THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

STUDIES OF THERMAL STABILITY OF POLYMERS

BY

THERMAL VOLATILISATION ANALYSIS.

by

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Contents

Summary

Studies of Thermal Stability of Polymers by Thermal Volatilization Analysis (TVA).

A great deal of work has been carried out on the degradation of polystyrene in order to elucidate the mechanism of the reactions involved.

Most of the workers have assumed that transfer reactions are taking place and included them as a factor in the theoretical treatments of the kinetics of degradation. Other workers have shown, by indirect experimental work, that transfer reactions to take part in the degradation process of this polymer.

However, this work is a direct attempt to show that intermolecular transfer is a major factor taking part in the degradation process.

The technique used was the TVA where the small pressure which exists in a continously evacuated system between a hot sample, decomposing to volatile products, and a cold trap placed some distance away is recorded continuously as the temperature of the sample is increased in a linear manner. The TVA curve indicates the variation of rate of volatilization of the sample with temperature.

The degradation method used was that of comparing the thermal stability of very thin films of polymer with that of the thicker films. Degradation was carried out under conditions of temperature rise of $10^{\circ}C$/min. or at isothermal temperatures.

Thin films of polystyrene were observed to be thermally more stable than the bulk material. The molecular weight dropped more sharply in the case of thick films when compared with thin films of the same sample weight. More styrene monomer was produced from degraded thin films than from the thicker films. Also, the shape of the curve of the rate of volatilization against percentage conversion in thin films resembled that of poly (α- methyl styrene) where the zip length is much greater than the chain length.

This behaviour was considered to be due to the reduction of intermolecular transfer reactions in thin films of polystyrene.

Polymers where transfer reactions are well established such as polypropylene, poly (isobutene) and some elastomers were also examined and showed an effect of thin film stability similar to that observed in polystyrene.

Poly (methyl methacrylate) was also examined in the form of thin and thick films and in powder form. The results suggested that transfer reactions of the secondary hydrogen atoms might be taking place to some extent.

Poly (methyl acrylate) which contains a tertiary hydrogen atom showed an effect similar to that observed in polystyrene; while there was no change in thermal stability of thin and thick films of poly (tert. butyl methacrylate).

Very few useful conclusions could be drawn from results obtained from the degradation of thin and thick films of PVC, PVA and poly (vinyl alcohol).

Chapter One

General Introduction

1.1 Introduction

The realisation in the last two decades, of the commercial importance of the synthetic polymers, especially those with high thermal stability, has led to a wide interest in the study of the chemistry of degradation of polymers. [1,2,3,4,5]

Polymers lose their desirable properties under the influence of an energy transfer agency such as heat, light, infra red, ultra violet or gamma radiation, as well as ultrasonic and mechanical stress.

As well as being technically important the chemistry of thermal degradation is scientifically interesting because it helps to reveal the molecular structure and also throws some light on the strength of the various bonds holding the polymer molecule together, on the mechanism and kinetics of depolymerisation, on the effects of time, pressure, temperature, and on the nature of the products.

Similarly, studies on thermal degradation of polymers are of extreme importance from a practical point of view. They not only explain the behaviour of polymers under conditions of high temperatures, but also help in selecting the right kind of polymer for specific uses where high temperatures are encountered, and might suggest the design and synthesis of new materials to meet special requirements.

The applications of polymers in industry and technology and in providing finished articles are so numerous that it is almost difficult to count them. Some of the recent applications of thermally stable polymers are in space technology and in production of Carbon fibres.

Experimentally, thermal degradation is one of the easiest types to study, since the main requirements are a source of heat and an accurate measurement of the temperature of the polymer. Despite this fact, the mechanism by which most polymers degrade thermally is still not fully understood.

The literature pertaining to the degradation of polymers is most formidable both in its quantity and diversity.

Pyrolysis of polymers in vacuum was carried out as early as 1860 when natural rubber was degraded by destructive distillation and products were analysed [6]. Polystyrene was first degraded in vacuum by Staudinger in 1935 [7].

1.2 Degradation in Vacuum:

Thermal degradation carried out in vacuum provides a better understanding of the mechanisms involved during the reaction. On the other hand, when the polymers are heated in gaseous atmosphere, even if it is inert, the diffusion out of the polymer of volatile products which are formed inside it is retarded so that these products may undergo secondary reactions. Moreover, an external gas which does not belong to the system will hinder the escape of the volatile products from the hot zone, so that they could undergo further secondary reactions in the gaseous state. If pyrolysis is carried out in air or in oxygen then the thermal effects of degradation of the polymer will be masked by the chemical reaction of the products, volatile and non-volatile, with oxygen.

Another advantage of carrying out pyrolysis of polymers in vacuum lies in the fact that collection and fractionation of volatile products are thus facilitated.

In theory, the ideal system by which to study the mechanism of degradation of a given linear polymer would be to degrade a single isolated extended polymer chain. In practice, however, this is not possible. But to approach this ideal situation, it is feasible to follow the degradation of an extremely thin polymer film which may be considered as a two dimensional lattice where the chains are not overcrowded and as little interaction between the molecules as possible will occur.

1.3 Types of Thermal Degradation:

Depolymerisation in general is more involved as a process than polymerisation. The reason is that intermediate products take part in further reactions which cause the kinetics to be more complicated and not straightforward as in polymerisation.

The thermal decomposition reactions in polymers may be broadly classified into two groups :- chain scission reactions and substituent reactions.

a) <u>Chain Scission Reactions</u>:

Scission of the polymer main chain, which occurs either in the middle or at labile ends, may result in depolymerisation to monomer as in poly (methyl methacrylate) and poly (α- methyl styrene), or in the production of a wide range of fragements as in the case of polypropylene and polyethylene. The residue may retain the chemical characteristics of the parent material, in that monomer units are recognisable in it.

b) <u>Substituent Reactions</u>:

The elimination or modification of pendant groups may take place as in the case of poly (vinyl chloride) and poly (acrylonitrile). The resulting residue progressively changes in character from the original starting material, as the reaction goes to completion. In effect, monomer is not produced and the residue acquires a new structure.[57]

1.4 Degradation of Polystyrene:

Systematic investigations on the kinetics and mechanisms of thermal degradation of polystyrene began in the late twenties[7] and early thirties [8]. Despite the massive amount of research carried out on this subject there is a lack of general agreement on the precise processes of the mechanisms involved in the initial rapid fall in molecular weight followed by a slower drop after 30 per cent volatilisation, and the production of volatile substances consisting of monomer, dimer, trimer etc. in decreasing quantities.

Polystyrene degradation might be considered as free radical reaction, the reverse of polymerisation, and having initiation, transfer reactions, propagation and termination.

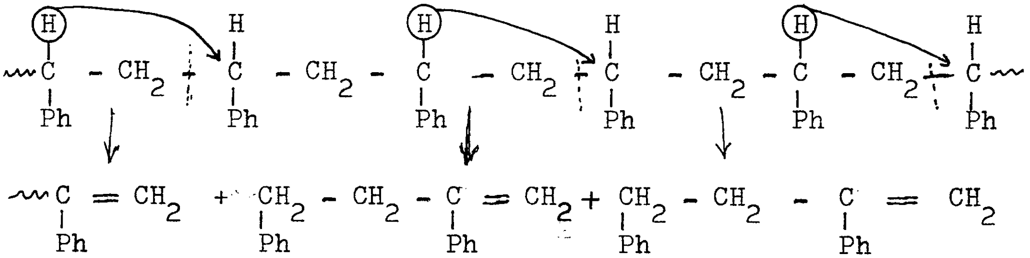
Due to the diversity of views on this subject, the work of various groups of workers will be briefly reviewed.

(A) Staudinger and Co-workers [7,8]

Some of the early investigations were made by these workers on the bulk degradation of polystyrene samples. One was commercially prepared and another was prepared in the laboratory under strict oxygen free conditions. Staudinger found that the latter was thermally more stable than the commercial sample. It was concluded that the oxygen which was incorporated in the polymer chain as peroxide groups was the cause for the lower thermal stability in the commercial polystyrene. The oxygen formed hydroxyl groups on adjacent carbon atoms at some points along the chain and the bond between such adjacent carbon atoms would be thermally weaker than the normal c-c bond.

Achhammer [9], found no evidence for the presence of hydroxyl groups when he examined samples of polystyrene by infra red spectroscopy, but this does not exclude the presence of a very small concentration of hydroxyl groups.

Later Staudinger and Steinhofer [8] suggested a picture for the mechanism of degradation. They pointed to the fact that a c-c bond "beta" to a double bond is weaker than a normal c-c bond. They also took into account that the α- hydrogen atom is more reactive and mobile, and considered that a scission in the main chain takes place followed by migration of an α - hydrogen atom.



(B) Investigations carried out by Jellinek:

Jellinek [10,11] studied the thermal degradation of polystyrene under high vacuum. He rejected the theory that the reaction could be explained by a random scission mechanism for the following reasons:

1 - Monomer is produced early in the reaction.

2 - The activation energy of 44.7 K cal/mole was lower than that expected for random scission.

3 - Plots of (Molecular weight)$^{-1}$ against time were non-linear in contrast to the case for random scission.

4 - The molecular weight distribution was narrower than that predicted for random scission.

Jellinek assumed that degradation is initiated by scission at "weak links" randomly distributed along the polymer chain.

To summerise Jellinek's findings on the thermal bulk degradation of polystyrene in vacuo, it can be put as follows:

At the start a rapid random degradation takes place owing to "weak links". For each random break a number of monomer units are split off the newly formed chain end. The rapid reaction comes to an end when all "weak links" are destroyed. Then a reverse, polymerisation process takes place consisting in chain end initiation, propagation and termination. At the same time a slight random degradation reaction occurs. Also he suggested the possibility that a small amount of cross-linking takes place during the later stages of the degradation.

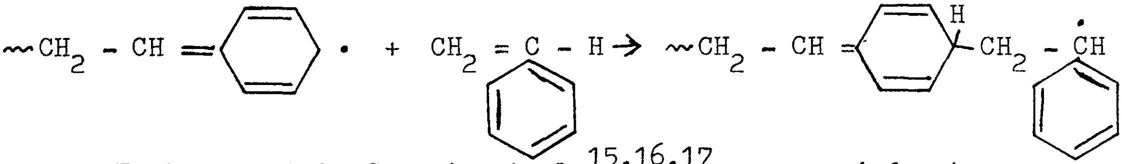
Thus, it is clear that Jellinek never considered the possibility of intermolecular transfer as a major factor taking part in the degradation process of polystyrene.

Jellinek and Spencer[12] carried out degradation of polystyrene in tetralin and naphthalene solutions. The reaction in tetralin showed no loss in weight of the polymer, which meant that the fall in molecular weight was not accompanied by the production of volatiles. This result was taken to support the "weak link" theory and as evidence against the views of Madorsky, which are discussed subsequently.

(C) Investigations by Grassie and Co-workers:

Grassie and Kerr[13] concluded from their work that chain scission occurred at "weak links", resulting in the formation of molecules rather than radicals. They also postulated that volatiles were produced by initiation at chain ends after scission at those weak points had taken place. The initial low rate of production of volatiles, rising to a maximum at about 35 per cent conversion, was ascribed to scission at "weak links" followed by immediate recombination of the pair of large radicals in a "cage", since they could not easily diffuse away from each other. Therefore a disproportionation reaction takes place and an unsaturated chain ends is thus produced which would be an initiation site for depolymerisation.

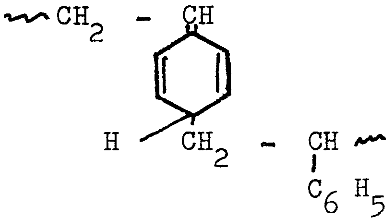
Kerr [14] has concluded that head to head abnormalities do not account for the number of bonds broken per molecule which may be less than unity, or for the lower rate of chain scission of poly (α - Deuterostyrene). Therefore, a process which might occur during the propagation step of polymerisation was suggested :-



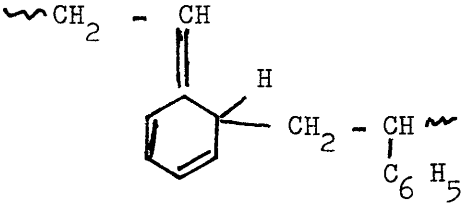
Further work by Grassie et al [15,16,17] was carried out on polystyrene degradation in experiments designed to test the "weak link" theory. They found that the presence of oxygen during polymerisation, the mode of polymerisation initiation, and branching exhibit no correlation with the initial rapid fall in molecular weight. However, some correlation was found with the polymerisation temperature, that the proportion of "weak links" is found to increase with the temperature of polymerisation.[57] Also abnormal structures in the polymer chain might be affecting the initial stages of the decomposition. Head to head, linkages were eliminated by a study of the degradation of styrene/stilbene compolymers.[17]

Grassie and Cameron [16] compared the bulk degradation of polystyrene in vacuum with its degradation in naphthalene and tetralin solutions in sealed tubes at high pressures, and found that in both cases the molecular weight decreases rapidly. But in tetralin solution, the production of volatiles and further drop in molecular weight were inhibited, while the radical chain depolymerisation process was retarded in naphthalene.

The same authors in another communication[18], suggested the transfer of the active site to the benzene nucleus and addition of monomer to give the structures of para and ortho quinonoid type, since the high stability of the polystyryl radical is attributed to resonance involving structures with the radical centre in the benzene ring.



para



ortho

Evidence in favor of associating "weak links" with main chain unsaturation came from a comparison of thermal and ozone degradation. It was found that ozonolysis followed by treatment with zinc and acetic acid to break the ozonide resulted in a molecular weight fall similar to that obtained by thermal degradation.

(D) Investigations by Madorsky and Co-workers:

Madorsky [19] and Wall [20], studied the degradation products of polystyrene and showed that:

1 - A maximum yield of 42 per cent monomer was obtained from isothermal degradation at 420°C.

2 - The composition of products was independent of time and temperature of degradation.

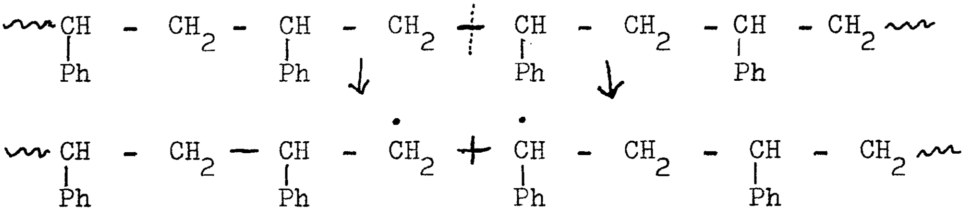
3 - Small chain fragments obtained consisted of dimer, trimer and tetramer in diminishing amounts.

Madorsky [21,22] investigated the rate of degradation in the temperature range 335 - 365°C by means of weight loss, using a tungsten spring balance. A rate maximum was found to occur in the production of volatiles around 30-40 per cent volatilisation. The rapid initial fall in molecular weight was also observed to take place during the first few per cent loss of weight of sample to about 80,000. Beyond this, the drop is slow and gradual until it reaches a limiting value between 40,000 - 60,000 then the decrease is even slower. This level of stabilisation is independent of the initial molecular weight or of the molecular distribution in the polymer, and also independent of its purity unless the sample is very impure.

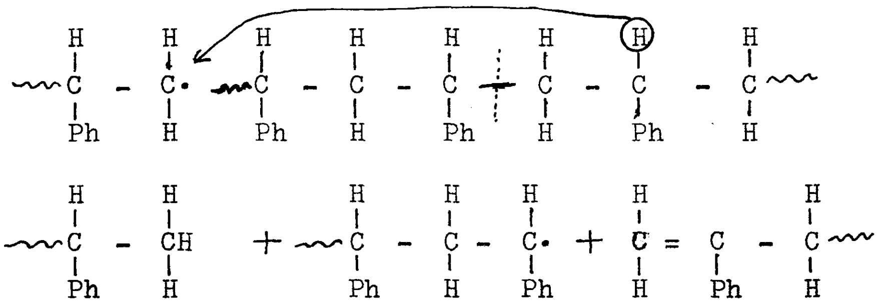
Madorsky[5] considered the rapid drop in molecular weight may be due partially to scission at "weak links" in the polymer, but is mainly caused by thermal scission in the chain. As a result saturated, unsaturated and free radical ends are formed. A small loss of weight takes place due, partly to evaporation of fragments, but mainly to the escape of monomers and dimers which unzip at the free radical chain ends.

However, in some cases a hydrogen transfer causes a break.[27]

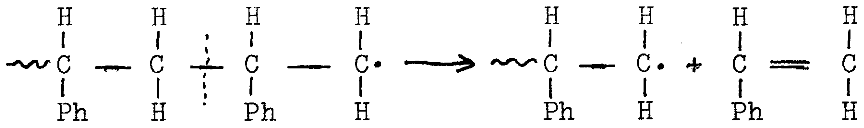
1. Scission without hydrogen transfer:



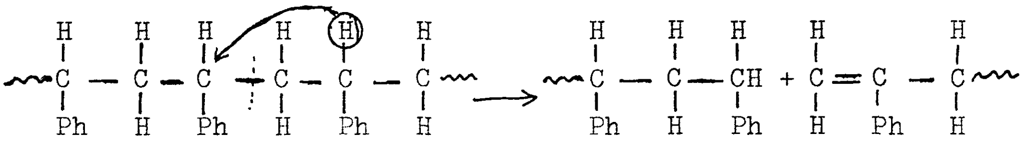
Each radical can remove a hydrogen atom from the same chain or from an adjacent one to cause a new scission:



Or the radical will unzip to produce monomer :



2. Scissions accompanied by hydrogen transfer:



The resulting unsaturated chain end is a labile site capable of depolymerisation.

(E) Simha, Wall and Collaborators [23,24,25]

Using a kinetic scheme involving end and random initiation, depropagation, transfer and termination, these workers predicted a rate maximum at or below 26 per cent conversion. This was at variance with Madorsky's experimentally obtained values of 30 - 40 per cent. Increasing the transfer parameter increased the maximum towards but never beyond 26 per cent.

Studies with deuterated polymers [26] have shown that when the(α) position of the styrene units is deuterated, the initial molecular weight drop is decreased by a factor of one half. This suggests at least, that intermolecular transfer occurs. The high monomer yield of 70% for poly (α - deuterostyrene) confirms that inter and intramolecular transfer is responsible for the nonmonomeric fractions. On the other hand, β - deuteration had no effect on the monomer production. This reaction was explained by the slower abstraction of the deuterium from the(α)site, thus favouring depropagation to monomer.

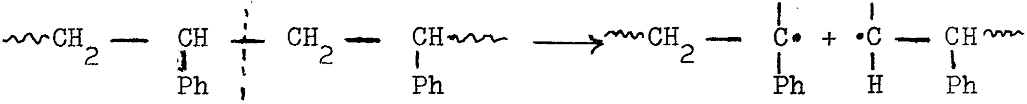
Wall et al., at the National Bureau of Standards, concluded that the degradation of polystyrene was a free radical chain reaction involving random scission, depropagation, inter and intramolecular transfer, and termination by disproportionation.

They rejected the "weak link" theory and suggested intermolecular transfer as being responsible for main chain scission. However, their mathematical treatment based on this explanation was not in complete agreement with experimental results, as pointed out above.

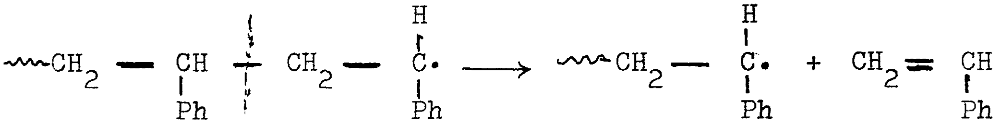
Wall and Flynn [28] agree with Madorsky's findings and explain the reaction for a polymer of large molecular weight as follows:

Initiation by a simple random scission at least to a certain degree, and depolymerisation at chain ends. A portion of the decrease in molecular weight as the result of the transfer reactions. The reaction might take place as follows:

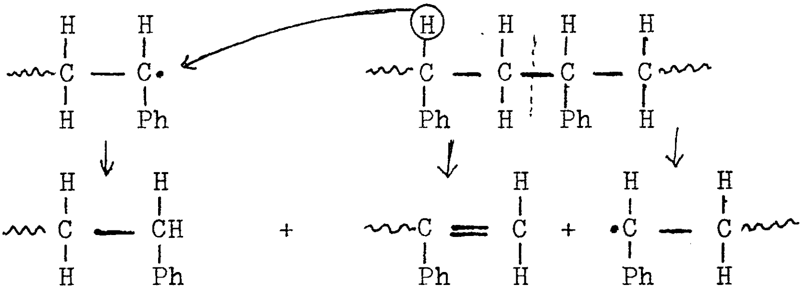
Initiation



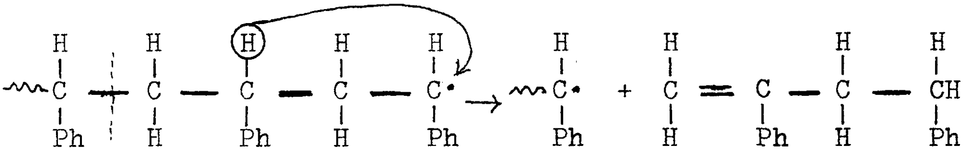
Propagation



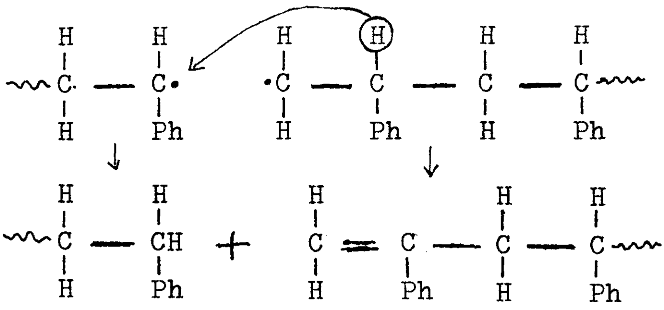
Intermolecular transfer



Intramolecular transfer



Termination (Disproportionation)



(F) Other Investigators:

MacCallum [29] used available results on polystyrene [10,11], polyethylene [30] and polypropylene [31] and calculated theoretically the weak bonds present in the macromolecules. But his treatment was sensitive to temperature and resulted in higher concentration of weak bonds at higher temperatures of degradation. This treatment was valid only when no volatilisation occurs.

Boon and Challa [32], Nakajima et al [33], studied isotactic polystyrenes prepared using the Zeigler - Natta catalysts and obtained an activation energy of 39 k cal/mole for random scission, in a zero order reaction. They found no evidence for 'weak links". They concluded that volatile products and chain fragments were formed by initiation at chain ends to give unzipping and intramolecular transfer.

Gordon [34] used results obtained by Grassie and Kerr [13,15], and Madorsky [21,22], in a kinetic treatment and showed that volatiles are produced by initiation at chain ends. In order to do this, a small amount of random splitting or "weak link" scission or transfer reaction were superimposed on the chain end initiated zipping reaction. But Grodon considered that involving "weak links" is an unnecessary complication.

Wall and Flynn [28] asserted that this result does not necessarily require that end initiation occurs in the original polymer.

Cameron [35] in a theoretical treatment on data from the literature showed that volatiles are produced by chain end initiation and not by random initiation during the degradation of polystyrene.

Cameron suggested that intramolecular transfer occurs and the giant radical either forms an active macroradical and a small volatile fragment, or the depolymerisation is terminated by evolving a small volatile radical leaving the main chain with an inactive unsaturated end which can reinitiate degradation.

Cameron and Kerr [36] studied the degradation of thermally and anionically prepared samples of polystyrenes at temperatures not exceeding 320°C at which volatile formation is negligible, and the weight loss was less than 3 per cent.

These authors found that anionic polystyrene prepared at low temperature contained no "weak links" and degraded in a simple random fashion, but the thermally prepared polymer showed the presence of "weak links". It was therefore, concluded that these "weak links" are distributed at random within the polymer chain, and some might be at chain ends.

McNeill and Haider [37] have estimated the unsaturation present in polystyrene, prepared by a cationic mechanism, by a method of using radiochlorine. It was found that unsaturation was exclusively terminal and every chain contained one unsaturated end. The fall in molecular weight on degradation of this polymer sample was shown to be similar to that reported for polymers prepared by free radical mechanism, despite the total absence of main chain unsaturation. It was concluded therefore, that the unsaturation present in the main chain of polystyrene prepared by free radical mechanism cannot be associated with "weak links".

McNeill and Makhdumi [38] have used the method of radiochlorine to estimate unsaturation in two types of polystyrene samples, one prepared by free radical mechanism using benzoyl peroxide as initiator and the other by thermal initiation. These authors have observed that the benzoyl peroxide initiated samples contained double bonds in the main chain and none present at chain ends. The thermally prepared samples however, have more double bonds and some of them are situated at chain ends.

Unsaturation was estimated in partially degraded samples and it was found, as predicted, to increase owing to double bonds formed by scission following intermolecular transfer.

It was also shown that temperature of polymerisation had no effect on the number of double bonds. It was therefore, concluded that double bonds were not associated with "weak links".

Richards and Salter [39] on the other hand, claim that both "weak links" and intermolecular transfer are contributing to the initial rapid fall of molecular weight of polystyrene.

In blends of poly (α- methyl styrene) with polystyrene, the former being less stable than polystyrene, induced its degradation at lower temperature and acted as a radical producing agent which initiates the polystyrene by hydrogen abstraction.

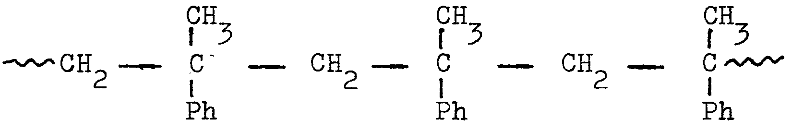
A polystyrene containing "weak links" at known positions along the polymer chain was synthesised by these workers. The "weak links" were in the form of head-to-head structures. This polymer being less thermally stable would also induce thermal degradation in normal polystyrene at low temperatures.

Polystyrene containing a specific number of thermally "weak links" at known points along the polymer chain was thermally degraded at temperatures between (280 - 285°C) in the presence of Carbon -14 labelled polystyrene as diluent or blend. Radicals produced from the scission at the specified "weak links" caused scission at the labelled polystyrene by transfer of a tertiary hydrogen atom. This was measured from the activity of the degradation products.

It is clear from the work on polystyrene, reviewed above, that the mechanism of the initial decrease in molecular weight during degradation is still unresolved: "weak links"; transfer, or both?

1.5 Degradation of Poly (α - methyl styrene)

The structure of this polymer differs from that of polystyrene by having a methyl group instead of the hydrogen atom in the α - position to the phenyl group [5].



$$\sim CH_2 - \overset{CH_3}{\underset{Ph}{C^{\cdot}}} - CH_2 - \overset{CH_3}{\underset{Ph}{C}} - CH_2 - \overset{CH_3}{\underset{Ph}{C}} \sim$$

The monomer yield is almost 100 per cent when this polymer is pyrolysed in a vacuum, in the temperature range 200 - 500°C.

Poly (α - methylstyrene) is considerably less stable than polystyrene [27]. This is believed to be owing to the presence of quaternary carbon, which weakens the adjacent c-c bond.

In contrast with polystyrene, when poly (α- methylstyrene) is pyrolysed below 500°C, hydrogen transfer is completely blocked from the sites of chain scissions by the presence of CH_3 groups in the α- position. Therefore, the ends of the chains at the points of scissions are in the form of free radicals which unzip into monomer. The zip length is estimated to be much longer than the degree of polymerisation and the radicals formed by scission depropagate to monomer.

However, transfer has been suggested to be taking place to a slight extent [28], especially at high percentage conversion, although it is difficult to distinguish between transfer and random scission.

1.6 Poly (m - methylstyrene) and Poly (P - methylstyrene):

Substitution of a hydrogen atom on the benzene ring in polystyrene was found to have less effect on the thermal behaviour of the polymer than when the substitution is made in the α- position on the polymer chain [5].

These two polymers degrade in the same way and yield similar amounts of monomer, and their mechanisms of degradation are considered to be similar.

From studies made on poly (m - methylstyrene) [27], it was found that its thermal degradation also resembled that of polystyrene. The rate curves indicate maxima at about 23 per cent volatilisation. Beyond that the rate decreases linearly to 100 per cent conversion, indicating a first order reaction. In the case of polystyrene however, the rate curves show maxima between 35-40 per cent volatilisation [5]. The monomer yield is slightly higher than that of polystyrene at 350°C.

1.7 Polypropylene:

In the degradation of polypropylene, transfer is a well established mechanism taking part in scissions of the main polymer chain [5]. This polymer differs from polystyrene in that it contains a methyl group instead of the phenyl group. The methyl group, being small, does not present much of an obstacle to a hydrogen transfer. Therefore, the scissions of c-c bonds in the chain are predominantly associated with hydrogen transfer at the site of scission. As a result the monomer yield is extremely small owing to the absence of an appreciable zip length. A wide spectrum of chain fragments of various molecular sizes is thus formed.

1.8 Polyisobutene:

In polyisobutene where each alternate carbon is quaternary, the chain c-c bonds are weaker than those of polypropylene [5]. Polyisobutene is less thermally stable than polypropylene.

On degradation polyisobutene produces about 18 per cent monomer at temperatures up to 500°C. The presence of the two methyl groups on every alternate carbon atom hinders transfer owing to steric effects. Therefore, scission of the main chain results in the formation of free radicals which unzip to yield monomers. However, an appreciable number of scissions accompanied by hydrogen transfer results in the formation of fragments.

McNeill and McGuchan,[48,49] have studied the thermal degradation of polyisobutene and found that it shows behaviour intermediate between that of poly (methylmethacrylate) and polypropylene or polyethylene.

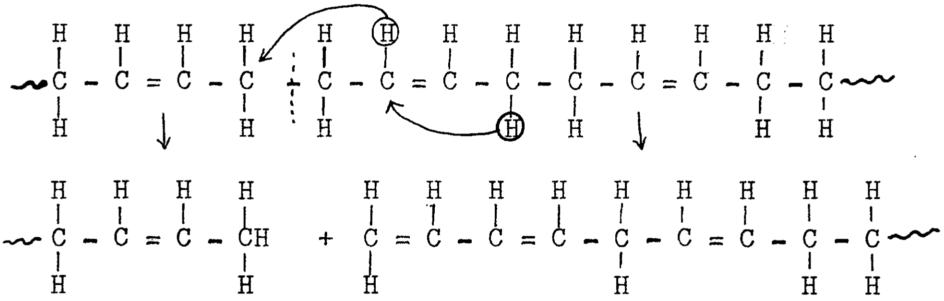
The pairs of methyl substituents in the polymer chain stabilize the polymer radicals and hinder transfer reactions to some extent. However, polyisobutene produces fragments as well as monomers and it resembles polystyrene in this respect.

These authors put more emphasis on intramolecular rather than intermolecular transfer. Hence, the mechanism of degradation of polyisobutene is believed to consist of initial thermal breaks of bonds at random in the chain, followed by depropagation to monomer and intra and intermolecular transfer reactions of the radicals thus produced to form the chain fragments.

1.9 Poly (butadiene)

Wall[20] has analysed the degradation products of this polymer when it was heated up to 400°C, and showed that the monomer yield was about 1 per cent.

The polymer is more thermally stable than polystyrene. Since the yield of monomer is very small,[5] it is assumed that most of the random scissions of the c-c bonds in the chains are accompanied by a hydrogen transfer.



The rate of thermal degradation of polybutadiene starts high and beyond 20 - 30 per cent loss of weight the rate decreases gradually and follows a straight line to 100 per cent loss.

1.10 Polyisoprene:

This polymer is less thermally stable than polyisobutene and polybutadiene.[4,5]

Polyisoprene between 300° - 400°C yields about 5 per cent monomer, and the monomer yield tends to increase at higher temperatures.

This is believed to be caused by dimerisation of the isoprene at lower temperatures. This is shown by the increase of dipentene in the products at lower temperatures.

The mechanism of breakdown of the polymer chain is considered to be taking place by scissions of c - c bonds either accompanied by a hydrogen transfer or not.

1.11 Butyl Rubber:

This polymer consists mainly of isobutene with a small amount of isoprene, about 1 - 5 per cent, copolymerised with it.

Its thermal behaviour is similar to that of polyisobutene.

1.12 Poly (methyl methacrylate):

Methyl methacrylate polymers have been extensively investigated over the past twenty five years by a number of workers.[40,41,42,43]

Grassie and Melville[40] have shown that the decomposition of poly (methyl methacrylate) is a radical chain depolymerisation process, taking place in two stages. The first is a fast reaction which takes place at low temperatures in the region of 240 - 270°C. This reaction consists of unzipping to monomer units of radicals produced exclusively at unsaturated end structures, if such structures are present, which depends on the mode of polymerisation. At temperatures above 300°C, the main backbone of the polymer becomes unstable, and a slow random scission of carbon-carbon bonds occurs producing radicals which again unzip to monomer as the sole product. The zip length is believed to be very large in both reactions, about 3000.

Melville and Cowley [46], noting the very high monomer yield, 95 per cent, and the fact that the molecular weight remains high during the decomposition, concluded that the initiation is proportional to the number of molecules, the zip length is so great that the molecules unravel completely, and the initiation probably occurs at chain ends.

However, it is observed in Grassie's results that the molecular weight of poly (methyl methacrylate) drops after 20 per cent conversion, especially in polymers having molecular weights over 90,000. This fall in molecular weight is greater than that expected from the theoretical curves plotted for cases where there is no transfer and no end initiation. [25]

Hart [44] has studied the change in molecular weight with increasing conversion at 300°C of two poly (methyl methacrylate) samples. Sample A was prepared by a free radical mechanism and its molecular weight was 150,000. Sample B was prepared under vacuum at -25°C to a molecular weight of 5×10^6.

On pyrolysis, it was observed that there was a sharp drop in the molecular weight of sample B up to 15 per cent volatilisation, then the rate of fall slows down.

The fall in molecular weight of sample A was not so drastic.

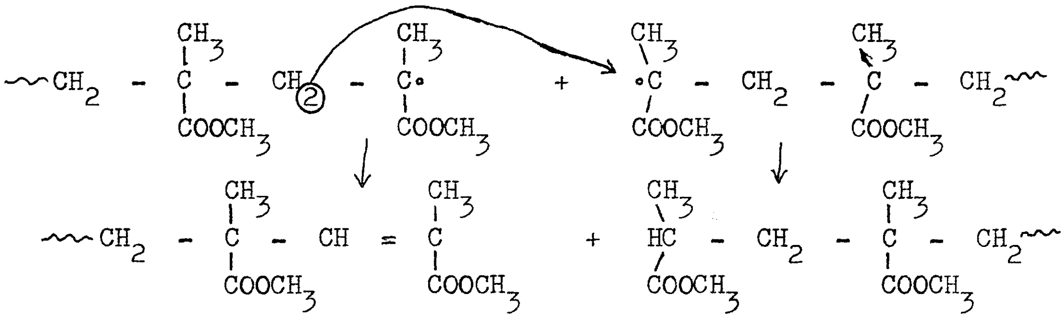
Cameron [43] studied the slow second reaction stage which takes place at temperatures above 300°C.

Cameron considered two possible processes which are often assumed to occur during the slow reaction of poly (methyl methacrylate) at elevated temperatures. The first, when the mean zip length is greater than the mean chain length, involves simple random initiation and unzipping to monomer, i.e., the molecules unravel completely before the depolymerisation is interfered with. But, secondly, if the zip length is shorter than the chain length, then a termination or transfer step must be introduced.

Cameron based his argument on the analysis of results obtained by other workers, and showed that during the second stage of the depolymerisation of poly (methyl methacrylate) there is a measurable contribution from chain end initiation until the zip length becomes equal to the chain length.[41] These labile chain ends must be produced by some mechanism during this slow phase, since all the original unsaturated chain ends have already been removed from the system during the first fast stage of reaction.

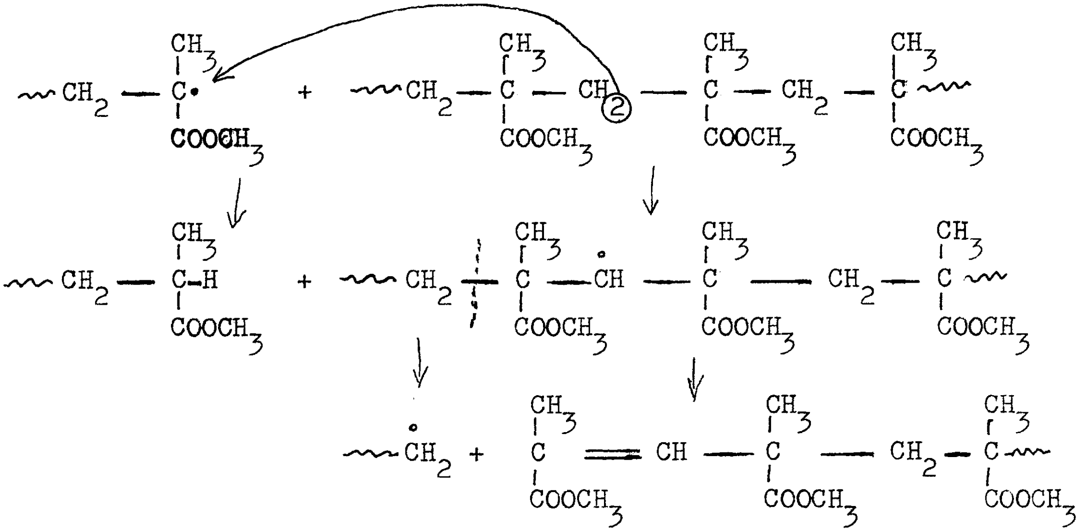
The following mechanism was then suggested to account for the production of these labile chain ends:

If the zip length ≪ chain length, then termination might occur:



A new unsaturated labile chain end is thus formed wich is capable of initiation reaction.

