THE EFFECTS OF SMALL MOLECULES ON THE THERMAL DEGRADATIONS OF SOME VINYL POLYMERS

by

ROBERT C. McGUINESS

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SUPERVISOR : DR. I.C. McNEILL

Chemistry Department,
University of Glasgow.
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"The Road goes ever on and on
    Out from the door where it began.
Now far ahead the Road has gone,
    Let others follow it who can
Let them a journey new begin,
    But I at least with weary feet,
Will turn towards the lighted inn,
    My evening-rest and sleep to meet."

J.R.R. TOLKIEN.

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SUMMARY

In the introductory chapter, the development of research into thermal degradation is traced from study of homopolymers, through copolymers and binary polymer blends, to the present study of polymer/small molecule blends.

Following a chapter describing the experimental techniques employed, Chapter Three consists of results, abstracted into tabular form, of a survey of the effects of various small molecules on the thermal degradation of a range of polymers. On the basis of this survey, three blends were chosen, for reasons given in Chapters Four, Five, and Six, to be studied in detail.

Zinc bromide was found to exert a massive effect on the thermal degradation of poly(methyl methacrylate) by combining with pendant ester groups to form a co-ordination complex, which subsequently allows cyclisation reactions at low temperature, with liberation of methyl bromide. A complete reaction mechanism for blend degradation is proposed.

The effect of zinc bromide on poly(vinyl acetate) degradation, again thought to proceed through complex formation, is of a catalytic nature, resulting in liberation of acetic acid at temperatures much lower than those required

for release of acetic acid from poly(vinyl acetate) alone.

Chapter Six deals with the effect, on poly(methyl methacrylate) degradation, of zinc oxide, a widely used commercial additive. In this case, the effect is less marked, with zinc oxide promoting some decomposition of methyl methacrylate units at high temperature, accompanied by some reduction to zinc in the process.

In overall conclusion, it can be seen that, whereas some small molecules do not affect polymer degradation, a large number exert a significant influence. The type of effect depends on particular polymer/additive selection, but on the basis of Chapters Four and Five, one possible generalisation is that the likelihood of low temperature degradation is increased if polymer - additive complex formation is possible.

CHAPTER ONE

INTRODUCTION

The increasing use of synthetic polymers to replace traditional materials such as wood, metal, and natural fibres has stimulated research into more versatile polymeric structures with an even wider range of properties. It is now desirable to "tailor" polymer composition to a specific use, which can be accomplished by

(a) synthesis of a copolymer with well-defined properties, or

(b) modification of an existing polymer by the addition of a suitable compounding ingredient.

COPOLYMERS AND POLYMER-POLYMER BLENDS

There are many examples of this currently in use, e.g. a styrene-butadiene copolymer has much greater impact resistance than brittle polystyrene.[1] The so-called ABS "engineering plastics" consist of block or graft terpolymers of acrylonitrile-butadiene-styrene.[2] Whereas poly(vinyl chloride) (PVC) is liable to degradation in the course of processing, copolymers of vinyl chloride with vinyl acetate are more readily processed and more flexible.[3] In this case PVC is said to be internally plasticized. Finally, it is possible to improve the impact resistance of poly(methyl methacrylate) (PMMA) by synthesis of a copolymer of MMA with butyl acrylate.[4]

Binary polymer blends, i.e. physical mixtures of two polymers, also have extensive commercial application. High impact styrene polymers consist of blends of polystyrene (PS) with natural or synthetic rubber. PVC is the subject of numerous modifications, e.g. for impact resistance it is blended with butyl rubber, whereas it can also be compounded with polymeric oils which act as external plasticizers. Polystyrene is plasticized by any one of a large number of vinyl polymers, and lastly, both polypropylene and polyethylene are toughened by the addition of butyl rubber.[5]

PREVIOUS WORK

In recent years, in recognition of the growing importance of copolymers and blends in the commercial field, the amount of research conducted into these systems has been increasing steadily.

Early work by Mizutani[6] showed that the presence of vinyl polymers such as PS or PMMA during pyrolysis causes acceleration of polypropylene (PP) decomposition, with the additional result of forming block or graft copolymers due to interaction of vinyl polymer radicals with the PP chain.

Richards and Salter[7] studied the pyrolysis of PS in the presence of poly($\underline{\alpha}$-methyl styrene) (PαMS), concluding that PS is caused to commence degradation at a temperature at which it is normally stable. This effect was ascribed to the fact that PαMS is known to be less stable thermally than PS, and as it depolymerises, radicals are produced which initiate PS decomposition by abstraction of hydrogen atoms.

With the exception of a study of blends of polypropylene/polyethylene, which were found to have increased thermal stability relative to polypropylene,[8] most other research has concerned compositions containing PVC, and latterly, poly(vinyl acetate) (PVA).

In these cases, researchers have pursued parallel courses of study, information being gathered on copolymers of the relevant monomers as well as on blends of the homopolymers. Barlow, Lehrle and Robb carried out an investigation into the stability of VC-MMA copolymers relative to PVC/PMMA blends,[9] concluding that the latter are more stable. In a similar study, Zutty and Welch[10] detected methyl chloride, absent from the degradation products of both homopolymers, in the products obtained from pyrolysis of a PVC/PMMA blend. This is clear evidence of interaction between the degrading polymers.

In a more detailed study of PVC/PMMA blends,[11,12] McNeill and Neil interpreted this interaction in terms of initial chlorine radical attack on PMMA, causing the polymer to undergo chain scission followed by depolymerisation.

Interaction of two degrading polymers cannot be assumed automatically, however, as was shown in a comparison of the thermal degradation of S-MMA copolymers with that of PS/PMMA blends. In this case, it was found that copolymer degradation behaviour is intermediate between those of the homopolymers, but in the mixed system no interaction was detected between the two polymers during decomposition.[13]

Study of a series of VA-VC copolymers[14] showed that at each extreme of the composition range, incorporation of the co-monomer results in a copolymer of reduced stability relative to the homopolymer, an effect caused by the influence of neighbouring co-monomer units on the ease of elimination of the first acid molecule, prior to a chain reaction. A strong interaction also occurs in PVA/PVC blends with HCl liberated from PVC causing an acceleration in the deacetylation of PVA.[15] It is true, however, that in both these cases, no reaction is found which does not occur in degradations of the homopolymers alone; such behaviour is not true of VA-MMA copolymers[16] and PVA/PMMA blends.[17]

In the case of the copolymer, an intramolecular cyclisation takes place, involving adjacent VA and MMA units. This leads to the elimination of methyl acetate, behaviour analogous to that of VC-MMA copolymers. In blends of PVA/PMMA, interaction again occurs leading to accelerated breakdown of PMMA, caused by acetate radicals from degrading PVA initiating chain-scission and subsequent depolymerisation of PMMA. Anhydride units are detected in the degrading PMMA chain, another example of behaviour similar to that of PVC/PMMA blends.

Finally, in contrast, both VA-S and VA-ethylene (E) copolymers exhibit degradation behaviour which is largely predictable from studies conducted on the homopolymers alone.[16] In the blend of PVA/PE no interaction is detected,[18] and in a mixture of PVA with PS there is found only a very slight interaction of PS macroradicals with the carbonaceous residue produced on deacetylation of PVA. The deacetylation reaction was found to be only slightly retarded.[19]

POLYMER-SMALL MOLECULE BLENDS

As stated previously, it has been necessary to expand the range of useful polymeric materials by various means, the most common of which, by far, is compounding of a polymer with various small molecule additives.

In the field of commercial plastics, polymers are regularly blended with fillers, reinforcing agents, and plasticizers, often in addition to being blended with other polymers, as described previously. The most common materials which are added in large amount to polymer compositions are glasses, asbestos, carbon black, metallic oxides such as zinc oxide, or carbonates such as calcium carbonate, and clays. A wide variety of chemicals may be added in minor amounts to function as pigments, lubricants, anti-oxidants, curing agents, flame retardants etc. For example, zinc stearate functions as a lubricant and stabilizer for many polymers, the most common of which is PVC.[20] Titanium dioxide, when compounded with PP, acts not only as a pigment, but has been found to improve weathering resistance.

Vinyl polymers are known to be particularly susceptible to oxidative degradation, and so this is prevented by the addition of antioxidants, typically hindered phenols.[21] Finally, as well as being included in various composites as a filler, as a pigment, and as a fire retardant,[22] zinc oxide is also used as a curing agent for ethylene-propylene copolymers.[23]

In view of the widespread occurrence of polymer-small molecule composites, it seems reasonable that the logical progression in the field of thermal degradative research is a movement from studies of homopolymers, copolymers and blends, as described, ultimately to studies of polymer-small molecule systems, a movement not yet reflected in the amount of work carried out on polymer-additive blends.

PREVIOUS WORK

The pyrolysis of PMMA in the presence of some acid or acid-generating species was studied by Gruntefest and Young, who determined by mass spectrometry that the major degradation product is not MMA as in the case of PMMA alone, but dimethyl ether. After the degradation was completed, a black residue remained,[24] in direct contrast to the behaviour of PMMA alone, which leaves no residue.

PMMA/silver acetate blends were studied by Jamieson,[18] who found that depolymerisation of PMMA is markedly increased in the presence of the silver salt, indicative of an interaction between polymer and additive during degradation. The explanation given is that radicals produced from decomposition of silver acetate attack the polymer chain, causing chain-scission and subsequent depolymerisation, via a hydrogen abstraction process.

Finally, the effect of the presence of small amounts of zinc chloride on the thermal decomposition of poly(methyl acrylate) (PMA) and of MA-MMA copolymers has been the subject of recent investigation.

Kochneva[25] found that $ZnCl_2$ affects both free radical stages in the degradation of PMA. The formation of a complex between $ZnCl_2$ and the ester carbonyl group of PMA leads to the formation of methanol and hydrogen.

In the case of MA-MMA copolymers,[26] Kopylova also found that $ZnCl_2$ alters the mechanism of degradation, causing increased production of CH_3OH, CO_2, CO and H_2O, with decreased production of MMA and MA, relative to the degradation of the copolymer alone.

RADICAL POLYMERISATION IN THE PRESENCE OF SALTS

The progression of degradation studies from polymers to binary polymer blends to polymer-additive mixtures has been quoted previously as an argument in favour of studies being carried out on polymer-additive blends. A further argument in favour of the study of such mixtures arises from the widespread trend of including various inorganic salts in vinyl polymerisation systems, a subject recently reviewed in some detail by Zubov and Kabanov.[27]

Research has shown that the presence of salts such as $ZnCl_2$, $ZnBr_2$, LiCl, $MgCl_2$ and $AlBr_3$, increases the rate of radical polymerisation of vinyl monomers such as MMA, AN, and VC. Molecular weights, composition, and structure of copolymers are also affected.

It is thought that the salts, which form co-ordination complexes with the functional groups of reacting species, affect the rate and mechanism of all the stages in radical polymerisation i.e. initiation, propagation, transfer, and termination. In the opinion of Zubov and Kabanov, one of the deficiencies of usual free radical polymerisation is that the rate constants of the mechanism depend on the chemical nature of the monomer, which leads to difficulty in controlling chain propagations and, therefore, total rate, molecular weight, and composition of the products. The object of inclusion of salts in this type of polymerisation is to establish new methods of controlling radical synthesis of macromolecules, by complex formation with propagating radicals. Since it is considered that the field will continue to expand[28] it is very desirable to evaluate the effect on polymer behaviour of any residual salt.

GENERAL SURVEY

On the basis of these arguments, it was decided to conduct first an exploratory survey of the effects of various small molecules on vinyl polymer degradation.

To achieve this, different types of additive were used e.g. nonvolatile species such as LiCl; Lewis acids such as $ZnBr_2$, $FeCl_3$; additives which themselves decompose to yield products capable of interaction with the degrading polymer, such as potassium nitrite, as well as additives widely used in the field of commercial plastics, such as zinc oxide and zinc stearate.

The principal experimental technique employed in conducting the survey and also used extensively throughout the subsequent work was Thermal Volatilization Analysis, (TVA), a technique developed by McNeill specifically for the study of thermal degradation of polymers. The technique is described in detail in Chapter Two.

After the results of the completed survey, which is reproduced in full in Chapter Three, had been assessed, it was decided to focus attention on several particular polymer-additive compositions and subject these to detailed investigation. The compositions chosen (for reasons which will be elaborated subsequently) were PMMA/$ZnBr_2$, PVA/$ZnBr_2$ and PMMA/ZnO blends.

CHAPTER TWO

APPARATUS AND EXPERIMENTAL TECHNIQUES

PREPARATIVE METHODS

Purification of Monomer

Methyl methacrylate (Hopkin and Williams, Ltd.) was freed from inhibitor by washing with dilute aqueous alkali, followed by distilled water, before drying over anhydrous calcium chloride. The monomer was distilled twice under vacuum before polymerisation.

Purification of Initiator

Azobisisobutyronitrile (Eastman Kodak, Ltd.) was purified by twice recrystallising from ethanol, the solution being filtered hot to remove any insoluble material arising from polymerisation of initiator decomposition products.[29]

Purification of Additives

Zinc bromide (Hopkin and Williams, Ltd.) and Cobalt (II) bromide (B.D.H. Ltd.) were purified by sublimation under vacuum, any previously absorbed water being condensed out in a liquid nitrogen trap.

Zinc oxide (B.D.H. Ltd, AR grade) was used without further purification.

Polymerisation Technique

Three polymer samples, viz. poly(methyl methacrylate) (PMMA) of two different molecular weights, along with poly(vinyl acetate) (PVA), were used in this work, and a brief account of their history including number average molecular weight is given in Table 2-I.

The PVA was a laboratory sample supplied by B.D.H.Ltd., which was then purified by precipitation in petroleum ether from benzene solution. The process was repeated before drying the sample in a vacuum oven at 40°C for several days.

Both PMMA samples were prepared by free radical initiation, in Pyrex glass dilatometers with graduated stems. The required amount of initiator was washed into the dilatometer with acetone (AR) which was then removed under vacuum. Methyl methacrylate was degassed three times under vacuum, following standard procedure, before the calculated volume was distilled into the dilatometer from a graduated reservoir. The dilatometer was then sealed under a vacuum of better than 10^{-5}mm Hg.

Polymerisations were carried out in a thermostat tank controlled to ±0.01°C, the extent of reaction being followed by monitoring volume contraction, in order to restrict conversion to 10%.

PMMA was precipitated by adding the solution to a large volume of methanol, the resulting polymer being purified by reprecipitation in methanol from chloroform solution. The polymer was then dried in a vacuum oven for several days.

Polymer	$\overline{Mn}$	History
PMMA	610,000	Bulk·Polymerisation at 60°C using azobisisobutyronitrile (0.05% $^W/V$).
PMMA (2)	40,000	Bulk Polymerisation at 75°C using azobisisobutyronitrile (4% $^W/V$).
PVA	45,000	BDH sample, purified by reprecipitation.

Table 2-I

Polymer Sample History

Molecular Weight Determinations

Number average molecular weights ($\overline{Mn}$) of the polymers were determined at 25°C by osmometry, using a Mechrolab Model 501 High Speed Membrane Osmometer fitted with a Sylvania 300 grade cellophane membrane, with toluene as solvent.

BLENDS

Polymer-Polymer Blends in General

In contrast to the normal behaviour of small molecules, if two polymers are dissolved in a common solvent, the resulting solution will generally separate into two phases. The polymers are said to be incompatible. Films cast from such solutions are opaque, as a result of the different refractive indices of the two polymer phases.[30] In pyrolysis of such samples, interaction of the two components can take place only at phase boundaries, or by diffusion of small molecule products from one phase into the other.

Since homogeneity depends on the heat and entropy of mixing,[31] the frequent occurrence of polymer-polymer incompatibility is ascribed to a small entropy of mixing for large polymer molecules, coupled with an endothermic heat of mixing.[32]

Preparation and Structure of Polymer-Additive Blends

For the most part, polymer-additive blends were prepared as films cast from a common solvent by the method employed by McNeill.[11] In the cases subsequently discussed, viz. blends of PMMA, and of PVA, with $ZnBr_2$, the films were found to be completely transparent, a property which previously has been taken as evidence that the components of a mixture are compatible.[11]

This compatibility indicates that the Free Energy for the mixing process must now be negative: this could be caused either by a larger entropy gain for a polymer-small molecule system than for a polymer-polymer system, or by an exothermic heat of mixing due to some association between the polymer and the small molecule, or a combination of both. As a result, sample form was found to be reproducible, and the homogeneities of the samples ensured maximum effect of the additive on polymer degradation during pyrolysis.

In the case of blends involving zinc oxide, however, mixing had to be achieved by grinding a mixture of solid oxide with solid polymer, since no suitable common solvent could be found. In this case, blending is possible only after fusion of the polymer, and the test of sample preparation procedure is reproducibility of degradation behaviour.

Blend Study by Visible Spectroscopy

After considering the suitability of physical techniques such as IR and UV spectroscopy for study of initial blend structure, it was decided that the technique liable to yield most information on possible complex formation, prior to degradation, was Visible Spectroscopy.

Thus, solid reflectance spectra were obtained for several samples comprising combinations of PMMA, acetone and $CoBr_2$, using a Beckmann DK-2A spectrophotometer; samples were either films cast from a common solution, prepared in a dry-box, or powder samples pressed into discs.

The reasons for this choice of technique, along with reasons for sample selection and interpretation of results are discussed in the appropriate section of Chapter Four.

Thermal Volatilization Analysis

Thermal Volatilization Analysis as a technique has been developed by McNeill, and its application to the study of polymer degradation is the subject of a number of publications.[33-35]

Since TVA studies are of prime importance in this work, it will be useful to describe some theoretical, as well as practical, aspects of the technique.

Principle of TVA

TVA is a physical technique which involves a continuous measurement of the pressure exerted by volatile products released from a heated polymer. Degradation is carried out under vacuum, ensuring that volatiles are immediately pumped from the sample, past a Pirani Pressure Gauge, into a cold-trap. Pirani response is recorded continuously as a function of oven temperature, producing a measure of the rate of volatilization of the sample. Discrete reactions which produce volatiles give rise to peaks on the TVA trace.

Description of the Apparatus

A schematic picture of the general experimental layout is given in Fig. 2.1, while Fig. 2.2 shows the usual sample heating assembly, and Fig. 2.3 shows the modified degradation tube head assembly used extensively throughout this work.

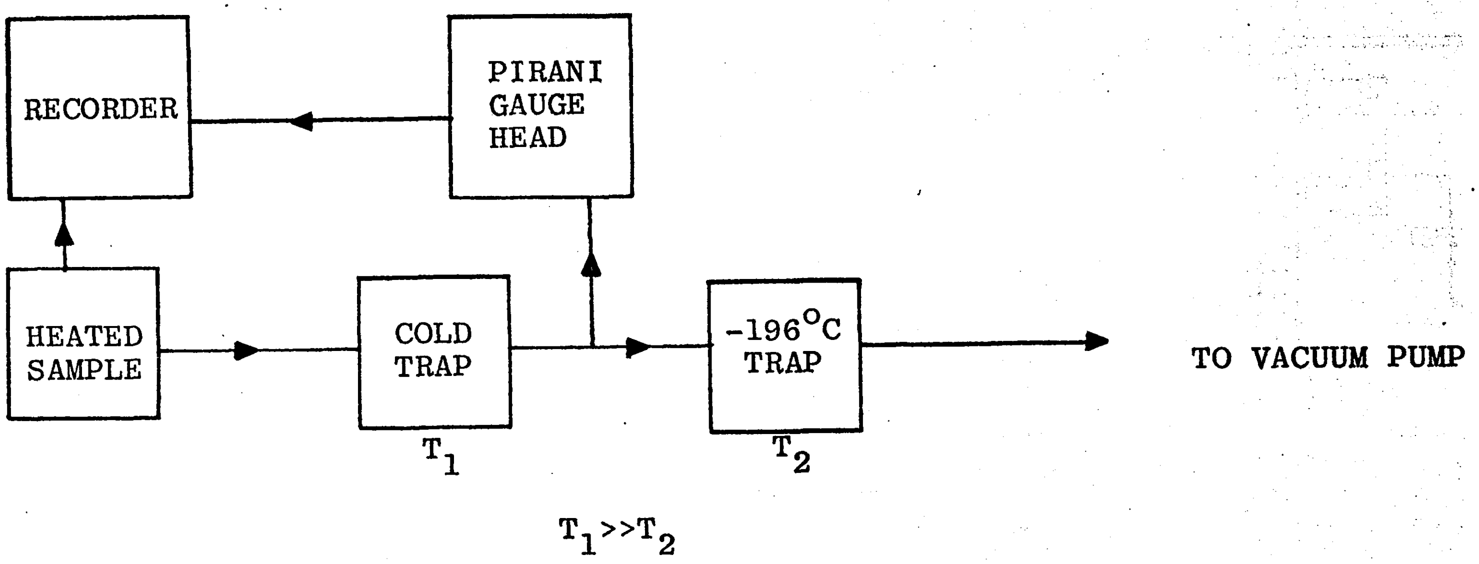


Figure 2.1. Principle of TVA

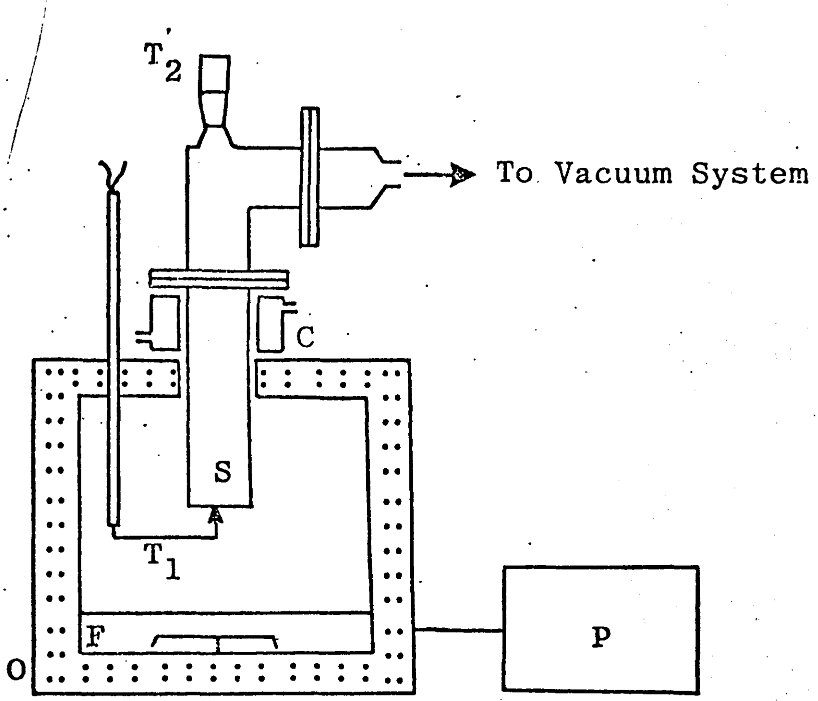
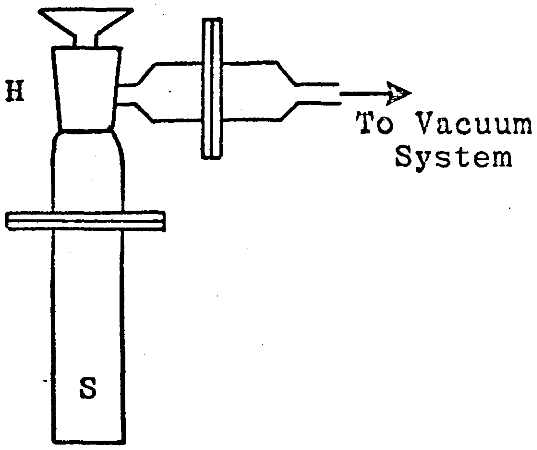


Figure 2.2 Heating Assembly

C.	Water Jacket
F.	Fan
O.	Oven
P.	Temperature Programmer
S.	Degradation Tube
T_1	Oven Thermocouple
T_2	Port of Calibration Thermocouple



H.	Degradation tube head incorporating stopcock, large bore, right angle type.
S.	Degradation Tube

Figure 2.3 Modified Assembly.

This slight modification enables sample preparation to be carried out in a dry-box, and subsequent transfer of the sample to the vacuum system to be made without contact with atmospheric moisture.

The polymer sample, usually in the form of a fine powder or a film cast from a suitable solvent, is heated on the base of a glass tube, 15cm. long, 3.5cm. in diameter, constructed from a Pyrex FG 35 flange. The top of the tube and the greased flange joint are cooled by a water-jacket ("cold-ring") during the experiment. Heating is carried out by a Perkin Elmer F11 oven in conjunction with a linear temperature programmer, which allows the sample to be heated isothermally, or programmed linearly from ambient temperature to 500°C at heating rates from 1 to 40°/min. Oven temperature is recorded by means of a Chromel-Alumel thermocouple fixed near the base of the degradation tube.

Determination of Sample Temperature

The temperature recorded during an experiment is that of the oven, as measured by thermocouple T_1 shown in Fig. 2.2, and not the actual sample temperature which is found to lag behind. The magnitude of this lag depends upon temperature, heating rate, particular degradation tube, and position of the oven thermocouple; it is caused by the insulating effect of Pyrex glass, coupled with heat loss to the cooling jacket.

For a particular apparatus and heating rate, the temperature lag is consistent,[34] and it may be plotted as a function of temperature (Fig. 2.4) by recording sumultaneously the outputs of the oven thermocouple and that of another thermocouple making contact with the inner base of the degradation tube. A small bead of Apiezon "L" grease is used to improve thermal contact between thermocouple junction and glass, and to simulate molten polymer.[34]

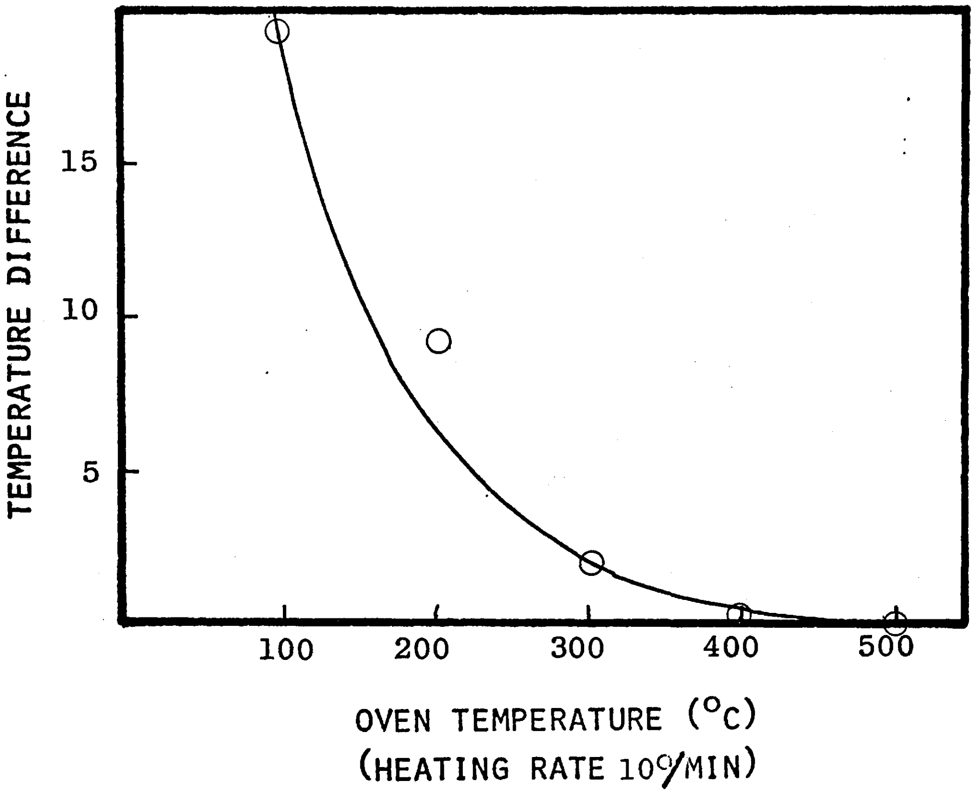


Fig. 2.4

Temperature Calibration Plot

From the graph, it is apparent that thermal lag falls, with increasing temperature, approaching zero in the high temperature region.

This thermal lag was found to be reproducible for a particular tube and particular heating rate (10^{o}/min in this work).

Since the degradation tube is massive relative to the sample, the large heat capacity of the tube ensures that exothermic or endothermic reactions in the degrading polymer should have little effect on sample temperature.

Differential Condensation TVA[36]

This is a development of the basic TVA system, designed to yield information on the nature of volatile products. The principle is the same as that of TVA, viz. Pirani Gauges used to monitor the passage of volatile products from degrading sample to liquid nitrogen trap (-196°C).

In this case, shown schematically in Fig. 2.5, the volatiles are pumped along four geometrically equivalent routes to liquid nitrogen traps. Each of the four routes contains a secondary cold-trap, normal temperatures for which are 0, -45, -75, and -100°C respectively. Each trap, including the final cold-trap, is followed by a Pirani Gauge which will register only the pressure of those volatiles not condensed in the particular trap. The outputs of these Pirani Gauges, along with that of the oven thermocouple, are transmitted via a multi-gauge head unit to a twelve channel recorder. Thus volatile products arising from the degrading sample are fractionated, according to whether or not they condense at each of the five temperatures, and a differential condensation TVA trace obtained. Inspection of this, in the light of previously determined behaviour of various compounds in the different traps, often yields a qualitative picture of the degradation.

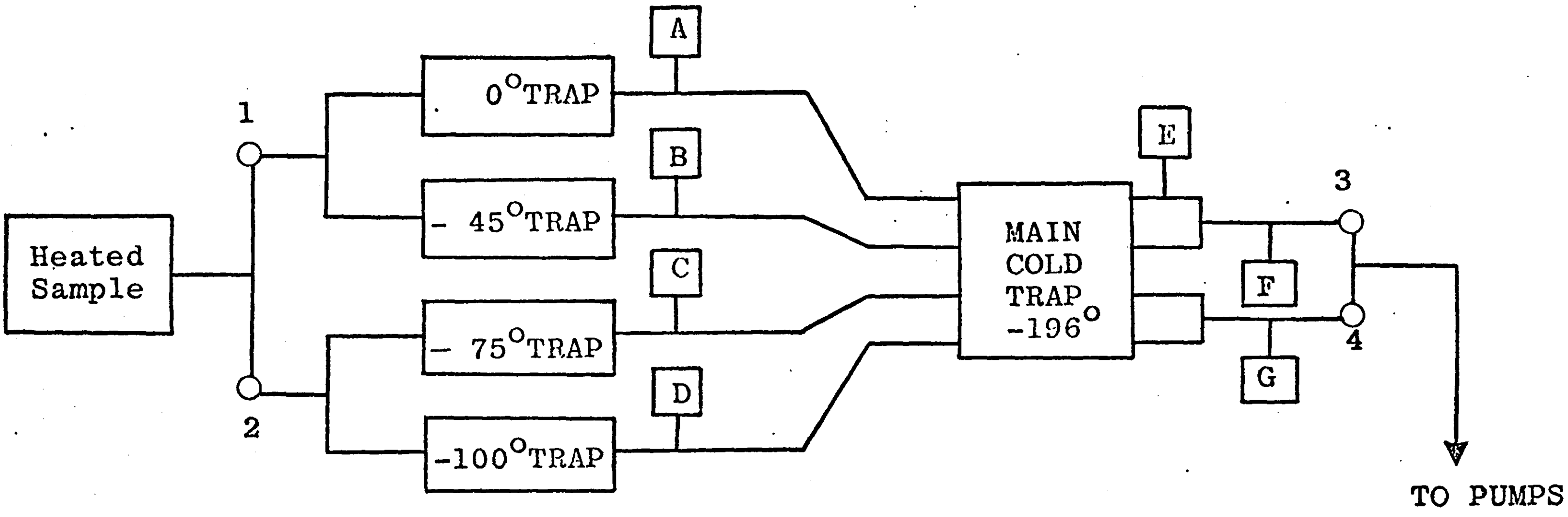


Figure 2.5 Differential Condensation TVA

A, B, C, D, E : Pirani Gauge Heads

F, G : Sample Collection Points

1, 2, 3, 4 : Right Angled Stopcocks

Product Analysis of TVA Fractions

Products arising from degradation in the TVA apparatus fall into one of two categories:

(a) The involatile residue

(b) Volatile products, which can be further subdivided into three classes:

(i) Those products which are volatile at the temperature of degradation, but involatile at ambient temperature (Cold-Ring Fraction, CRF).

(ii) Those products volatile at degradation temperature, but involatile at -196°C (Condensables).

(iii) Those products volatile at degradation temperature and volatile at -196°C (Non-Condensables).

The involatile residue, which remains on the tube base, may be subjected to study by Infra-Red Spectroscopy, carried out in the form of a KBr disc, pressed under vacuum. Products forming the cold-ring fraction are found to collect on that upper part of the degradation tube which is cooled by the water-jacket. This fraction is particularly useful for studying the nature of the polymer chain after the occurrence of substituent reactions, but before the molecule is grossly fragmented. These products may be analysed by IR Spectroscopy either in the form of a KBr disc, or as a solution obtained by wiping the tube with a tissue moistened with suitable solvent, followed by solvent extraction.

Condensable products may be isolated by closing the taps after degradation, and distilling the products into a receiver, identification then being possible by IR Spectroscopy Gas-Liquid Chromatography (GLC), or other techniques. Non-condensables cannot be isolated in such a way, since these pass through the liquid nitrogen trap under the continuous pumping conditions of TVA. These, typically carbon monoxide, methane and hydrogen, may be collected by using a closed system, consisting of an IR gas-cell fitted with a cold-trap to condense the less volatile products, as described by McNeill and Neil.[37] Identification is possible by IR Spectroscopy and by Mass Spectrometry.

Limitations of TVA

TVA is only a semi-quantitative technique since Pirani response is not linear with rate of volatilization for responses greater than one millivolt. It is also found that Pirani response per mole depends on the material distilling, making impossible direct comparisons of amounts of different volatiles even at low Pirani response unless calibration experiments are carried out.[38]

In addition, only those products which are sufficiently volatile to reach the Pirani filament are recorded, and so not all the processes which would be detected by thermogravimetry (TG) are detected by TVA. This is not strictly a disadvantage, because comparison with TG sometimes reveals chain fragmentation without small volatiles formation.

Advantages of TVA

One advantage of TVA is the fact that because of the sensitivity of the Pirani Gauge, a TVA trace is obtained even if only a small proportion of the weight of the sample is lost as volatiles.

In addition, temperature gradients within the sample are minimised because of the enormous mass of the degradation tube relative to the sample, and finally, continuous pumping throughout an experiment ensures swift and efficient removal of volatiles from the degrading sample, minimising the possibility of diffusion-controlled processes and secondary reactions. TVA is the only routine thermoanalytical technique yielding information about the nature of the volatile degradation products (in terms of their volatility) and changes in composition of products in the course of the heating programme, prior to chemical or spectroscopic analysis. Fractionation of the products can also be carried out without removal from the apparatus, as discussed below.

Separation of Condensable Products

As described previously, the main technique for analysis of condensable products, after thermal degradation in the TVA system, is IR analysis, carried out after distillation of the total condensable products into an IR gas-cell. The most serious disadvantage of this is the fact that many different compounds are present in the gas-cell. This results in the possibility of an important peak in the spectrum being hidden by a more intense absorption at a similar wavelength caused by some other compound. The presence of many overlapping absorptions within a particular region of the spectrum also rules out the possibility of quantitative estimation of a product by measurements made on an absorption peak which falls within that region.

In order to overcome these limitations in identification and analysis, a technique has been evolved, based on a combination of sample degradation in the TVA system with a development of the separation technique used by Ackerman and McGill.[39] In general terms, TVA may be applied to the study of volatilization of material from any sample under controlled rate of increase of temperature, provided that the sample is completely involatile at the initial temperature chosen, under the operating conditions of TVA.

In applications of TVA previously published, studies have been confined to the temperature range ambient - 500°C, limiting sample choice to material involatile at ambient temperature. It can be shown, however, that the scope of the method may be extended to include the temperature range -196°C - ambient, making possible study of substances which are volatile liquids, or gases, at ambient temperature. The technique requires controlled rate of increase of temperature from a trap initially cooled to -196°C, and it has been found that in certain studies on mixtures, substances volatilize independently during warm-up, i.e. some separation is effected.

This type of application of TVA will be referred to subsequently as Sub-Ambient TVA.

Principle of Sub-Ambient TVA

The technique is based on the principle that when a frozen mixture of different compounds is allowed to warm slowly, under high vacuum conditions and with continuous pumping, fractionation occurs as the separate components of the mixture evaporate at different rates, dependent on temperature.

Description of the Sub-Ambient TVA Apparatus

The apparatus is described schematically in Fig. 2.6. Sample preparation and heating assembly are the same as for conventional TVA, condensable volatiles from the degrading sample being collected in a main liquid nitrogen cold-trap, (1). On completion of degradation, with taps A and C closed and tap B open, the condensable products are distilled into a trap surrounded by benzene frozen to -196^{o}C (Fig. 2.7). With tap B now closed and tap C open i.e. under conditions of continuous pumping, the outer liquid nitrogen trap is removed from around the benzene, which is allowed to warm very slowly by heat transfer from the surroundings. In practice, this occurs reproducibly so that a controlled (although non-linear) rate of temperature increase is obtained. The separate products distill into cold-trap (2), and a Chromel-Alumel thermocouple is used to measure the temperature at which each distilling product exerts its maximum pressure on the Pirani Gauge, 4 , whose output is transmitted to a recorder.

A typical sub-ambient TVA trace is shown in Fig. 2.8.

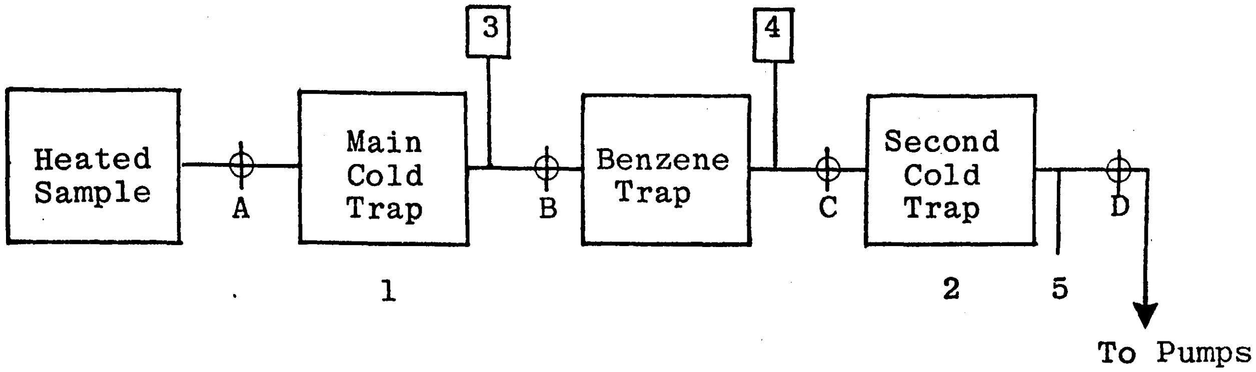


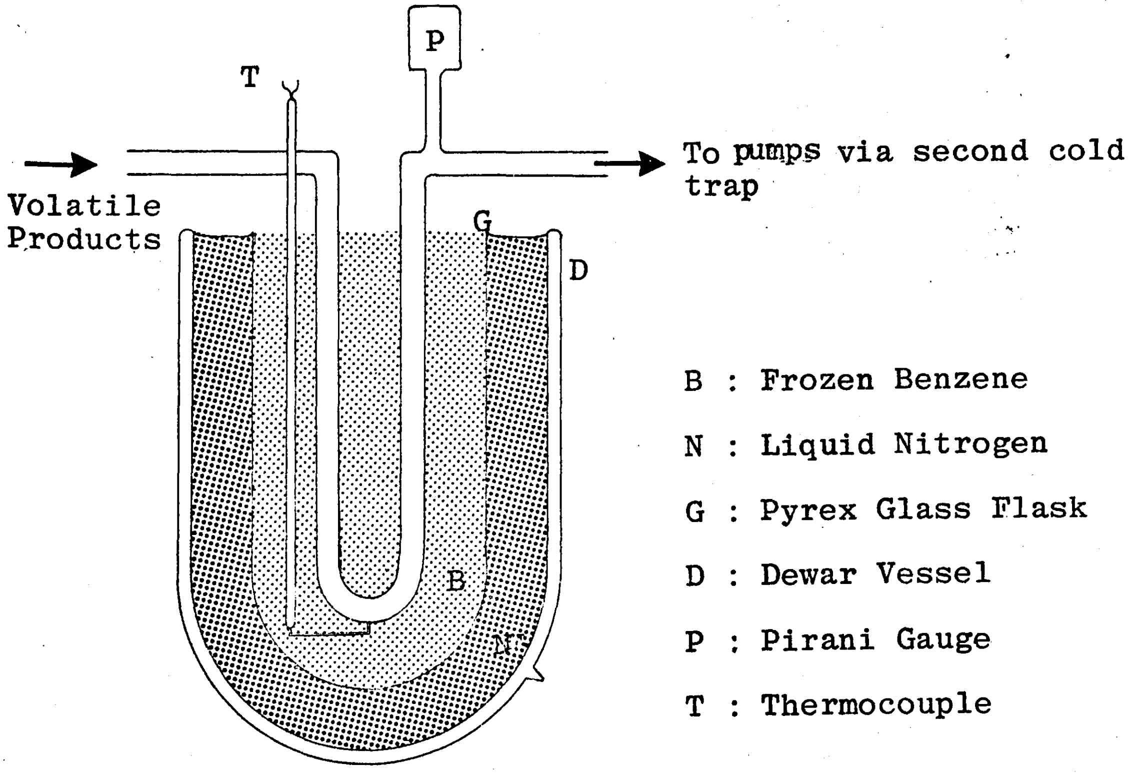
Figure 2.6 Sub-Ambient TVA.

1, 2 : Liquid Nitrogen Traps

3, 4 : Pirani Gauges

5 : Sample collection point.

A, B, C, D : Stopcocks



B : Frozen Benzene

N : Liquid Nitrogen

G : Pyrex Glass Flask

D : Dewar Vessel

P : Pirani Gauge

T : Thermocouple

Figure 2.7 Detail of Benzene Trap.

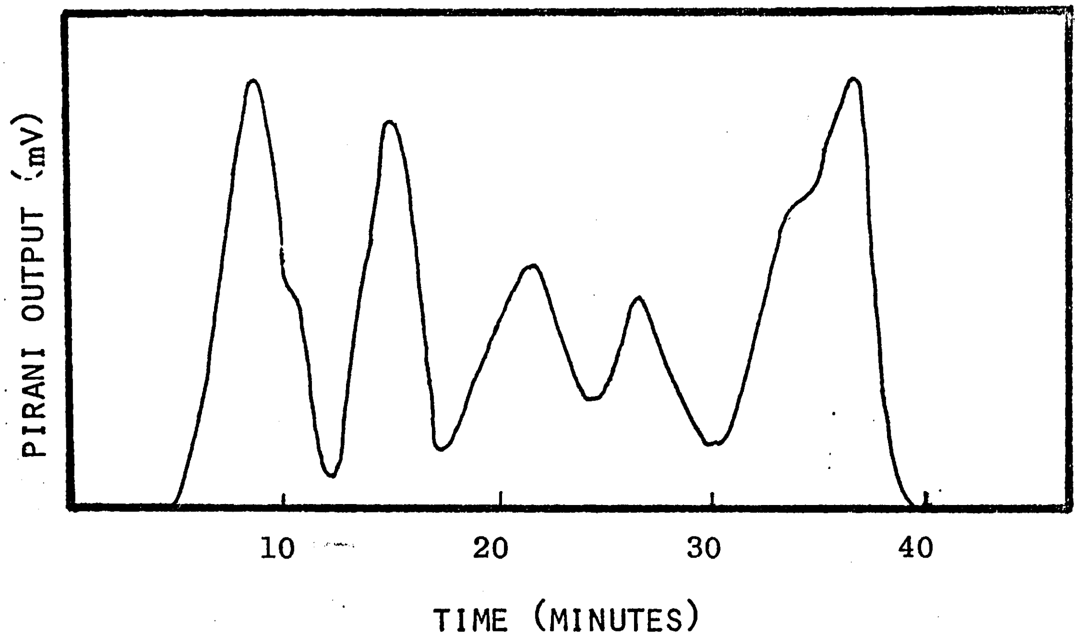


Fig. 2.8

Typical Sub-Ambient TVA Trace.

