates a roughly linear correlation between the two. This suggests that some factor which increases the gel forming tendnecy of the polymers also increases their thermal instability.

2.3.3. Summary

The results in Sections 2.3.1 and 2.3.2. show that conditions of polymerisation which favour branching, due either to the nature of the diluent or to the extent of conversion, also tend to increase the proportion of gel formed during pyrolysis. These experiments also show that the temperature of polymerisation has a profound effect on gel formation during pyrolysis. The relationship between G_{20} values and the temperature of polymerisation is not as simple as was originally envisaged and the curves relating the two quantities show distinct minima around 50°C.

PMA samples which have a strong tendency to form gel on pyrolysis tend to be relatively thermally unstable.

It is believed that concentration of chain branches in polymer samples may be the factor involved in these effects. Possible causes and reasons will be examined in Section 4. of this chapter.

2.4. AGING

2.4.1 Effects of storage

When PMA(7) was degraded in the series of runs which gave the rate and molecular weight data (Chapter III) the pyrolysed residues were completely soluble in benzene and no yellow discolouration developed.

Some months after the completion of this work, a sample of PMA(7) was degraded to provide a residue for spectrometric examination and it was noted that the residue was discoloured and that insolubility had developed on heating.

These effects were attributed to oxidative attack on the polymer during storage. Poly (m-diethynylene benzene) is also known to undergo aging during storage.[102]

2.4.2. Accelerated Oxidative Aging

To check whether the aging effects in PMA(7) could be caused by oxidative attack, some simple experiments were carried out on PMA(2), a polymer which showed little tendency to form gel.

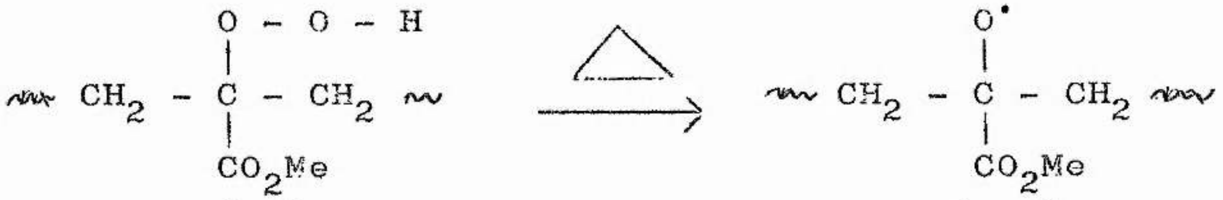
A sample was heated in an oven for 10 days at 60°C. The volatilization during this time was 3.5%. The sample, now called PMA(2A), had turned deep yellow but was still completely soluble in benzene. Degradations of 100 mg. samples were done at 290°. Results are tabulated below (Table 27) together with a comparable degradation on PMA(2).

Table 27

Comparison of gel formation in aged and non-aged PMA(2).

Run	Sample	T.O.H. hr.	S.I.W. mg.	Wt.loss mg.	% C.	%insol.	C.M.R.cm.Hg Fr.IIIA	Fr.III A+B
128	2	6	93.0	10.8	11.6	0.0	1.65	4.55
129	2A	6	102.9	21.9	21.1	84.0	>12	>15
130	2A	2	93.0	9.5	10.2	84.0	>12	>15

These figures demonstrate the enormous effect that the presence of oxygenated structures in the chain can have on the degradation characteristics of PMA. Accelerated oxidative aging greatly increases the tendency of the polymer to gel. The probable primary product of oxidative attack on PMA would be the hydroperoxide (VI) which can decompose to the radical (VII). Radical (VII) might be involved in crosslinking reactions.



$$\sim CH_2 - \underset{CO_2Me}{\overset{O-O-H}{C}} - CH_2 \sim \xrightarrow{\Delta} \sim CH_2 - \underset{CO_2Me}{\overset{O^{\bullet}}{C}} - CH_2 \sim$$

(VI) (VII)

The actual rate of volatilization is also increased, possibly due to the more rapid rate of breakdown of oxygenated structures. It is also noted that the proportions of gaseous volatiles increase considerably. A similar increase in volatile production has been attributed in the oxidative degradation of poly (ethyl acrylate), [51] to the more ready breakdown of oxygenated end structures, which are the primary products of hydroperoxide breakdown.

2.5. DAA AND GEL FORMATION

Results are presented in Table 28 which show that incorporation of DAA into the polymer melt eliminates gel formation, at least up to 25% volatilization.

The presence of DAA also eliminates the yellowing of the pyrolysed residue.

Table 28

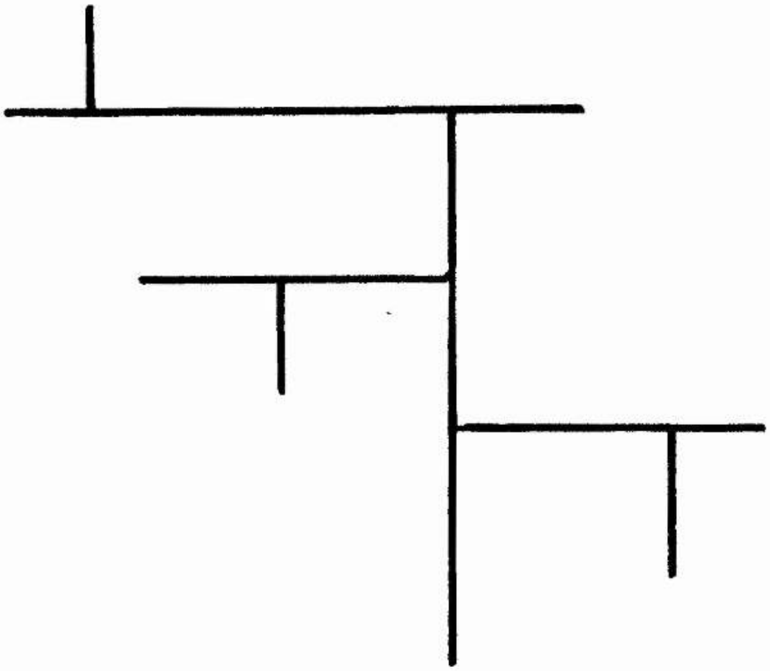
Effect of DAA on gel formation at 290°C

Run	Sample	T.O.H. hr.	% volat.	% insol.	Wt. DAA mg.
94	7	7.5	26.6	30.8	0
98	7	8.5	21.7	0.0	2.0
143	19	4.76	15.5	26.4	0
149	19	6.0	16.6	0.0	2.0

3. COLOURATION

Colouration, especially yellowing is a typical manifestation of degradation of polymers and has been noted on many occasions. Yellowing is very frequently linked with oxidative attack on the polymer. In vacuum pyrolyses of poly (methacrylonitrile), [34] poly (acrylonitrile), [33] poly (vinyl chloride), [31] and poly (methyl vinyl ketone), [103] the colouration reactions have been closely studied and explained in terms of well defined processes which make major contributions to the overall degradation. On the other hand, the yellowing produced on vacuum pyrolyses of poly (ethylene terephthalate), [104] (which is caused by small amounts of an aromatic methyl ester), and of poly (tetramethylene oxide), [105] is due to structures produced in secondary radical reactions of minor importance.

The colouration produced in PMA degradation falls into this latter category, and has not been thoroughly investigated as isolation of the colouring matter, as in the case of poly (ethylene terephalate), can often be both tedious and unrewarding. However, the following facts



VIII

IX

Figure 33 Representation of branched and crosslinked polymer molecules VIII, branched; IX, crosslinked.

concerning colouration have emerged from other investigations.

(i). There is no bathychromic shift of absorption as volatilization proceeds (Section 3.4., Chapter IV).

(ii). The presence of DAA can eliminate the colouration. (Section 2.5., this chapter).

(iii). The colouration can be produced by oxidative aging. (Section 2.4.2., this chapter).

(iv). Colouration can be produced in the apparent absence of crosslinking reactions. (Section 2.2., this chapter). Despite these observations the source of the colouration is still obscure. It is fairly certain, nevertheless, that the colouration is a further ramification of the overall free radical chain process.

4. DISCUSSION

It has been suggested that the gel formation, which is such an important feature of the degradation of the twelve polymer samples described, is due to crosslinking. Branched and crosslinked molecules are schematically represented in Figure 33, as structures (VIII) and (IX) respectively. Structure (VIII) has been produced by branching, which could have been brought about by chain transfer during polymerisation, and although very large molecules of this type can be formed, branching reactions alone cannot lead to gel formation.[106] The most obvious difference between these structures resides in the functionalities of the polyfunctional units. Branching involves only trifunctional units, crosslinking generally involves tetrafunctional units. Crosslinking, in fact, refers to a specific type of branching.

The purpose of this discussion is to provide explanations for the experimental results described in Section 2 of this chapter, and to suggest possible mechanisms which would fit into the overall degradation scheme.

The crosslinking reaction of the type apparently taking place in PMA is an entirely novel process among vinyl polymers undergoing thermal degradation.

The observations that crosslinking in PMA on pyrolysis can be induced by oxidative aging before pyrolysis, and that PMA(7) developed a tendency towards gel formation on storage suggests superficially, that the crosslinking on degradation may only be a "pseudo" effect, brought about by the incorporation of oxygen into the polymers on preparation. However, the hydroperoxide structure (VI) which is thought to be a precursor to oxidative crosslinking cannot be formed during polymerisation. Also, the precautions taken in storage of the 2F polymers make it extremely unlikely that a sufficient concentration of hydroperoxide groups could be present at tertiary carbon sites to cause the effects observed. Finally, the overall consistency and the peculiar nature of the dependence of the gel formation on temperature of polymerisation can hardly be accounted for by invoking the presence of hydroperoxide intermediates in the samples.

For these reasons the theory that hydroperoxide structures alone are responsible for the bulk of the insolubility is untenable, and an explanation more in agreement with the experimental facts must be sought. The relationship between the extent of gel formation and the percentage volatilization, coupled with the unusual temperature preparation effect suggest that crosslinking is promoted by structures which are present in the polymer sample to begin with. There are two features of the polymerisation of methyl acrylate which may account for the relation between gel formation and temperature of polymerisation.[101, 107] These features are the ready occurrence of chain transfer, and the existence of a low temperature "popcorn" polymerisation when the catalyst concentration is low.

In vinyl addition polymerisations branches can be introduced by chain transfer between a growing chain and either monomer or polymer. Chain transfer alone cannot produce an infinite network, but the complex structures generated by extensive chain transfer offer favourable circumstances for the formation of such networks through the assistance of independently occurring intermolecular or intramolecular combinations.

The polymerisation of methyl acrylate is perhaps the most unusual involving a vinyl monomer. Fox and Gratch[101] have made a very thorough theoretical analysis of the process and they concluded that transfer to polymer is the only chain transfer process which is important. Due to the large reactivity of the propagating radical and to the presence of the labile hydrogen atoms, Fox and Gratch concluded further that in bulk polymerisation transfer should result in the appearance of insoluble gel around 80% conversion. In fact, gel formation occurs at as low as 5% conversion in bulk polymerisation, [55] and there seems little doubt that in polymerisation in solution branched structures are formed at fairly low conversions. It therefore appears that gel formation can arise by the transition (and this need involve only a small number of intermolecular combinations) from complex branched structures into insoluble crosslinked networks. Both the branched structures, and the transfer reactions necessary to produce the radicals for combination are present during the pyrolysis of PMA, and it is postulated that the insoluble gel arises in this way.

The normal increase in branch concentration with increase in temperature of polymerisation therefore, explains the rise in G_{20} values for all the samples as the polymerisation temperature increases from 50 - 70°C. In the following paragraphs the "inverse" temperature effect, by which the G_{20} values decrease with rise in temperature from 40 - 50°C, will be seen as an additive effect, in which a branch concentration arising in another way is superimposed on the normal increase in branch concentration with temperature.

This inverse temperature effect in which increase in temperature between 40 and 50°C lowers the tendency of samples to form gels may also be explained in terms of the processes occurring in the polymerisation of methyl acrylate. This monomer is unique among mono-olefins in that "popcorn" polymer formation can occur in the total absence of crosslinking agents. The nature of "popcorn" polymerisation, which leads to the formation of small nodules of insoluble polymer is not very well understood. However, it is necessary to work at temperatures of below 50°C to obtain "popcorns" of PMA, [107, 108] and to use low initiator concentrations. [108] Breitenbach and Fally [109] have found a relationship between initiator/monomer ratio and the "popcorn" formation at 20°C. The initiator/monomer ratio used in the preparation of the present 1F and 2F polymers was approximately 10^{-4} which lies in the range in which "popcorns" may be formed. Fox and Gratch consider that in some circumstances crosslinking by self-termination of branch radicals growing on the same back-bone chain might occur with greater probability than termination with other free radicals, and that minute crosslinked networks, microgel particles, may result. They calculate that this may be significant with methyl acrylate at 1% conversion and suggest that these particles are the "popcorn" nuclei.

It seems possible that the conditions at 40°C in the present polymerisations may have allowed the formation of microgel particles, and that these particles would be present in addition to the normal branched structures as nuclei for later gel formation.

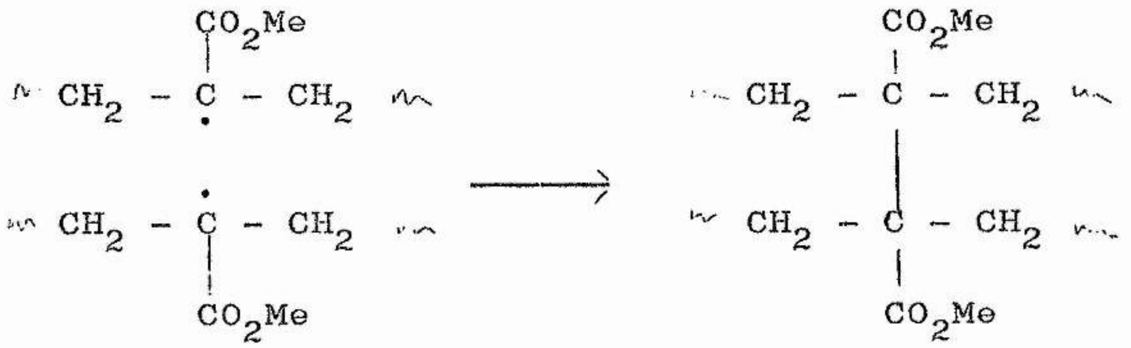
The gel formation tendency can therefore be explained in terms of polymer sample structure caused by the unusual conditions realised in the methyl acrylate polymerisation.