Also the radical might attack an inactive polymer molecule in the vicinity, produces an active radical and another unsaturated labile chain end:



The radical $\sim\sim\overset{\circ}{C}H_2$ is a very active radical, and it is more likely to take part in a transfer reaction or termination reaction rather than depropagate.[45]

In a study of photo-initiated thermal depolymerisation[46], transfer has been suggested as an explanation of the rate remaining in proportion with the square root of the intensity at low molecular weights and the existence of a kinetic chain length greater than the degree of polymerisation.

Simha and Wall[25] suggested a slight transfer could cause the premature decrease in molecular weight which has been discussed above in Grassie's results.

Transfer[28], therefore, may take place to a slight but important extent in the thermal degradation of poly (methyl methacrylate).

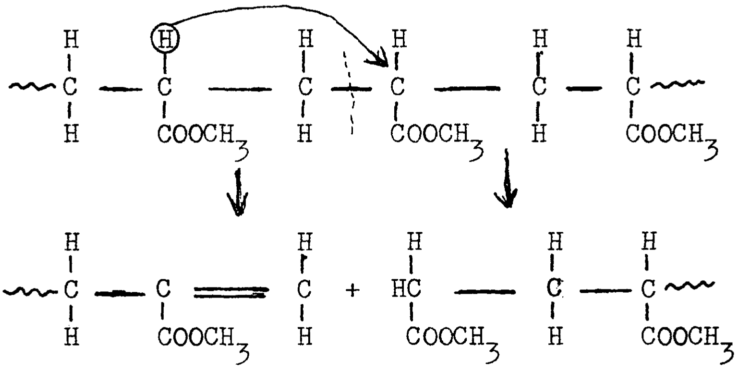
1.13 Poly (methyl acrylate):

This polymer yields very little monomer on pyrolysis. At temperatures between 300° - 400°C the yield is about 0.7 per cent monomer.[27]

The methyl group attached to the carbon atom in the backbone of poly (methyl methacrylate) is replaced by a hydrogen. This hydrogen, being a tertiary, is very reactive and takes part in reactions involving transfer.

Since a large amount of chain fragments are formed in the pyrolysis of this polymer, the following mechanism is proposed by Madorsky.[27]

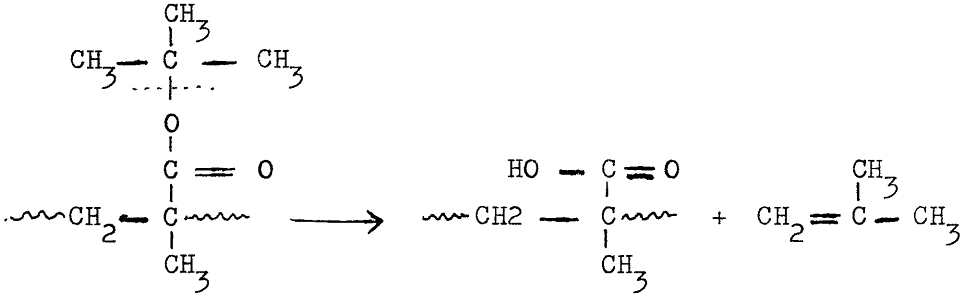
Scission by intramolecular transfer:



Methanol and carbon dioxide are also produced during the degradation of this polymer. Madorsky offers no mechanism for the formation of methanol, but he suggests that the process is not associated with the formation of free radicals during c-c bond scissions in the chain.

1.14 Poly (tert. butyl methacrylate):

This polymer is different from other polymethacrylates in the fact that it yields no monomer on degradation, despite the presence of a quaternary carbon atom.[63] Instead, isobutene splits off as a volatile fragment leaving behind an isolated unit of methacrylic acid in the polymer chain.

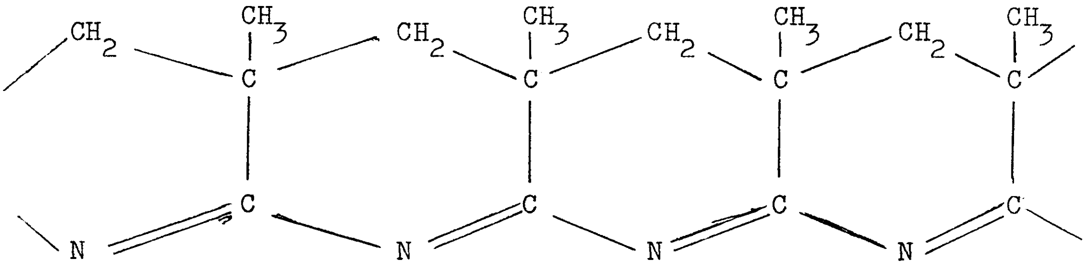


The elimination of isobutene is initiated autocatalytically to give an almost theoretical yield. The polymethacrylic acid which is left, yields water at about 200°C, to form six membered anhydride rings. These will undergo subsequent decomposition at elevated temperatures to give products which include carbon monoxide and dioxide.[59]

1.15 Poly (methacrylonitrile):

Grassie and McNeill [55,56], have investigated the degradation of this polymer at various temperatures. At low temperatures about (120° - 220°C), colour from yellow to red develops, without loss of volatiles, owing to impurities present in the monomer used to prepare the polymers. If the monomer was carefully purified, the colouration does not appear at low temperatures and the polymer degrades to almost 100 per cent monomer when heated at temperatures above 300°C.

The colouration is shown to be due to the progressive linking up of adjacent nitrile groups to produce conjugated carbon-nitrogen sequences.



The molecular weight drops slightly down to 25 per cent volatilisation.

The initial rate of volatilisation was found to be less for higher molecular weights when the polymer was degraded under vacuum at temperatures of 256°C.

1.16 Poly (vinyl chloride) PVC :

On thermal degradation, PVC liberates hydrogen chloride leaving a coloured residue. It has been established that the colouration is caused by the formation of unsaturation in the polymer chain.

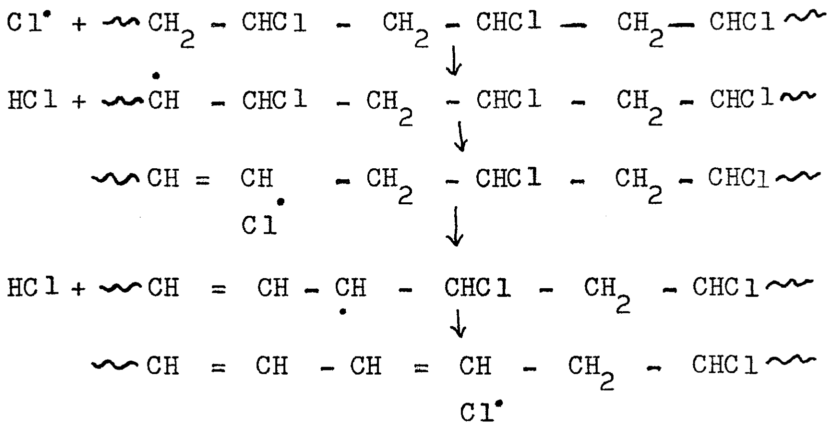
$$\sim \mathrm{CH_2 - CHCl - CH_2 - CHCl} \sim \xrightarrow{-\mathrm{HCl}} \sim \mathrm{CH = CH - CH = CH} \sim$$

At elevated temperatures, cross-linking takes place through the polyene rearrangement, benzene and hydrocarbons are produced leaving a carbonaceous residue.

Stromberg et al [50] studied the thermal degradation of PVC and proposed a radical mechanism by which HCl is produced as shown below :-

Initiation: $\mathrm{PVC} \longrightarrow \mathrm{Cl}^\bullet$

Propagation:



$$\mathrm{Cl^\bullet} + \sim\mathrm{CH_2 - CHCl - CH_2 - CHCl - CH_2 - CHCl}\sim$$

$$\downarrow$$

$$\mathrm{HCl} + \sim\mathrm{\dot{C}H - CHCl - CH_2 - CHCl - CH_2 - CHCl}\sim$$

$$\downarrow$$

$$\sim\mathrm{CH = \underset{Cl}{\dot{C}H} - CH_2 - CHCl - CH_2 - CHCl}\sim$$

$$\downarrow$$

$$\mathrm{HCl} + \sim\mathrm{CH = CH - \dot{C}H - CHCl - CH_2 - CHCl}\sim$$

$$\downarrow$$

$$\sim\mathrm{CH = CH - CH = \underset{Cl^\bullet}{CH} - CH_2 - CHCl}\sim$$

Termination: $Cl^{\circ} + Cl^{\circ} \longrightarrow Cl_2$

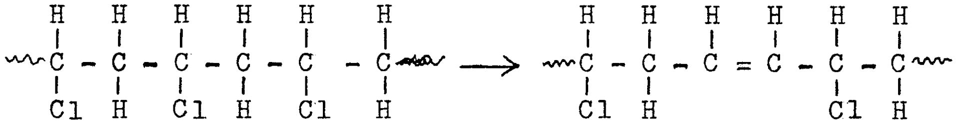
$$R_1^{\bullet} + R^{\circ}_2 \longrightarrow R_1 + R_2 \text{ or } R_1R_2$$

$$R^{\bullet} + Cl^{\bullet} \longrightarrow R\,Cl$$

where $R^{\bullet}$ = Polymer radical, R = Polymer molecule.

The evidence for this mechanism is circumstantial, rather than conclusive.

Another possible reaction mechanism for the dehydrocholorination of PVC at temperatures below 300°C is as follows: [5] The C - Cl bond is the weakest in the polymer, so that it is the first to rupture. This is followed immediately by an abstraction of hydrogen atom from an adjacent carbon and formation of a double bond in the chain.



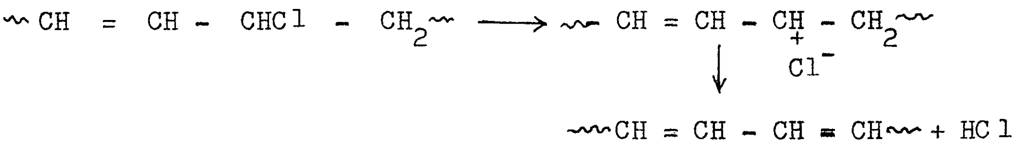
The chlorine atoms in β - position to the double bond are now more likely to break away from the carbon atoms to which they are attached than the other chlorine atoms. Thus, the process of formation of HCl and of conjugated double bonds could proceed by a chain reaction without the existence of a seperate chlorine free radical as an intermediate.

Bamford and Fenton [64] degraded PVC in labelled toluene at 180°C. It was observed that the radio-active atoms from the toluene became incorporated into the polymer chain, and the amount of activity in the polymer chain increased linearly with extent of dehydrochlorination.

It was therefore concluded that the degradation of PVC involved free radical intermediates.

McNeill and Neil [51] in a recent communication have shown that when a mixture of PVC and PMMA is degraded in the TVA apparatus [58,59], abnormally early degradation of PMMA was caused by chlorine radicals migrating from their sites on the PVC and abstracting hydrogen atom from the PMMA leading to a macroradical which undergoes scission and depolymerisation.

Marks et al [52] have suggested that PVC degrades by an ionic mechanism:



$$\sim CH = CH - CHCl - CH_2\sim \longrightarrow \sim CH = CH - \underset{+}{CH} - CH_2\sim \quad Cl^-$$

$$\downarrow$$

$$\sim CH = CH - CH = CH\sim + HCl$$

A third view, suggested by Druesdow and Gibbs [53], is that dehydrochlorination of PVC polymers may be initiated without the intermediate formation of either radicals or ionic species. The loss of HCl is initiated at a labile centre in the molecule by a unimolecular process. In this mechanism the chlorine radical or ion is not fully separated from the PVC molecule and does not migrate, but tends to attack the adjacent hydrogen.

It seems therefore, that there is no agreement on the mechanism of HCl liberation in the process of PVC degradation.

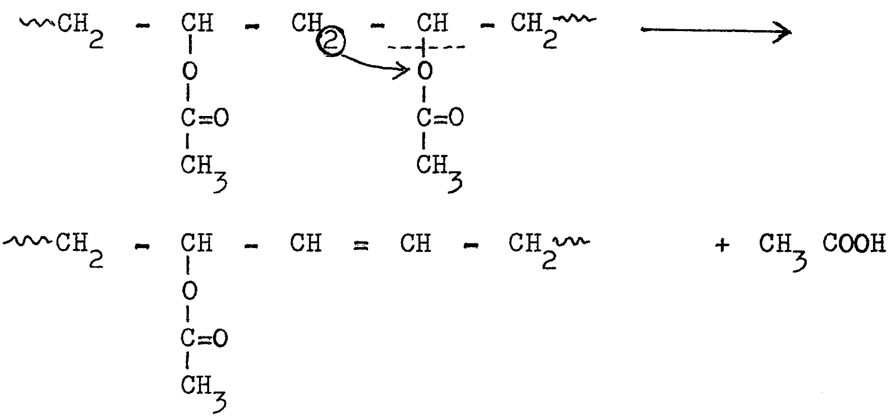
1.17 Poly (vinyl acetate) and Poly (vinyl alcohol):

Grassie[54] studied the degradation of poly (vinyl acetate) and found that this polymer when heated above 190°C decomposes into acetic acid and polyacetylene. Acetic acid was found to be produced almost quantitatively.

Servotte and Desreux[60] recently reported 95 per cent yield of acetic acid when poly (vinyl acetate) was degraded at 300°C, under high vacuum.

The mechanism proposed by Grassie is a chain reaction which is initiated by the loss of an acetic acid molecule at the end of the polymer chain, and the formation of a double bond.

Formation of acetic acid by a chain reaction in the pyrolysis of poly (vinyl acetate) could also be initiated at sites other than ends, by the scission of a C - O bond followed by an abstraction of hydrogen from an adjacent carbon to form acetic acid:



$$\sim CH_2-CH(OCOCH_3)-CH_2-CH(OCOCH_3)-CH_2\sim \longrightarrow \sim CH_2-CH(OCOCH_3)-CH=CH-CH_2\sim + CH_3COOH$$

Thus double bonds are formed in the main chain. The C - O bond in β-position to the double bond is weak and breaks to form another acetic acid molecule.

Thermal degradation of poly (vinyl alcohol) at low temperatures results in the elimination of water.[3,5,66] The degradation of this polymer apparently follows the same mechanism of a substituent reaction as in the case of poly (vinyl acetate). The hydroxyl group abstracts a hydrogen and forms a water molecule. A wide range of minor products are also observed.[62]

Chapter Two

Apparatus and Experimental Technique

2.1 Thermal Volatilization Analysis (TVA):

The fundamental features of TVA apparatus are described in detail by McNeill elsewhere.[58,59]

In this work the TVA apparatus, with some modifications, has been used very widely as the primary means of carrying out degradation. Therefore, it is thought useful to describe the apparatus in relation to the modifications made to increase its sensitivity for detecting very small amounts of volatile products.

A - Principle

The sample is heated in a continuously evacuated tube at a linear rate of temperature rise, or at isothermal temperatures. Pirani gauges are situated between the sample tube and the cold traps of the vacuum system and these respond to the increase in pressure when degradation products are distilling from the hot zone into the cold trap. The Pirani output, which is recorded as a function of temperature (time), is related to the rate of degradation on a non-linear scale which is compressed at higher outputs and also varies from one product to another.[65]

B - Apparatus

The apparatus used is shown in (fig. 2.1). The oven (A) and linear programmer designed by Perkin-Elmer for the model F11 Gas Chromatograph were used. The temperature range was up to 520°C. The degradation tube (C) was 6 inches long and constructed from a pyrex Quickfit FG35 flange fitted with a flat base. The lid (E) was constructed from two FG35 flanges at right angles, with a B14 socket (F) at the top for temperature calibration purposes as well as a site for fitting a Pirani head (P) during degradation experiments. The degradation tube went through a water cooled jacket (D) before it entered the oven. Thus the upper part of the degradation tube is kept cooled to prevent the grease at the flanged joint from softening during the course of an experiment. This set up is connected to two paralled "U" shaped cold traps (T) by a narrow bore tube (M) of 3 mm internal diameter. The cold traps (T) were provided with outlets (R) to facilitate collection of degradation products. Alternative Pirani gauge sites, before and after the cold traps, were provided at (G, H and J).

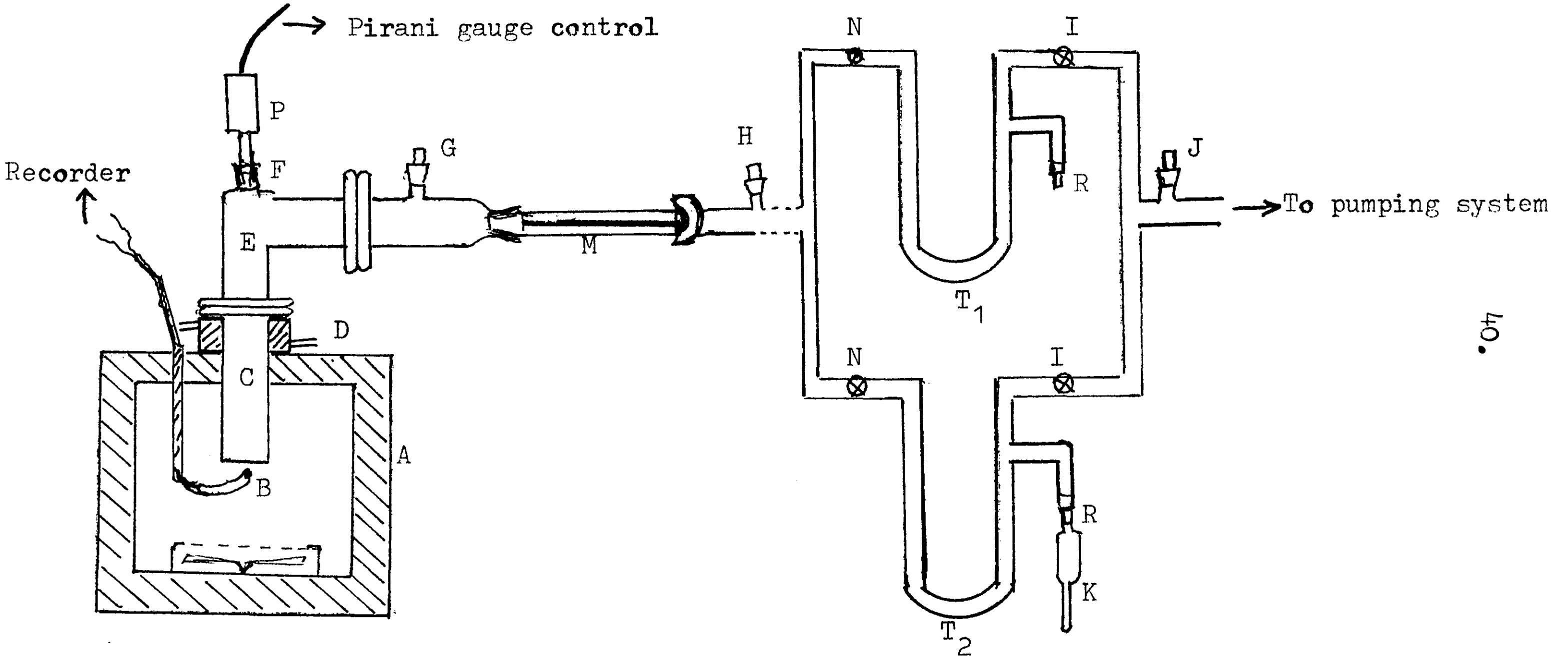


Figure 2.1 The TVA Apparatus Layout.

A. Oven.

B. Chromel-Alumel Thermocouple Junction.

C. Degradation Tube.

D. Cooling Jacket

E. Removable, Flanged Lid

F,G,H,J,R. B14 Ground Glass Sockets.

P. Pirani Gauge Head.

M. Narrow bore tube (3 mm inside diameter).

N,I. two way tap.

K. Finger tube for products collection.

T_1, T_2 cold traps.

The vacuum system in general was constructed of pyrex glass medium wall tubing of 0.5 inch internal diameter.

High vacuum was maintained by liquid nitrogen traps and vacuum pumps (Edwards model E01 vapour diffusion pump, backed by a model 2 SC20A rotary oil pump).

An Edwards "Speedivac" model 8-2 Pirani gauge control unit with provision for the use of two heads (model G5-C2) was employed.

C - Modifications:

In order to increase the sensitivity of the TVA apparatus to its maximum, three simple modifications were introduced:

1 - The Pirani head was placed at (F), see fig. 1, near to the sample. This increases the response of the Pirani gauge to volatile products coming off the sample, since McNeill and Neil [65,67] have shown that there is a gradient of pressure increasing from the cold trap towards the sample site. Thus the pressure at (F) is higher than that registered at (G).

2 - A six inches long narrow bore tube, 3 mm internal diameter, was inserted in position (M). This was found to be sufficient to increase the response of the Pirani

without causing any appreciable delay in pumping down the volatile products from the hot zone to the cold trap, especially when small samples are degraded. Thus T_{max}, the temperature at which the rate of volatilisation reaches a maximum, is not shifted when small sample sizes are degraded. But when a large sample, 20 mgs or more, is degraded a slight delay in pumping out the volatile products caused a small shift in T_{max}, by about 3^{o} - 5^{o}C, to higher temperatures.

3 - The Pirani output was fed to a recorder giving, at maximum sensitivity, 1 mv full scale deflection (f.s.d.).
For the larger sample sizes studied, 10 mv f.s.d. was used. The Pirani gauge response is non-linear for high rates and it is very compressed at high pressures. However, it may be considered as fairly linear at low output up to 2mv. This has been shown for styrene monomer, for example, by McNeill and Neil.[65,67]
Therefore, when a very small sample size of polymer is degraded the volatile products caused a response of less than 1mv on the recorder chart, so that the response for the small samples could be assumed to be a linear function of rate of volatilisation.

By making these simple veri~~fic~~ations to the apparatus it was found possible to degrade a very small weight of polymer, as small as 5 μg in the case of polystyrene, and still get very well defined peaks.

A Rikadenki 3-pen recorder, model B341, was used to record the emf output of the Pirani gauge and of the thermocouple.

2.5: 1 potential divider was provided for the thermocouple channel to enable a full scale deflection of 25 mv to be obtained.

The chart speed normally used throughout the work was 40 cm./h ; other speeds were also available.

D - <u>Degradation Tubes</u>:

The degradation was carried out mainly in pyrex tubes with flat bases to make it easy to cast as uniform a film as possible.

To investigate differences in thermal behaviour for various film thicknesses without changing the sample size of the polymer, a number of tubes with various base areas were constructed.

Tube No. 1 in (fig. 2.2) had a flat base of area of approximately 10 cm^2, and was similar to (C) in (fig. 2.1).

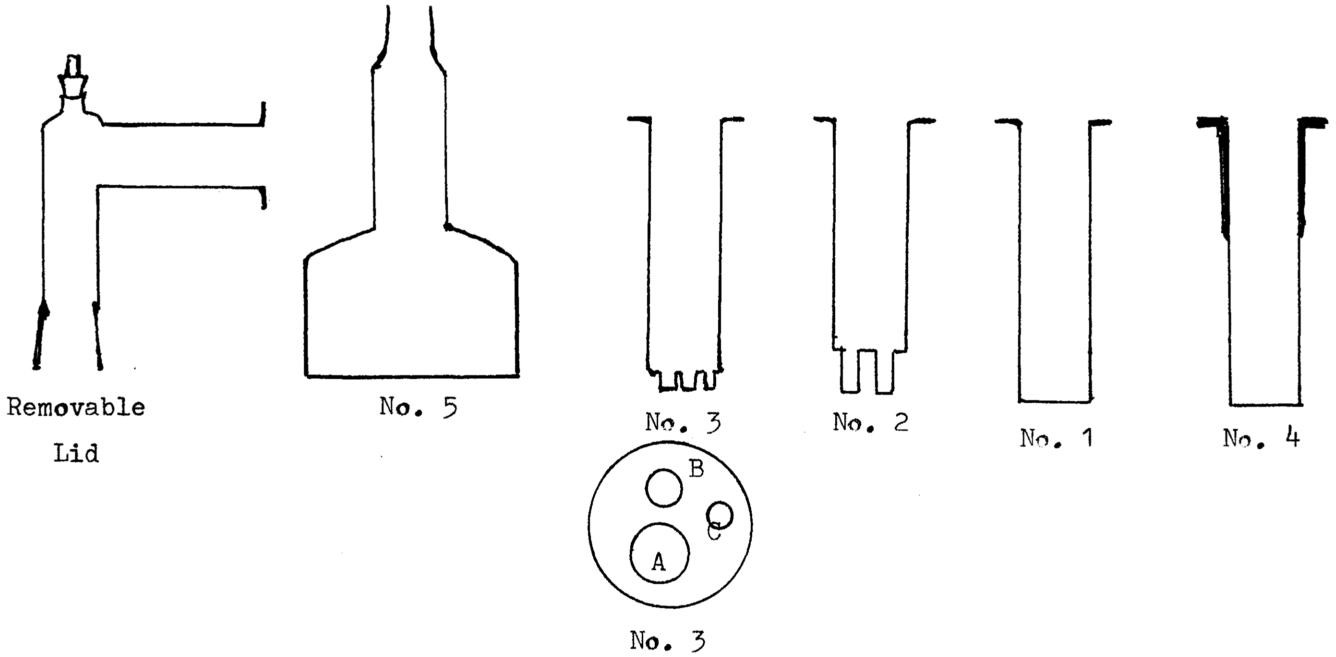


Figure 2.2 Degradation tubes.

1. Glass tube (base area 10 cm^2).
2. Glass tube provided with two limbs (1 cm^2 each).
3. Glass tube provided with three limbs (A, 1 cm^2, B, 0.4 cm^2 and C, 0.12 cm^2).
4. Stainless steel tube (10 cm^2).
5. Glass tube with large base area (about 64 cm^2).

No. 2 was provided with two limbs of area about 1 cm^2 each. Tube No. 3 had three limbs and was constructed as tube No. 2 except that it was fitted with three tubes of different diameters, (A) 9, (B) 7 and (C) 4 mm internal diameter, thus the areas of the bases of these small limbs were 0.64, 0.4 and 0.12 cm^2 respectively. The limbs were about 1 cm deep.

Tube No. 4 was similar to No. 1 in dimensions but made of thin wall stainless steel tubing, strong enough to withstand high vacuum without collapsing.

The large tube No. 5 was constructed from pyrex tubing of medium wall thickness. The base was a flat pyrex disc of 9 cm diameter. The top of the tube was fitted with a B34/35 Quickfit Cone, instead of the flange, to make it possible to insert it through the oven and the cold ring jacket.

The base area of this tube was about 64 cm^2. An extra lid E in (fig. 2.2), provided at one arm with a B34/35 socket, was constructed to be used with this tube.

2.2 Differential Condensation Thermal Volatilisation Analysis:

The vacuum system between the hot zone and pumps was split into four parallel lines, each of which consisted of two

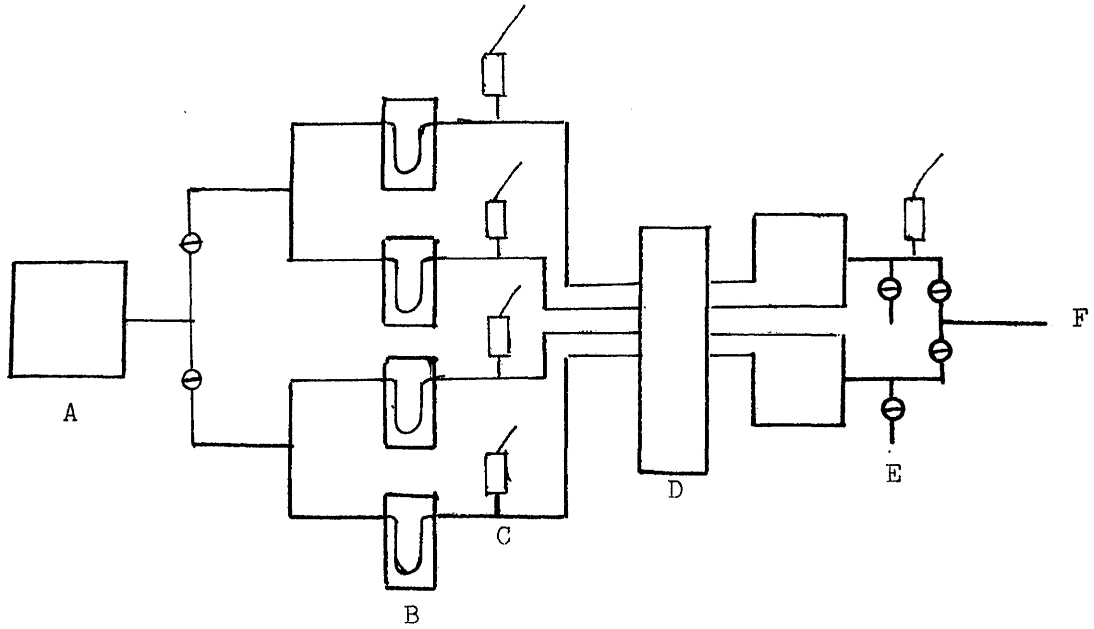


Figure 2.3 Differential Condensation TVA Apparatus.

A. Oven, Heated sample. D. Common Cold trap.

B. Secondary Cold trap E. Receiver for Products.

C. Pirani Gauge Head. F. To pumping system.

"U" shaped traps with Pirani gauge to record the pressure in the short line between them (fig. 2.3). The trap nearer the sample was maintained at 0, - 45, - 75 or - 100°C, the second trap is kept at - 196°C under liquid nitrogen. A fifth gauge was situated after the - 196°C traps.

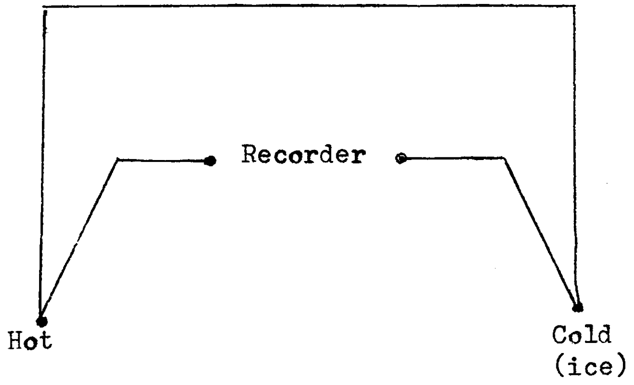
The Pirani gauges were connected to the control unit of a multipoint recorder through variable potentiometers adjusted so that the responses from the gauges were as close as possible throughout the pressure range when a completely non-condensable gas was passed through the system.[66]

2.3 Temperature Calibration:

Chromel - Alumel thermocouples (20 gauge, Leeds and Northrup Ltd.) were used.

The recorder was operated with a 10 mv range and 2.5 : 1 potential divider on the temperature channel.

The thermocouple circuit was as shown below:



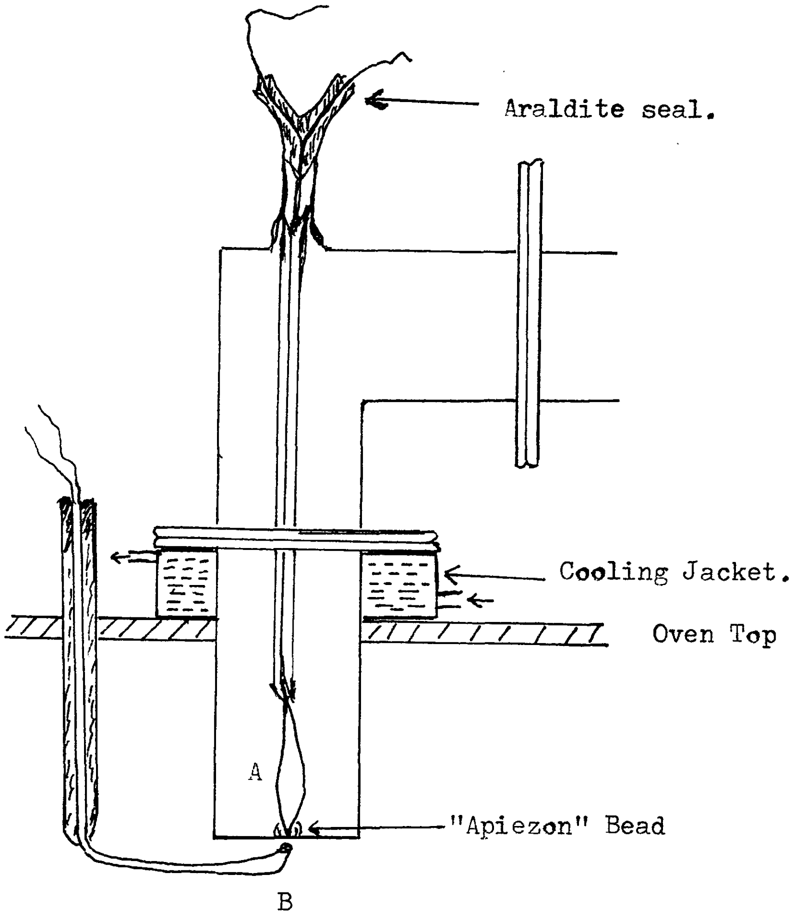


Figure 2.4 Arrangement for temperature calibration.

A. Thermocouple junction (inside tube).

B. Thermocouple junction (oven).

The reading obtained on the chart by applying known potentials through the potential divider to the recorder was determined and thus the chart reading could be related to temperature by the use of Chromel - Alumel thermocouple tables.

The temperature reading obtained during degradation was measured by the oven thermocouple B (figs. 2.1, 2.4) and recorded on the recorder chart. Since it was the sample temperature which was of interest, and this was different from oven temperature due to the thermal gradient across the base of the degradation tube, it was necessary to calibrate the tube for the temperature lag at the specified heating rate, 10°C/min., and at the isothermal heating temperatures used in this work, by comparing the outer thermocouple output with that of a thermocouple touching the inside surface of the tube base. The tip of the thermocouple on the inside was made slightly flat and was also made to exert a small pressure against the tube base to ensure good contact; again for the same reason a small bead of Apiezon "L" grease was put at the point of contact between thermocouple and the tube base, which also simulated molten polymer samples (fig. 2.4).

Several calibration runs were made under high vacuum

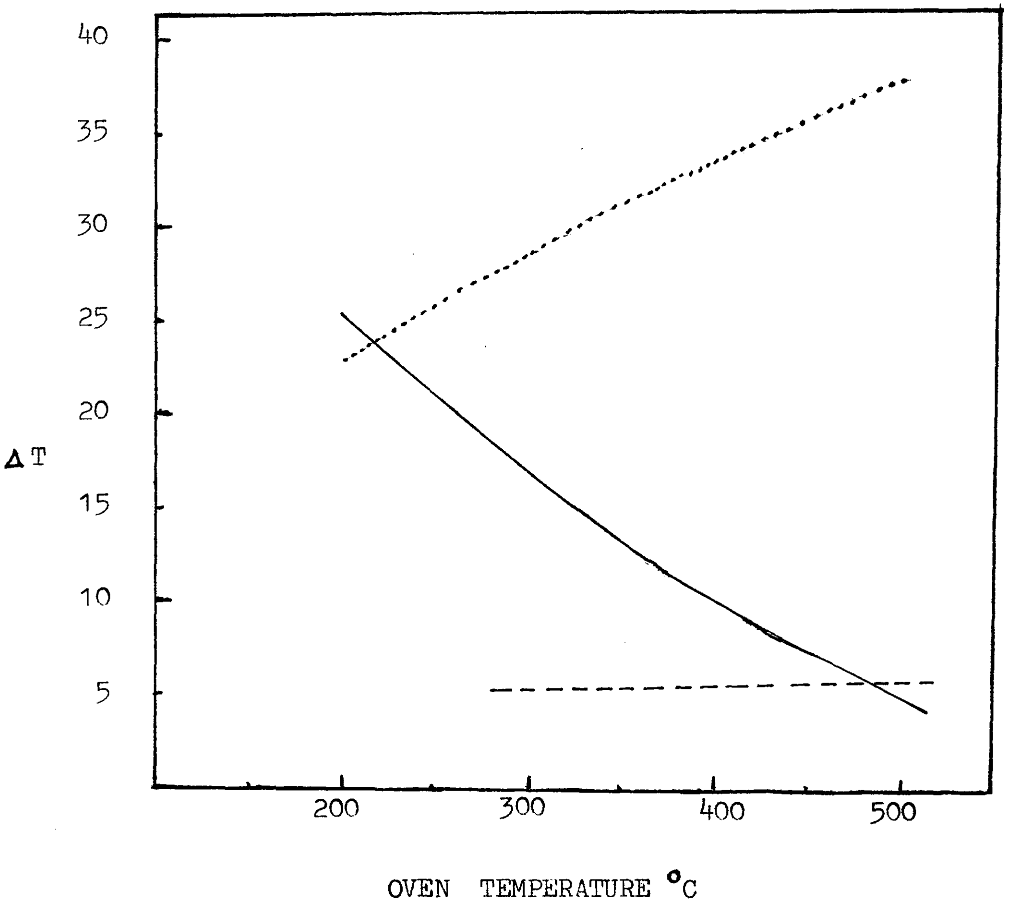


Figure 2.5 Temperature calibrations for degradation tubes:

———	Tube No. 1
....	stainless steel tube .
-------	tube No. 2

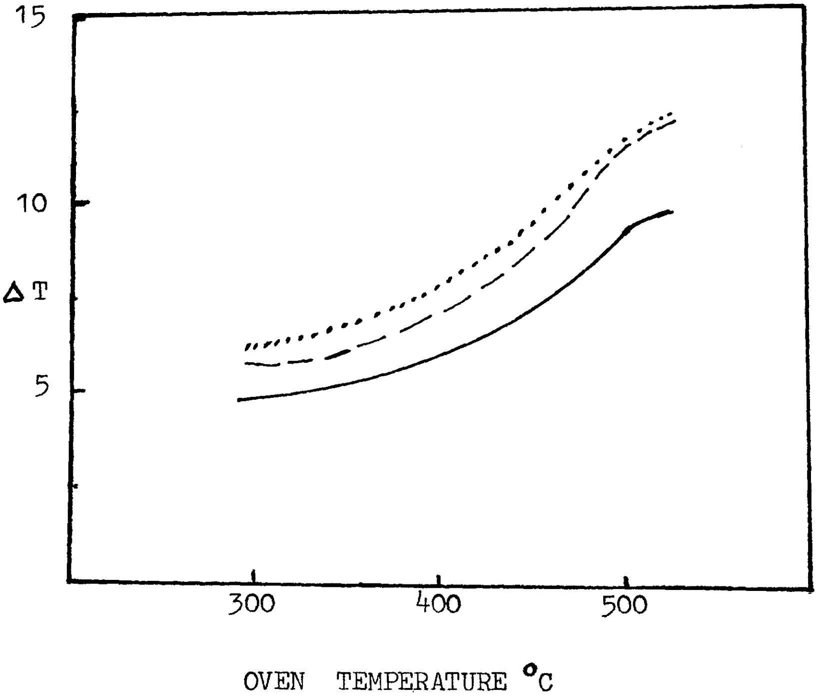


Figure 2.6 Temperature calibration for tube No. 3.