Collection of the Separated Products

Products responsible for separate peaks in the sub-ambient TVA trace can be collected separately in the following manner:-

The benzene trap is allowed to warm, as described, but on production of the first "peak" on the trace, tap C is closed and the benzene re-frozen to -196°C. The product responible for this first peak can now, with taps C and D closed, be distilled into a suitable collecting vessel and removed for analysis. After re-evacuation of trap 2, it is again cooled to -196°C, taps C and D are opened, the benzene allowed to warm, and the product responsible for the next peak collected in a similar manner. In this way, products which give rise to separate peaks on the trace may be separated.

This separation technique was especially helpful in the present work in obtaining clear IR identification evidence for the presence of methyl formate and methyl acetate, whose IR absorptions were largely masked in a spectrum of the total volatile products.

The main value of the technique in the present work, however, was its ability to isolate methyl bromide from the mixture of condensable products. This made possible quantitative estimation, by IR spectroscopy, of methyl bromide produced in the degradation of PMMA/zinc bromide blends.

ANALYSIS OF DEGRADATION PRODUCTS

Infra-Red Spectroscopy

Spectra, both qualitative and quantitative, were recorded on a Perkin Elmer 257 spectrophotometer. Polymer samples and residues were examined as KBr discs or as thin films cast on NaCl plates, cold-ring fractions were examined either in solution (CCl_4) or as KBr discs, and volatile products were examined in the gaseous phase. Residues, as CsI discs, were also examined, for the presence of metal oxide, using a Perkin Elmer 225 grating spectrophotometer, over the range 700 - 250cm^{-1}.

Quantitative estimations of methyl bromide were carried out after calibration of a gas cell whose volume had been obtained by filling it with acetone from a burette.

Pure methyl bromide was introduced into the cell using standard vacuum technique, the pressure of this gas being controlled and measured by means of a mercury manometer.

In this way, IR spectra corresponding to a series of pressures on CH_3Br in the cell were obtained, peak heights at 1316cm^{-1} were measured, and a graph obtained of optical density of the peak versus pressure of CH_3Br (Fig. 2.9).

The number of moles (n) of CH_3Br isolated in the cell during an expermiment was calculated after relating optical density measurements to pressure by referring to the calibration plot, and applying the equation

$$PV = nRT$$

where P = pressure of CH_3Br
V = volume of gas cell
R = gas constant
T = absolute temperature.

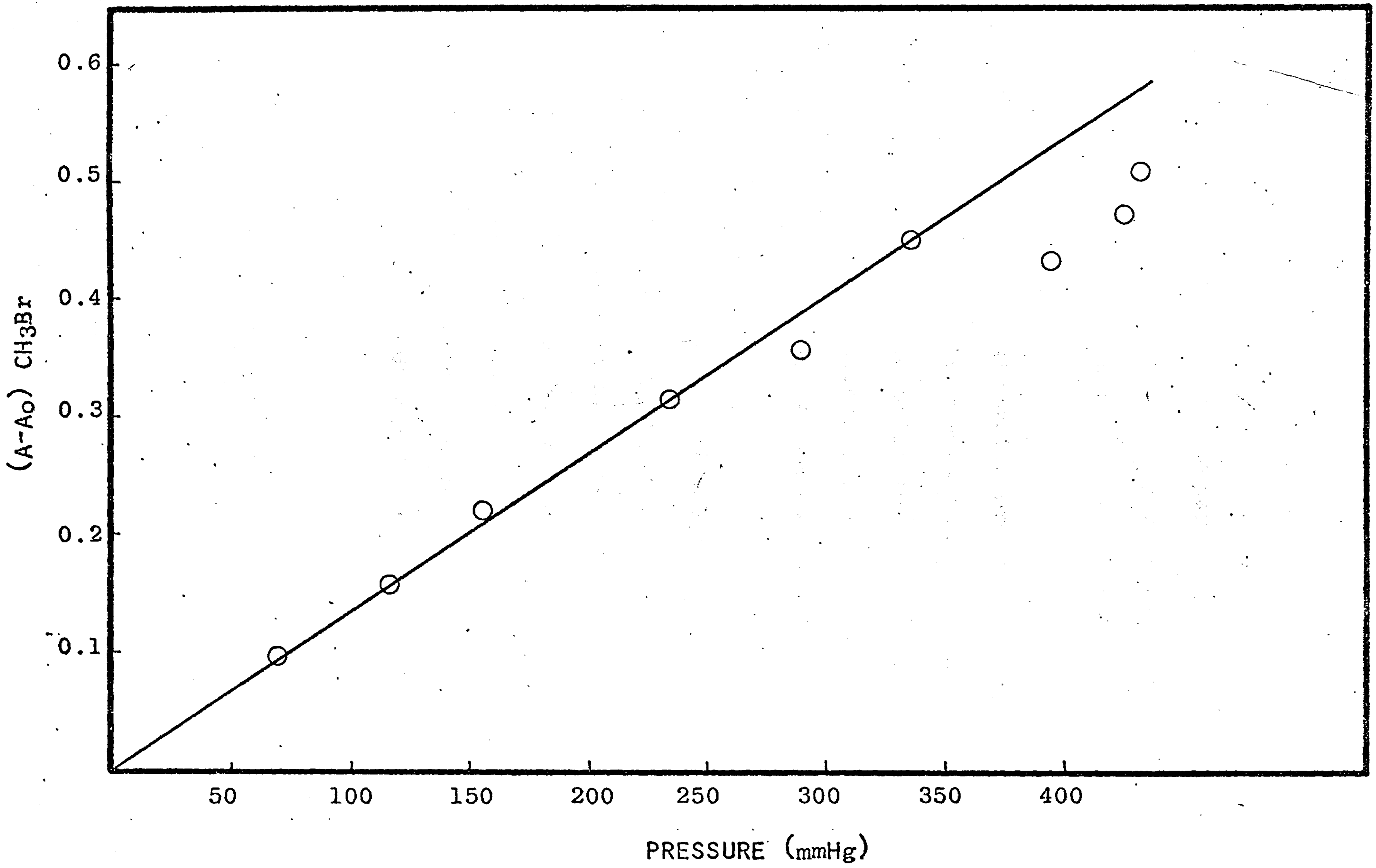


Figure 2.9 Calibration plot for CH_3Br

Gas-Liquid Chromatography (GLC)

Almost all the GLC data were collected using a Microtek GC-2000 Research Chromatograph with flame ionization detector; only a qualitative separation of methyl acetate and acetone was carried out using a Perkin Elmer F-11 instrument, equipped with a thermal conductivity detector.

When the liquid degradation products from PMMA/$ZnBr_2$ blends were isolated, these were found to consist of two immiscible layers, and so prior to quantitative estimation of methanol and methyl methacrylate, dioxane solvent was added to render the products completely miscible.

Quantitative data for MeOH and MMA were obtained by adding a known weight of n-propanol, as internal standard, to the solution of liquid products. A series of pure samples of both MeOH and MMA in turn were mixed with weighed amounts of the internal standard and run on the chromatograph in order to determine the sensitivities of the product compounds relative to n-propanol.

Measurements of peak areas were obtained using an Infotronics Microprocessor for GLC, Model 309.

The Sensitivity Factor, (K), is defined such that

$$K = \frac{As.Wx}{Ws.Ax}$$

where Ws, Wx are weights of internal standard, and product X, and As, Ax are areas of the respective peaks on the Chromatogram. The calibration plots for MeOH amd MMA are shown in Figures 2.10 and 2.11 respectively.

These data can be used to determine the number of moles, Nx, of product X in the sample of degradation products, i.e.

$$\mathrm{Nx} = \mathrm{K}.\ \frac{(\text{Peak area of X})}{(\text{Peak area of standard})} \cdot \frac{(\text{Weight of standard})}{(\text{Weight of 1 mole of X})}$$

Mass Spectrometry

Volatile products were analysed using an EI MS12 mass spectrometer. Products, collected under vacuum, were either directly introduced into the instrument, or fractionated by means of a liquid nitrogen trap, to separated condensable and non-condensable products. In the present work, this technique is particularly important for the detection of hydrogen.

Estimation of Acetic Acid.

Acetic acid produced in the degradation of poly(vinyl acetate) was estimated by titration with 0.01M NaOH using phenolphthalein as indicator.

The results are tabulated in Chapter Five.

Ultra-Violet (UV) Spectroscopy

UV studies of different blends were carried out on a Unicam SP 800A UV Spectrophotometer equipped with a deuterium lamp, by direct casting of films, as described previously (Page 13), onto a silica degradation tube suitable for direct UV examination of the blend before and after heating.

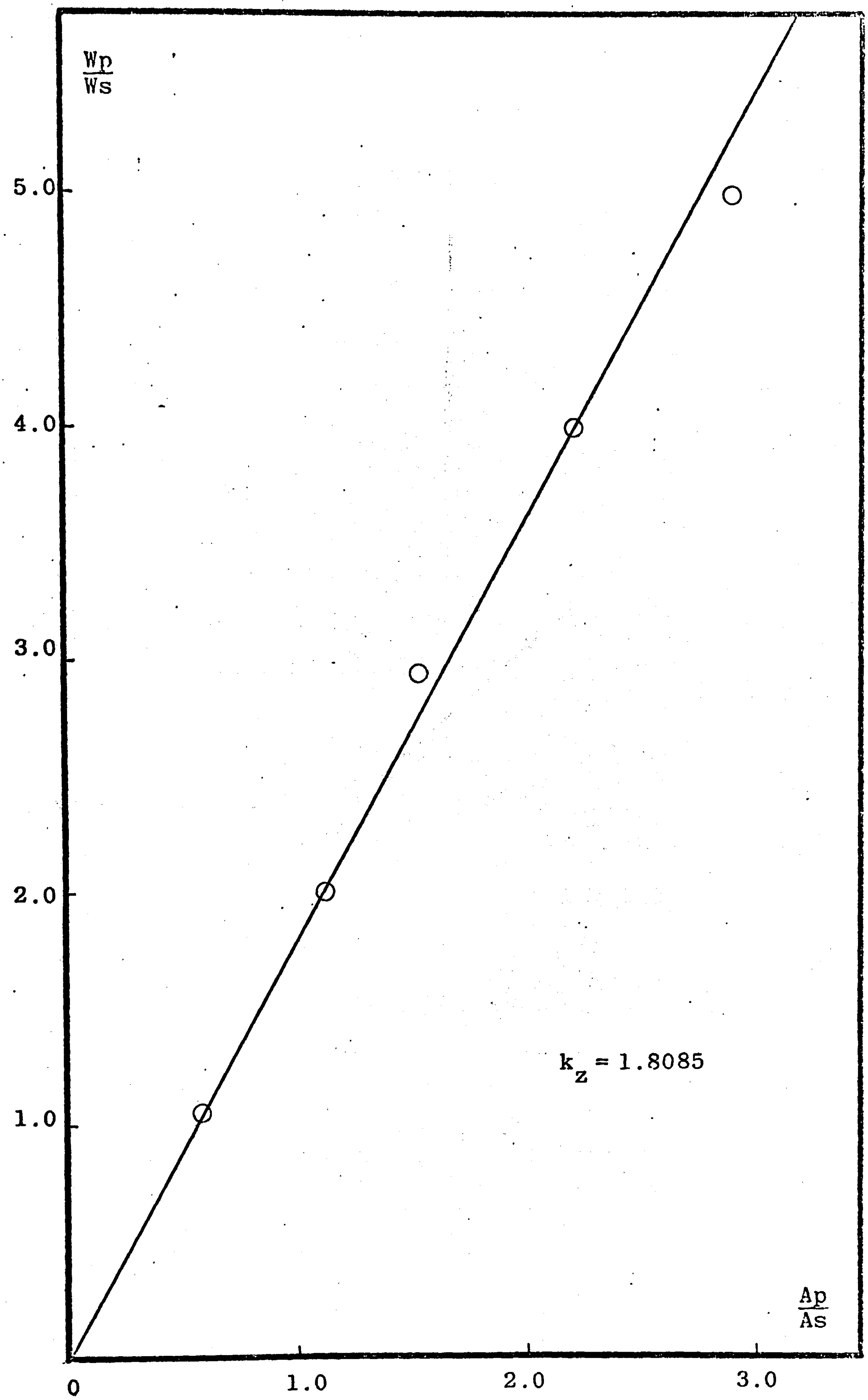


Figure 2.10 Sensitivity Factor for Methanol

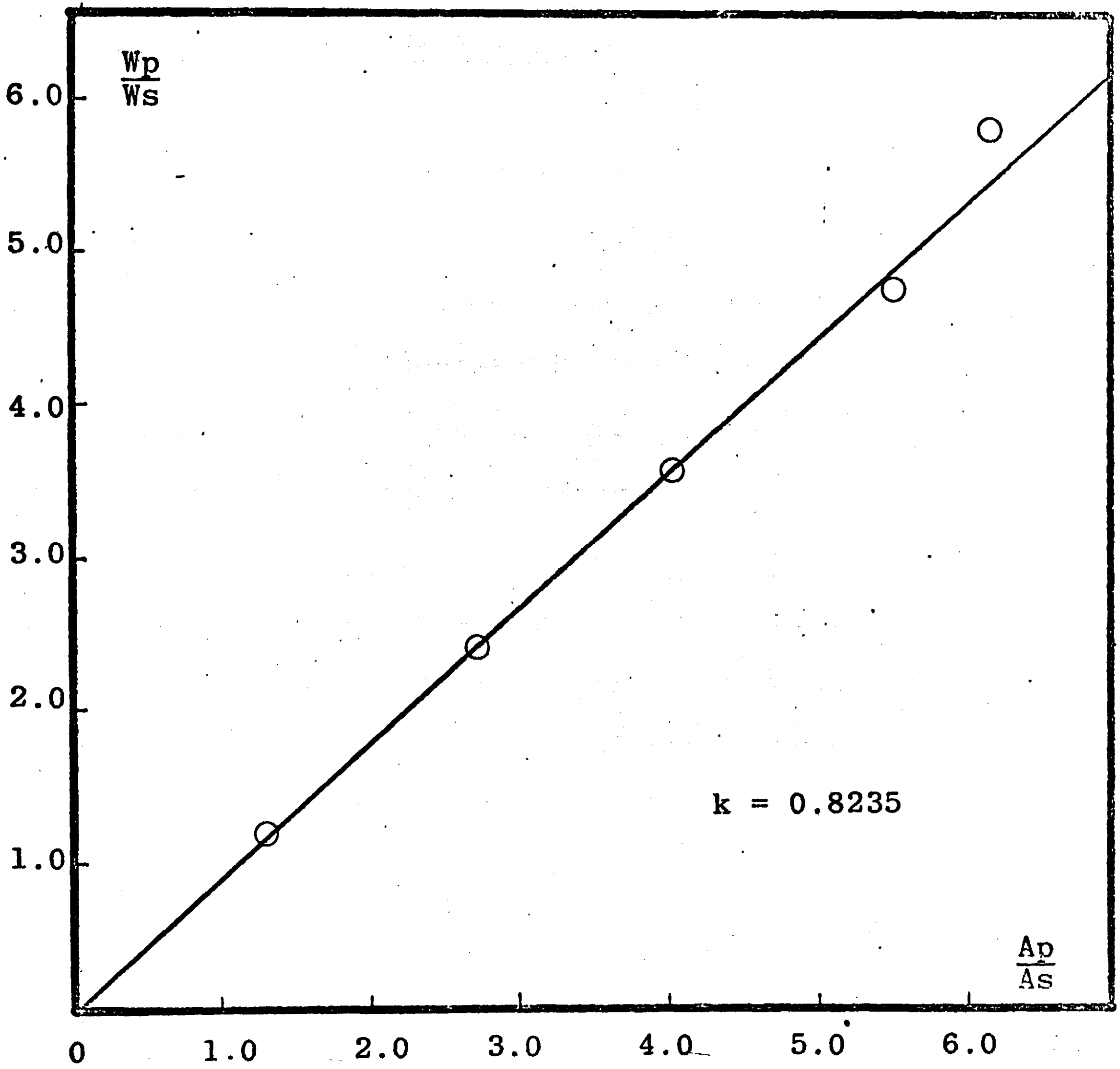


Figure 2.11 Sensitivity Factor for MMA

CHAPTER THREE

GENERAL SURVEY OF ADDITIVE EFFECTS ON POLYMER DEGRADATION

A survey of the effect of various small molecule additives on polymer degradation was initiated in these laboratories by Dr. M. A. J. Mohammed, and completed by the author. The survey was necessarily qualitative in nature, additive effects, if any, being deduced solely by comparing and contrasting TVA traces.

Owing to the large number of traces involved, it was felt necessary to summarise the results in tabular form, and so an explanation of column headings is required.

Explanation of Column Headings

(1) Type: two types of blend were studied. "Powder " denotes a physical mixture of polymer and additive ground together, whereas "film" refers to both films cast from a mixture of polymer and additive solutions, and also to films cast from polymer solutions containing dispersed insoluble additive.

(2) Threshold: this refers to the temperature at which volatile products first begin to appear, detected by at least one Pirani gauge output signal

separating from the baseline of the trace.

N.B. All temperature values quoted in this survey are sample temperatures.

This column is further divided into separate threshold temperatures for condensable and non-condensable products (as defined in the description of TVA in Chapter Two).

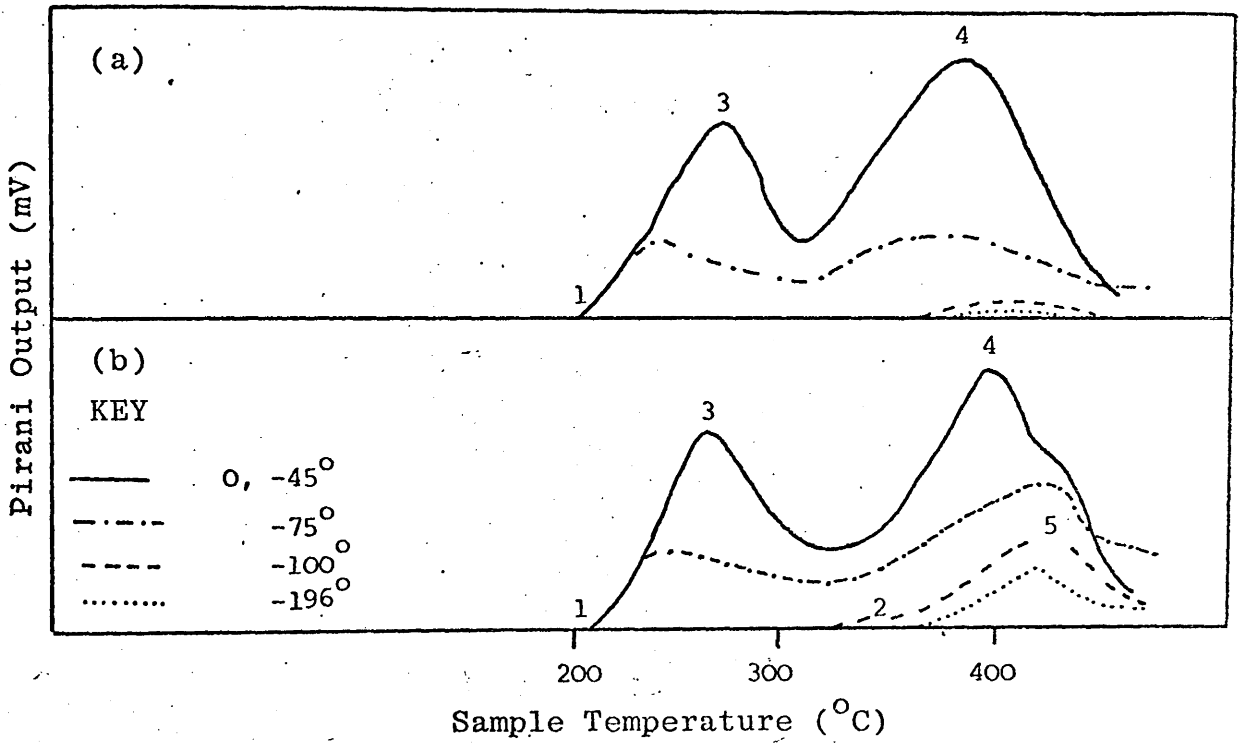
(3) Main Peaks: peak maxima are obtained in TVA traces when maximum rate of volatilization, for a particular reaction, is reached. The temperature corresponding to this maximum rate is denoted Tmax. for the reaction, and in this column, Tmax. values for the different reactions occurring are listed.

It is extremely important to note that the reaction responsible for the first Tmax. in one trace may differ from the reaction responsible for the first Tmax. in another trace. Thus direct comparisons of reaction temperatures cannot be made by comparison of Tmax. values from different traces in the absence of further information.

(4) Additive Effect: comments in this column are based solely on comparisons of different TVA traces, by the author.

Example of Tabulation Procedure.

The example of PMMA ($\overline{Mn}$ 40,000) plus $MgBr_2.6H_2O$ is demonstrated in Fig. 3.1 and Table 3-I.



1, 2 Threshold Temperatures.

3, 4, 5 Main Peaks, Tmax Values.

Figure 3.1 TVA traces of (a) PMMA ($\overline{Mn}$ 40,000) and (b) PMMA ($\overline{Mn}$ 40,000) + $MgBr2.6H_2O$

These results would be tabulated as shown below in Table 3-I.

Blend	Type	Threshold (°C)		Main Peaks	Effect
		Condensables	Non-Condensables	(°C)	
PMMA	Powder	196	none	290, 372	-
PMMA + $MgBr_2.6H_2O$	Powder	216	343	290, 378 420	Small production of non-condensables

Table 3-I

TVA traces from Fig 3.1 in tabular form.

In all cases, TVA traces were obtained for blends comprising 50mg polymer plus 50mg additive, heated from ambient temperature to 500°C at 10°/minute. Residual solvent peaks and peaks resulting solely from additive decomposition prior to any polymer degradation were ignored.

Tabulated Results

Results detailing additive effects on PMMA, poly(vinyl acetate) (PVA), poly(vinyl chloride) (PVC), polystyrene (PS), polyacrylonitrile (PAN), and polymethacrylonitrile (PMAN), are summarised in Tables 3-II – 3-VI.

Blend	Type	Threshold (°C) Condensables	Non-Cond.	Main Peaks, Tmax (°C)	Additive Effect
PMMA(1)	Powder	228	none	295, 366	-
PMMA(1) + Zinc Acetate	Powder	229	none	297, 368	Negligible effect
PMMA(1) + Zinc Oxalate	Powder	244	none	291, 360	Negligible effect
PMMA(1) + Ammonium Dichromate	Powder	255	none	288, 351	Negligible effect
PMMA(1) + Caesium Bromide	Film	226	none	291, 362	Negligible effect
PMMA(1) + Lithium Chloride	Film	239	376	321, 376, 432	Small production of non-condensables
PMMA(1) + Zinc Stearate	Film	254	356	305, 392, 426	Large production of non-condensables
PMMA(1) + Magnesium Bromide Hexahydrate	Film	242	340	294, 387, 420	Small production of non-condensables
PMMA(1) + Zinc Fluoride	Powder	241	none	288, 365,	Negligible effect
PMMA(1) + Zinc Chloride	Film	178	178	253, 400, 450	Enormous production of non-condensables
PMMA(1) + Zinc Bromide	Film	215	238	257, 396, 450, 483	Enormous production of non-condensables

Table 3-II

The effect of additives on the thermal degradations of PMMA(1), $\overline{Mn}$ 610,000, and PMMA(2), $\overline{Mn}$ 45,000.

Blend	Type	Threshold (^{o}C)		Main Peaks, Tmax (^{o}C)	Additive Effect
		Condensables	Non-Cond.		
PMMA(1) + Zinc Iodide	Film	144	199	266, 406, 455	Enormous production of non-condensables
PMMA(1) + Potassium Nitrite	Powder	237	306	344, 369, 416, 443	Large production of non-condensables
PMMA(1) + Silver Acetate	Powder	187	214	247, 342	Production of non-condensables at low temperature
PMMA(1) + Cupric Bromide	Film	243	314	403	Large production of non-condensables
PMMA(1) + Zinc Oxide	Powder	269	382	317, 405, 445	Large production of non-condensables
PMMA(2)	Powder	196	none	290, 372	-
PMMA(2) + Magnesium Bromide Hexahydrate	Powder	216	343	290, 378, 420	Small production of non-condensables
PMMA(2) + Cupric Bromide	Film	172	304	291, 392, 420	Large production of non-condensables
PMMA(2) + Cuprous Bromide	Film	243	326	301, 385, 420	Small production of non-condensables
PMMA(2) + Zinc Bromide	Film	141	166	291, 403, 448	Enormous production of non-condensables

Table 3-II (contd.)

Blend	Type	Threshold (^{o}C) Condensables	 Non-Cond.	Main Peaks, Tmax (^{o}C)	Additive Effect
PMMA(2) + Cupric Chloride	Film	237	237	317, 397	Small production of non-condensables at low temperature
PMMA(2) + Zinc Nitrate	Powder	145	172	240, 309, 373, 416, 451	Continuous production of non-condensables from low temperature

Table 3-II (contd.)

Blend	Type	Threshold (^{o}C)		Main Peaks,	Additive Effect
		Condensables	Non-Cond.	Tmax (^{o}C)	
Poly(Vinyl Acetate) (PVA)	Film	260	302	369, 464	-
PVA + Lithium Chloride	Film	259	279	355, 480	Small increase in production of non-condensables
PVA + Zinc Oxide	Film	233	279	356, 482	Small increase in production of non-condensables
PVA + Zinc Oxalate	Film	239	269	271, 330, 451	All Tmax values lowered
PVA + Zinc Stearate	Film	256	279	352, 476	Small increase in production of non-condensables
PVA + Zinc Acetate	Film	235	279	304, 352, 481	Additional peak. Small increase in production of non-condensables
PVA + Magnesium Bromide Hexahydrate	Film	173	194	253, 371, 496	Temperature of first reaction lowered. Increased production of non-condensables
PVA + Zinc Chloride	Film	144	229	193, 335, 491	Temperature of first reaction lowered. Increased production of non-condensables
PVA + Zinc Bromide	Film	144	287	178, 441	Temperature of first reaction lowered. Enormous production of non-condensables

Table 3-III

The effect of additives on the thermal degradation of PVA, $\overline{Mn}$ 45,000.

Blend	Type	Threshold (°C)		Main Peaks	Additive Effect
		Condensables	Non-Cond.	Tmax (°C)	
Poly(Vinyl Chloride)-1 (PVC)	Film	223	339	298, 316, 455	-
PVC(1) + Zinc Acetate	Film	196	207	222, 460	Small production of non-condensables at low temperature
PVC(1) + Zinc Oxalate	Film	288	336	221, 265, 457	Temperature of first reaction lowered
PVC(1) + Zinc Sulphite	Film	178	314	310, 456, 476	Additional reaction at high temperature
PVC(1) + Zinc Dust	Powder	206	207	233, 287, 458	Production of non-condensables at low temperature
PVC(1) + Lithium Chloride	Film	227	334	307, 460	Negligible effect
PVC(1) + Magnesium Sulphate	Film	206	320	288, 321, 463	Negligible effect
PVC(1) + Ammonium Dichromate	Film	123	215	221, 254, 318, 470	Enormous production of non-condensables, starting at low temperature
PVC(1) + Ammonium Thiocyanate	Film	177	177	202, 255, 443, 471	Production of non-condensables at low temperature

Table 3-IV

The effect of additives on the thermal degradations of PVC(1), $\overline{Mn}$ 16,000 and PVC(2), $\overline{Mn}$ 45,600.

Blend	Type	Threshold		Main Peaks,	Additive Effect
		Condensables	Non-Cond.	Tmax. (^{o}C)	
PVC(1) + Ferric Chloride	Film	151	355	256, 463	Enormous production of non-condensables in second peak
PVC(1) + Zinc Bromide	Film	139	307	195, 416, 467	Enormous production of non-condensables
PVC(2)	Film	202	315	315, 463, 482	-
PVC(2) + Zinc Sulphite	Film	204	316	316, 463	Negligible effect
PVC(2) + Zinc Carbonate	Film	177	319	221, 271, 475	Tmax of first peak lowered
PVC(2) + Zinc Stearate	Powder	195	350	221, 259, 304, 491	First stage split into three peaks
PVC(2) + Zinc Acetate	Film	202	310	224, 454	Enormous production of non-condensables in second peak
PVC(2) + Zinc Nitrate	Film	91	91	227, 446, 461	Production of non-condensables at very low temperature
PVC(2) + Potassium Nitrite	Film	199	199	255, 451	Tmax of first peak lowered

<u>Table 3-IV (contd.)</u>

Blend	Type	Threshold (^{o}C)		Main Peaks,	Additive Effect
		Condensables	Non-Cond.	Tmax (^{o}C)	
Polystyrene (PS)	Film	338	none	407	-
PS + Ammonium Thiocyanate	Film	346	none	413	Negligible effect
PS + Ammonium Carbonate	Film	330	none	419	Negligible effect
PS + Ammonium Persulphate	Film	335	none	416	Negligible effect
PS + Lithium Chloride	Film	322	none	413	Negligible effect
PS + Calcium Chloride	Film	325	none	414	Negligible effect
PS + Magnesium Sulphate	Film	322	none	413	Negligible effect
PS + Zinc Oxalate	Film	318	none	416	Negligible effect
PS + Zinc Fluoride	Film	319	none	415	Negligible effect
PS + Zinc Chloride	Film	329	none	419	Negligible effect

Table 3-V

The effect of additives on thermal degradation of PS, $\overline{Mn}$ 169,000.

Blend	Type	Threshold (°C)		Main Peaks, Tmax (°C)	Additive Effect
		Condensables	Non-Cond.		
PS + Zinc Bromide	Film	330	none	421	Negligible effect
PS + Zinc Iodide	Film	330	none	420	Negligible effect
PS + Ferrous Chloride	Film	355	370	441, 468	Small production of non-condensables
PS + Ferric Chloride	Film	333	333	439, 471	Small production of non-condensables
PS + Ammonium Chromate	Film	298	408	422, 451	Very slight production of non-condensables
PS + Ammonium Dichromate	Film	232	232	341, 456	Large production of non-condensables, starting at low temperature
PS + Potassium Nitrite	Film	254	254	413, 470	Large production of non-condensables, starting at low temperature

Table 3-V (contd.)

Blend	Type	Threshold (^{o}C)		Main Peaks,	Additive Effect
		Condensables	Non- Cond.	Tmax (^{o}C)	
Polyacrylonitrile (PAN)	Powder	285	377	303, 480	-
PAN + Zinc Bromide	Powder	211	211	320, 378, 456	Enormous production of non-condensables, starting at low temperature
Polymethacrylonitrile (PMAN)	Film	269	353	325, 385, 406	-
PMAN + Ammonium Thiocyanate	Film	266	287	373, 423, 481	Large production of non-condensables
PMAN + Ammonium Carbonate	Film	260	260	374, 416, 482	Enormous production of non-condensables
PMAN + Zinc Bromide	Film	244	244	387, 431, 480	Enormous production of non-condensables

Table 3-VI

The effect of additives on the thermal degradations of PAN, $\overline{Mn}$ 1,000,000 and PMAN, $\overline{Mn}$ 68,000.

CHAPTER FOUR

INTRODUCTION

After the general study of additive effects on polymer degradation considered in Chapter Three, this chapter deals with a detailed investigation into the effect of zinc bromide on the thermal decomposition of PMMA.

The reasons for interest in polymer/additive systems in general have already been outlined.

The $ZnBr_2$/PMMA system was chosen for detailed study for several reasons:
PMMA was selected as the polymer component since its thermal degradation is relatively simple and now well understood; the exact mechanism is discussed below.
$ZnBr_2$ was selected as the small molecule additive for the reasons:
(i) from results tabulated in Chapter Three, it is clear that $ZnBr_2$ exerts a profound influence on the degradation mechanisms of several important vinyl polymers, including PMMA.
(ii) $ZnBr_2$ does not decompose thermally, in the manner of zinc oxalate, for example, to give volatile products which could subsequently affect polymer degradation. This fact ensures that any effect on the polymer degradation mechanism

can be related directly to the additive without fear of complication by decomposition products whose formation might be subject to modifying influences, either chemical or physical.

(iii) it is relatively involatile, and as a result, any changes which occur on heating can be related directly to chemical processes without the complications of change in composition due to evaporation loss.

As a prerequisite to the study of PMMA/$ZnBr_2$ blends, the thermal degradation mechanisms of PMMA and of $ZnBr_2$ must be discussed, and their separate behaviours during study by TVA described.

THE THERMAL DEGRADATION OF PMMA

First studied by Grassie and Melville,[40] and later reviewed by MacCallum,[41] the degradation process has been shown to be the reverse of polymerisation, termed depolymerisation, producing quantitative yields of monomer. The mechanism of degradation is described as a free-radical process, in accordance with the general scheme for chain scission reactions proposed by Simha, Wall, and Blatz,[42,43,44] except that transfer reactions are relatively unimportant. Degradation is known to be a two-stage process, initiation of depolymerisation taking place either at unsaturated chain-end structures, or by random scission of the polymer backbone; chain-end initiation occurs at temperatures above 200°C whereas random scission begins to dominate at temperatures of over 300°C during isothermal degradation experiments. More recent work has confirmed these early findings, and, latterly, the application of TVA to the study of this degradation[35,36] has proven especially useful in presenting a clear picture of the two separate stages in decomposition, which appear as two peaks on the TVA traces. These TVA studies also show that the mechanism of degradation is affected, not only by the method of preparation of the polymer, but also by the molecular weight of a particular polymer sample.

Since the first depolymerisation reaction depends on the presence of unsaturated chain-ends for initiation, it follows that this type of degradation will be absent in the case of a polymer prepared by anionic polymerisation, since this contains no such structures. This type of polymer is found to be stable to slightly higher temperatures, initiation being possible only by random scission of the polymer backbone.

Unsaturated chain-end structures in a polymer chain are formed as a result of free-radical polymerisation being terminated by disproportionation reactions, and since low molecular weight polymers contain a higher concentration of unsaturated chain-ends, the maximum rate of monomer production from the first depolymerisation reaction occurs at progressively lower temperatures as the molecular weight of the sample is lowered.

TVA STUDY OF PMMA

The dependence of the low temperature reaction on molecula weight is illustrated in Figures 4.1(a) and (b) which contain

TVA traces of PMMA(1), $\overline{Mn}$ 610,000 and PMMA(2), $\overline{Mn}$ 40,000, respectively. Both of these polymers were prepared by free radical polymerisation.

It should be noted that although the sole product from degradation of PMMA is known to be MMA monomer, it appears from both TVA traces that some products are passing through the 0° and -45° traps, some being condensed in the -75° trap, and the remainder are being condensed in the -100° trap. The explanation is that MMA produced passes through the 0° and -45° traps before partially condensing in the -75° trap. However, MMA is sufficiently volatile to distil slowly from the -75° trap into the main trap, causing Pirani output from the -75° trap to register as a plateau on the TVA trace. This is known as limiting rate behaviour, a valuable feature of the TVA technique since the limiting rate at a given trap temperature is characteristic of a particular substance in the apparatus.

THERMAL BEHAVIOUR OF ZINC BROMIDE

Brewer has shown[45] that when subjected to heat, $ZnBr_2$ is not dissociated to zinc metal at its boiling point, nor is there any dissociation to the monovalent state; it has been found, rather, that sublimation takes place.

TVA STUDY OF $ZnBr_2$

The TVA trace from a "film" comprising 20mg $ZnBr_2$ cast from acetone solution is shown in Figure 4.2.

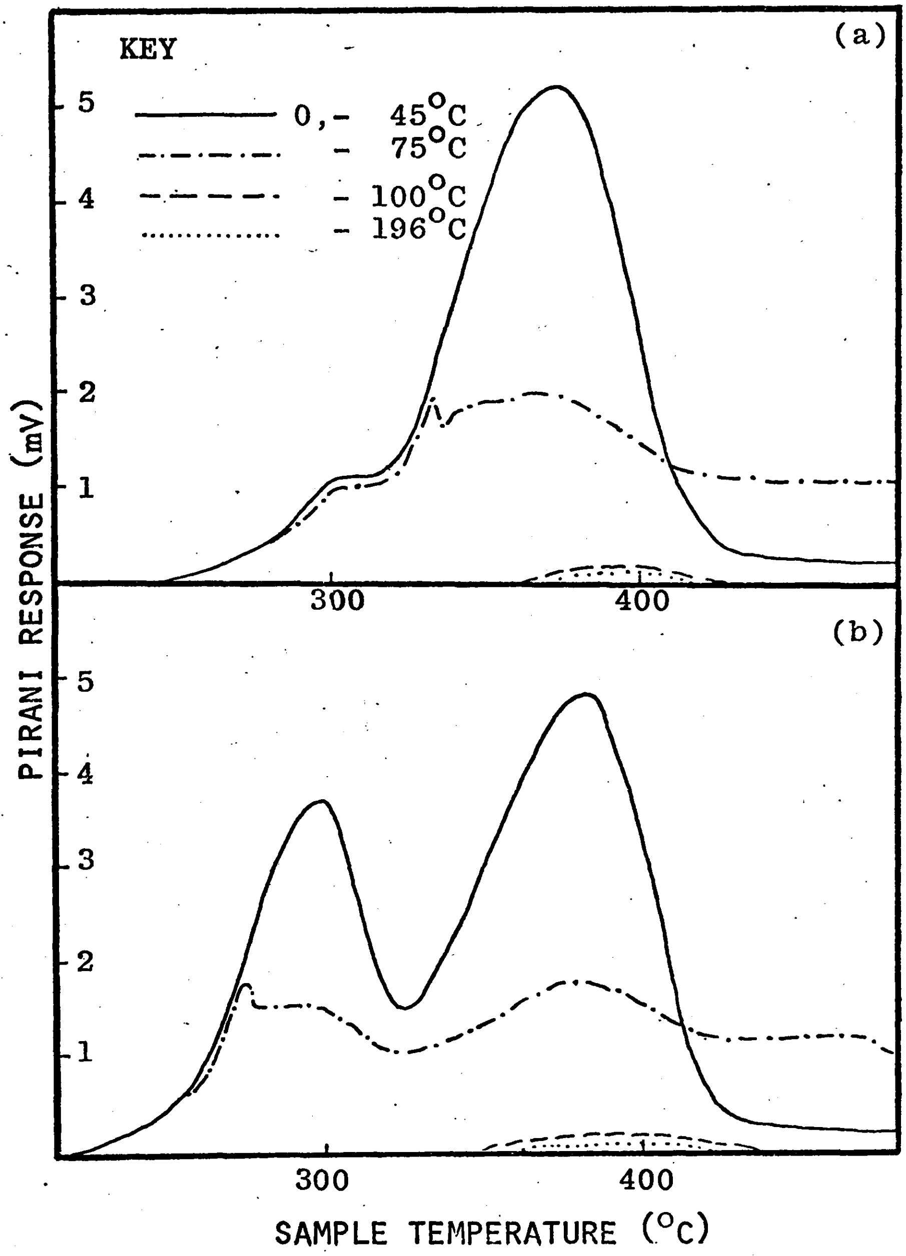


Figure 4.1 (a) TVA trace for PMMA(1), $\overline{Mn}$ 610,000.

(b) TVA trace for PMMA(2), $\overline{Mn}$ 40,000.

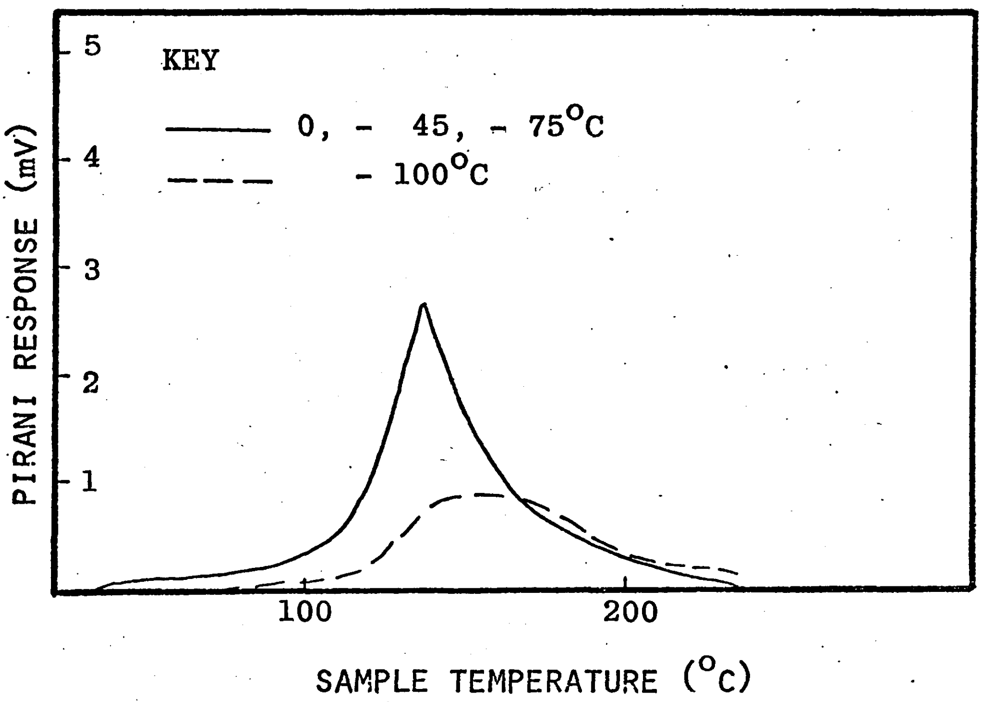


Figure 4.2 TVA trace for "film" of $ZnBr_2$ from acetone solution.

The single peak, Tmax. 135°C, is due to acetone solvent, which is seen to exhibit a limiting rate effect in the -100°C trap, behaviour characteristic of acetone.

$ZnBr_2$ is not represented on the trace, since it sublimes from the base of the sample tube to the cold-ring, thus never reaching the Pirani filaments. It has been found, however, by observation of the temperature at which $ZnBr_2$ is seen to appear in the cold-ring, that $ZnBr_2$ sublimes at 323°C under the operating conditions of TVA used.

TVA STUDY OF PMMA/ZnBr$_2$ BLENDS

Samples were examined as films cast from mixed solutions of polymer and salt in acetone. In each case, the sample comprised 30mg polymer compounded with the appropriate weight of ZnBr$_2$ for the particular blend. In all cases, the heating rate employed was 10^{o}C/minute.

Throughout this work blends made up of three different polymer salt compositions were studied. These are listed in Table 4-I, expressed in terms of MMA units in the polymer chain relative to molecules of ZnBr$_2$, and are also on a weight to weight basis. In all cases the figure quoted first refers to PMMA.

	Ratio of PMMA(1):ZnBr$_2$	
	(i) No. of moles	(ii) by weight
Blend 1	11.25:1	5:1
Blend 2	2:1	1.13:1
Blend 3	1:1	1:2.25

Table 4-I PMMA(1)/ZnBr$_2$ Blend Compositions

TVA traces for blends 1, 2, and 3 are reproduced in Figures 4.3, 4.4 and 4.5 respectively.