The relationship between gel forming tendency and rate of volatilization established in Figure 32 can also be explained by associating the occurrence of insolubility with branched structures. It is known that the presence of branches, in polyethylene [67] in particular, causes its rate of volatilization to be unexpectedly rapid as far as 20% volatilization. Branch points act as a source of weakness in a polymer [110] and in addition favour breakdown by intramolecular transfer [16] which, in turn, causes more rapid evolution of short chain fragments. Generally hydrocarbon polymers containing branches are more thermally unstable at low conversions [111] than the corresponding linear polymers. It is notable, therefore, that the G_{20} values for the 2F polymers increase with rates of volatilization, (see Figure 32), and this feature provides further support for the theory that gel formation is linked with the presence of branched structures in PMA.

The lack of gel formation at higher degradation temperatures (Section 2.2.) must result from changes in the relative extents of the competing processes in the radical chain reaction. In particular, the stability of the tertiary radical (IV), (Section 4, Chapter IV), may be greatly affected by a temperature increase from 290° to 320°C. The ratio $\frac{\text{tertiary radicals combining}}{\text{tertiary radicals undergoing scission}}$ may be reduced at 320° to a value incompatible with effective crosslinking.

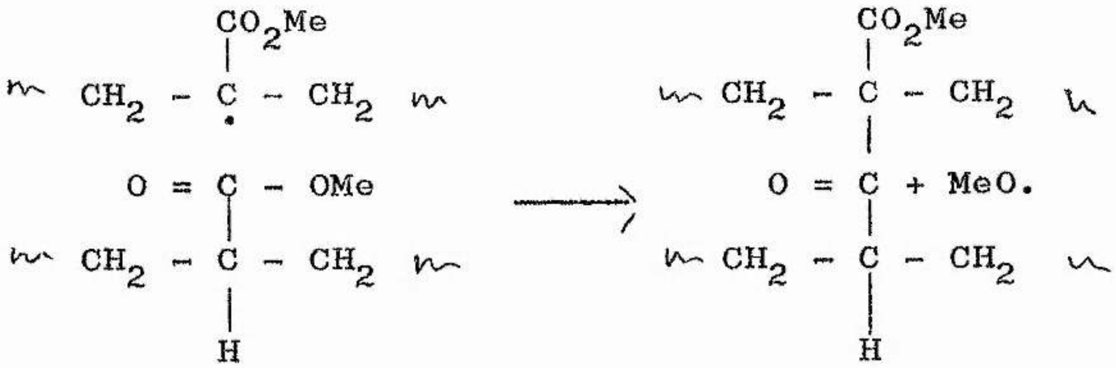
As yet there is insufficient evidence to specify the exact way in which DAA acts in eliminating gel formation.

Crosslinking as a combination process between two radicals has been discussed, but the actual nature of the combining radicals has not been considered. The most likely reaction leading to crosslinking is combination of two tertiary chain radicals.



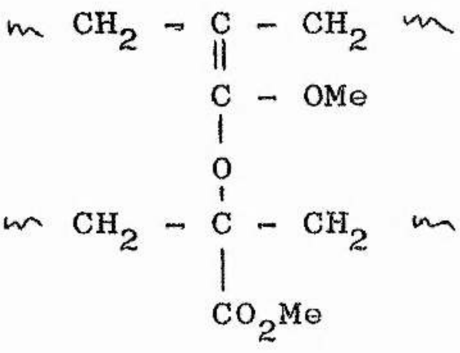
This type of crosslink, is believed to be formed in the ultra-violet irradiation of poly (ethyl acrylate), [112] as it has been established that the crosslinks cannot be hydrolysed by alkali. It is probable that similar links would be formed in PMA during pyrolysis.

Crosslinks which would also be impervious to alkaline hydrolysis could be formed by less conventional routes as follows. Attack by the tertiary radical on the carbonyl carbon of the ester side group would produce a ketonic link as shown. (Scheme 7).

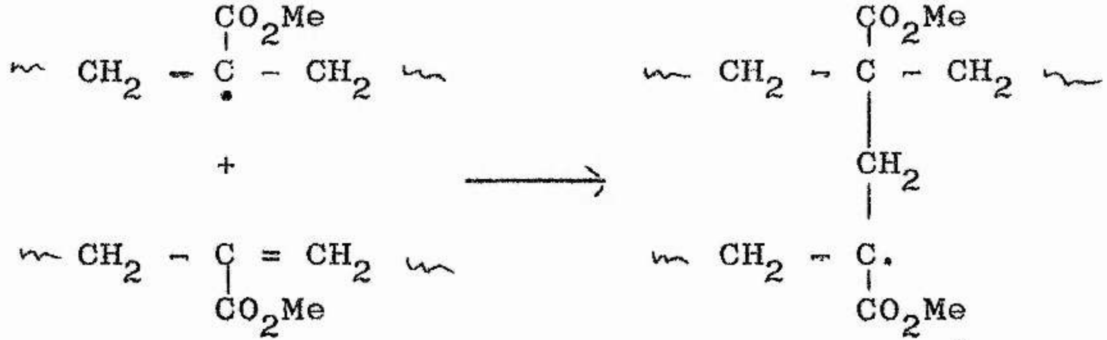


Scheme 7

There are no precedents for this type of behaviour and even although the mechanism would provide a ready additional mode of production of methanol it is considered highly speculative. The resonance mesomer (V), (Chapter IV, Section 4), of the tertiary radical could also be involved in combination to give the structure below.



A final interesting way in which crosslinks could be formed is by radical addition to one of the double bond ends produced during the degradation.



(X)

Linking of any chain to the tri-branched radical (X) would result in a crosslinked structure. Initial scission radicals may take part in this way in the crosslinking reaction. Ethylenic double bonds at each end of the molecule attacked as above could result in the formation of quite complex structures.

If a series of reactions of the type discussed above is responsible for crosslinking in PMA pyrolysis it is immediately obvious how oxidation prior to pyrolysis can increase gel formation and thermal instability. Assuming that hydroperoxides are formed at the tertiary carbon atoms these will breakdown on heating to radicals of the type (VII) (Section 2.4.2.). The net effect of this breakdown would be to increase the back-bone radical concentration and the probability of two or more initially separate chains linking up by one of the schemes described above.

4.1. SUMMARY

It is suggested that the relationship between gel forming tendency and conditions of polymerisation is due to variations in the structure of the original polymer. As the temperature of polymerisation is increased above 50°C the concentration of branches increases giving samples with greater tendencies to gel on pyrolysis. Samples polymerised to high extents also form gel more readily for the same reason. Polymers prepared below 50° show an inverse effect, a decrease in temperature of polymerisation favouring ready insolubilization during degradation. It is thought that this effect is due to the presence of microgel particles which form nuclei for gel formation.

Pre-oxidation or aging of PMA samples also promotes gelation on pyrolysis, and it is suggested that this pre-treatment gives rise to hydroperoxide units at tertiary carbon atoms. When these breakdown on heating they produce an abnormally high concentration of free radicals which accelerate crosslinking.

The precise mechanism of crosslinking is not completely clear, but it is a free radical process. Several possible reactions have been suggested.

Table 29

Degradation of PMA(19) at 290°C
Values plotted in Figure 29.

Run	T.O.H. hr.	S.I.W. mg.	Wt. loss mg.	% volat.	% insol.
139	3.0	96.2	14.7	15.3	20.9
143	4.7	98.8	19.3	19.5	26.4
152	6.0	98.6	21.6	21.9	37.0
155	14.0	95.9	40.2	41.9	62.3
156	15.8	96.9	41.9	46.4	67.4

CHAPTER VI

DEGRADATION OF POLY (BENZYL ACRYLATE)

Poly (benzyl acrylate) (PBA) is a tough rubbery polymer similar in appearance to PMA. The literature contains virtually no references to either the preparation or the reactions of PBA, and the polymer does not appear to have been used commercially in any way.

This chapter describes some preliminary experiments carried out on the degradation of PBA. These investigations are by no means exhaustive but in the time available it was most useful to attempt, by analogy, to throw more light on the degradation of PMA, and to provide a survey of the degradation of PBA which would indicate firstly, the most satisfactory conditions and secondly, the most promising points of departure for a more extensive and detailed study.

1. CLASSIFICATION AND NATURE OF DEGRADATION PRODUCTS

The division of pyrolysis products into fractions is not so clear cut for PBA as it was for PMA. Preliminary degradations which were carried out in the molecular still apparatus (Figure 1), followed by chromatographic analysis of the products, indicated that benzyl alcohol was a major product of the pyrolysis. Benzyl alcohol boils at 205.3° at 760 mm. 53 and could not be distilled quantitatively to the manometer system under vacuum. In addition, a yellow oily liquid condensed in the vacuum line between the still A and the cold-trap E (Figure 1). This was thought to be the counterpart of Fraction II from PMA. The molecular still apparatus, therefore, was not suitable for quantitative examination of the pyrolysis products of PBA, and the alternative degradation apparatus (Figure 7) was adopted. The products obtained when PBA was pyrolysed in this apparatus separated into four fractions as follows.

(i). The pyrolysis residue. This remained at the foot of stem G, and was found to be long chain PBA.

(ii). The liquid products. These collected partly at bend I and partly distilled to cold-trap L, and were composed almost entirely of roughly equal quantities of short chain fragments and of benzyl alcohol.

(iii). The products condensable between -76° and -194°C.

(iv). Non-condensable gaseous volatiles.

The division into fractions is not quite the same as that for PMA and hence Madorsky's terminology [50] is not used.

It was found convenient to study these products in the order, non-condensable gaseous volatiles, condensable gaseous volatiles, liquid products, and pyrolysis residue. The products will be discussed below under these headings.

Only two samples of PBA were prepared and used.

2. ANALYSIS OF DEGRADATION PRODUCTS

2.1. NON-CONDENSABLE VOLATILES

The non-condensable gases produced by the degradation of PBA (1) in Run 190 B † were collected and analysed by mass spectrometry. The cracking pattern is shown below in Table 30.

---

† The letter B indicates that the run was carried out in the apparatus shown in Figure 7.

Run 190B was carried out for 6 hrs. at 315°C to 48% volatilization on PBA (1).

Table 30

Cracking pattern of non-condensable gases collected from PBA(1) in R 190B

Mass/charge ratio m/e	Peak height mv. units
1	.0
2	15.5
14	11.0
15	18.0
16	22.5
28	168.5
29	9.0

From this pattern the components were identified as carbon monoxide, methane and hydrogen, constituting approximately 70, 20, and 10 molar percent respectively of the non-condensable gases. The peaks at m/e values of 14 and 29 are rather high, although their appearance is justified by the presence of methane and carbon monoxide. There is no obvious explanation for this.

In two degradation runs the pressure of the non-condensable gases was measured as described in Section 4.4. of Chapter II. The pressure measurements, combined with the knowledge of the volume of the system (250 ml.) and the gas analysis, allowed the absolute weights of the components to be calculated. The weight percentage of the non-condensable gases, based on the total weight loss in degradation, in both cases was approximately 1%.

2.2. CONDENSABLE GASEOUS VOLATILES

The condensable gaseous volatiles were collected and analysed by mass spectrometry. The cracking pattern obtained was almost identical to that included in Table 7 of Section 2.2.3., Chapter III, showing that carbon dioxide was the only component.

A series of degradations was carried out in the molecular still (Figure 1), and the pressure of the carbon dioxide for each run was measured in the constant volume manometer ($V_o = 8.15$ ml.). Corrected manometer readings are plotted against weight loss in Figure 34, which shows that the carbon dioxide liberated increases linearly with weight loss. From Figure 34 it is calculated that carbon dioxide represents 4.7% of the total weight loss in the range 10 - 50% volatilization.

2.3. LIQUID PRODUCTS

Gas chromatography was the main technique employed in the analysis of the liquid products. The number and, as far as possible the nature of the products was first determined.

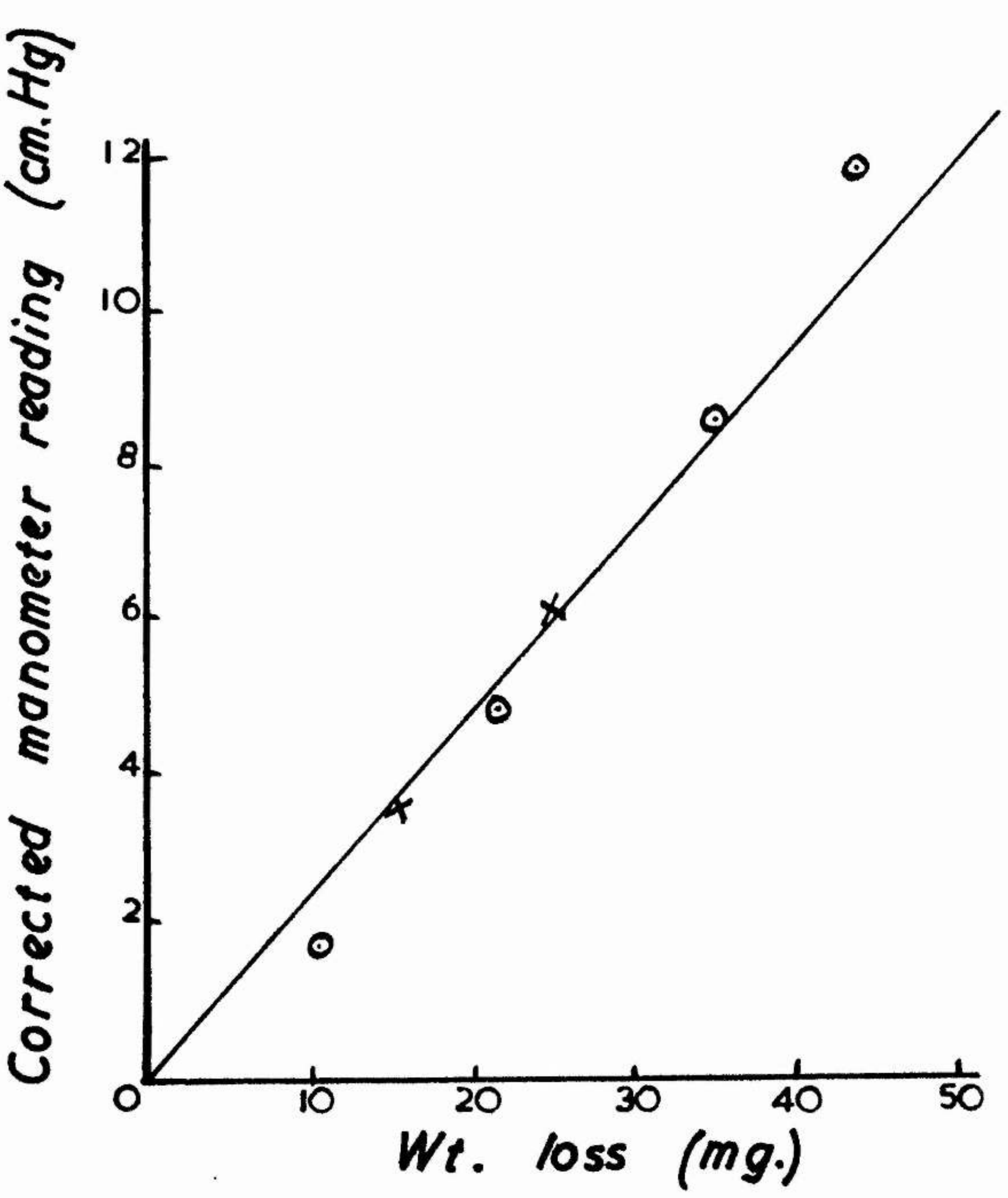


Figure 34 Corrected manometer readings (for CO_2) against weight loss for degradation of PBA(I) ×, at 260°C ; ⊙, at 270°C. Molecular still used.