——— Limb (A)

------ Limb (B)

•••••• Limb (C)

for each tube and for each limb. Graphs were plotted for temperature lag against oven temperature, (figs. 2.5 and 2.6).

2.4 Thermogravimetry (TG):

TG is a well established thermal analysis technique in which the weight of a sample is continuously recorded while the temperature is raised linearly. TG curves quickly provide a measure of the total extent of degradation, but require to be differentiated to obtain rates of reaction. The temperatures at which rate maxima occur are much less accurately measured than in TVA. A more detailed comparison between the two techniques is given by McNeill [65] and Neil [67].

TG curves were obtained from a Du Pont 900 Differential Thermal Analyser with accessory 950 TG module. The thermobalance was of the null deflection type employing a photoelectric system to detect and compensate for movements of the quartz beam from which the platinum sample pan was suspended. The heat was supplied by a programmed furnace into which the silica tube enclosing the balance beam, sample pan and thermocouple slid horizontally.

Samples were degraded in an atmosphere of nitrogen flowing at 50 ml/min., or under vacuum which was as good as

10^{-4} mm Hg.

Thermogravimetry had the advantage that it could be used to study degradations at temperatures above 500°C.

2.5 Sample preparation:

Polymer samples were usually degraded in the form of films of various thicknesses. These films were prepared by delivering 1 ml of solution of appropriate concentration into the degradation tube. The solvent was removed by passing a slow flow of nitrogen gas over the surface of the base of the degradation tube, at room temperature, using the apparatus arrangement of fig. 2.7.

1 per cent polymer solutions were prepared in 10 ml standard flasks. Successive 10 fold dilutions, of the 1 per cent solution, were also prepared down to a 0.001 per cent concentration.

5 per cent solutions were also made to provide larger sample weights.

Sample weights varied from 10 µg up to 20 mgs in most cases, except for polystyrene were it was between 5 µg and 100 mgs, i.e. (5×10^{-6} and 10^{-1}g).

The films are formed at the base of the degradation tube when the solvent is swept off. More solvent is given off by the

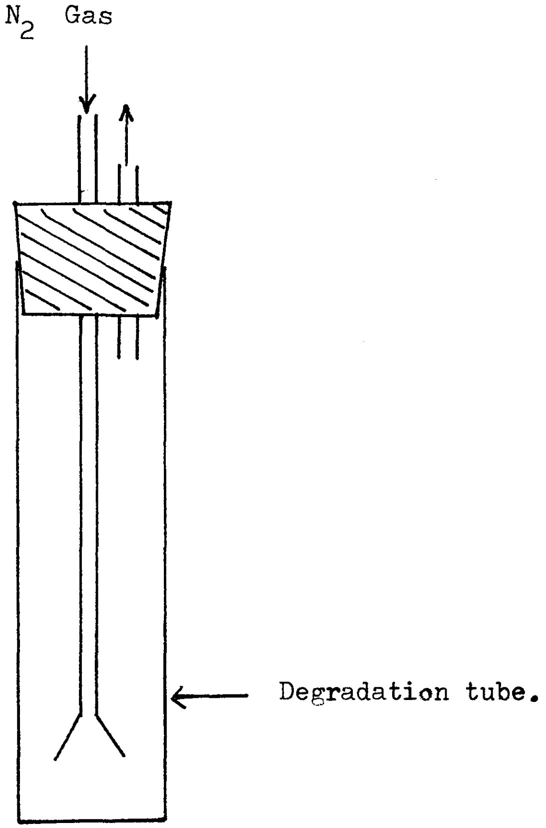


Figure 2.7 Arrangement for film preparation.

film when it is exposed to high vacuum and the rest of the retained solvent is released in the early stages of temperature rise.

Polymer samples in the form of fine powder (or small pieces for polymers which could not be ground) were degraded in order to compare their results with those obtained from very thin films. Extra care was taken to ensure an even distribution of the polymer powder onto the base of the degradation tube, and not on the inside walls. This precaution is important to secure uniformity of sample temperature during degradation.[65]

Various solvents were used to make up the polymer solutions, such as benzene, toluene, acetone, cyclohexanone, 1,2 - dichloroethane, ethyl methyl ketone and others which will be mentioned in each case. These solvents were of A.R. grade, and used with no further purification unless it is otherwise stated.

The sources of the various polymer samples, and the details of preparation of those made specially for this study, are given in the appendix.

The usual procedure of degradation carried out throughout this work was that polymer samples were degraded either at the programmed heating rate of 10°C/minute or at various isothermal temperatures.

Chapter Three

Degradation of Polystyrene

3.1 The shift in the Rate Maximum Temperature (T_{max}) for polystyrene as Thin Films:

Polystyrene ($\bar{M}n$ 140,000) prepared by free radical mechanism (see appendix) was degraded in the form of films, using degradation tube No. 1 with 10 cm^2 base area (fig. 2.2). Sample weights varied from 5×10^{-6} gm up to 10^{-1} gm, forming film thicknesses from 10^{-6} cm up to 10^{-2} cm respectively.

The degradation was carried out under a programmed temperature rise of 10°C/min. in the TVA apparatus.

The graph of T_{max} against log (sample weight) was step shaped showing two clearly defined horizontal portions differing in temperature by about 60°C (fig. 3.1), the thin film portion of the graph being in the higher temperature region. The section on the graph related to thin films represents weights between 5×10^{-6} and 10^{-4} gm, i.e. thickness of about 5×10^{-7} up to 10^{-5} cm. This section is followed by a sharp drop in the region of 2×10^{-4} to 2×10^{-3} gm, then the curve levels off at constant T_{max} for larger sample sizes.

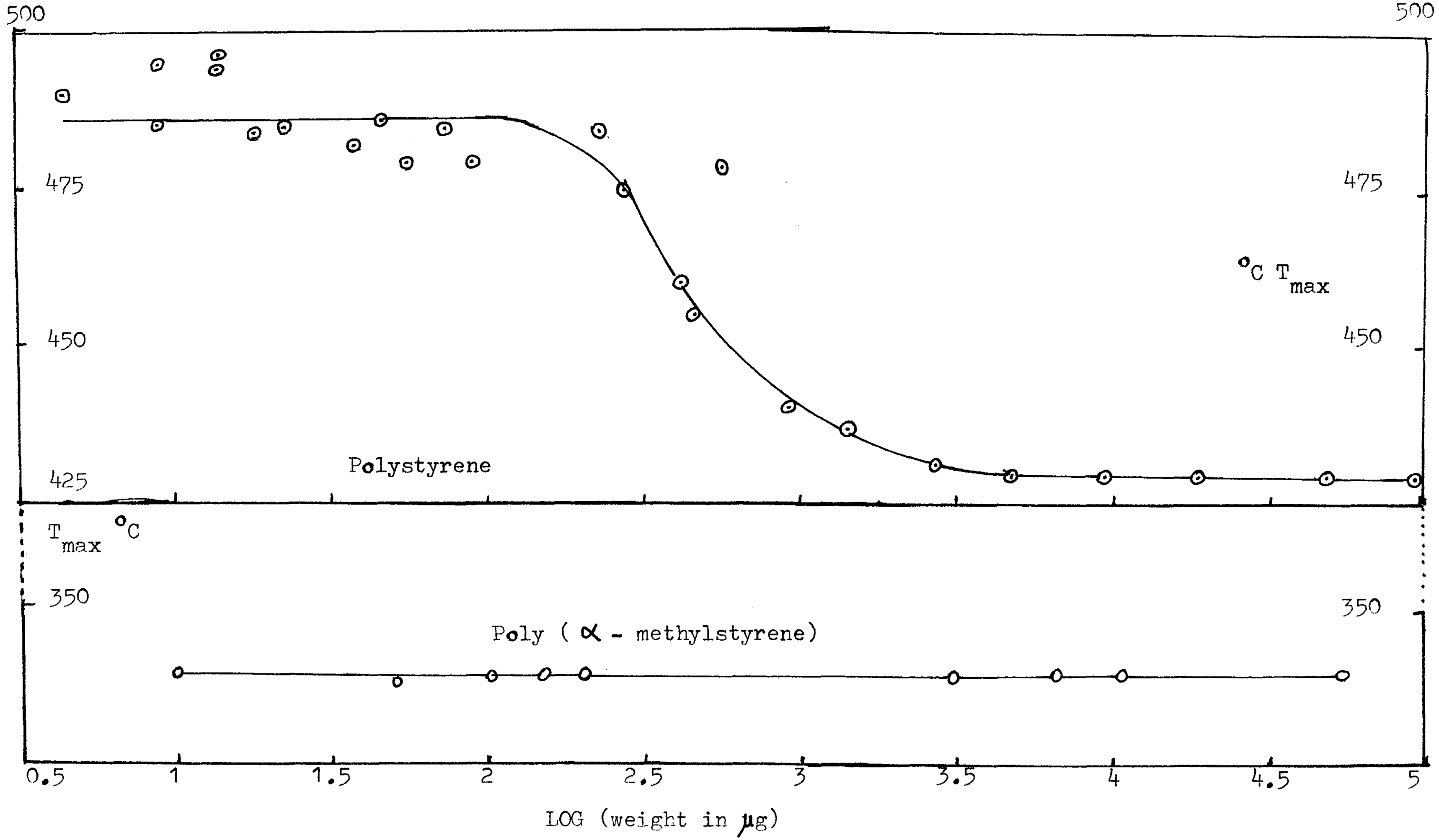


Figure 3.1 T_{max} Vs. log (sample weight) for films of various thicknesses degraded in tube No. 1 (10 cm^2) of polystyrene and poly (α - methylstyrene).

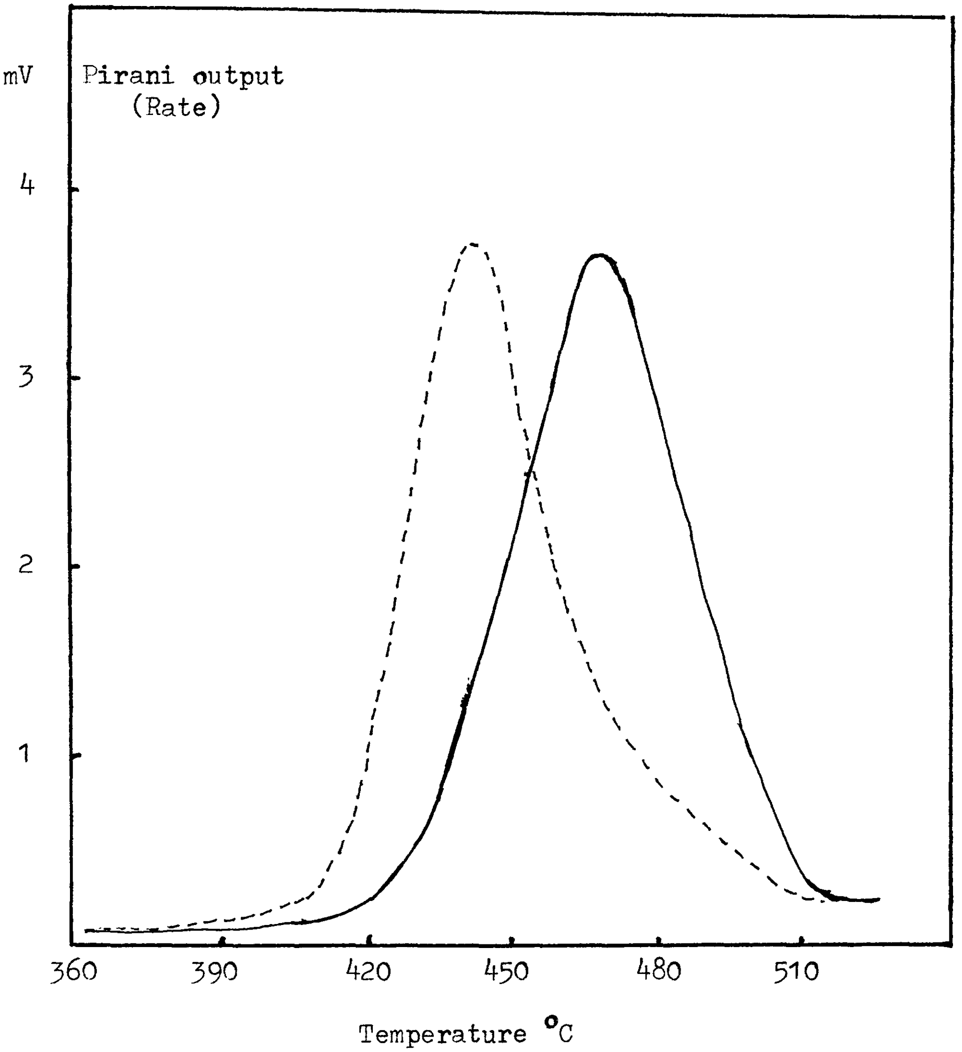


Figure 3.1a Degradation of 0.2 mg film samples of polystyrene (cationic $\overline{M}_n$ = 108,000).

——— film degraded in tube No. 1 (10 cm^2).

-------- film degraded in tube No. 2 (1.2 cm^2).

The same polymer was also degraded in the powder form and T_{max} was the same for small and large sample sizes, and corresponded to values of T_{max} represented by the lower section of the curve in (fig. 3.1).

3.2 Authenticity of the Thin Film Effect:

When extremely thin films of polystyrene, 10^2 - 10^3 Å thick, were degraded under vacuum in the TVA apparatus, the rate maxima temperatures, T_{max}, were observed to be higher by about 60°C than those for films more than one micron thick.

This remarkable phenomenon of apparently enhanced thermal stability of thin films was the subject of detailed investigation.

A number of tests were carried out to show that this effect was due to changes in the mechanism of breakdown of polymer molecules and not caused by other external factors related to characteristics of the apparatus or sample preparation.

a) Surface effects on glass were excluded when the same shift in T_{max} occurred when the polymer film was cast and degraded in a stainless steel tube specially constructed for this purpose, (fig. 2.2).

b) The possibility that the effect might be due to slow transfer of minute amounts of styrene monomer as a

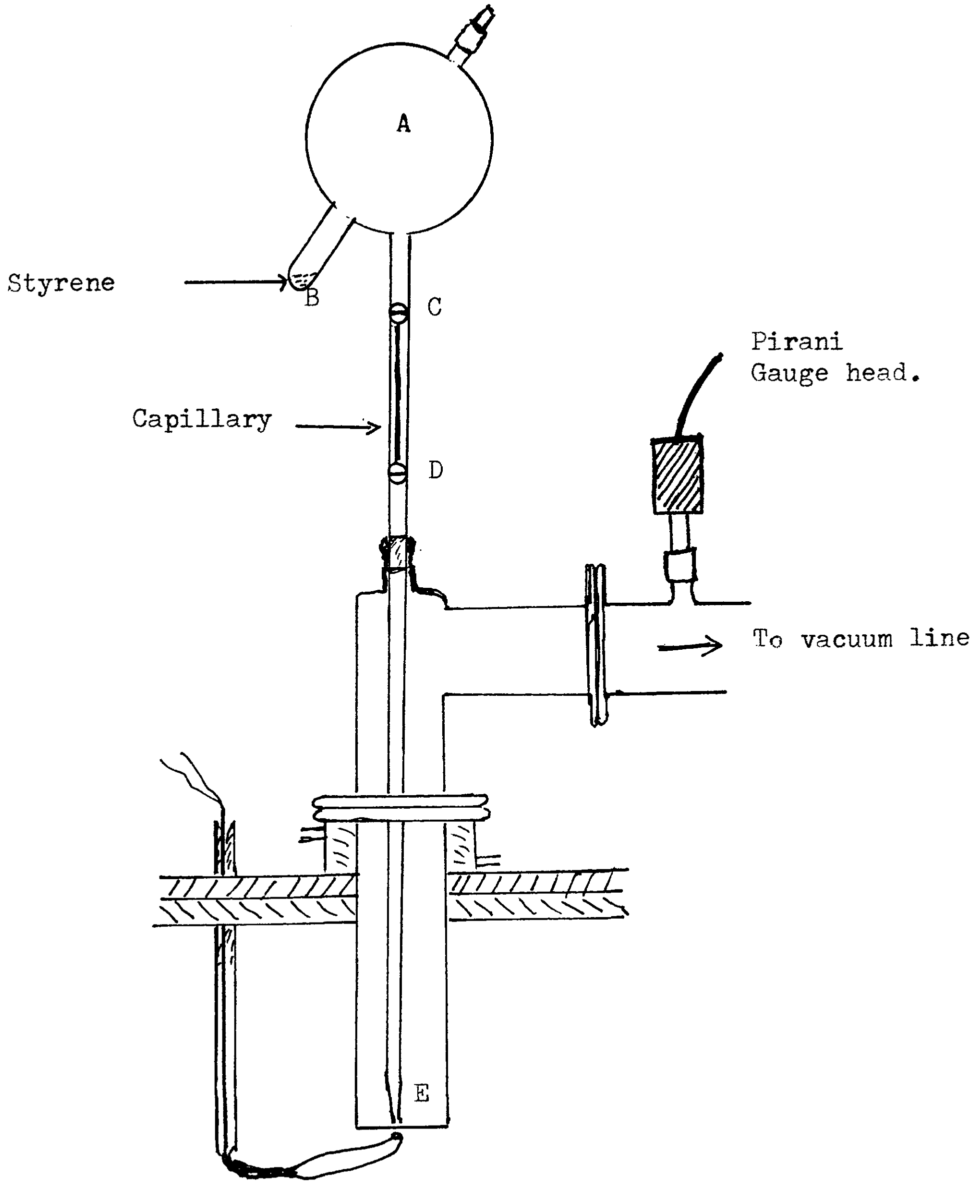


Figure 3.2 Arrangement for the Pirani Gauge response to styrene monomer.

product of degradation owing to adsorption on the walls of the apparatus, for instance, was tested by admitting very small amounts of styrene into the apparatus at 420°C at a given instant and noting the time taken for the Pirani gauge, some distance away, to respond.

The apparatus used in this experiment comprised a round bulb (A) in (fig. 3.2) of about 1 litre volume with a short side tube (B), constructed of pyrex glass. A tube 20 inches long was attached to it. It consisted of a 4 inches long capillary between taps (C) and (D), followed by a B14 air leak and a narrow tube the end of which (E) almost touched the base of the degradation tube.

A small amount of styrene monomer, 2 ml, was introduced into the side tube (B) and was completely degassed by freezing it and opening bulb (A) to the vacuum line several times. Finally, while the monomer was kept frozen, bulb (A) was opened again to the vacuum system until a high vacuum was obtained. Tap (D) was then closed and the monomer was allowed to thaw. Thus bulb (A) and capillary were filled with styrene vapour. Tap (C) was then closed; the oven temperature was brought up to 420°C. (D) was opened to let styrene vapour inside the capillary to pass through to the hot base of the degradation tube.

The response of the Pirani gauge was instantaneous in every case, indicating that slow transfer of products of degradation is not the explanation for the effect referred to above.

It was also observed that when a blank run was carried out, i.e. when there was no polymer sample in the degradation tube, adsorbed gases were released from the inside walls of the degradation tube only in the very early stages of temperature rise.

c) In a further test, a polystyrene thin film, of 0.01 mg sample weight, was preheated beyond its T_{max} and just before its complete conversion into volatile products, heating was stopped and the oven was allowed to cool down to room temperature. When the residual polymer was heated again, the TVA curve showed a small peak, due to products resulting from the minute residue, was observed (see fig. 3.3). This observation shows that the degradation is not complete until the TVA curve has reached the base line.

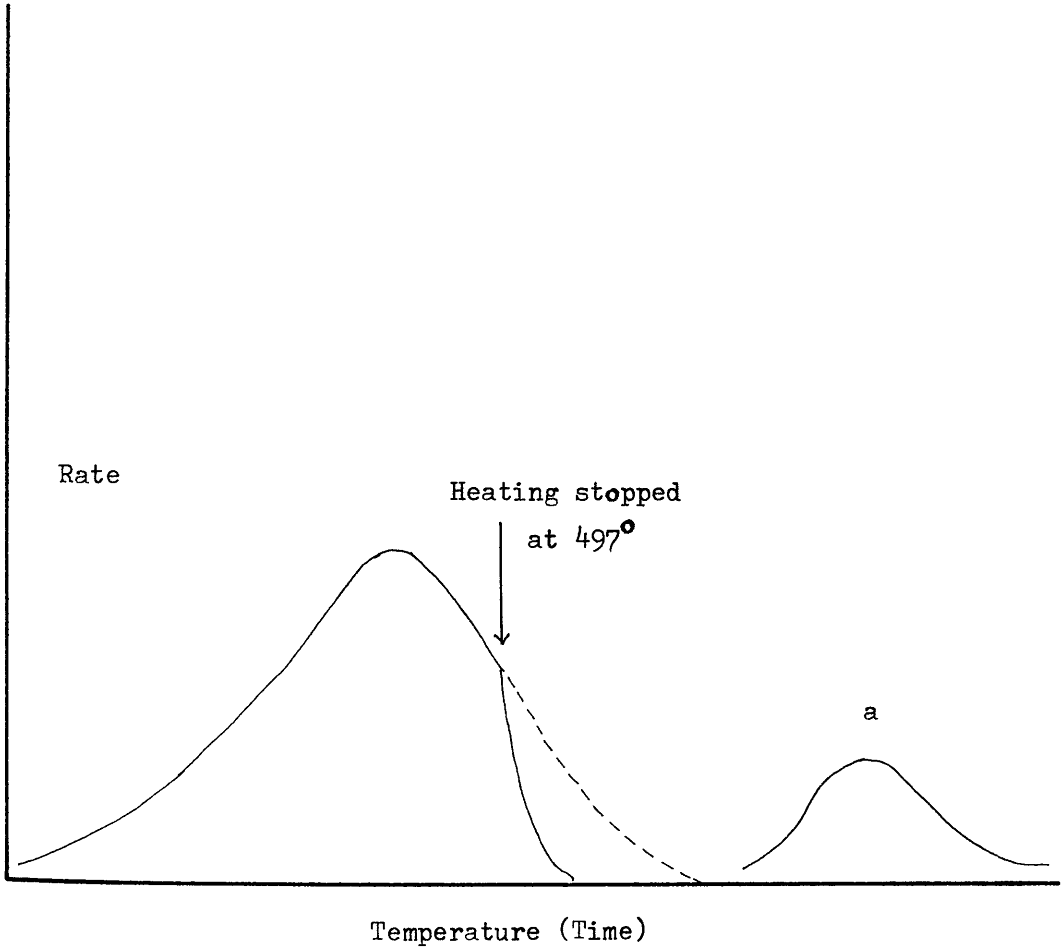


Figure 3.3 0.01 mg PS thin film heated at 10°/min up to 497°C and then cooled down to room temperature.

--------- if degradation was continued.

a, peak due to residual polymer when it was degraded again.

This would support the earlier experiment in that the removal of products is instantaneous and the time lapse for volatiles to travel from the hot zone to the cold trap is not long enough to allow for the wide shift observed in T_{max} along the temperature scale.

3.3 Possible causes of the shift in T_{max}:

A - Ease of volatilization from the polymer surface:

It is well established that free radicals are formed during the degradation of polystyrene (see Introduction). The smaller radicals, produced during the degradation, diffuse through the molten polymer mass causing further scissions by abstracting an α- hydrogen atom at sites on the same chain or on another molecule.

When the polymer is degraded as an extremely thin film it is possible, therefore, that the small radicals might escape from the vicinity of the polymer film surface without causing any further degradation in the neighbouring sites.

This was tested by attempting to cause some delay or to hinder the small radicals from escaping the film surface.

d. Coating the polystyrene film with a thermally more stable polymer:

Polyparaxylylene (PPX) which degraded at a higher temperature than that of polystyrene and did not interact with it, was used.

Thin films of 0.1 mg polystyrene were prepared as previously described and a thin covering of 50 mgs (PPX) in the form of thin sheets (since it was found difficult to grind (PPX) into a fine powder) was distributed so as to cover the polystyrene film.

However, T_{max} for polystyrene thin films showed the same shift as in the absence of (PPX) covering.

Individually degraded (PPX) and Polystyrene (cat. D.N. see appendix) showed T_{max} of 510°C and 430°C respectively.

A 0.1 mg polystyrene powder and 50 mg (PPX) placed at separate locations in the degradation tube No. 1 were degraded. The same sample weight of polystyrene film covered with the same amount of (PPX) was also degraded, and the T_{max} was observed to be higher by 30°C (fig. 3.4) in the latter case.

Since the peak for 0.1 mg polystyrene appeared only as a small sholder on the (PPX) peak, the experiment was

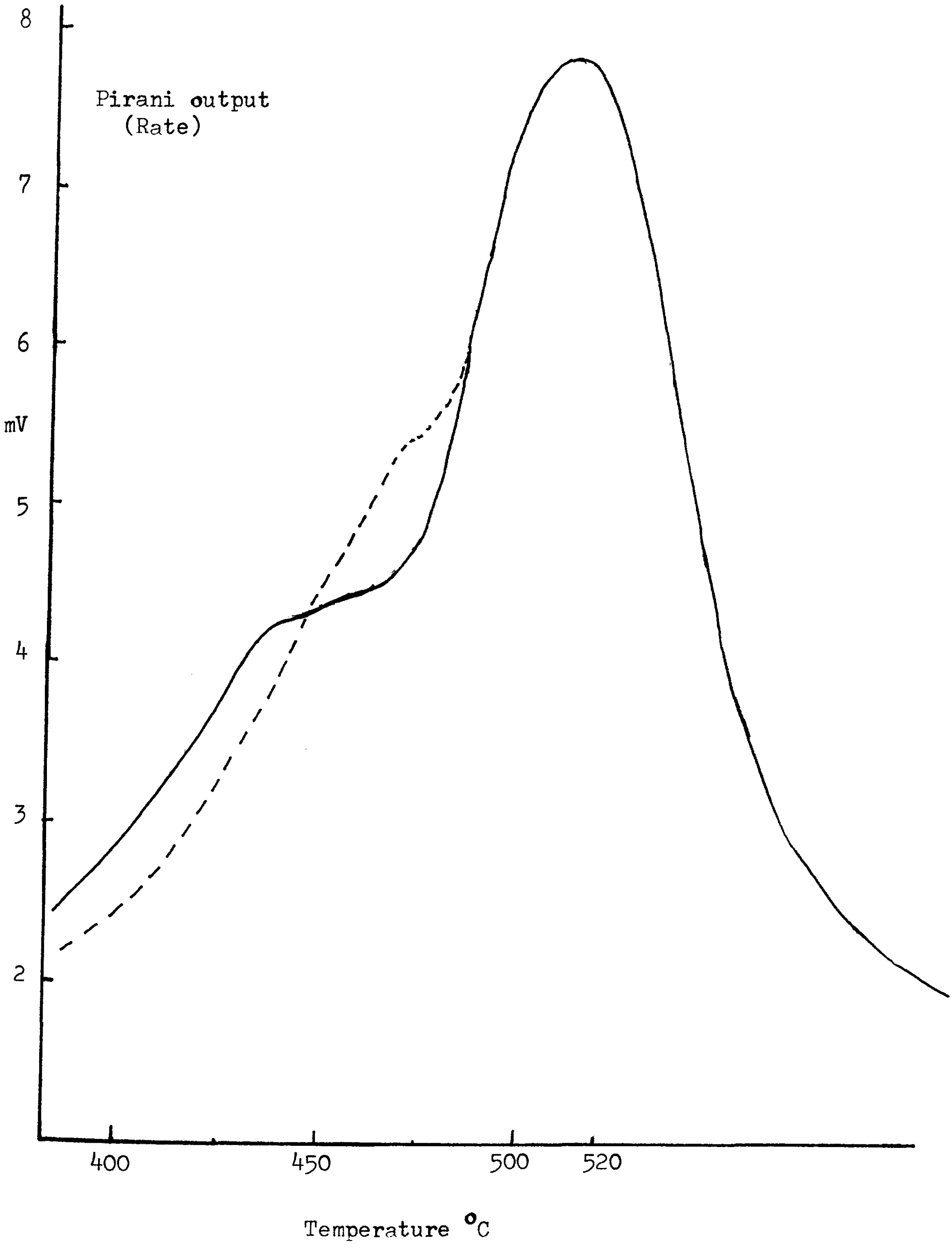


Figure 3.4 Degradation of 0.1 mg PS (cationic) covered with PPX.

——— 0.1 mg PS Powder + 50 mg PPX placed separated in tube No. 1

------- 0.1 mg PS film covered with 50 mg of PPX.

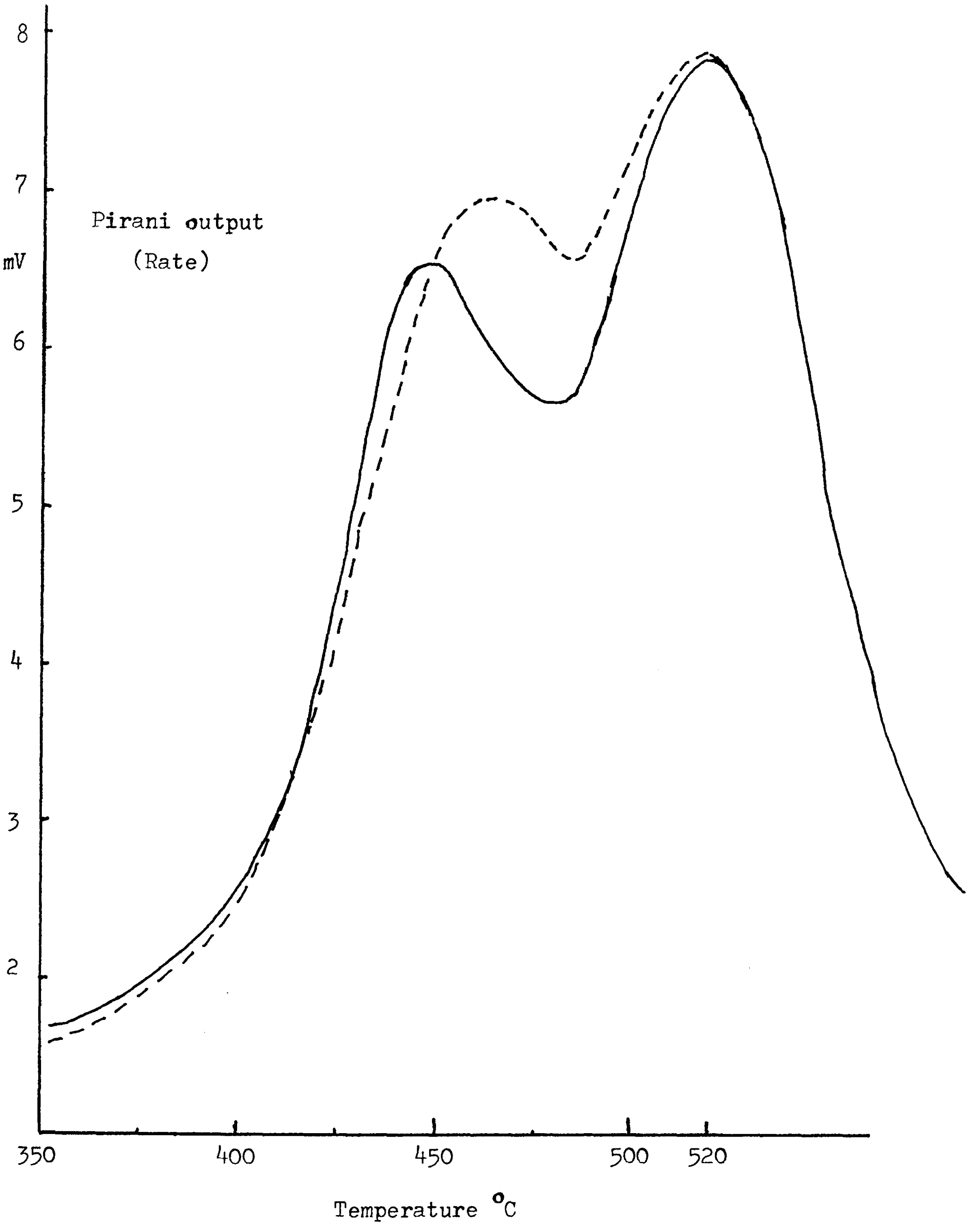


Figure 3.5 Degradation of 0.5 mg PS (cat.) covered and uncovered with PPX.

——— 0.5 mg PS Powder + 50 mg PPX placed separated in tube No. 1.

------ 0.5 mg PS film covered with 50 mg PPX.

repeated with a polystyrene sample of weight of 0.5 mg instead of 0.1 mg. The same shift was observed as is shown in fig. 3.5.

b) Degradation in a closed system:

When the pressure over the polymer sample is increased, the ease with which volatile products, including small radicals, leave the polymer surface will be reduced. This pressure would therefore favour further attacks by the small radicals on the polymer chains. To test this possibility the pressure over the polymer sample was increased as follows:

1. The films were prepared as previously described, and the system was maintained initially at high vacuum, before the degradation tube was isolated from the pumping system by closing taps I in fig. 2.1. The cold trap (T_1) was kept at -196°, -78°, -40° and at room temperature for different experiments.

Thin films were degraded under these conditions and the cold traps acted as pumping system. T_{max} was observed to be higher in the case of thin films than those for thicker films to the same extents previously observed.

Three polystyrene samples were used, PS D.N. cat., PS. F.R. $\bar{M}n$ 228,000, and PS_1 thermal (see appendix).

2. Trap T_1 in fig. 2.1 was kept at room temperature, and the diffusion pump was disconnected. The rotary pump was connected and supported by a cold trap which was kept at - 40°C. The pressure was increased to about 10^{-2} Torr. Experiments for degrading polystyrene thin films were carried out. The T_{max} for thin films was observed to be higher than those for thick films by about 30° - 40°C.

These attempts described in a and (b.1 and 2) above, though not conclusive, may suggest that ease of volatilisation from the polymer surface is not a major factor responsible for the enhanced stability of very thin films of polystyrene.

B - The effect of oxygen gas:

The effect of traces of oxygen during film preparation was excluded when films prepared under a flow of oxygen gas showed the same shift in T_{max} when degraded.

Films were also prepared under air or simply left overnight at room temperature for the solvent to evaporate, when degraded, T_{max} was found to be higher for thin films than those for thick films by more than 50°C. For example, T_{max} for a 4 mg film prepared under oxygen was 432°C. While that of a thin film of sample weight 0.05 mg prepared under the same conditions was 488°C.

This suggests that the atmosphere under which films were prepared has little or no influence on the stability of the thin films.

C - The effect of solvents used:

To test the effect of solvents on the polymer film, various solvents were used in the polymer film preparation, such as benzene, toluene, cyclohexane, ethyl methyl ketone and 1,2-dichloroethane.

It is well established that polymer molecules are more extended in a thermodynamically good solvent than in a poor solvent. Therefore, the polymer molecules in different solvents might also align themselves differently when thin films are formed.

Films prepared from various solvents were degraded, and it was observed that values of T_{max} obtained from thin films were higher than those for thick films by the same extent as previously described in all cases.

This suggests that the solvent power has no effect on the enhanced stability of thin films.

D - The effect of solvent impurities:

Analytical Reagent grade solvents used in this work contained, according to the suppliers specifications, small amounts of impurities.

Therefore, it was considered essential to examine the possible effect of these impurities and to see whether these produced volatiles in appreciable quantities or not.

20 - 30 ml of benzene or toluene were evaporated under nitrogen gas in the degradation tube No. 1 with no polymer present. The tube was then attached to the vacuum system and a TVA experiment was carried out. Very little volatiles were given off at about 300°C and there was no defined peak but just a deflection of about 0.02 mV. This deflection is insignificant and it has no contribution to the area under the TVA curve of 0.1 or 0.01 mg of polystyrene sample, since only one ml of solvent is used in each case and not 30 ml.

Therefore, it seems that T_{max} refers to the peak formed from the volatiles given off the sample itself and not to solvent impurities.

Furthermore, the same solvents were also used for those polymers, discussed subsequently, which did not exhibit any shift in T_{max} according to film thickness.

3.4 Du Pont TG Machine:

TG curves were obtained for polystyrene samples heated at 10°C/min. under a dynamic atmosphere of nitrogen gas.