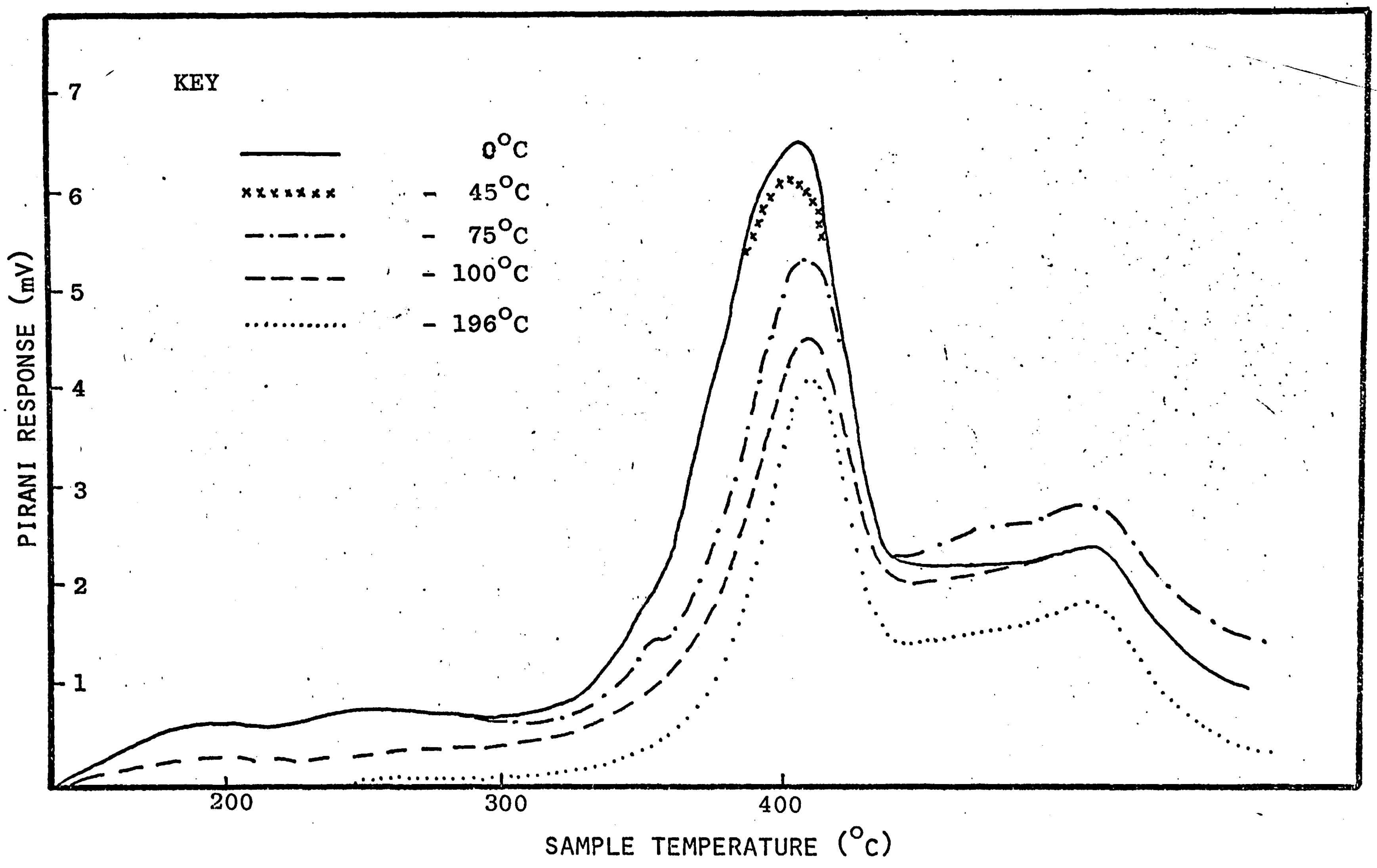


Figure 4.3 TVA trace for Blend 1, comprising PMMA(1)/$ZnBr_2$ in the ratio 11.25:1 Molar.

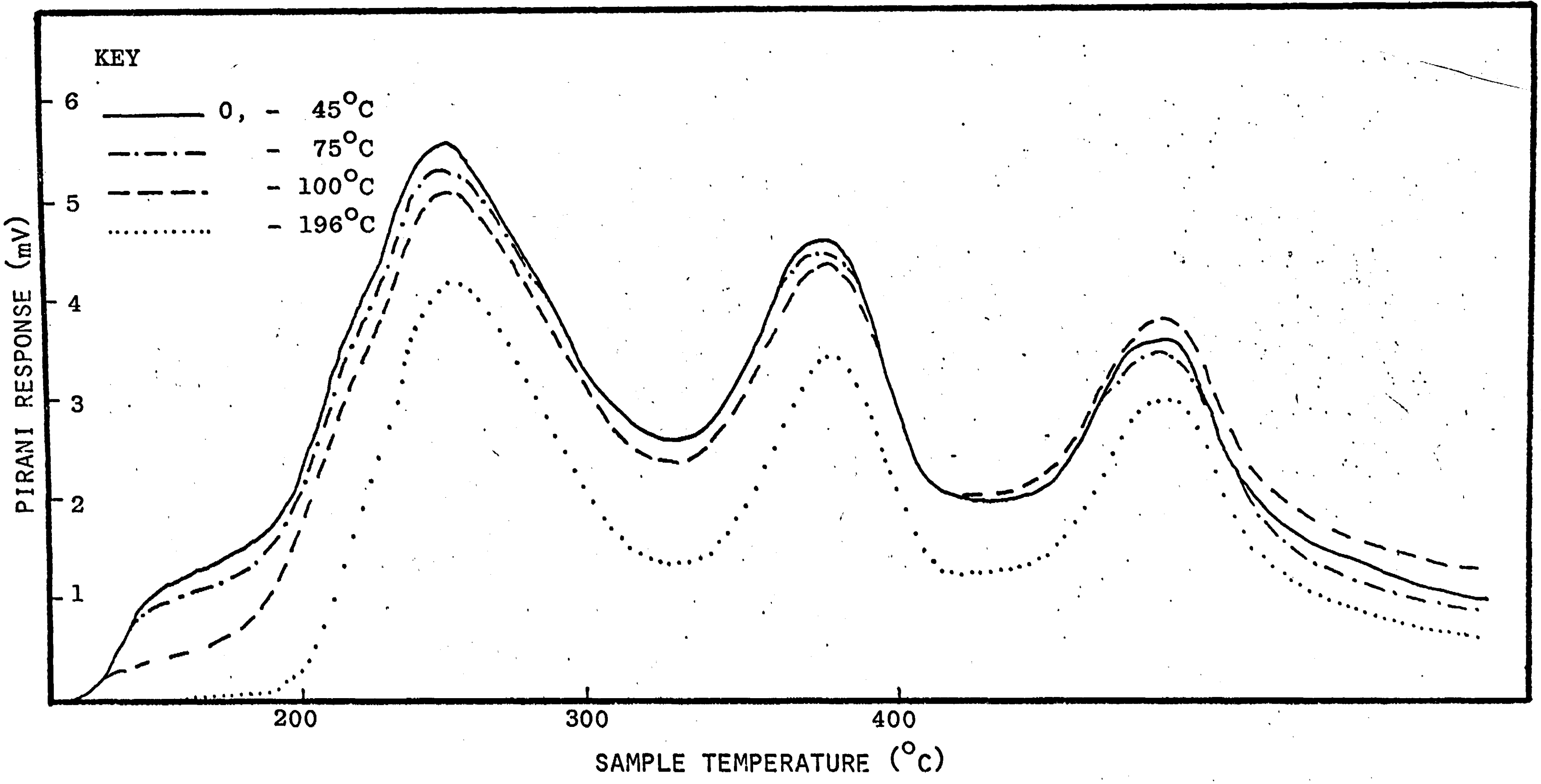


Figure 4.4 TVA trace for Blend 2, comprising PMMA(1)/$ZnBr_2$ in the ratio 2:1 Molar.

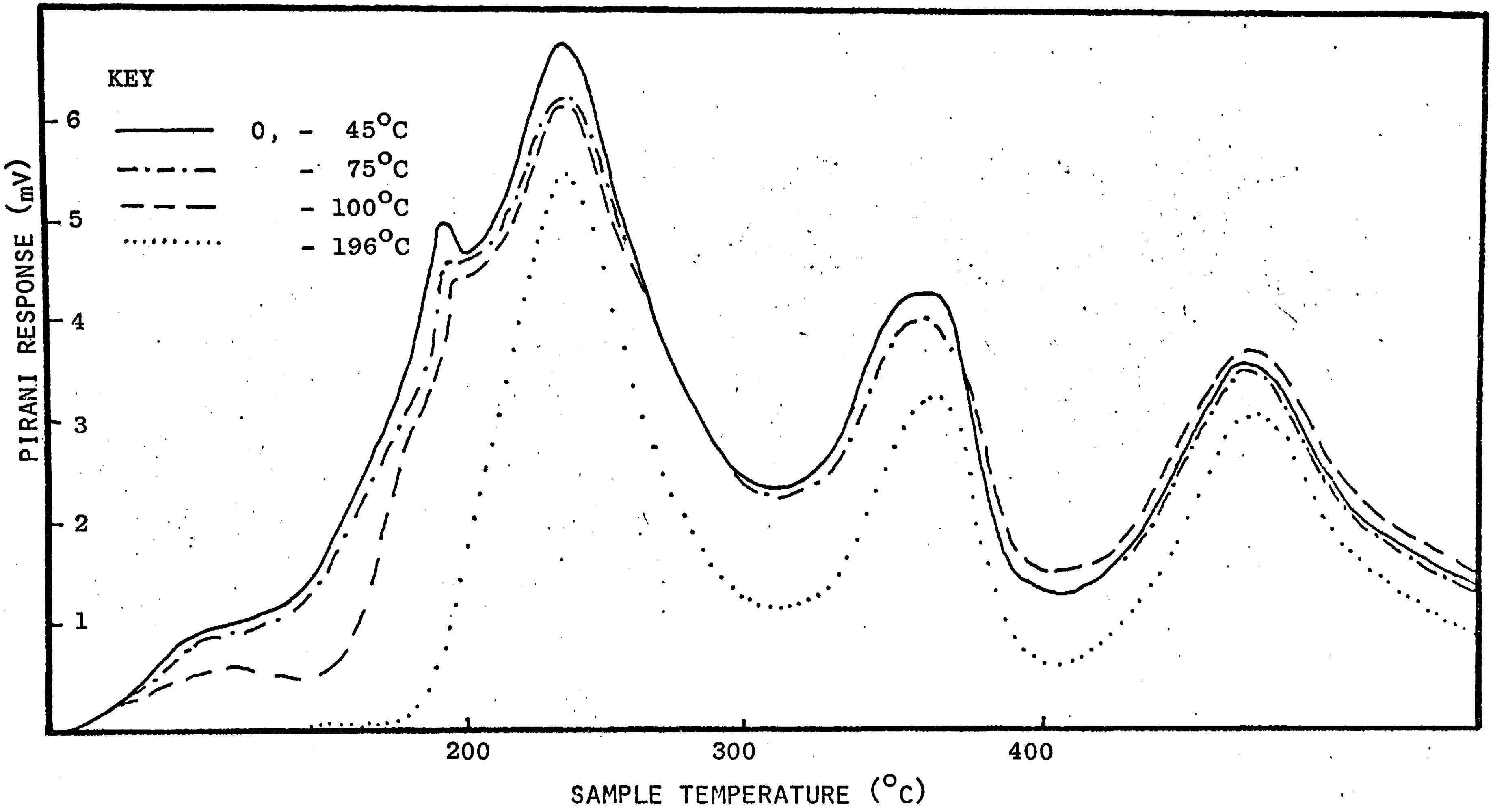


Figure 4.5 TVA trace for Blend 3, comprising PMMA(1)/$ZnBr_2$ in the ratio 1:1 Molar.

DISCUSSION

It is immediately apparent, on comparison of the TVA traces for the PMMA/salt blends with the trace for PMMA(1) only (Fig. 4.1(a)), that the prsence of $ZnBr_2$ causes the thermal degradation mechanism to become substantially more complex than simple depolymerisation to monomer. The most striking feature to arise in the cases of the blends is a massive production of non-condensable products, commencing at low temperature, a hitherto unknown development in work concerning degradation of blends involving PMMA.

BLEND ONE: PMMA(1)/$ZnBr_2$ in the ratio 11.25:1 molar. The trace consists essentially of three peaks, Tmax. values 247, 402 and 485°C, the early part of the first peak being due to residual acetone, which is known to be partially condensable at -100°C. The evolution of acetone at this stage was later confirmed by IR spectroscopy.

The first peak is relatively small, containing only a very small production of non-condensables, initiation of which commences at 236°C. This peak appears to be due almost entirely to materials condensed either at -100°C or -196°C. This is consistent with production of CH_3Br, CH_3OH and methyl acetate (CH_3OAc), in addition to the presence of residual solvent, all of which are known to show limiting rate behaviour at -100°C (CH_3OH,[46] acetone,[46] CH_3OAc[18]), or are non-condensable at -100°C but condensable at -196°C (CH_3Br[47]).

The second peak is the largest peak in the trace, and at this stage, some product is evolved which exhibits limiting rate behaviour at -75°C, consistent with production of MMA. Tmax for this peak occurs at 402°C, however, as compared to a Tmax value of 372°C for the main peak in the TVA trace for PMMA(1) alone, i.e. the peak which represents production of MMA initiated by random scission of the polymer backbone. This indicates that during degradation of blend 1, some low temperature process may be occurring, resulting in the formation of structures in the polymer chain which block depolymerisation to MMA. Since an "unzipping" reaction is prevented, the polymer chain remains largely intact until some reaction other than depolymerisation occurs at a slightly higher temperature.

This view is supported by the massive evolution of non-condensable products at this stage, although it should be noted that the sensitivity of Pirani filaments to non-condensable products tends to exaggerate the quantity of non-condensables present relative to condensable products.

Besides non-condensables, and material which exhibits limiting rate behaviour at -75°C, there is also evidence, at this peak, for material condensable at -196°C.

Finally, there is a third stage in the degradation, occurring at relatively high temperature, Tmax. 485°C. Apart from the plateau described by the -75°C trace, resulting from previously condensed MMA distilling slowly into the main liquid nitrogen trap, the products seem to consist of low-boiling material, either non-condensable, or condensable only at 196°C.

This evidence is consistent with the findings in previous work, where such high temperature reactions have generally been found to consist of breakdown of residual chain fragments.

BLEND TWO: PMMA(1)/$ZnBr_2$ in the ratio 2:1 molar.
This blend had previously been heated to 150°C to remove excess acetone, and excluding the small shoulder at the beginning of the first peak, caused by residual solvent, the degradation once more consists, essentially, of three stages. These are represented by three peaks whose Tmax.values are 246°C, 375°C and 462°C.

The first peak has now assumed considerable importance, being the largest peak in the trace, and containing evidence of a massive quantity of non-condensable material, production of which begins at a temperature well below 200°C. There is also evidence for the presence of a small quantity of material condensable at temperatures above -100°C, but most of the condensable material present is completely condensable only at -196°C, consistent with the findings from blend 1.

The second peak, Tmax. 375°C, is due almost entirely to material either non-condensable, or condensable only at -196°C, and it can be seen that after completion of the second peak, to the end of the trace, the highest pressure reading is recorded on the Pirani gauge following the -100°C trap. This behaviour is probably caused by a type of limiting rate effect, whereby materials condensed or partially condensed in the -100°C trap in the early stages of degradation (e.g. acetone, MeOH) distil more rapidly into the main liquid nitrogen trap as the temperature of the -100°C trap begins to rise slightly towards the end of the experiment.

The final stage in the degradation, Tmax. 462°C, again consists mainly of production of non-condensables, or material condensable only at -196°C, in complete agreement with the results from blend 1.

BLEND THREE: PMMA(1)/$ZnBr_2$ in the ratio 1:1 molar
This blend was also pre-heated to 150°C to remove excess acetone, and excluding the early shoulder caused by residual solvent, the trace again consists of three main peaks, Tmax. values 232°C, 362°C, and 463°C.

The first stage of degradation has now become even more dominant, being responsible for easily the largest peak in the trace. In general, the trace exhibits the same features as those of the trace for blend 2, limiting rate behaviour again occurring in the -100°C trap during later stages of the experiment.

One additional feature of this trace is the emergence of a sharp peak, Tmax. 193°C, in the early stages of degradation. This is indicative of some reaction which results in very rapid production of large quantities of material partially condensable at -100°C, material which later evidence identifies as MeOH. On close examination of the TVA trace for blend 2, a slight shoulder at temperature 210°C can be detected, indicating the occurrence to a lesser extent, of a similar reaction during the degradation of blend 2.

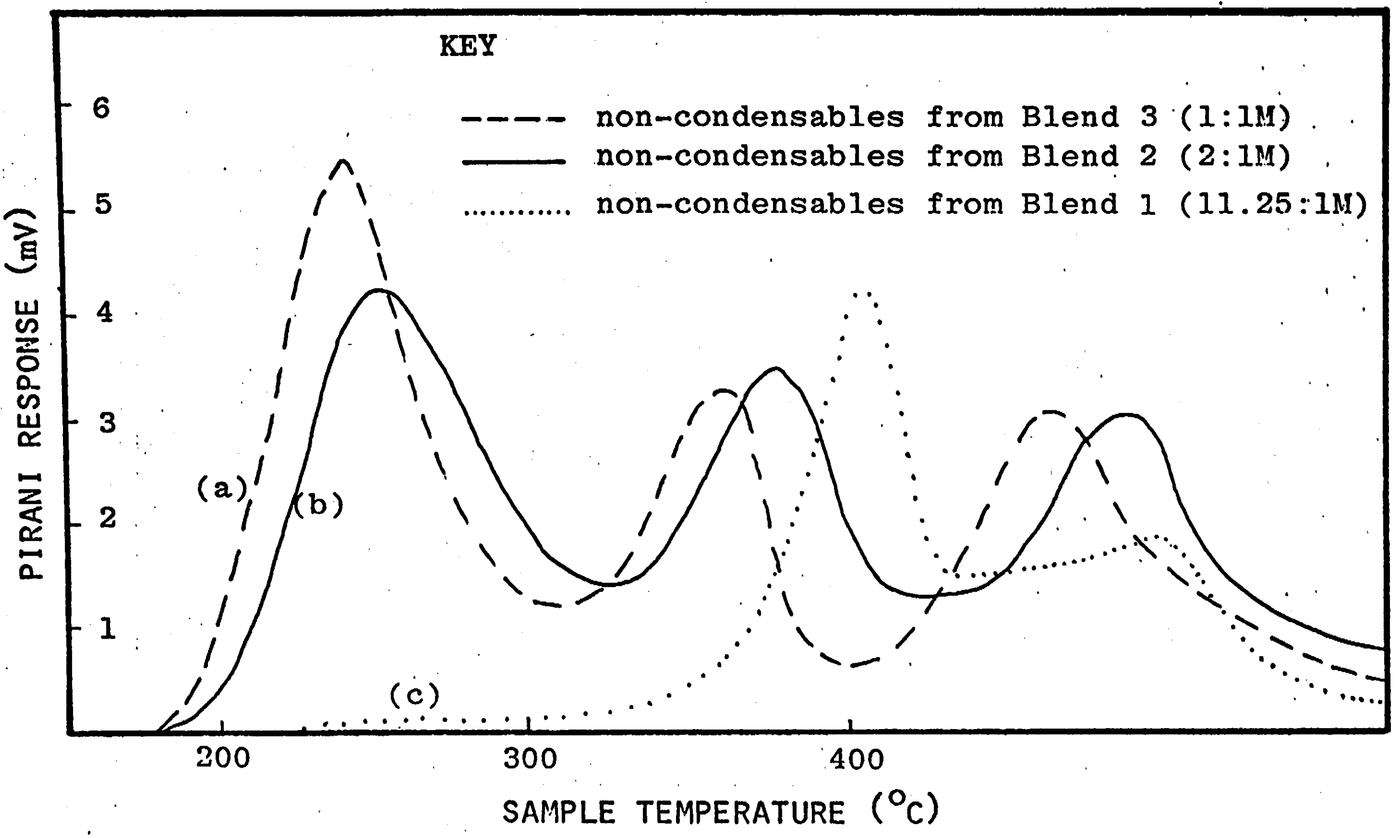
GENERAL TRENDS

In order to illustrate the general trends which emerge from degradation of the three blends, Figure 4.6 depicts the non-condensables portion only of the TVA trace for each blend superimposed onto the same scale.

By inspection of this composite picture, it is apparent that as the concentration of $ZnBr_2$ in the blend increases, the relative size of the first peak increases markedly, indicating the growing importance of some early reaction which can be attributed to the presence of $ZnBr_2$. It can also be seen that as the amount of $ZnBr_2$ present is increased, all three stages in the degradation occur at lower temperatures. This is shown by the progressive movement, to lower temperatures, of all three Tmax. values in each trace.

The overall picture is, therefore, one in which depolymerisation of PMMA to monomer is prevented by production of blocking units, perhaps cyclic structures, in the polymer chain as a result of some substituent reaction involving $ZnBr_2$ at low temperature. An additional piece of evidence to support this view is the TVA study of a film containing 50mg PMMA(2) and 10mg $ZnBr_2$, shown in Figure 4.7.

Comparison with the TVA trace for PMMA(2) alone, shown in Fig. 4.1(b), P.53 shows that the peak representing depolymerisation to monomer, initiated at unsaturated chain-end structures, which is considerable in the trace for polymer alone, is virtually absent from the trace depicting



<u>Figure 4.6</u> Composite TVA trace showing non-condensable products only from Blends 1, 2, 3.

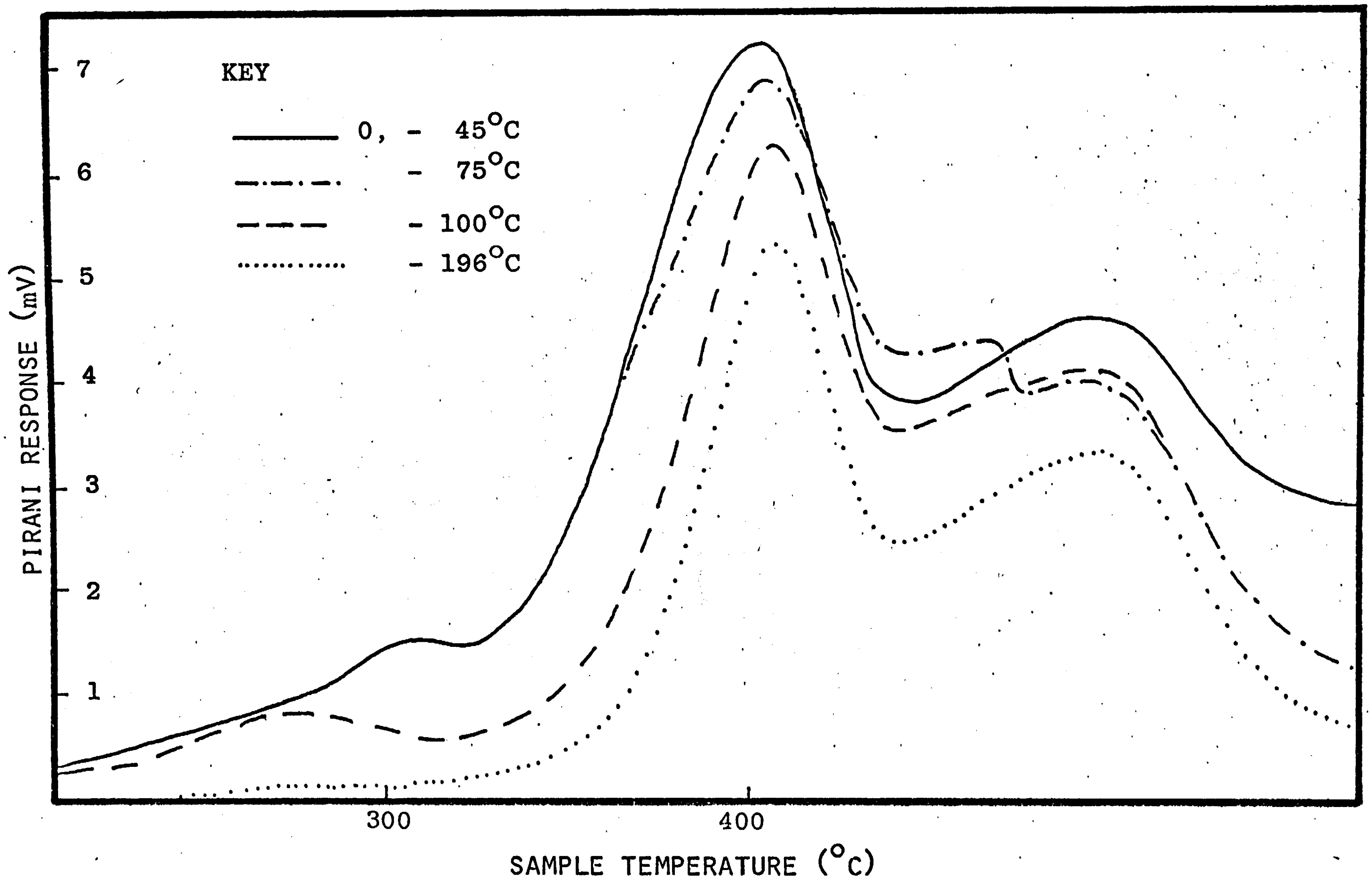


Figure 4.7 TVA trace for film comprising PMMA(2)/$ZnBr_2$ in the ratio 11.25:1 Molar.

degradation of the blend. This gives another indication that the depolymerisation mechanism is somehow blocked.

ANALYSIS OF VOLATILE PRODUCTS BY IR SPECTROSCOPY

Spectra were obtained of the gaseous degradation products from film samples of each of the three blend compositions described in Table 4-I, P.56. Samples consisted of 100mg polymer plus the required weight of $ZnBr_2$, and degradations were carried out under normal TVA conditions, viz. heating at 10^{o}/minute to $500^{o}C$, with the exception of collection of non-condensable products, for which a closed system was used.

It was found that the degradation products were almost identical for all three blends, any differences being in their relative amounts. The only major difference is a near absence of MMA absorptions in the spectra of products from blends 2 and 3.

In general, spectra were found to be so complicated that unambiguous assignments of absorptions is not possible from any one trace, and so three spectra obtained from degradations of a 2:1M blend are shown in Figures 4.8(i) and (ii) and 4.9.

Figure 4.8(i) shows non-condensable products only, from which CH_4 and CO are easily identified by absorptions at 3005 and $1305cm^{-1}$ for CH_4, and $2120cm^{-1}$ for CO.

Figure 4.8(ii) shows the total products, condensables plus non-condensables, from which several compounds are

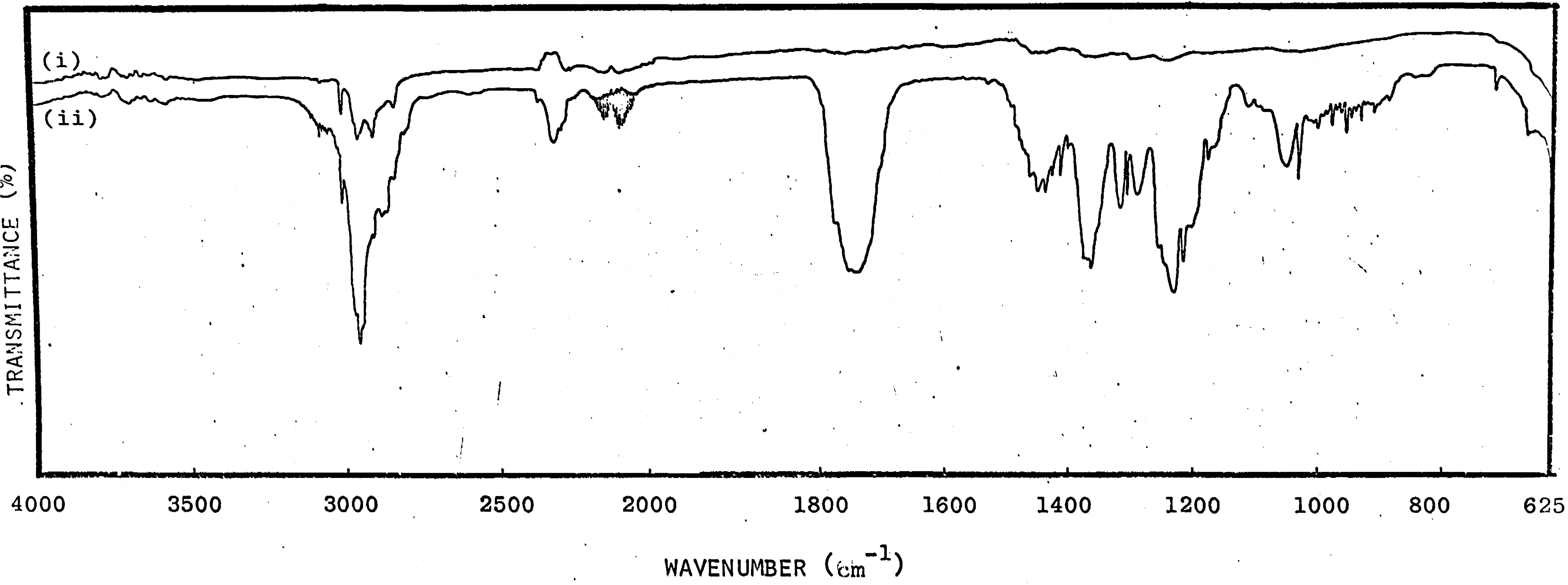


Figure 4.8 (i) non-condensable products

(ii) condensable + non-condensable products from degradation to 500°C of a Blend of PMMA(1)/$ZnBr_2$, 2:1 Molar.

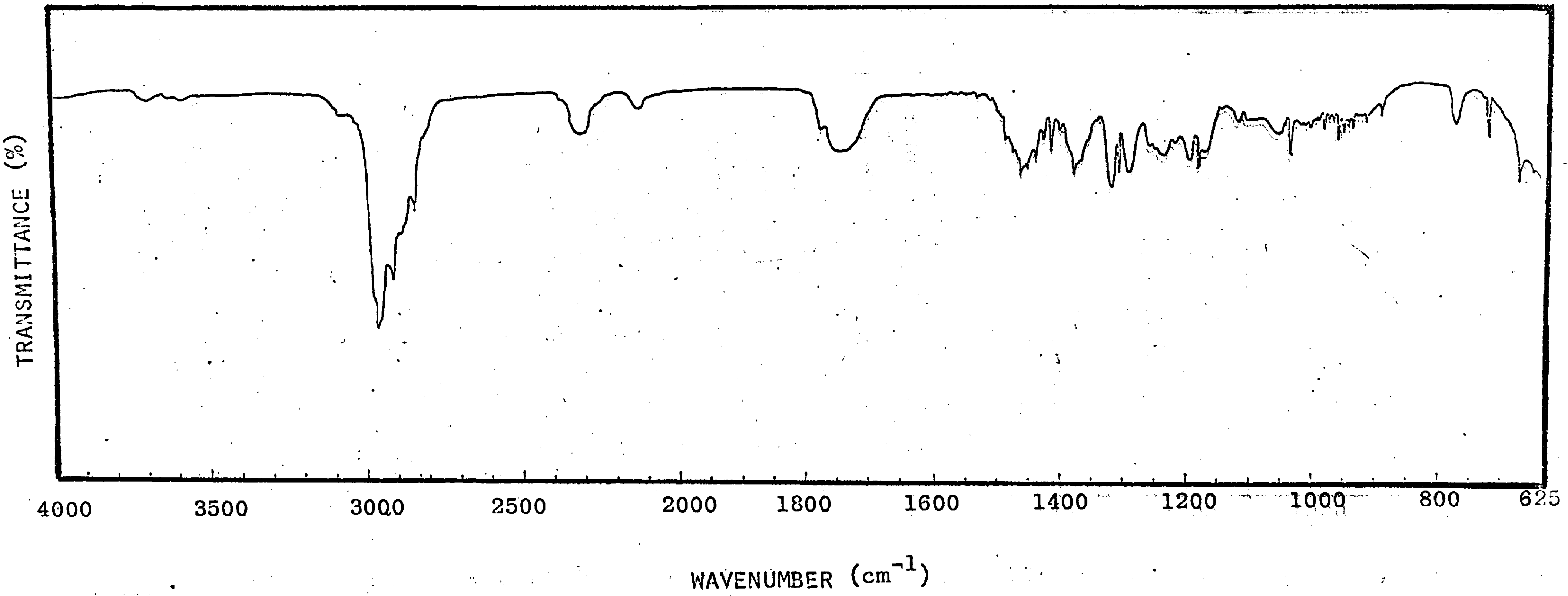


Figure 4.9 IR spectrum of condensable products only from degradation of a PMMA/ZnBr$_2$ blend, 2:1 Molar.

detected. CH_3OH is recognised from its characteristic sharp peak at 1035cm^{-1}; CO_2 absorptions at 2320cm^{-1} and 670cm^{-1} are present, and but-1-ene and isobutene are identified by peaks at 912cm^{-1} and 890cm^{-1} respectively.

Finally, Figure 4.9 shows only the condensable products from a similar 2:1M blend. Thus CH_3Br may be identified without any complication from CH_4, by comparison of the triplet absorption at 1290, 1306 and 1316cm^{-1} with the peaks of a reference spectrum, and in the absence of CO, some ketene species is identified by an absorption at 2120cm^{-1}.

Since there are many overlapping absorptions in these spectra, it was decided to effect a crude separation of the total degradation products obtained from such a blend. Each separate product fraction was then subjected to IR analysis in the hope of establishing the presence of compounds whose absorptions are "swamped" in a spectrum of the total products.

Separation was carried out by sub-ambient TVA, as described in Chapter Two, and the resultant trace is shown in Figure 4.10. Compounds whose presence was detected in a particular fraction, by comparison of IR spectra of the fraction with reference spectra, are also tabulated.

All volatile products identified by infra-red analysis are listed in Table 4-II. Acetone, mesityl oxide, and water are excluded from this list, since acetone is merely

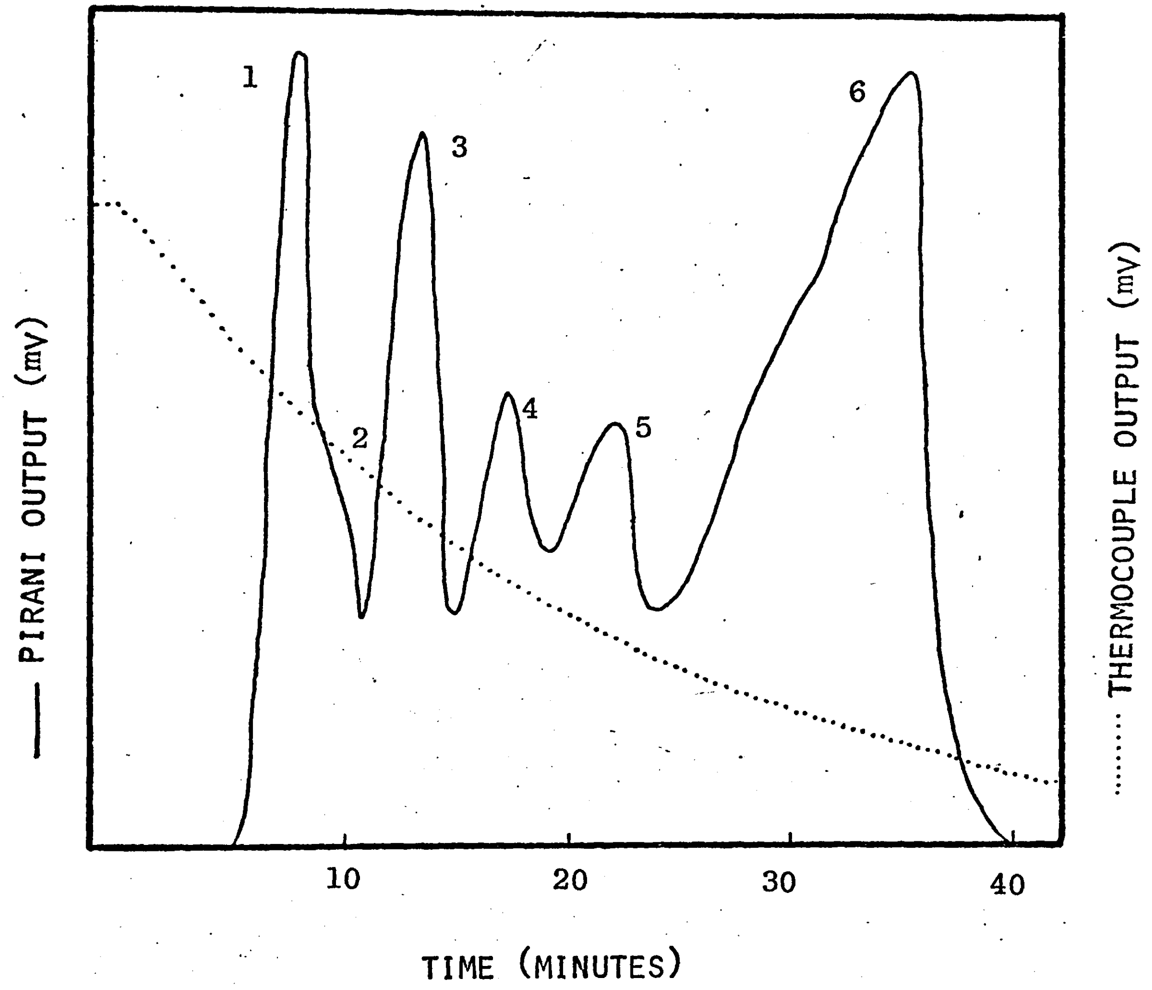


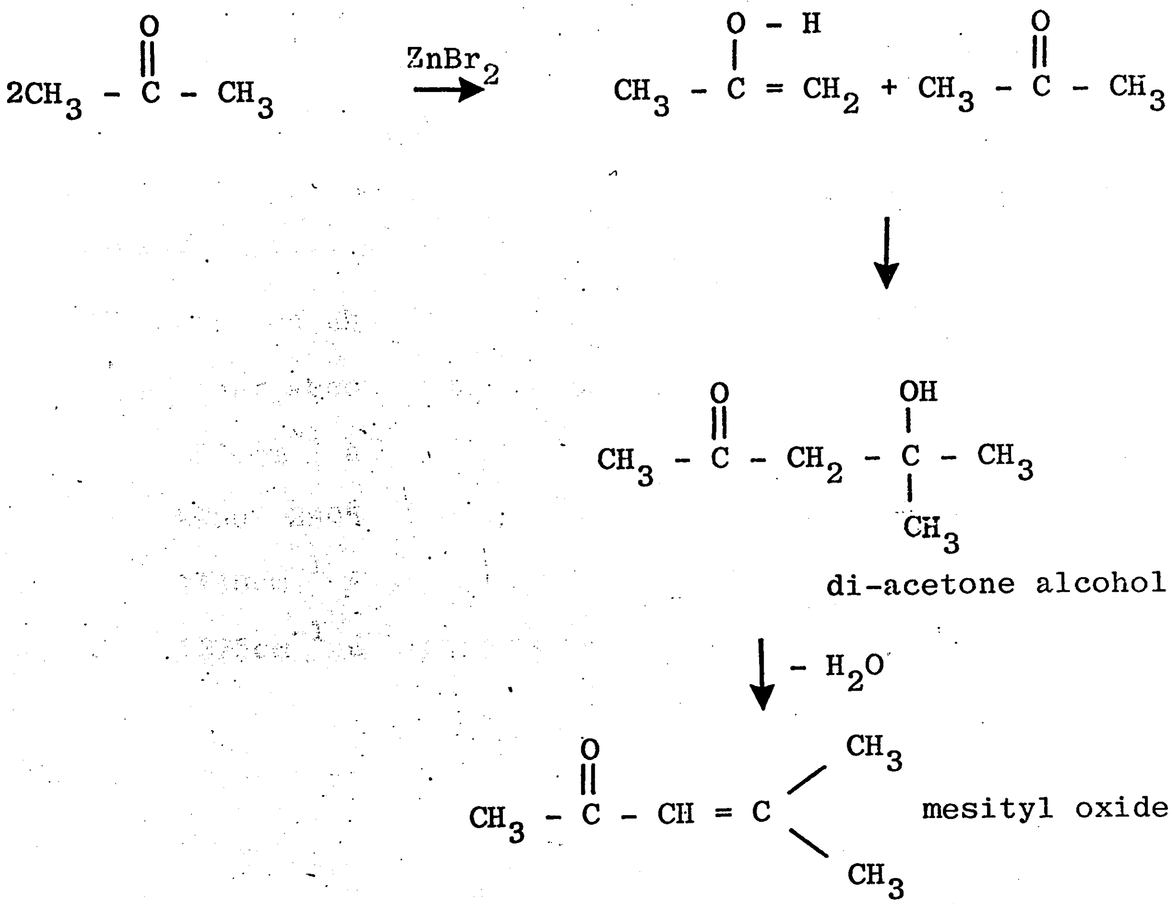
Figure 4.10 Sub-ambient TVA trace for PMMA(1)/ $ZnBr_2$, 2:1 Molar.

Peak No.	Main Constituent(s).
1	CO_2, CH_3OCH_3, isobutene
2	methyl acetate, methyl formate
3	methyl bromide
4	methanol
5	acetone (solvent)
6	mesityl oxide, H_2O

PRODUCT	MAIN PEAKS (cm^{-1})
<u>non-condensables</u>	
carbon monoxide	2110, 2180
methane	3002, 1301
<u>condensables</u>	
methyl methacrylate	1740, 1750
methanol	1032
methyl bromide	1305
methyl acetate	1775, 1245
dimethyl ether	1180
carbon dioxide	2320, 670
dimethyl ketene	2120
isobutene	890
but-1-ene	912
ethylene	950
methyl formate	1210

Table 4-II Volatile products identified by IR analysis.

solvent, and mesityl oxide plus water are produced in the solvent removal process, i.e. when heated to $120^{\circ}C$, it seems that in the presence of $ZnBr_2$, acetone undergoes a condensation reaction to form di-acetone alcohol, which then decomposes into mesityl oxide and water.



Mesityl oxide was identified by IR analysis, and later, by gas-liquid chromatography.

IR ANALYSIS OF COLD-RING FRACTION

Although the degradation of PMMA alone yields no cold-ring fraction, degradation of all three blends results in a deposit of yellow-brown material in the cold-ring. IR spectra of this material were obtained as KBr discs, CCl_4 solutions, and films cast from $CHCl_3$ solutions onto sodium chloride plates. Spectra from all three blends were found to be similar, all consisting of broad peaks which cannot be assigned to a particular compound. The sole exception is a sharp absorption at $1600cm^{-1}$ in spectra of samples run as KBr discs, an absorption characteristic of $ZnBr_2$.

The other absorptions occur at:

$3510cm^{-1}$ assigned to uptake of H_2O
2950, 2905, $2860cm^{-1}$ assigned to C-H stretching
$1440cm^{-1}$ assigned to C-H deformation
$1375cm^{-1}$ assigned to $-CH_3$ deformation

These data are not particularly helpful, leading only to the assumption that the CRF consists of a mixture of hydrocarbons and $ZnBr_2$.

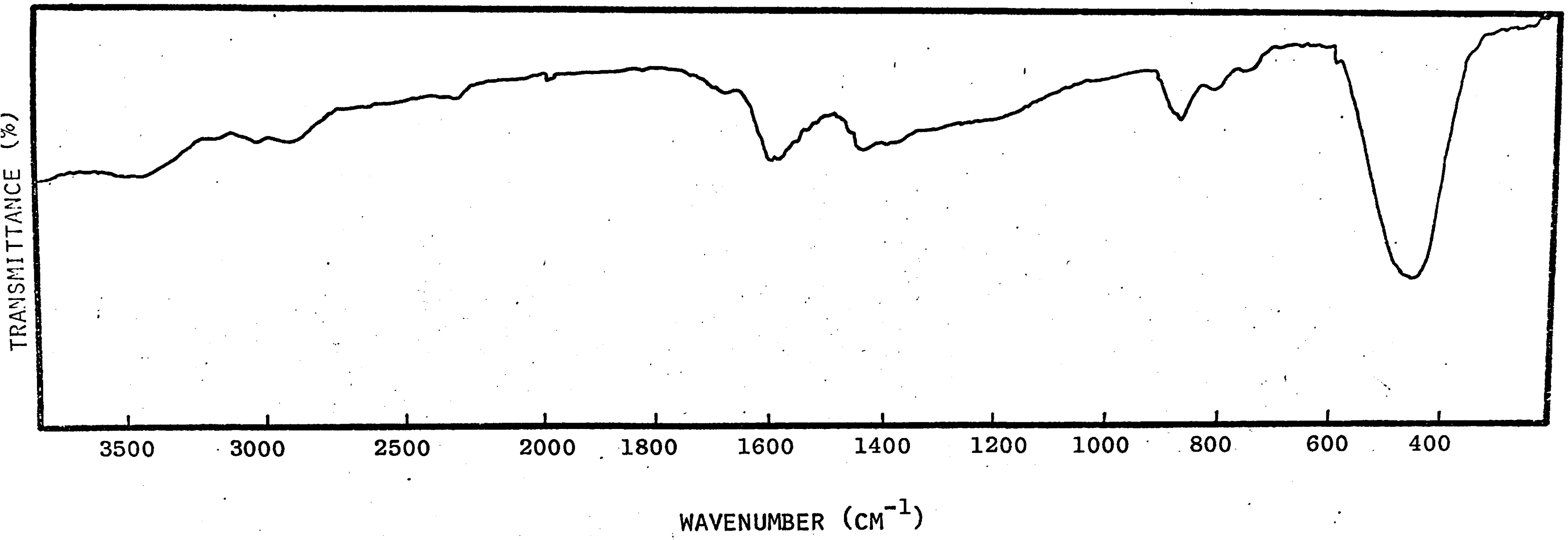
In the final stages of degradation, just below 500^oC, a metallic mirror, obviously zinc, is deposited on the upper parts of the degradation tube. This is thought to be the result of interaction between zinc oxide, formed during degradation, and the carbonaceous residue from PMMA.

i.e. $ZnO + C \longrightarrow Zn + CO$

RESIDUE ANALYSIS BY IR SPECTROSCOPY

After heating to 500°C, all three blends leave a black residue on the base of the degradation tube, again in contrast to the behaviour of PMMA alone which leaves no residue.