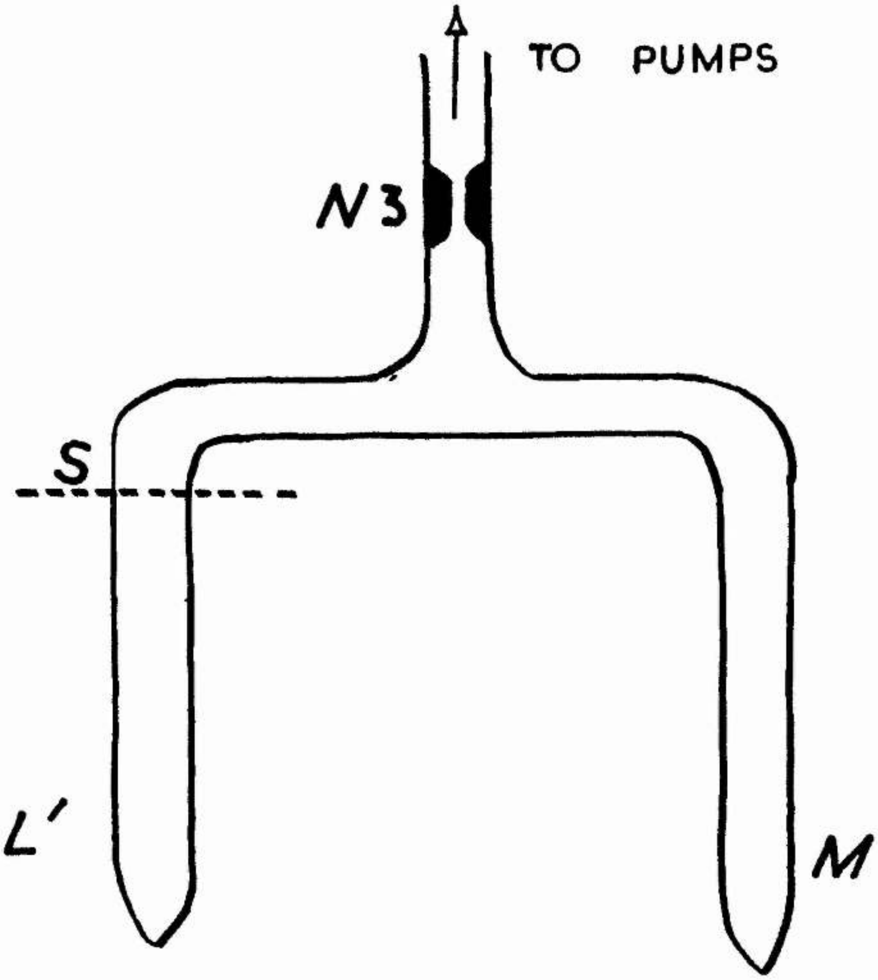


Figure 35 Apparatus for fractionation of liquid products from PBA degradation

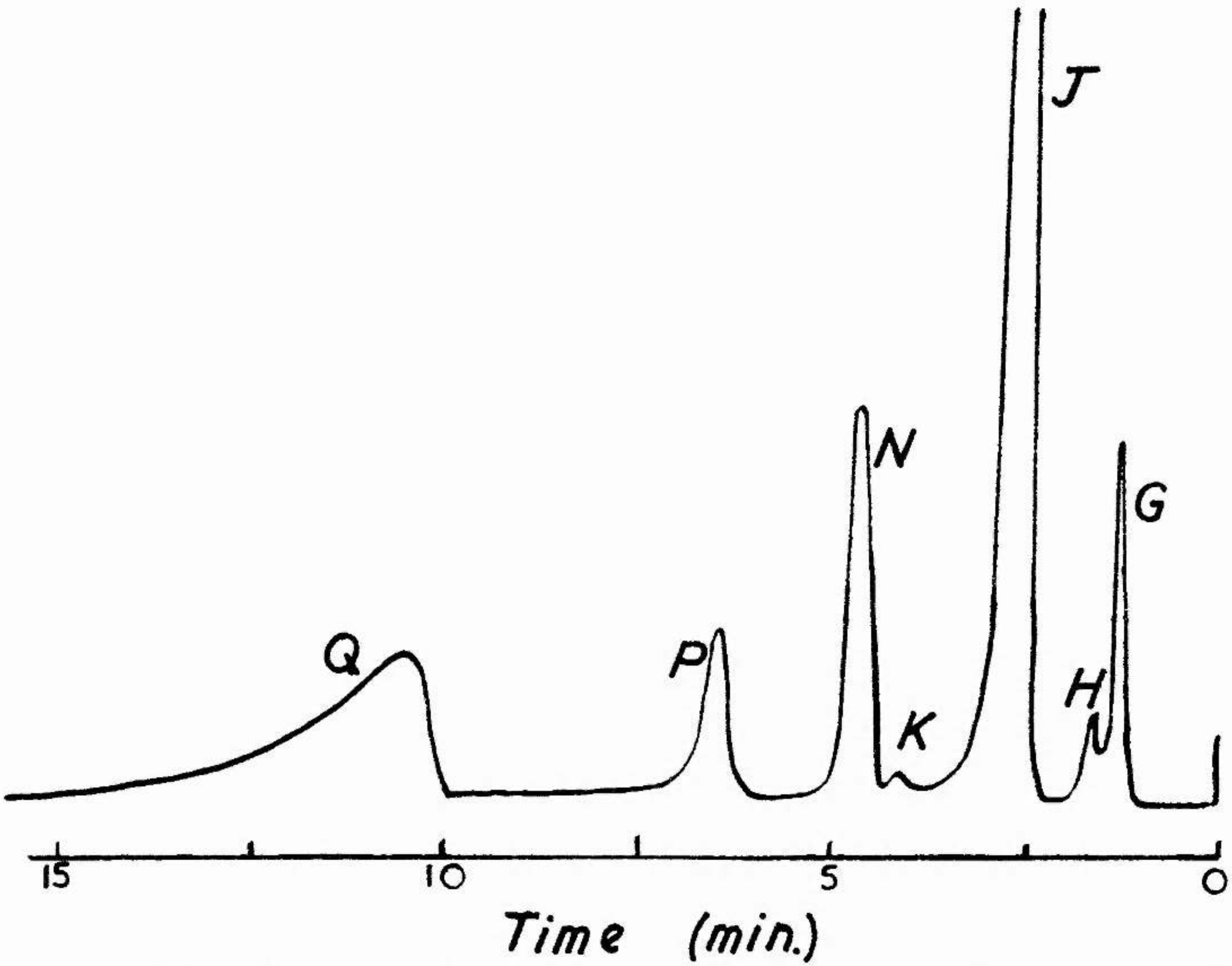


Figure 36 Gas chromatogram of Fraction B(i) from PBA(1) 40.3% volatilized in Run 192 B

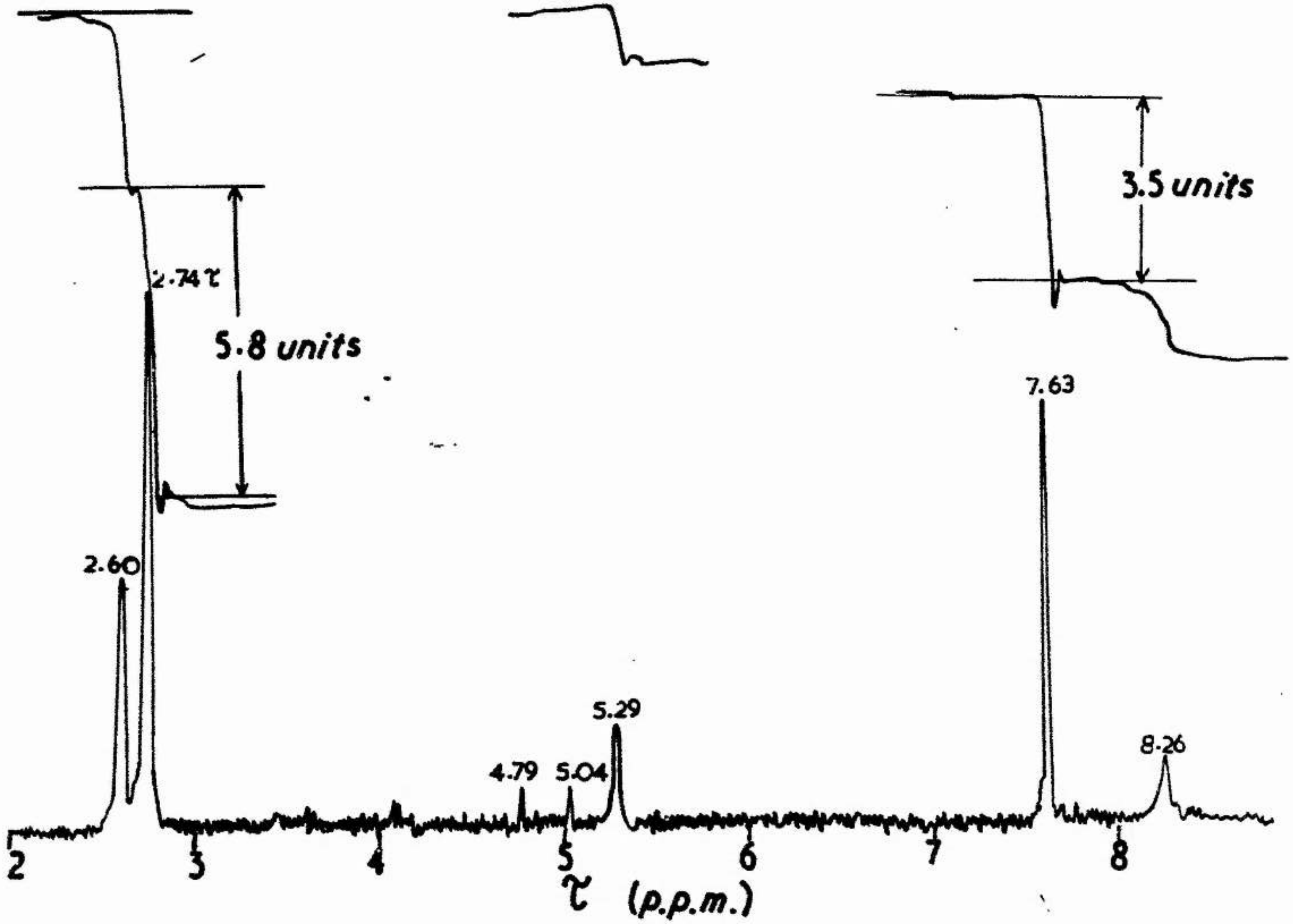


Figure 37 N.M.R. spectrum of the most volatile of the liquid products from PBA(2) 78.5% volatilized in Run 225B