A 0.2 mg polystyrene sample was degraded in the powder form and the same sample weight was also degraded as a thin film. The thin film was introduced to the platinum pan by delivering 0.05 ml solution of an appropriate concentration. The TG apparatus was operated at maximum sensitivity. From comparing the two TG curves in (fig. 3.6), it appears that the thin film is more thermally stable than the powder by 10° - 15°C, this confirms the effect observed by TVA.

The shape and size of the platinum pan, which was about 1cm^2 area, did not allow very thin films to be formed, because the pan had no flat base.

The balance mechanism was not sensitive enough for weights less than 0.2 mg due to noise and vibration of the balance beam of the sample holder.

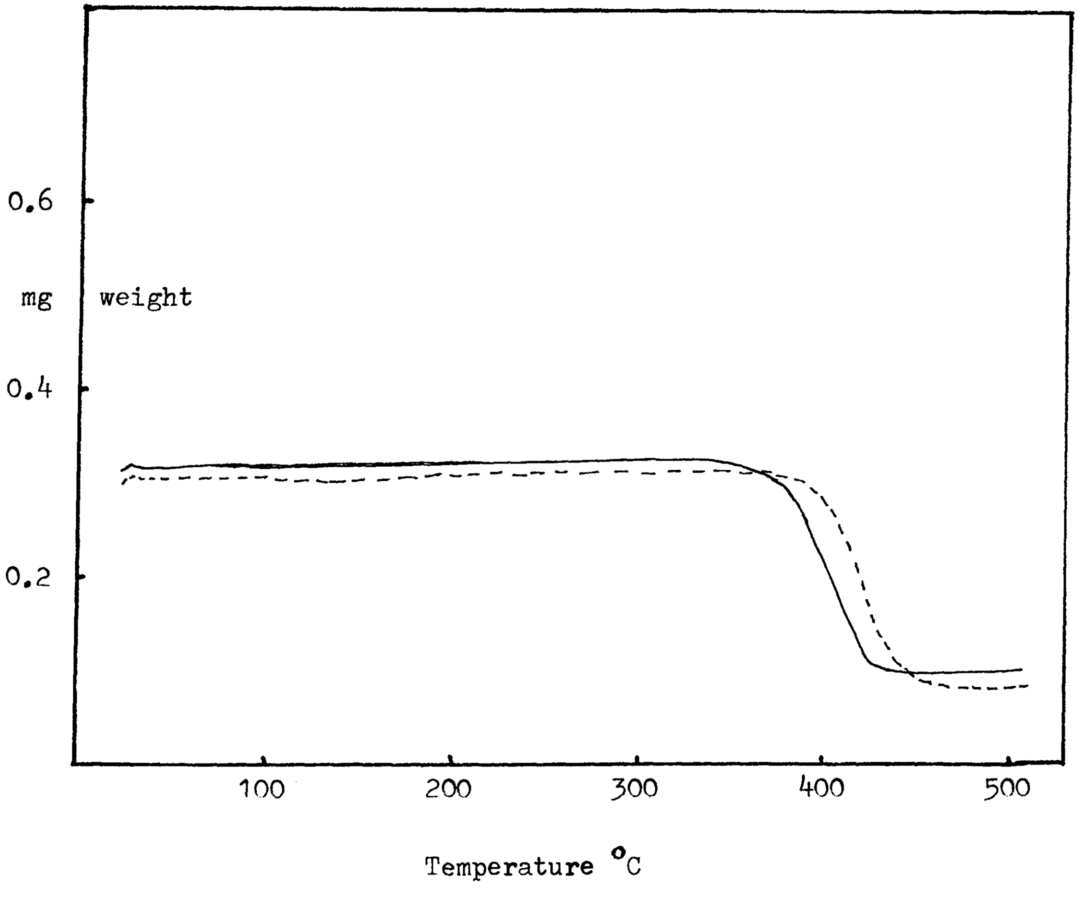


Figure 3.6 Degradation of 0.2 mg samples of polystyrene in the TG Du pont machine, under dynamic atmosphere of N_2 gas.

________ powder sample

-------- film sample.

3.5 Degradation of various types of polystyrene:

A number of samples of polystyrene, prepared by various polymerisation mechanisms, such as free radical, thermal, anionic and cationic (see applendix), were examined by the TVA apparatus. The molecular weight ($\bar{M}n$) of these polymers ranged from 2000 to 600,000.

20 mg, 0.1 mg and 0.01 mg sample weights were degraded for each polymer in the form of films.

T_{max} for thin films of sample weights of 0.1 and 0.01 mg were observed to be higher than those obtained from degrading 20 mg samples (see table 3.1).

Mode of polymerisation seemed to have no significant influence on the position of T_{max}. However, values of T_{max} obtained from 20 mg samples were observed to be higher for low molecular weight polymers than those obtained from high molecular weight polymers, (see fig. 3.7).

3.6 Isothermal Degradation of Polystyrene:

A 3.2 mg polystyrene powder sample (cationic D.N. see appendix) was degraded in the TVA apparatus isothermally at 400°C. Degradation started after 7½ minutes during the heating up period, when the sample temperature was about 250°C and still rising.

POLYSTYRENE			T_{max} °C.		
SAMPLE	TYPE	$\bar{M}_n$	20 mg.	FILMS 0.1 mg	0.01 mg
PS	BZ_2O_2	140,000	431	480	488
PS ST11	BZ_2O_2	130,000	426	451	487
ST 8	BZ_2O_2	60,000	428	485	490
PS	BZ_2O_2	184,000	427	482	485
PS	BISTO	75,000	430	491	488
PS	BISTO	228,000	425	489	485
ST.2.	Thermal	605,000	422	486	488
ST.7	Thermal	420,000	426	480	486
PS.706	Thermal	136,000B	424	460	461
L 13	Anionic	48,000N	433	478	488
L 2.	Anionic	44,600	431	465	482
PS.705	Anionic	175,000N	429	470	474
PS DN	Cationic	108,000	430	472	480
PS	Ionic?	4,000	440	488	-
PS	Ionic	2,000	441	483	-

B = Broad Distribution

N = Narrow Distribution

Table 3.1 T_{max} values for various polystyrene samples degraded as films in tube No. 1 (10 cm^2).

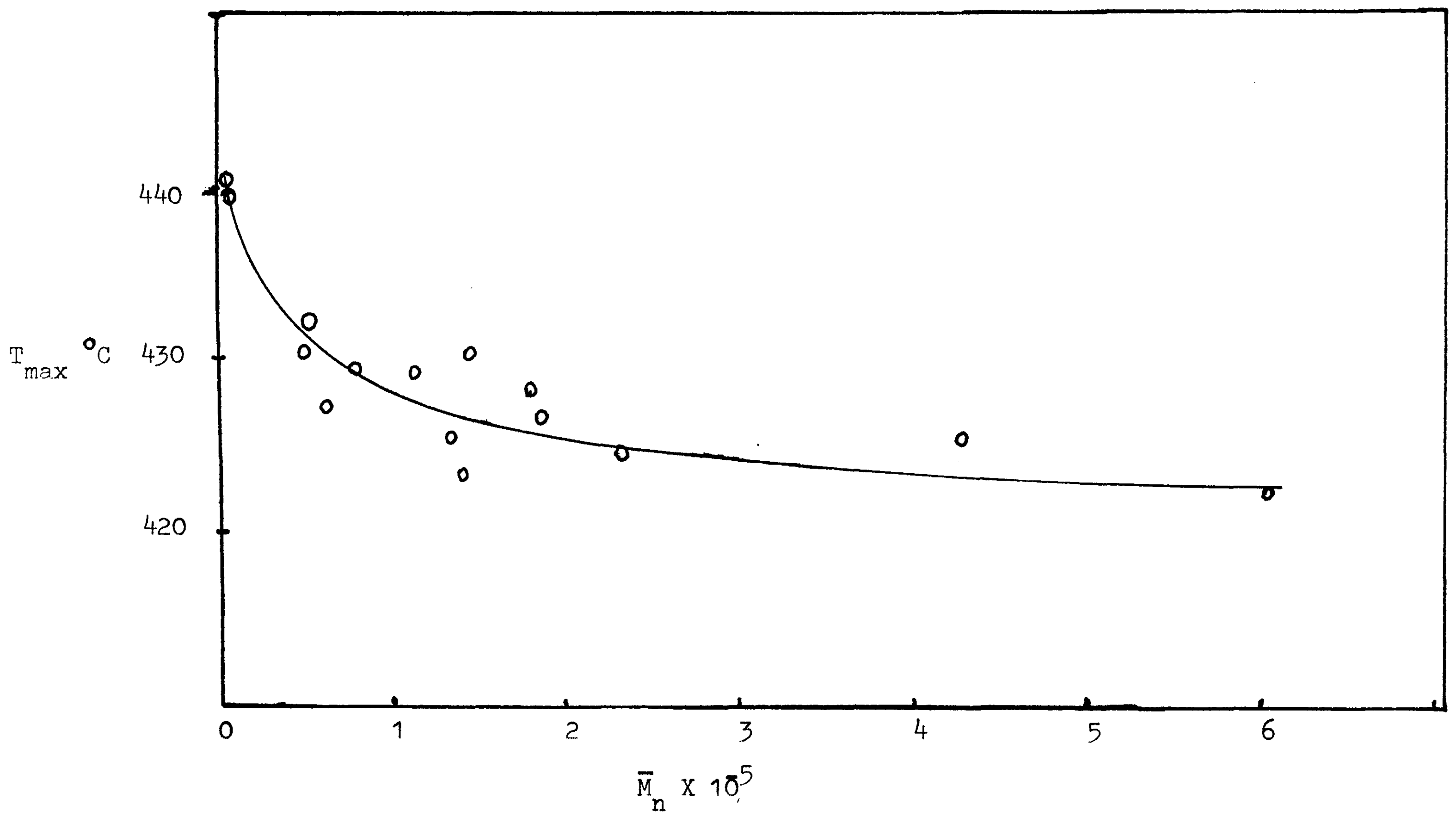


Figure 3.7 Rate maximum temperatures (T_{max}) for polystyrene samples of various molecular weights, ranging from 2000 to over 600000, and 20 mg sample weight.

Complete conversion to volatiles was attained after about 30 minutes, (see fig. 3.8). The curve obtained from this isothermal degradation, appears to be a broad peak and the rate of degradation was very high.

In contrast, a 0.2 mg film sample of the same polymer was degraded isothermally at 410°C. Volatilisation began at a temperature of about 380°. The rate reached a maximum after 7 minutes at about 400°C. Then degradation continued at a smaller rate of volatilisation for more than 70 minutes towards complete conversion (fig. 3.9).

In another set of experiments, 1.0 mg sample weights were degraded isothermally in the TVA apparatus using degradation tube No. 1 which has 10 cm^2 base area. The samples were in the powder and film forms. The thin film was degraded at 360°C and the powder sample at 350°C. The results are compared in (fig. 3.10).

The curve representing the thin film is shifted altogether towards the right along the time scale, although the temperature is higher than in the case of the powder form.

The reason that the two samples were not degraded at the same temperature was that volatilisation from the thin film did not begin to be noticed for 30 minutes when it was heated at

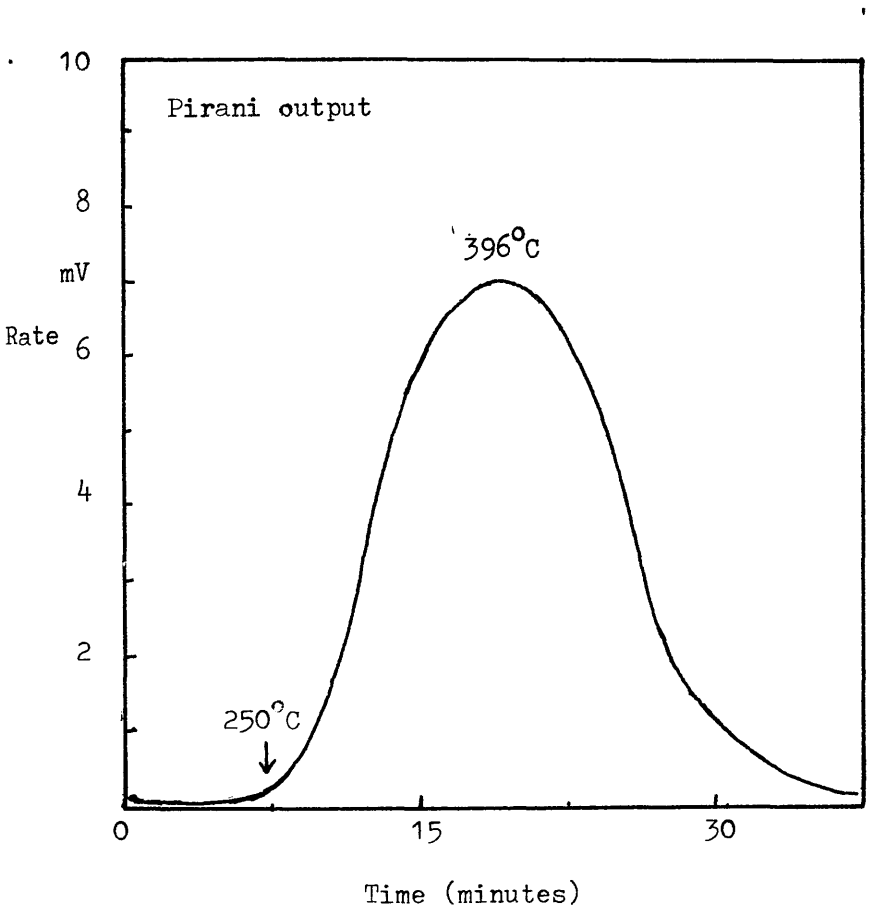
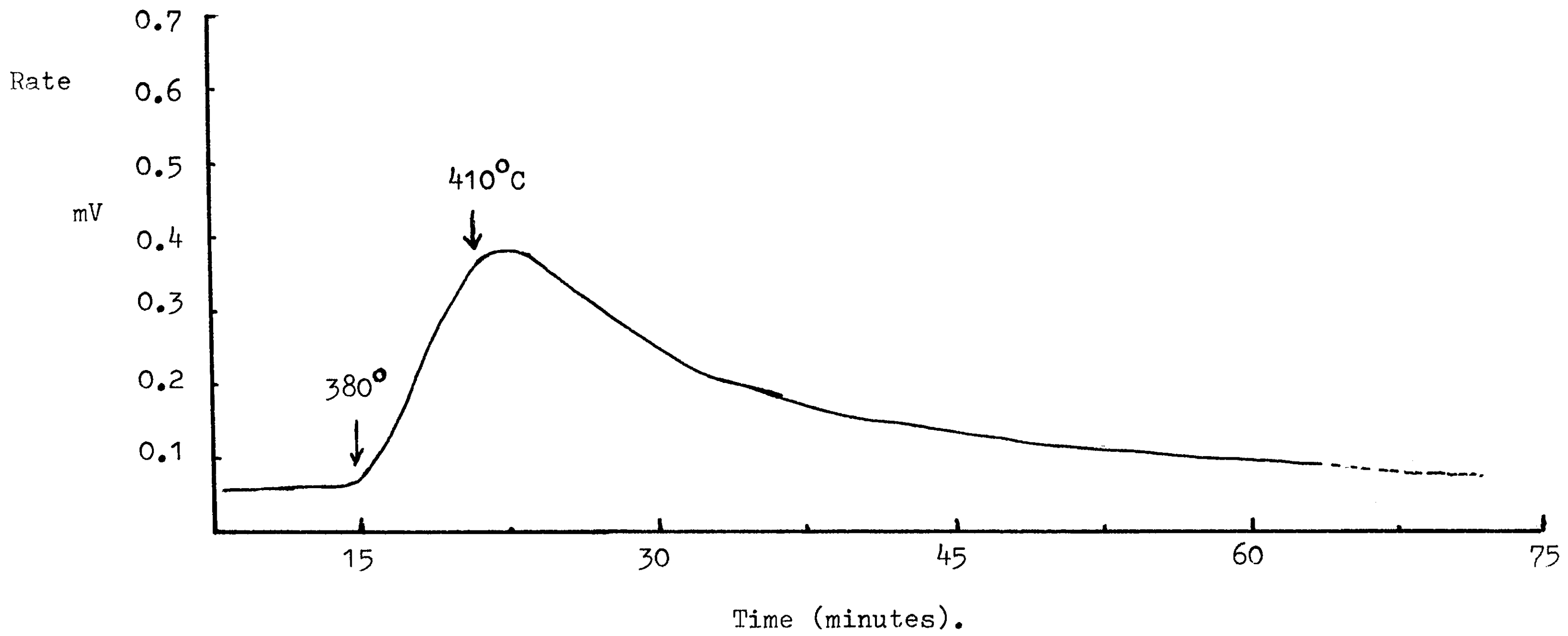


Figure 3.8 Isothermal Degradation of 3.2 mg powder sample of polystyrene at 400°C.



<u>Figure 3.9</u> Isothermal Degradation of 0.2 mg film sample of polystyrene at 410°C.

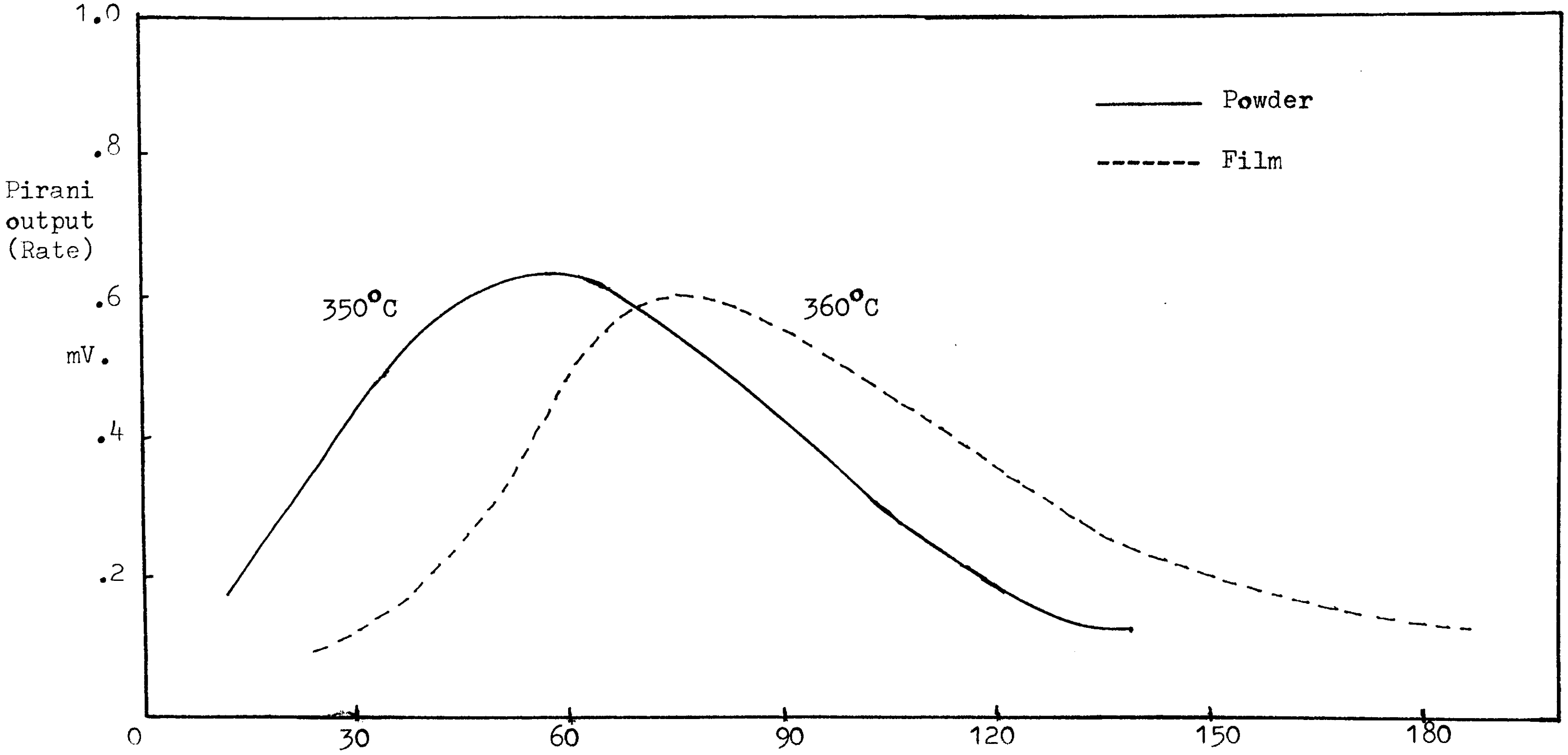


Figure 3.10   Isothermal degradation of 1.0 mg samples of Polystyrene.

350°. On the other hand, the powder sample degraded so rapidly at 360°C, causing a deflection of more than 1 mV Pirani output, that the response was no longer linear with the rate.

When a 0.1 mg film sample of the same polymer was heated at 350°C for 60 minutes, no volatile products were detected. As soon as the temperature was raised to 400° the film started to degrade very slowly, and the rate increased only when the temperature was raised to above 400°C.

All these observations indicate greater thermal stability of thin films compared with thicker films or powder samples.

3.7 Degradation of Poly (methyl styrenes):

Solutions of poly (α - methyl styrene), poly (meta-methyl styrene) and poly (para-methyl styrene) (see appendix), were made in benzene and toluene. Various appropriate concentrations were used to enable accurate weights to be delivered into the degradation tube by measuring 1 ml aliquots containing 20 mg, 10 mg, 1 mg, 0.1 mg and 0.01 mg. Films were prepared as described previously.

The sample weights of poly (α - methyl styrene) covered the same range of weights as polystyrene, i.e. from 0.01 mg to 50 mg. Poly (α - methyl styrene) was degraded at a heating rate of 10°C per minute under similar conditions as used for polystyrene. It

It was observed that the T_{max} values were the same for all sample sizes as it is shown in fig. 3.1.

Poly (m - methyl styrene) and poly (p - methyl styrene), however, both showed significant shifts in T_{max} for extra thin films as shown in table 3.2.

3.8 Degradation of other polymers:

Polymers for which intra and intermolecular chain transfer has been well established as playing a part in the degradation process were examined.

a) Polypropylene

Polypropylene normally shows a great deal of intra and intermolecular transfer on degradation. Although it was difficult to dissolve this polymer in benzene or toluene, an attempt was made to dissolve it in refluxing methyl ethyl ketone which has a boiling point of 80°C.

A 0.1 mg polymer film sample was formed in degradation tube No. 1 as previously described and degraded in the TVA apparatus at 10° per minute temperature rise. T_{max} was observed to be higher than that for the corresponding bulk sample of similar weight and for that of 20 mg. weight by about 40°C.

POLYMER	$T_{Max.}$ °C.		
	20 mg	0.1 mg	0.01 mg
Poly (α- methylstyrene)	338	338	339
Poly (m-methylstyrene)	410	477	478
Poly (p-methylstyrene)	417	474	471
Poly (propylene)	460	508	-
Butyl Rubber MD 501.	395	404	423
Poly (isoprene)	374	374	395
Poly (butadiene)	398(461)	398 (466)	- (473) Not clear
Poly (isobutene) IB IV	391	414	426

Table 3.2 Rate Maximum Temperatures for films of various polymers.

However, it was difficult to get a wide range of film thicknesses owing to the rapid precipitation of the polymer in cold solution. The results obtained for this polymer are collected in table 3.2.

b) Poly (isobutene):

Since this polymer resembles polystyrene with the phenyl group replaced by a methyl group, as discussed in the Introduction, its degradation was studied in some detail.

The polymer IB $\overline{\underline{IV}}$, $\bar{M}n = 10^5$ see appendix, was degraded in bulk and as thin films in the TVA apparatus as described earlier. Solutions were prepared in benzene as being a poor solvent and in cyclohexane as being a very good solvent for this polymer. The films were prepared in the same way as for polystyrene. T_{max} values of samples degraded as thin films were observed to be higher than those of thick films by about 30°C (see table 3.2).

Further experiments to show the effect of film thickness on the position of T_{max} were carried out. The method consisted of degrading the same sample weight formed as films on two different areas. Tube No. 1 with 10 cm^2 area and tube No. 3c with an area of 0.12 cm^2 were used (see fig. 2.2). 2μl of 0.5 per cent polymer solution, containing 0.01 mg sample weight, were introduced by a microsyringe into limb (c) of tube No. 3. Also, 1 ml of the polymer solution containing the same amount of polymer, i.e. 0.01 mg, was delivered into tube No. 1. The average thickness of the thin film was 100 Å, and that of the film in tube 3C was 100 times thicker. The films were prepared as previously described and were both degraded in the TVA apparatus under identical conditions at a heating rate of 10°C per minute. Their TVA curves are compared in fig. 3.11, which indicate that the thin film is more thermally stable than the thick film.

As previously discussed in the case of polystyrene the comformations of polymer molecules in solution varies according to the solvent power. Thus, when the solvent is evaporated, leaving a thin polymer film, the molecules in films formed from different solvents might have different alignments or might acquire different comformations.

Therefore, thin films prepared from a poor and from a good solvent were degraded in the TVA apparatus under similar conditions. The T_{max} values were observed to be the same in both cases.

The rate with which the solvent was removed, during film preparation, also had no effect on the position of the T_{max}

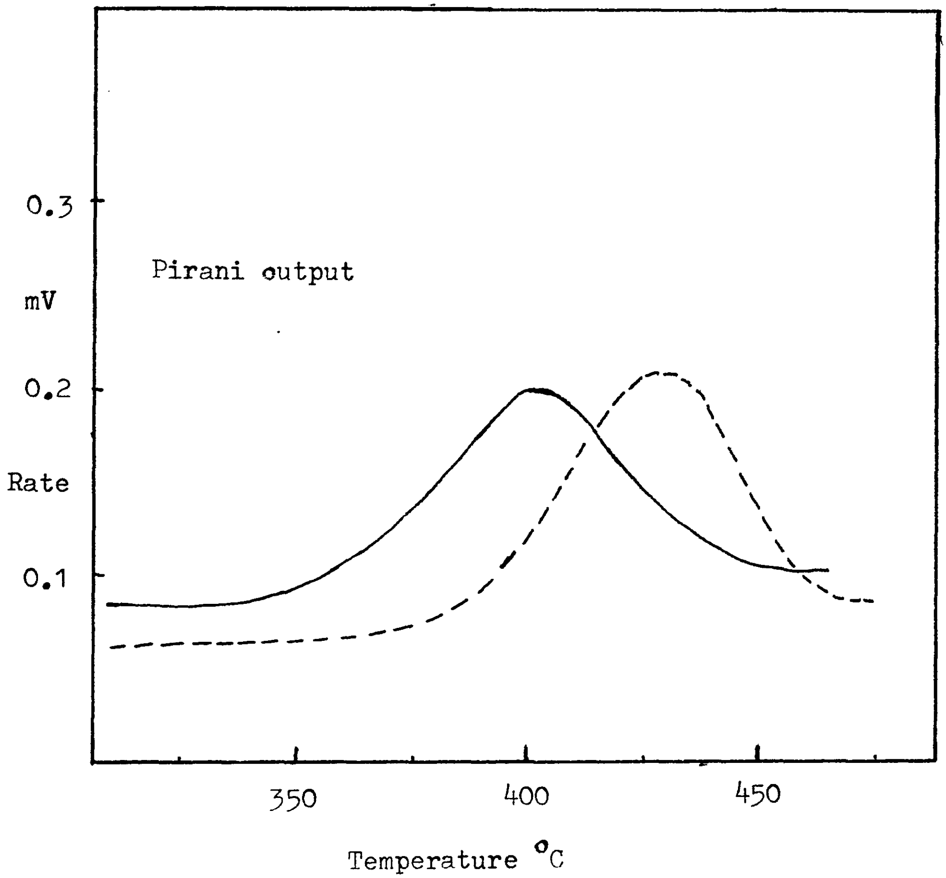


Figure 3.11 Degradation of 0.01 mg Poly (isobutene) films of different thicknesses.

----- film prepared in tube No. 1 (10 cm^2).

——— film prepared in tube No. 3C (0.12 cm^2).

values of the degraded thin films, as long as the thickness of the film was not severely affected by blowing the solution to the sides of the degradation tube by the flow of nitrogen gas.

This was tested by degradation of 0.1 mg thin films prepared by removing the solvent rapidly within 5 minutes, or very slowly over a period of 2 hours. This was carried out for both solvents and 1 ml solution was used in each case, and tube No. 1 was used.

These observations may suggest that solvent power has no effect on the position of T_{max}, and confirm the conclusion reached in similar experiments in the case of polystyrenes.

c) Poly (isoprene), Poly (butadiene) and Butyl Rubber:

These three polymers, obtained from industrial sources (see appendix), were purified from stabilisers. The method used was to dissolve the polymer in benzene and reprecipitate twice in a large excess of methanol. The polymer was then collected and dried under vacuum at room temperature for two days.

Solutions of appropriate concentrations were prepared as previously described and films of various thicknesses were degraded in the TVA apparatus.

T_{max} values on the TVA curves were observed to be higher for thin films than those for thick films, as listed in table 3.2.

Chapter Four

4.1 Investigations into molecular weight changes of Polystyrene:

To understand the mechanism of breakdown of polystyrene molecules in thin films it is essential to know how the molecular weight falls and at what rate, during degradation.

Due to the very small sample weights used in this work, it was not possible to measure the changes in molecular weight by using standard techniques. Other possible approaches were investigated, which might give some indication, even if only qualitative, of molecular weight changes in ultra small samples.

The molecular weight of a polymer is directly proportional to its solution viscosity. Solvent retention in the polymer film will also be directly proportional to viscosity hence to molecular weight. A thin film of polymer retains some of the solvent for some time even under vacuum at room temperature.

The use of radioactive traces offers a promising approach to determination of minute quantities of material. Measurements of radioactive solvent retained in a polymer film might therefore be related quantitatively to viscosity or molecular weight of the polymer.

1,2-dichloroethane (13.8 mg) labelled with Cl^{36} was supplied by the Radiochemical Centre, the specific activity was 14.6 μci/mM and the total activity was 20.4 μci. This radioactive material was diluted with 50 ml 1,2-dichloroethane which have been distilled three times, the middle portion having been collected each time.

Solutions of polystyrenes ST.2, ST.7 and ST.11 of three different molecular weights (see appendix) were made in A.R, 1,2-dichloroethane of concentration 1mg/ml.

A ratemeter (EKCO Electronics type N522C) and Geiger tube (Mullard type MX 168/01) were used in the counting experiments.

Uranyl Acetate solution was used to calibrate for the optimum voltage. A curve for voltage versus pulses per second (PPS) was obtained (fig. 4.1), and 450 volts were found to be the voltage where the counts were independent of voltage fluctuations.

A 0.5 mg film for each of the three polystyrenes were made on one inch diameter shallow aluminium dishes. The films were dried at 60° under vacuum for several hours.

0.2 ml of the radio-active solvent was added to each films and was left to evaporate at room temperature. When the film was visibly dry it was placed under the Geiger tube and count readings were taken on the ratemeter every five minutes. Readings were also taken

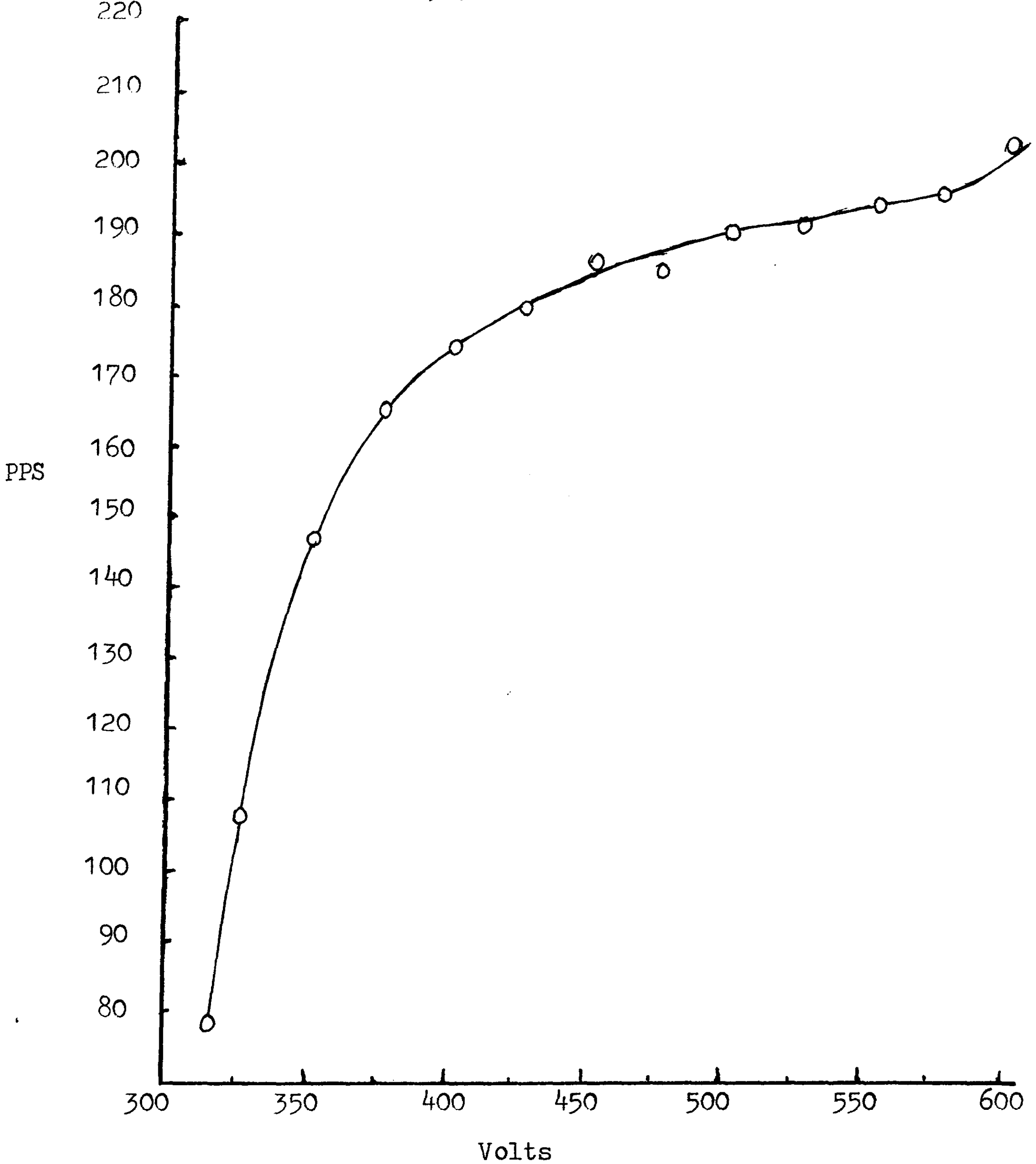


Figure 4.1 Counts per second Vs. Voltage on ratemeter using Tube MX 168.

for blank dishes which contained no polymer films but radio-active solvent was added to count for adsorpiton on the metallic dish.

Although it was observed that the films retained appreciable amounts of the radio-active material for 20-30 minutes, no significant correlation could be found between radio-activity retained by the polymer film and the molecular weight of the polymer.

A more sophisticated instrument such as the liquid scintillation counter (Nuclear Chicago, Mark I) was also used.

0.5 mg films of the polymers were prepared in duplicates in small bottles. All bottles were kept in the vacuum oven at 60°C for several hours.

0.2 ml of the radio-active solvent was added to each of the polymer films and to two other bottles which contained no polymer films, and the solvent was left to evaporate at room temperature.

10 ml of scintillation fluid, comprising 4 mg PPO and 50 mg POPOP per litre of toluene, were added to each bottle and to two extra blank bottles.

The results of counting the solutions were inconclusive.

4.2 Viscometry:

A sharp drop in the molecular weight of a polymer would obviously cause a drop in the intrinsic viscosity of its solution.

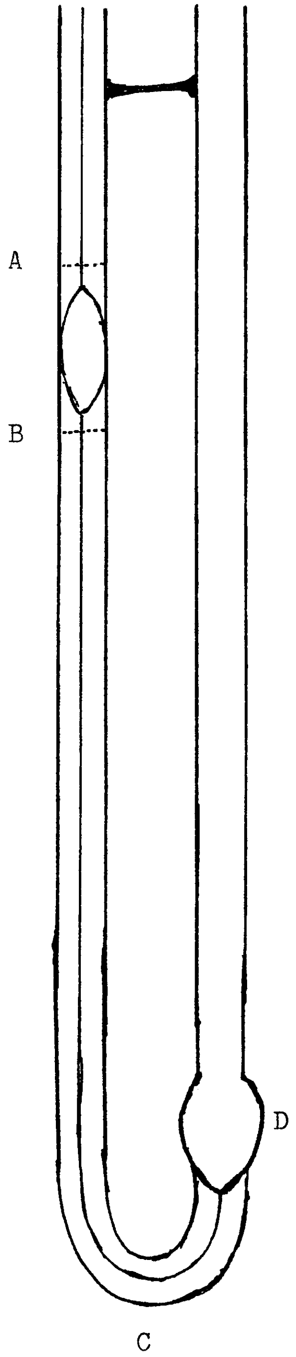


Figure 4.2 Semimicroviscometer,

Volume of AB is about 0.4 ml.

Volume of D is about 0.7 ml.

The sample sizes employed in this work, however, were much too small to permit use of conventional viscometers with any accuracy. Two methods were used to gain increased sensitivity.

To increase the sample weight of the polymer film without altering its thickness a large base degradation tube No. 5 (see fig. 2.2) was constructed, with base area 64 cm^2.

A semimicroviscometer was also specially constructed for viscosity measurements of small volumes of solutions of low concentration.