The residue from each of the three blends was subjected to IR analysis, over the range 4000 - 250cm^{-1}, samples being examined in the form of CsI discs. A typical spectrum, obtained from the residue from a 2:1M sample is reproduced in Figure 4.11, from which it can be seen that the most informative absorption is a massive peak at 450cm^{-1}. This is evidence of the presence of ZnO, and the absence of other absorptions suggests that any residue from the polymeric part of the blend is largely carbon.



<u>Figure 4.11</u> Residue after degradation to 500°C of a film comprising PMMA(1)/$ZnBr_2$, 2:1 Molar.

VOLATILES ANALYSIS BY MASS SPECTROMETRY

Analysis, by mass spectrometry, of the total volatile products from degradations of the three blends was carried out as described in Chapter Two.

Following isolation of the products in a receiver cooled to liquid nitrogen temperature, non-condensable products alone were introduced into the spectrometer, and only after re-evacuation of the instrument were the condensed products introduced. Results were found to be similar for all three blends, and so discussion will be confined to the 2:1M blend.

Study of the non-condensable products provides evidence for CO, at $^{M}/E$ value 28 (complicated by the presence of traces of atmospheric N_2), CH_4, $^{M}/E$ value 16, and H_2, $^{M}/E$ value 2. The peak interpreted as H_2 is of low intensity in relation to the peak for CH_4, and although the sensitivity of the instrument to different ions may vary slightly, it seems that no large scale production of H_2 occurs during degradation.

The spectrum obtained from examination of the condensable products is reproduced in Figure 4.12, from which it can be seen that the most intense peaks may be assigned to CH_3Br. Evidence is found for the presence of all of the major products identified by IR, although it should be noted that, in some cases, the same molecular fragment could have arisen from more than one parent compound.

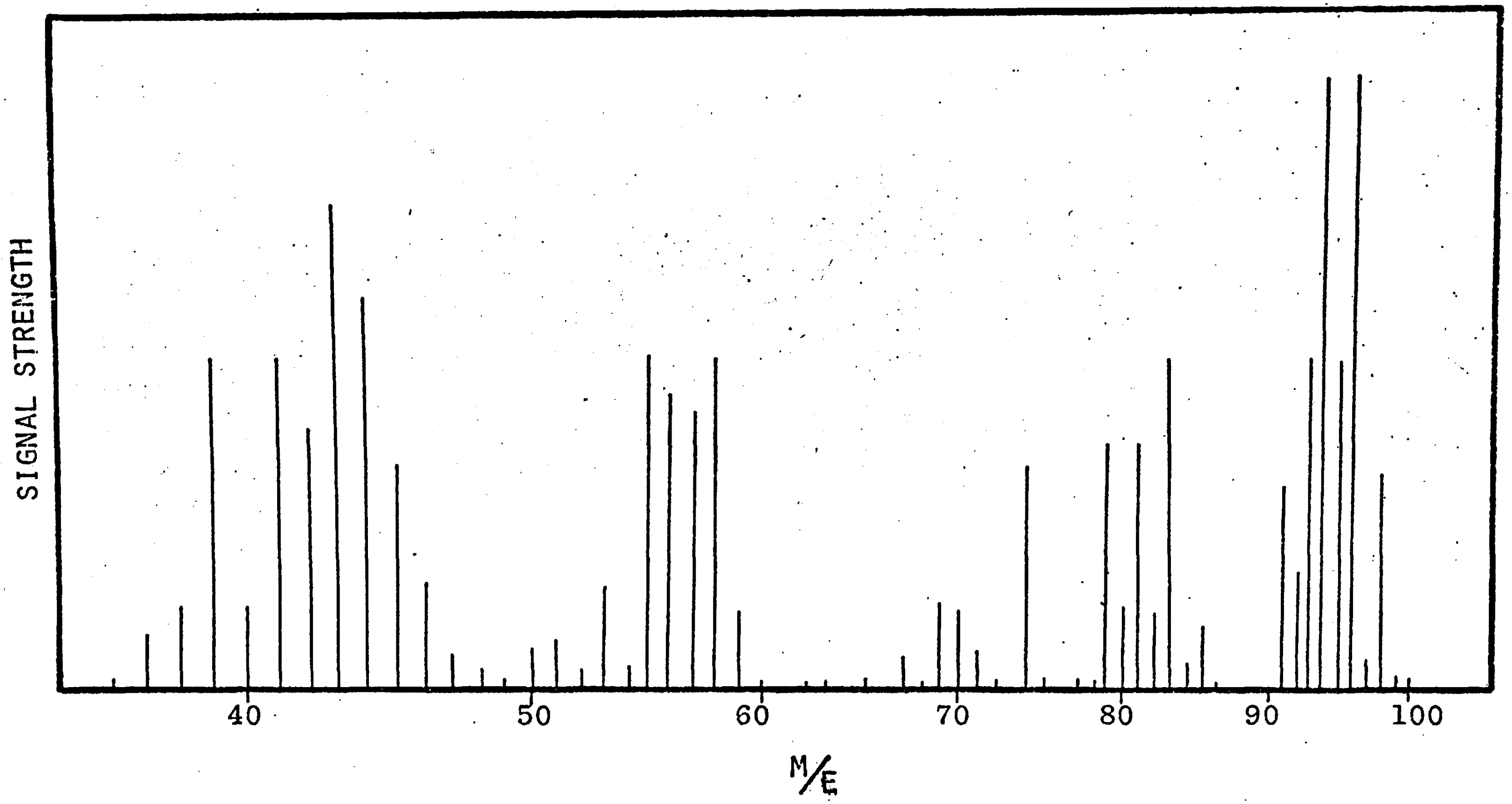


Figure 4.12 Mass spectrum of the condensable products from degradation of a 2:1 Molar blend, PMMA(1)/$ZnBr_2$.

Assignments of peaks in the mass-spectrum to particular compounds are made in Table 4-III, and on the whole it appears that results from mass spectrometry are in close agreement with results from IR spectroscopy.

M/E	PRODUCT
100, 85, 69, 59, 41	methyl methacrylate
98, 83, 55, 42	mesityl oxide
96, 94, 81, 79, 15	methyl bromide
32, 31, 15	methanol
74, 59, 43, 42	methyl acetate
44, 28	carbon dioxide
46, 31, 15	dimethyl ether
58, 43, 15	acetone
70, 42, 41	dimethyl ketene
56, 55, 54, 41	isobutene butene

Table 4-III Assignment of peaks from mass spectrum of condensable volatile products.

STRUCTURE OF THE POLYMER-SALT BLEND

On the basis of results from TVA studies of polymer/salt blends and analyses of the resultant degradation products, it is apparent that there is considerable interaction between PMMA and $ZnBr_2$ during the course of degradation.

Since the blends were studied as films cast from acetone solutions, and, as previously stated, these films are invariably transparent, indicative of the compatibility of the components, it was decided to examine the structure of these polymer/salt blends. The aim was to establish whether or not any interaction can be detected prior to the onset of degradation.

This investigation is particularly necessary in order to evaluate the role played by acetone, since a $ZnBr_2$/acetone molecular complex has previously been characterized,[48] complex formation being due to co-ordination of the lone-pair electrons of the carbonyl oxygen with Zn^{2+}.

TECHNIQUES CONSIDERED

Methods of study which could possibly yield relevant information were thought to be IR, UV, and visible spectroscopy; it was decided, however, that the first two were unsuitable, for the following reasons:

(i) IR Spectroscopy

In the IR region, complex formation between $ZnBr_2$ and PMMA should be accompanied by a lowering in energy required to stretch the PMMA carbonyl group, detected by a shift to lower wavenumber of the polymer carbonyl absorption. This is "masked", however, by the presence of the carbonyl absorption of acetone which normally occurs at lower wavenumber than that of PMMA, and so, for the blend, only a broad carbonyl peak covering a range of frequencies is obtained, from which no firm conclusions can be drawn.

(ii) UV spectroscopy

In the ultraviolet region of the spectum, both PMMA and acetone absorb strongly, and thus make impossible interpretation of the broad absorptions obtained for polymer/salt blends.

(iii) Visible spectroscopy

In the visible region of the spectrum, however, PMMA and acetone have no absorptions, and so it was felt that useful information could be obtained from visible spectroscopy studies. Unfortunately, Zn^{2+} does not exhibit d-d electronic transitions since the ion, a d^{10} system, contains completely filled 3d orbitals, and so $ZnBr_2$ is not suitable for study by visible spectroscopy. In order to overcome this limitation, the approach adopted was one previously used by various workers in enzyme studies, who have investigated the stereochemistry of structures involving Zn^{2+} by replacing the zinc ion with a metal ion which does exhibit d-d transitions.[49] In order to gain information about the enzyme carboxypeptidase A, for example, Zn^{2+} in the active site was replaced by Co^{2+} to allow spectroscopic studies to be carried out.[50]

Thus it was decided, in this work, to study a blend of PMMA(1)/$CoBr_2$, 1:1 molar ratio.

Before any spectroscopy was carried out, however, it was necessary to study the thermal degradation of a blend of PMMA(1)/$CoBr_2$. The composition chosen was in the ratio 5:1 by weight, in the form of a film, which was found to be transparent.

The TVA trace for this blend is given in Figure 4.13, and comparison with the TVA study of the equivalent blend involving $ZnBr_2$ (P. 57) shows the traces to be of similar form. IR analysis shows the volatile products from the $CoBr_2$ blend to be identical to those from the $ZnBr_2$ blend, and on this basis, it seems reasonable that the structure of a blend involving $CoBr_2$ is similar to that of a blend involving $ZnBr_2$.

Visible spectroscopy studies were then carried out on samples, in the form of both powders and films, to provide solid reflectance spectra which are reproduced in Figure 4.14.

INTERPRETATION OF THE SPECTRA

1. Anhydrous $CoBr_2$, powder. λmax. 626nm

In this case the ligand to Co^{2+} is Br^-, and the structure is tetrahedral.[51]

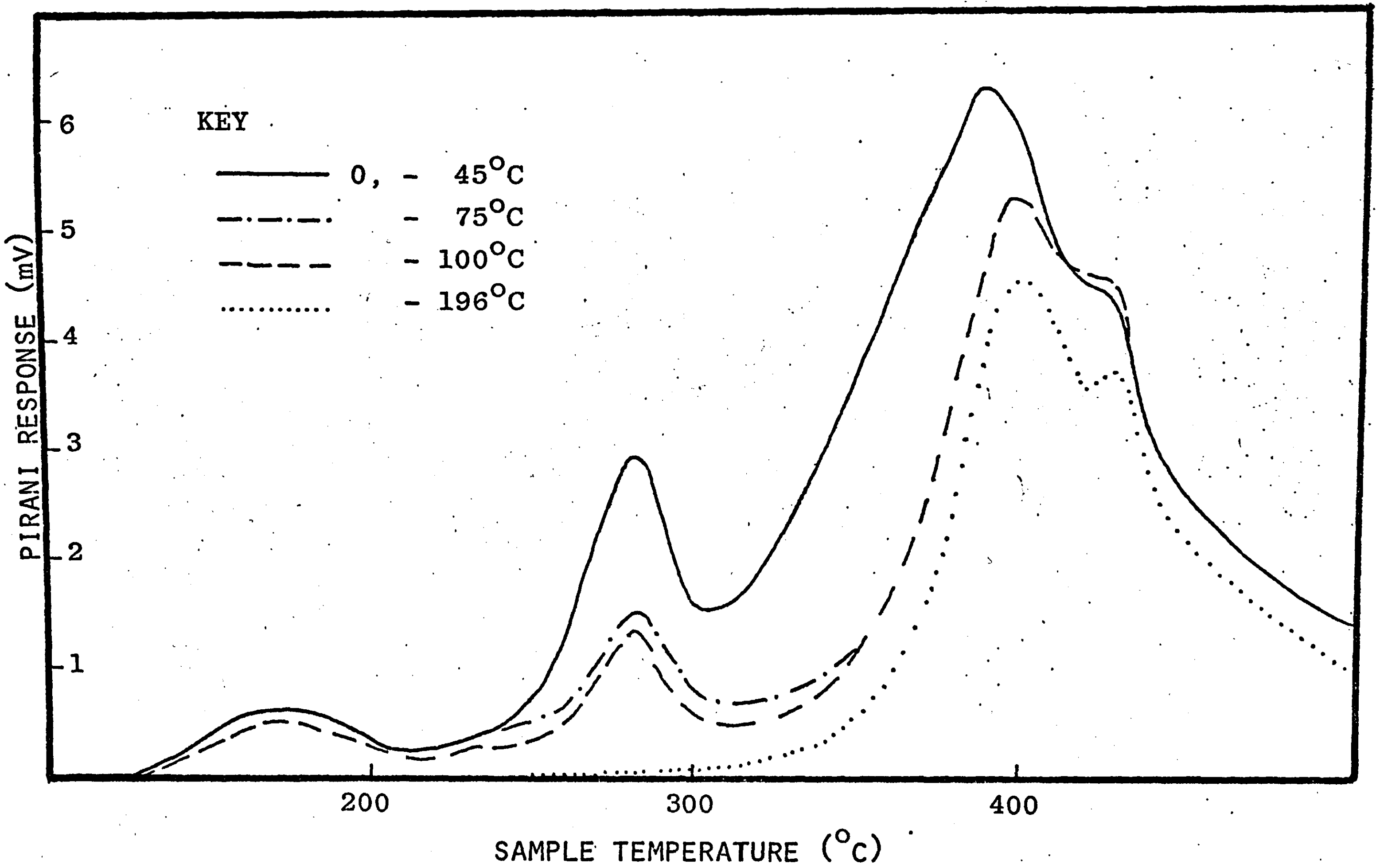


Figure 4.13 TVA trace for a film comprising PMMA(1)/$CoBr_2$ in the ratio 5:1 by weight.

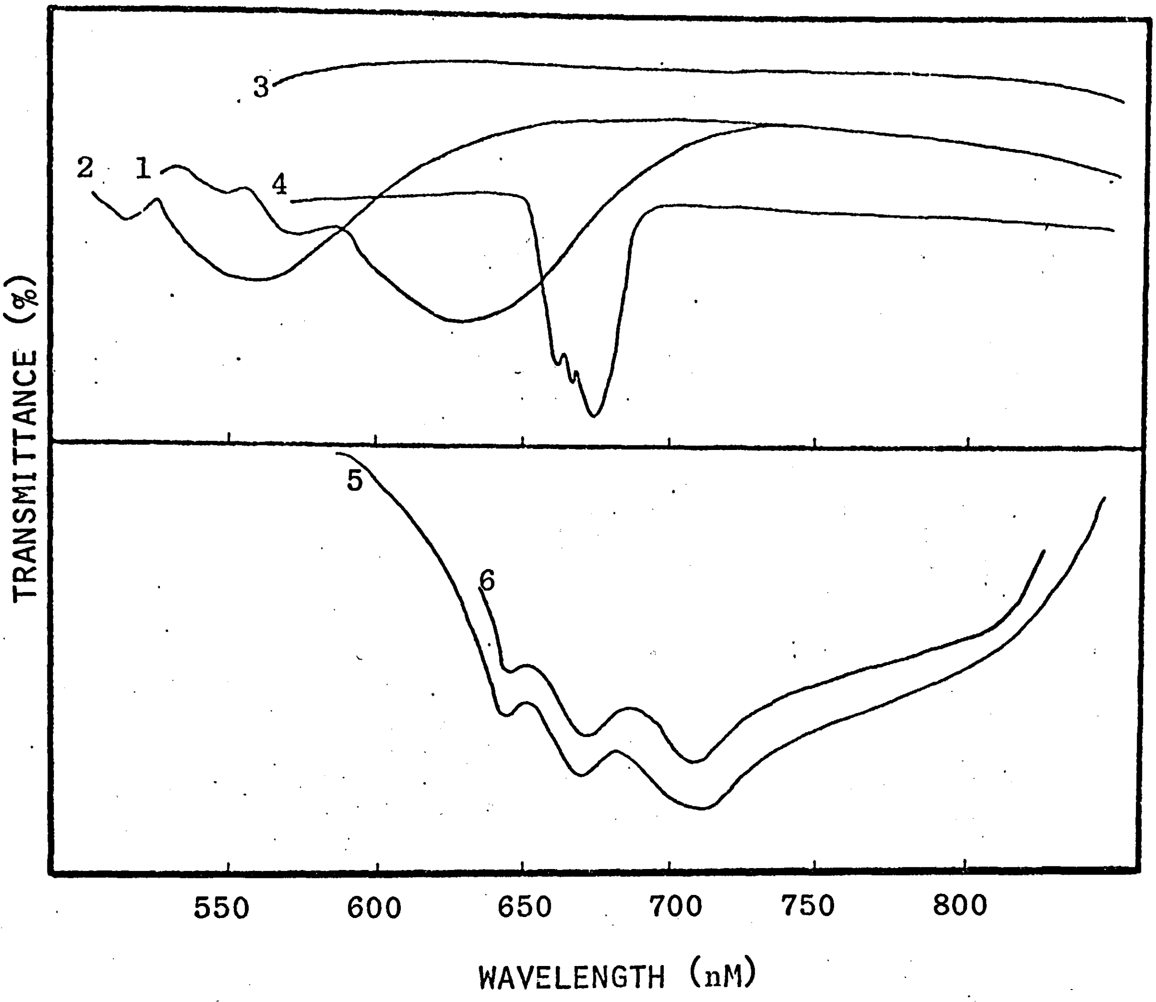


Figure 4.14 Visible Spectra of :

1. Anhydrous $CoBr_2$, powder
2. $CoBr_2$ powder allowed to absorb H_2O
3. PMMA(1), powder
4. "Film" of $CoBr_2$ from acetone
5. Film of PMMA(1)/$CoBr_2$, 1:1M
6. Film in 5 heated to 170°C to remove acetone

2. $CoBr_2$, powder, after the uptake of H_2O. λmax 558nm.

In this case, Br^- is replaced as ligand to Co^{2+} by H_2O, a "stronger" ligand in terms of the spectrochemical series. The shift of λmax. to higher energy is a movement towards octohedral co-ordination, but since the extinction co-efficient remains similar, the structure can only be pseudo-octohedral which would result in an extinction co-efficient an order of magnitude smaller.

Pseudo-octahedral geometry may be explained by the possibility of two Br^- ligands, in cis positions, which would prevent the structure from possessing a centre of symmetry..

3. PMMA(1) only. Powder.

This shows no absorption. PMMA powder was then physically ground with anhydrous $CoBr_2$, and a spectrum of the resultant mixed powder obtained. This was found to be identical to spectrum 1 , i.e. that of anhydrous $CoBr_2$ alone, showing that no interaction is detected when the components are in the powdered state.

4. "Film" of $CoBr_2$ from acetone. λmax 675nm.

In this case acetone replaces Br^- as the ligand to Co^{2+}. The fact that λmax occurs at slightly lower energy than for $CoBr_2$ suggests that acetone is a slightly weaker ligand than Br^-, and the reason for Co^{2+}-acetone complex formation may be that acetone is present in such excess.

The position of λmax for this Co^{2+} - acetone complex is once more consistent with tetrahedral geometry, being in the lower energy range of the visible region.

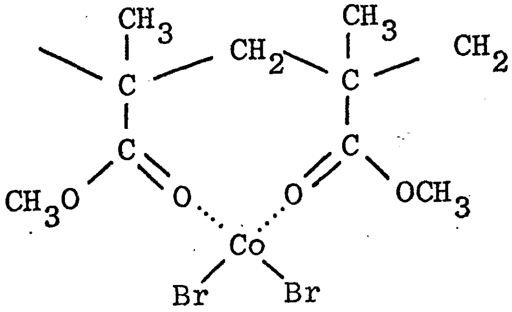
5. Film of PMMA(1)/$CoBr_2$, 1:1M, from acetone. λmax 712nm.

6. The above film heated to 170°C to remove acetone.

It can be seen that spectra 5 and 6 are identical, both consisting of three absorptions with λmax 712nm.

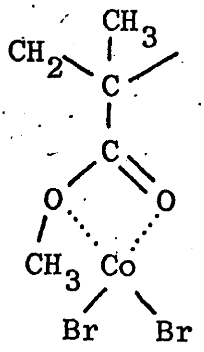
This spectrum is completely different from that of the $CoBr_2$ - acetone complex, 4 , and λmax has shifted to lower energy, consistent with the formation of some complex between $CoBr_2$ and PMMA. Since, in this case, λmax has shifted to low energy relative to the $CoBr_2$ - acetone complex, which is tetrahedral, the geometry of the polymer-salt complex could be described as pseudo-tetrahedral, especially since absorption continues beyond 800nm.

These facts are compatible with a polymer-salt complex of the type:



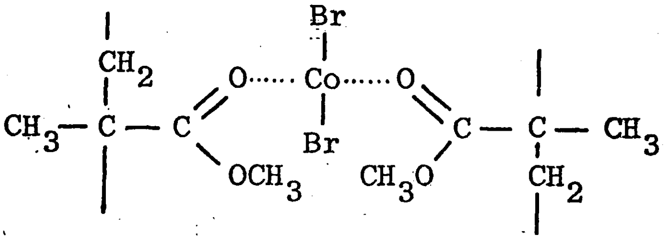
(a)

Other possibilities are



(b)

where the ester group acts as a bidentate ligand, and



(c)

where $CoBr_2$ effectively crosslinks the polymer..

Viscometry experiments failed to yield any evidence for (c), however, and it is felt that structure (a) is most likely as a result of the favourable positions occupied by adjacent carbonyl groups, which would best allow the metal to exhibit tetrahedral geometry.

This argument applies equally well to $ZnBr_2$ since zinc favours tetrahedral geometry even more than does cobalt.

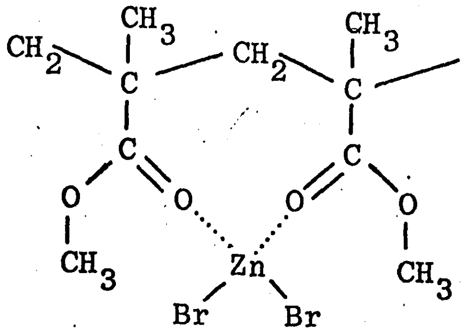
REASONS FOR FORMATION OF A POLYMER-SALT COMPLEX

Under normal circumstances, the carbonyl group of an ester would be expected to be a less effective donor ligand than the carbonyl group of a ketone, as a result of the electron - withdrawing effect of the ester alkoxy group. In this instance, however, there are two reasons why the ester carbonyl in PMMA should replace acetone as the ligand to Zn^{2+}.

1. There will be a type of chelate effect when the polymer complexes with the salt, i.e. there will be an overall gain in entropy when two separate acetone molecules are released, replaced by ester groups constrained by the polymer chain.

2. Co-ordination complexes such as $ZnBr_2$ - PMMA are weak, with bonds continuously breaking and re-forming. Since the sample films are formed by the passage of nitrogen over a solution, and are then continuously pumped to high vacuum, acetone will be progressively removed, whereas PMMA will not. Thus a PMMA - $ZnBr_2$ complex is also favoured statistically.

On this basis, a PMMA - $ZnBr_2$ complex, of the type shown, is thought to form during film preparation from solution, prior to degradation.



Probable structure of complex

OPTIMUM BLEND COMPOSITION

If the above deduction is correct, optimum conditions for blend preparation should be a 2:1 molar ratio of PMMA:$ZnBr_2$. This hypothesis was tested in the following way:

(i) A film of composition PMMA(1)/$ZnBr_2$, 1:1 molar was cast from acetone solution. This was heated to 170°C to remove solvent, prior to microanalysis. All original Br^- should still be present, and the results found were

	Found	Theory (1:1M)
%Br	45.67	49.14

When it had been established, on the basis of IR evidence, that the complex is soluble in $CHCl_3$, the above sample was dissolved in $CHCl_3$, in which $ZnBr_2$ alone is insoluble. After filtration to remove excess $ZnBr_2$, followed by reprecipitation into petroleum ether, the sample was finally heated to remove solvent. Thus only $ZnBr_2$ complexed with

PMMA should now be left in the sample.

Comparison of the analysis figures found for Br in this case with the theoretical figure for the proposed structure (shown above) suggests that PMMA/$ZnBr_2$, 2:1 Molar is the favoured ratio i.e.

	Found	Theory (Proposed Structure)
%Br	38.8	37.6

POSSIBLE REACTION PATHWAY

These results suggest that one possible explanation for the unusual behaviour of PMMA during degradation in the presence of $ZnBr_2$ is that the effect is caused by some low temperature reaction (between $ZnBr_2$ and the pendant ester groups of PMMA) which occurs through a co-ordination complex formed during sample preparation from solution.

This hypothesis is to some extent borne out by the result of a TVA study made on a powder blend of PMMA(1)/$ZnBr_2$, 2:1M, shown in Figure 4.15.

In the case of mixed powders, complex formation cannot occur at temperatures below the Tm of the polymer, and comparison with the TVA trace for a similar blend cast from solution (Fig 4.4, P.58) where complex formation does occur, shows that the first peak in the trace is much smaller for the mixed powder blend. This is taken as evidence that the first stage in degradation is reaction between $ZnBr_2$ and the ester groups of PMMA, a reaction which is facilitated by the intimate polymer-salt contact of a complex.

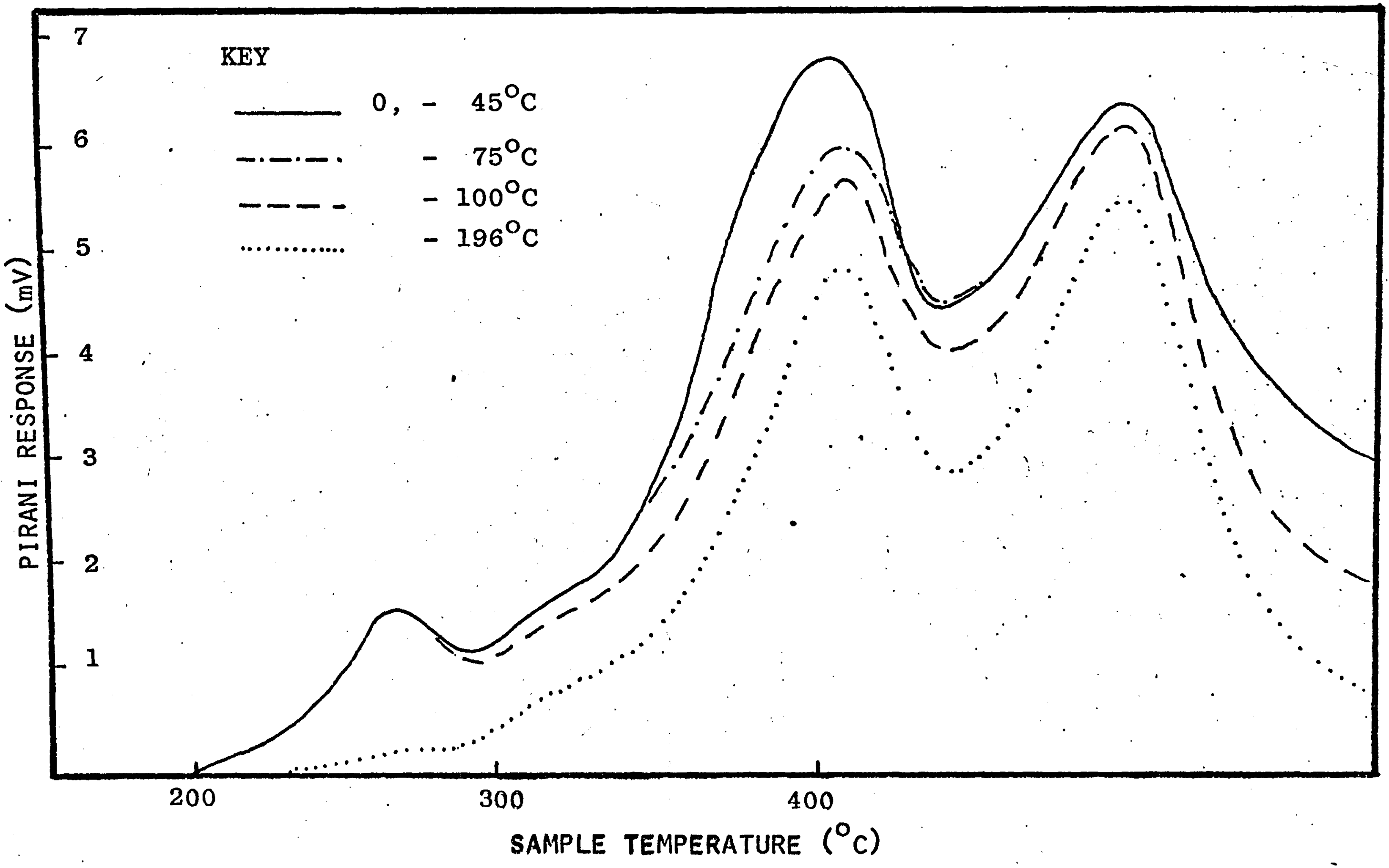


Figure 4.15 TVA trace for a Powder Blend, comprising PMMA(1)/$ZnBr_2$, 2:1 Molar.

THE ROLE OF WATER

$ZnBr_2$ is known to be extremely hygroscopic, and it was found that polymer-salt sample films could absorb atmospheric moisture. It was, therefore, necessary to establish whether or not any H_2O present in a blend prior to heating had an effect on the degradation mechanism.

The approach adopted was a comparative study of two samples, blends of PMMA/$ZnBr_2$ in the ratio 1:1 Molar, whereby one was allowed to come into contact with atmospheric H_2O and the other was prepared for study under rigorous drying conditions.

It was found that if the first blend, previously heated under vacuum to remove solvent, was left exposed to the atmosphere, it absorbed 12 - 14% of its own weight of water, and then stabilized. This behaviour was found to be reproducible, after a similar study had been conducted using several other samples.

The precautions taken to exclude moisture from the "dry" blend during sample preparation were as follows:

(i) The solvent used was acetone (AR, max. 0.2% H_2O) which was distilled under vacuum, onto molecular sieves, and used immediately.

(ii) $ZnBr_2$ was sublimed under vacuum, previously absorbed H_2O being condensed in a liquid nitrogen trap. The $ZnBr_2$ was then used immediately.

(iii) Solution preparation and mixing was carried out in a dry-box.

(iv) Excess solvent was removed by distillation, carried out on a vacuum-line.

(v) Samples for study by TVA were added to the degradation tube in a dry-box; the tube was sealed off using the degradation tube head described in Figure 2.3, P.17, and the sample was then connected to the TVA apparatus.

Results of degradation studies on such blends were found to be reproducible, TVA traces being similar to the trace shown in Figure 4.5, for a 1:1M blend.

When comparable samples which had been allowed to achieve maximum H_2O content were studied, TVA traces were similar to those obtained for "dry" samples, the only real difference being that for the sample which contained moisture, a peak appeared at around 120°C in the TVA trace, corresponding to removal of H_2O. It was also found, by IR analysis, that for both blends, volatile products, cold-ring fractions, and residues were identical.

This is taken as evidence that H_2O plays no part in the degradation mechanism. There is one complicating factor, however. As has been stated previously, when PMMA/$ZnBr_2$ films are heated, some acetone condenses with itself during solvent removal, in the early stages of TVA. The products are mesityl oxide and water.

Thus, even samples prepared under anhydrous conditions must come into contact with some H_2O. However, it can be seen from the TVA traces shown in Figures 4.3 - 4.5 that the extent to which thermal degradation of PMMA is altered increases enormously with increasing concentration of $ZnBr_2$.

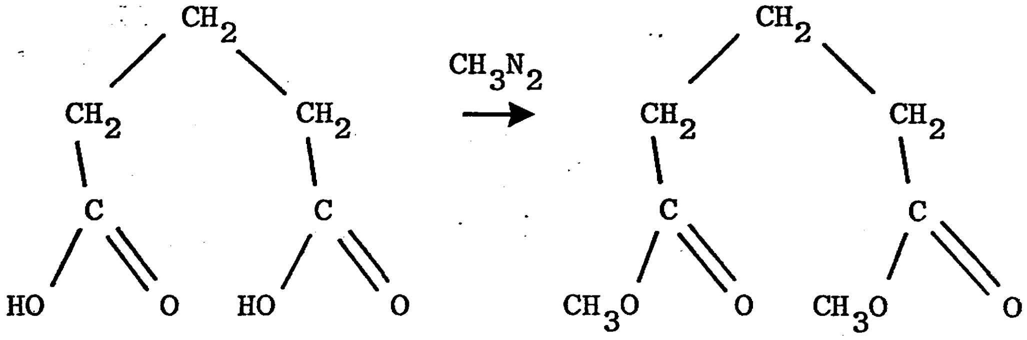
It is unlikely, however that the number of moles of water produced from the condensation reaction will increase sufficiently from blend 1 to blend 3 to result in the increasing magnitude of the effect on PMMA degradation experienced as the concentration of $ZnBr_2$ is increased. The effect on polymer degradation is thought, therefore, to be a direct result of the presence of $ZnBr_2$, rather than a secondary effect caused by H_2O produced from acetone.

MODEL COMPOUND

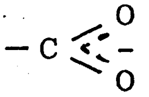
In general, attempts to correlate the thermal degradation of polymers with the breakdown of low molecular weight model compounds have been largely unsuccessful. This is thought to be due mainly to the intimate contact between reactive sites in a polymer, affording the possibility of chain reactions, as well as to the occurrence of occasional "weak links" in the polymer structure. Consequently, low molecular weight analogues tend to show higher thermal stability.

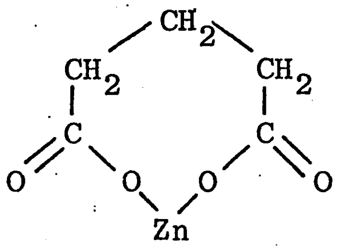
In the case of blends of PMMA with $ZnBr_2$, however, it was thought that structural changes in the polymer were occurring as a result of reaction between $ZnBr_2$ and pendant ester groups, and it was felt that some insight into this process might be gained by substitution of a model compound for PMMA.

The model compound chosen, mainly due to ease of preparation, was dimethyl glutarate, which, although not ideal, could still yield useful information. Preparation was by esterification of glutaric acid, using diazomethane, to yield a clear liquid:

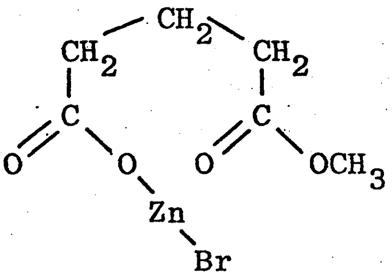


Dimethyl Glutarate (DMG)

DMG was then refluxed with anhydrous $ZnBr_2$, and was found to yield large quantities of a white solid. IR analysis of this solid, Figure 4.16., showed a new absorption at $1550cm^{-1}$, evidence of the carboxylate group,  $-\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{O}}{}^{-}$. This is perhaps indicative of some structure of the type:



or



Attempts to extend this approach to MMA + $ZnBr_2$ were unsuccessful, due to the added complication of the methacrylate double bond, which was probably involved in complex formation with $ZnBr_2$, and also led to polymerisation on heating.

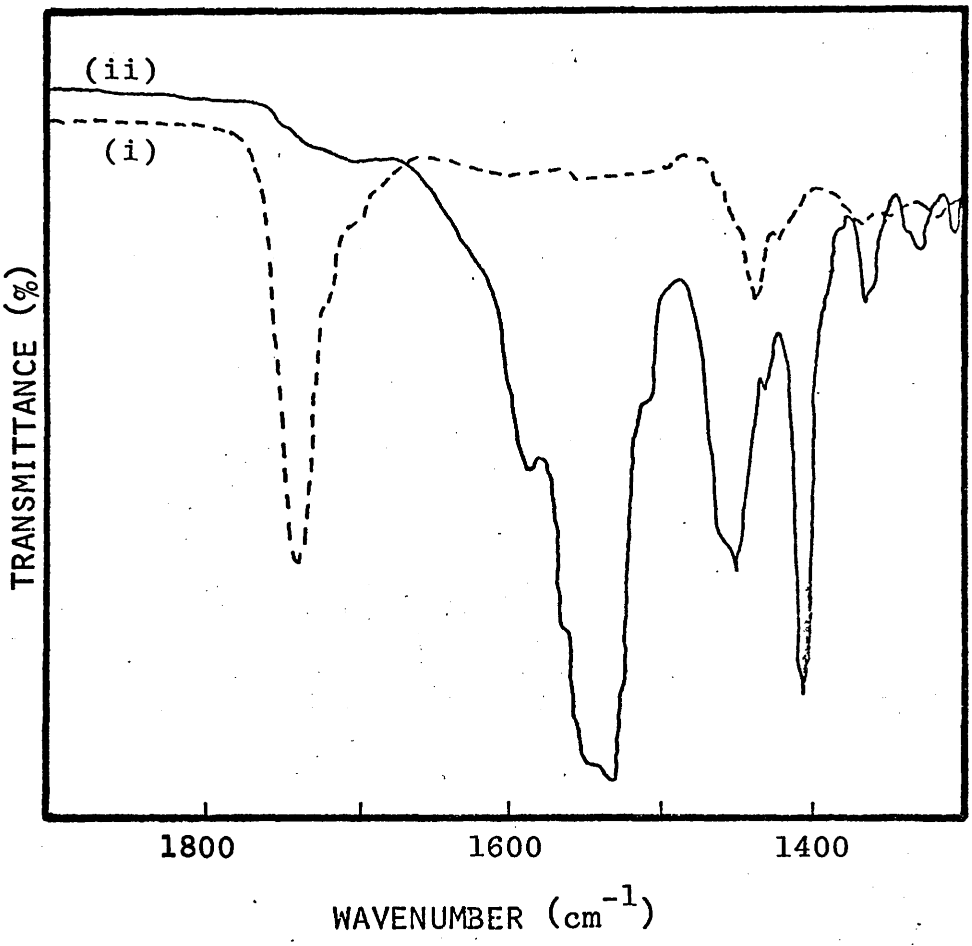


Figure 4.16 (i) IR of DMG, liquid film on NaCl plate.

(ii) IR of solid product after reflux of DMG + $ZnBr_2$. KBr disc.

STRUCTURAL CHANGES DURING BLEND DEGRADATION

In order to study the structural changes which occur in PMMA during degradation in the presence of $ZnBr_2$, a film containing PMMA(1):$ZnBr_2$ in the ratio 2:1 molar was cast onto a sodium chloride plate. This was then subjected to IR analysis after having been heated isothermally at various temperatures for 1 hour periods, as shown in Figure 4.17.

Trace (a) shows the blend prior to any heating. Since it has already been shown, by visible spectroscopy, that a PMMA - $ZnBr_2$ complex forms at room temperature, this should be reflected in an IR study showing the PMMA carbonyl absorption.

In theory, since carbonyl groups of PMMA are acting as donor ligands to Zn^{2+}, the carbonyl stretching frequency, normally 1745cm^{-1}, should occur at lower energy i.e. lower wavenumber.

Interpretation is made more complicated, however, by the presence of acetone solvent, the carbonyl group of which normally absorbs at lower wavenumber than that of PMMA, viz. 1720cm^{-1}.

In fact, the overall carbonyl absorption in spectrum (a) is broad, as expected from a peak composed of two different absorptions, but the fact that absorption occurs over the relatively low range 1720 - 1670cm^{-1} seems to indicate that the carbonyl absorptions of both PMMA and acetone are lowered

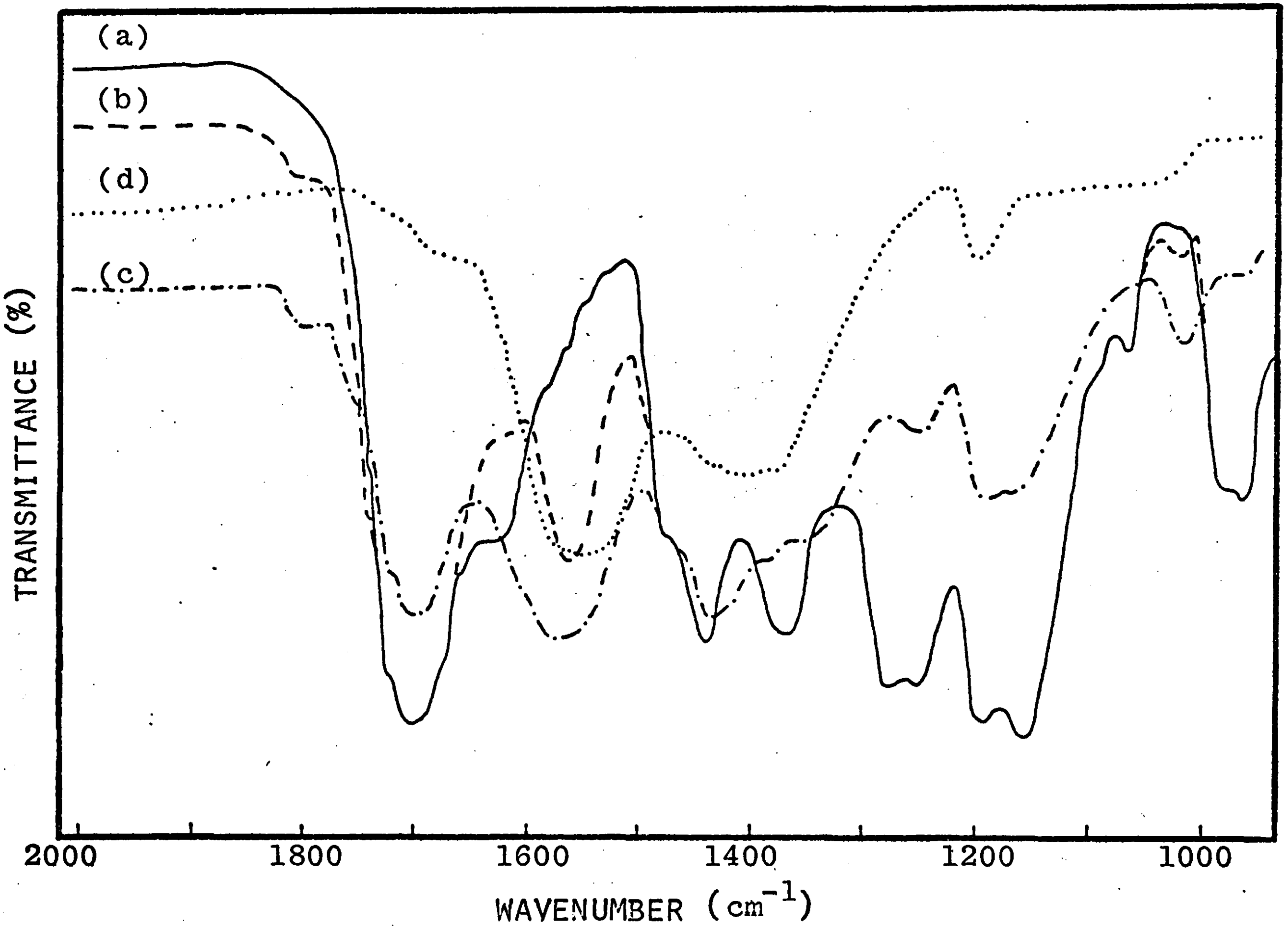


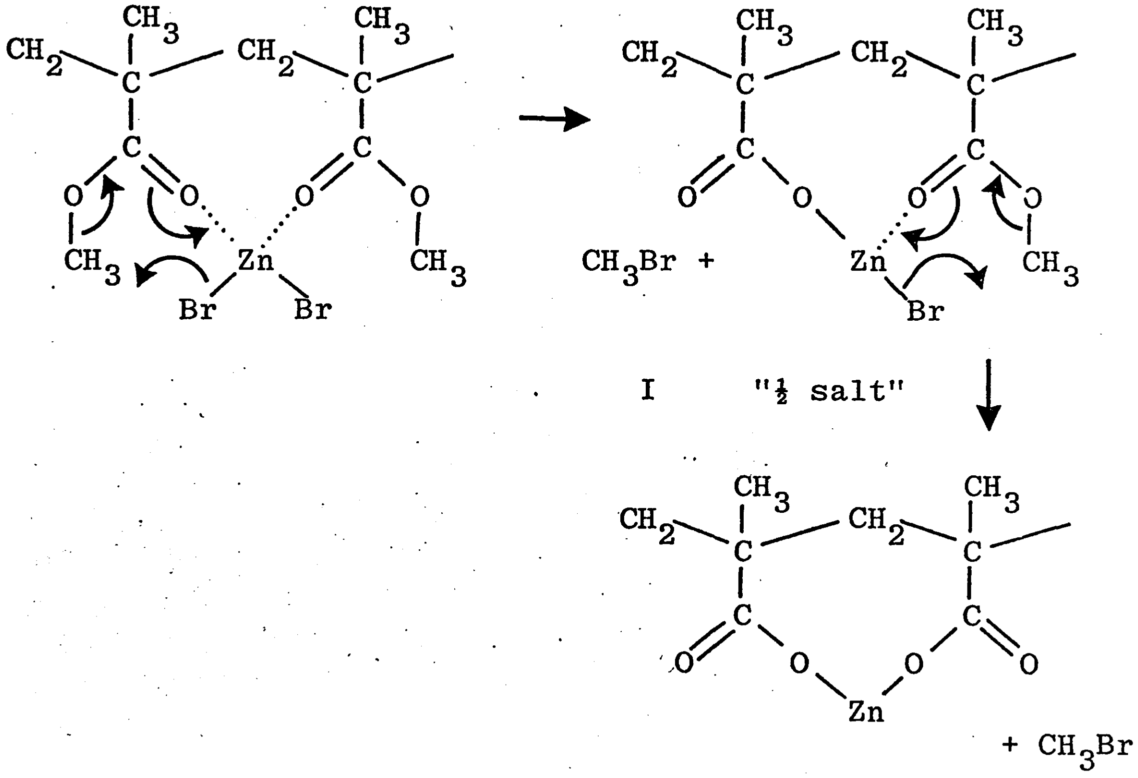
Figure 4.17 IR spectra showing structural changes on heating PMMA(1)/$ZnBr_2$, 2:1 Molar.

as a result of separate complex formations with $ZnBr_2$.