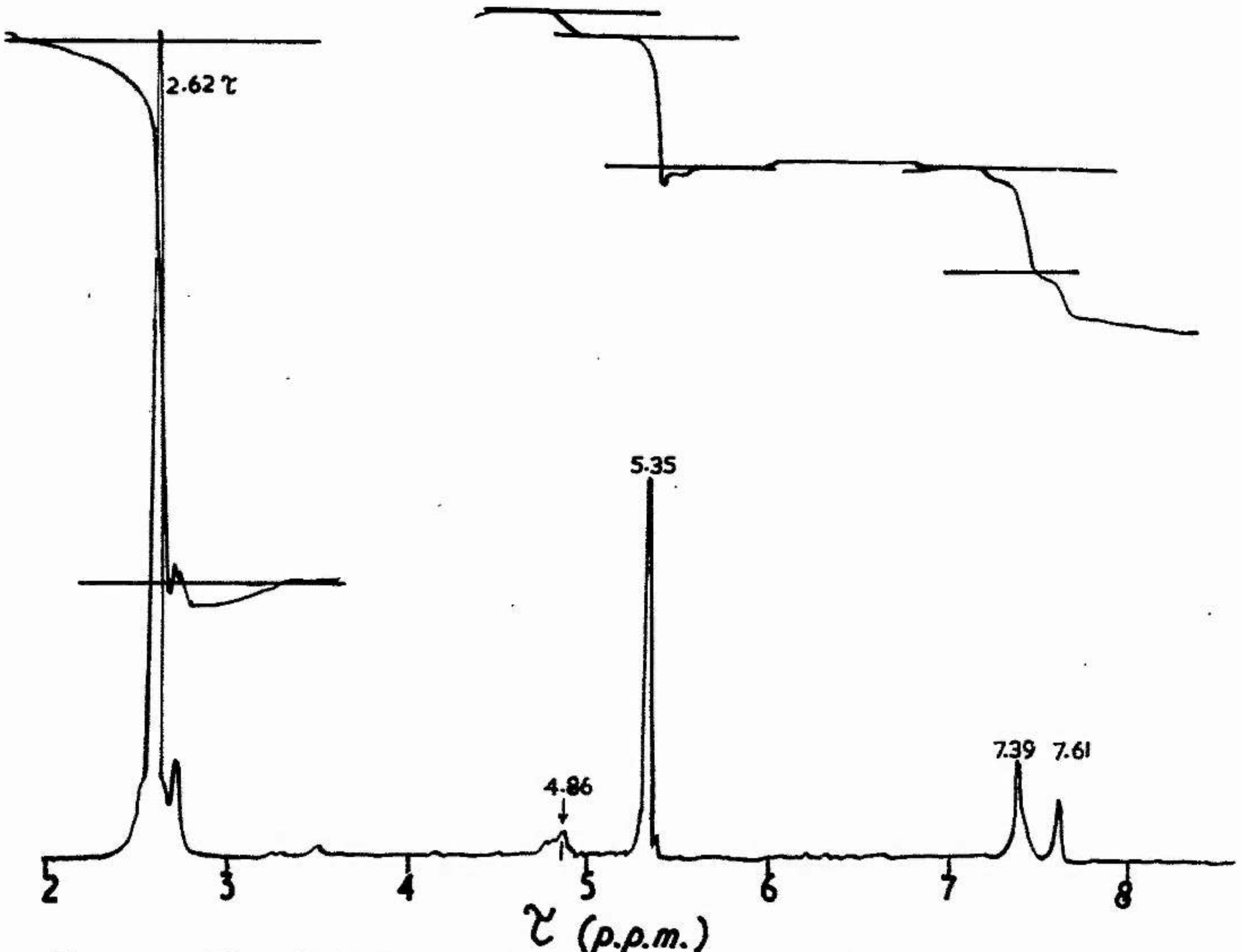


Figure 38 N.M.R. spectrum of unfractionated liquid products from PBA(2) 50% volatilized in Run 212 B

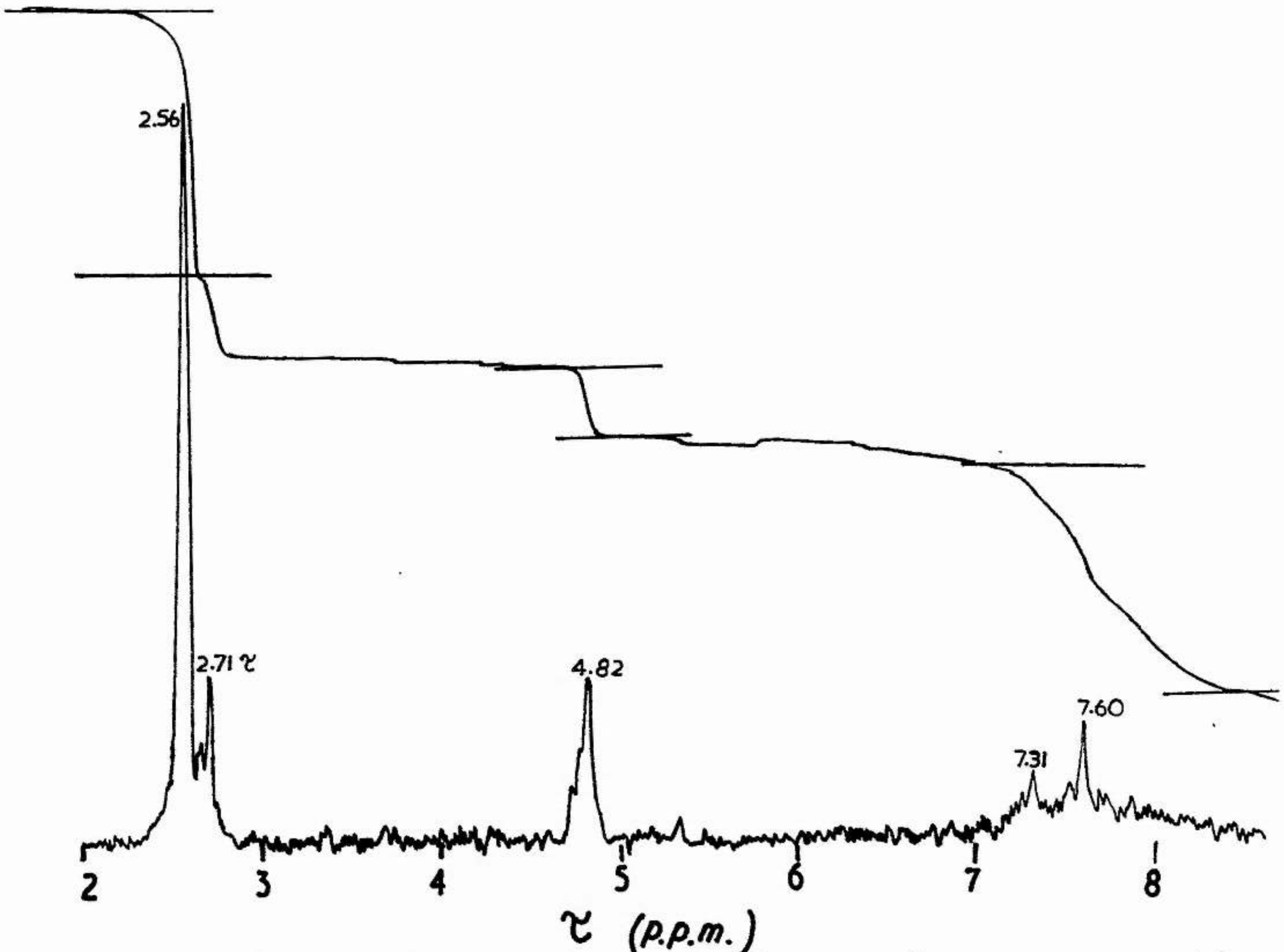


Figure 39 N.M.R. spectrum of Fraction B(ii) from PBA(2) 50% volatilized in Run 212B

In later runs a marker compound was added for quantitative analysis of the liquid products. In addition liquid products were examined by I.R. and N.M.R. methods.

2.3.1. Qualitative analysis

The short chain fragments did not come off the column at the temperatures used for analyses, and the predominance of benzyl alcohol in the remaining fraction of the products caused difficulties in the determination of the other components. The short chain fragments and benzyl alcohol were the most involatile of the components, and preliminary fractionations, which made qualitative analysis easier, were achieved in the following manner.

The condensable products were collected in the stem L (Figure 7), which was then sealed off under vacuum. The top of stem L was quickly cracked off, and the bottom section L′, in which the liquid products were held condensed, was quickly sealed on at S to a part of the vacuum line as shown in Figure 35. With L immersed in liquid air, the inverted U tube was pumped out and sealed off under sticking vacuum at contriction N3. Only when this was accomplished was the liquid air cold-trap removed from L′, and placed around stem M. Stem L′ was then allowed to warm to room temperature. The cold-trap was kept around M for 12 hr. The more volatile of the liquid products, Fraction B (i), distilled to M, while the bulk of the benzyl alcohol and short chain fragments, Fraction B (ii), remained at the foot of L′.

Both fractions were analysed using a column of 10% silicone oil on celite at 110°C. The chromatogram of Fraction B(i) contained seven distinct peaks, (see Figure 36). Peak Q was identified as belonging to benzyl alcohol and peak J had the same retention time as toluene. Toluene plus the other components comprised less than 3% by weight of the total degradation products, and the other components were not identified.

Traces of benzyl acrylate were detected from preliminary degradations using the molecular still, but the monomer was not found in the above experiments. It is believed to have been re-polymerised during the flaming of the system which was required to drive the products into L.

Samples of Fraction B (ii) were run on the silicone oil column and benzyl alcohol was the sole peak in the chromatogram.

The presence of toluene in the liquid products was established by N.M.R. measurements. The liquid products from a sample of PBA(2) were allowed to collect at bend I, but some distilled to L providing a very elementary fractionation. Stem L was then sealed off leaving the bulk of the products at I. An N.M.R. spectrum of the liquid products from L is shown in Figure 37. The peaks at 2.60, 5.29 and 8.16 τ are due to benzyl alcohol. The peaks at 2.74 and 7.63 τ are attributed to toluene on account of position, (τ values for 7.5% solution of toluene in deuterochloroform are 2.83 and 7.68), [113] and on account of the integral ratio, $^{5.8}/_{3.5}$ which agrees with the theoretical value. An unsaturated structure could be responsible for the very small absorptions at 4.79 and 5.04 τ.

Direct evidence for the existence of short chain fragments in the liquid products was also obtained by N.M.R. studies. Figures 38 and 39 show the spectra of the unfractionated liquid products and of Fraction B (ii) respectively, produced by volatilization of PBA(2) to 78.5%. In the unfractionated liquid products benzyl alcohol apparently predominates, and the peaks at 2.62, 5.35, and

8.39 τ (Figure 38) are due to this component. (The position of the hydroxyl proton peak, can vary with the concentration of the benzyl alcohol solution). The peak at 4.86 τ in this spectrum, is assigned to methylene protons in the ester groups of chain fragments. The spectrum of the Fraction B (ii) in Figure 39 shows much stronger absorption at 4.82 τ and broad absorption between 7.2 and 8.4 τ which can only be due to chain methine and methylene protons. This latter absorption proves that short chain fragments are present. The peak at 7.61 τ in Figures 38 and 39 cannot be accounted for satisfactorily.

No peaks attributable to aldehyde or carboxyl protons could be detected in the N.M.R. spectra of the liquid products.

2.3.2. Quantitative analysis.

Quantitative analysis of the liquid products was carried out by gas chromatography using a column of 10% silicone oil on celite at 110°C, with a pressure of nitrogen carrier gas of 15 p.s.i. The marker compound employed was phenyl methyl acetate which came off the column after benzyl alcohol and hence did not interfere with the resolution of the liquid products. The phenyl methyl acetate was itself chromatographically pure. The products of five degradations of PBA(1) at 300°C were analysed. In each case the operating accuracy and reproducibility of performance of the gas density balance throughout the loadings were checked by running known samples of benzyl alcohol and phenyl methyl acetate in ether, before and during the liquid product loadings.

The mean weight percentages of benzyl alcohol, (weight percentage based on total weight loss), were calculated from four or more consistent analyses, except for those of runs 199B and 201B when two consecutive, consistent results were used. The results obtained are listed in Table 31.

Table 31

Gas chromatographic analysis of liquid products of degradation of PBA(1) at 300°C

Run	S.I.W. mg.	Wt. loss mg.	% volat.	Mean wt. % $PhCH_2OH$	% other components
199B	105.7	54.8	51.9	32.0	2.4
204B	89.3	41.0	45.9	38.5	2.5
203B	86.3	37.8	43.8	40.0	2.9
201B	105.3	42.4	40.3	40.5	3.9
219B	94.3	34.6	36.8	44.2	–
				MEAN	2.9

In each degradation listed in Table 31 the marker was added to the total liquid products, except for degradation 219B. For this analysis a weighed portion of the liquid products was added to a known weight of marker. The percentage weight of benzyl alcohol in the weight of liquid products used was found and converted to the percentage of the total loss in weight. Run 219B, in particular, proves conclusively that about half of the liquid products did not leave the column at 110°C, and this confirmed the results from the four previous runs. The non-elution of certain products is additional evidence that there were involatile chain fragments present in the samples.

The amount of benzyl alcohol evolved was not directly proportional to the total weight loss. The plot of weight percentage of benzyl alochol against percentage volatilization shown in Figure 40 establishes a definite relation between the two quantities. It is clear, therefore, that as volatilization proceeds, the amount of benzyl alcohol produced per unit weight loss decreases. The amount of other components evolved was very low and apparently remained constant throughout the degradation.

2.4. PYROLYSIS RESIDUE

It will be clear from the experiments described in this section that the pyrolysis residue was long chain PBA. Degradation of PBA was carried out in the molecular still (Figure 1) at 260 and 270°C. The results obtained from these experiments are listed in Table 33.

The residue developed both a yellow colouration and insolubility on pyrolysis.

2.4.1. Volatilization and limiting viscosity number data

The plot of percentage volatilization against time

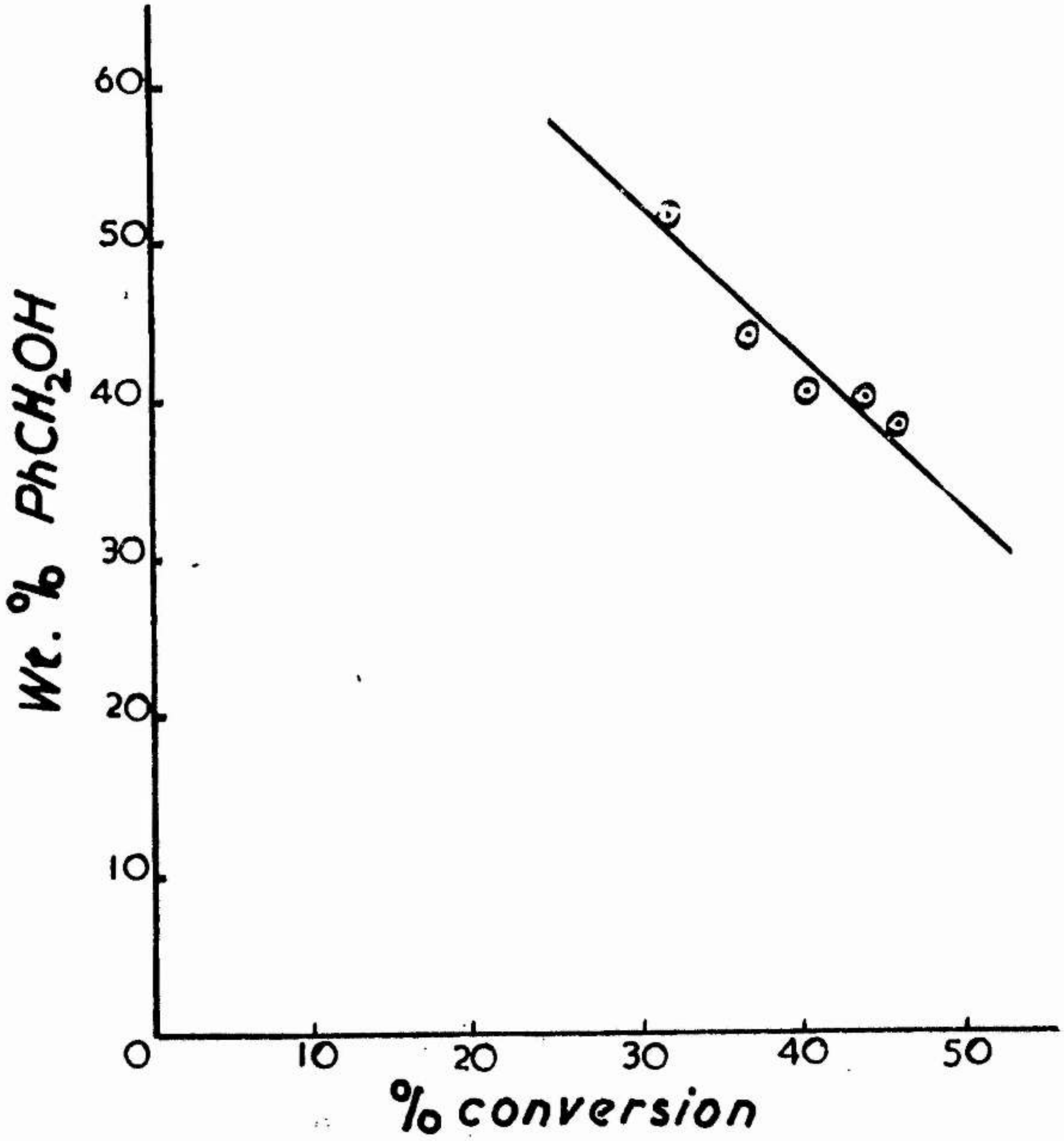


Figure 40 Weight percentage yield of benzyl alcohol against percentage volatilization for degradation of PBA(I) at 300°C
$PhCH_2OH$ analysis by gas chromatography.