A) <u>The Viscometer</u>:

A "U" shaped semimicroviscometer was constructed from pyrex glass tubing of 4 mm inside diameter joined to a section of "Veridia" precision bore capillary tubing of 0.35 mm diameter see (fig. 4.2). The total length was 35 cm. The constant volume between A and B was about 0.4 ml and bulb D was about 0.7 ml capacity. The capillary between B and C was 23 cm long.

B) <u>Testing of Viscometer with samples of known M. Wt.</u>

The viscometer was cleaned with hot chromic acid and rinsed with water several times and left to dry in an oven. It was then rinsed again with A.R. toluene several times and dried and kept in a vertical position in a thermostated water bath at 25°C ± 0.02°.

Viscosity measurements were made on polymers of known number-average molecular weights (obtained from osmotic pressure measurements) ST2, ST7, ST11 and FR I (see appendix) using the semimicroviscometer.

1 per cent W/V solutions in A.R. toluene were prepared for each polymer. Each solution was used to prepare 0.8, 0.5, 0.2, 0.1, 0.05 and 0.02 per cent concentrations.

A stop watch reading to 0.1 second was used. The mean flow time of toluene at 25°C was 174 seconds. Flow times for the above solutions were determined several times. Results are given in (table 4.1) and η_{sp}/C VS. C plots are shown in (fig. 4.3).

To calculate molecular weights, the relationship, $[\eta] = K\bar{M}_v^a$ was used, where the values of (K) and (a) for polystyrene in toluene at 25°C are 11.8×10^{-5} and 0.72 respectively.[68]

The viscosity average molecular weights obtained from these measurements for the polymers above, were of the same order as their number average molecular weights.

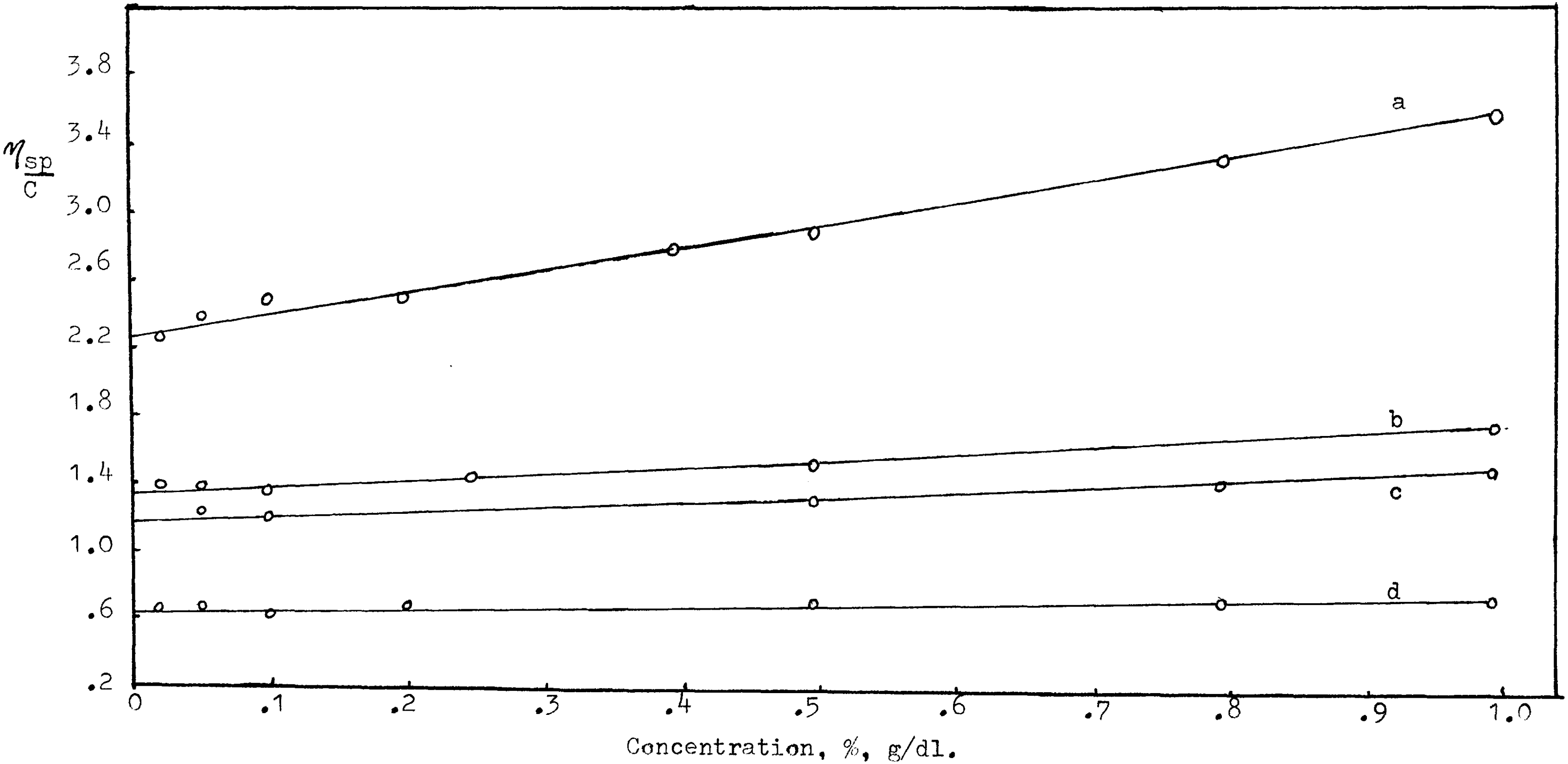


Figure 4.3 Viscosity measurements of four known molecular weight polystyrenes using the Semimicroviscometer.

a - 853,500 $\bar{M}v$

b - 428,700 $\bar{M}v$

c - 359,000

d - 153,000

	concentration%	Flow time sec.	η_{sp}/C		concentration%	Flow time sec.	η_{sp}/C
a) ST2	1	807.3	3.637	b) ST7	1	481.3	1.764
	0.8	637.5	3.328		0.5	310	1.561
	0.5	425.3	2.874		0.25	236.9	1.443
	0.4	369.3	2.802		0.1	198	1.373
	0.2	263.5	2.509		0.05	186.5	1.424
	0.1	218.6	2.557		0.02	179.0	1.407
	0.05	195	2.406				
	0.02	182	2.269				
c) FRI	1	434.4	1.495	d) ST11	1	301.0	0.7290
	0.8	372.8	1.427		0.8	275.1	0.7251
	0.5	289.5	1.325		0.5	235.9	0.7099
	0.1	195.6	1.235		0.2	197.4	0.6692
	0.05	185.0	1.252		0.1	185.2	0.6375
	0.02	178.8	1.350		0.05	179.8	0.6548
					0.02	176.4	0.6606

Table 4.1 Results of viscosity measurements of four PS samples of known M.wt. using the semimicroviscometer. These results are plotted in (fig. 4.3).

c) Determination of percentage conversion during degradation:

The determination of extent of degradation in cases where the sample size is too small to permit estimation of products by conventional methods presents special problems.

The method used for calculating the percentage conversion of a partly degraded sample was as follows: A 0.5 mg polymer sample in the form of thin film was completely degraded isothermally. Since the pirani response causes a recorder deflection not more than 0.6 mV, it may be considered as a linear measure of rate of production of styrene monomer (see page 42). Hence the area under the TVA curve, which is a rate VS. time plot; is a measure of quantity of volatile material. The area under the TVA curve due to the volatile products from a 0.5 mg sample of polystyrene thin film degraded under isothermal conditions was measured. The area determined in three experiments was found to be 670 ± 6 cm^2 and was considered to represent 100 per cent conversion.

A similar size of sample was degraded isothermally in tube No. 3C which has a very small area (0.12 cm^2) so that the film was more than 100 times thicker than that formed in tube No. 5, with large base area. The area under the TVA curve was considered as a measure of 100 per cent degradation as was described above. In three experiments in this case, the area was found to be 614 ± 4 cm^2.

The average thickness of the thin film was less than 1000 Å over an area of about 64 cm^2, while that of the thick film in tube No. 3C was about 10^5 Å.

In the isothermal degradation experiments, thin films were degraded at 410°C while thick films were degraded at 360°C. The different temperatures were necessitated by the considerable differences in rate previously discussed.

To obtain various percentage conversions, the heating was stopped at different stages along the TVA curve in each experiment and the area under the TVA curve was calculated. This area was then compared with that for complete conversion (see fig. 4.4) to give the percentage conversion.

D) Degradation of thin polymer films to various degrees of conversion:

High molecular weight polystyrene ST2 ($\bar{M}v$ = 853,500) was used, see appendix. The films were prepared, as previously described, by transferring 1 ml solution, containing 0.5 mg of the polymer, into the degradation tube No. 5 with the large base area.

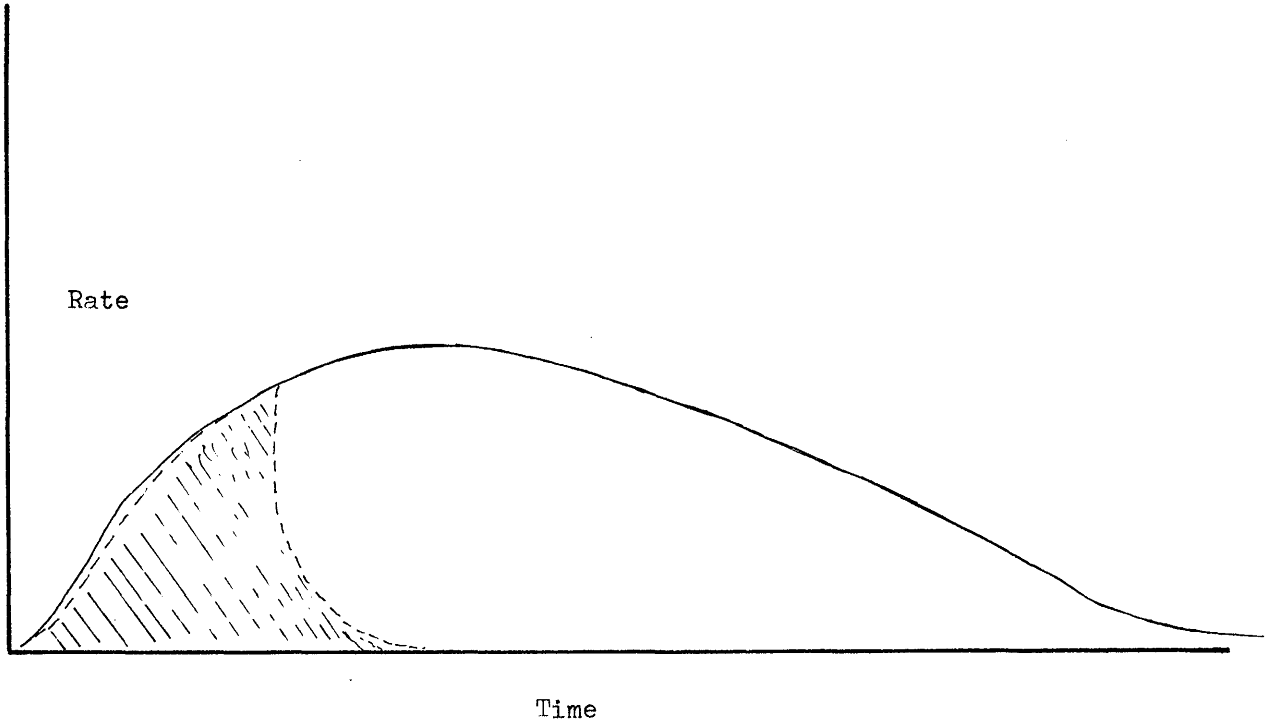


Figure 4.4 Isothermal Degradation of PS samples for calculations of % conversion.

________ Complete conversion to volatiles (100%)

-------- Shaded area for partly degraded sample.

Degradation was carried out to a different degree of conversion for each experiment, starting from 4.5 per cent up to 48 per cent degradation.

The method used was as follows:

The heating was stopped and the sample was left to cool down to room temperature. Then the degradation tube was disconnected from the vacuum line and the partly degraded polymer film was dissolved in 1 - 2 ml of toluene. The solution was then transferred with great care to a 10 ml bottle which had been cleaned with chromic acid, rinsed several times, dried and kept in a dessicator. The degradation tube was rinsed several times with solvent and the rinsings were transferred to the small bottle to ensure removal of all traces of polymer. The solvent was then removed from the solution in the bottle by a slow flow of dry nitrogen gas. The partly degraded polymer was then redissolved in 0.7 ml of toluene accurately measured by using a 1 ml graduated pipette. This solution was kept at 25°C and a 0.5 ml portion was accurately measured by a semimicropipette and delivered into the viscometer which was kept in a vertical position in the water bath. After allowing a few minutes for temperature equilibration the flow time of the solution between A and B (fig. 4.2) was measured five times and the mean value was taken in each experiment.

The concentration of the solution was calculated as follows, from the estimated conversion: e.g. When a 0.5 mg sample was partly degraded, say to 16 per cent conversion, 0.42 mg was left in the degradation tube. When this 0.42 mg was made into 0.7 ml toluene solution, the concentration was calculated to be 0.06 per cent W/V.

$[\eta]$ was obtained from a single viscosity measurement by plotting the point for $\frac{\eta_{sp}}{c}$ VS. C, where η_{sp} is specific viscosity and C is concentration in per cent weight/volume.

$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o}$, where η is the viscosity of polymer solution, η_o is the viscosity of pure solvent. By extrapolating from this point to infinite dilution or zero concentration along a parallel to the nearest line representing a known molecular weight polymer (fig. 4.3), $[\eta]$ was estimated from the intercept and the molecular weight was calculated from the relationship $[\eta] = K M^a$, given above, for polystyrene in toluene at 25°C.

This single-point method for estimating molecular weight was considered to be of sufficient accuracy because of the fairly low concentrations used.

E) Degradation of thick films:

Thick films were made in tube No. 3C in the same way as described above, except that a very small volume of a more concentrated solution was required. Therefore, 50 µl of a 1 per cent solution were transfered by a microsyringe fitted with a 5 inches long needle.

Degradation was carried out at 360°C. The polymer was partly degraded to various degrees of conversion in each TVA experiment and the undegraded residue was disolved in toluene and transfered for viscosity measurements as described in the previous section.

The calculated molecular weights for partly degraded samples of thin and thick films were plotted against their degrees of conversion and two clearly separate curves were obtained as shown in figs. 4.5 and 4.6.

The drop in molecular weight of thick films is seen to be sharper than that of the thin film samples. Both curves level off and come closer to each other at about 60,000 - 70,000 molecular weight, at about 40 per cent conversion.

F) Analysis of volatile products by GLC:

It was observed, as mentioned before, that the area under TVA curve for a completely degraded thin film sample of

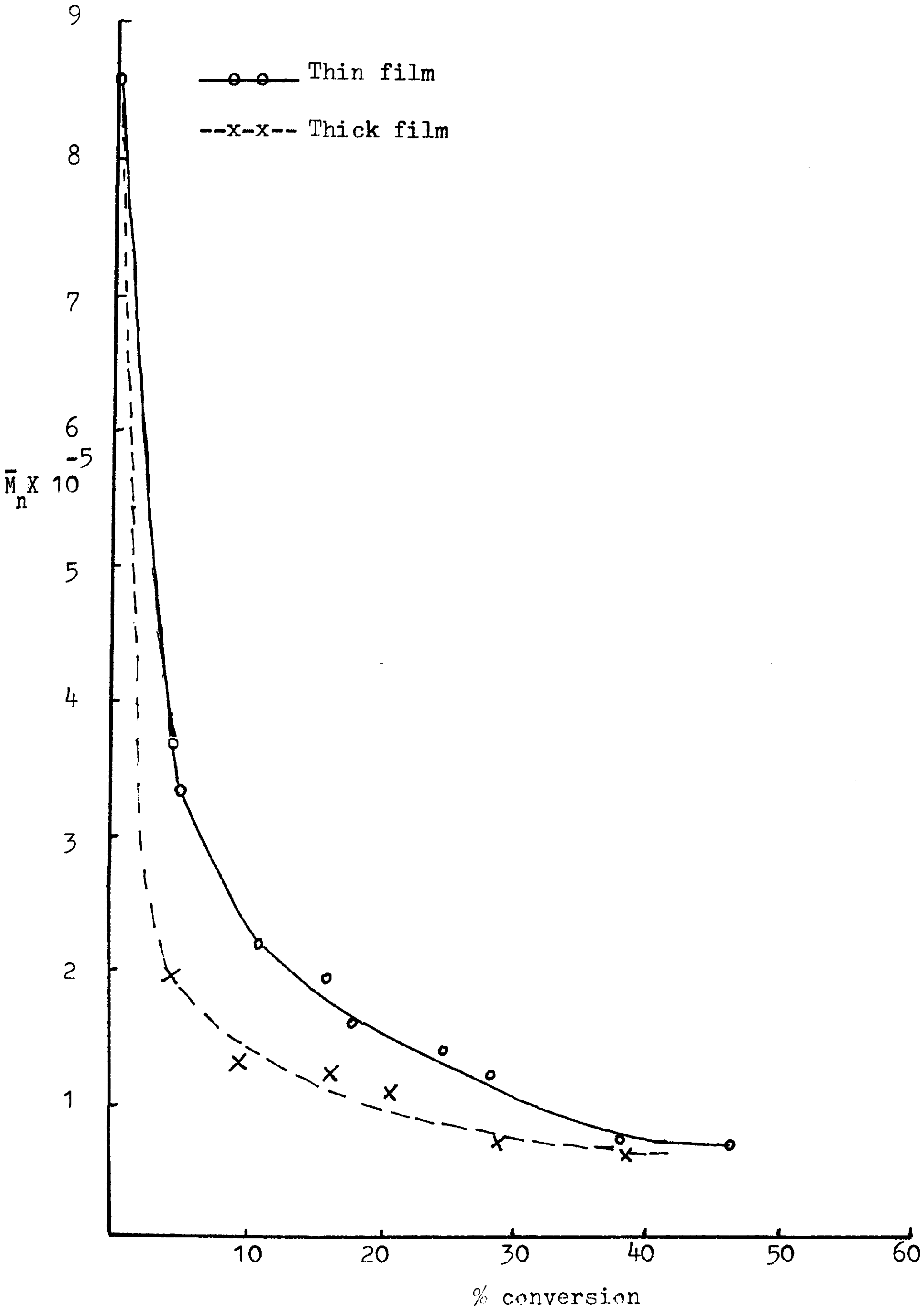


Figure 4.5 The effect of degradation on the molecular weight of polystyrene.

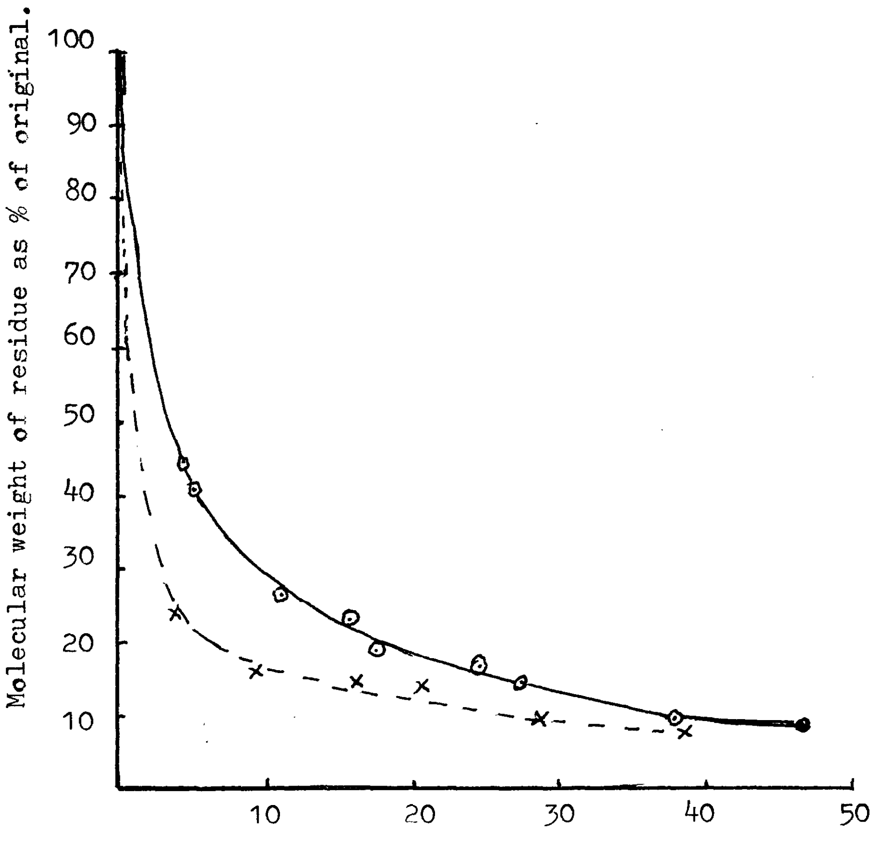


Figure. 4.6 The effect of degradation on the molecular weight of PS in the form of thin and thick films

—o—o— Thin film

-x--x- Thick film.

Thin film

conversion %	concentration%	Flow time sec.	η_{sp}/C	Mv
0	0.05714	195.7	2.2	821,400
4.5	0.06821	188.2	1.2055	368,000
5	0.068	187.6	1.12	334,200
11	0.06359	183.4	0.8591	216,800
16	0.06	182.1	0.7859	195,000
18	0.05857	180.7	0.6676	160,300
25	0.05357	179.6	0.61186	140,500
28	0.05143	178.7	0.5444	121,300
38.5	0.04393	176.8	0.3890	74,500
47	0.03786	176.1	0.33415	70,000

Thick film

conversion %	concentration%	Flow time sec.	η_{sp}/C	Mv
4	0.068	183.1	0.77	195,000
9.5	0.065	180.3	0.567	127,700
16.5	0.060	179.6	0.545	121,300
21	0.0564	179.0	0.520	110,000
29	0.0507	177.3	0.3856	74,500
39.3	0.04336	176.5	0.345	64,000

Table 4.2 Viscosity measurements of PS, ST2, degraded as thin and thick films to various degrees of volatilisation for the study of changes in M.wt. sample size is 0.5 mg.

polystyrene ST2 (high M.wt.) was about 670 cm^2 and that of a thick film was about 610 cm^2. There is a difference therefore, of about 10 per cent in area between the two. It was found useful to analyse products of degradation in both cases, using gas liquid chromatography.

0.5 mg sample weights of polystyrene ST2 were completely degraded as both thin and thick films respectively.

The retained solvent in the polymer film was removed in the early stages of temperature rise and collected in trap T_1 in fig. 2.1 and as soon as degradation commenced, the cold trap T_1 was closed and volatile products were then collected in cold trap T_2 at liquid nitrogen temperature.

When degradation was completed T_2 was closed and volatile products were distilled into a small cold finger (K) in fig. 2.1 kept at - 196°. The products were completely transfered into the cold finger (as shown by checking on the pressure after 30 minutes). Then the cold finger was removed from the vacuum line and a 50 μl portion of ethyl benzoate was very quickly injected by a microsyringe into the cold finger which was immediately closed by a small cap.

This process was repeated, after a pilot experiment, three times for each thin and thick films.

Ethyl benzoate was used as a solvent because it had a longer retention time in the GLC column than that of styrene monomer. Other solvents such as chloroform, toluene or benzene tend to interfere with styrene and mask its peak.

In another two sets of similar degradation experiments for both types of films, toluene was injected into the cold finger as a solvent for degradation products instead of ethyl benzoate. This attempt was made in order to identify any dimer or possibly larger fragments which might be present.

GLC measurements

Three different GLC machines were used.

1. The Pye Argon Chromatograph had a radio-active detector of strontium 90, (20 mci). The instrument was set at 1000 volts and X3 sensitivity. The column was 4 feet long and kept at 100°C. The argon gas flow rate was 60 cc/min, and the chart speed was 15"/h.

   0.1 μl portions were injected from each sample for both types of products of thin and thick films.

   There was some evidence that more styrene monomer was present in the products from thin films than from thick films, but there was no evidence of any dimer or larger fragments present (see fig. 4.7).

2. Perkin Elmer F11 Gas Chromatograph, Flame ionization, was used isothermally at 100°C, and at a programmed temperature rise of 10° and 5° per minute to check the above results. A 1 per cent SE 30 column, 4 feet long, was used. The results were consistent with the previous measurements, and again no evidence for dimer or larger fragments was found (see fig. 4.8).

3. Techmation - Microtik, GC. 2000 - R:
This research Gas Chromatograph, with ionization detector, was also used isothermally at 100°C and programmed at 5° per minute between 60° and 200°C. A 5 per cent SE 30, 6 feet long, column was used.

The results confirmed the previous sets.

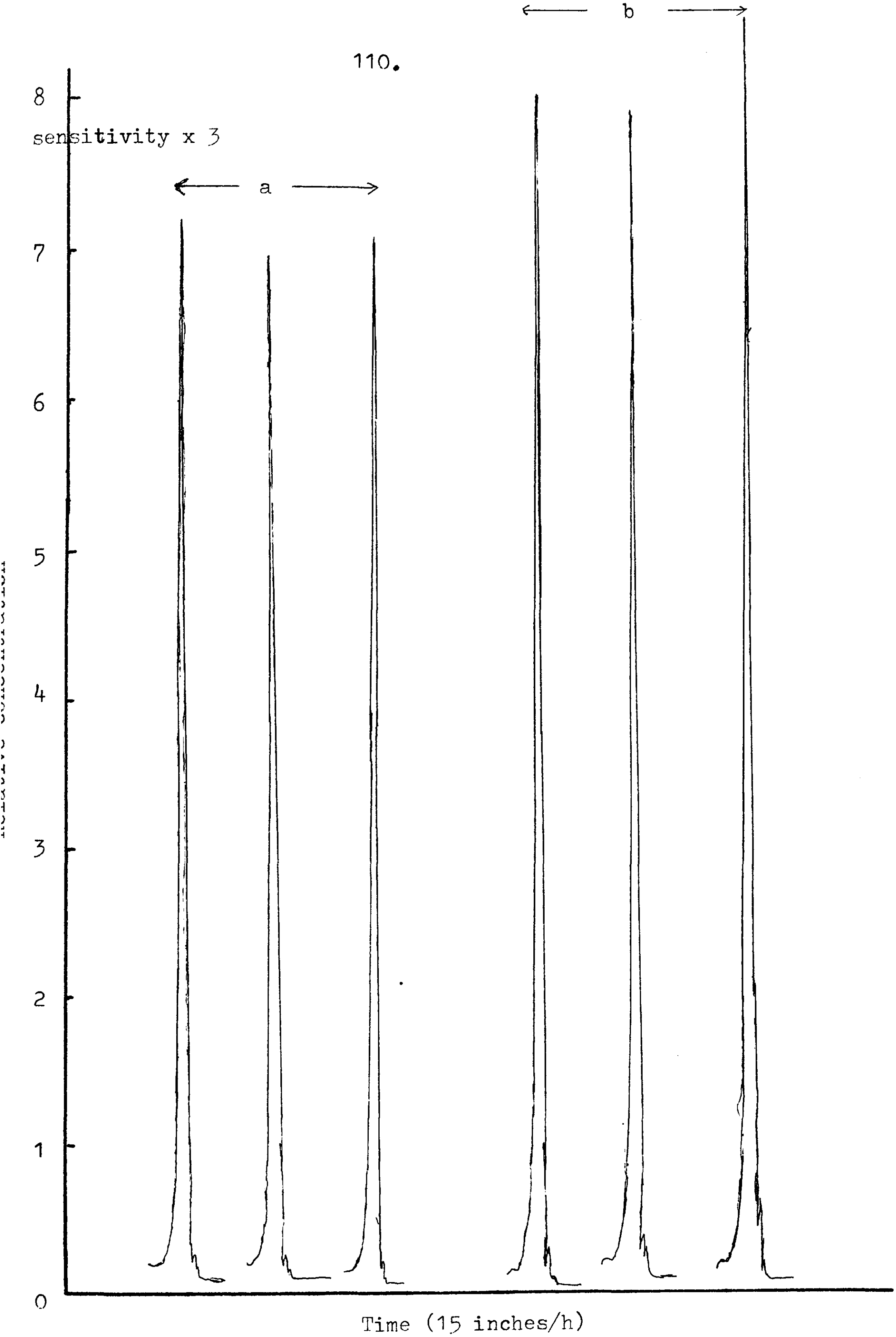


Figure 4.7 GLC traces (Argon Chromatograph). $0.1\ \mu l$ injected at 100°C (Isotheral). Solvent peaks are not shown.
a) styrene monomer from thick films b) styrene monomer from thin films

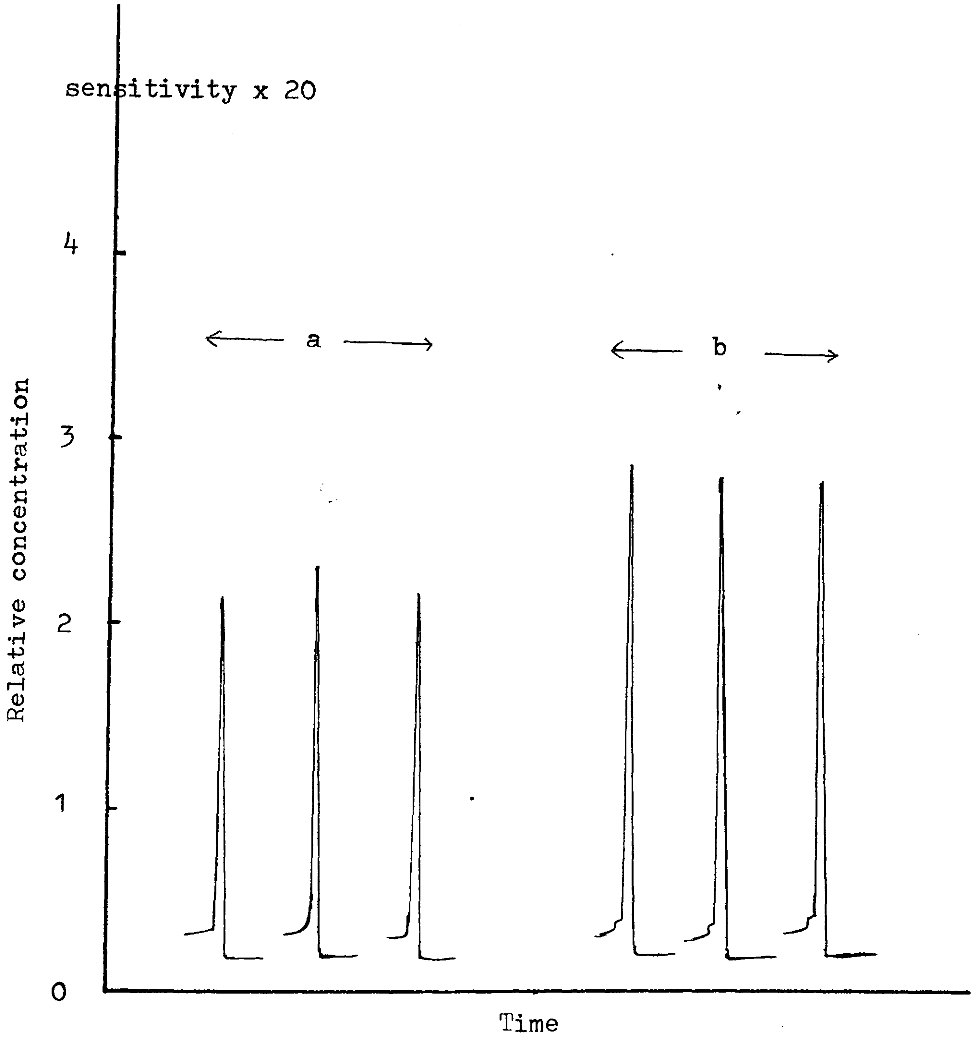


Figure 4.8 GLC Perkin - Elmer F11.
1 μl injected at 100°C (Isothermal)
a, monomer from thick films b, monomer from thin films
Solvent peak is not shown.
Chart speed is 5 mm/minute.

Chapter Five

Results And Discussion For Polystyrene

It appears from figs. 3.1 and 3.1(a) that very thin films of polystyrene are thermally more stable than the thick films or powder samples. This behaviour suggests that some change in the mechanism of degradation of thin films from that of the bulk material is occurring. Although there is some scattering in the values of T_{max} in the region of thin films, i.e. the upper section of the curve in fig. 3.1 for polystyrene, it is evident that all these values lie well above the values of T_{max} for thick films which are at about 428°C. This scattering in T_{max} values may be attributed to variations in thicknesses of some films caused by the fluctuations of the flow rate of nitrogen gas during film preparation.

Fig. 3.1(a) shows a significant difference in the thermal stability of the two films which differ in thickness by approximately 10 times. Also, it is observed that the initial rate of formation of volatile products for the thicker film is higher than that for the thin film.

Table 3.1 gives results obtained from degradation of thin films and thick films of polystyrene samples prepared by various methods of polymerisation and having a wide range of molecular weights. It is observed from these results that thin films prepared from all these samples exhibited greater thermal stability.

In contrast, it is seen in fig. 3.1 and in table 3.2 that for poly (α- methyl styrene) where hydrogen transfer reactions are known to be absent, there was no shift in T_{max} values with respect to changes in film thickness.

It is reasonable to assume that the molecules of polystyrene are rather less crowded in thin films than in the case of thick films and the powder samples. Therefore, radicals formed during the degradation in thick films or in powder samples have more chance of abstracting a tertiary hydrogen atom from sites nearby, whereas such reactions may be restricted in the case of thin films.

In the case of poly (α- methyl styrene) however, there should be no change in thermal stability according to film thickness, which is indeed the case found from the experimental results obtained for this polymer, since there is no transfer mechanism to be restricted. [71]

The effect observed in the degradation of polystyrene in the TVA apparatus, takes place also to some extent when thin films were degraded in the TG apparatus as shown in fig. 3.6. The thin film starts to degrade at a temperature higher than that of the powder sample.

These findings suggest that intermolecular transfer is an important factor taking part in the degradation process of polystyrene. When this transfer mechanism is restricted, as in the case of thin films the thermal stability of the polymer is enhanced.

Fig. 3.10 compares the results of isothermal degradation of thin film and powder of the same sample weight. Despite the higher temperature at which the thin film was degraded, it showed higher thermal stability than the powder sample. Degradation started later in the thin film than that in the case of the powder and tailed off for about 40 minutes longer to complete conversion.

Comparing figs. 3.8 and 3.9, it is interesting to see how the shape of the two curves differ from each other. Although the powder sample was again degraded at a temperature 10°C lower than that of the 0.2 mg film, it started to degrade at 250°C and the rate reached a maximum at 396°C, while the film started to decompose at 380°C. Degradation of the powder is nearly complete in 38 minutes, whereas the film continues to degrade for considerably longer.

Eggertsen and Stross [75] carried out experiments on the degradation of 0.02 mg samples deposited as films on a filament heated at 365°C. The volatile products were monitored by G.C. These authors found that the rate reached a maximum after about 8 minutes. It gave a curve similar to that in fig. 3.9, but the temperature is lower probably due to the thicker film formed on the filament which obviously has much less surface area than that of degradation tube No. 1 (10 cm^2). It was also observed, in the work of the same authors, that the monomer yield produced from 0.2 - 0.3 mg samples degraded at 6°C/min. up to 550°C was 85%.

Lehrle and Robb [72], and Barlow [73] have carried out work on flash pyrolysis of thin films. The method those authors used was passing a triggered discharge through a filament of nichrome or a ribbon filament; small samples as films were coated on the filament and the charge suddenly passed for a few seconds and the products of degradation were swept away and passed through the G.C. by the carrier gas. This means that the polymer sample is exposed to high temperatures for a very short time and completely destroyed. The authors found that thin films are thermally less stable than thick films which is contrary to results obtained in this work. This may be explained by the difference in the techniques used; since destroying a polymer film at high temperature and in a very short time tells very little about its stability and gives little opportunity to follow the mechanism of the reaction. Also this method does not permit information about the fall in molecular weight to be obtained. Therefore, it may be difficult to compare it with results obtained in this work.

Polymers for which hydrogen transfer is a well established degradation mechanism were degraded as thin films and in bulk; all showed similar behaviour to that of polystyrene. Those polymers which have elastomeric properties such as poly (isobutene), poly (isoprene), butyl rubber and poly (butadiene) showed a shift in T_{max} values less than that observed in polystyrene thin films as is seen in table 3.2. This may be attributed to the fact that in these polymers the molecular interaction is much greater than the interaction between these molecules and the glass surface of the degradation tube. Therefore, the molecules would tend to pull each other and cause the film to shrink rather than spread, hence form a thicker discontinuous film than that expected from the available surface area.