"ORGANIC SALT" FORMATION

Trace (b) shows the spectrum obtained after heating the blend isothermally at 200°C for one hour. The most striking feature is the emergence of an absorption at $1550cm^{-1}$, indicative of the carboxylate group, as previously detected when $ZnBr_2$ was refluxed with the model compound for PMMA..

This could be the result of a reaction between the polymer ester groups and $ZnBr_2$, liberating CH_3Br, to leave zinc methacrylate - type units in the polymer chain.



II "Organic Salt"

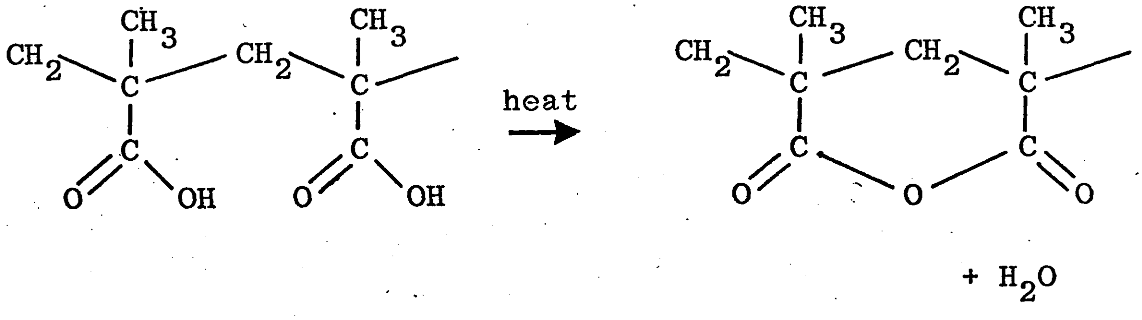
The carboxylate absorption could be produced by either I or II. N.B. Structures of this type are discussed throughout this work, and so, for convenience, ths terms "½ salt" and "organic salt" have been adopted for their description.

This type of structure has also been detected by Khilivitskii et al.[52] who recently studied the degradation of PMMA in the presence of small amounts of $ZnCl_2$.

ANHYDRIDE FORMATION

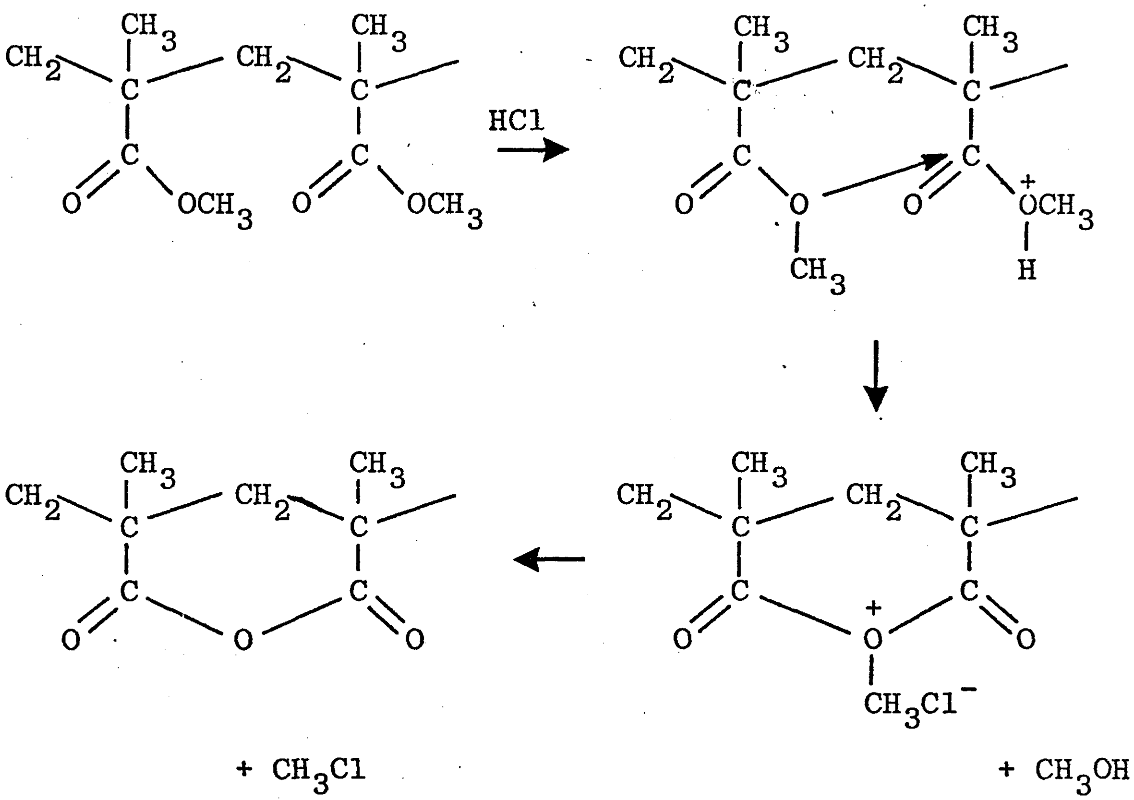
Another feature of spectrum (b) is the appearance of small peaks at 1795cm^{-1} and 1020cm^{-1}, which become more clearly developed in spectrum (c) which shows the blend structure after heating isothermally at 300°C for one hour.

Absorptions of this nature have been attributed, by Grant and Grassie, to six-membered anhydride structures in the polymer chain. These workers showed[53] that methacrylic acid, on heating, is converted to anhydro poly(methacrlyic acid).



The anhydro poly(methacrylic acid) so formed, showed characteristic absorption peaks at 1795 and 1750cm^{-1} (twin carbonyl peaks) and 1022cm^{-1} (C - O - C stretch).

Similar anhydride structures have been detected during studies of degradation of blends involving PMMA e.g. in a study of blends of PVA with PMMA, McNeill and Neil detected absorptions at 1800cm^{-1} and 1020cm^{-1} in IR spectra.[12] They suggested that anhydride structures could be formed as a result of reaction between HCl and PMMA as follows:



The possibility was not discarded, however, that HCl may effect hydrolysis of the polymer ester groups to yield methacrylic acid units, pairs of which can dehydrate to form anhydride structures.

In a study of PMMA/PVA blends,[18] Jamieson also found anhydride structures in the PMMA chain, identified by IR absorptions at $1800cm^{-1}$, $1762cm^{-1}$ (actually only a shoulder) and $1018cm^{-1}$. In this case anhydride production is attributed to the effect of acetic acid on PMMA.

It is interesting to contrast these findings with those of Straiton,[47] who studied MMA-vinyl bromide copolymers, using TVA. IR analysis of the subsequent CRF yielded bands at (i) $1765cm^{-1}$, (ii) $1020cm^{-1}$ and (iii) a shoulder at $1800cm^{-1}$, his interpretation being that these peaks represent γ-lactone (i, ii) and six-membered anhydride structures (ii, iii) respectively.

It is apparent, therefore, that there is great similarity in the IR absorptions of γ-lactone and anhydride structures, since both absorb at around $1020cm^{-1}$, and both also have an absorption around $1760cm^{-1}$.

The main difference is that anhydrides show absorption at $1800cm^{-1}$, which lactones do not possess, and that the peak at $1765cm^{-1}$ is the strongest absorption in the spectrum of a γ-lactone. Thus it is apparent that differentiation would be difficult if both structures were contained within the same polymer chain, probably yielding only broad IR absorptions.

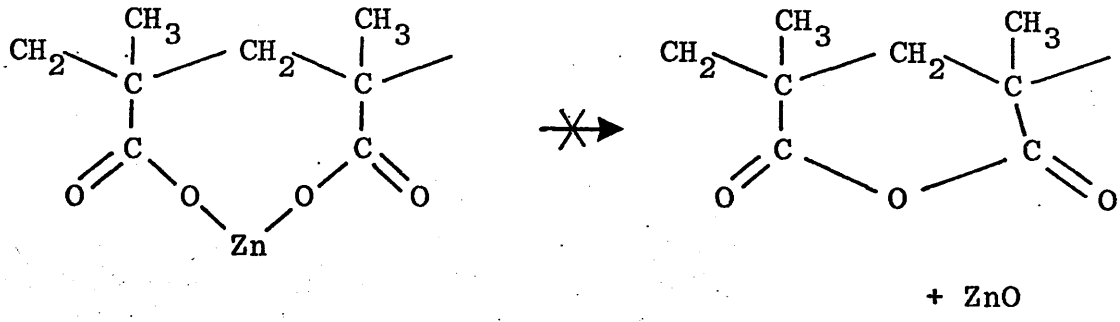
In the case of trace (c) which depicts the PMMA/$ZnBr_2$ blend after heating isothermally at 300°C, peaks at $1795cm^{-1}$ certainly suggest anhydride structures, although the additional presence of γ-lactone structures cannot be ruled out completely.

MECHANISM OF ANHYDRIDE FORMATION

There are two possible routes for anhydride formation in this case, either from decomposition of previously formed zinc methacrylate structures, or by some reaction which completes with "organic salt" formation to form anhydrides by direct combination of adjacent ester groups in the PMMA chain.

The first route is ruled out, on two counts:

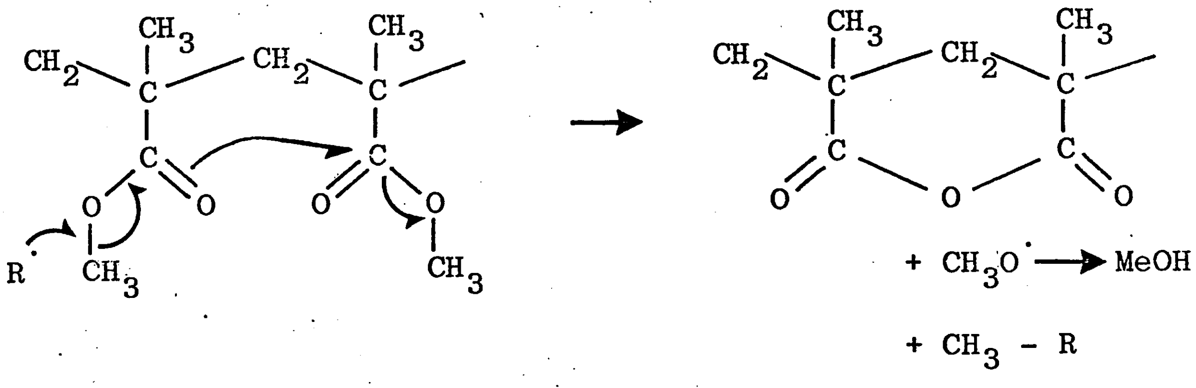
(i) in a study of the thermal degradation of zinc polymethacrylate,[54] Zulfiquar considered the possibility of zinc methacrylate units decomposing to yield anhydride units plus zinc oxide:



Infra-red studies gave no indication of anhydride structures, however, and so decomposition was assumed to follow a different route.

(ii) In the present study, trace (d) in Figure 4.18 represents the PMMA/$ZnBr_2$ blend after it has been heated isothermally at 350°C for one hour. Examination of this spectrum shows that organic salt structures are still present, identified by the absorption at $1550cm^{-1}$, whereas the characteristic anhydride absorptions have disappeared, an indication that the anhydride structures have decomposed. Thus, since anhydrides undergo decomposition before organic salt structures do so, anhydrides cannot be formed as a result of organic salt breakdown.

On this basis, it is likely that anhydride structures are formed in the PMMA chain by some reaction of the type:



where R· could be a radical produced as a result of interaction between PMMA and $ZnBr_2$. One possibility is $CH_3 - O - \underset{\underset{O}{\|}}{C}\cdot$,

since substantial quantities of $CH_3 - O - \underset{\underset{O}{\|}}{C} - CH_3$ have been detected by IR spectroscopy. This type of mechanism also results in production of methanol, another compound the presence of which has been verified by IR spectroscopy.

DECOMPOSITION OF CYCLIC STRUCTURES

Earlier studies of poly(methacrylic acid),[36] and of zinc polymethacrylate,[54] have shown that anhydrides and organic salt structures exhibit comparable thermal stability, in both cases Tmax. for the decomposition reaction occurring between 400°C and 450°C during programmed degradation.

It is surprising, therefore, that in the present work, anhydride structures are found to decompose after isothermal heating at 350°C for one hour, whereas organic salt structures do not disappear completely until they have been heated at 450°C for one hour.

One possible explanation is that the carbonyl groups in anhydride structures may remain co-ordinated to Zn^{2+}. This could result in a general weakening of bonds in the structure, perhaps by some inductive effect, causing decomposition to occur at a relatively low temperature. This argument is in agreement with the results shown in Figure 4.6, P. 65, from which it can be seen that the overall trend in degradation of PMMA/$ZnBr_2$ blends is for reactions to occur at progressively lower temperatures as the $ZnBr_2$ content of the blend is increased.

SUMMARY OF STRUCTURAL CHANGES

On the basis of IR evidence presented in Figure 4.17, it appears that the sequence of events during degradation of a 2:1M blend of PMMA/$ZnBr_2$ is

(i) formation of organic salt

(ii) a competing reaction, whereby anhydrides and organic salt structures are both formed.

(iii) anhydride decomposition

(iv) organic salt decomposition.

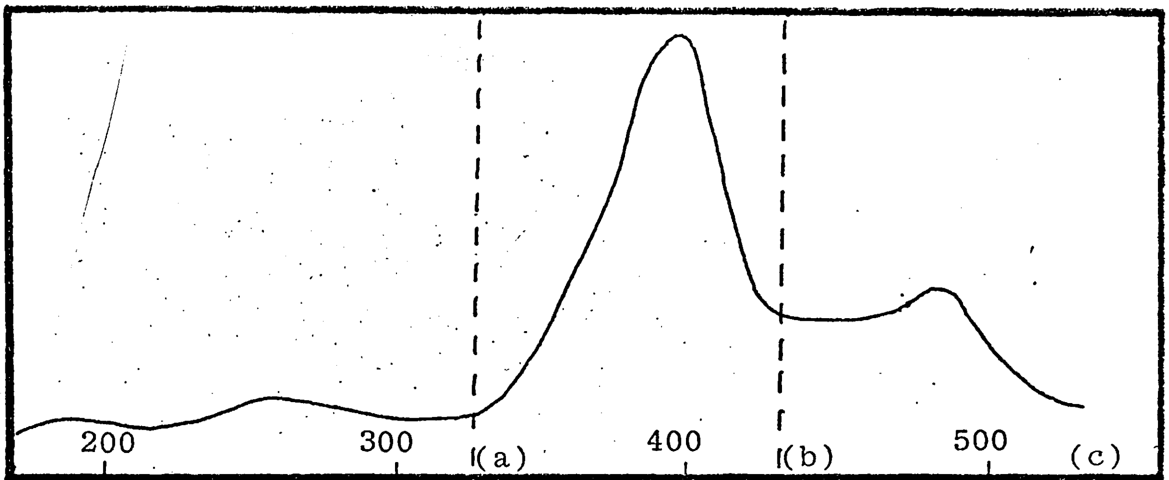
STEPWISE DEGRADATION

The next step was an attempt to identify the volatile products released during particular stages of blend degradation. Since the TVA trace for each of the three blends studied consists of three peaks (Figures 4.3 - 4.5), the approach adopted was to identify the volatile products responsible for each separate peak. This was achieved by heating the particular blend to that temperature, obtained from the appropriate TVA trace, at which Pirani output falls to a minimum before beginning to rise again as soon as a further production of volatiles occurs.

Volatile products were collected, as described previously, for analysis by IR spectroscopy. A sample of the blend residue, at each stage, was also removed for IR analysis (CsI disc).

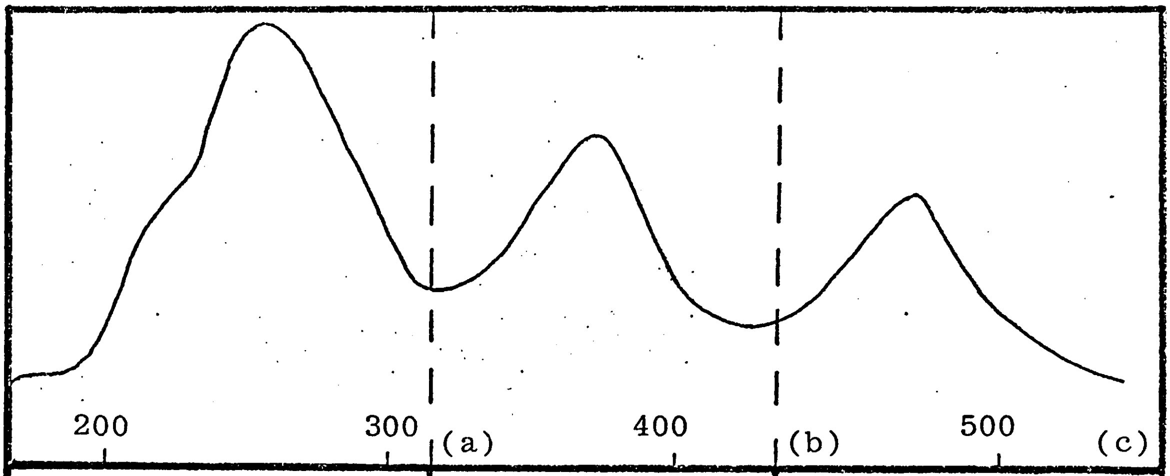
In this way it was possible to ascertain at which stage of the degradation a particular product is formed.

Results for blends 1 , 2 , and 3 are listed in Tables 4-IV, 4-V and 4-VI respectively. In each case, an outline of the TVA trace is included, to show the temperatures at which heating was interrupted, and below this, those products responsible for the particular peak are listed. The exception is residual solvent, (acetone), which, although always released during the first stage of degradation, is omitted from the lists.



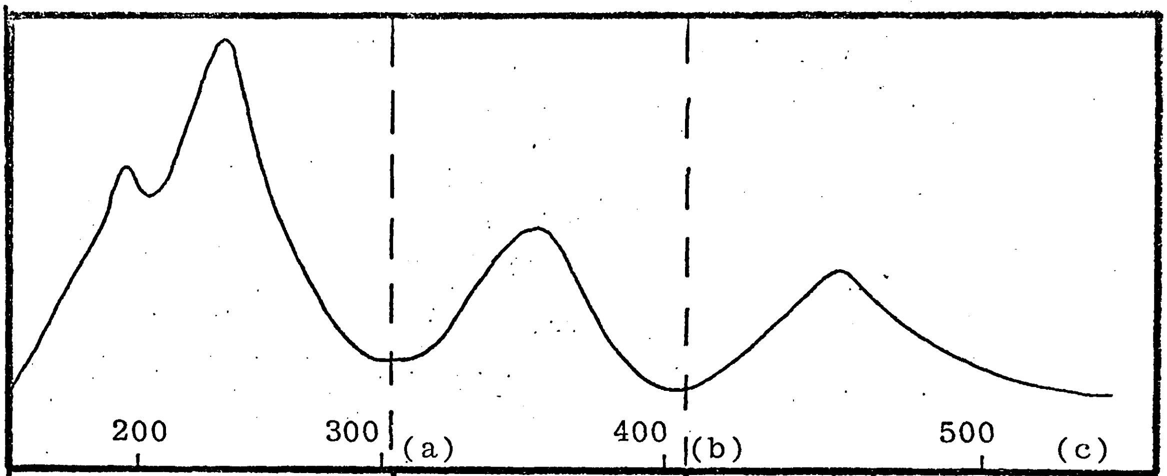
Volatile Products 1	Volatiles 2	Volatiles 3
CO MMA CH_3OH CH_3Br CH_3COOCH_3 CH_3OCH_3	CO CO_2 MMA CH_3OH CH_3Br isobutene butene	CH_4 CO, CO_2 dimethyl ketene isobutene but-1-ene ethylene
Residue at (a)	Residue at (b)	Residue at (c)
organic salt anhydride $ZnBr_2$ ZnO (trace)	organic salt ZnO (trace)	ZnO C Zn

Table 4-IV Products identified, by IR, at each stage in the degradation of blend 1.



Volatile Products 1	Volatiles 2	Volatiles 3
CO CH_3OH CH_3Br CH_3COOCH_3 CH_3OCH_3 MMA (trace)	CH_4 CO CO_2 CH_3OH isobutene but-1-ene	CH_4 CO dimethyl ketene butene (trace) isobutene (trace) ethylene
Residue at (a)	Residue at (b)	Residue at (c)
organic salt anhydride $ZnBr_2$ ZnO (trace)	organic salt ZnO (trace)	ZnO C Zn

Table 4-V Products identified, by IR, at each stage in the degradation of Blend 2.



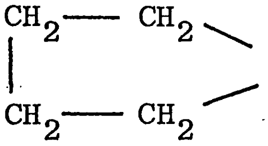
Volatile Products 1	Volatiles 2	Volatiles 3
CO	CH_4	CH_4
CH_3OH	CO	CO
CH_3Br	CO_2	CO_2
CH_3COOCH_3	CH_3OH	dimethyl ketene
CH_3OCH_3	isobutene	isobutene
MMA	but-1-ene	but-1-ene
$HCOOCH_3$ (trace)		ethylene
Residue at (a)	**Residue at (b)**	**Residue at (c)**
organic salt	organic salt	ZnO
anhydride	ZnO (trace)	C
$ZnBr_2$		Zn
ZnO (trace)		

Table 4-VI Products identified, by IR, at each stage in the degradation of Blend 3.

THE EFFECT OF Br· RADICALS ON PMMA

IR studies on blend structure and on volatile products have shown that in the early stages of degradation of a PMMA/$ZnBr_2$ blend, some reaction takes place which results in formation of CH_3Br.

It is known that discrete Br^- ions do not exist in $ZnBr_2$, since the metal - halide bond exhibits considerably less ionic character than that in ZnF_2[51] or $ZnCl_2$, the actual degree of ionic character in the Zn-Br bond being 65%.[55] It was decided, therefore, to investigate the effect of Br· radicals on the degradation of PMMA. A convenient source of Br· radicals is N-Bromo succinimide (NBS),



which is known to effect bromination of many organic compounds by production of Br· radicals following homolytic fission of the almost non-polar N-Br bond.[56]

The study was carried out by degrading, to 500°C, a blend of PMMA/NBS, 1:1 molar, since Zeigler has shown[57] that 50% of the available bromine in NBS is released as Br· by heating at 80°C for one hour. It is established, therefore, that Br· radicals will be produced at sufficiently low temperature to undergo possible reaction with PMMA, prior to the onset of normal polymer degradation.

The TVA trace showing degradation of a PMMA/NBS blend is shown in Figure 4.18, along with the trace for degradation of a similar blend, comprising PMMA/succinimide, 1:1 molar.

Since the blend involving succinimide yields a TVA trace identical to that for PMMA alone, it can be assumed that any effect caused by NBS is a result of Br· radicals, as opposed to later decomposition products of NBS.

In fact, NBS is seen to have only a relatively small effect on the degradation of PMMA, resulting in the emergence of an additional reaction at high temperature, indicated by the appearance of non-condensables. This behaviour is consistent with the occurrence of a modification of the polymer chain, whereby some MMA units are prevented from depolymerising to monomer. These units then decompose at higher temperature to yield CH_3OH and CO, both of which were detected by IR analysis, in this case.

CH_3Br was not detected (nor was any other Br-containing species). On this basis, it appears that in degradations of blends of PMMA/$ZnBr_2$, early production of CH_3Br depends on complex formation between the polymer and the Lewis Acid, since CH_3Br production is not achieved by Br· radicals alone (assuming Br· radicals are produced in this case).

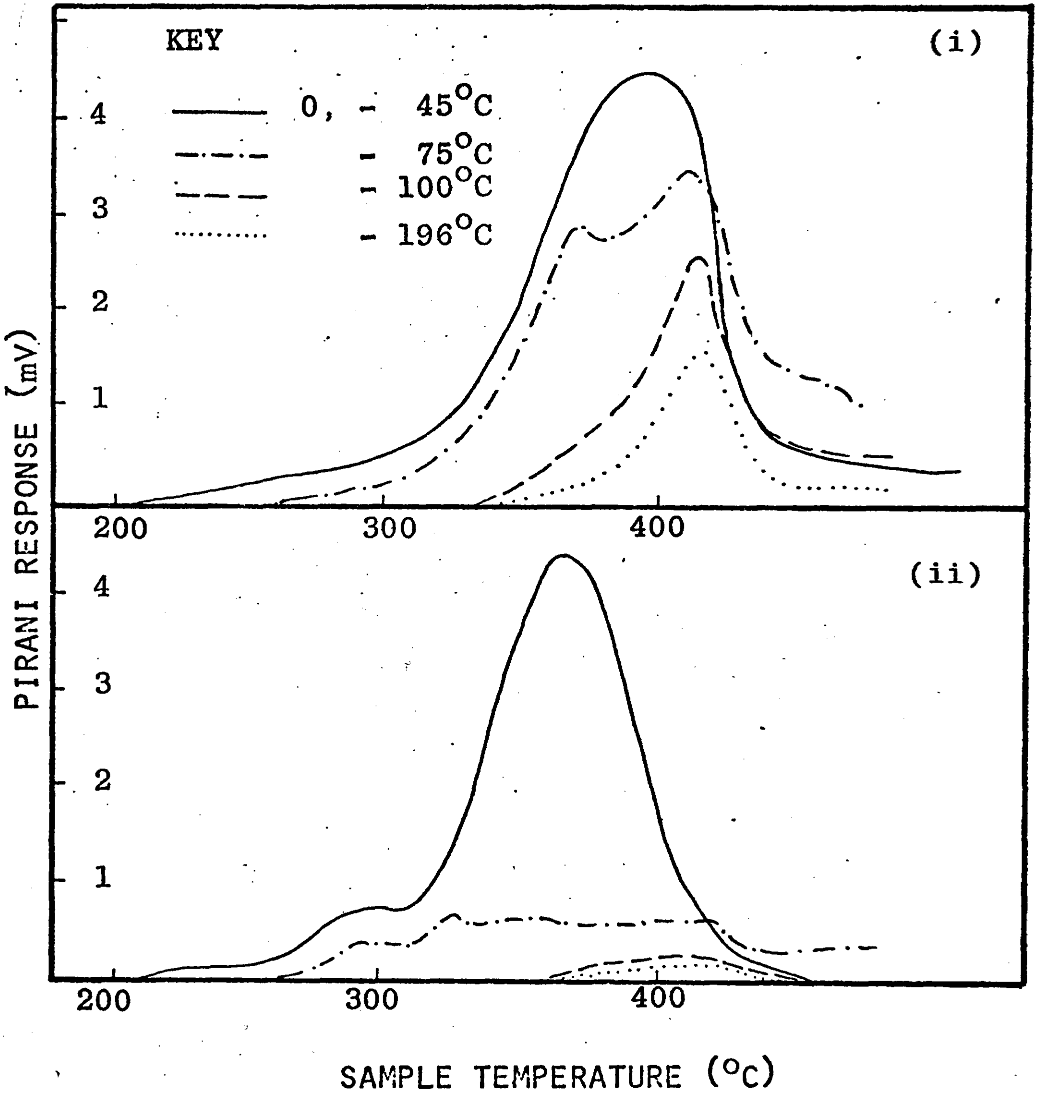
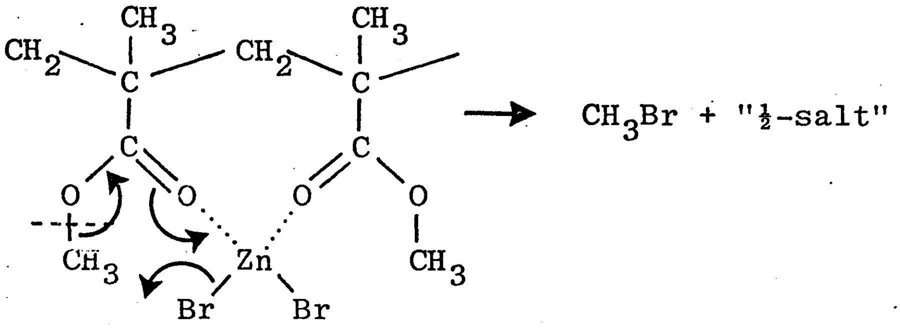


Figure 4.18 (i) TVA trace for PMMA(1)/NBS in the ratio 1:1 molar.

(ii) TVA trace for PMMA(1)/Succinimide, in the ratio 1:1 Molar.

FORMATION OF CH_3Br

The process takes place as follows:



Under normal circumstances, the carbon - oxygen bond is not expected to break and the fact that it does, in this instance, may be explained by a weakening of this C - O bond as a result of donation of electron density from the carbonyl group to Zn^{2+}. CH_3Br can thus be the product of the concerted molecular reaction shown above.

ANALYSIS OF LIQUID PRODUCTS BY GLC

The total liquid products obtained from programmed degradation, to 500°C, of all three blends, each containing 65mg polymer, were analysed using GLC.

Product collection and analysis was as described in Chapter Two, using dioxan as solvent, n-propanol as internal standard, and separation being effected by a column containing 10% ethylene glycol adipate supported on chromosorb P. A trace representing the total liquid products obtained from degradation to 500°C of a sample of blend 2 is given in Figure 4.19.

Identification of the peaks was achieved by injection of reference compounds into the chromatograph, and subsequent comparison of retention times with those of the separated products. The small, early, peaks are believed to correspond to gaseous products, such as CH_3OCH_3, dissolved in the liquid fraction, and the larger peaks are identified in Table 4-VIII.

METHYL ACETATE (MeOAc) DETECTION

One major failing of this set of analysis conditions is the inability to separate acetone from methyl acetate, thus ruling out any possibility of quantitative estimation of the latter. Such an estimation would have been useful, since MeOAc is known, from IR studies, to be produced in the early stages of degradation.

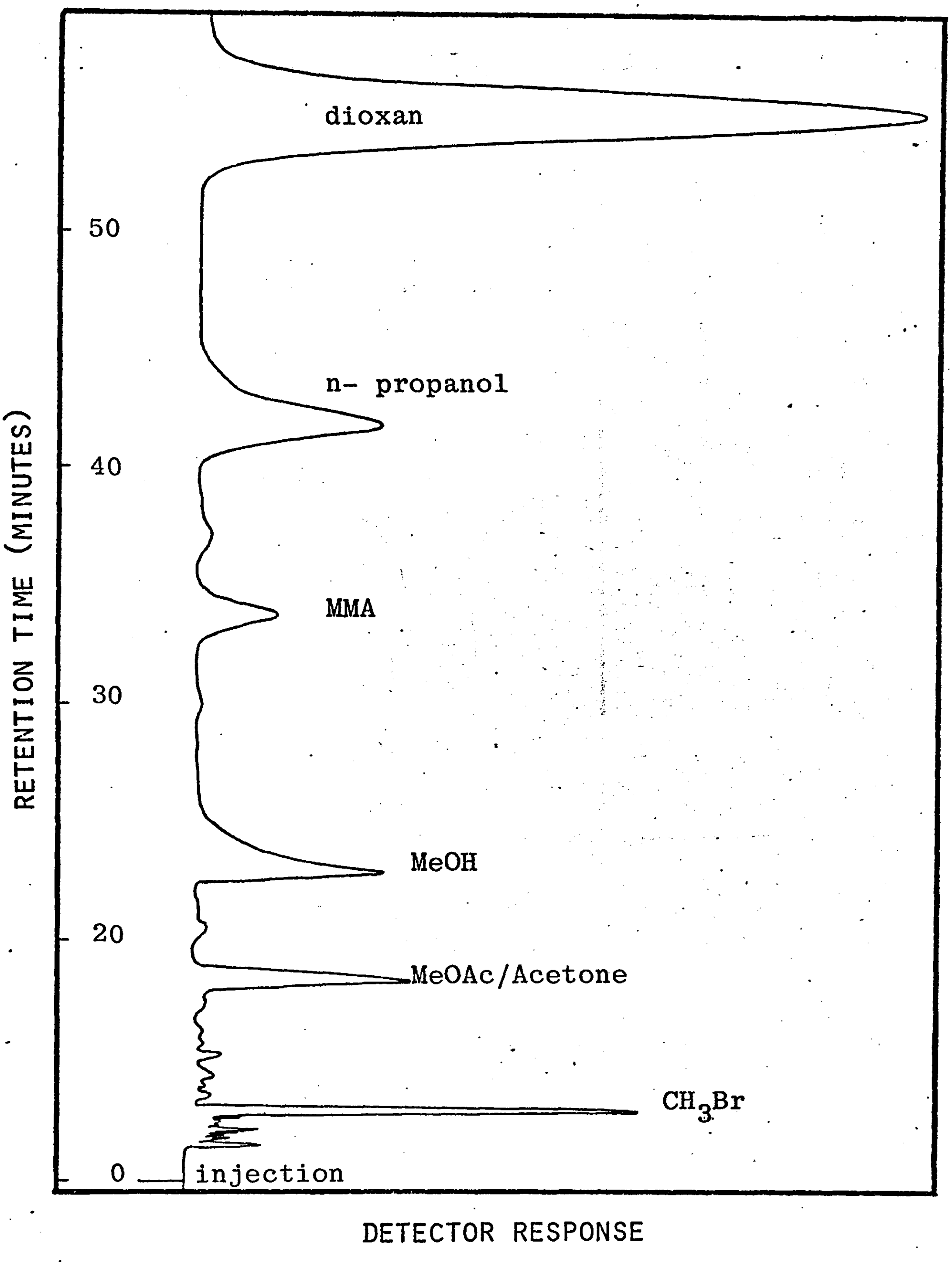


Figure 4.19 GLC analysis of the liquid products from degradation to 500°C of PMMA(1)/ $ZnBr_2$, 2:1 Molar.

Peak No.	Retention Time (minutes)	Compound
1	2.4	methyl bromide
2	5.5	methyl formate
3	8.6	methyl acetate/ acetone
4	13.1	methanol
5	24.1	methyl methacrylate
6	32.25	n- propanol
7	45.4	dioxan
8	68.0	mesityl oxide

Table 4-VII Assignment of peaks from GLC analysis of liquid products from PMMA(1)/$ZnBr_2$, 2:1 Molar.

It was possible, however, to obtain some information on methyl acetate production. Liquid products were injected into a column containing 13½% MEA and 6½% di-2-ethyl hexyl sebacate supported on chromosorb, from which it was shown that when blend 2 is heated isothermally at 180°C for one hour, MeOAc is produced. The relevant trace is shown in Figure 4.20, from which it can be seen that separation is not sufficiently good for quantitative measurement, but is adequate for confirmation of methyl acetate production at this stage in the degradation.

MeOH AND MMA DETECTION

Prior to quantitative measurements of MeOH and MMA produced during degradation, it was necessary to determine at which stage of degradation these products are evolved. The approach adopted was to select a 2:1M blend, heat this thermally at 160°C for one hour, and then analyse the liquid products by GLC. The blend was then heated at 170°C for one hour, the liquid products collected and analysed, and the procedure repeated at 180°C, etc. In this way, the blend was heated isothermally, for periods of one hour, at twenty different temperatures, rising in 10° stages from 100°C - 350°C.

Results showed that MeOH was produced during heating at 180°C and 190°C but was not detected in the products after heating at 200 - 250°C, and larger amounts of MeOH were found after heating at 300°C, the temperature at which MMA is first detected. One interpretation of these data is that

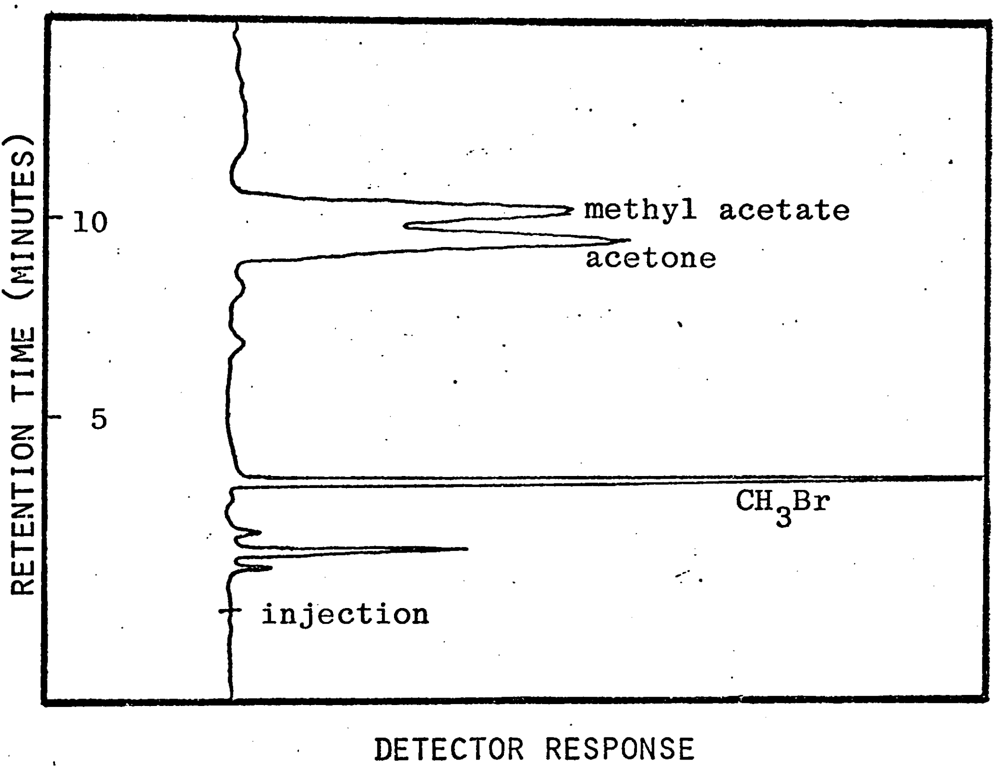


Figure 4.20 GLC analysis of products after heating a 2:1 Molar blend at 180°C for 1 hour.

during degradation of the blend, there are two separate reactions in which MeOH is formed.

It is also possible, however, that MeOH detected at 150°C could be precipitant which had been trapped in the polymer since the sample of PMMA studied had been prepared by precipitation from $CHCl_3$ solution into MeOH. In an attempt to clarify this point, two experiments were conducted:

(i) 65mg of the PMMA(1) sample alone were heated at 180°C for one hour, after which any liquid products collected were dissolved, as before, in dioxan , and injected into the column. MeOH was not detected.

(ii) A 2:1 molar blend of PMMA/$ZnBr_2$, in which the PMMA was taken from a sample which had been precipitated in petroleum ether, and had, therefore, never come into contact with MeOH, was heated at 180°C for one hour. When a solution of the liquid products was injected in the column, MeOH was detected.

On the basis of these findings, it appears that in the course of degradation of the blend, there are two separate reactions which result in MeOH production.

QUANTITATIVE ESTIMATION OF MeOH AND MMA

As before, blends 1 , 2 , and 3 , PMMA:$ZnBr_2$ ratios 11.25:1, 2:1 and 1:1M respectively, were examined. Estimation of MeOH was carried out by:

(i) heating the sample, firstly at 180°C for one hour, then at 210°C for one hour, treatment designed to obtain all the MeOH produced via the first reaction.

(ii) subsequently heating the sample at 300°C for successive periods of one hour, until MeOH production had ceased.

Total MeOH production is shown in Figure 4.21, and MeOH produced at 300°C only, i.e. via the second mechanism, is shown in Figure 4.22. MMA measurements were made at 300°C, and results are shown in Figure 4.23, which includes, for comparison, a curve describing corresponding production of MMA from similar treatment of a sample of PMMA(1) alone.
Note: The results are expressed such that 100 mole% of MeOH, for example, would mean that every unit of MMA in the sample gives rise to one molecule of MeOH.

These results show that the total amount of MeOH evolved increases with increasing content of $ZnBr_2$ in the blend. It can be seen that the first production of MeOH is enhanced by increasing the amount of $ZnBr_2$ present, but production of MeOH from the second reaction is lowest for the 1:1M blend. The importance of these trends will be discussed later.

From Figure 4.23, it is clear that production of MMA falls dramatically as $ZnBr_2$ concentration increases. A possible interpretation of this is that increased $ZnBr_2$ results in increased cyclisation reactions involving adjacent MMA units, which in turn "block" depolymerisation to MMA.

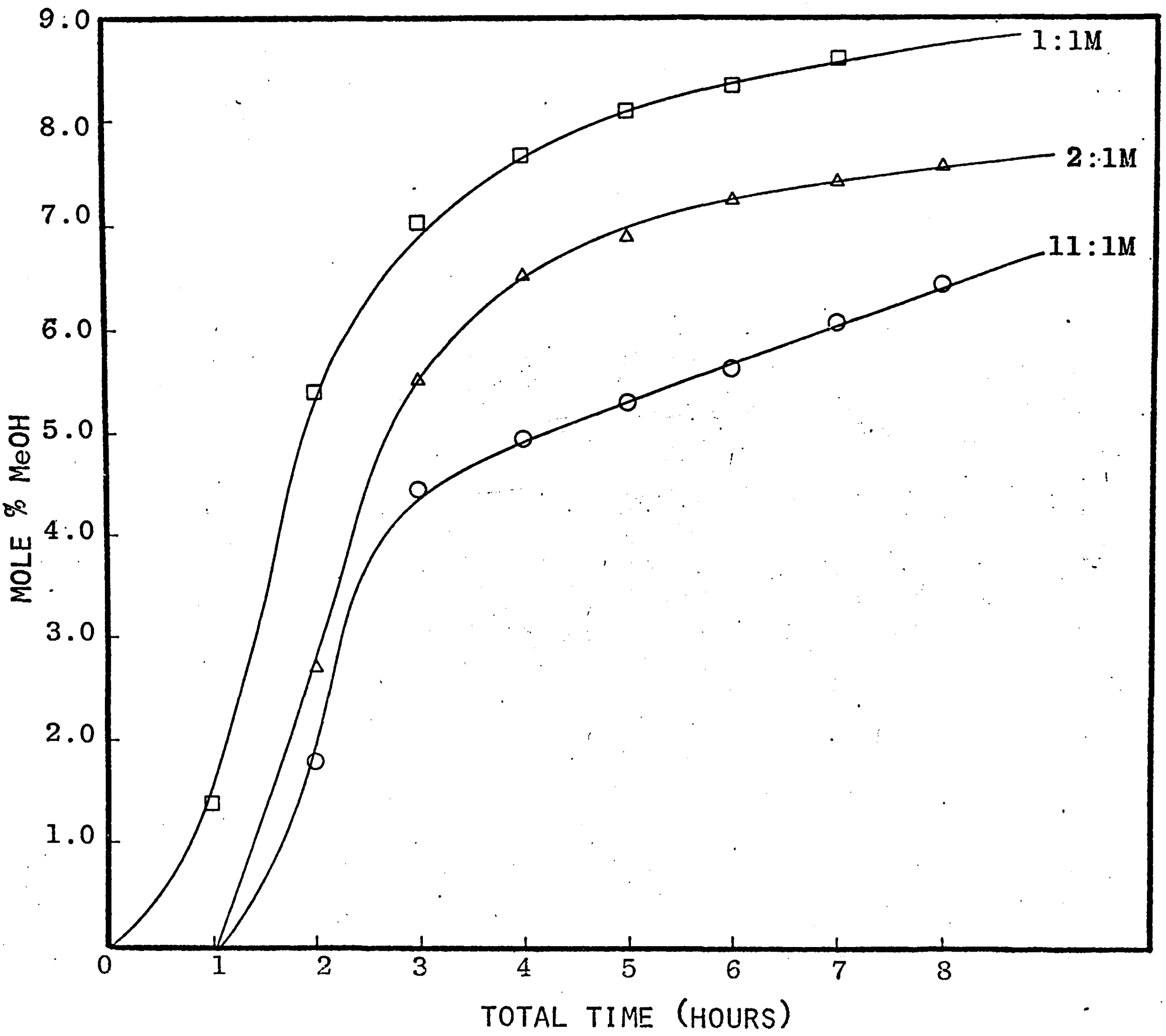


Figure 4.21 Total MeOH production after heating a blend of PMMA/$ZnBr_2$ (2:1M) for 1 hour at 180°C, 1 hour at 210°C and then at 300°C.