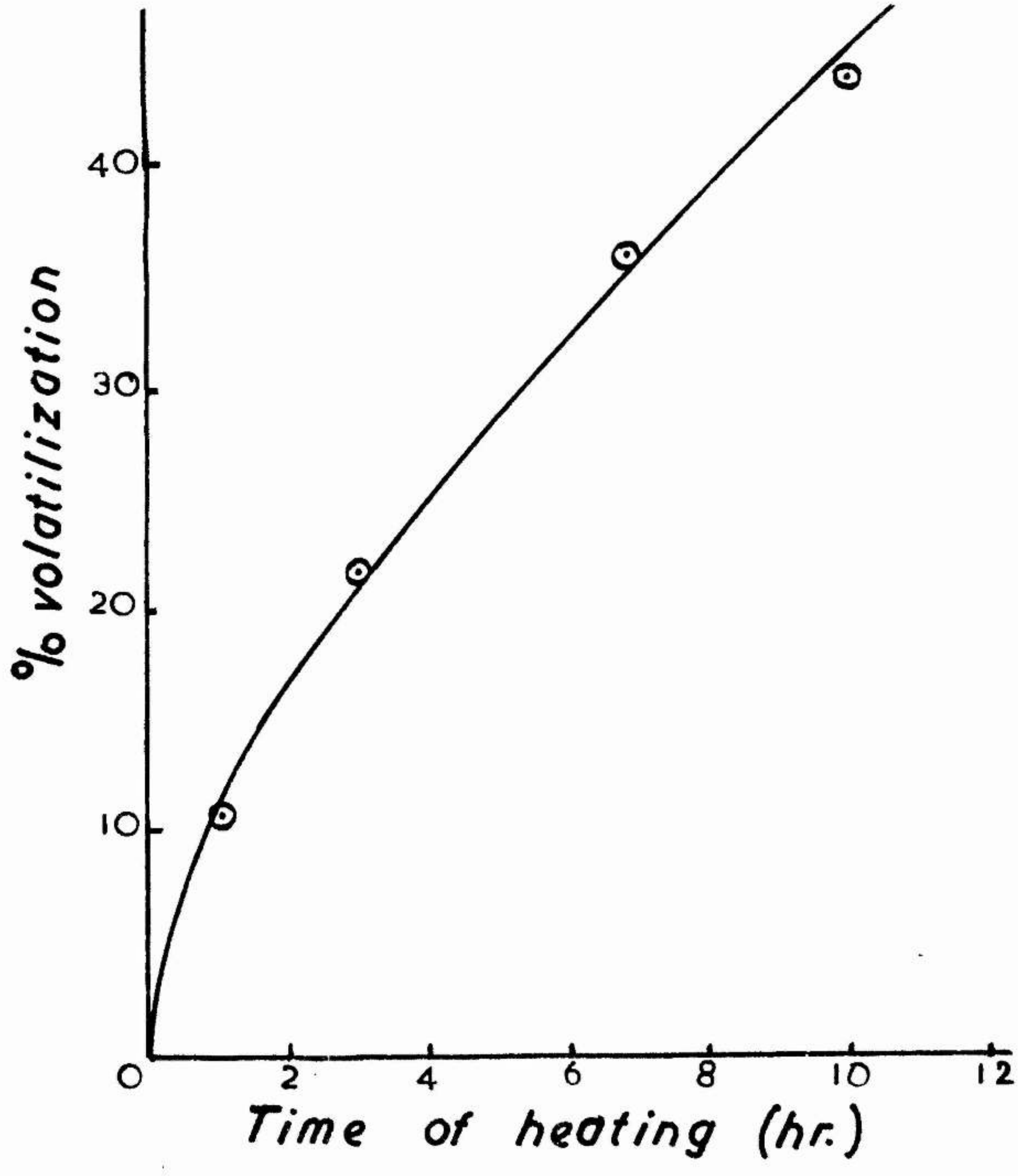


Figure 41 Percentage volatilization against time of heating at 270° C for PBA(I)
Molecular still used.

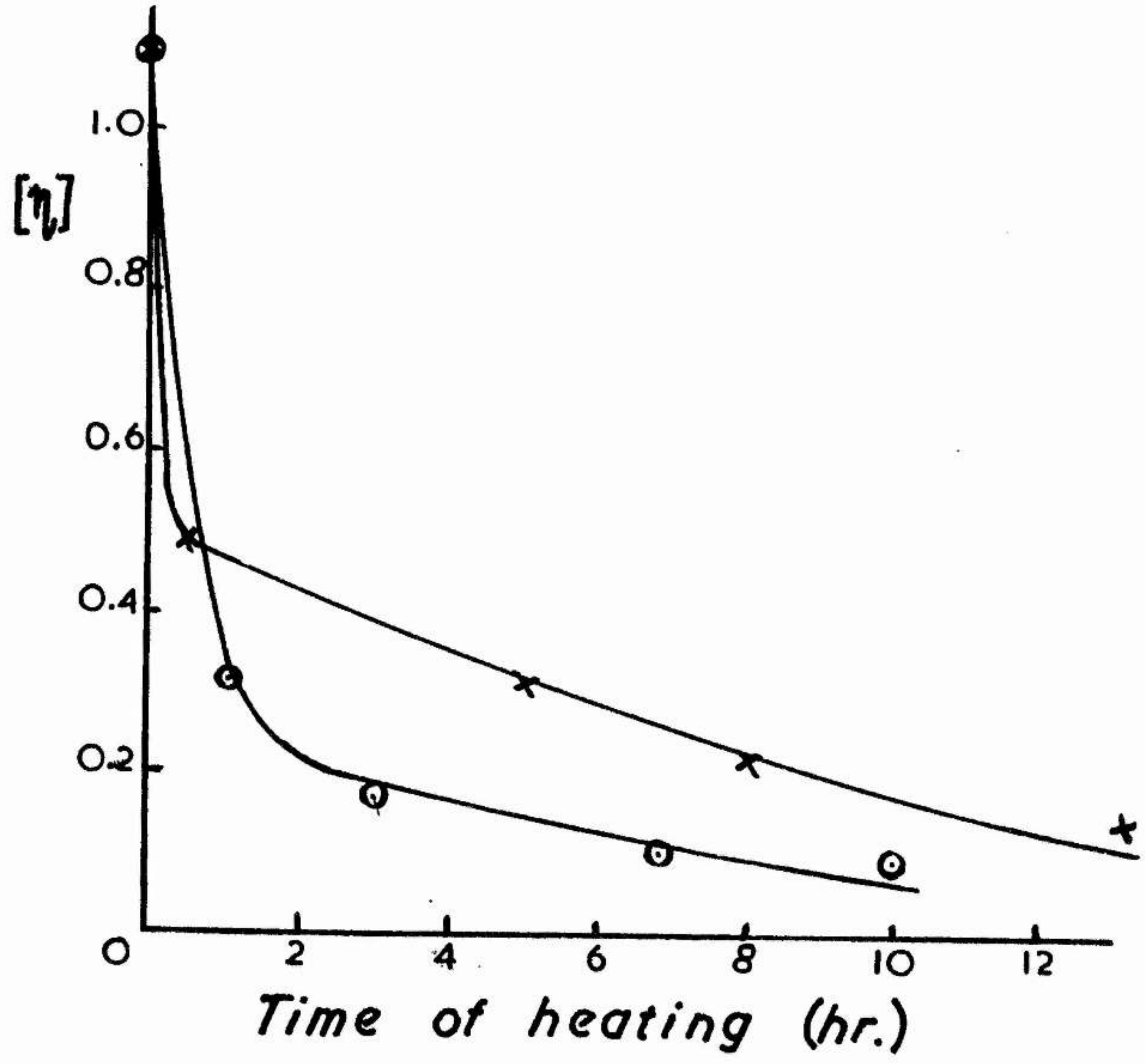


Figure 42 Limiting viscosity number [η] of pyrolysed residues against time of heating for degradation of PBA(I)

X , *at* 260° C ; *at* 270° C .

Molecular still used.

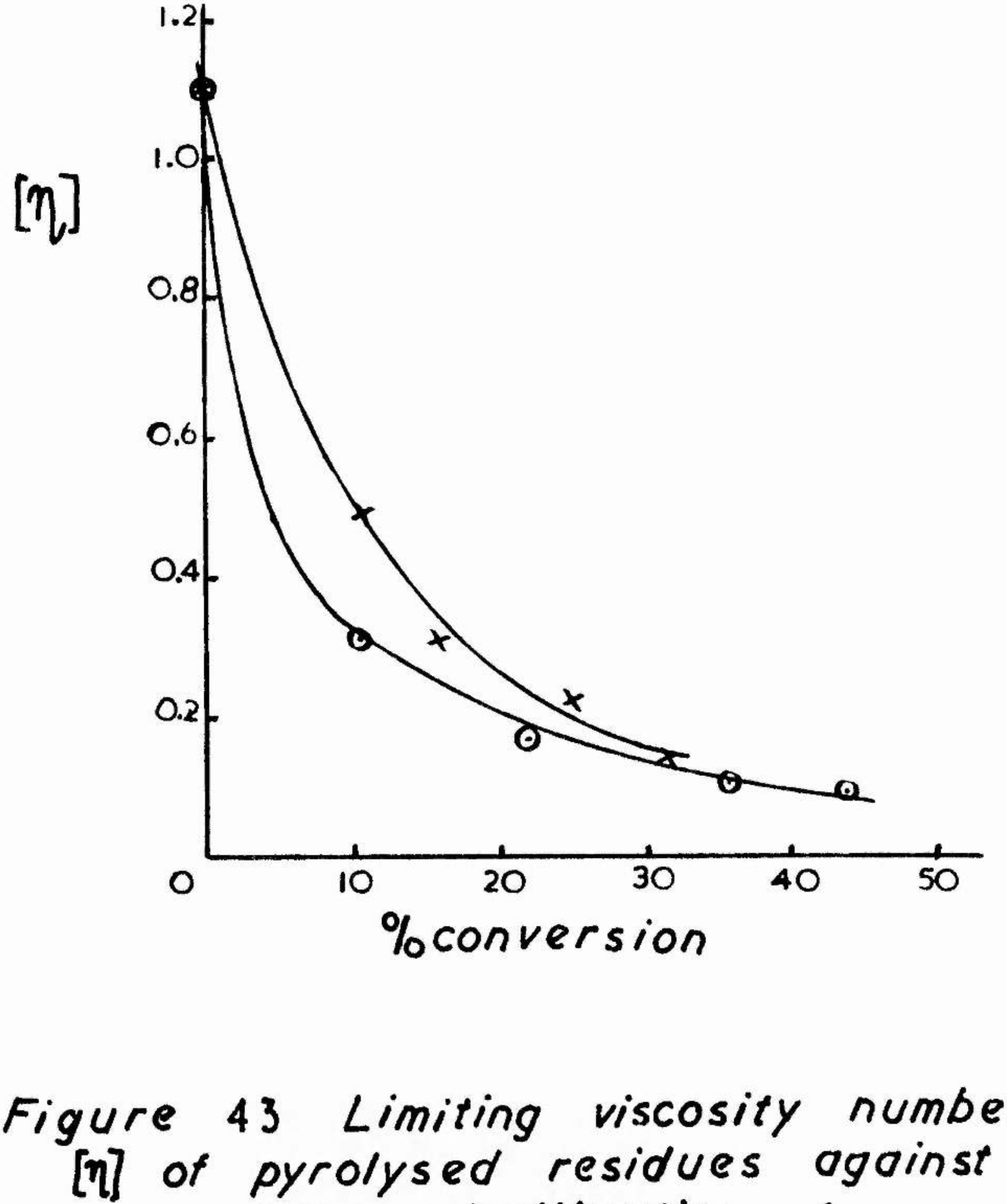


Figure 43 Limiting viscosity number [η] of pyrolysed residues against percentage volatilization for degradation of PBA(1)

×, 260°C ; ⊙ , 270°C .

Molecular still used .