From fig. 5.1(a) it is shown that the curves for rate of degradation against percentage conversion in the case of thick films have a maximum between 30-40 per cent degradation which is in good agreement with Madorsky's results.[5] On the other hand, the thin

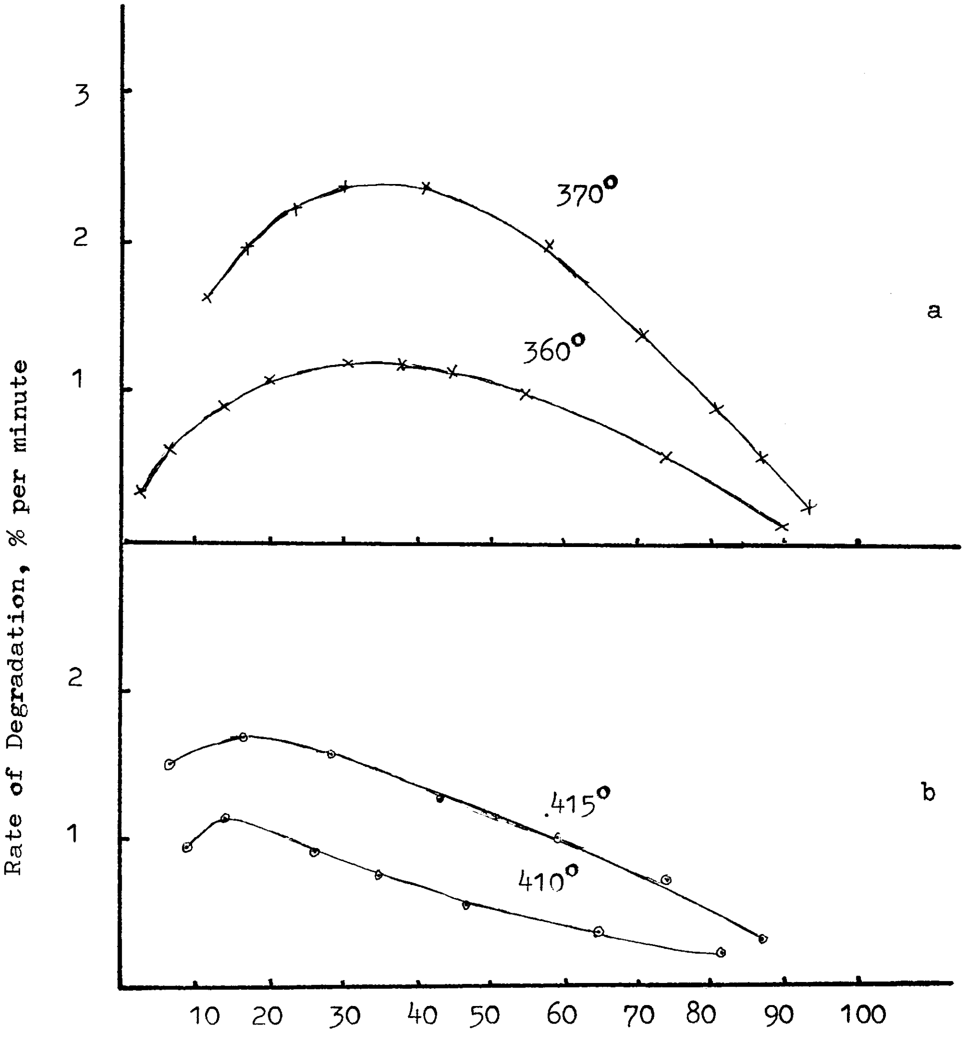


Figure 5.1 Rate of thermal degradation of polystyrene ($\bar{M}n$ = 605,000). Sample size being 0.5 mg.

a, Thick film

b, Thin film

Thick Film (370°)		Thick Film (360°)	
Amount Volatilised %	Rate of Volatilisation % of sample /min.	Amount Volatilised %	Rate of Volatilisation % of sample /min.
10.5	1.65	2.0	0.35
16.25	2.0	6.25	0.65
22.67	2.24	13.2	0.90
29.7	2.46	19.56	1.1
40.7	2.46	30.0	1.22
57.7	2.0	37.36	1.22
70.5	1.4	44.5	1.15
80.8	0.9	54.5	1.0
87.3	0.57	73.8	0.57
93.75	0.25	90.0	0.11
Thin Film (415°)		Thin Film (410°)	
6	1.52	8.5	0.95
16	1.7	13.5	1.15
28.2	1.58	26.0	0.9
43	1.26	34.5	0.75
59.5	1.0	46.5	0.55
74.6	0.70	65.0	0.35
87.6	0.30	82.0	0.2

Table 5.1 Results of thermal degradation of thin and thick films of 0.5 mg PS ST2.

films of the same sample size (fig. 5.1-b) show a different trend. The rate reaches a maximum between 10-20 per cent degradation then falls down with almost a constant slope. This behaviour of thin films is somewhat similar to that of poly (α - methyl styrene).[71]

The sharper drop in molecular weight, in the very early stages of degradation, of thick films than that of thin films is shown in figs. 4.5 and 4.6. Although the thick films were degraded at a lower temperature than the thin films, it is seen from fig. 4.5 that the molecular weight drops more steeply than that in the case of thin films. This is contrary to results obtained by Jellinek [4,77] where he found that the molecular weight of polystyrene degraded in bulk, drops to a limiting value, and this value is lower the higher the temperature of degradation.

Since a rate maximum at 25 per cent or greater conversion and a rapid initial fall in molecular weight are both characteristic of degradation involving intermolecular transfer, the rate and molecular weight results of this work suggest that this enhanced thermal stability of thin films is due to a reduction of intermolecular transfer.

The GLC results of figs. 4.7 and 4.8 show that more styrene monomer is produced from thin films than thick films of the same weight. Since transfer causes fragmentation and the production of small fragments such as dimers, trimers, tetramers and pentamers in diminishing quantities, then it is reasonable to assume that the production of more monomer is due to the reduction of the transfer reactions. This would mean that, in thin films, the kinetic chain length for depropagation is greater than that in the thicker films.

Jones and Moyles [74] and Knight [76] have shown that more monomer is produced from very small samples of polystyrene deposited as thin films on a filament. Samples in the microgram level produced more monomer. However, the method and techniques these authors used were of flash pyrolysis and direct analysis of the degradation products by gas chromatography.

The fall in molecular weight, the rate of volatile products and the amount of styrene monomer produced, in thin and thick films, discussed above, also suggest that intermolecular transfer is a major factor taking part in the degradation process of polystyrene.

The reactions taking place during the degradation of bulk samples or thick films may be explained as follows:

At low temperatures, the polymer molecules are ruptured at sites randomly distributed, forming radicals which stabilise themselves rapidly by recombination or by abstracting tertiary hydrogen atoms in a disproportionation reaction, or by transfer causing further scissions. At higher temperatures the radicals start either to depolymerise by unzipping into monomers or attack other sites on the same molecule or on other molecules in the neighbourhood and abstract tertiary hydrogen atoms causing more scissions. The molecular weight thus falls down very rapidly. Depolymerisation continues and the kinetic chain length becomes greater than the chain length of the molecules present in the reaction at this stage. The molecules start to unravel and disappear from the system at a faster rate than the transfer reaction. Therefore, little further drop in molecular weight is observed and the molecular weight reaches a limiting value. Termination takes place by disproportionation or unravelling of whole molecules.

Results shown in fig. 3.7, where the higher the initial molecular weight the lower was the T_{max} value, may be explained as follows:

Transfer reactions take place in the high molecular weight polymers producing more initiation sites. Thus, the rate of formation of volatile products increases very rapidly and reaches a maximum at a temperature lower than that for the low molecular weight samples. In the case of very low molecular weight (4000, for example) once initiation starts the transfer reactions have little opportunity to be effective because of the zip length being much greater than the chain length. Therefore, the rate increases more gradually due to the dominent reactions of random scission and depolymerisation. Thus the rate reaches a maximum at a higher temperature than that of the high molecular weight polymers.

Reactions taking place during the degradation of thin films on the other hand may be explained as follows:

The radicals present in the reaction have very little opportunity to cause intermolecular transfer, since the molecules are very thinly distributed. Therefore, unzipping into monomers is more predominent. This would account for the shape of the rate curves in fig. 5.1 - b and for the higher yield of styrene monomer than that in the case of thick films.

However, the polymer molecules are not distributed in an ideal unimolecular layer in thin films. Therefore, some intermolecular transfer is expected to be taking place to a limited extent. This may account for the initial drop in molecular weight in the case of thin films, although this would not entirely exclude the possibility of the presence of "weak links".

Chapter six:

6.1 Degradation of Poly (methyl methacrylate) PMMA:

Poly (methyl methacrylate) shows different TVA curves according to its polymerisation mechanism. Polymers prepared by the free radical polymerisation mechanism usually contain unsaturated chain ends which initiate thermal degradation at an early stage as described in chapter one. Thus such polymers produce two peaks in the TVA curve, the first peak, which is related to the first fast reaction stage, varies in size according to the number of unsaturated chain ends present, i.e. according to the number average molecular weight. Polymers prepared by anionic polymerisation mechanism, on the other hand, contain no unsaturated chain ends and show only one peak in the TVA curve, which corresponds in temperature range to the second reaction stage above, consisting of random chain scission and unzipping to monomer.

Polymers prepared by free radical mechanisms having various molecular weight (samples, D6, D10, D12, I.C., FRI nad AI) were degraded in the TVA appartus. An anionic polymer sample was also available (see appendix).

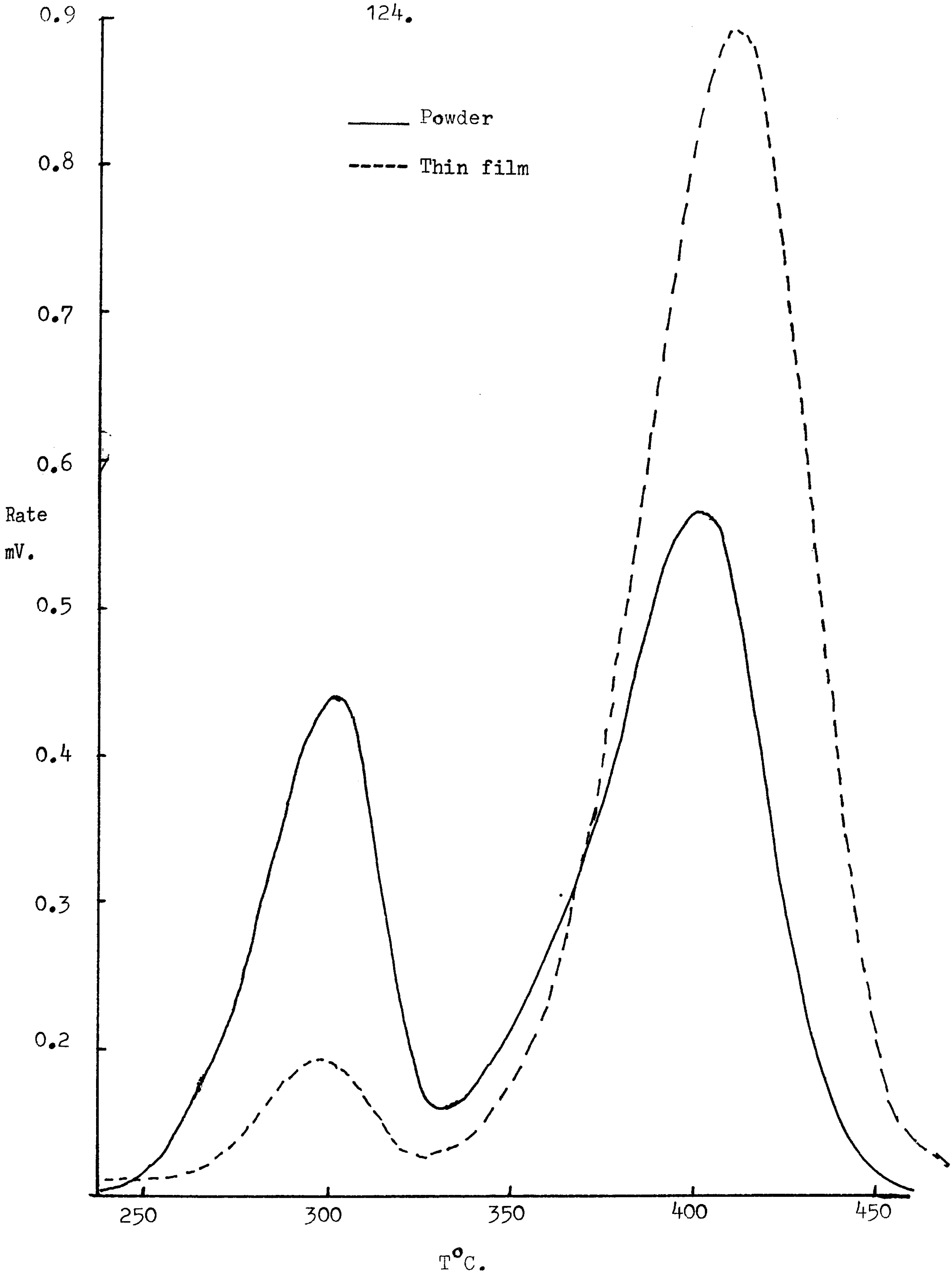


Figure 6.1 Degradation of 0.3 mg of PMMA samples (D10) in tube No.1 (10 cm^2).

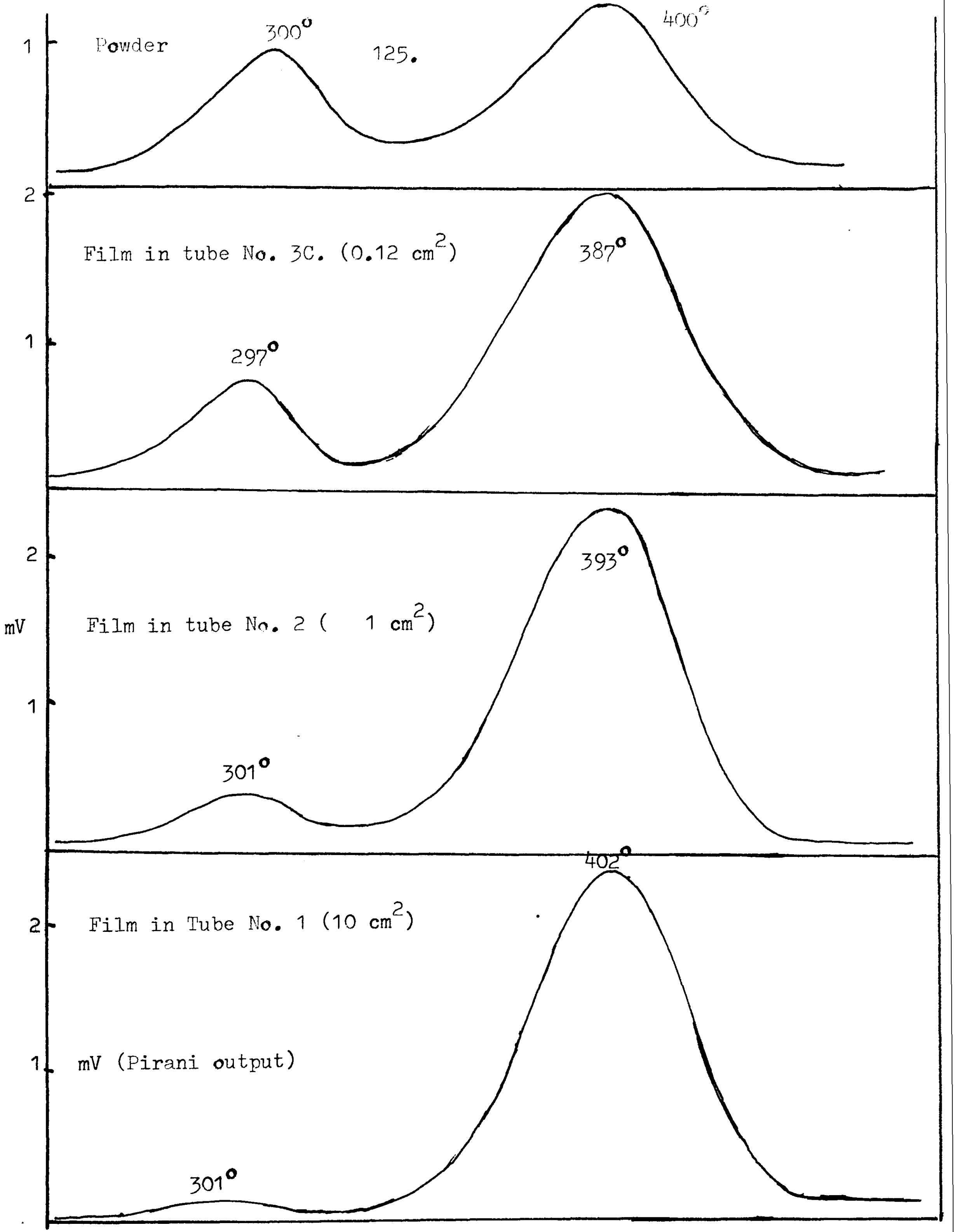


Figure 6.2 Degradation of 0.1 mg sample weights of PMMA (D10) as films and powder.

A 0.3 mg sample of polymer D10 was degraded in tube No. 1 (10 cm^2) in the powder form and in the film form. The first peak was observed to be very much smaller in the film than that of the powder as seen in fig. 6.1.

1.0, 0.1 and 0.01 per cent W/V solutions of the polymers were prepared in benzene and in toluene as was described in the case of polystyrene. 0.1 mg sample weights of polymer D10 were degraded in the powder form as well as in the film form in three different tubes Nos. 1, 2 and 3C with base areas of 10, 1 and 0.12 cm^2 respectively.

The first peak which is related to volatile products produced during the first stage of chain end initiated reaction was observed to be smaller in thin films than that of the thick film. The first peak for the same sample weight in powder form is larger than any of the corresponding peaks in the thin films of three different thicknesses, as shown in fig. 6.2.

6.2 Degradation of PMMA by T.G.

Poly (methyl methacrylate) sample D10 was degraded in the TG apparatus under a vacuum of about 10^{-4} torr at 10°/minute heating rate.

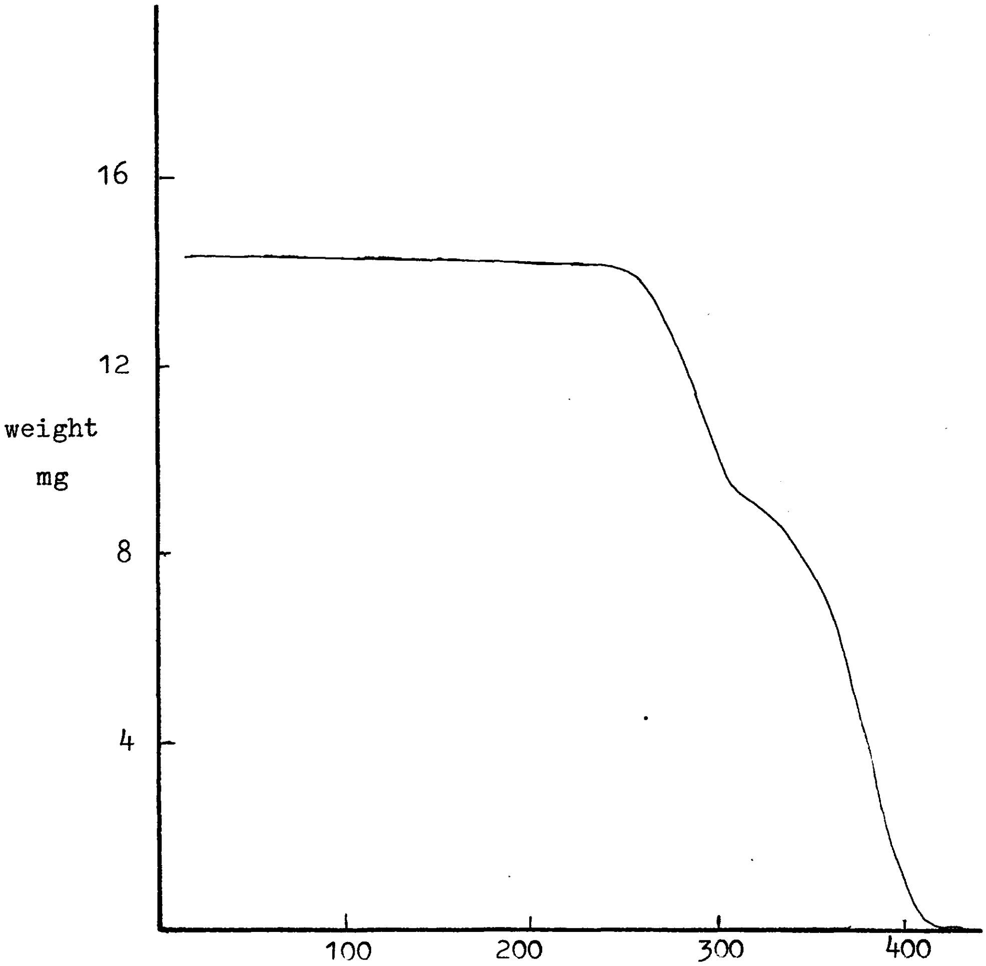


Figure 6.3 Degradation of PMMA sample D10 in the TG apparatus, in the powder form.

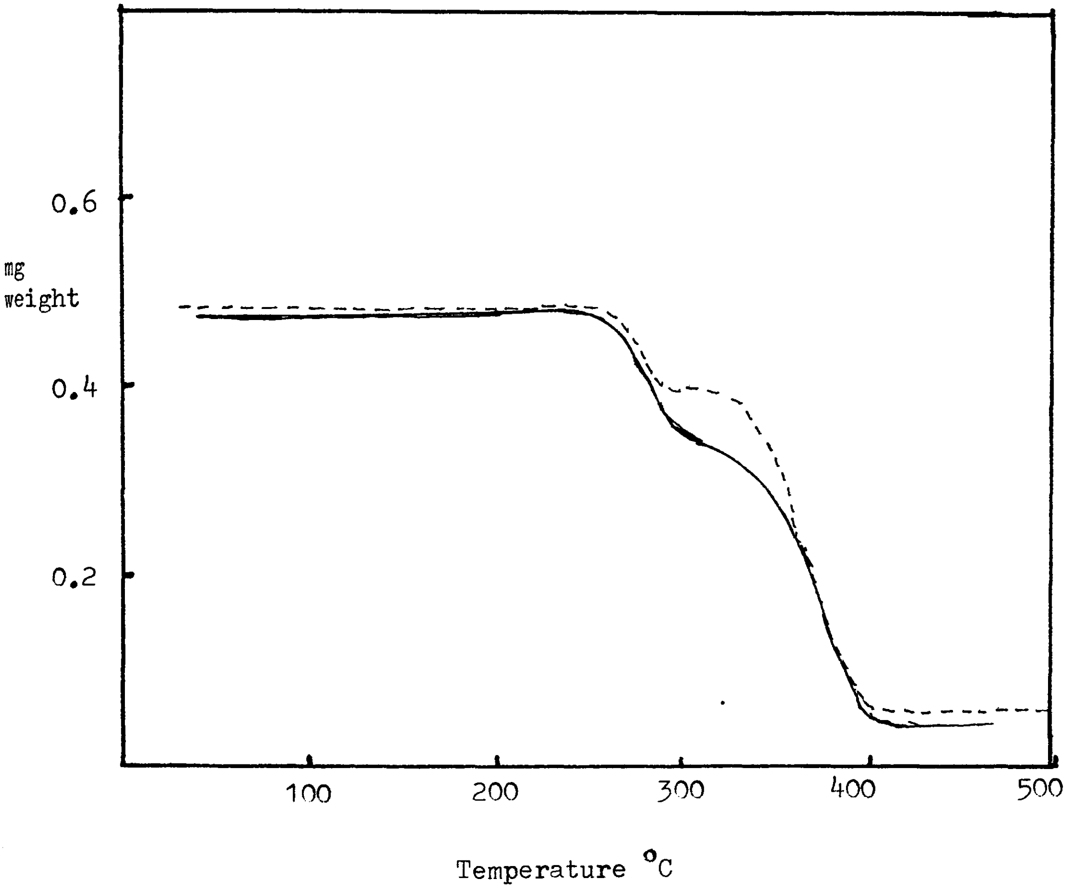


Figure 6.4 Degradation of poly (methyl methacrylate) sample D10 (0.4 mg weight) in Du Pont TG machine.

______ powder sample

------- film sample

A powder sample of 14.3 mg weight was degraded and the weight loss corresponding to the first reaction stage was observed to be about one third of the total weight (see fig.6.3).

A 0.4 mg film sample was formed on the platinum sample holder of the TG apparatus by transferring a few drops of the polymer solution of 0.5 per cent concentration. The benzene solvent was allowed to evaporate before the apparatus was connected to the vacuum line. The film was degraded at a heating rate of 10°C per minute. The same sample weight in the powder form was also degraded under the same conditions.

From fig. 6.4 it is seen that the first stage of the reaction is about one third of the total weight of the powder sample. While it is only one fifth of the total weight of the film sample.

The weighing system of the TG apparatus was set at maximum sensitivity. The small size of the platinum container and its shape, which is curved, deep in the middle, made it difficult to cast a thin film. Therefore, it was not possible to get meaningful results for sample weights smaller than 0.4 mg.

6.3 Degradation of sample AI by TVA:

Since this polymer ($\bar{M}n$ = 28,000) contained a large number of unsaturated chain ends (see appendix) it showed a large peak for the first reaction stage of the TVA curve.

When a 1 mg sample of A1 was degraded in the powder form in tube No. 1 (10 cm^2), the first peak, which is related to chain end initiated reaction, was higher than the second peak which is related to random chain scission, whereas in the film, the reverse was observed, i.e. the first peak was much smaller than the second, as shown in fig. 6.5.

6.4 Degradation of other PMMA samples:

Poly (methyl methacrylate) samples D6, D12 and I.C. all showed the same effect of reduction in the first stage of degradation when they were degraded in the form of thin films.

Sample DN contained no unsaturation at chain ends, since it was prepared by an anionic polymerisation mechanism, see appendix, it showed only one peak in the TVA curve, which is related to the second stage of reaction. Sample FRI had a high molecular weight ($\bar{M}n = 1.5 \times 10^6$) therefore, the number of chain ends is small and it showed only a small sholder on the second peak of the TVA curve. The latter two samples therefore, did not show significant differences in behaviour as thin films.

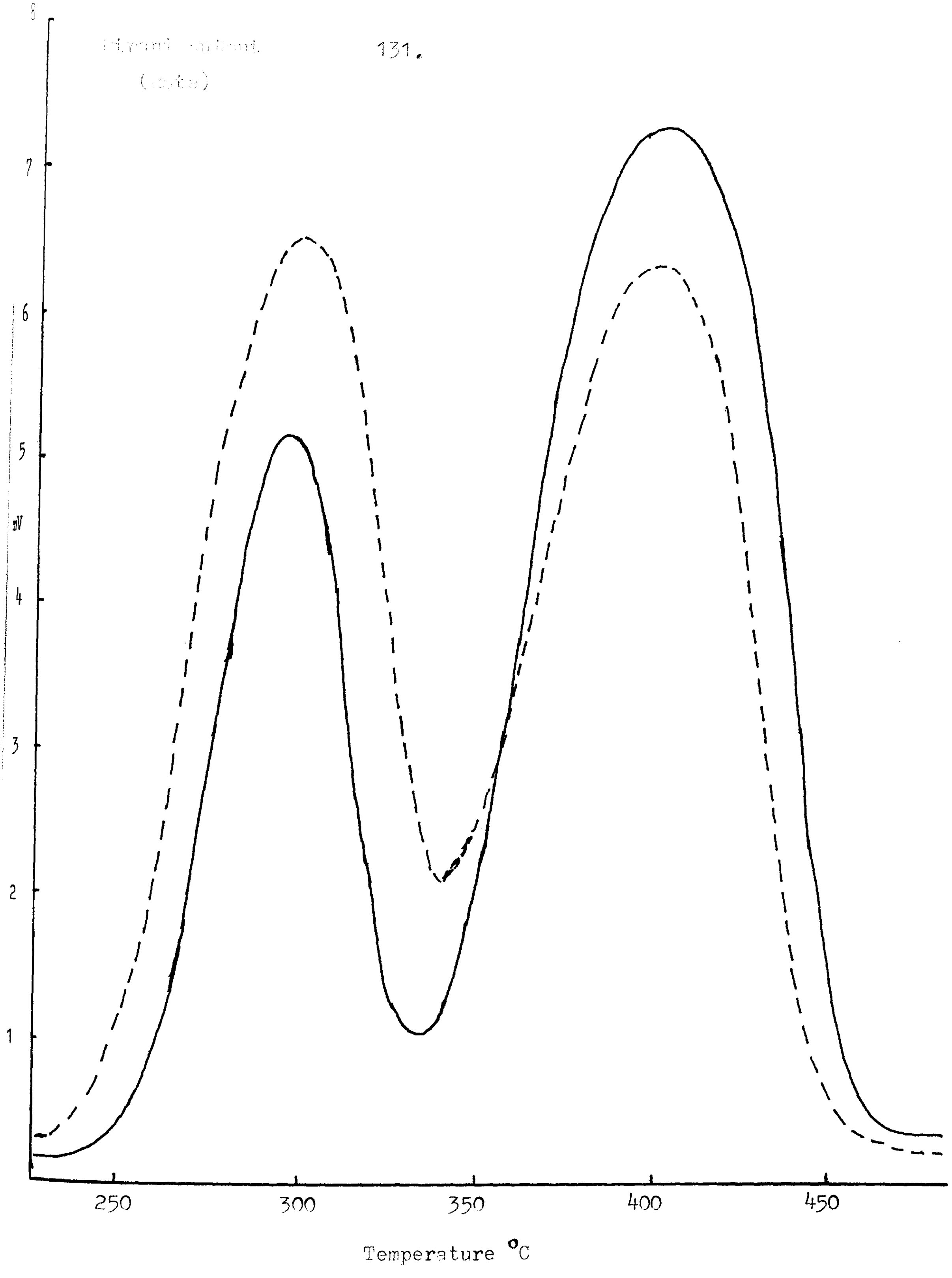


Figure 6.5 Degradation of 1 mg samples of PMMA (A1) in tube No. 1 ($10\ cm^2$).

——— Film sample ------ Powder sample.

6.5 Degradation of PMMA Blends:

Polymers DN and FRI, as have been shown above, showed no significant first peak. If however, a very small amount of polymer A1, which contains a large number of unsaturated chain ends, is mixed with each of these two polymers, an increase in the first peak might be expected. Therefore, a mixture of A1 and DN of ratio 1:9 weight by weight was made respectively. A similar blend of A1 and FRI was also made. The mixtures were made into 1 per cent W/V solutions in toluene. Thus, 1 mg of either mixture contained 0.1 mg of A1 and 0.9 mg of DN or FRI polymer.

The films were prepared as previously described. 1 mg samples of the mixtures were degraded in the TVA apparatus using degradation tubes Nos. 1 and 2 of base areas 10 and 1 cm^2 respectively. A 0.1 mg of polymer A1 was degraded in tubes No. 1 and 2 to compare the size and height of the first peak with that resulting from the blends.

It was observed that the first peak in the TVA curve of the blends was larger than the corresponding peak when a 0.1 mg of polymer A1 was degraded alone as shown in figs. 6.6, 6.7, 6.8 and 6.9. It is also seen that the thinner the film the smaller was the first peak.

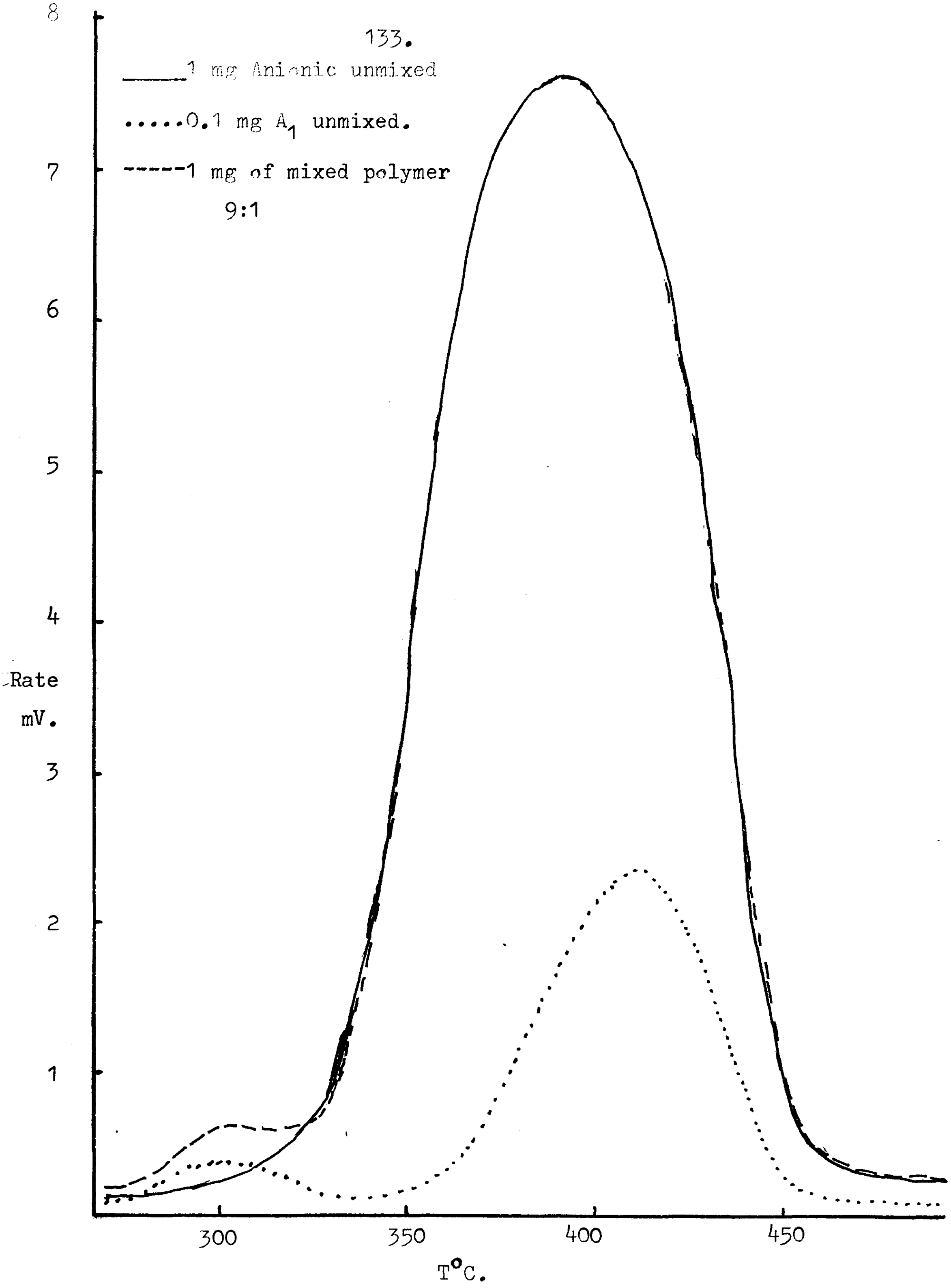


Figure 6.6 Degradation of PMMA, mixed and unmixed, samples in tube No. 1 (10 cm^2).

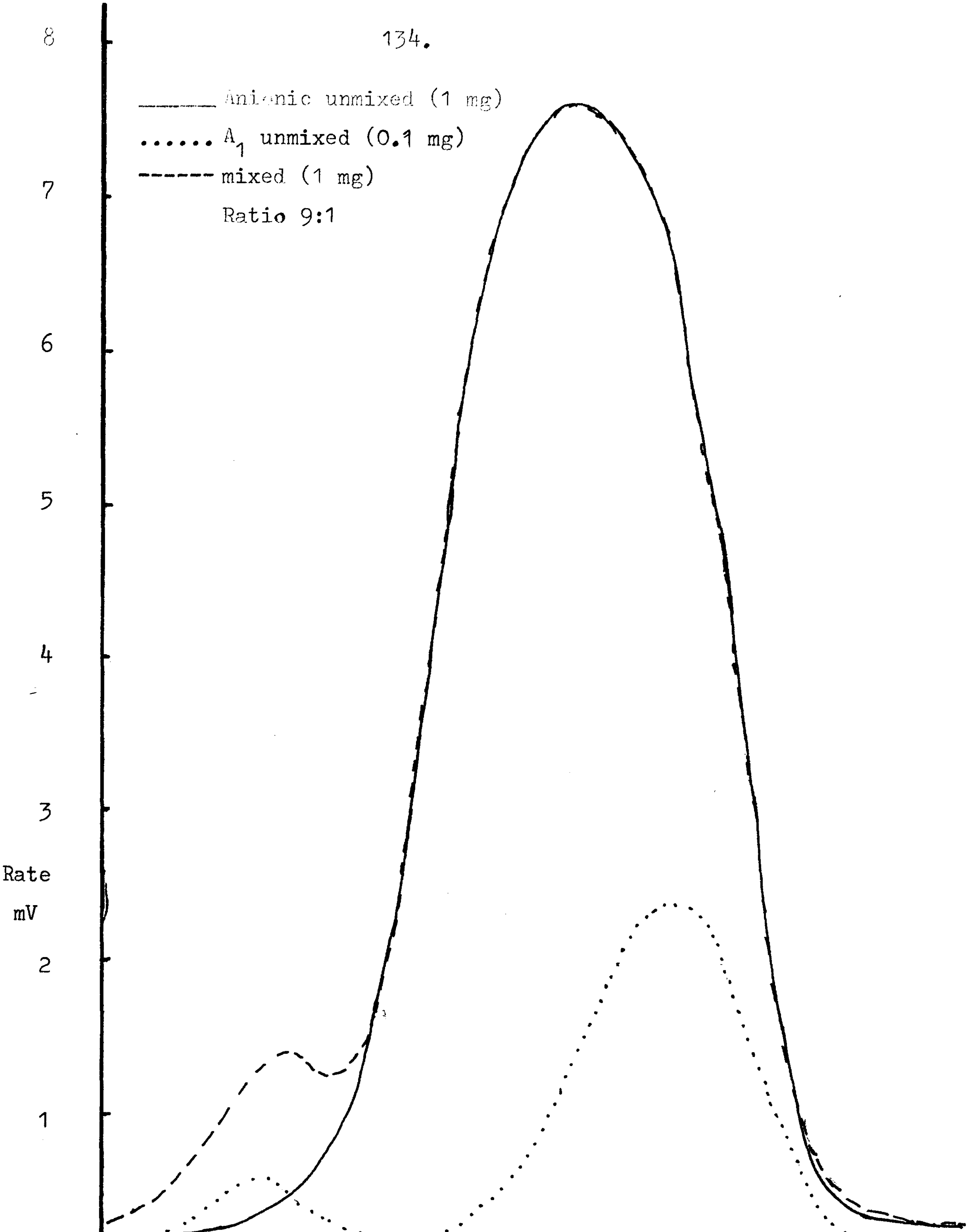


Figure 6.7 Degradation of PMMA, mixed and unmixed, samples in tube No. 2 (1 cm^2).