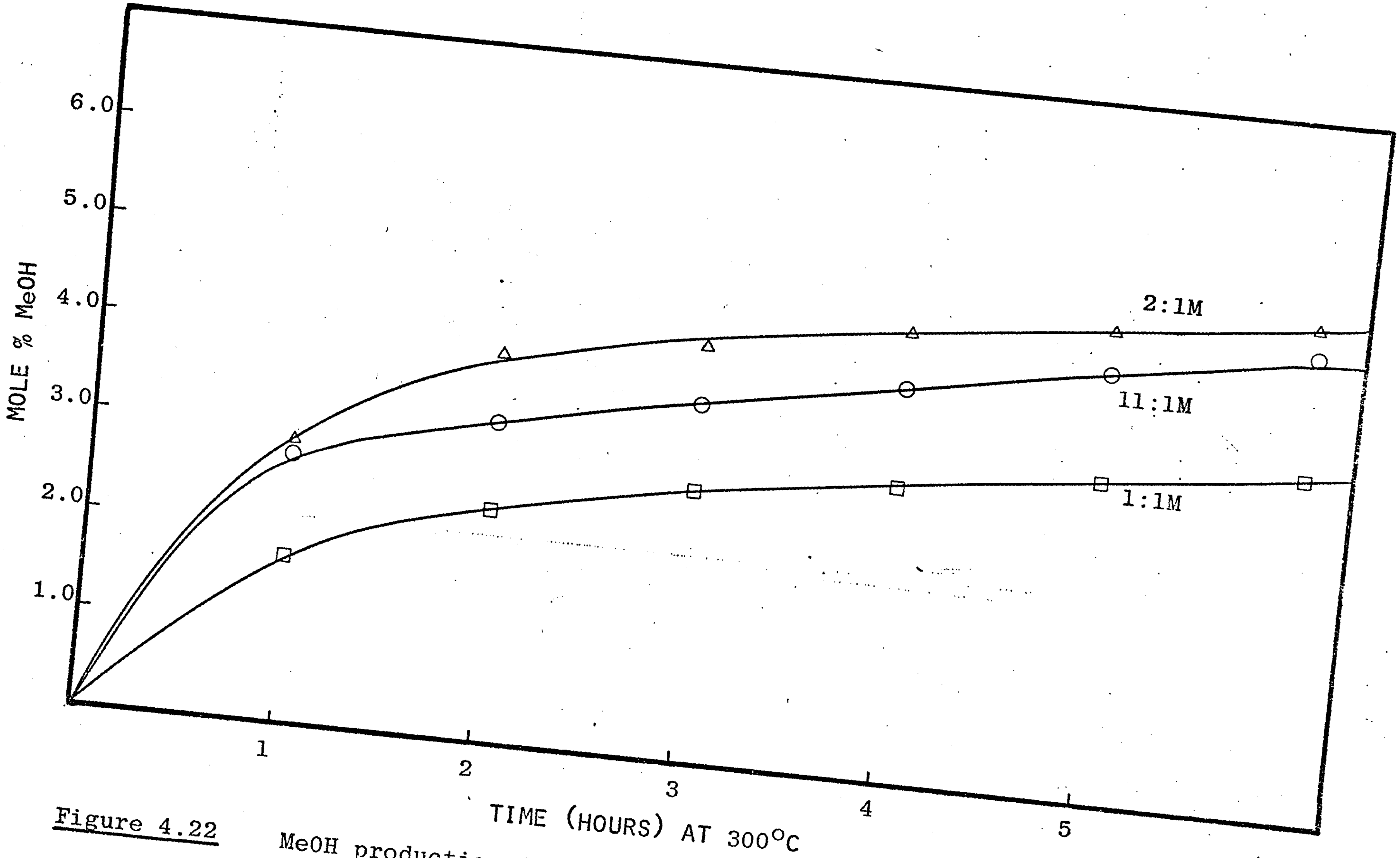


Figure 4.22 MeOH production from heating a blend of PMMA/$ZnBr_2$(2:1M) at 300°C.

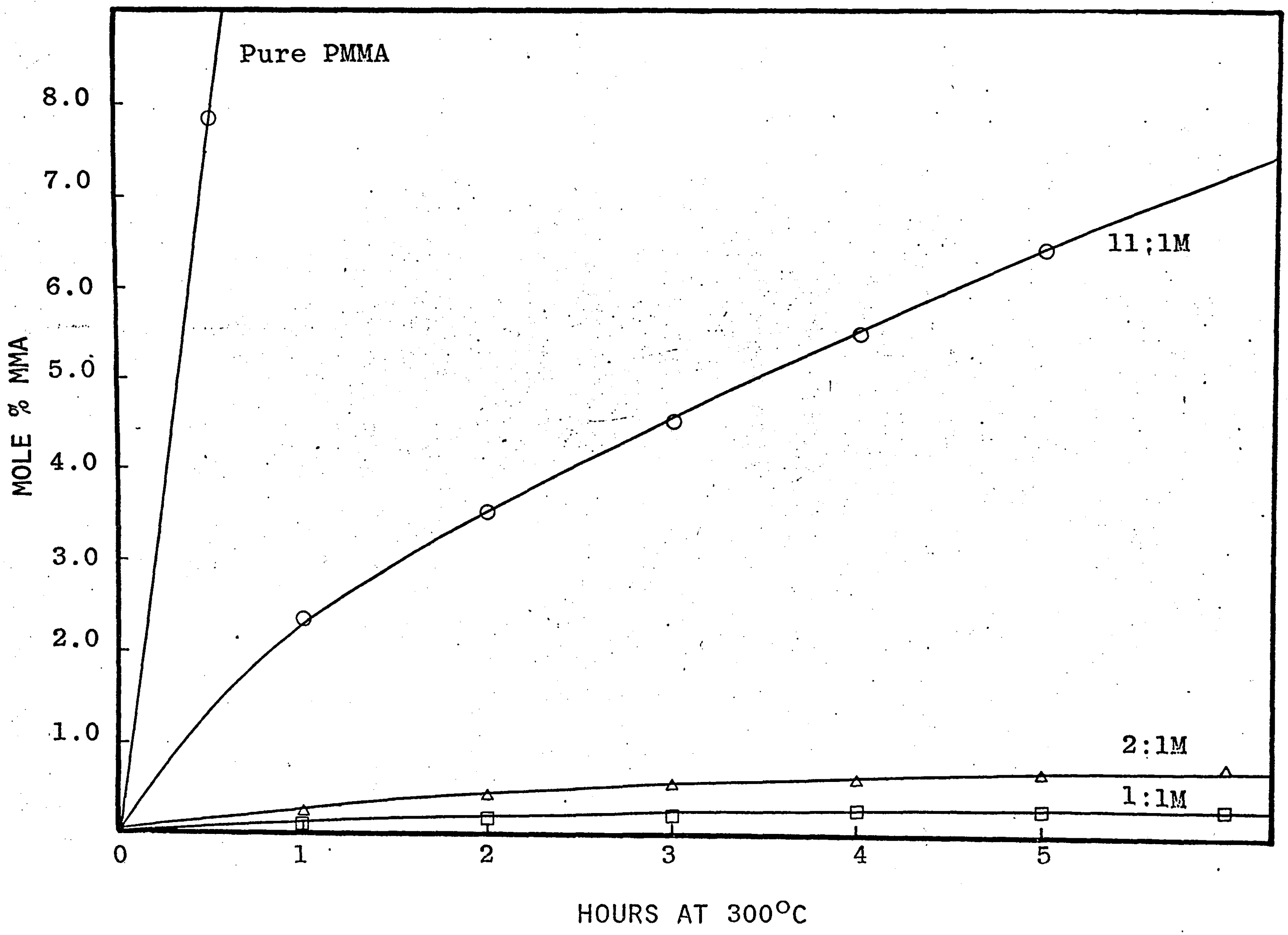


Figure 4.23 MMA produced from heating, at 300°C, a blend of PMMA/$ZnBr_2$, 2:1M.

QUANTITATIVE ESTIMATION OF CH_3Br

Although CH_3Br was detected qualitatively by GLC, quantitative measurements could not be made by the technique used for MeOH and MMA since CH_3Br, Boiling Point 4°C, is a gas at room temperature. For this reason, quantitative measurements were made by IR spectroscopy, as described in Chapter Two. As explained previously, in IR spectra of the total volatile products from degradations of all three blends, methyl bromide may be identified by its characteristic absorption at $1305cm^{-1}$ (Figure 4.8, P.69). Quantitative measurements cannot be made, however, since absorptions due to the presence of other products overlap with those of CH_3Br.

MEASURMENT TECHNIQUE

If the total products collected are subjected to sub-ambient TVA, however, a separation is effected (Figure 4.10, P. 73), whereby methyl bromide can be isolated by collection of fraction 3 only. This knowledge was used to establish a technique for the estimation of CH_3Br.

The process consisted of:

(i) heating the blend under normal conditions of TVA, followed by collection of the condensable products in a liquid nitrogen trap.

(ii) distillation of these products into a benzene trap at -196°C, followed by separation using the sub-ambient TVA technique.

(iii) collection of the CH_3Br fraction only, in a liquid nitrogen trap.

(iv) distillation of the CH_3Br into an IR gas-cell, of known volume, which was then removed for analysis by IR.
A sample spectrum, of CH_3Br produced by heating a 1:1 molar blend at 180°C for one hour, is shown in Figure 4.24. This is identical to a reference spectrum of CH_3Br, and as a result, quantitative estimations were carried out, using optical density measurements made on the peak at $1316cm^{-1}$.

In this way, production of CH_3Br from the three blends was studied.

ISOTHERMAL MEASUREMENTS

The blends were initially heated at 160°C for several one-hour periods, when it was found that CH_3Br production appeared to reach a maximum, and then cease (Figure 4.25). The blends were then heated at 300°C, whereupon another large production of CH_3Br was detected (Figure 4.26), indicating that there are also two separate reactions for CH_3Br production during degradation. The fact that almost all the CH_3Br produced from the second reaction is obtained after the first hour at 300°C suggests that the reaction actually occurs at some lower temperature.

From the graphs shown, it can be seen that:

(i) for the 11.25:1M blend, the second production of CH_3Br is much larger than the first.

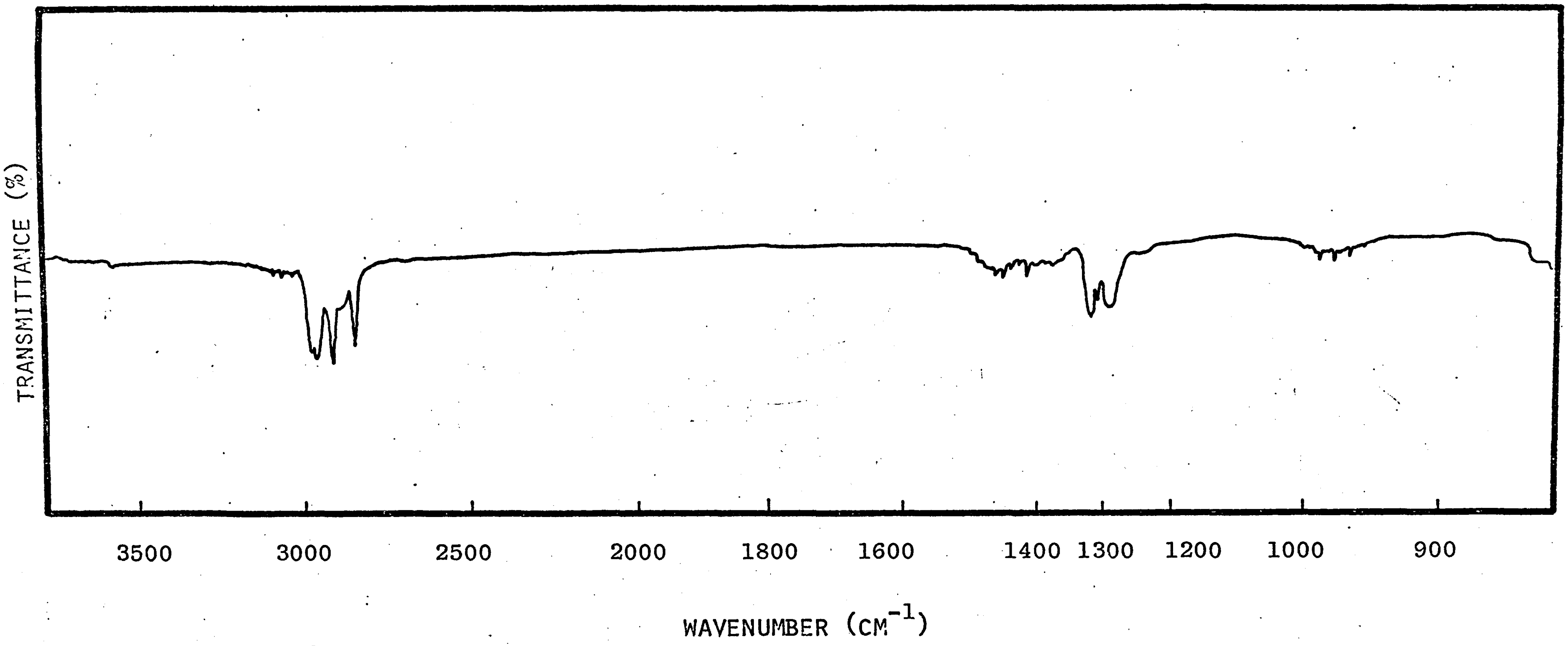


Figure 4.24 . IR spectrum obtained from CH_3Br produced on heating a PMMA/$ZnBr_2$ blend, 1:1M at 180°C for 1 hour. CH_3Br was isolated using sub-ambient TVA.

(ii) on increasing the $ZnBr_2$ content, to give a 2:1M blend, CH_3Br figures for the first and second reactions are similar, and

(iii) when the $ZnBr_2$ content is increased further, to a 1:1M blend, the first production of CH_3Br now exceeds the second.

These figures and trends will now be discussed, in conjuction with all of the results previously listed, with the aim of formulating a possible reaction mechanism.

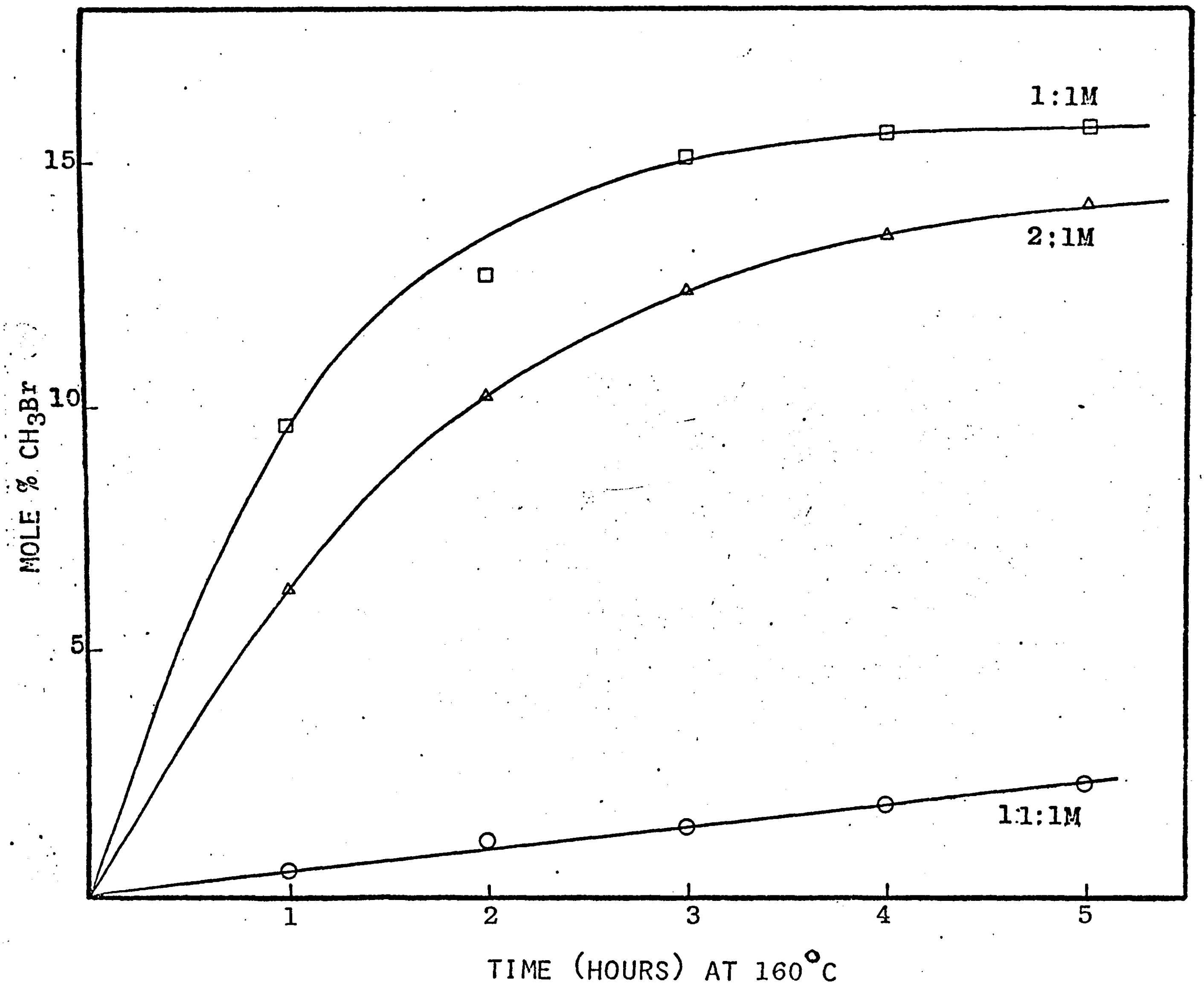


Figure 4.25 CH_3Br production on heating PMMA/$ZnBr_2$ blends at 160°C.

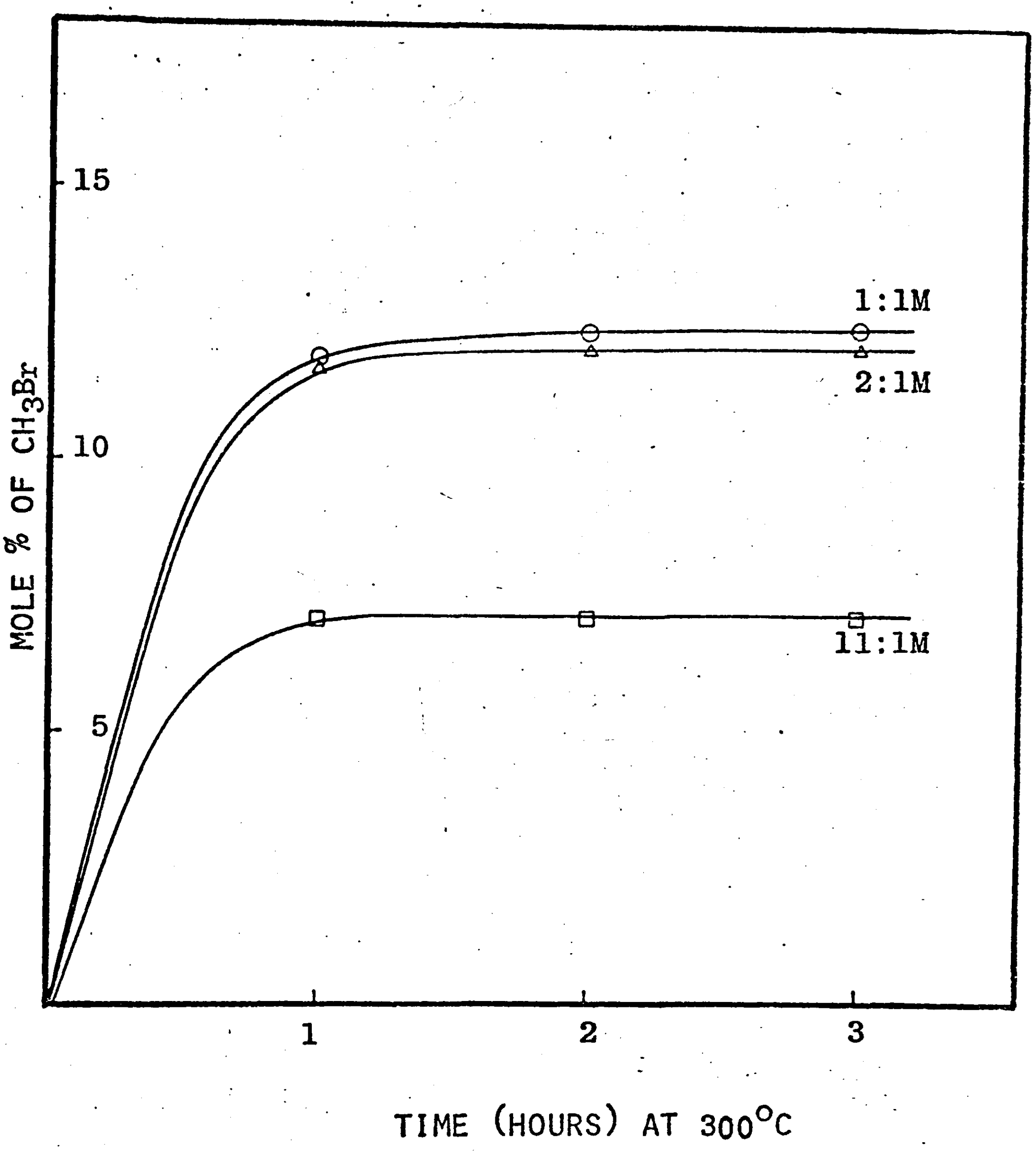
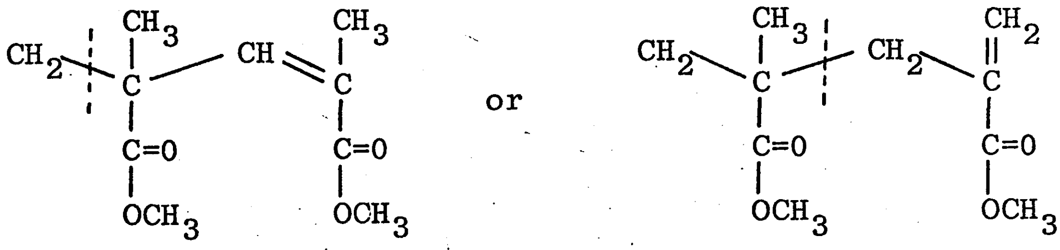


Figure 4.26 CH_3Br produced on heating PMMA/ $ZnBr_2$ blends at 300°C (after previous heating at 160°C).

INTERPRETATION OF RESULTS AND DISCUSSION

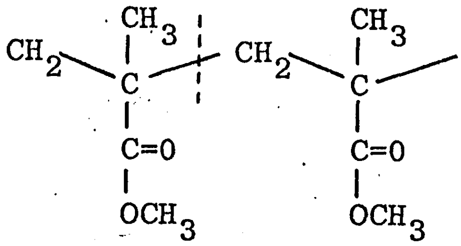
In the broadest terms, the results obtained show that the effect of $ZnBr_2$ on PMMA degradation is, through the formation of a co-ordination complex, to weaken bonds in the MMA unit which would not normally be expected to break.

Grassie and Melville[40] have shown that in the degradation of PMMA alone, the first bond to break is the C - C bond shown below.

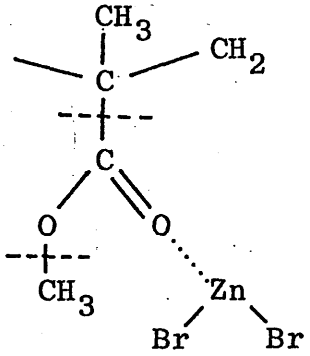


One reason for this is that these are weakened due to the fact that the allylic radicals formed by their scission are resonance stabilized.

Grassie and Melville also showed that when unsaturated chain-end structures have been eliminated, the bond most likely to break during a random scission process is a C - C bond in the polymer backbone.



In the presence of $ZnBr_2$, however, donation of electron density from the carbonyl group of MMA to Zn^{2+} causes an inductive effect which weakens the bonds shown, allowing the possibility of these breaking before the onset of depolymerization.



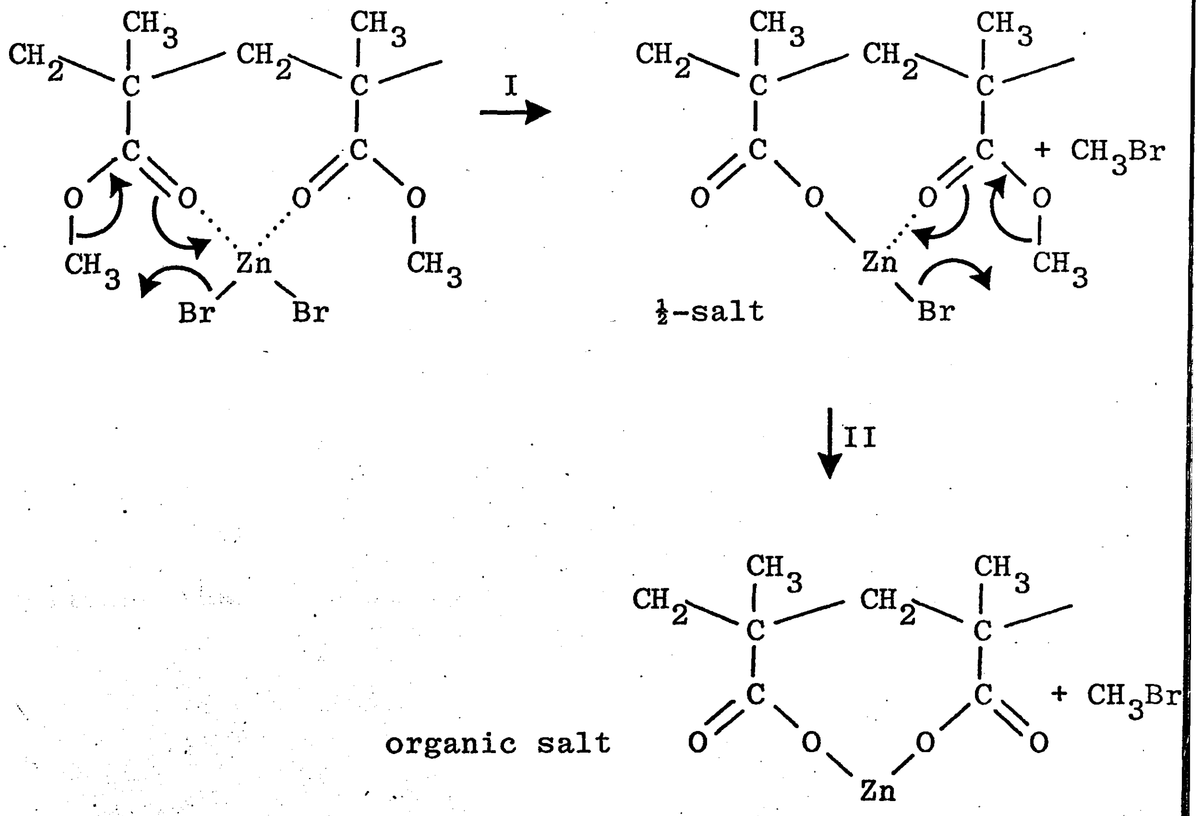
As a result, substituent reactions occur, to produce cyclic structures which have been shown to block "unzipping" to monomer.

The degradation mechanism of PMMA/$ZnBr_2$ blends consists, essentially, of three stages.

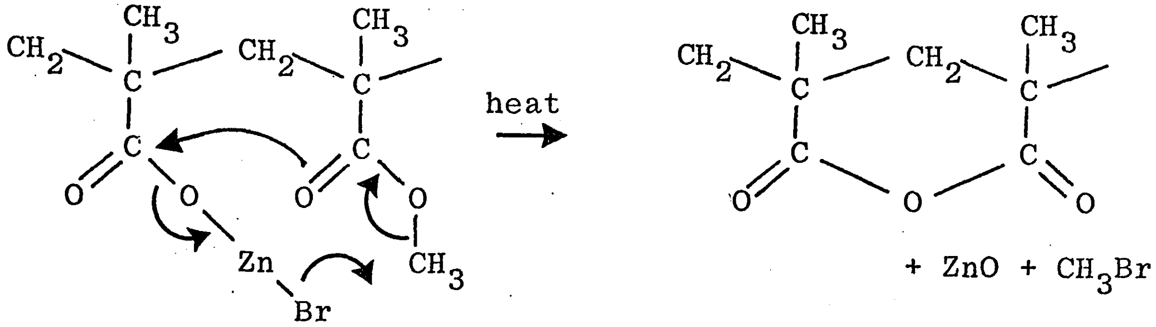
STAGE ONE

The first stage, responsible for the first peak in the TVA traces, is by far the most complex, consisting of a number of competing reactions which result in formation of organic salt and anhydride structures in the polymer chain, in addition to the production of some non-condensable materials.

It appears that the first process to occur is production of a "½-salt" structure, liberating CH_3Br. As the temperature is raised, this ½-salt then liberates another molecule of CH_3Br to form a cyclic organic salt structure, i.e.



The two reactions shown are thought to be the two separate productions of CH_3Br mentioned previously. There is the added possibility that the ½-salt structure could yield an anhydride structure, producing zinc oxide in addition to methyl bromide:



However, since only trace amounts of ZnO could be detected in the blends at relatively low temperatures, it is felt that although this reaction perhaps occurs to a slight extent, it is of no great importance in the general reaction scheme.

CH_3Br PRODUCTION

If the reaction scheme: complex → ½-salt → organic salt is correct, then, in theory, the yield of CH_3Br from reaction I should be equal to the yield of CH_3Br from reaction II.

From the curves shown in Figures 4.25 and 4.26, it is established that this is approximately true of the 2:1M blend.

In the case of the 11.25:1M blend, however, it appears that the amount of CH_3Br produced in the second reaction is much greater than the amount produced in the first reaction. There is an explanation for this, however.

In the cases of all the blends before heating, there will be competition between acetone and polymer to act as ligands to Zn^{2+}, resulting in the setting up of an equilibrium between two complexes i.e.

$$\begin{array}{ccc} \mathrm{ZnBr_2} + \mathrm{PMMA} & \rightleftharpoons & \text{complex} \\ + & & \\ \mathrm{CH_3COCH_3} & & \\ \upharpoonleft\!\downharpoonright & & \\ \text{complex} & & \end{array}$$

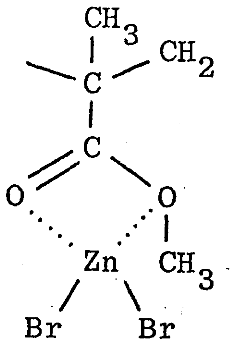
As the blends are heated isothermally at 160°C, acetone is steadily removed, and the equilibrium moves towards a polymer-salt complex. However, at this temperature, the polymer-salt complex undergoes chemical reaction to form a ½-salt structure, liberating one molecule of CH_3Br.

The reason for the apparently small mole % figure for CH_3Br produced during the first reaction in blend 1 may be that the amount of acetone still remaining is sufficient to complex a relatively large proportion of the available $ZnBr_2$. This means that only a small proportion of the available $ZnBr_2$ is in the form of a polymer-salt complex. As the blend is heated, any PMMA/$ZnBr_2$ complex present does react to form the ½-salt structure, and as acetone is removed equilibrium moves towards the PMMA - $ZnBr_2$ complex. There is therefore a slow but continuous production of CH_3Br, in agreement with experimental results which show CH_3Br production to continue to rise slowly. Thus, in this case, CH_3Br production is incomplete after six hours at 160°C, and the large percentage of CH_3Br obtained when this blend was heated at 300°C is actually composed of the remainder of CH_3Br produced from reaction I, and the total CH_3Br produced from reaction II.

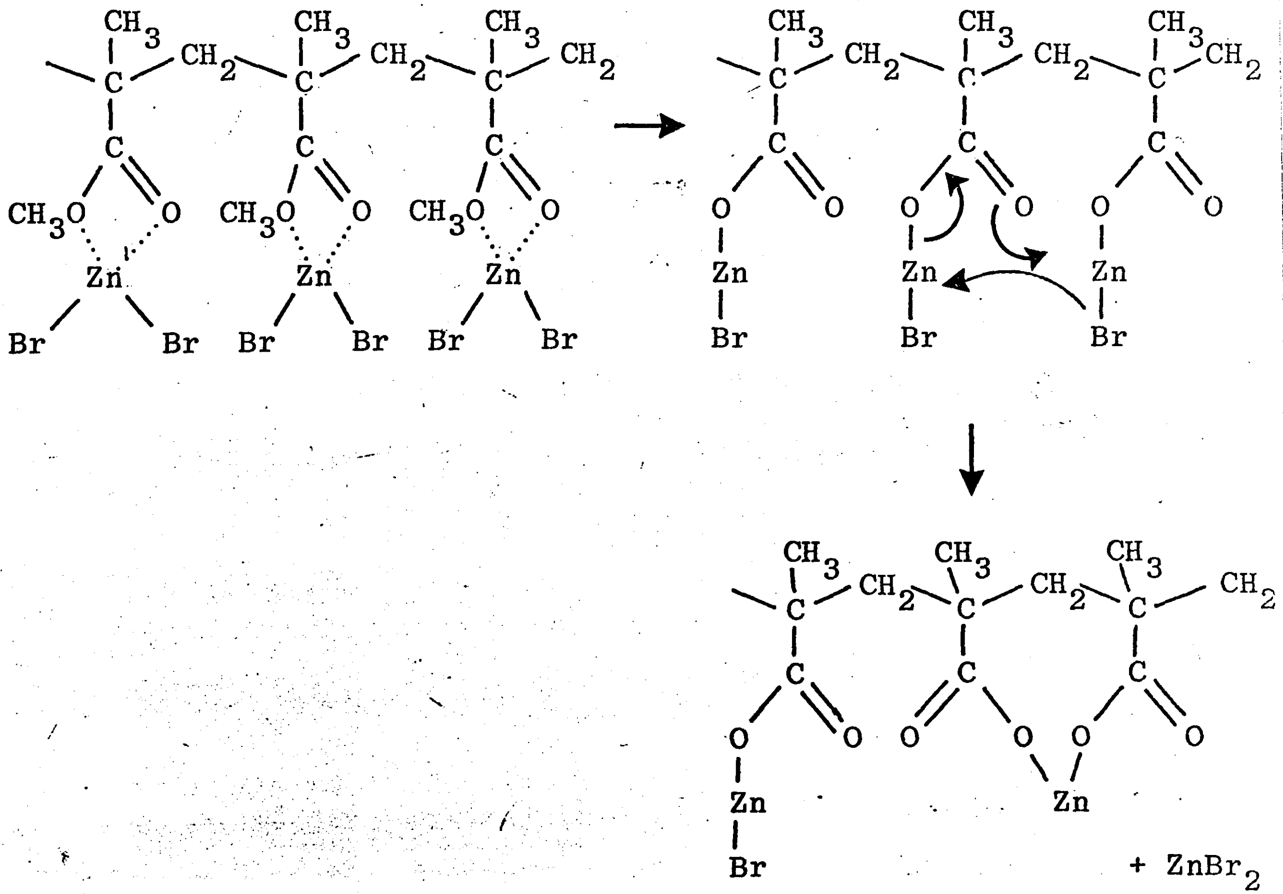
As the amount of $ZnBr_2$ in the blend is increased, there will still be an equilibrium between two complexes. The amount of residual acetone after film preparation will not increase in proportion to $ZnBr_2$ content, however, and so in blends 2 and 3, the fraction of $ZnBr_2$ complexed to acetone is small compared with the fraction complexed to PMMA.

In the case of the 1:1 Molar blend, the amount of CH_3Br produced from reaction I is almost double the amount produced in reaction II. This indicates that not all the ½-salt structures, formed by liberating one molecule of CH_3Br, then liberate a second CH_3Br molecule during organic salt formation.

Since there are, in this blend, an equal number of $ZnBr_2$ molecules and PMMA ester units, it is possible that rather than two carbonyl oxygens from adjacent MMA units complexing with one Zn^{2+}, each ester group acts as a bidentate ligand. This would involve a complex, whose geometry could remain pseudo-tetrahedral, where the ligands to Zn^{2+} are the ether oxygen and carbonyl oxygen of the same ester group, i.e.



A series of such structures along the polymer chain could result in a series of adjacent ½-salt structures:



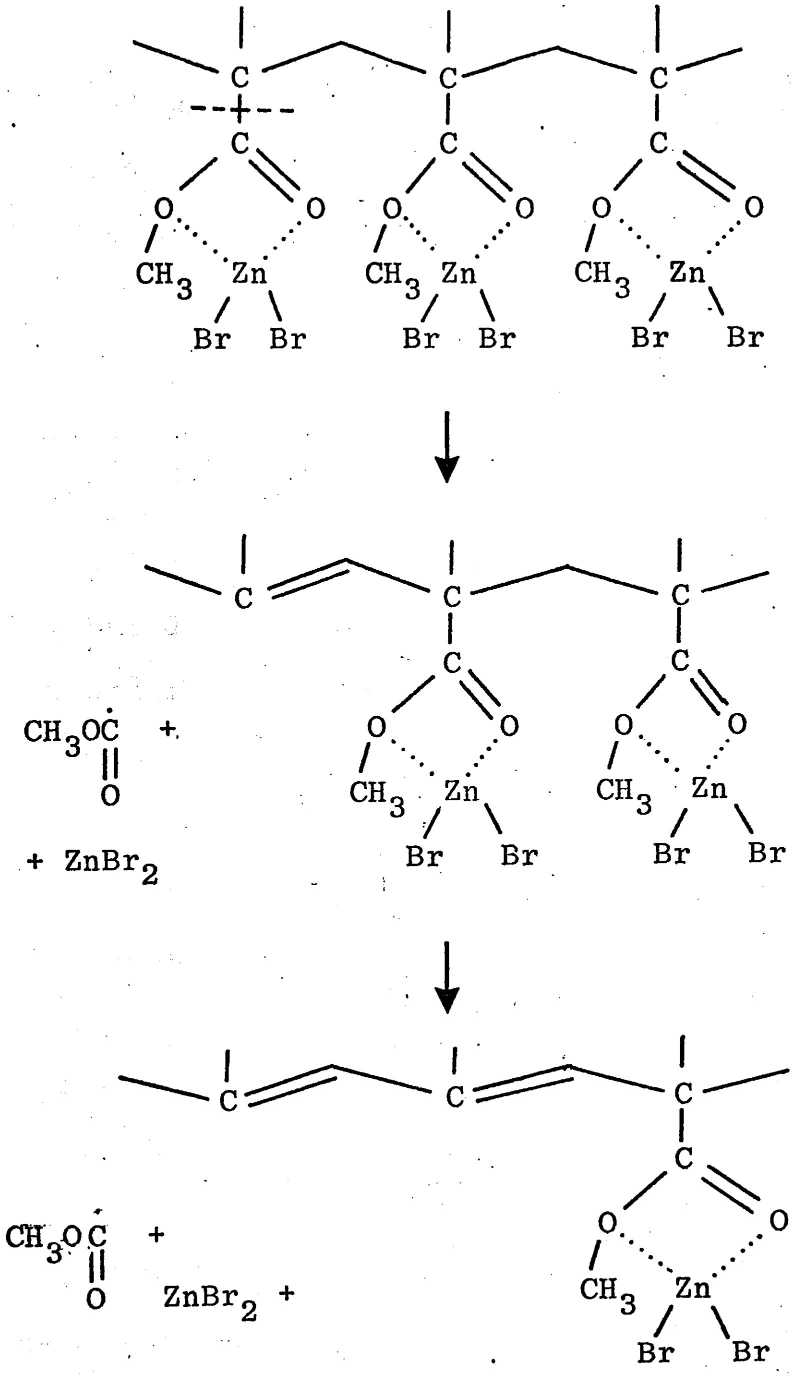
Cyclisation could then take place as shown, liberating not CH_3Br, but $ZnBr_2$ which could later sublime. The "driving - force" for such a reaction would be the stability associated with the cyclic structure.

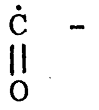
EARLY NON-CONDENSABLES

TVA traces have shown that production of non-condensables in the first peak increases markedly as the $ZnBr_2$ content of the blend is increased. These products have been identified, by IR analysis, as carbon monoxide, and are thought to arise from regions of the polymer chain where each $ZnBr_2$ molecule is complexed to only one ester group.

Such regions will obviously be most prevalent in the 1:1M blend, and will be rare in the 11.25:1M blend, and this is in agreement with observed production of non-condensables in TVA traces for the different blends.

In such equimolar regions, in competition with possible cyclisation mechanisms, it is thought that there is successive scission of C - C bonds, as shown, with H abstraction leading to C = C formation:

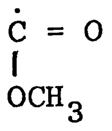

CH3OC + ZnBr2
CH3OC + ZnBr2 +

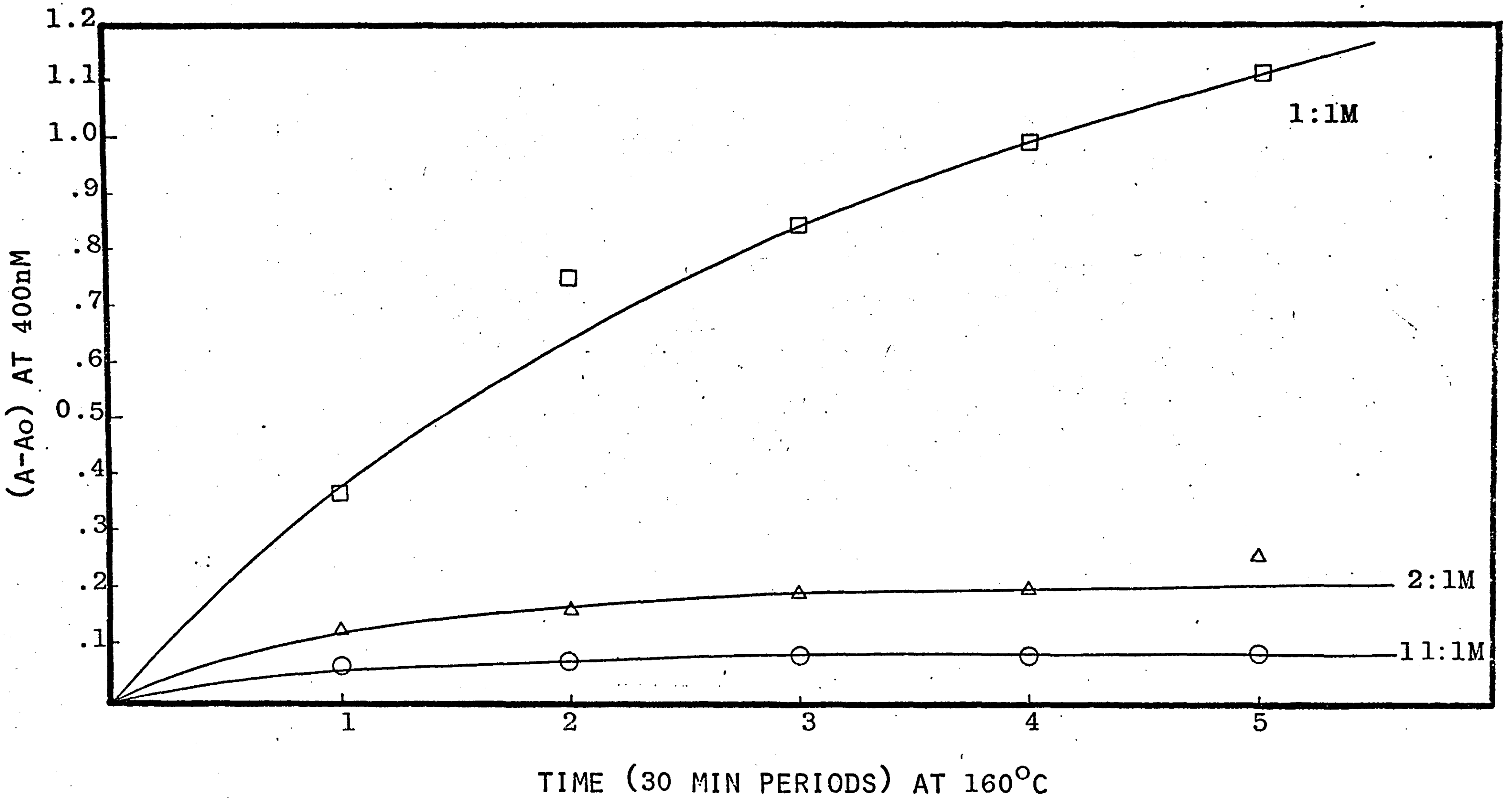

$\dot{C}(=O)-OCH_3$ radicals released can decompose to form

$$CO + CH_3O^{\bullet} \longrightarrow CH_3OH$$

The fact that quantitative measurements of MeOH show that MeOH produced below 200°C is largest for largest $ZnBr_2$ concentration supports this theory, and the above process is thought to constitute the first reaction producing methanol.