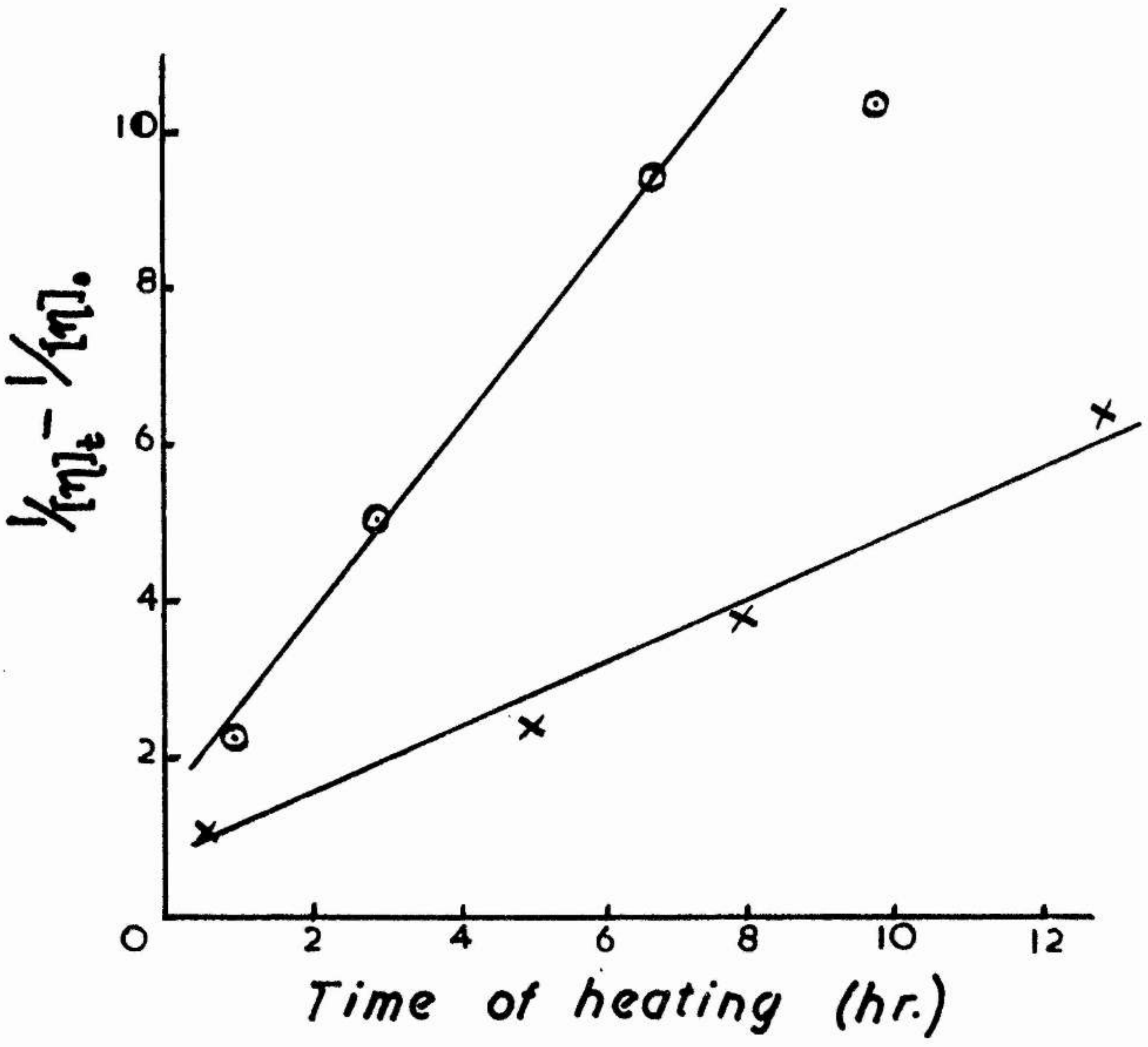


Figure 44 Plot of $1/[\eta]_t - 1/[\eta]_0$ against time of heating for degradation of PBA (I)
×, at 260°C ; ⊙, at 270°C .
Molecular still used

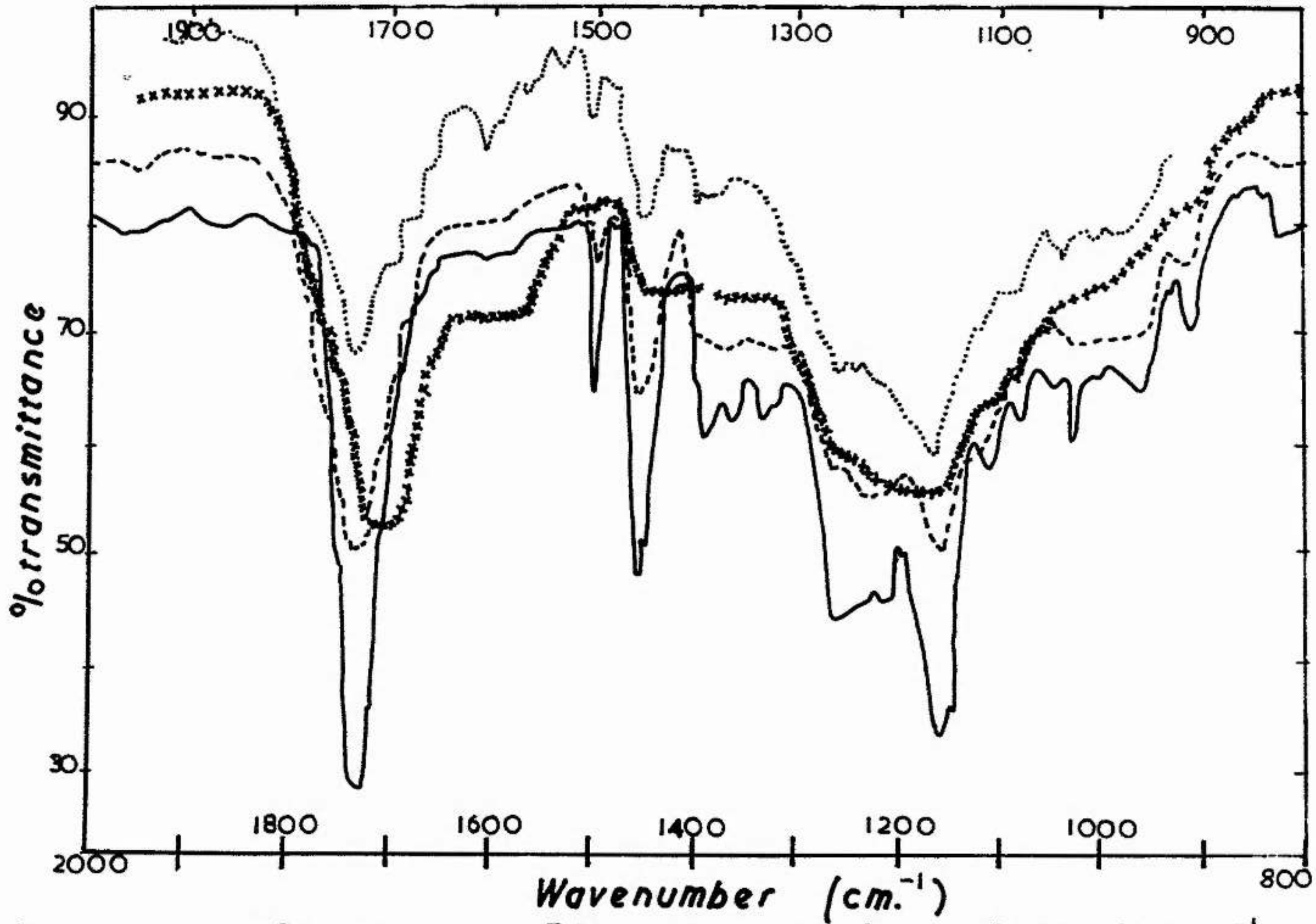


Figure 45 Section of I.R. spectrum from 2000—800 cm.$^{-1}$ for PBA (I) and pyrolysed residues of PBA(I) Undegraded, —— ; 31.5 % pyrolysed (R221), ------- ; 48 % pyrolysed (R190B), × × × × ; 67.5% pyrolysed (R194B), ········· .

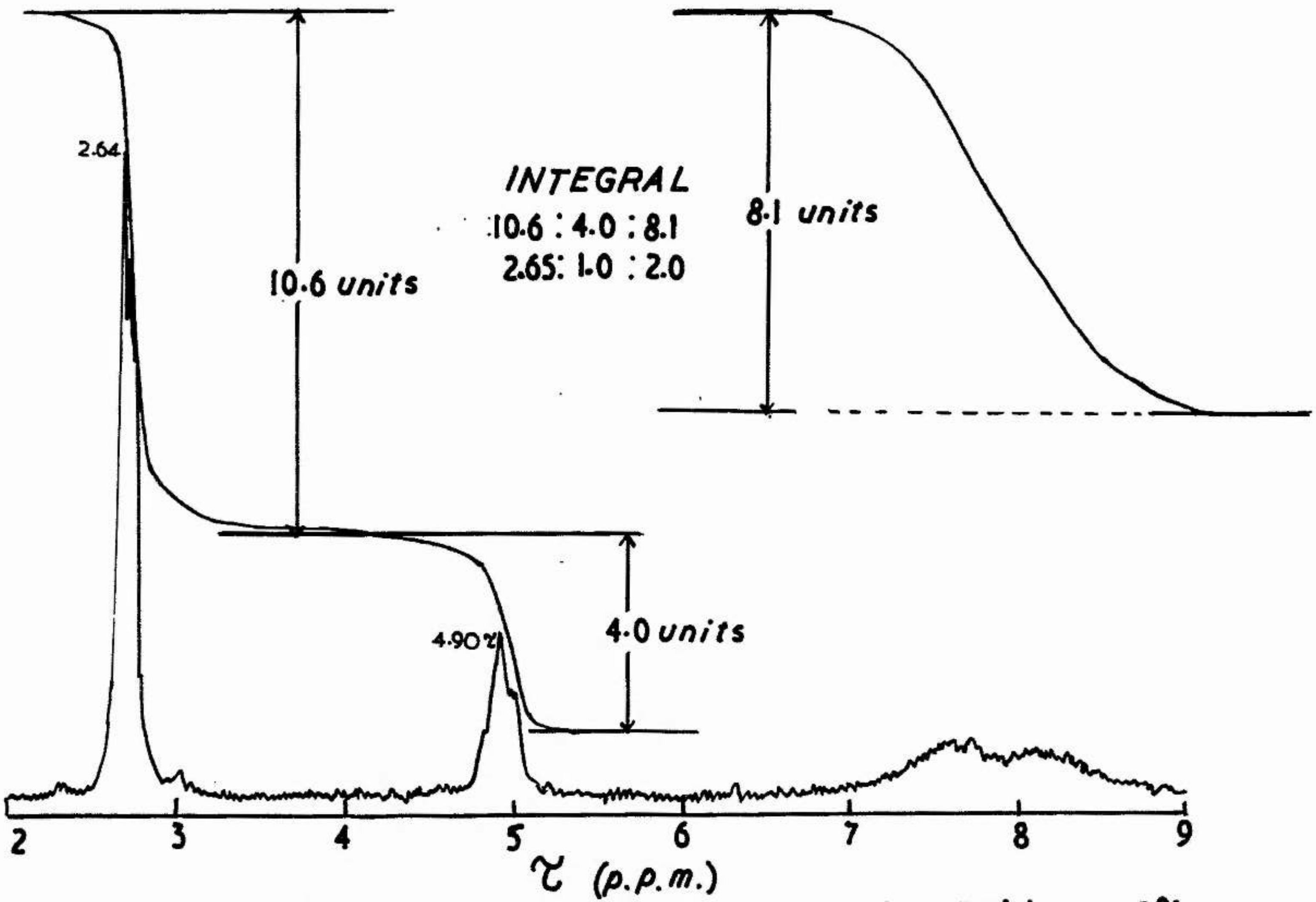


Figure 46 N.M.R. spectrum of residue of PBA(I) 44.5% pyrolysed in R180

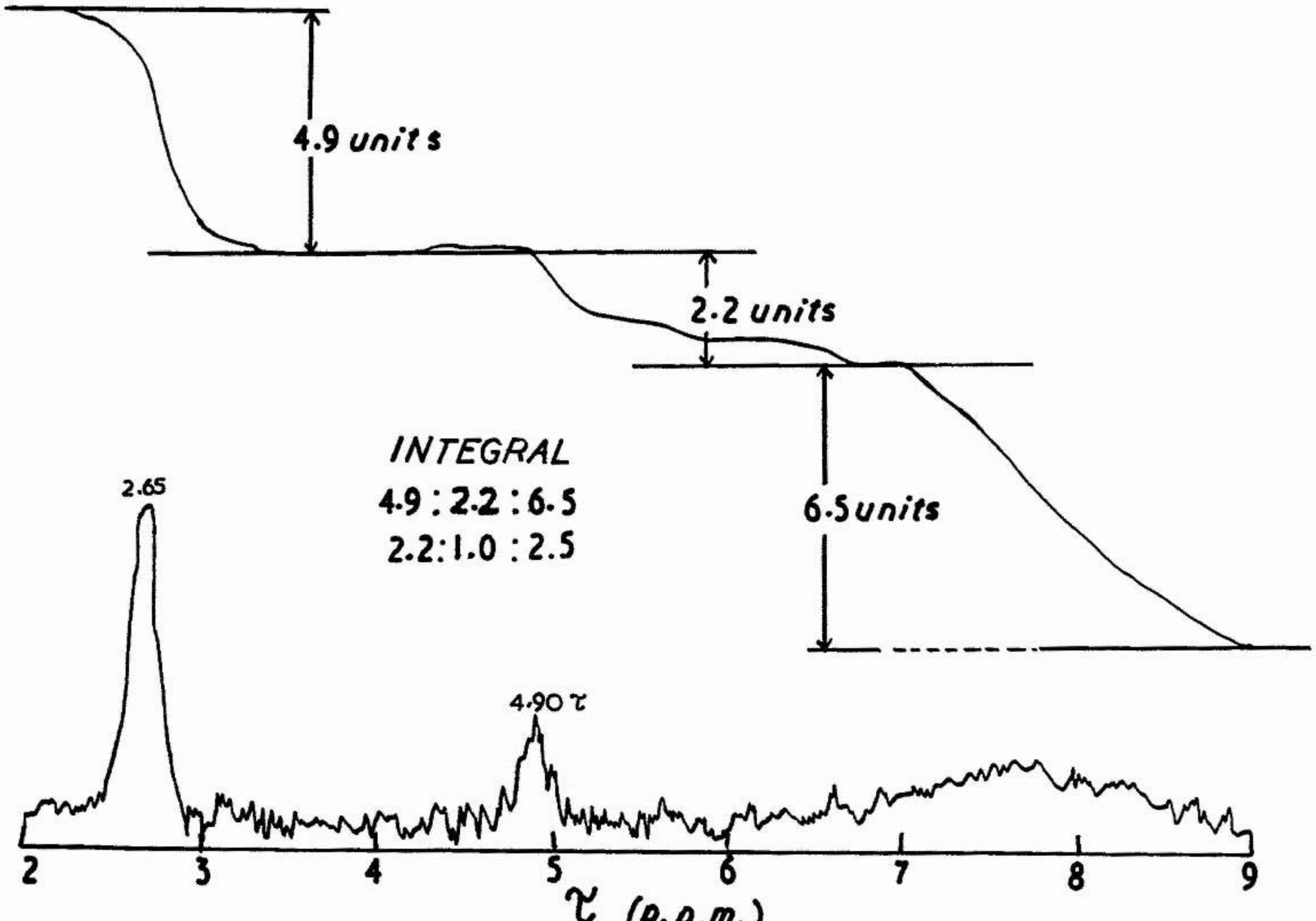


Figure 47 N.M.R. spectrum of residue of PBA(I) 67.5 % pyrolysed in R194B

of heating at 270°C (Figure 41) shows no unusual features, and the plots of limiting viscosity number against time of heating at 260 and 270°C are consistent with a polymer undergoing random breakdown. (See Figure 42).