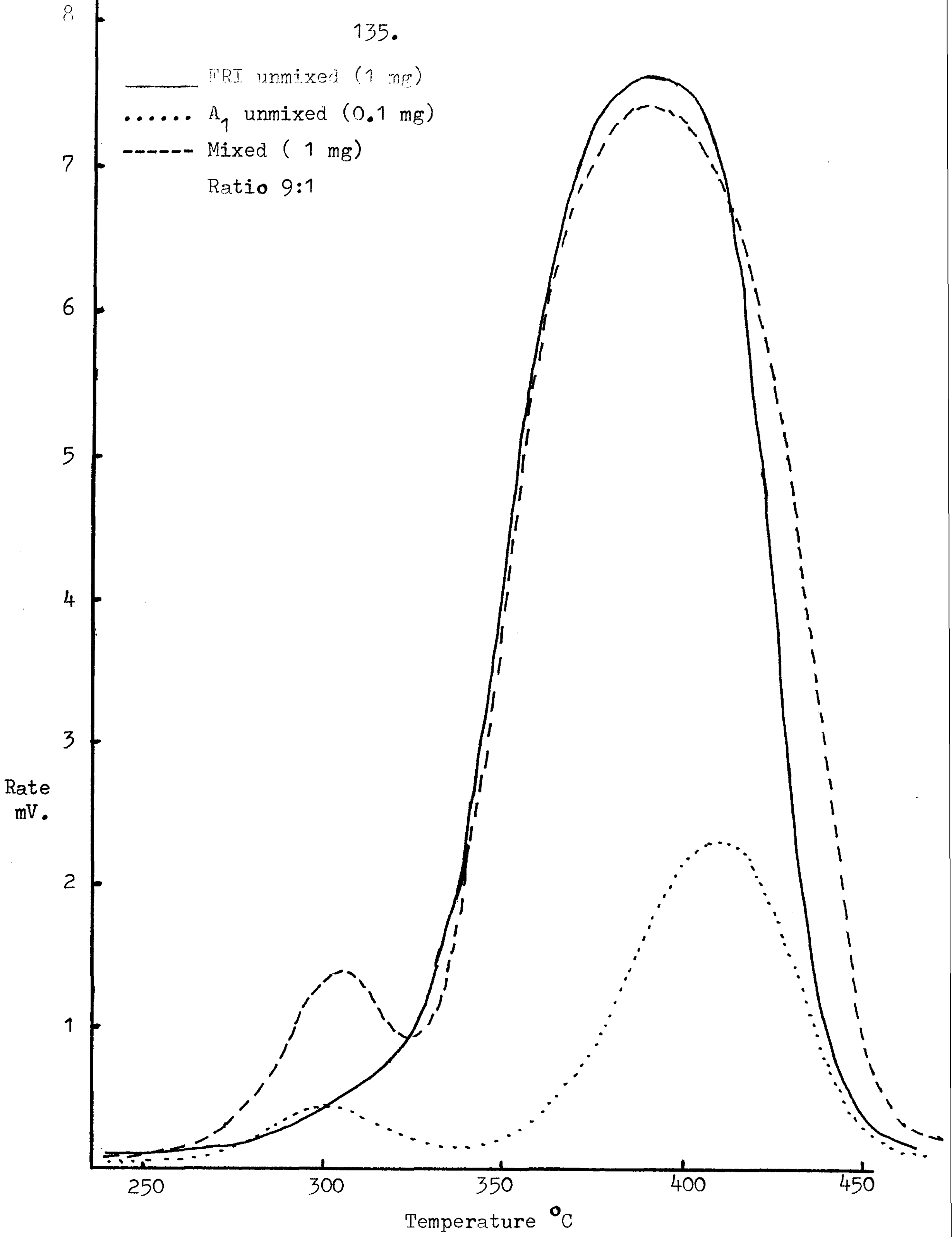


Figure 6.8 Degradation of PMMA mixed and unmixed samples in tube No. 1 (10 cm^2).

Sample size is 1 mg of mixed polymer.

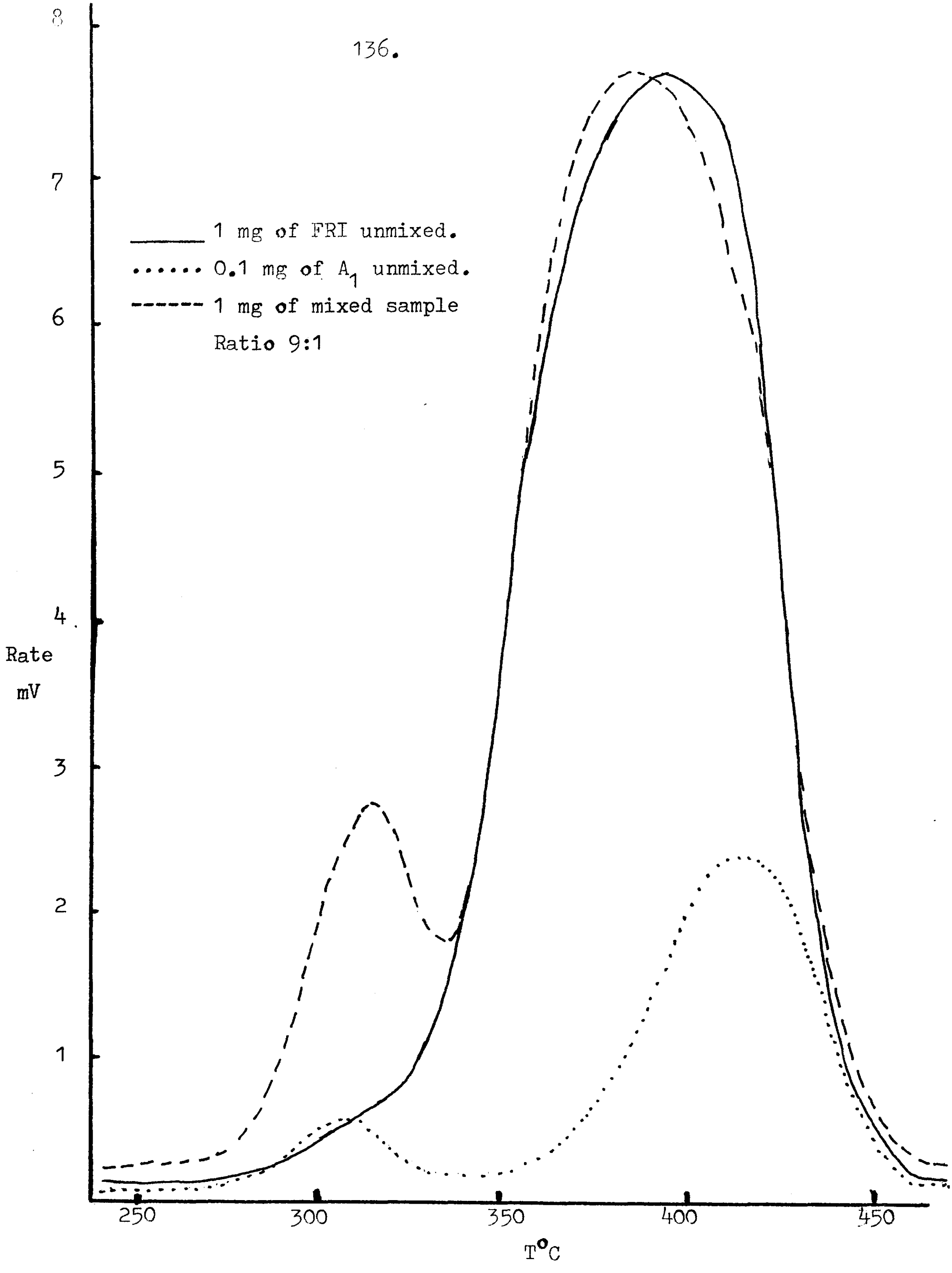


Figure 6.9 Degradation of mixed and unmixed of PMMA samples in tube No. 2 (1 cm^2).

Ratio FRI: A_1 is 9:1.

6.6 Discussion of Results for Poly (methyl methacrylate):

In fig. 6.1 it is observed that there is a significant reduction in volatiles produced during the first reaction stage, which is due to chain end initiation, when the polymer is degraded as a thin film. This behaviour is also illustrated in fig. 6.2 where various film thicknesses were compared with the powder sample. This suggests that radicals formed during the chain end initiation are taking part, to some extent, in a transfer reaction, in case of thicker samples.

As discussed in the Introduction in Chapter One, the radicals may abstract a secondary hydrogen atom causing scission and forming new labile sites which may take part instantaneously in volatile production. The available hydrogen atoms for transfer reactions are those in the secondary position, since the primary hydrogen atoms on the methyl groups are more difficult to be abstracted by a radical. Although the secondary hydrogen atoms are ten or eleven times less reactive than tertiary hydrogen atoms, the possibility of a transfer reaction is not negligible.

Results obtained from degradation experiments carried out in the TG apparatus shown in fig. 6.3 indicate that the volatiles produced in the first reaction stage amount to about one third of the total weight of the powder sample. Fig. 6.4 compares the weight loss during the first stage between film and powder samples of the same weight. It is very clear from fig. 6.4 that the first stage in the film sample has been reduced very significantly. This also confirms results obtained from degradation carried out in the TVA apparatus.

In fig. 6.5, the same effect is observed for a powder of a low molecular weight (A1,28200, see appendix) which contains a large number of unsaturated chain ends and shows a large first peak in the TVA curve.

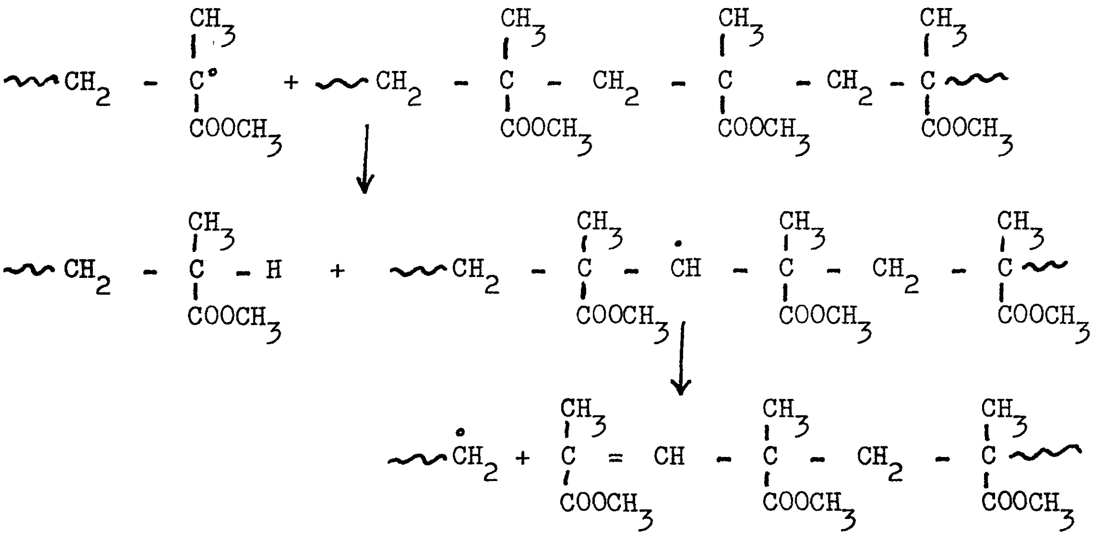
In figs. 6.6 and 6.7, where A1 was mixed with an anionic polymer sample, which does not usually show chain end initiated degradation, in the ratio 1:9, as previously described, it is observed that the volatiles from the first reaction stage have increased in thicker films.

The same effect was observed when polymer A1 was mixed with a very high molecular weight sample which contains few unsaturated chain ends, as is shown in figs. 6.8 and 6.9.

All these observations suggest that some transfer, at least to a limited extent, may be taking place in the degradation of the polymer. This is in agreement with the mechanism suggested by Cameron and Kerr [43] and MacCallum [45], discussed in the Introduction.

Therefore, the degradation reaction probably proceeds in the following way:

Initiation takes place at chain ends and radicals start to depolymerise producing monomers. Some of these radicals may abstract hydrogen atoms on secondary carbon atoms of polymer molecules. This is followed by scissions in the activated molecules and new unsaturated chain ends are thus formed which take part in a new initiation reaction. Hence a larger number of depolymerisation sites is produced and the volatile products from the first reaction stage are thus increased.



$$\sim CH_2-\underset{COOCH_3}{\overset{CH_3}{C^{\circ}}} + \sim CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\sim$$

$$\downarrow$$

$$\sim CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-H + \sim CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-\dot{C}H-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\sim$$

$$\downarrow$$

$$\sim \overset{\circ}{C}H_2 + \underset{COOCH_3}{\overset{CH_3}{C}}=CH-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\sim$$

Thus a new labile chain end is produced and the very active $\sim\overset{\circ}{C}H_2$ radical may take part in transfer or termination reactions rather than depolymerise to produce monomer.

In the second stage, random scission and depolymerisation into monomers predominate. The zip length becomes much greater than the chain length and the molecules unravel and disappear from the reaction zone.

If the initial molecular weight is too high, then the number of unsaturated chain ends is very small, and the first reaction stage is expected to be very limited and it appears as a small sholder on the peak of the second reaction stage in the TVA curve. In the second reaction stage, random scission and some transfer may take place which cause some fall in molecular weight observed in results obtained by Grassie and Melville [40], and Hart [44].

In contrast, when a thin film is degraded the possibility of transfer is considerably reduced, and volatile products appear to be less in the first reaction stage. The reaction in thin films may be explained in the following way:

Initiation starts at chain ends and monomer is produced. Transfer reactions however, are greatly reduced and may be completely eliminated. Therefore, the mechanism explained above is highly restricted and new labile chain ends are not formed. Thus the volatile products during the first reaction stage are less in thin films than that in thick films. The second reaction stage proceeds as in the case of thick films by random scission and depolymerisation into monomers.

6.7 Degradation of Poly (methyl acrylate):

Films were made from solutions of this polymer in benzene, as previously described.

0.3 mg samples were degraded as a thin film and as a small piece of solid polymer respectively, in the TVA apparatus, using degradation tube No. 1 (10 cm^2).

The thin film was slightly more stable than the bulk sample, and showed a T_{max} value 15°C higher than the corresponding value obtained from the bulk polymer (see fig. 6.10).

A 20 mg sample was degraded in bulk and showed a peak similar to that of polystyrene but with a T_{max} value of 400°C.

Fig. 6.10 shows an enhanced stability of the thin film. This is similar to results obtained from degradation of polystyrene films.

The shift in T_{max} values of thin films appear to be less than that observed in polystyrene. This may be due to the slight elastomeric properties of this polymer causing the film to be thicker than expected, as previously explained in the case of elastomers.

This polymer degrades largely by intermolecular transfer. Restriction of this in the thin films is a reasonable explanation for the enhanced stability since this polymer like polystyrene also contains tertiary hydrogen atoms which are labile and easily abstracted by a radical.

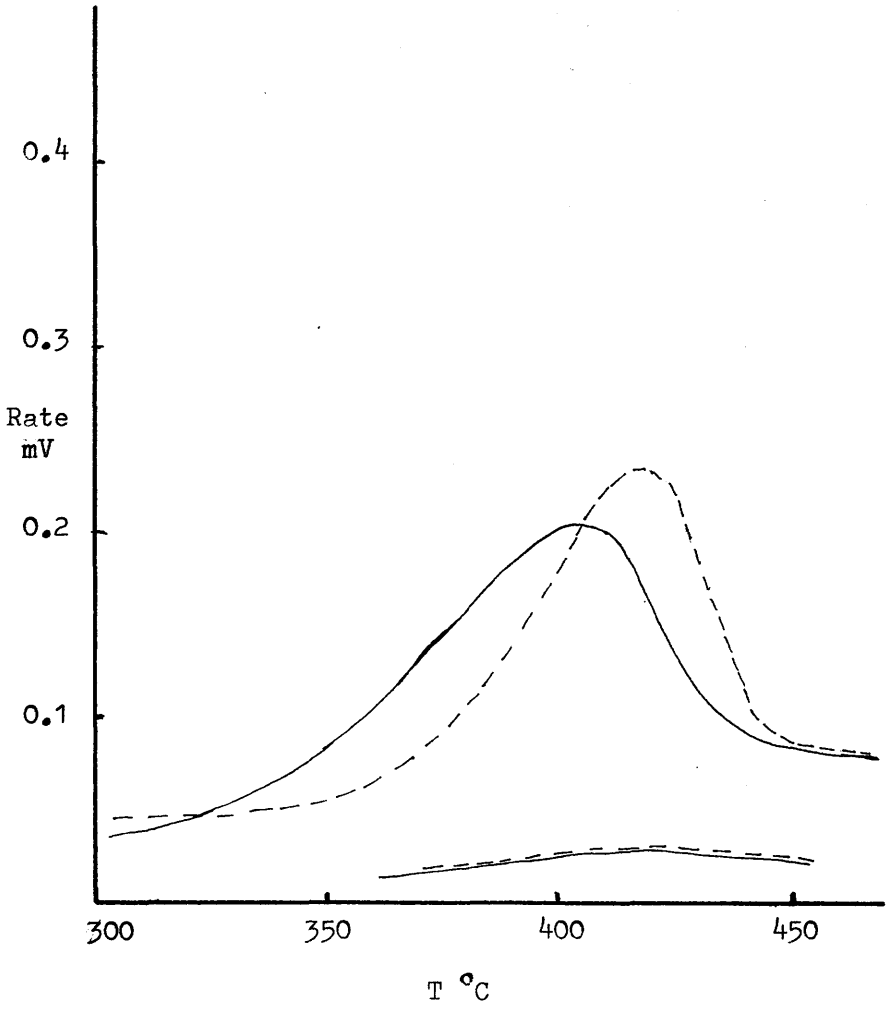


Figure 6.10 Degradation of 0.3 mg samples of poly (methyl acrylate) in tube No. 1

——— Powder.

------ Film

6.8 Degradation of Poly (methacrylonitrile):

A solution of this polymer was made in cyclohexanone, and films were prepared under nitrogen gas as previously described.

0.3 mg Polymer samples were degraded in the form of powder and thin film. This polymer showed an effect similar to that observed in poly (methyl methacrylate) i.e., the first peak was smaller in thin films than that of the powder samples, as shown in Fig. 6.11.

T_{max} values were 332°C for the first peak and 400°C for the second peak.

Fig. 6.11, shows some reduction in the size of the first peak, non reproducibility may be due to uneven thicknesses of thin films.

In this polymer the reaction is like that of poly (methyl methacrylate) initiated at chain ends. Since there was a slight drop in molecular weight shown in results obtained by Grassie and McNeill [55], transfer might be taking place to a small extent through the β-hydrogen atoms

6.9 Degradation of Poly (tert. butyl methacrylate):

A 1 per cent solution was made in acetone and films were prepared as in the case of polystyrene.

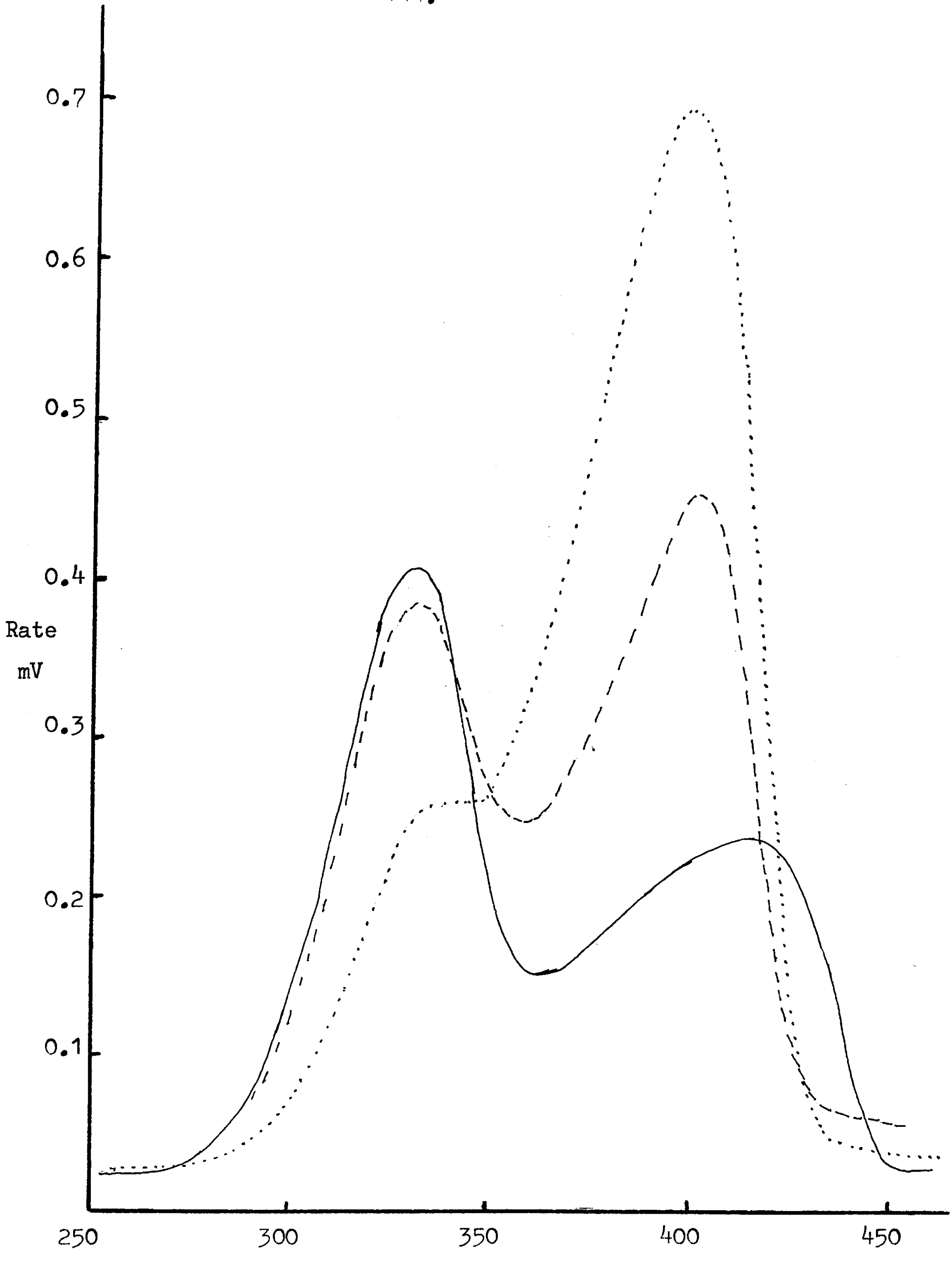


Figure 6.11 Degradation of 0.3 mg samples of Poly (methacrylonitrile) in tube No. 1.

——— Powder ······· film ----------- film

A 20 mg sample was degraded in the TVA apparatus and the curve showed three peaks at temperature 180°, 256° and 440°C respectively. The same values were obtained when the polymer was degraded in small sample weights and as a very thin film.

These results should be expected since this polymer behaves entirely different from other methacrylates as was discussed in the Introduction.

In the early stages of temperature rise some monomer is produced. Then the elimination of isobutene commences autocatalytically. Water is also eliminated intramolecularly which is not affected by film thickness.

Therefore there seems to be no change in the mechanism of degradation of this polymer according to variations in film thickness.

6.10 Degradation of Poly (vinyl chloride) PVC:

Solutions of PVC, Geon 101 (see appendix), were prepared in cyclohexanone and in tetrahydrofuran (THF) as previously described.

5 mg samples were degraded in tube No. 1 (10 cm^2) in the powder form and as a film. It was observed that the initial rate of production of HCl in the powder sample was higher than that of the film, as is shown in fig. 6.12. This difference

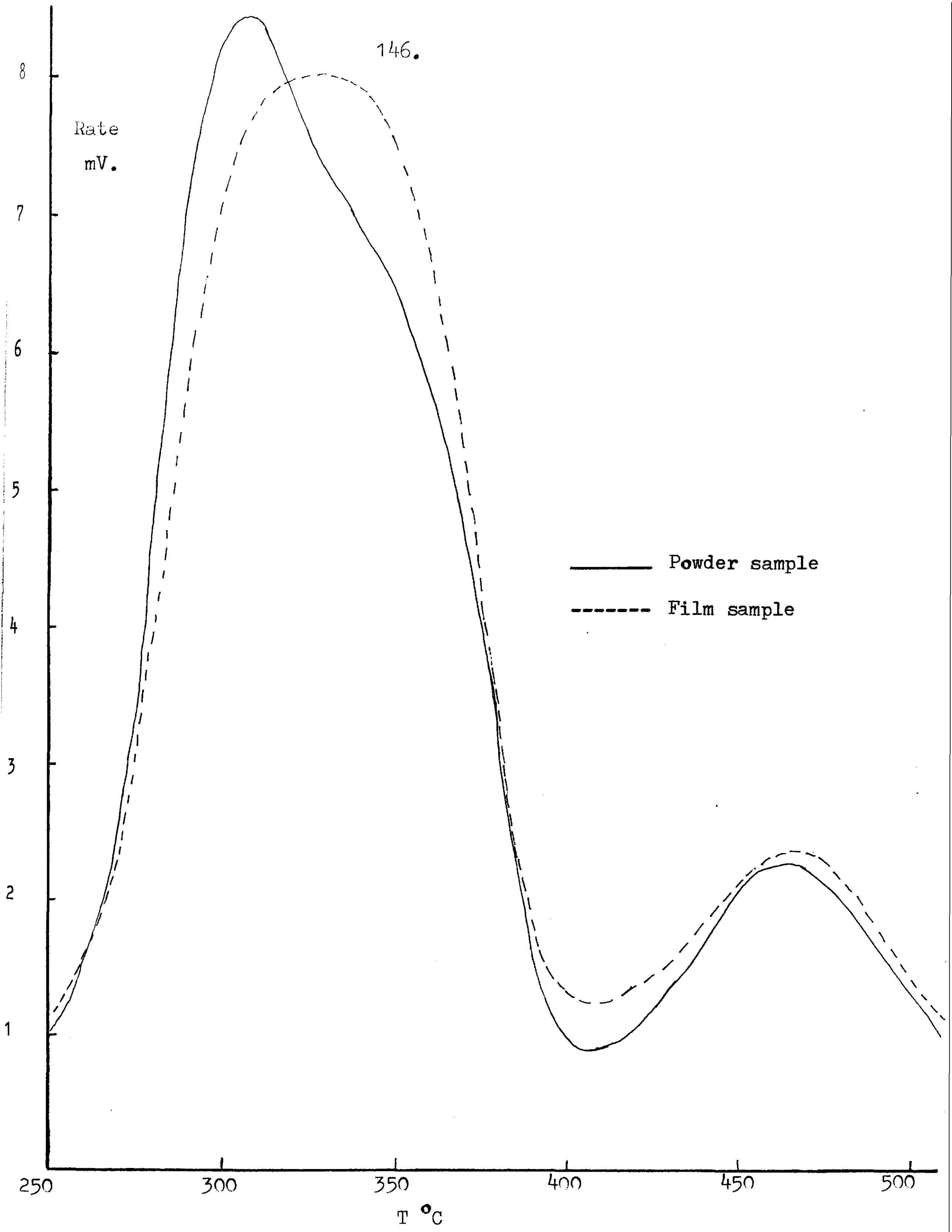


Figure 6.12 Degradation of 5 mg samples of PVC (Geon 101) using tube No.1, in the TVA apparatus.

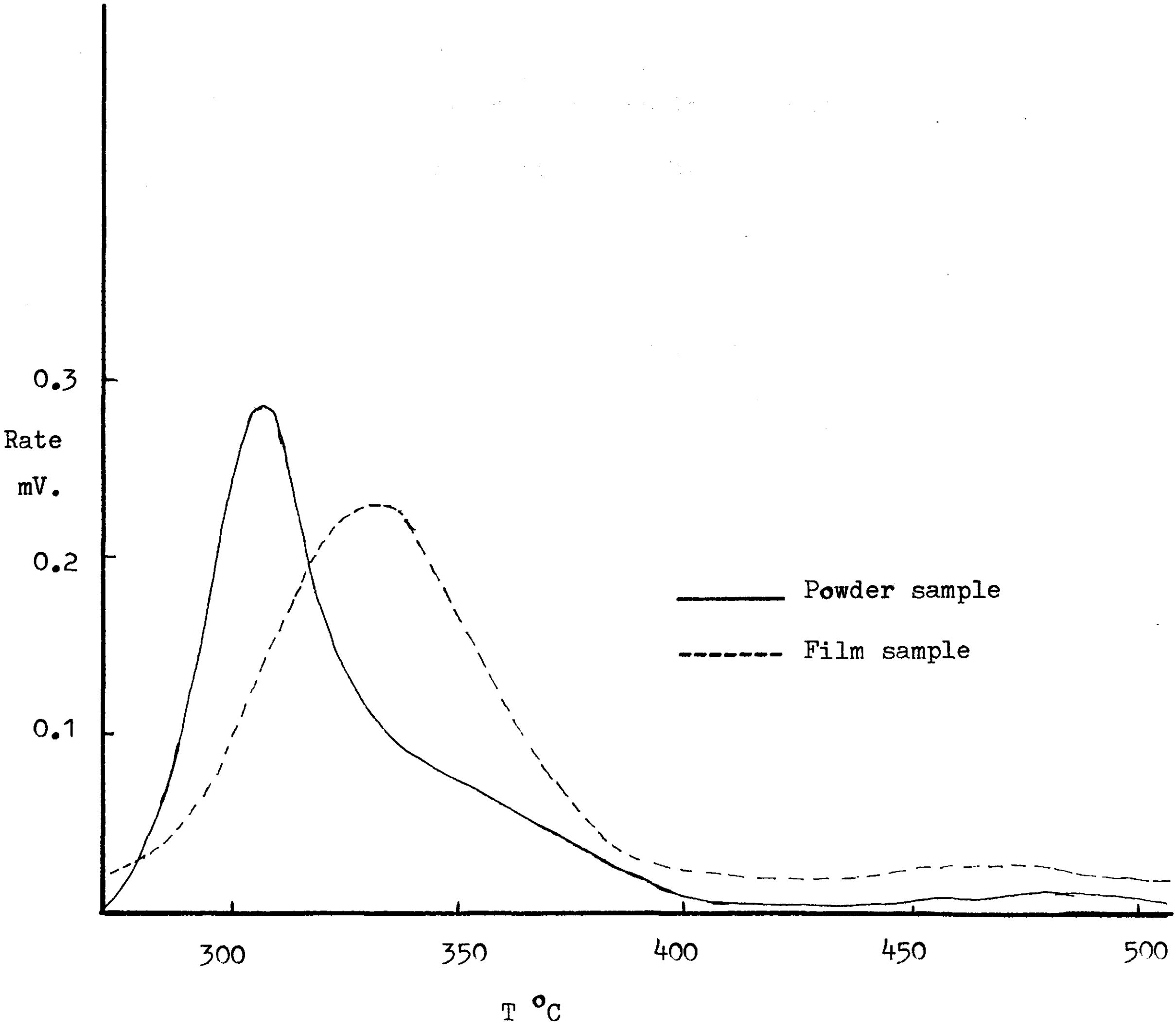


Figure 6.13 Degradation of 0.3 mg samples of PVC (Geon 101) using tube No. 1 in TVA apparatus.

in the initial rate of production of HCl caused an apparent shift in T_{max} of the film by about 20°C. There was no shift in T_{max} of the second peak which is due to decomposition of the conjugated structure which is left after the elimination of HCl.

0.3 mg samples were also degraded as powder and as thin film. The same behaviour was observed as is shown in fig. 6.13, i.e. the initial rate of HCl production is much greater in the powder sample than that of the film. The broad second peak became very small and almost unidentifiable.

After degradation was complete, a brown residue was observed on the base of the degradation tube. The residue did not dissolve in organic solvents, but came off when it was wiped with a tissue paper soaked in chloroform.

The effect shown in figs. 6.12 and 6.13 may be different from the effect of film thickness observed in other polymers such as polystyrene and poly (methyl methacrylate) previously discussed, since it is observed in films of considerably greater thickness.

The higher rate of production of HCl in the powder sample may be due to autocatalysis by HCl, while in the thin film the liberated HCl escapes very readily from the reaction zone, before autocatalysis can occur.

Attention has already been drawn to the influence of sample thickness in PVC degradation, by Geddes [61].

6.11 Degradation of Poly (vinyl acetate):

Solutions of this polymer were made in benzene. When this polymer was degraded in the TVA apparatus, it showed two peaks, one at T_{max} 345°C and the second at 450°C.

A 0.2 mg thin film sample showed one peak at 345°C and the second peak was not visible. Thus, there was no shift in T_{max} values and the initial rate of production of acetic acid was the same for the solid sample and the film.

This may suggest that the elimination of acetic acid takes place by an intramolecular mechanism as discussed in the Introduction.

The second peak appears to be very small in the TVA curve especially for the thin films. The first peak is particularly large in PVA breakdown, so that the maximum Pirani response extends into the region for which the response is far from linear with rate. Therefore it is difficult to make valid comparisons of the relative sizes of the two peaks in the TVA curve for samples which differ in size, as in these experiments.

6.12 Degradation of Poly (vinyl alcohol):

A solution of this polymer was made in hot distilled water.

A 4.5 mg polymer sample was degraded in the powder form. The TVA curve showed two peaks, the T_{max} values of which were 260° and 380°C respectively.

A 1 mg sample was degraded as a thin film in Tube No. 1 (10 cm^2). T_{max} value of the first peak, which is related to the elimination reaction of water molecules, was shifted to a higher temperature by about 50°C as shown in fig. 6.14.

Since little is known about the mechanism of degradation of this polymer it is difficult to explain this behaviour from this little information. But it is evident that thin films are more thermally stable, and the elimination of water molecules is somehow hindered.

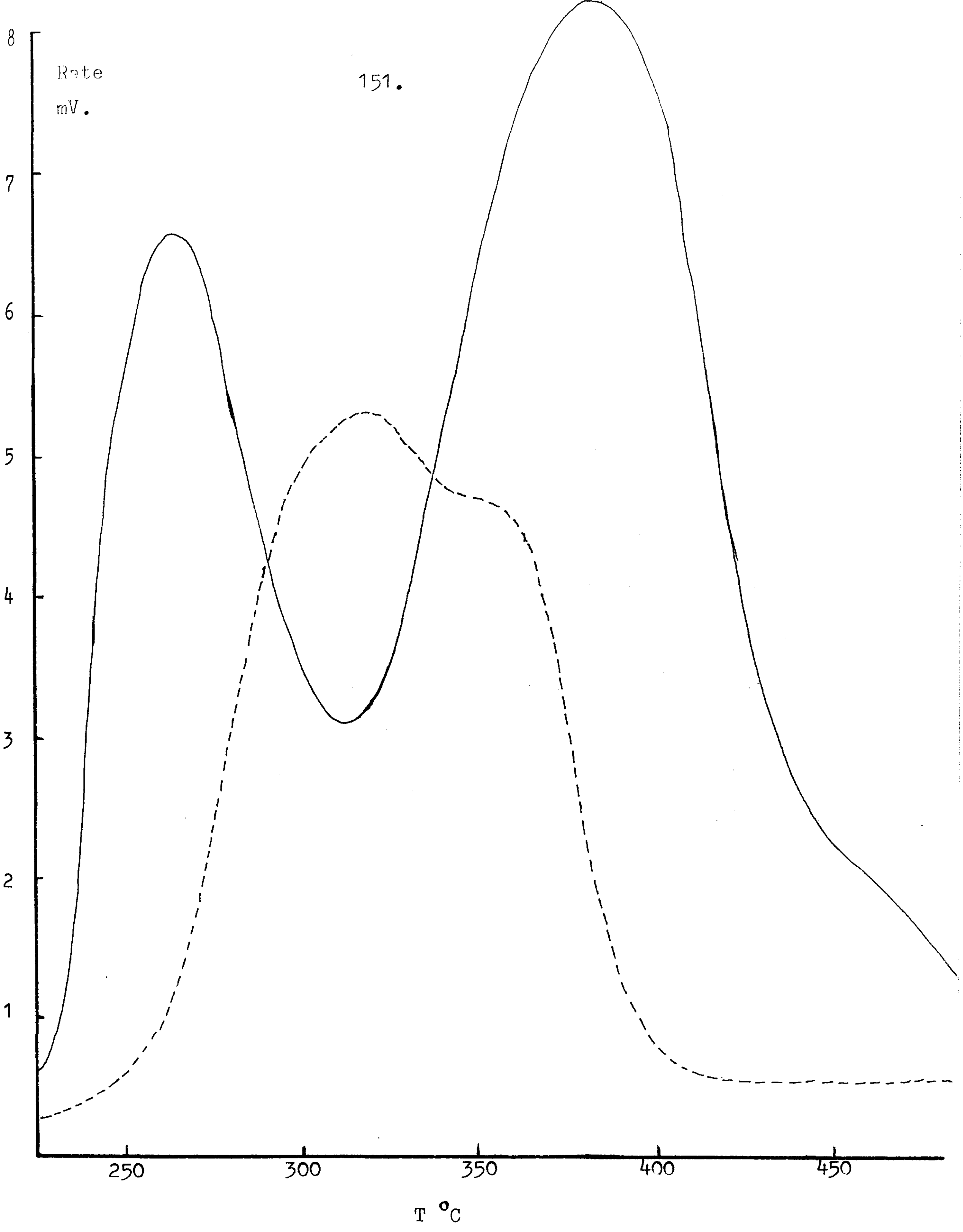


Figure 6.14 Degradation of poly (vinyl alcohol) in tube No. 1 in the TVA apparatus.