An additional source of information to support this mechanism is a study, by UV spectroscopy of the three blends. It was felt that if the above process does take place, there must be a build up of conjugated double bonds in the polymer backbone, and in order to investigate this hypothesis, each blend in turn was heated isothermally at 160°C for one-hour periods, and then subjected to study by UV. Results are given in Figure 4.27, a plot which shows absorption at a chosen wavelength vs. time.

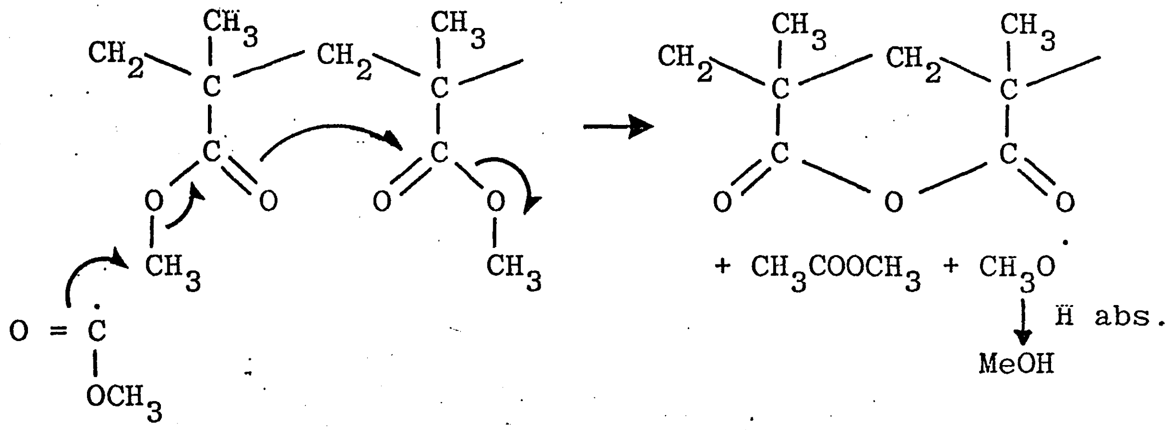
It can be seen that at this low temperature, there is a build-up in absorption at 400nm, greatest for blend 3 , smaller for blend 2 and almost non-existent for blend 1 . This is in agreement with the mechanism proposed, and proves that any  $\dot{C}(OCH_3)=O$ radicals produced at this stage do not come from MMA units trapped between cyclic structures, since absorption at 400nm is characteristic of seven C = C bonds in conjugated sequence.



<u>Figure 4.27</u> PMMA/$ZnBr_2$ blends heated at 160°C. Build up in conjugation is shown by absorption at 400nm

METHYL ACETATE PRODUCTION

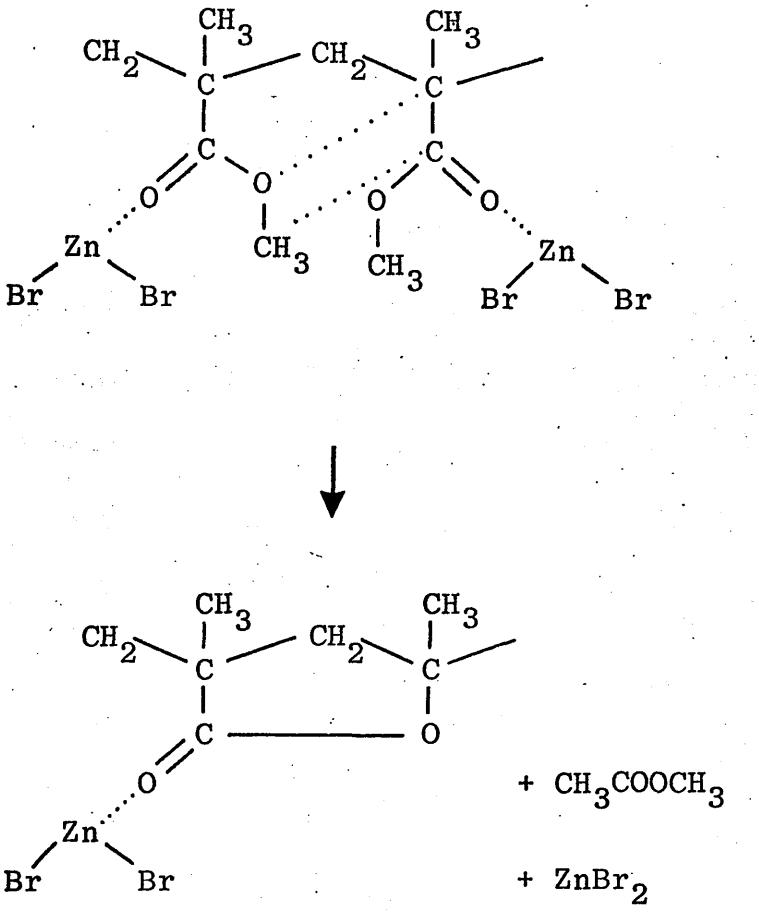
In addition to production of CO and MeOH, $\underset{\underset{O}{\|}}{\dot{C}} - OCH_3$ radicals can also give rise to anhydride structures, as previously detected in the polymer chain i.e.



The evidence for this process is identification, by IR analysis and GLC, of substantial quantities of methyl acetate in the products during the early stages of degradation, and the occurrence of anhydride residues in the polymer chain, detected by IR spectroscopy.

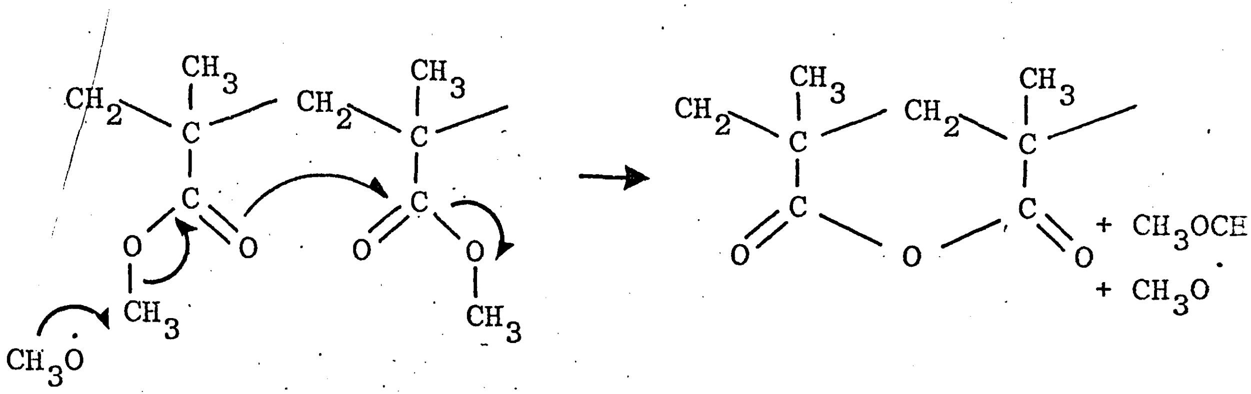
This process must occur immediately on formation of $\cdot COOCH_3$ radicals, since these will have a very short lifetime. Any MeOH formed from this mechanism is, therefore, formed at the same time as MeOH arising from decomposition of $\overset{\overset{O}{\|}}{\cdot C} - OCH_3$, followed by hydrogen abstraction.

It should be noted that methyl acetate could also arise from lactone formation between two adjacent MMA units: .



This is considered to be unlikely, however, since no clear IR evidence for lactone structures has been detected.

Dimethyl ether was also detected during the first stage of degradation, and this is thought to arise, either by dimerisation of MeOH in the presence of $ZnBr_2$, or during anhydride production in a manner similar to methyl acetate production i.e.



This process results in the production of one molecule of CH_3OCH_3 accompanied by liberation of a $CH_3\dot{O}$ radical, which can either continue with this mechanism, or form MeOH by hydrogen abstraction.

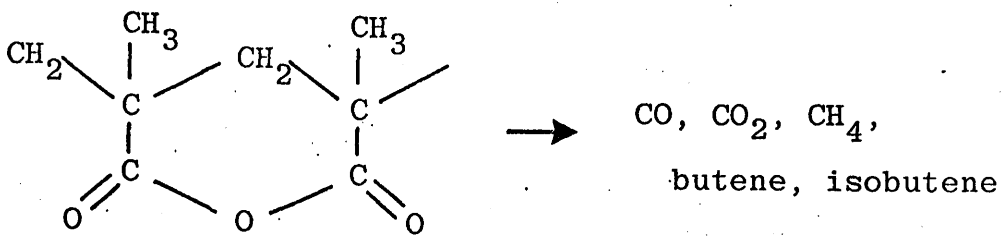
SUMMARY

Thus, to summarise, the first peak in the TVA traces consists of formation of organic salt and anhydride, accompanied by liberation of CO, CH_3Br, CH_3OH, CH_3COOCH_3 and CH_3OCH_3.

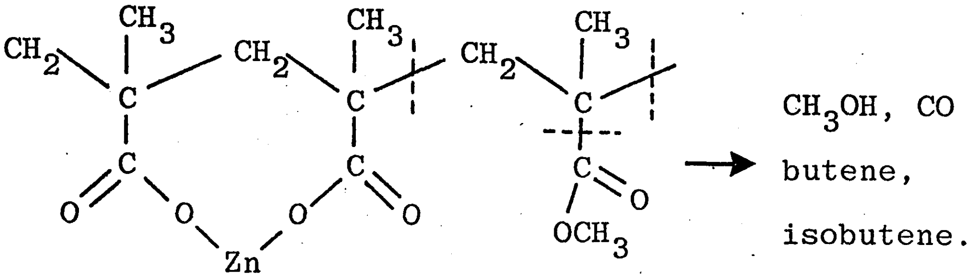
STAGE TWO

The second stage in blend degradation, as described by the second peak in the appropriate TVA traces, consists of anhydride breakdown similar to that described by McNeill and Neil, accompanied by decomposition of any uncomplexed MMA units trapped between cyclic structures.

(i)



(ii)

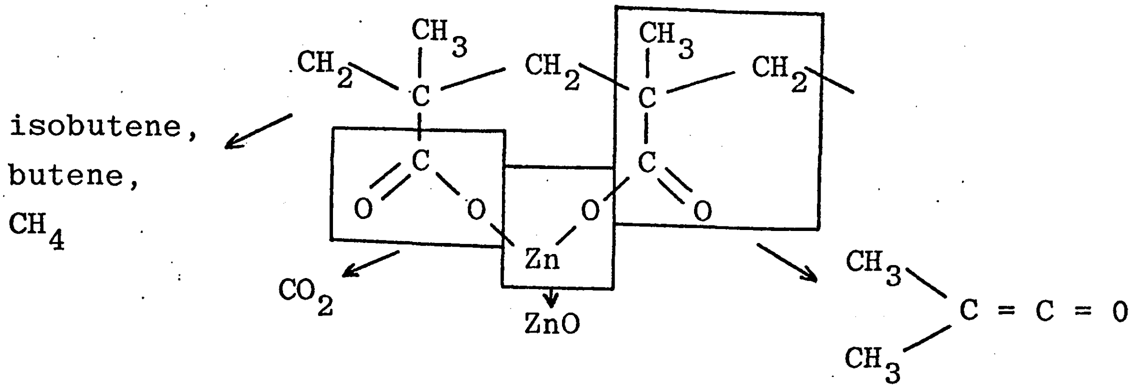


This is thought to constitute the second production of MeOH. Figure 4.22, P.128 shows MeOH production at this stage to be smallest for the blend containing highest $ZnBr_2$ concentration, a reasonable finding, since high $ZnBr_2$ content will result in the smallest proportion of MMA units not already involved in cyclisation or decomposition reactions as a result of complex formation.

Depolymerisation to monomer also occurs at this stage, but takes place only in regions of the polymer chain which have been unaffected by $ZnBr_2$. As a result, depolymerization is important only in the case of blend 1 , where initial $ZnBr_2$ concentration is small. This is in agreement with results, Figure 4.23, which show MMA to be detected in substantial amounts only in the case of blend 1 .

STAGE THREE

The third stage in blend degradation, peak three in the TVA trace, is believed to consist of breakdown of organic salt units, accompanied by decomposition of residual backbone.



The products detected at this stage in the degradation were in good agreement with those found by Zulfiquar[54] after degradation of zinc polymethacrylate.

It is believed that some ZnO produced by decomposition of organic salt structures then reacts further with the carbonaceous residue from PMMA, to form CO, seen as non-condensables in the TVA trace, and metallic zinc which remains in the degradation tube

$$ZnO + C \longrightarrow CO + Zn$$

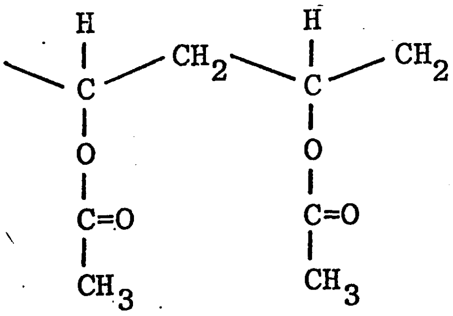
The feasibility of this reaction under the conditions employed was confirmed by a separate TVA experiment performed on a mixture of zinc oxide and charcoal, which showed CO to be formed at temperatures from 450 - 500°C.

Finally, residual polymer backbone structures which may consist of sequences of conjugated double bonds, or possibly crosslinked sections, also decompose during this stage in the degradation to yield some methane and, to a lesser extent, ethylene.

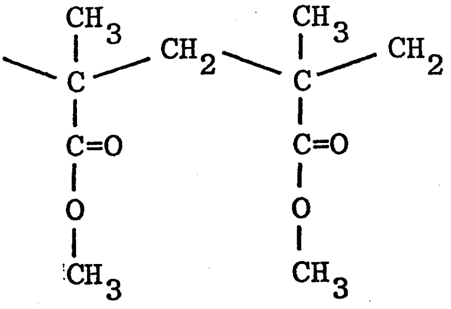
CHAPTER FIVE

INTRODUCTION

In the preceding chapter, where the effect of $ZnBr_2$ on the thermal degradation of PMMA was discussed, it was shown that the presence of the salt results in formation of several species not found in the products of degradation of PMMA alone. Since it is thought that $ZnBr_2$ alters the degradation pathway of PMMA via reactions facilitated by the existence of a complex between the salt and the pendant ester groups of the polymer, it was decided to study the effect of $ZnBr_2$ on the degradation of some other polymer which affords the possibility of ester-salt complex formation. The polymer chosen was PVA, which also contains suitable pendant groups, but unlike PMMA, these are attached to the polymer chain by carbon-oxygen bonds



PVA



PMMA

This chapter, therefore, deals with the effect of $ZnBr_2$ on the thermal degradation of PVA.

THERMAL DEGRADATION OF PVA

Initial work on thermal degradation of PVA was carried out by Grassie twenty five years ago,[58] and although more recent workers have questioned some of the details of that study, the overall characteristics of PVA degradation as proposed by Grassie are still accepted. The basic view is that acetic acid is produced in almost quantitative yield, one molecule of acetic acid being liberated from each monomer unit. On liberation of one such acetic acid molecule, a double bond is formed in the polymer chain, which facilitates deacetylation from the adjacent monomer unit by allylic activation.

Grassie identified the volatile products of isothermal degradation at 200 - 250°C as up to 95% acetic acid, the remaining 5% being carbon dioxide and ketene which were thought to form by decomposition of acetic acid.

Servotte and Desreux[59] agreed that on heating the polymer at temperatures from 235 - 305°C, 90 - 95% of the volatile degradation products consist of acetic acid, although they failed to identify CO_2 or ketene. Their hypothesis was that these products had been formed, in Grassie's experiments, as a result of catalytic decomposition of CH_3COOH, the catalyst being copper powder which had been added to the degrading polymer to ensure uniform temperature distribution.

These workers found that the rate of degradation was independent of polymer molecular weight, thereby discounting Grassie's theory that initiation of degradation occurs at unsaturated chain ends.

Servotte and Desreux also reported that, using IR spectroscopy, they had detected very little evidence of absorption due to sequences of conjugated double bonds, sequences which one would expect to find if Grassie's idea of a chain reaction were correct (although it should be stated that IR spectroscopy is not a very sensitive technique for this purpose). Such sequences have, in fact, been detected using UV spectroscopy by Zimmerman[60], and in more recent work by Gardner and McNeill[61] and Jamieson[18]. These latter workers also reported ketene, CO_2, CO and CH_4 among the degradation products, thus verifying Grassie's early observations. Jamieson[18] has postulated a degradation mechanism whereby the first step in degradation is random thermal scission of a C-O bond, liberating an acetate radical. The double bond then formed in the polymer chain facilitates deacetylation from an adjacent monomer unit. Subsequent deacetylations proceed until the polyene sequence contains about twelve double bonds, by which time resonance stabilization associated with the conjugated sequence outweighs any allylic activation tending to promote further deacetylation. The final stage in the degradation, which takes place at a temperature above 400°C is described as a general break-up of the conjugated polyene chain to form non-condensable products. On the basis of experiments carried out on PVA/PMMA polymer blends, Jamieson and McNeill[17] concluded that the degradation of PVA occurs by a radical process, as opposed to a molecular mechanism which would involve liberation of molecules of acetic acid. Their view is that initiation of degradation is by random thermal scission of a C-O bond, to yield an acetate radical. This, they suggest, can explain why PVA becomes insoluble at an early stage in its degradation, i.e. intermolecular reaction between pairs of PVA macroradicals leads to crosslinking. Finally, Jamieson and McNeill, also on the basis of results obtained from degradation of PVA/PMMA blends, propose that the minor products of degradation (ketene, CO_2, CH_4, CO, H_2O) are formed not by acetic acid decomposition as thought by earlier workers, but by decomposition of acetate radicals released from the polymer chain.

TVA STUDY OF PVA

The TVA trace obtained from degradation of a 25mg sample of PVA (BDH, Ltd.), $\overline{Mn}$ 45,000, is shown in Figure 5.1. The polymer was in the form of a film, cast from acetone solution, and the sample had previously been heated to 150°C to remove any residual solvent.

From this diagram, similar to the one obtained by Jamieson and McNeill[17], it can be seen that the degradation is essentially a two stage process, in keeping with the reported

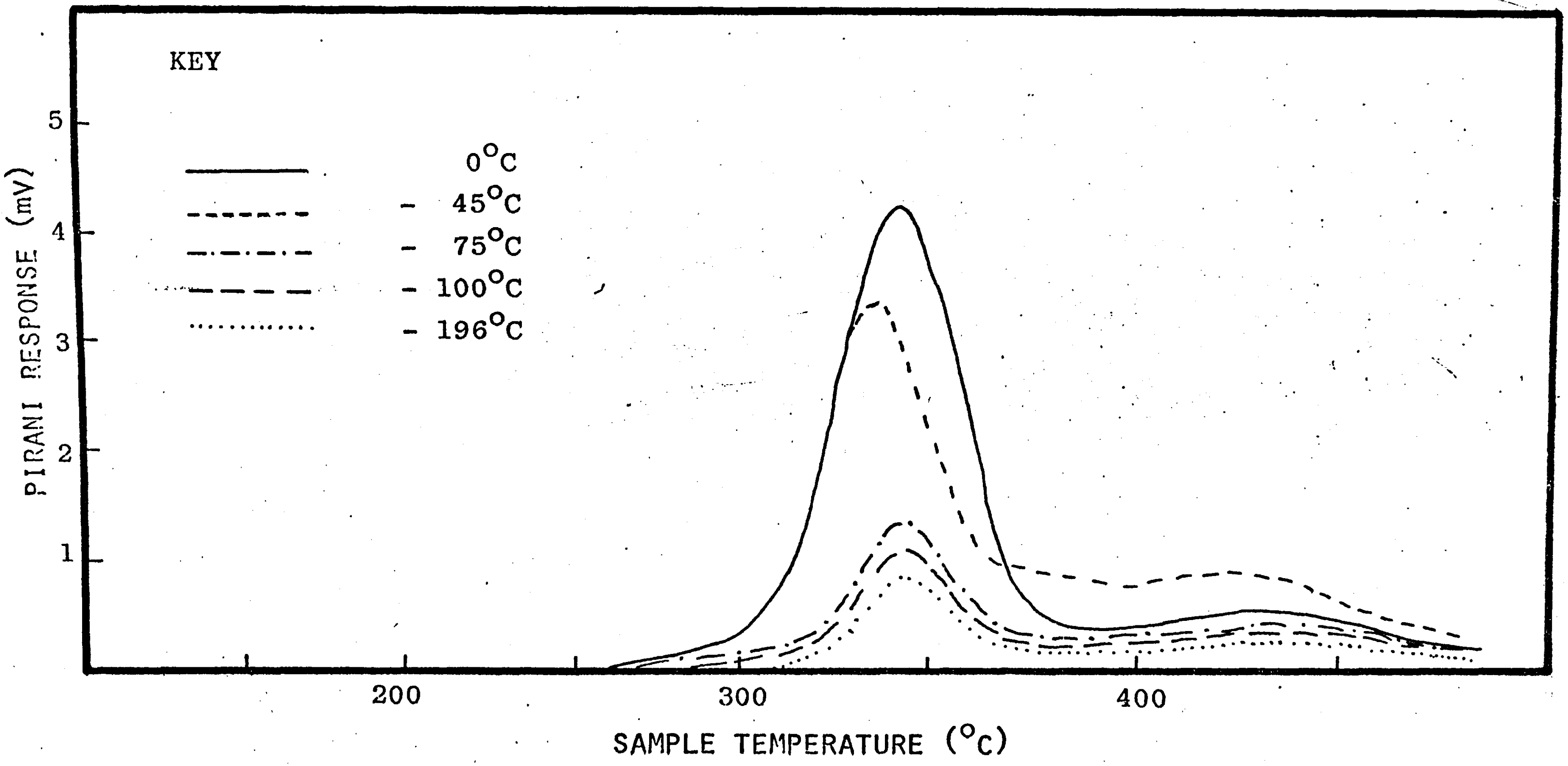


Figure 5.1 TVA trace for PVA, $\overline{Mn}$ 45,000. (25mg sample, heating rate 10°/min.)

findings of previous workers. The large peak, Tmax, 340°C corresponds to a deacetylation reaction producing mainly acetic acid. This is completely condensed in the -196°, -100° and -75°C traps, but at -45°C exhibits a limiting rate effect (as defined previously), causing the -45°C trace to remain a constant height above the -75°C trace. In addition to acetic acid, it can be seen that there are also volatiles produced at this stage in the reaction which are non-condensable at -75°, -100°, and -196°C. The differences in Pirani response between the -75° and the -196°C traces are thought to be due to ketene, water and carbon dioxide, and the peak in the -196°C trace to be due to the non-condensables methane and carbon monoxide. The smaller peak, with Tmax at 433°C, results from volatile products evolved during breakdown of the highly conjugated polymer backbone structure left after deacetylation. The products consist mainly of non-condensables; a carbonaceous residue remains, at 500°C.

THERMAL BEHAVIOUR OF $ZnBr_2$

As described in Chapter Four, it has been found that $ZnBr_2$ sublimes on heating. As a result, the sole peak in the TVA trace (page 54) is one at Tmax, 135°C caused by release of acetone solvent.

TVA STUDY OF PVA/$ZnBr_2$ BLENDS

Samples were again examined as films cast from mixed solutions of polymer and salt in acetone. In each case, the sample comprised 25mg polymer blended with the calculated weight of $ZnBr_2$ to give the desired molar ratio. The heating rate was 10°/minute.

Since, from previous experiments on PMMA/$ZnBr_2$ blends, the optimum polymer:salt ratio for complex formation is 2:1 molar, the blend first studied was PVA/$ZnBr_2$, 2:1 molar.

The results of variation in concentration of $ZnBr_2$ present are shown in Figures 5.3 and 5.4 which show TVA traces for blends of PVA/$ZnBr_2$ 1:1 molar and 10:1 molar respectively.

BLEND ONE PVA/$ZnBr_2$ in the ratio 2:1 molar (Figure 5.2) This trace is similar in general form to the one representing PVA degradation, except that Tmax., for the deacetylation reaction occurs at 164°C as opposed to 342°C for PVA alone. The small shoulder present in the early part of the deacetylation peak is due to release of acetone solvent (verified by IR analysis). Although the sample had been pre-heated to remove acetone, complete removal prior to the onset of polymer degradation was impossible due to the very low temperature at which deacetylation begins. The presence of acetic acid is suggested by the limiting rate behaviour of the -45°C trace, and the difference between the -75°C

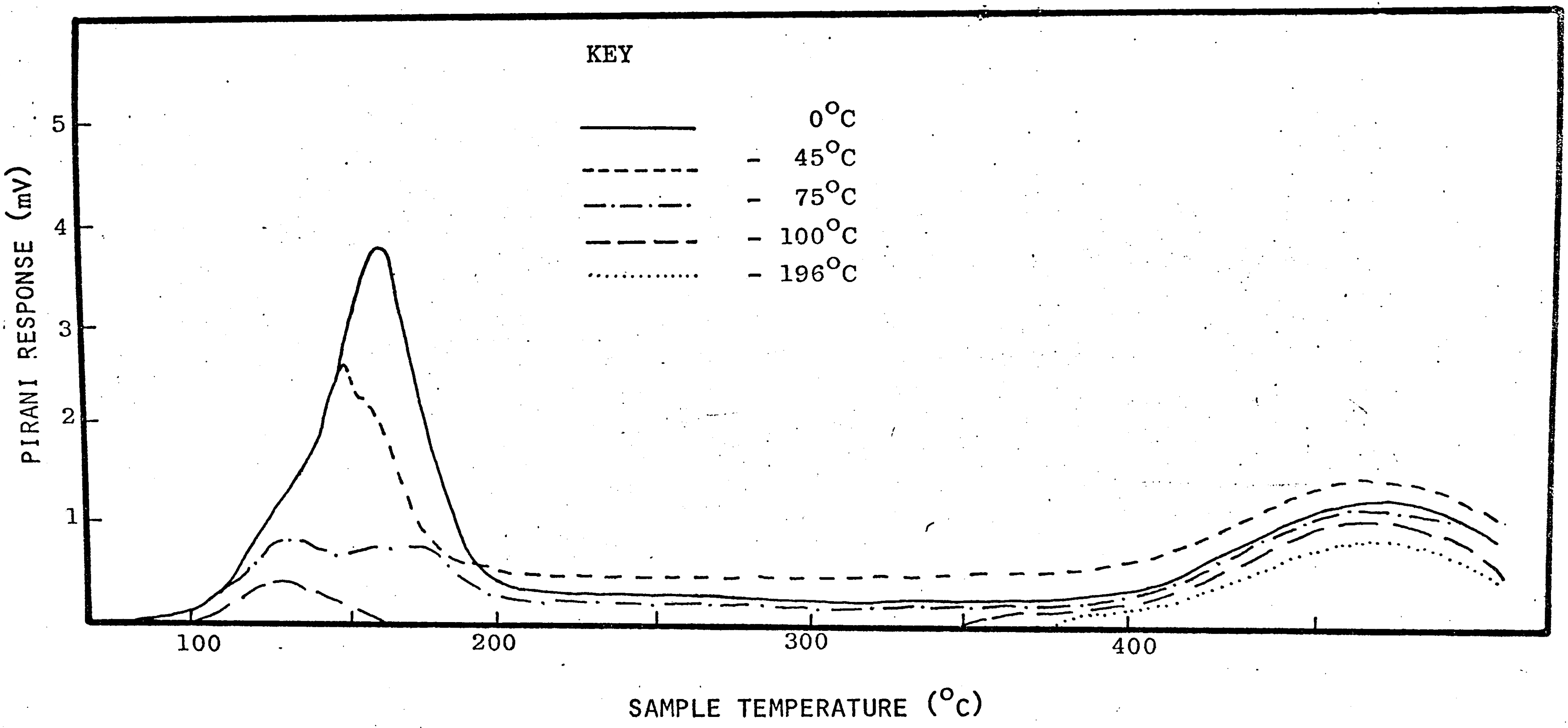


Figure 5.2 TVA trace for PVA/$ZnBr_2$, 2:1 Molar.

trap and the $-196^{o}C$ trap again provides evidence of small amounts of products which could be ketene, carbon dioxide and water (the displacement of the $-100^{o}C$ trace at this point is more clearly seen in TVA traces produced by larger samples). No non-condensable products have been detected at this stage.

The high temperature peak, above $400^{o}C$, is thought to result from volatile products evolved during breakdown of the unsaturated polymer backbone, in a manner similar to the second stage in the degradation of PVA alone.

The above interpretation of the trace suggests that the effect of $ZnBr_2$ is not to initiate any new degradation reaction, but to promote deacetylation at a much lower temperature, resulting in a very substantial destabilisation of the polymer.

<u>BLEND TWO</u> PVA/$ZnBr_2$ in the ratio 1:1 molar (Figure 5.3) Interpretation of this trace is as for blend one, Tmax. for deacetylation now occurring at an even lower temperature, i.e. $154^{o}C$.

<u>BLEND THREE</u> PVA/$ZnBr_2$ in the ratio 10:1 molar (Figure 5.4). The form of this trace is as before, one peak corresponding to a deacetylation reaction (with an early shoulder caused by residual acetone), and a later peak corresponding to backbone scission. In this case, with a relatively small concentration of $ZnBr_2$ present, the temperature at which deacetylation proceeds has been lowered by a smaller amount than was found in the cases of the previous two blends.

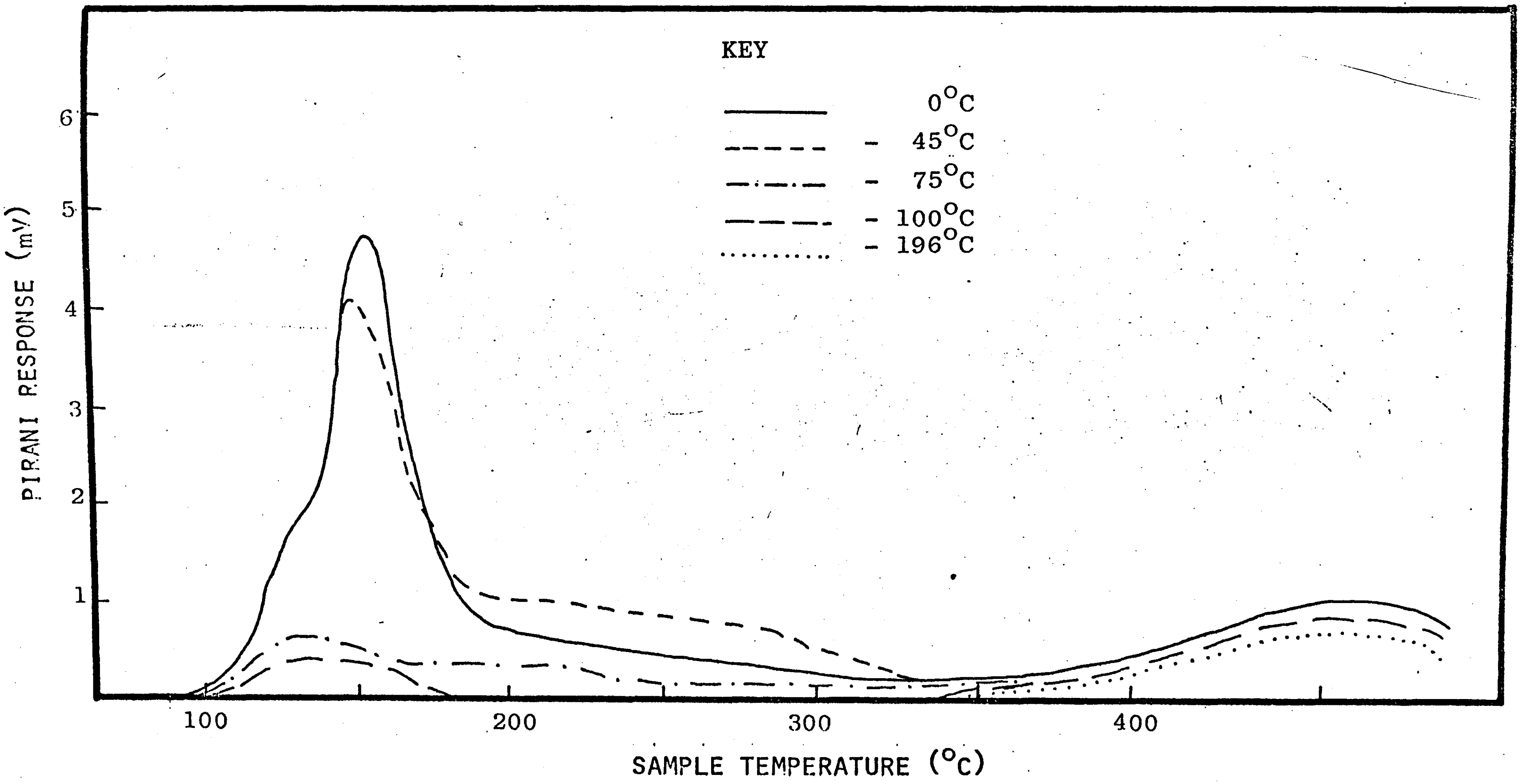


Figure 5.3 TVA trace for PVA/$ZnBr_2$, 1:1 Molar.

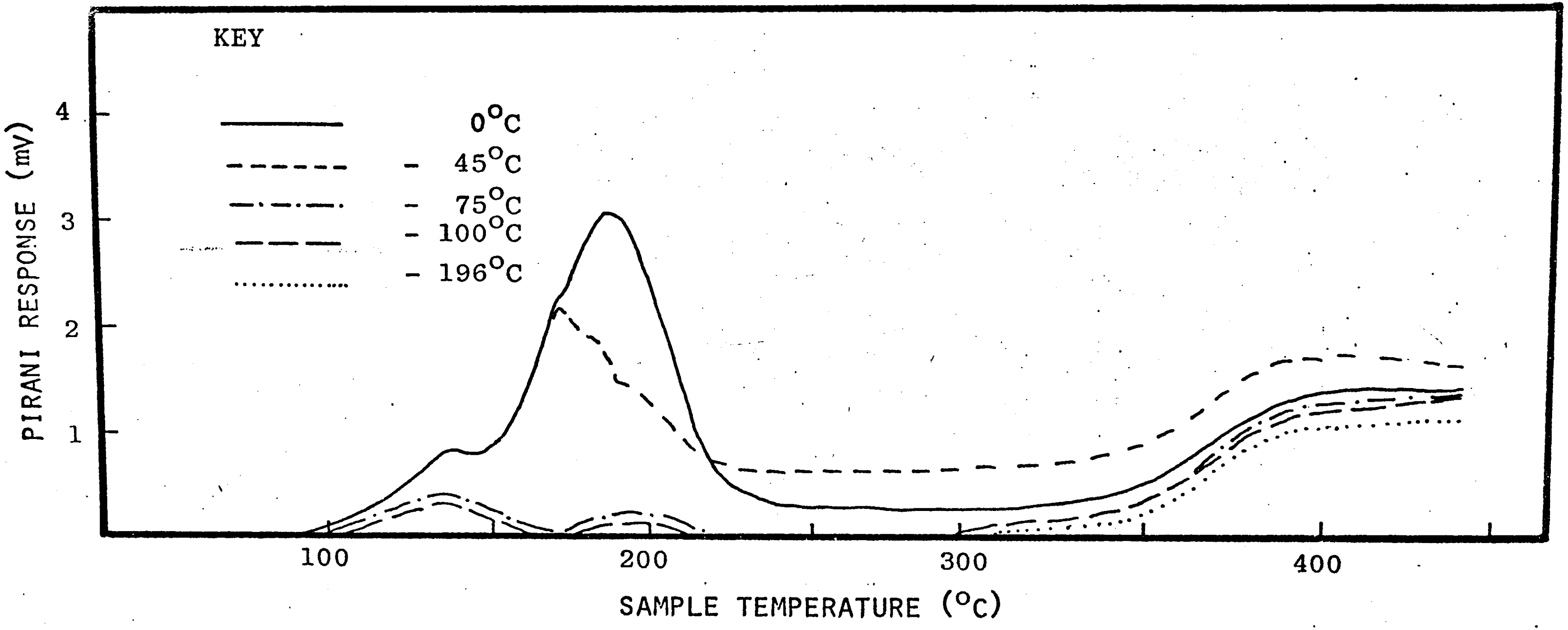


Figure 5.4 TVA trace for PVA/$ZnBr_2$, 10:1 Molar.

Tmax in this case occurs at 190°C.

Comparison of the TVA traces for all three blends with that for PVA alone suggests that the presence of $ZnBr_2$ in the degradation serves only to lower substantially the temperature of deacetylation, this temperature falling progressively with increasing concentration of $ZnBr_2$ in the blend. Evidence in support of this view was obtained from analysis of degradation products.

ANALYSIS OF DEGRADATION PRODUCTS BY IR SPECTROSCOPY

Spectra were obtained of the volatile degradation products from each of the three blend compositions, namely 1:1, 2:1, and 10:1 molar PVA/$ZnBr_2$. These were compared with the spectrum of the products obtained from similar degradation of PVA alone. In all cases, the sample consisted of 50mg polymer blended with the required amount of $ZnBr_2$, and degradations to 500°C were carried out under normal operating conditions of the TVA apparatus, as described previously. The exception, as before was the technique used to isolate non-condensable products, for which a closed system had to be used.

It was found that the products identified from degradation of PVA alone were fully consistent with those reported previously by several workers,[17,18,58,61] the main difference being a failure, in this work, to detect CO. This is thought to be a result of the small polymer sample (50mg) degraded in this case. In previous studies which have reported CO, sample size has been 100mg, leading to the larger production necessary to ensure that there is sufficient pressure of CO in the closed system for detection by IR analysis. Volatile products identified from degradation of PVA (50mg) are listed in Table 5-I.

Condensables	Non-Condensables
CH_3COOH	methane
CO_2	
ketene	
butene/isobutene	

Table 5-I Volatile Degradation Products of PVA identified by IR Spectroscopy.

It should be noted that butene and isobutene were identified only after the volatile products had been fractionated using the sub-ambient TVA technique, described in Chapter Two, and the separated fractions subjected to IR analysis.

When spectra of the total volatiles from each of the three blends were studied, it was found that methane was present in all cases, but that the only condensable product which could be identified with confidence was CH_3COOH. When the condensable products from degradation of a further sample of the 2:1M blend were then fractionated using sub-ambient TVA, IR analyses of the individual fractions provided clear evidence for the presence of ketene, CO_2, butene and isobutene. No evidence was found to suggest the presence of CH_3Br or any other bromine-containing species.

Analyses of the small cold-ring fractions obtained from blend degradations showed the organic products to be identical to those from PVA alone, thought to be polyene containing chain fragments arising from polymer chain scission. Cold-ring fractions arising from blend degradations also contained large amounts of $ZnBr_2$, identified by an IR absorption peak at $1600cm^{-1}$.

Finally, analyses of residues after degradations of both PVA alone, and of the blends, failed to provide any useful information, all spectra containing only small, very broad, absorptions. When a sample of the residue from degradation of the 2:1M blend was studied as a CsI disc, IR analysis over the range $4000 - 250cm^{-1}$ did not detect ZnO.

ANALYSIS OF VOLATILE PRODUCTS BY MASS SPECTROMETRY

Analysis of the condensable products obtained from degradation of PVA was carried out as described in Chapter Two. Results are similar to those obtained by Jamieson and McNeill,[17] and are presented in Table 5-II.

Condensable Products
CH_3COOH
ketene
CO_2
butene/isobutene

Table 5-II Volatile Products from Degradation of PVA, identified by Mass Spectroscopy.

These can be seen to confirm IR analysis data.

Mass spectrometric analysis was then carried out on the condensable products of degradation of a 2:1M blend of PVA(50mg) and $ZnBr_2$. Evidence for all of the products identified in the analysis of volatiles from PVA was found in the spectrum, which contained no new peaks. Thus, product analysis by both IR spectroscopy and mass spectrometry seems to confirm the initial interpretation of TVA traces. This is that $ZnBr_2$ does not participate in any chemical reaction with the degrading polymer to produce species not found in PVA degradation, but interacts with the polymer in some way which lowers the temperature at which deacetylation can take place.

In order to test this theory further, several different blends were heated isothermally at a temperature too low for normal production of CH_3COOH from PVA, and quantitative measurements made on CH_3COOH evolved.

QUANTITATIVE ESTIMATION OF CH_3COOH

A number of PVA/$ZnBr_2$ blends, prepared as films cast from acetone solution, were subjected to isothermal heating at 129°C (at which temperature $ZnBr_2$ is involatile) for periods of several hours. The blends consisted of 30mg PVA plus the calculated amount of $ZnBr_2$, and are described in Table 5-III.

Blend Number	PVA:$ZnBr_2$ (Molar Ratio)	
1	1	2
2	1	1
3	2	1
4	5	1
5	10	1
6	100% PVA	

Table 5-III Blend Compositions Subjected to Isothermal Heating at 129°C.

Volatiles evolved were isolated prior to quantitative measurements of CH_3COOH being made by titrating the products with NaOH(0.01M) to the phenolphthalein end-point.

On the basis of TVA, infra-red and mass spectrometric analyses, it was felt that deacetylation is similar, in this case, to the process which occurs during degradation of PVA alone, whereby volatiles consist of around 95% acetic acid and there is no evidence of any other acidic species which would render invalid measurements based on such titrations. When similar estimations were made of acetic acid evolved during programmed degradation, to 500°C, of these blends, in all cases actual CH_3COOH production was over 90% of the theoretical maximum (one molecule of CH_3COOH per VA unit).

It is useful, at this stage, to consider quantitative results obtained by previous workers studying PVA degradation. These are that heating for 1 hour at 253°C produced less than 5% volatilization of the sample[58], or that more than 3 hours at 275°C were required to give complete production of CH_3COOH[17]. As stated above, samples in this work were heated at 129°C, the results being shown in Figure 5.5.

On examination of these curves, it is immediately obvious that no acetic acid is produced from PVA alone, and that the rate of acetic acid production increases with increasing concentration of $ZnBr_2$, up to a maximum. It can be seen that this maximum rate of production of CH_3COOH occurs for the 1:1M blend, and an increase in the amount of salt present, to give a 1:2 molar ratio, does not result in any further rate increase. These results can, once more, be explained in terms of degradation occurring more readily through a polymer-salt complex.