However, the plot of limiting viscosity number against percentage volatilization for degradations at 260 and 270°C (Figure 43) differs from that for PMA. The points for 260° and 270° for PBA fall on different curves, while the limiting viscosity numbers of residues of PMA(7) pyrolysed at 286, 290, and 300°C, plotted against percentage volatilization, fall on a single smooth curve. The plot of $1/[\eta]_t - 1/[\eta]_o$ against time of heating for the PBA degradations is shown in Figure 44. The linear nature of the relationship between the two quantities illustrates the essentially random nature of the main-chain breaking process in PBA(1).

2.4.2. Infrared measurements

Infrared spectra of PBA(1) residues degraded to 31.5, 48, and 67.5% were examined. The section of the spectra from 2000 - 800 cm.^{-1} is shown in Figure 45. In this region the spectra of degraded residues differ from that of the undegraded polymer in a number of respects.

The carbonyl absorption at 1725 cm.^{-1} broadens markedly, particularly on the lower wavenumber side. It is not possible to tell, however, whether or not the carbonyl absorption decreases in extent. The only increases in absorption in this region of the spectrum occur between 1700 and 1450 cm.^{-1}, and are attributed [114] to the formation of conjugated structures - C = C - C = C - . The reduction in the peaks at 1500, 1450 and 1028 cm.$^{-1}$ reflects the diminishing concentration of aromatic rings in the polymer melt.[115] The sample pyrolysed to 67.5% has begun to show an increased absorption at 1450 cm.$^{-1}$ and this is thought to be associated[115] with the formation within polymer chains of sections containing up to six consecutive conjugated - C = C - linkages. The evolution of benzyl alcohol as degradation proceeds must cause a reduction in the main ester C - O concentration and hence the decrease in height of the peak at 1155 cm.$^{-1}$ [86]

Changes also occur in the region from 4000 - 2000 cm.$^{-1}$ Broad hydroxyl absorption appears in the residues produced by degradation in the apparatus in Figure 7. For the following reasons, this is believed to be produced by the presence of small amounts of benzyl alcohol which had not passed bend H, in pyrolysis, and had run back into the polymer melt.

(i). The absorption can be reduced although not completely removed, by keeping a film of the residue on the NaCl plates at 100°C in a vacuum-oven for 24 hr.

(ii). The residue pyrolysed to 31.5% in the molecular still does not show this absorption.

The aromatic ring is responsible for three peaks between 3100 and 3000 cm.$^{-1}$ in the undegraded polymer.[116] These diminish with increasing volatilization. A very weak absorption at 2720 cm.$^{-1}$ is found only in one residue pyrolysed to 60.8%, and may be due to aldehyde C - H linkages.

2.4.3. Nuclear magnetic resonance measurements

The spectrum of undegraded PBA(1) has peaks at 2.72, 5.03, 7.6, and 8.2 τ. These correspond to phenyl, ester - CH_2 -, methine, and chain methylene protons respectively. Benzyl acrylate monomer has peaks for phenyl protons at 2.72 τ and for - CH_2 - protons in the ester group at 4.85 τ. The integral evaluations of these peaks are as required by the formulae of the compounds.

Figures 46 and 47 show N.M.R. spectra of residues of PBA(1) pyrolysed to 44.5 and 67.5% respectively. Since the absorption of the ester - CH_2 - protons has moved largely from 5.03 τ to around 4.89 τ on pyrolysis, some change in the environment of these protons has occurred and it seems likely that at these extents of volatilization many of the ester groups remaining are attached to ethylenic carbon atoms, as in benzyl acrylate monomer. The peak position of the phenyl protons has also changed slightly to a lower τ value. The experimental integral evaluations for the pyrolysed residues can be compared with those which should be obtained theoretically, taking the weight percentage of benzyl alcohol produced as 40% of the total weight loss. At 44.5% volatilization two out of seven $PhCH_2O$- groups should be lost and the proton ratios should be 2.5 : 1.0 : 2.1. The value obtained from Figure 46 is 2.65 : 1.0 : 2.0 ; excellent agreement considering the approximate nature of this approach. For the 67.5% pyrolysed residue three out of five $PhCH_2O$-

groups should be lost from the polymer chains and the proton ratio should be 2.2 : 1.0 : 3.7. The experimental value is 2.2 : 1.0 : 2.5, which may indicate, as postulated earlier, that hydrogen atoms are stripped from the main chain at higher extents of volatilization.

No peaks were observed below 0 τ and therefore aldehyde and carboxyl protons are not present in detectable concentrations.

2.5. SUMMARY

Results obtained concerning the nature and the composition of the products are summarised in Table 32.

Table 32

Degradation products from PBA; pyrolyses below 305°C

Product	Components	Wt.% of total wt. loss	Comments
pyrolysis residue	long chain PBA	residue	yellow in colour; contains small amount of gel
liquid products	short chain PBA benzyl alcohol toluene and others benzyl acrylate	~ 50 ~ 40 2.9 trace	dependent on % volat. at least 5 other components
condensable gaseous volatiles	carbon dioxide	4.7	–
non-condensable gases	CO, CH_4, H_2 in molar ratio 7:2:1	~ 1	–

Spectroscopic investigations have shown with certainty the presence of double bonds in both the pyrolysis residue and the short chain fragments and isolated sequences of conjugated C = C bonds may occur in the former.

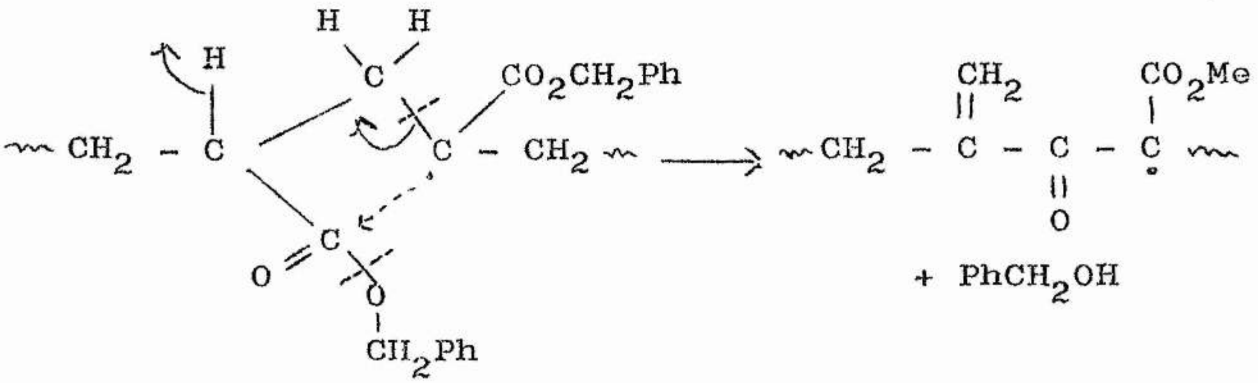
No other new structures can be recognised in the products.

3. DISCUSSION

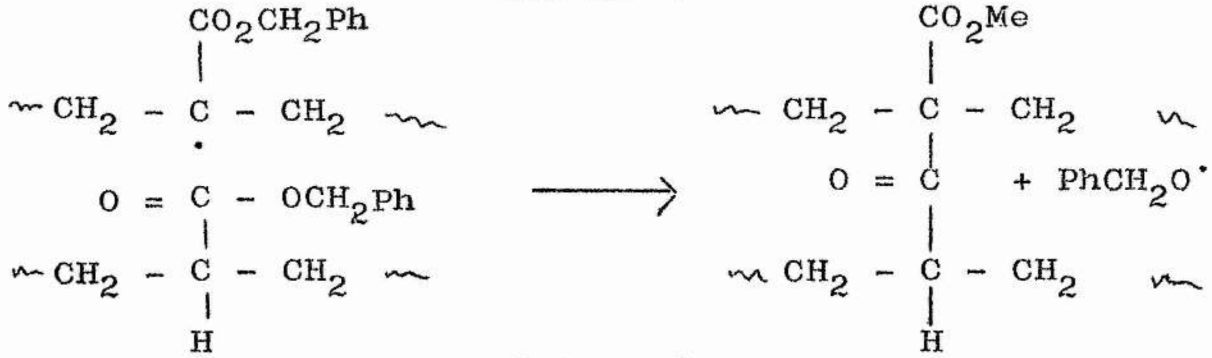
The degradation of PBA is in many respects similar to that of PMA. The exceptionally low monomer yield, the evolution of short chain fragments and the changes in limiting viscosity number show that PBA too degrades essentially by a random mechanism. An alcohol and carbon dioxide appear in appreciable amounts in the products from both polymers.

Two features of the degradation reaction, among others, are particularly indicative of a radical chain reaction. Firstly, the formation of insoluble gel, which cannot be explained convincingly by molecular or ionic mechanisms. Secondly, the relationship between the limiting viscosity number and percentage volatilization at different temperatures (Figure 43) can only be explained by a radical breakdown. The evolution of volatile materials is dependent on the size of the fragments produced in the melt reactions and the behaviour shown in Figure 43 can best be interpreted by postulating an increase in the ratio of intermolecular to intramolecular transfer as the temperature goes from 260 to 270°C. Intramolecular transfer, therefore, plays a larger part in the degradation process at lower temperatures. No other polymer is known to show an effect of this type, and this may be a weakness in the above explanation. One consequence of this behaviour is that the weight percentage of benzyl alcohol in the degradation products should decrease with temperature of pyrolysis for any given percentage volatilization, as intramolecular transfer produces a greater amount of short chain fragments. Limited data obtained at lower temperatures bear this out.

The considerable yield of benzyl alcohol proves the occurrence of a novel side group decomposition. The obvious broadening of the carbonyl absorption in the infrared spectrum indicates that new carbonyl structures are formed in the process. Efforts to determine the functionality of new carbonyl groups produced in this decomposition were again hindered by the ester carbonyl absorptions. The spectroscopic investigations did not produce evidence of any substantial carboxyl or aldehyde abscrptions to help to define the nature of the new carbonyl absorptions. This failure, in itself, supports the theory that on evolution of benzyl alcohol, a ketone structure is formed, since of possible functions, the ketone would be the most difficult to detect in company with the ester structure. It is therefore possible that routes analogous to Scheme 4 (Chapter IV, Section 4) and Scheme 7 (Chapter V, Section 4) may be responsible for the production of benzyl alcohol, and these are illustrated for PBA as Schemes 8 and 9.



Scheme 8



Scheme 9

Scheme 9, which involves a crosslinking reaction for the production of benzyl alcohol is supported by the complete insolubility of a residue pyrolysed to 78.5%.

The molar ratio of benzyl alcohol to carbon dioxide produced in the degradation of PBA is higher than that of methanol to carbon dioxide in PMA products. This supports the earlier suggestion that the formation of carbon dioxide is not linked at all with the alcohol formation. (See Chapter IV, Section 4).

The double bond formation in PBA may provide a contrast to that in PMA. Much of the double bond absorption in degraded PMA residues was obviously due to terminal methylenic groups, but there is no evidence for these in degraded PBA. On the contrary, the spectroscopic evidence from PBA residues suggests that numerous internal double bonds are formed between carbon atoms, and that isolated groups of conjugated - C = C - linkages may be present. Whether or not this indicates that benzyl alcohol is produced in reactions in which hydrogen atoms are stripped from the main chain is a matter of speculation. There is, however, no reason to believe that long sequences of C = C bonds are formed.

The question of the effect of the aromatic ring on the stability of acrylate polymers has been answered. It is estimated that PBA degrades as rapidly at 270° as PMA does at 290°C.

This preliminary investigation of the degradation of PBA shows that a more extensive study of certain features of the degradation might be worthwhile. A first step would be to obtain the rate curves for several degradation temperatures and determine the overall activation energy. Examination of the degradation at temperatures above 260°C would appear not to be very useful because of the competition between chain scission and benzyl ester side group decomposition. Further investigations should therefore be made at as low a temperature as possible, where one of these competing reactions might be very greatly suppressed, thereby permitting a more detailed study of the other. Finally, in view of the readiness of the side group decomposition in PBA it is possible that a similar decomposition might occur in poly (benzyl methacrylate) and perhaps compete with the characteristic depropagation reaction of the methacrylate polymers.

Table 33

Degradation of PBA(1) in molecular still.

Run	T.O.H. hr.	S.I.W. mg.	Wt.loss mg.	%volat.	$[\eta]$	$[\eta]_t - [\eta]_o$	%insol.	C.M.R. (CO_2) cm. Hg.
UNDEGRADED		PBA(1)			1.1	0.0		
At 260°								
209	0.5	94.2	9.9	10.5	0.49	1.1	11.6	-
210	5.0	95.3	15.2	16.0	0.31	2.3	5.7	3.5
220	8.0	99.6	24.9	25.0	0.22	3.6	3.6	6.8
221	13.0	98.2	30.9	31.5	0.14	6.2	6.8	-
At 270°C								
207	1.0	94.2	9.9	10.5	0.31	2.3	5.9	1.7
182	3.0	97.2	21.1	21.7	0.17	5.0	-	4.8
211	6.8	98.1	35.1	35.8	0.098	9.3	7.8	8.6
218	10.0	106.1	46.4	43.8	0.09	10.2	3.4	11.8

CHAPTER VII

REVIEW

The aim of this review is to summarise the work described in the preceding four chapters.