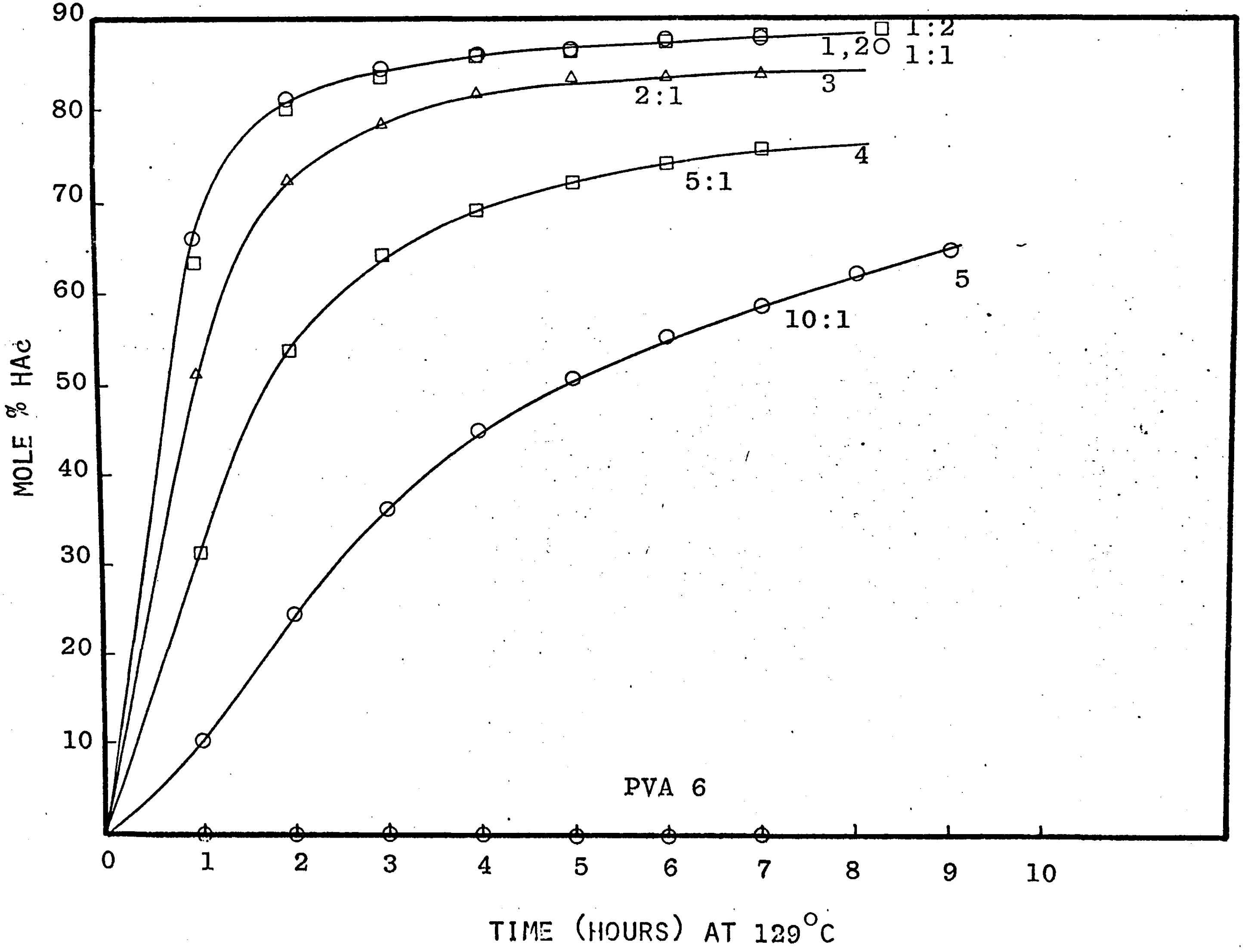
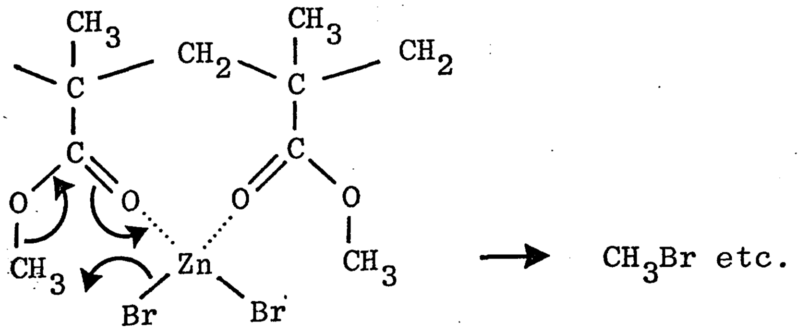


Figure 5.5 PVA/$ZnBr_2$ blends heated isothemally at 129°C

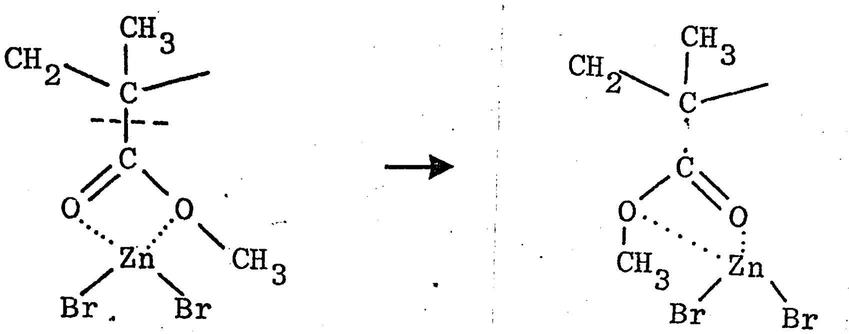
PVA-$ZnBr_2$ COMPLEX STRUCTURE

In the previous chapter, visible spectroscopy was used to confirm the existence of a PMMA-$ZnBr_2$ complex, the initial indication of such complex formation being that all the polymer-salt films studied were homogeneous and completely transparent. It has also been found that PVA/$ZnBr_2$ films are uniform and transparent even after solvent removal, and by analogy with PMMA, PVA is thought to form a complex with $ZnBr_2$ prior to degradation. If the respective structures of these polymer-salt complexes are now examined, an explanation can be found for the fact that $ZnBr_2$ takes part in the degradation of PMMA to the extent of being involved in formation of CH_3Br and eventually ZnO, whereas during degradation of blends involving PVA, $ZnBr_2$ merely aids deacetylation at abnormally low temperatures. Consider the structure of the optimum blend of PMMA/$ZnBr_2$ i.e. 2:1M.

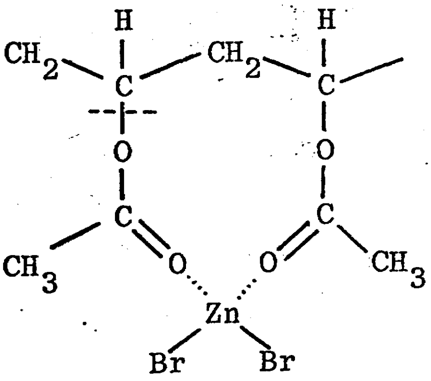


In this case, with $ZnBr_2$ complexed with two adjacent carbonyl groups, the geometry of the system allows a six-membered transition state to be set up, whereby a molecule of CH_3Br is released and a chemical bond formed between the polymer and zinc, ultimately leading to cyclisation.

When the concentration of $ZnBr_2$ is increased to give a 1:1M blend, it was shown that each $ZnBr_2$ tends to form a complex with the two oxygens of one ester group, and in addition to CH_3Br production, C-C scission occurs to liberate the pendant group:



In this case, $\dot{C}OOCH_3$ radicals are thought to be produced, and $ZnBr_2$ is released unaltered. In the case of a 2:1M blend of $PVA/ZnBr_2$, the analogous complex sturucture is



A similar mechanism leading to liberation of CH_3Br is clearly not possible, and the effect of $ZnBr_2$ is, therefore, to promote scission of the C - O bond shown, an effect similar to the one observed during degradation of 1:1M blends of $PMMA/ZnBr_2$. This is thought to be an inductive effect caused by the electrophilic nature of $ZnBr_2$. Such an explanation accounts for the fact that maximum rate of production of CH_3COOH occurs for the 1:1M blend of PVA/$ZnBr_2$ since each pendant group is complexed with one molecule of $ZnBr_2$. Any increase in $ZnBr_2$ concentration cannot lead to further complex formation, and thus cannot provide any increase in the inductive effect thought to be responsible for the production of CH_3COOH at low temperatures.

ENERGY OF ACTIVATION FOR CH_3COOH PRODUCTION

Although previous workers have arrived at quite different results for the absolute values of rates of deacetylation of PVA,[58,59] nevertheless good agreement has been reached in the values calculated for energy of activation. Using weight loss measurements, Servotte & Desreux[59] calculated an activation energy of 40 kcal/mole, an energy which must relate not to acetic acid production, but to the entire deacetylation process, including formation of small amounts of other minor products. Similarly, Jamieson,[18] using an identical weight loss method, calculated the activation energy to be 37.9 ± 2.0 kcal/mole.

In the present work, it was felt that the low temperatures of deacetylation must be reflected in the value of energy of activation, although it should be stressed that the method chosen to obtain this value is, necessarily, far from ideal, for the following reasons:

(1) The weight loss method used by previous workers is not applicable since blends containing $ZnBr_2$ absorb atmospheric moisture whilst in the thermobalance. It was felt, in any case, that some method should be adopted which yields a value for the activation energy for production of acetic acid, as opposed to the energy for deacetylation.

(2) The activation energy, E, for production of acetic acid was calculated by applying the Arrhenius Equation

$$k = Ae^{-E/RT}$$

where k is the rate constant for the reaction (rate of acetic acid production in this case).
Obviously $\log_{10}k = \log_{10}A - \frac{E}{2.303RT}$, and if several values of k are obtained, corresponding to the same reaction carried out at different temperatures, then a plot of $\log k$ vs. $\frac{1}{T}$ should yield a straight line. The value of E can be calculated from the gradient of this line.

In this work, a blend of PVA/$ZnBr_2$ (2:1M) containing 25mg PVA was selected initially and heated isothermally for periods of time at temperatures ranging from 118 - 148°C. After each time period, any CH_3COOH liberated was isolated and estimated by titration, the results being shown in Figure 5.6. Since the reaction is assumed to be of complex order (a conclusion reached by Jamieson[18] for PVA degradation in the absence of $ZnBr_2$) the method chosen to obtain values of k was to measure the initial rates of reaction (up to 10%) from the curves in Figure 5.6. At first sight, it would appear that the temperatures chosen are too high, yielding a large percentage of the available acetic acid in a short time. At temperatures below 118°C, which would result in a more modest rate of production of CH_3COOH, however, it was found to be impossible to remove acetone solvent. This process must be complete before any measurements are made on quantity of acetic acid liberated during heating under controlled conditions.

For these reasons, the value of E calculated here should

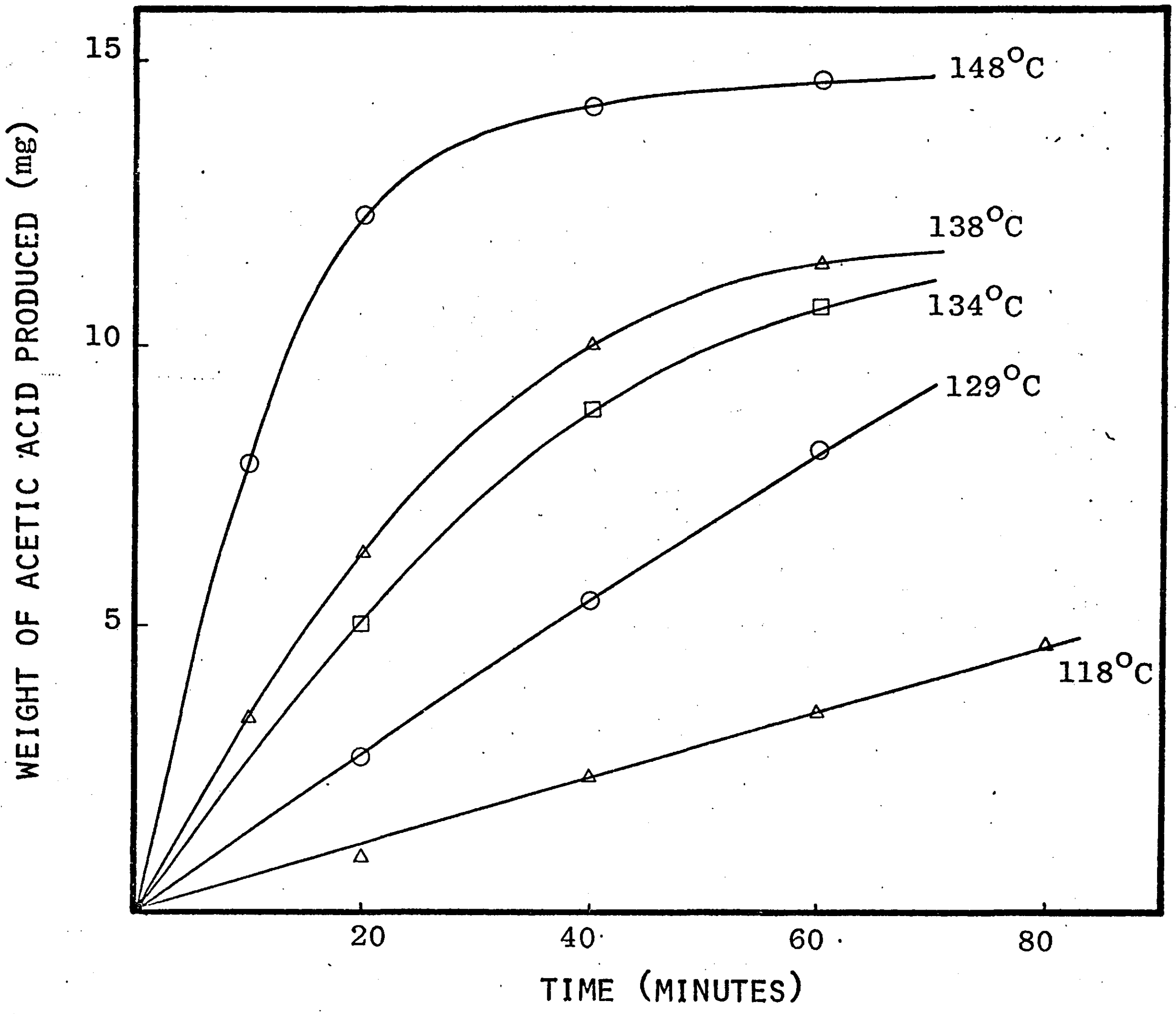


Figure 5.6 Rates of acetic acid production from isothermal heating at temperatures 118 - 148°C.

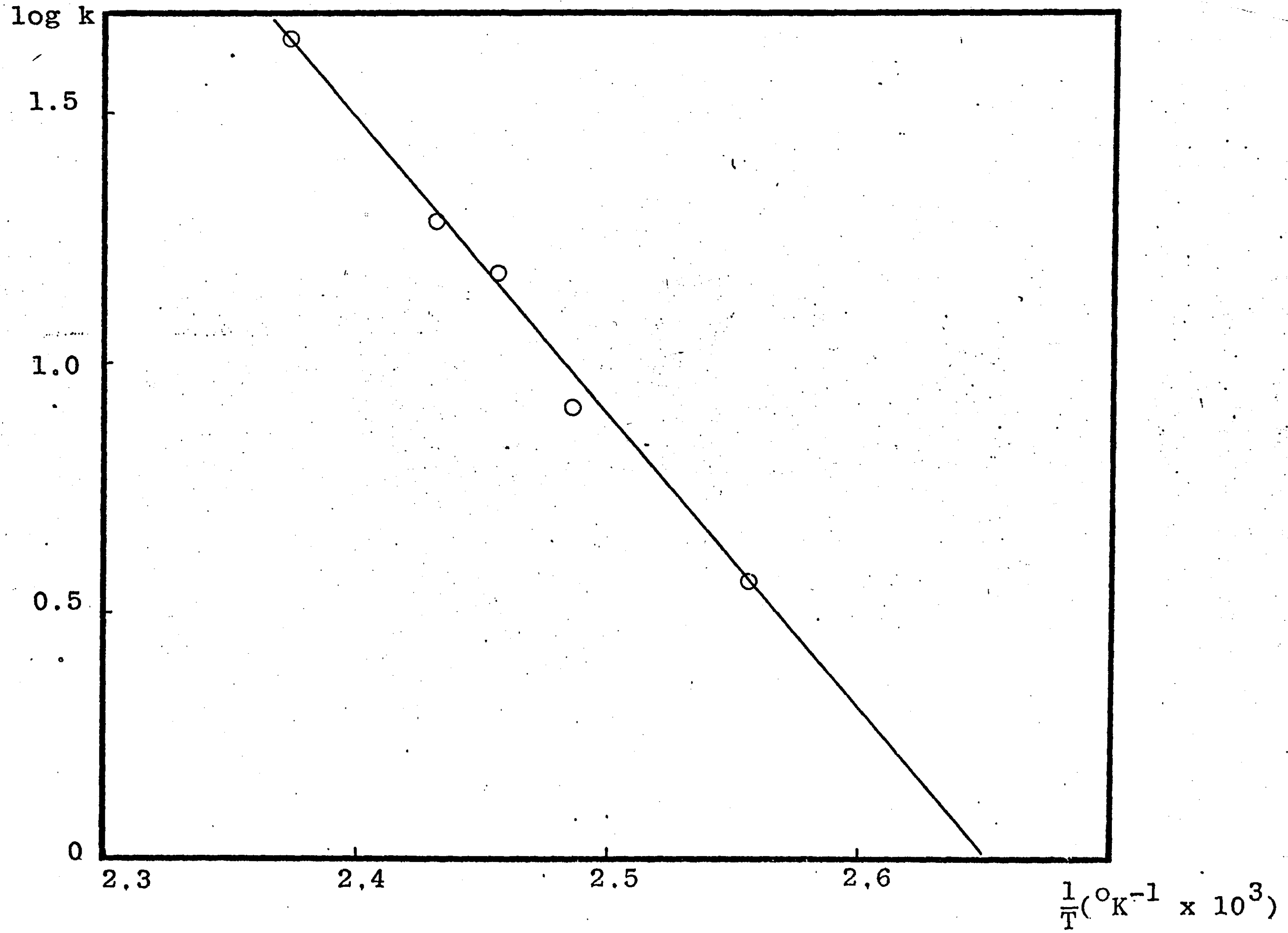


Figure 5.7 Arrhenius plot used to determine Activation Energy.

be considered merely to give an indication of the activation energy relative to those values already quoted.

The plot of (initial rate) vs. (reciprocal of absolute temperature) is shown in Figure 5.7, for which the gradient was calculated using the least squares method. The value calculated for E is

$$E = 27.0 \text{ kcal/mole},$$

which gives some impression of the magnitude of the catalytic effect of $ZnBr_2$ on PVA degradation.

NB. This value, as stated above, corresponds to a 2:1M blend of PVA/$ZnBr_2$. Since it can be seen from Figure 5.5 that the rate of CH_3COOH production is even greater from a 1:1M blend, it is apparent that were a similar calculation made using a 1:1M blend, the value of E obtained would be even lower.

MECHANISM OF DEACETYLATION

As stated in the introduction to this chapter, previous workers who have studied the thermal degradation of PVA have differed in their conclusions as to whether deacetylation is a molecular, or a free radical process, and whether minor products such as ketene arise from decomposition of acetic acid, or are formed directly from the polymer. In the most recent work on the topic, Jamieson and McNeill[17] concluded that deacetylation is a free radical process, and that the minor products arise from acetate radicals, not from acetic acid decomposition.

In this work, the issue is complicated by the presence of $ZnBr_2$, which, it could be argued, might alter the mechanism of PVA degradation even though blend degradation products are identical to those from PVA alone. Bearing in mind this reservation, it is possible to explain the results obtained in this study in terms of the mechanism proposed by Jamieson and McNeill.

It has been shown by Bamford and Dewar[62] that on pyrolysis of acetic acid in the temperature range 500 - 900°C, the reactions which occur are

$$CH_3COOH \longrightarrow CH_2 = C = O + H_2O \quad \ldots\ldots \quad (1)$$

$$CH_3COOH \longrightarrow CH_4 + CO_2 \quad \ldots\ldots \quad (2)$$

$$2CH_2 = C = O \longrightarrow CH_4 + C + 2CO \quad \ldots\ldots \quad (3)$$

$$2CH_2 = C = O \longrightarrow CH_2 = CH_2 + 2CO \quad \ldots\ldots \quad (4)$$

pathways 1 and 2 being the major processes.

Scotney[63] has also observed decomposition of acetic acid (in vacuo) to ketene at temperatures of 380°C, and the same author has postulated that during vacuum degradation of cellulose triacetate, acetic acid decomposes to ketene at 322°C. This is the lowest temperature at which thermal degradation of CH_3COOH to ketene has been claimed to occur.

In this work, however, a 2:1M blend of PVA/$ZnBr_2$ was heated, under vacuum in the TVA system, for one hour at 160°C. When the evolved volatiles were isolated and fractionated using the sub-ambient TVA technique, ketene, as well as a small amount of CO_2, was identified by IR analysis. It is impossible for this ketene to have arisen from CH_3COOH degradation, unless the decomposition is somehow catalysed by the presence of $ZnBr_2$. In order to investigate this possibility, a 1:1M mixture of $ZnBr_2$ and acetic acid was introduced into a tube, which, after the mixture had been cooled to -196°C, was evacuated and sealed. Thus CH_3COOH was heated in the presence of $ZnBr_2$, in a sealed, evacuated tube for one hour at 160°C. IR analysis of the resulting "products", again after attempted fractionation by sub-ambient TVA did not yield any evidence of ketene, nor was there any evidence of acetic anhydride, which may be formed by the reaction of ketene and acetic acid.

On this basis, it seems that in the case of PVA/$ZnBr_2$ blends, ketene arises, not from decomposition of acetic acid, but directly from the polymer side chain, possibly from decomposition of $CH_3CO\dot{O}$ radicals as in the interpretation of Jamieson and McNeill.

$$CH_3CO\dot{O} \longrightarrow CH_2 = C = O + \dot{O}H(\rightarrow H_2O) \quad .... \quad (5)$$

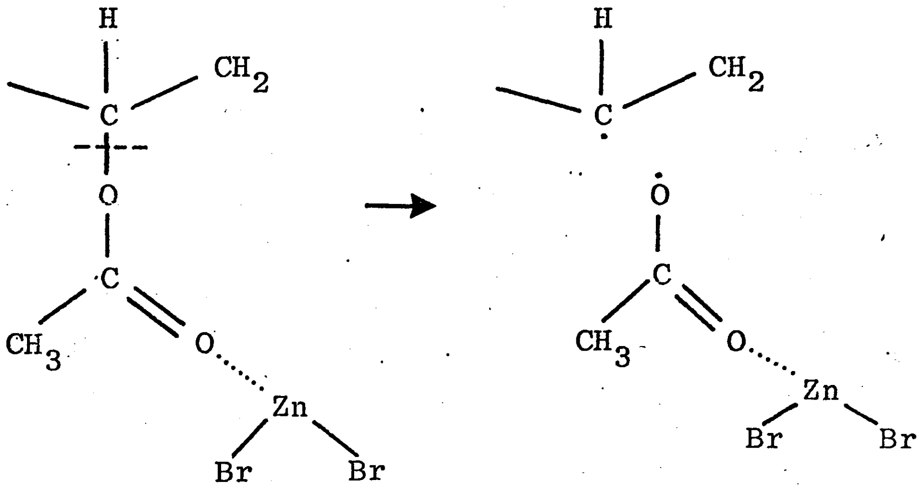
There is a second route for decomposition of acetate radicals, i.e.

$$\begin{aligned} CH_3CO\dot{O} \longrightarrow CO_2 + CH_3^{\bullet}(&\rightarrow CH_4) \quad .... \quad (6), \\ (\text{or}&\rightarrow C_2H_6) \end{aligned}$$

but although CO_2 was detected in small amounts after heating at 160°C, there was no evidence of CH_4. Examination of the TVA traces from the three PVA/$ZnBr_2$ blends, shown on pages 160-163, shows, also that no non-condensable products are evolved during the deacetylation reaction. It is possible, therefore, that the process shown in equation (6) does not take place in this case, and that CO_2 detected arose as an impurity in the sub-ambient TVA apparatus.

FREE RADICAL PRODUCTION

If the above theory of radical decomposition is correct, then it must be the case that $ZnBr_2$ in some way promotes homolytic scission of a C - O bond to yield free radical species



One possible explanation of this is that $ZnBr_2$ may confer some stability on the free radical formed, since there is a net withdrawal of electron density towards the zinc. This type of argument applies equally well to the production of $^{\cdot}COOCH_3$ radicals in PMMA/$ZnBr_2$ degradation, and has been used by previous workers in other fields e.g. Gould has suggested[64] that in the process

$$CHCl_3 \longrightarrow {}^{\cdot}CCl_3 + H^{\cdot}$$

the $^{\cdot}CCl_3$ radical gains some stability by distributing electron density over the three Cl's. Similarly, it has been demonstrated[65] that the bond dissociation energy for C - Br in CCl_3Br is 50 kcal/mole, whereas the C - Br dissociation energy in $CHCl_2Br$ is 54 kcal/mole i.e. it is easier, energetically, to form the free radical which contains more electron-withdrawing groups attached to the carbon.

SUMMARY AND CONCLUSIONS

When the interpretations of results presented in this chapter are drawn together to form a composite picture, it appears that the effect of $ZnBr_2$ on the thermal degradation of PVA is to lower the activation energy for acetic acid production as a result of complex formation with pendant acetate groups.

There are no products formed which are not formed in degradation of PVA alone, and in the case of a 2:1M blend of PVA/$ZnBr_2$, there is definite evidence of some process other than molecular elimination of acetic acid, in the early stages of degradation. Results obtained can be explained in terms of the free radical mechanism for PVA degradation proposed by Jamieson and McNeill, although it should be noted that evidence which shows some ketene to have arisen from a source other than acetic acid does not exclude the additional possibility of some molecular elimination of acetic acid from the degrading polymer.

CHAPTER SIX

INTRODUCTION

The small molecule component, $ZnBr_2$, of the blends studied in Chapters Four and Five was selected on the basis of chemical considerations, outlined on Page 49. Since one of the reasons for study of polymer/small molecule blends is the widespread introduction of various additives into polymeric systems to produce commercial plastics, it was felt that a complementary study should be made of related blends containing some commonly used additive.

The polymer chosen for study was PMMA, because of its well understood thermal degradation behaviour as explained in Chapter Four, and the additive selected was zinc oxide, for the following reasons: since the small molecule most studied in this work is $ZnBr_2$, it was felt that a zinc compound would be most relevant, and ZnO is commercially the most important compound of zinc,[66] widely used in rubber and paint technology.

THERMAL DEGRADATION OF PMMA

The thermal degradation of PMMA is discussed in Chapter Four, P. 50. The sample used in this study was PMMA(1), $\overline{Mn}$ 610,000, the sample used in the detailed study of PMMA/$ZnBr_2$ blends, and the TVA trace for polymer alone is reproduced, for reference, in Figure 6.1.

THERMAL BEHAVIOUR OF ZnO

Zinc oxide, normally a white powder, turns yellow on heating,[67] before subliming at 1975°C.[68] The ZnO used in this study was a B.D.H. Ltd. laboratory reagent (AR grade), used without further purification; since zinc carbonate is known to decompose to ZnO, liberating CO_2, at temperatures over 200°C,[68] a sample of ZnO was subjected to study by TVA, as a precautionary measure. The resultant trace showed no evolved volatiles, indicating that the oxide used was free from impurities which might decompose in the course of polymer pyrolysis.

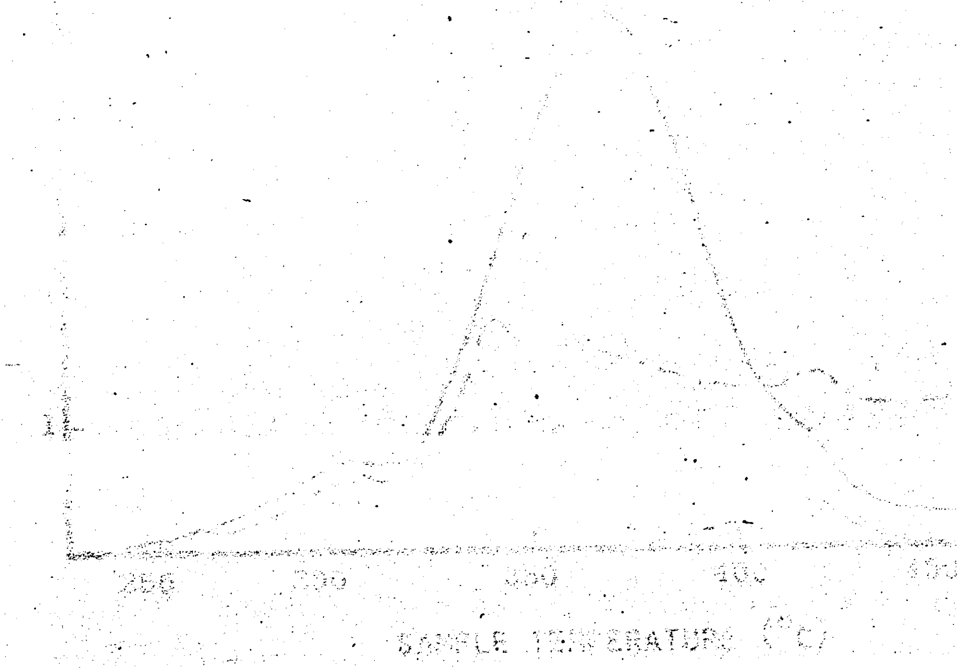
TVA STUDY OF PMMA/ZnO BLENDS

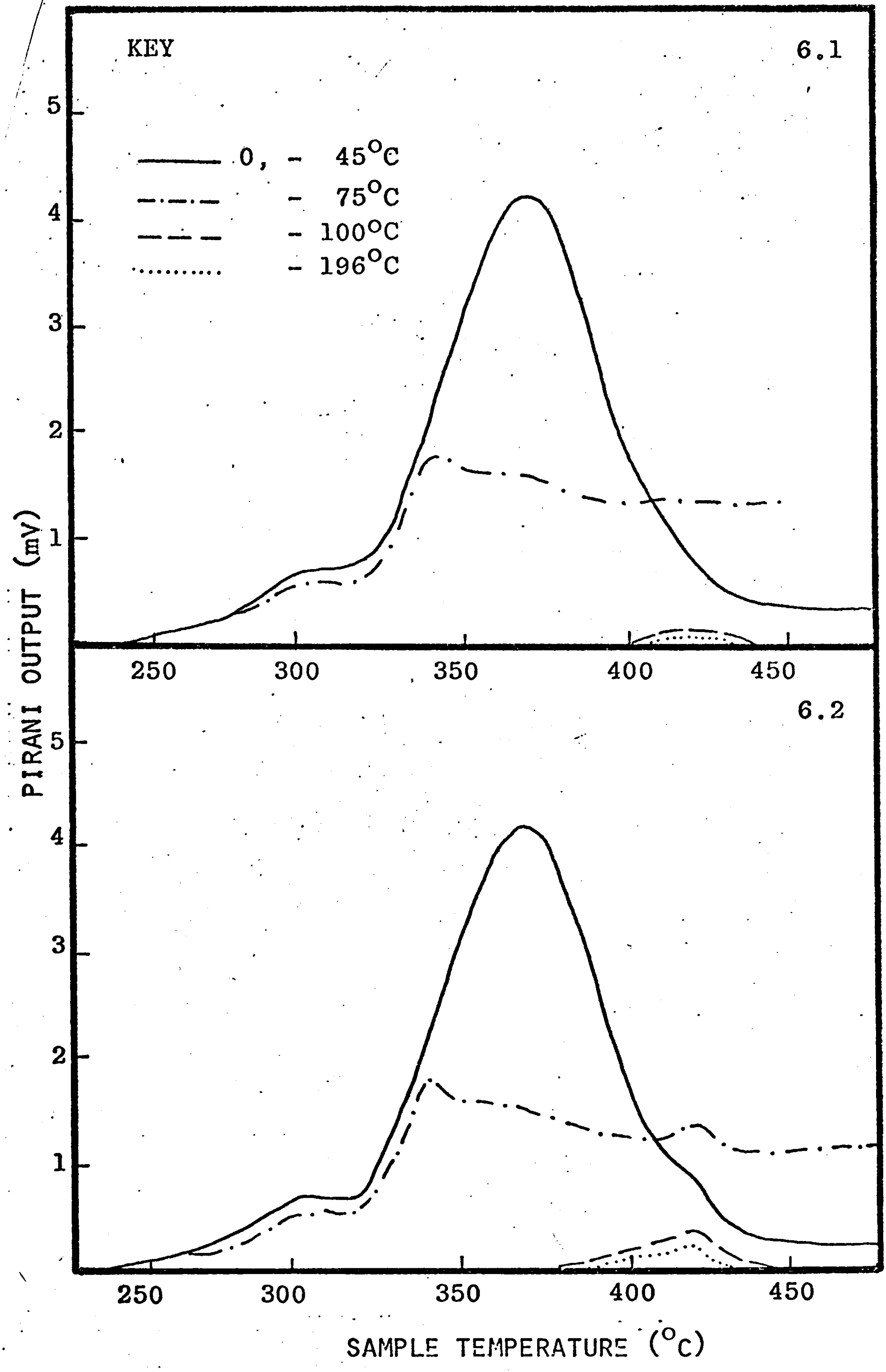
Due to the difficulty in obtaining a solvent system common to both polymer and oxide, samples were examined as mixed powders which had been physically ground together. In each case, the sample comprised 30mg PMMA compounded with the appropriate weight of ZnO. Heating rate was 10°/min. TVA traces for PMMA and for PMMA/ZnO blends 10:1, 2:1 and

1:1M are reproduced in Figures 6.1,2,3,4 respectively.

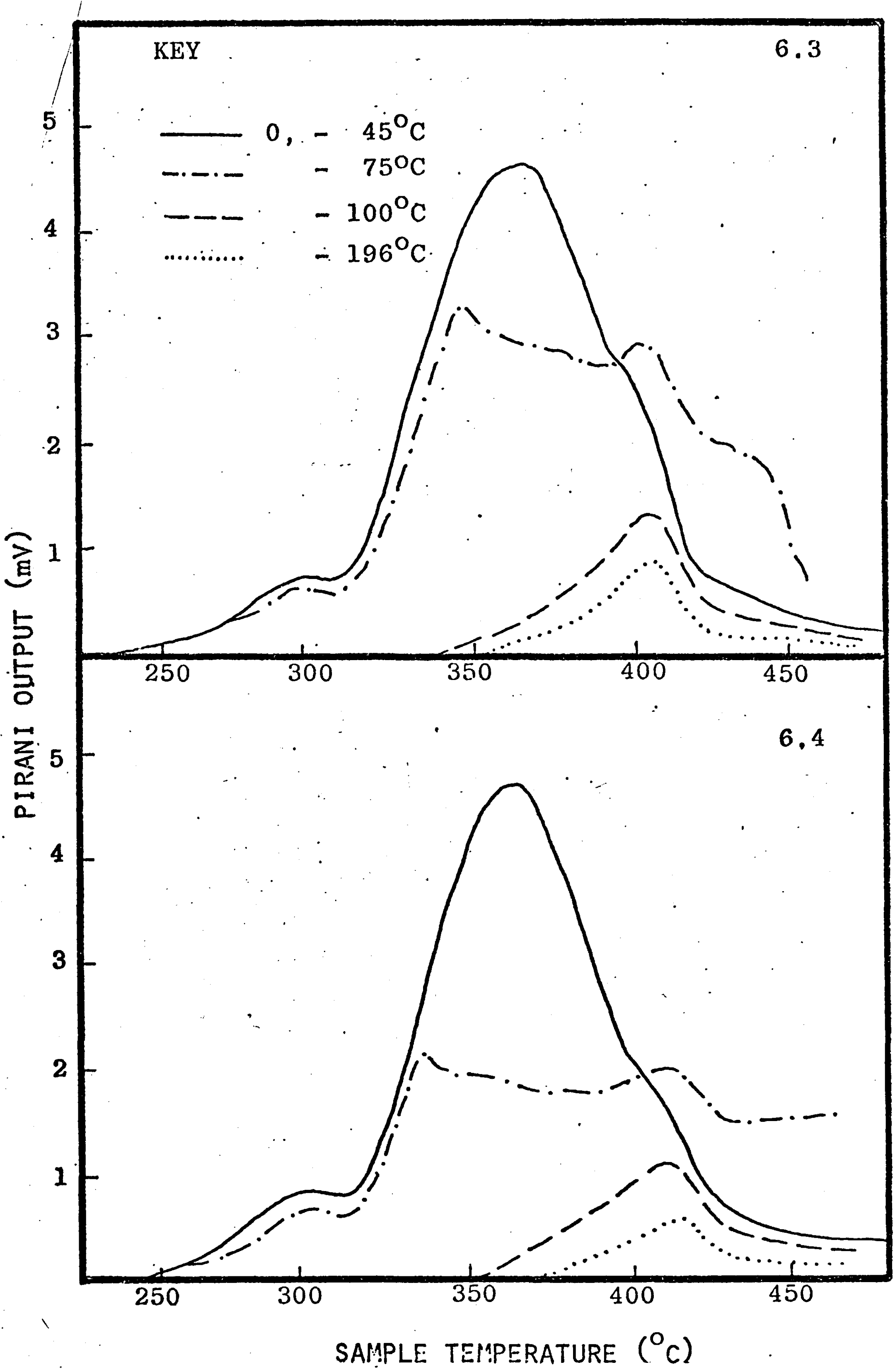
At first sight, all four traces are similar, (allowing for the fact that the -75°C trap was probably slightly warm during the experiment represented in Figure 6.3) the only slight difference being, in blend degradation, some additional high temperature reaction, Tmax. around 410°C, which results in production of material non-condensable at -100°C and -196°C.

Based solely on a comparison of peak magnitude in these traces, it appears that there is a similar quantity of this material produced from 2:1M and 1:1M blends, with a much smaller production from the 10:1M blend.





Figures 6.1 & 6.2 TVA traces for PMMA(1) and for PMMA/ZnO blend (10:1M) respectively.



Figures 6.3 & 6.4 TVA traces for PMMA/ZnO blends, 2:1M and 1:1M respectively.

PRODUCT IDENTIFICATION

(a) VOLATILE PRODUCTS - BY IR ANALYSIS

In the case of PMMA alone, the only condensable product detected was MMA monomer. There were no non-condensable products. In the case of the PMMA/ZnO blend (2:1M), condensable products identified were MMA, CH_3OH and CO_2. The presence of CH_3OH and CO_2 was verified by product fractionation using sub-ambient TVA prior to IR analysis. Non-condensables were examined after degradation in a closed system, as described previously. The presence of CH_4, and possibly trace amounts of CO, was confirmed.

(b) COLD-RING FRACTION

Neither PMMA alone, nor the PMMA/ZnO blend was found to yield any cold-ring fraction.

(c) RESIDUE

There was no residue after degradation of PMMA alone.

After blend degradation, the residue consisted mainly of an off-white powder, identified as ZnO by IR analysis, with some black carbonaceous residue, and a zinc mirror on lower parts of the degradation tube.

In order to confirm the presence of zinc metal in the residue, dilute HCl was added, whereupon the hydrogen produced was found to decolourize permanganate solution. A control experiment was carried out using HCl and the ZnO starting material, as a test for Zn as an impurity, but the permanganate retained its colour. Thus, some zinc oxide is reduced to zinc during blend degradation.

PARTIAL PYROLYSIS

On the basis of results from TVA and IR analysis, it is apparent that in the case of PMMA/ZnO blends there is some reaction occurring other than depolymerisation. Since it has been shown in this work that $ZnBr_2$ reacts with pendant ester groups of PMMA to yield zinc methacrylate units, it was decided to investigate the possibility of new polymeric structures being formed as a result of reaction between ZnO and degrading PMMA.

A 2:1M blend was heated to 360°C; the polymer fraction was isolated and subjected to IR analysis, which showed no structures other than that of PMMA to be present. This suggests either that PMMA depolymerises in the usual way and that the additional reaction is one between evolved MMA and ZnO, or that ZnO reacts with some depropagating radicals at high temperature, resulting in decomposition of MMA units.

POSSIBLE INTERPRETATION

It has been found in degradation studies of copolymers containing MMA that if depolymerisation to monomer can be prevented, MMA units decompose at high temperature. For example, in a study of the thermal degradation of methyl methacrylate - methacrylic acid copolymers, Jamieson and McNeill[69] discovered the formation of anhydride rings. One result of this is that depolymerisation is prevented, and MMA units trapped between cyclic structures were found to decompose to give methanol, and possibly carbon monoxide and methane.

In the present work, it has been shown that, during blend degradation, the polymer structure is not modified in any way which would inhibit depolymerisation, but the products of degradation indicate a possible breakdown of MMA units. Since the additional reaction takes place at a temperature no higher than that at which MMA is released intact during normal PMMA degradation it may be that MMA decomposition to methanol, carbon monoxide and methane is catalysed by ZnO.

Carbon monoxide thus produced could reduce zinc oxide to zinc, liberating CO_2

$$CO + ZnO \longrightarrow CO_2 + Zn$$

It is certainly known for molecules to be chemisorbed on ZnO, both acetone[70] and carbon monoxide[71] having been studied, for example, and it may be that in blend degradation, when

MMA released at around 400°C diffuses through the ZnO, some monomer decomposes on the oxide surface. It could also be the case that ZnO interacts with the depropagating radical to promote decomposition of MMA units. Carbon monoxide produced would then be in the required intimate situation for further reaction to produce Zn and CO_2. A previous study of the reduction of ZnO by low pressure CO has shown the process to take place at 645°C.[72] It has already been shown (P.151), however, that under the degradation conditions used throughout this work, ZnO is reduced by carbon at temperatures as low as 350°C.

CONCLUSION

The effect of ZnO on the thermal degradation of PMMA seems to be the provision of a surface on which a small fraction of MMA units can decompose to CH_3OH, CO and CH_4 at temperatures around 400°C. This effect is not merely a physical one induced by the presence of any powdered additive, since it can be seen from the general survey in Chapter Three that neither CsBr, nor ZnF_2 has any effect on PMMA degradation.

CHAPTER SEVEN

GENERAL CONCLUSIONS

Tabulated results in Chapter Three show that many additives affect polymer degradation, but it can be seen from the work carried out in subsequent Chapters that magnitude of effect is related to intimacy of polymer - additive contact. A good example of this is given in Chapter Four where the effect of $ZnBr_2$ on PMMA, notably at low temperature, is much greater for a film sample than for a mixed powder blend.

From visible spectroscopy studies, it was concluded that a polymer - salt complex is formed between PMMA and $ZnBr_2$, a complex which is thought to facilitate chemical reaction during pyrolysis, resulting in the formation of a large number of degradation products other than methyl methacrylate.

Blends of PMMA with $CoBr_2$, $CuBr_2$ and $ZnCl_2$ were also found to form transparent films, a possible indication of some complex formation, and thermal degradations of these resulted in volatiles similar to the products of degradation of PMMA/$ZnBr_2$ blends.

Further work (Chapter Five) on blends of $ZnBr_2$ with PVA, deliberatly chosen because its pendant ester groups were thought to afford the possibility of complex formation with the salt, showed once more how an additive in intimate contact with a polymer can affect its low temperature degradation. In this case the presence of $ZnBr_2$ does not result in the formation of new products, but promotes deacetylation at very low temperatures, probably through formation of a co-ordination complex.

Thus, although this work has shown (Chapter Three) that many different types of additive can affect polymer degradation in a variety of ways, on the basis of work described in Chapters Four and Five it seems reasonable to conclude that the likelihood of low temperature degradation of a polymer is markedly increased by the addition of some compound capable of formation of a co-ordination complex with that polymer. On the other hand, a polymer such as polystyrene, which is unsuitable for formation of co-ordination complexes,is unaffected by a large number of additives of different types.

In contrast, Chapter Six deals with the type of system more likely to be encountered in a commercial material, a blend of a powdered additive (ZnO) with a powdered polymer (PMMA). In this case, as might be expected if the effect of $ZnBr_2$ on PMMA in a powder blend is compared with the effect found in a film, there is no low temperature effect; there is however, a definite chemical effect at high temperature

A purely physical effect, caused by the presence of an additive, is unlikely since it is shown in Chapter Three that several powdered additives, including caesium bromide and zinc oxalate, exert no effect on the degradation of PMMA.

In conclusion, it must be stated that the mechanism of this type of effect has not been elucidated fully, and that further work is required.

SUGGESTIONS FOR FUTURE WORK

In order to gain an understanding into the mechanism of the effect of ZnO on PMMA degradation, the work described in Chapter Six could be extended to include studies of PMMA/ZnO blends of different compositions, with quantitative estimation of evolved MeOH and MMA. A study of the effect of ZnO on pyrolysis of some model compound for PMMA might also provide useful information.

The postulate that polymer degradation is accelerated at low temperature by formation of a co-ordination complex could be further tested by study of systems including a polymer component such as poly(methyl vinyl ketone) (PMVK) which would certainly lend itself to complex formation. Since the complexing moiety in this case is a pendant carbonyl group, one would expect a stronger complex with $ZnBr_2$ than that formed between the ester group of PMMA and $ZnBr_2$. The further possibility exists, therefore, that these proposed films will exhibit interesting electrical properties; the main problem in examining films in the ZnBr$_2$/PMMA system is uptake of atmospheric moisture, an effect to which a stronger PMVK/ZnBr$_2$ complex might be less susceptible.

Finally, one useful and interesting programme of work would be a parallel photochemical study. This could begin with a study of photochemical degradation of blends containing an additive unaffected by UV radiation, before moving on to blends containing additives themselves reactive to UV radiation. This would be especially useful in view of a recent development in the surface coatings industry, which uses UV radiation to "cure" polymer films, often acrylate in nature. In all such cases, unreacted photoinitiator, such as benzophenone, benzoin ethers, or substituted thioxanthones, remains in the cured polymer film, and, to date, the effects of this type of residue are unknown.

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