The vacuum thermal degradation of PMA has been thoroughly investigated, and a preliminary investigation of the degradation of PBA has been made. In the work on the degradation of PMA the nature of the products has been confirmed, and the rates of volatilization, activation energy, and changes in molecular weight during pyrolysis have been found. The effects of a free radical catcher, DAA, on the breakdown, and the factors affecting a gel formation reaction have been studied. Polymeric degradation products have been examined using spectroscopic techniques. For PBA the products of degradation have been qualitatively and quantitatively determined, and changes in limiting viscosity number during pyrolysis have been followed. Polymeric degradation products have been examined by infra-red and nuclear magnetic resonance spectroscopy.

Monomer is almost entirely absent from the degradation products of the two acrylate polymers studied. In the degradation of PMA the bulk of the weight loss is caused by the evaporation from the polymer melt of short chain fragments ($M_n = 704$). Carbon dioxide (4.8% of the total weight loss), and methanol (3.4%), are the next most abundant products of degradation. The value found for methanol may be low on account of partial decomposition of this component by copper surfaces within the still. The main products of degradation of PBA are short chain fragments and benzyl alcohol. The exact yields of these components are definitely dependent on the extent of volatilization, and probably on the precise temperature of pyrolysis. Under the conditions used in the present investigations benzyl alcohol comprises approximately 40%, carbon dioxide 4.7%, and short chain fragments around 50% of the total weight loss. Trace components have been detected in the pyrolysis products of both polymers.

The study of the effect of DAA on the breakdown of PMA demonstrated that the short chain fragments are produced, to a large extent, in a free radical chain reaction, and confirmed that transfer processes involving the tertiary hydrogen atoms on the polymer backbone are responsible for the formation of a large fraction of the short chain fragments. By analogy, it is virtually certain that transfer processes play a major part in the degradation of PBA.

The initiation step in the degradation of PMA is a random homolytic scission of the polymer back-bone. Chain-end initiation does not occur to any appreciable degree. Random chain scission followed by the evaporation of short chain fragments, produced mainly by transfer steps, allows the degradation to proceed almost as a completely random process. The plot of rate of volatilization R_1 against percentage conversion is close to the theoretical plot for a volatilization first order with respect to sample weight. The rate of volatilization R_2, (based on the weight of polymer remaining), remains virtually constant as far as 50% volatilization. A value of 37 k. cal./mole. was found for the activation energy of the overall process. For PBA an essentially similar picture may well prevail, but the degradation may approach ideal first order weight loss behaviour less closely because of the presence, to a significant degree, of a side group decomposition reaction.

The effects of time of heating, and of percentage volatilization at various pyrolysis temperatures on the molecular weight of the pyrolysed residue, for both retarded and unretarded degradations, can only be satisfactorily interpreted in terms of intramolecular transfer bringing about the bulk of the volatilization. Although there is no reason to believe that intermolecular transfer is entirely absent from the degradation, the following observations show that intramolecular transfer is the predominent transfer process.

(i). The plots of rate of volatilization R_1 against percentage volatilization for 286 and 290°C exhibit maxima around 10% volatilization.

(ii). The plot of relative molecular weight against percentage volatilization lies between similar plots for polymethylene, and polystyrene. The change in molecular weight with percentage volatilization for polymethylene is almost ideal for a linear polymer undergoing random chain scission, followed by solely intermolecular transfer. However, intramolecular transfer is known[73] to play a significant part in the degradation of polystyrene. It is possible that the intermediate behaviour of PMA is partly explicable in terms of molecules lost by complete "unbuttoning".

(iii). The molecular weight changes with time of heating and percentage conversion are almost unaltered by the presence of DAA.

For the degrading PBA system, the plots of limiting viscosity number against percentage volatilization for pyrolysis temperatures of 260 and 270°C fall on different curves. Such behaviour is unusual, and it is postulated that it provides evidence for the occurrence of both inter- and intramolecular transfer, and that, as a consequence, intramolecular transfer is more prominent at lower degradation temperatures.

Side group decomposition occurs in the breakdown of both PMA and PBA, as shown by the presence of carbon dioxide and the corresponding alcohol in the respective degradation products. The carbon dioxide and methanol from the degradation of PMA are largely produced in reactions, or reaction sequences, involving free radicals. Again by analogy, it is likely that radicals are involved in the formation of benzyl alcohol and carbon dioxide from PBA. Possible routes for the formation of these volatiles, particularly for methanol, have been considered. Methanol is not produced by the <u>combination</u> of straightforward acyl oxygen scission, and of subsequent hydrogen abstraction by the methoxyl radical. No completely satisfactory route to explain the formation of the alcohols has been formulated.

Spectroscopic analysis of the polymeric degradation products of PMA and PBA has failed to yield precise evidence of any new carbonyl structures formed during the pyrolysis. It is likely that in the infrared spectra of degraded residues the ester carbonyl absorption at 1725 cm^{-1} masks new absorptions in that region. On pyrolysis the 1725 cm^{-1} carbonyl absorption of PBA residues broadens markedly, and although this is taken to indicate that the environment of numerous $C = O$ linkages is changing, new carbonyl structures cannot be defined. Since aldehyde and carboxyl absorptions have not been detected, ketonic functions may be produced.

The spectral work has shown that ethylenic unsaturation is produced in both polymers during pyrolysis. Terminal methylenic structures have been determined in short chain fragments of PMA. Conjugated diene structures may be present in the pyrolysed residues of PMA. Groups and long chains of conjugated $C = C$ linkages are not formed in that polymer. On the other hand isolated groups of conjugated $C = C$ bonds may be present in the pyrolysed residues of PBA. There is no reason, however, to believe that long polyene chains are produced. N.M.R. evidence indicates that many of the ester groups in the short chain fragments of PBA are attached to doubly bound carbon atoms.

The pyrolysis residues of both PMA and PBA are not always completely soluble in benzene, and a yellow colouration develops during degradation. In the degradation of PMA both these reactions are free radical in nature, and therefore almost certainly likewise in the degradation of PBA. The factors affecting the crosslinking reaction occurring in the degrading PMA have been extensively examined. The gel formation tendency is dependent on the diluent, the percentage conversion to polymer, and the temperature in polymerisation. In addition, the extent of volatilization of the sample, and the temperature of degradation have an important bearing on the extent of insolubility produced during pyrolysis. These effects have been linked with the presence in the polymer of branched structures which are formed during polymerisation. It is postulated that such branched structures provide a framework for, and hence promote, the formation of insoluble crosslinked networks. Support for this theory has been obtained from data on the polymerisation of methyl acrylate, from the relation between gel formation tendencies and instability of degrading PMA samples, and from the observation that intramolecular transfer is predominant. (The presence of branches is known to favour intramolecular transfer at the expense of intermolecular transfer).[117] Combination of radicals produced by transfer reactions during pyrolysis can give rise to insolubilization; possible combinations are suggested.

The colouration, side group decomposition, and crosslinking reactions in degrading PMA are seen as ramifications of a free radical chain reaction, initiated by random homolytic scission and sustained by readily occurring transfer processes.

The pattern of degradation of PBA is believed to be basically similar to that of PMA. Further, but more detailed study of the degradation of PBA at temperatures rather lower than 260°C may prove worthwhile.

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THE THERMAL DEGRADATION OF POLY(METHYL ACRYLATE)

It has been proposed by Madorsky (1) that the pyrolytic degradation of poly(methyl acrylate) (PMA) is a random process probably involving transfer reactions. This conclusion was based only on the rate curves for the volatilization of degradation products and on the presence of large fragments (average molecular weight, 633) in these volatile products. In the course of studying this degradation in more detail, over the temperature range 286 to 300°C., we have measured molecular weights of the polymer residues at various stages of the reaction. Results are shown in Figures 1 and 2.

Similar curves to these are obtained during the thermal degradation of polyethylene and polymethylene (2) and this behavior has been shown to be consistent with a random mechanism (3). These results therefore support Madorsky's conclusion but do not exclude the possibility of some weak links in the chains. Such weak bonds could contribute to the initial rapid drop in molecular weight as appears to be the case with polystyrene (4).

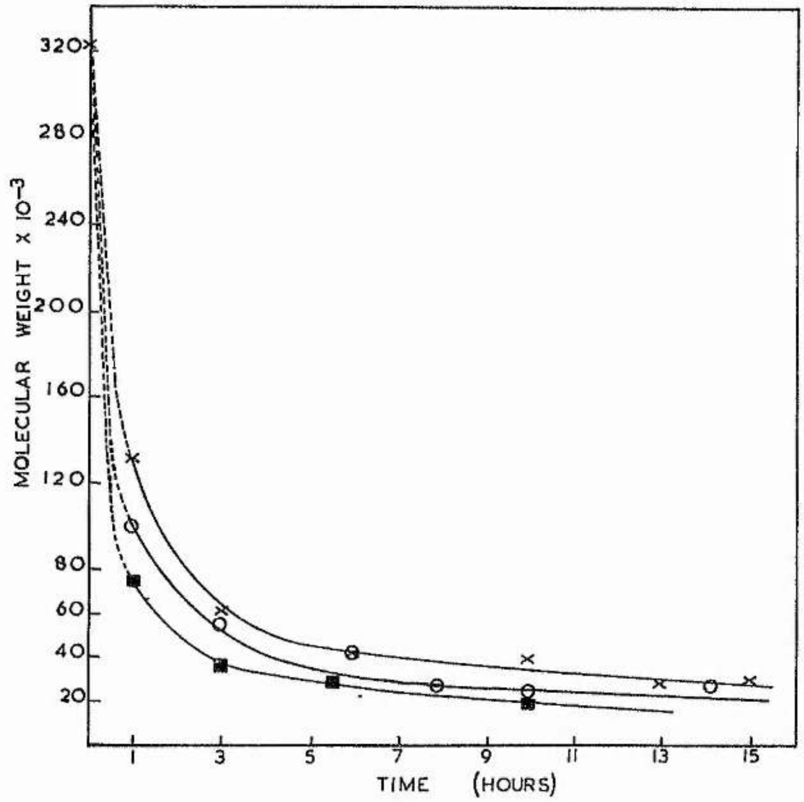

Fig. 1. Molecular weight of residue as a function of time of heating for PMA (7). Temperature of heating: (X) 286; (0) 290; (■) 300°C.

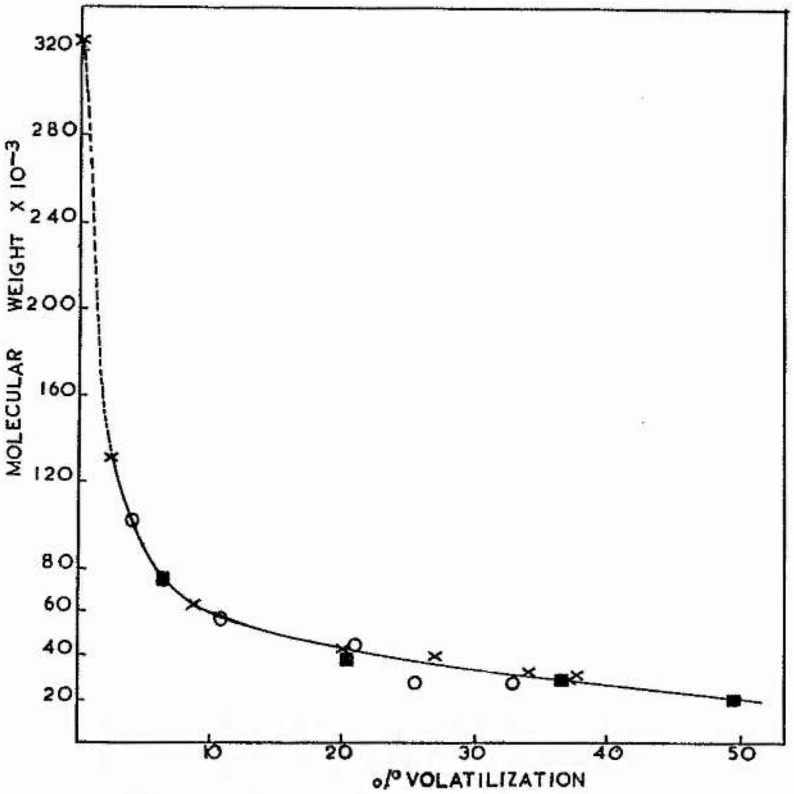

Fig. 2. Molecular weight of residue as a function of percentage volatilization for PMA (7). Temperature of heating: (X) 286; (0) 290; (■) 300°C.

The degraded polymer residues reported above were all soluble in cold benzene. Other samples of PMA, however, proved to contain a proportion of insoluble gel after degradation. The presence of this gel indicates a crosslinking reaction superimposed on chain scission. The proportion of gel in the polymer residue increases with the degree of volatilization of the sample as is seen from Table I. The results in Table I suggest that the amount of gel formed is not simply related to the initial molecular weight of the sample or to the degree of conversion during polymerization within the range studied, but rather to the temperature of polymerization. The effect might therefore be caused by subtle differences in structure such as differing degrees of branching.

Further work on the degradation of PMA is underway.

Experimental

Polymers were prepared in oxygen-free dilatometer tubes using benzoyl peroxide as initiator.

TABLE I

Polymer	Temp. of polymerization, °C.	Conversion, %	Solvent	Initial M.W.	% Volatilization at 286°C.	% Gel in residue
PMA (3)	60	22	Benzene	2.7×10^6	10.1	17.8
					18.3	37.8
					19.8	38.5
PMA (2)	55	23	Me acetate	3.2×10^6	12.9	<1.0
					30.6	1.3
					40.8	7.5
PMA (7)	45	12	Et benzene	3.2×10^5	8.8	0
					20.4	0
					37.1	0

Degradations were carried out in high vacuum in a modified version of the apparatus used by Grassie and Melville (5).

Molecular weights were determined by viscometry in benzene at 30°C. using the relationship $[\eta] = 1.28 \times 10^{-4} M^{0.7143}$ (6).

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