______ 4.5 mg sample in the powder form. ----- 1 mg sample as a thin film.

Chapter Seven

The Degradation of Copolymers of Vinyl acetate with ethylene and styrene.

7.1 Introduction:

The degradation of poly (vinyl acetate) is reviewed briefly in the Introduction in Chapter One.

Carbon dioxide and ketene, which were identified by Grassie's work [54], were not detected by Servotte and Desreux.[60] The latter authors also found some differences in the absolute rates which they suggested was due to the presence of copper in Grassie's apparatus, and no difference in rate among samples of molecular weights differing by a factor of 100 which is in contradiction to Grassie's postulate that initiation takes place at chain ends. Servotte and Desreux postualted a cross-linking reaction due to a chain breaking process occuring along with deacetylation.

The behaviour of copolymers of vinyl acetate with ethylene and styrene in which the acetate groups are next to methylene groups in the former case and next to phenyl groups in the latter case is examined here, in order to collect information about the effect of environment on the breakdown of vinyl acetate units.

7.2 Experimental:

Styrene monomer was purified of inhibitor by washing several times with 1N NaoH and then washed with water till it was neutral to litmus, and dried over unhydrous calcium chloride.

Vinyl acetate was purified of inhibitor by distillation (b.p. 71 - 72°C).

A few mls of benzene containing a known amount of initiator (Azobisisobutyronitrile) were added to the calibrated dilatometers. The benzene was then removed under reduced pressure.

Styrene monomer was degassed three times on a vacuum line and then distilled into a graduated flask from which the required quantity was then distilled into the dilatometer.

A similar procedure was carried out with vinyl acetate monomer except that degassing had to be carried out four or five times.

When the required amounts of styrene and vinyl acetate monomers had been added to the dilatometer, the dilatometer was sealed, placed in a thermostat at 60°C and the polymerisation was followed from the volume contraction.

The polymers were precipitated by adding the dilatometer contents to methanol, filtered off and redissolved in benzene. Reprecipitation was carried out by the slow addition of the solution through a dropping funnel to a large excess of methanol with stirring. The polymers were filtered off as before, collected and dried in a vacuum oven at room temperature.

Degradation behaviour was studied using differential condensation - TVA apparature[66], which is discussed in Chapter two (see fig. 2.3).

The heating rate used was 10°C/minute. The modifications for small sample sizes, discussed in Chapter two - C, were not applied in this work, because the samples used were of 50 mg or 100 mg. The apparatus was used with 10 mV full scale sensitivity for PVA, 2.5 mV for E/VA copolymers, and 1 mV for S/VA copolymers.

The main method used in product analysis was I.R. spectroscopy. Samples of the non-condensable (at - 75°) products were examined by two methods owing to the difficulty of distinguishing between Ketene and carbon monoxide. The first method involved degradation in a closed system and the second method involved degradation in a continuously evacuated system in order to remove CO gas (see fig. 7.1). Both methods involved collection of volatile products in a trap at - 196°C. At this point in the open system the vacuum pump was isolated. The temperature of the trap was then raised to - 75°C and non-condensables were distilled into a trap at - 196°C, which was attached to a gas I.R. cell (fig. 7.1). When equilibration had occurred the gas cell was isolated and allowed to come to room temperature and the I.R. spectrum was then obtained. The products isolated in the - 75°C trap were also collected and their I.R. spectrum obtained.

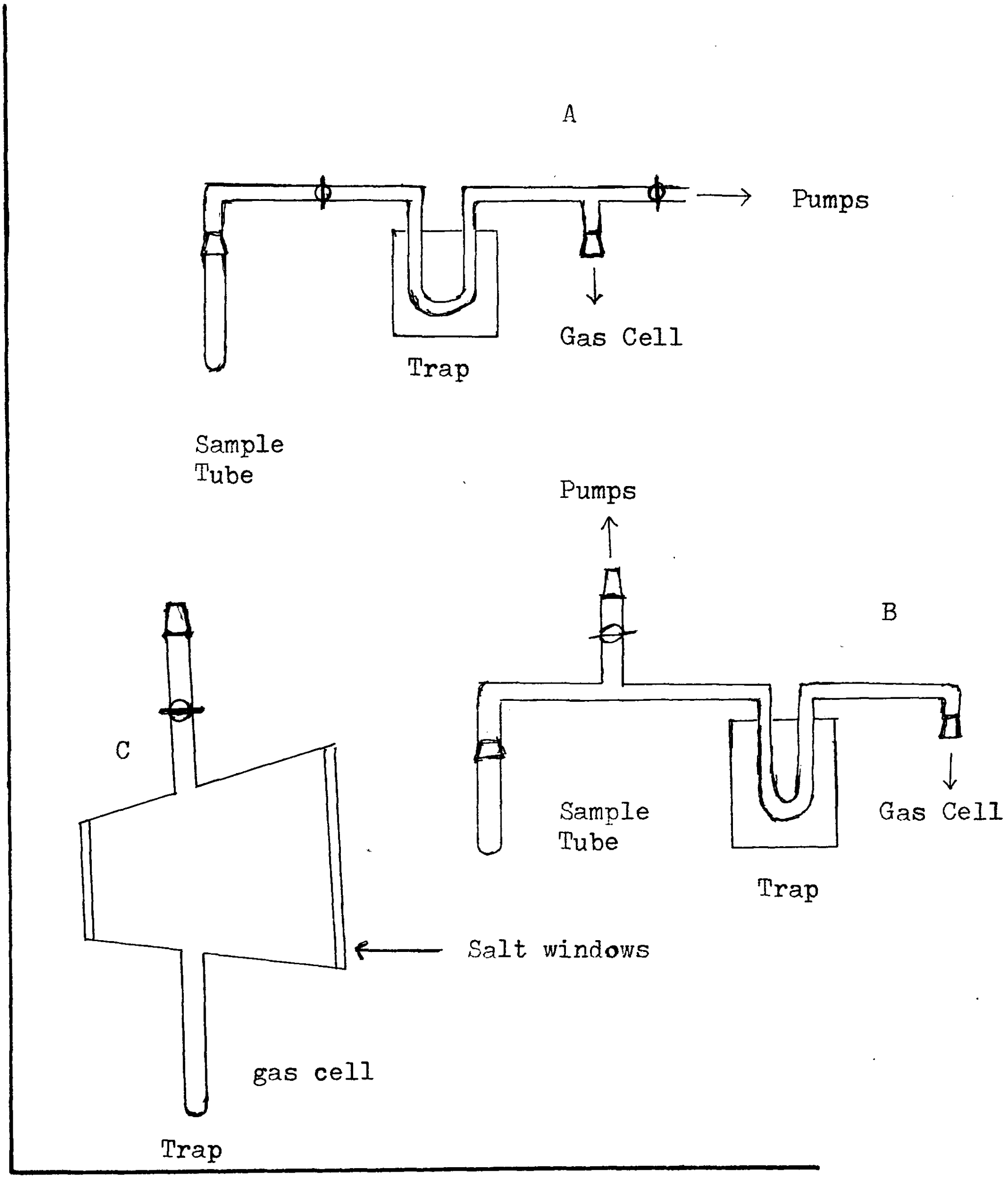
7.3 Results:

a) Polymers: The amounts of monomer necessary to give the required copolymer composition were calculated using the copolymer composition equation with the reactivity ratios r_1 and r_2 of styrene being 0.01 ± 0.01 and 55 ± 10 respectively.[69]

Polymer	Mole % Initiator	$\bar{M}_n$	Time of Poly. (hrs.)	% Polymerisation
12% E/VA	-	52,500	-	-
18% E/VA	-	43,000	-	-
33% E/VA	-	22,800	-	-
PV acetate	0.025%	356,000	-	10%
5% S/VA	0.05%	35,200	10	5%
10% S/VA	0.05%	22,100	28	5%
15% S/VA	0.2%	15,300	30	5%
20% S/VA	0.2%	11,000	48	5%
Polystyrene	0.05%	167,000	3	10%

The % copolymer composition always refers to the acetate content in the copolymer.

The reason for the styrene-vinyl acetate copolymerisation having such a slow rate is that styrene is about fifty times as reactive as vinyl acetate towards the styrene radical and the vinyl acetate radical prefers to add the styrene monomer by a factor of about one hundred as compared with addition of vinyl acetate. When, as in this case, the proportion of styrene monomer is very small, it acts as a retarder for the polymerisation of vinyl acetate. Vinyl acetate radicals are frequently converted to styrene radicals owing to the large



<u>Figure 7.1</u> A, continuously evacuated system.

B, closed system process.

C, Gas Cell, withsalt windows.

value of $\frac{1}{r_{VA}}$ and in spite of the low concentration of styrene. The less reactive styrene radical in turn adds vinyl acetate reluctantly; hence growth of the chain is delayed.[70]

b) TVA curves

The TVA curve in fig. 7.2 for polystyrene shows a single peak in which practically all the volatile products are condensed out in the - 75°C trap. However, as the acetate content in the copolymer increases the trace becomes broader and there is also a decrease in T_{max} and a decrease in the temperature where degradation begins (figs. 7.3 and 7.4). In the traces of 5% and 10% S/VA copolymers there is no evidence of any products which are not condensable at - 196°C, however in 15% and 20% S/VA copolymers there is a small quantity of non condensable products.

The fact that the products of the copolymer degradation are almost completely condensed out in the - 75°C trap indicates that the major products of the degradation are styrene monomer and acetic acid.

50 mg and 100 mg PVA samples were degraded, giving the curves shown in figures 7.8 and 7.9 respectively.

In fig. 7.9 the curve for products non-condensable at -45°C shows the Limiting Rate Effect.[69]

The first peak in the P.V.A. trace is due to deacetylation and a large quantity of acetic acid is condensed out at - 75°C, however there is also a quantity of products which are non-condensable at - 196°C. The second peak is due to the degradation of the unsaturated hydrocarbon produced by deacetylation (see Introduction in Chapter one).

The TVA curves of E/VA copolymers in figs. 7.5, 7.6 and 7.7 showed two peaks. The first peak, which did not vary in position (T_{max} was the same) in any of the copolymers, was due almost entirely to acetic acid. However, there was a significant quantity of non-condensable products.

There was no Limiting Rate effect similar to that observed in the 0°C and -45°C curves of PVAc since a sufficient quantity of acid is not produced in this degradation. The peak height increased with acetate content. The second peak is due to the degradation of the unsaturated hydrocarbon residue and most products are condensed out in the - 75°C trap but there is also a significant quantity of non condensable products.

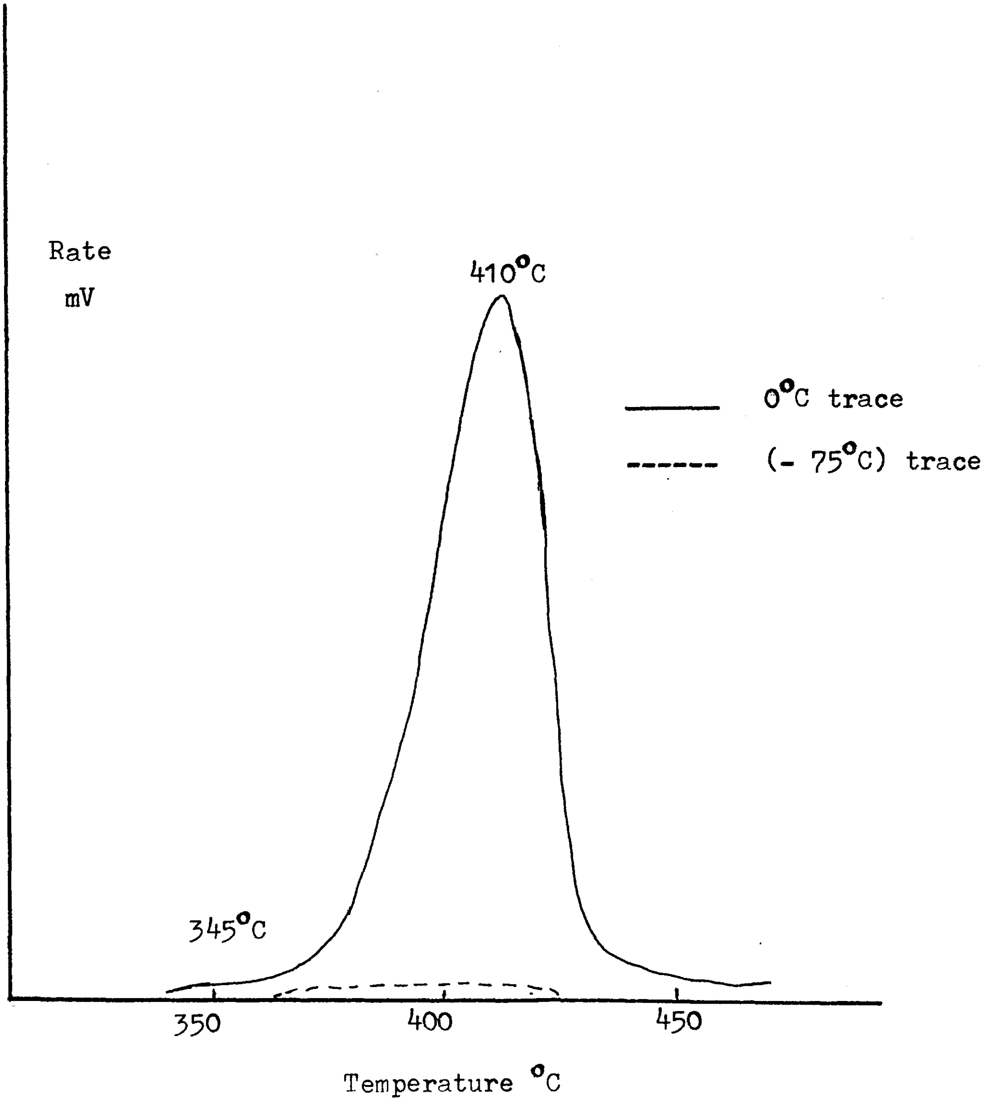


Figure 7.2 Degradation of 50 mg powder sample of PS in the TVA - DC apparatus.

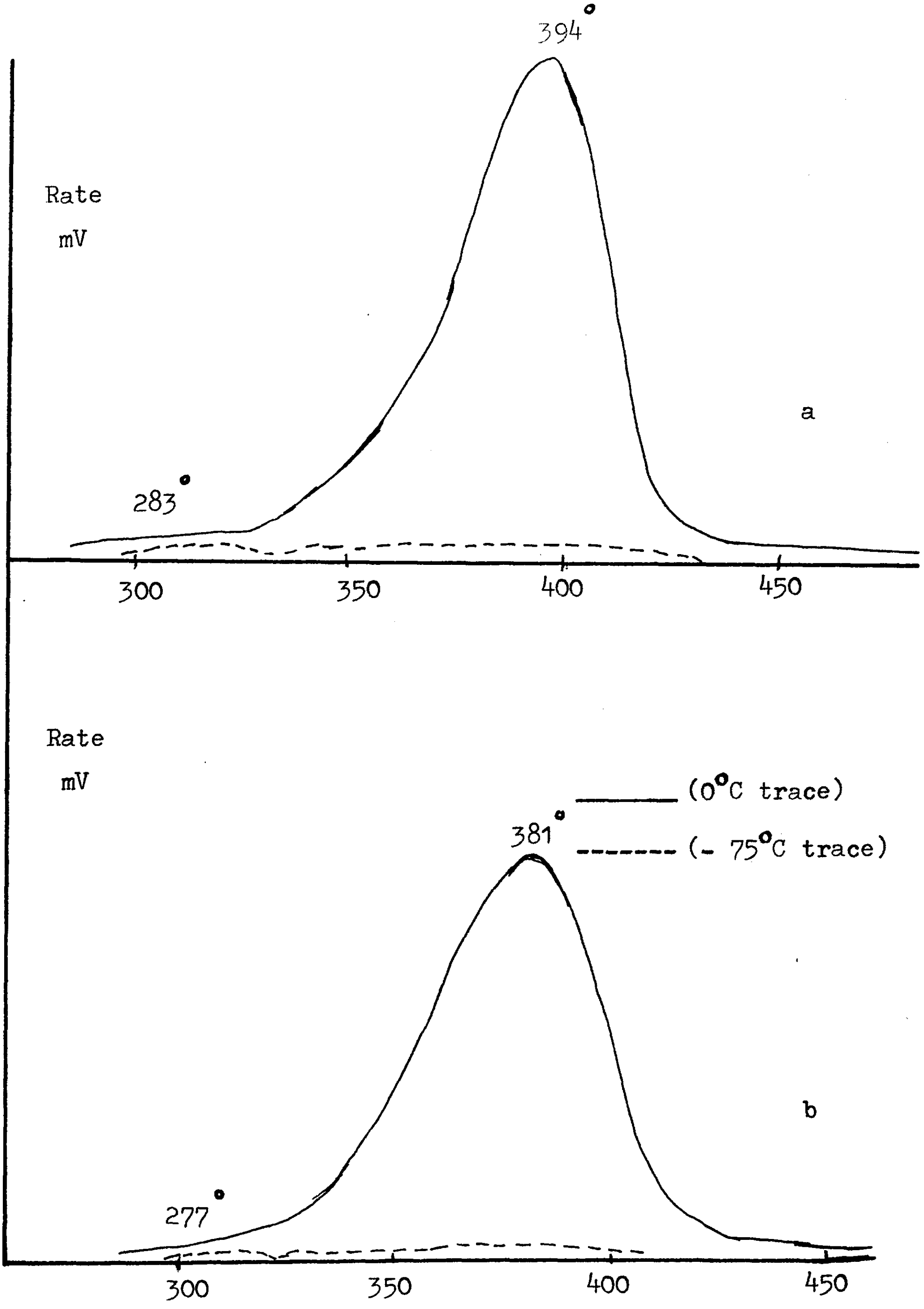


Figure 7.3 Degradation of 50 mg samples of styrene/vinyl acetate co-polymer in the TVA - DC apparatus.

a, 5% S/VA b, 10% S/VA

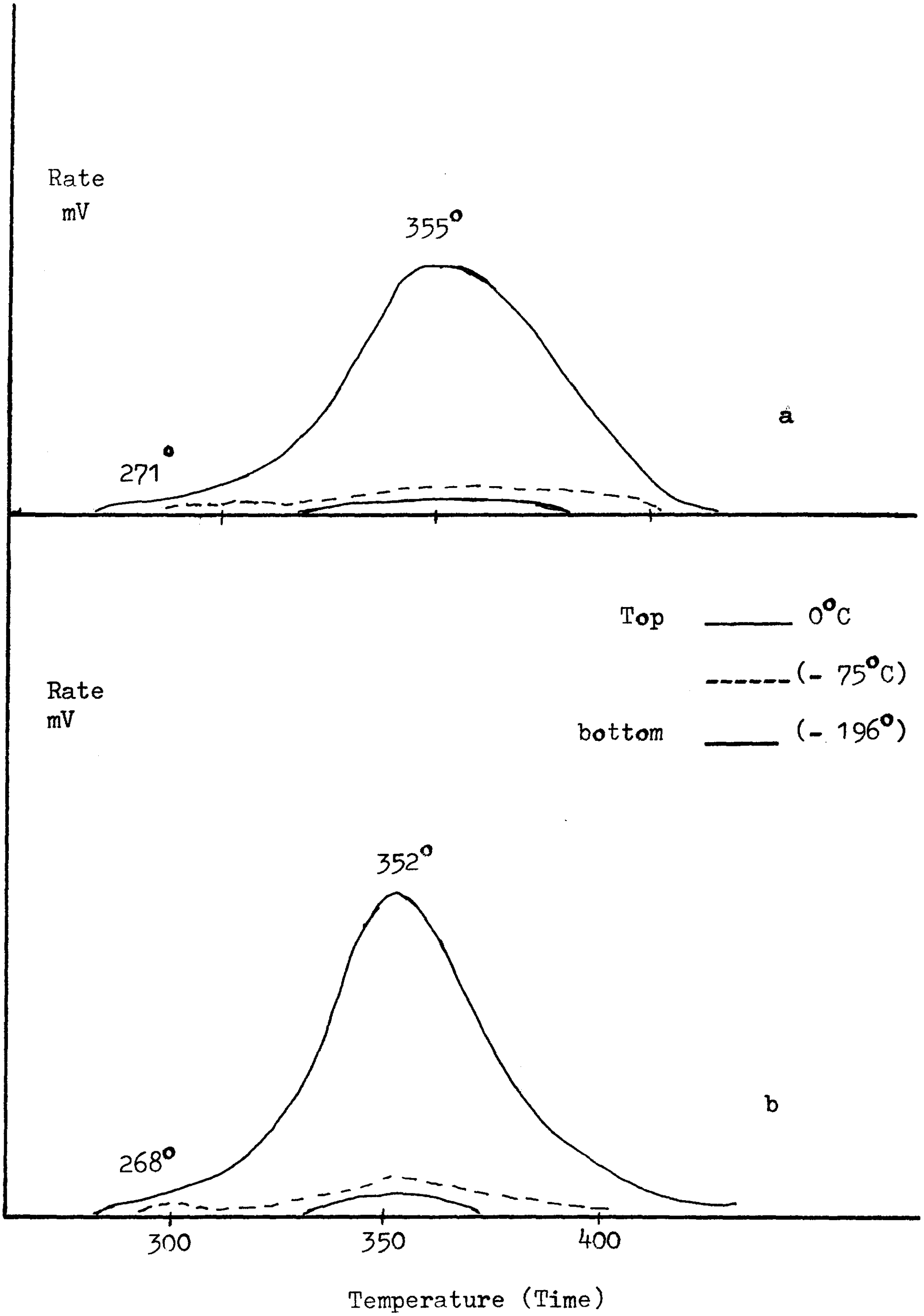


Figure 7.4 Degradation of 50 mg samples of styrene/vinyl acetate co-polymers in the TVA - DC apparatus

a, 15% S/VA b, 20% S/VA

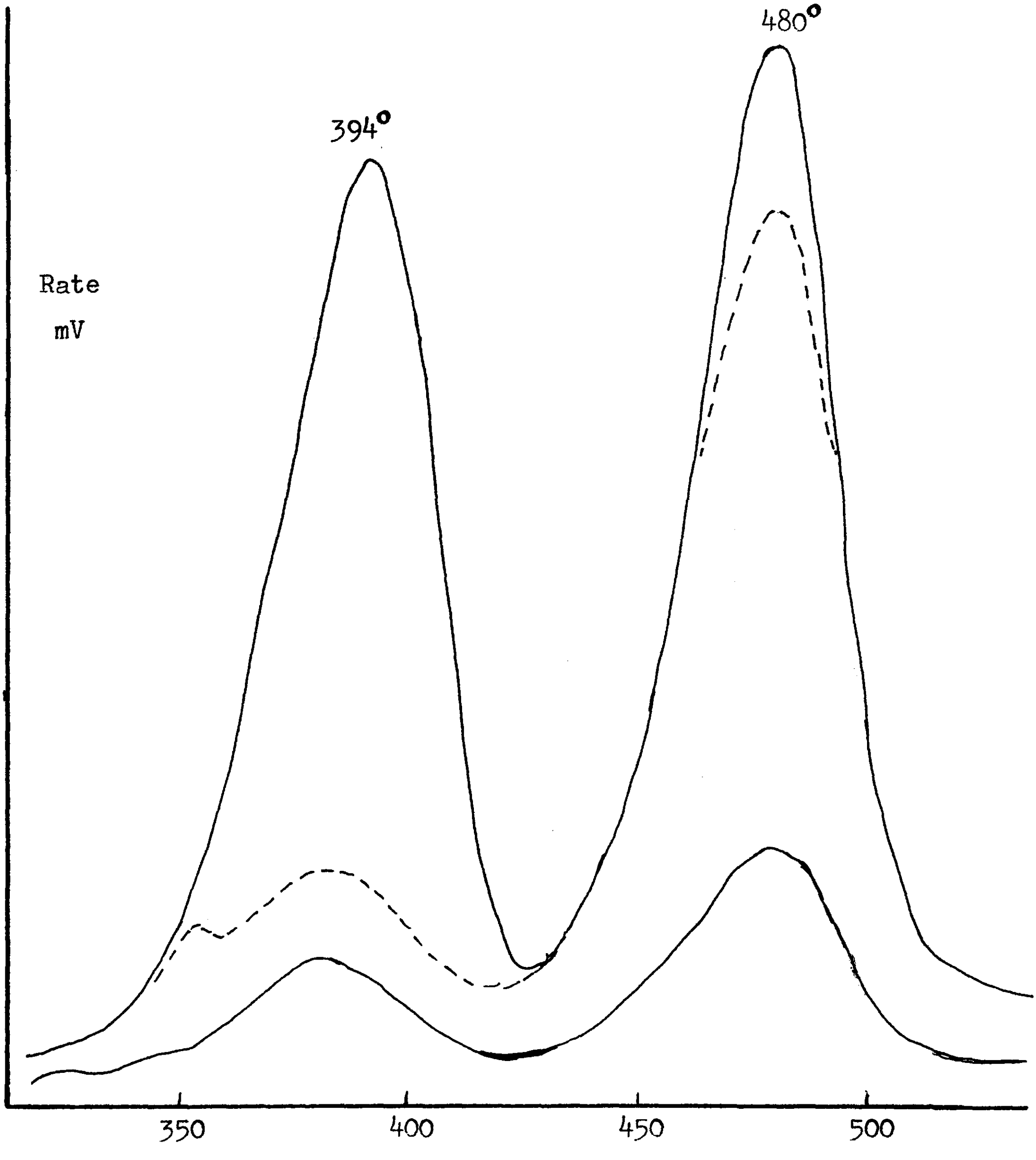


Figure 7.5 Degradation of 50 mg sample of ethylene/vinyl acetate, E/VA, co-polymer in the TVA - DC apparatus, 12% E/VA.

top _____ 0°C and (- 45°) ------(- 75°C)

bottom _______ (- 196°C)

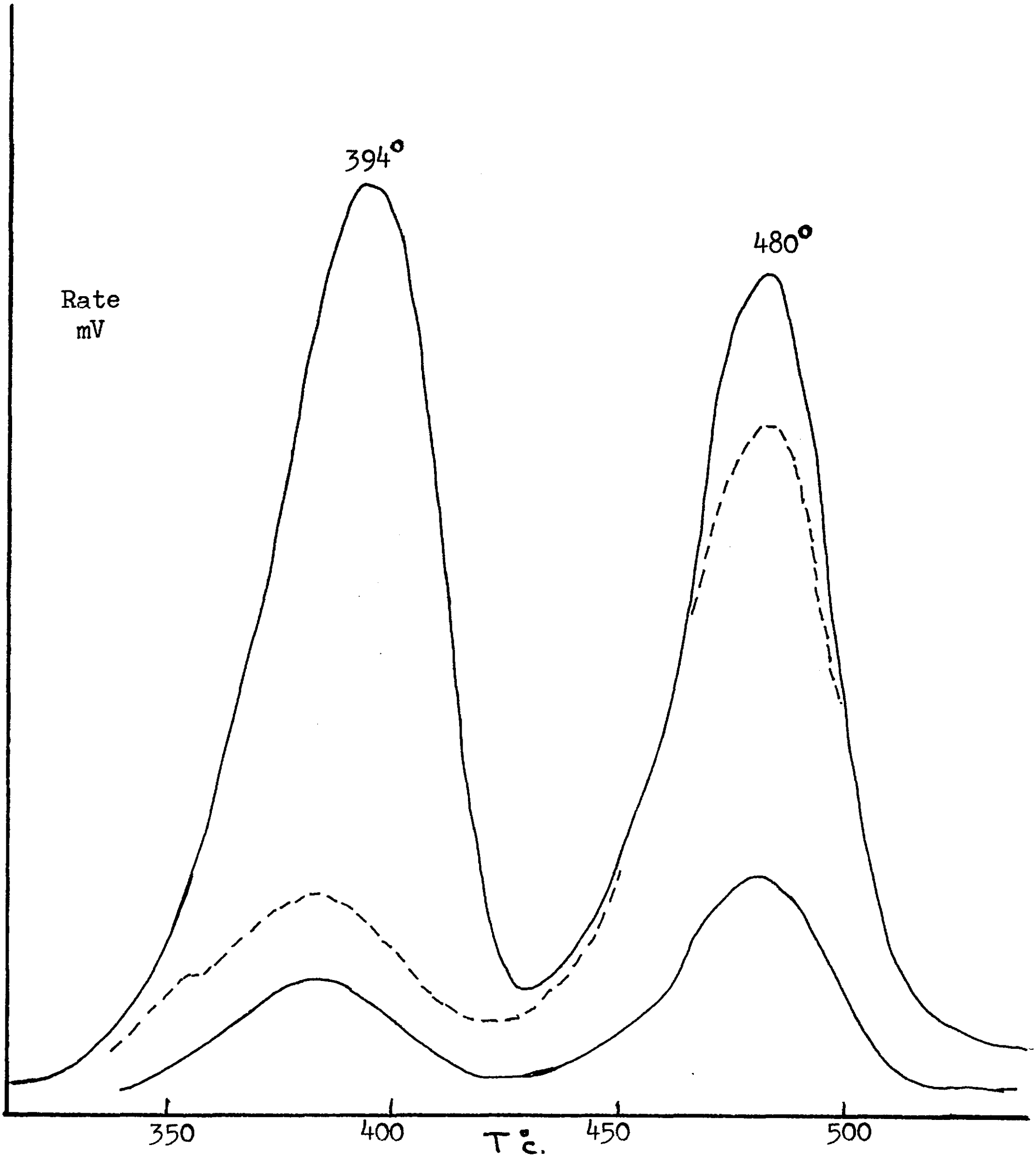
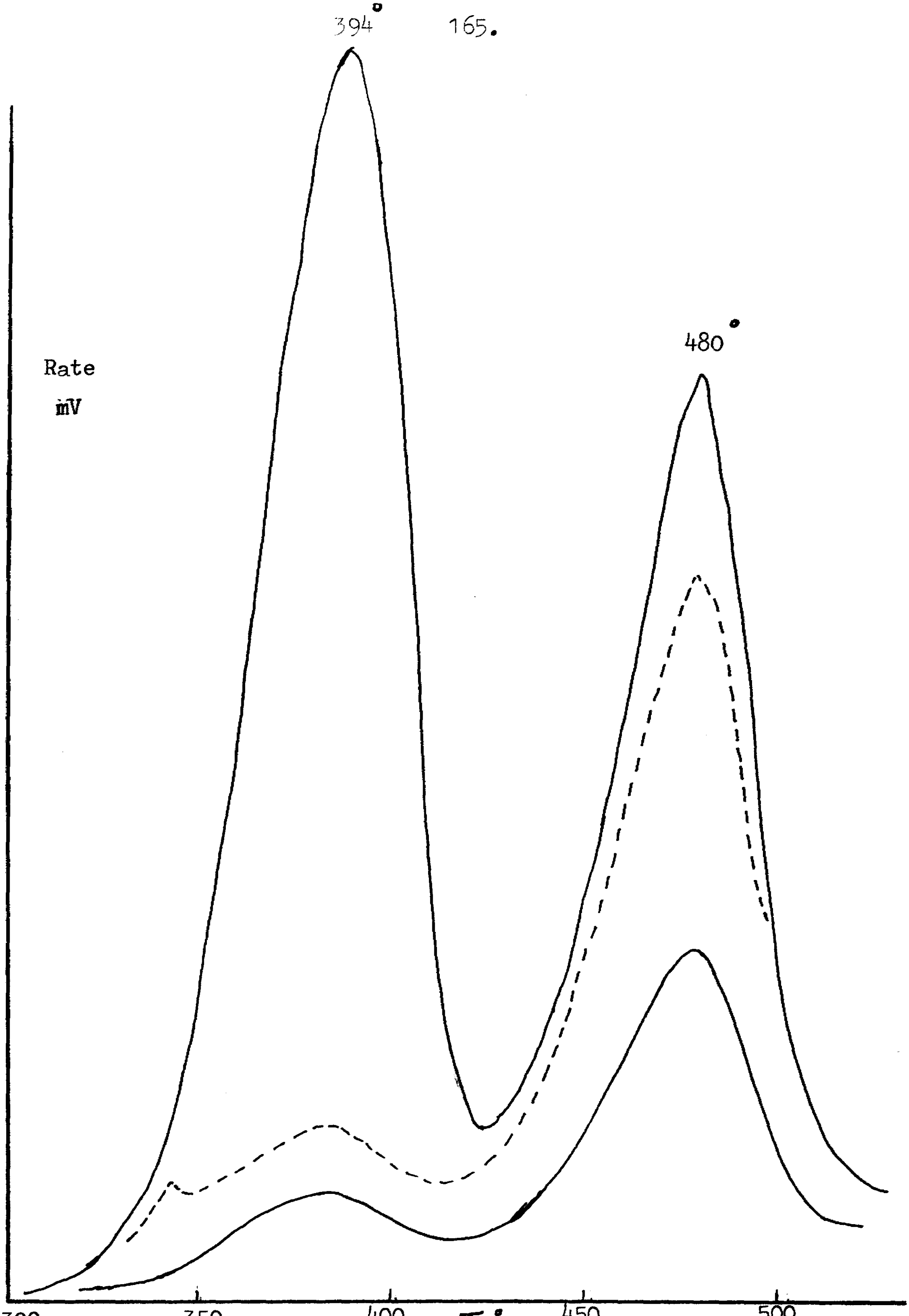


Figure 7.6 Degradation of 50 mg sample of 18% E/VA co-polymer.

top ____ 0°C and - 45°C ------ (- 75°C)

bottom ______ (- 196°C)



<u>Figure 7.7</u> Degradation of 50 mg sample of 33% E/VA co-polymer, in the TVA - DC apparatus.

top ——— 0°C and - 45° ----- - 75° bottom ——— - 196°

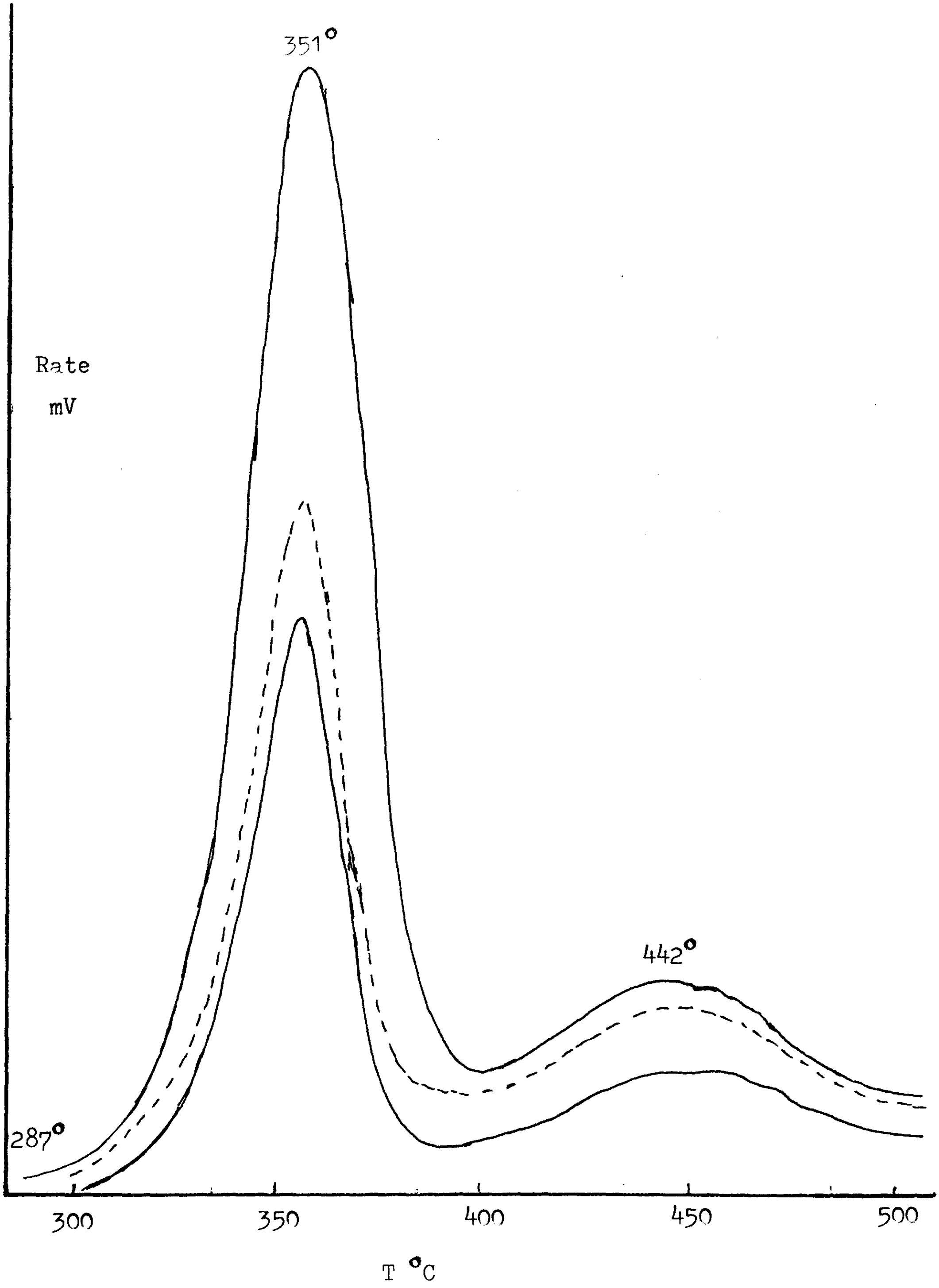


Figure 7.8 Degradation of 50 mg sample of poly (vinyl acetate) in the TVA - DC apparatus.

top _____ 0 °C and - 45°C ------- (-75°C and - 100°C)

bottom _____ (- 196°C)

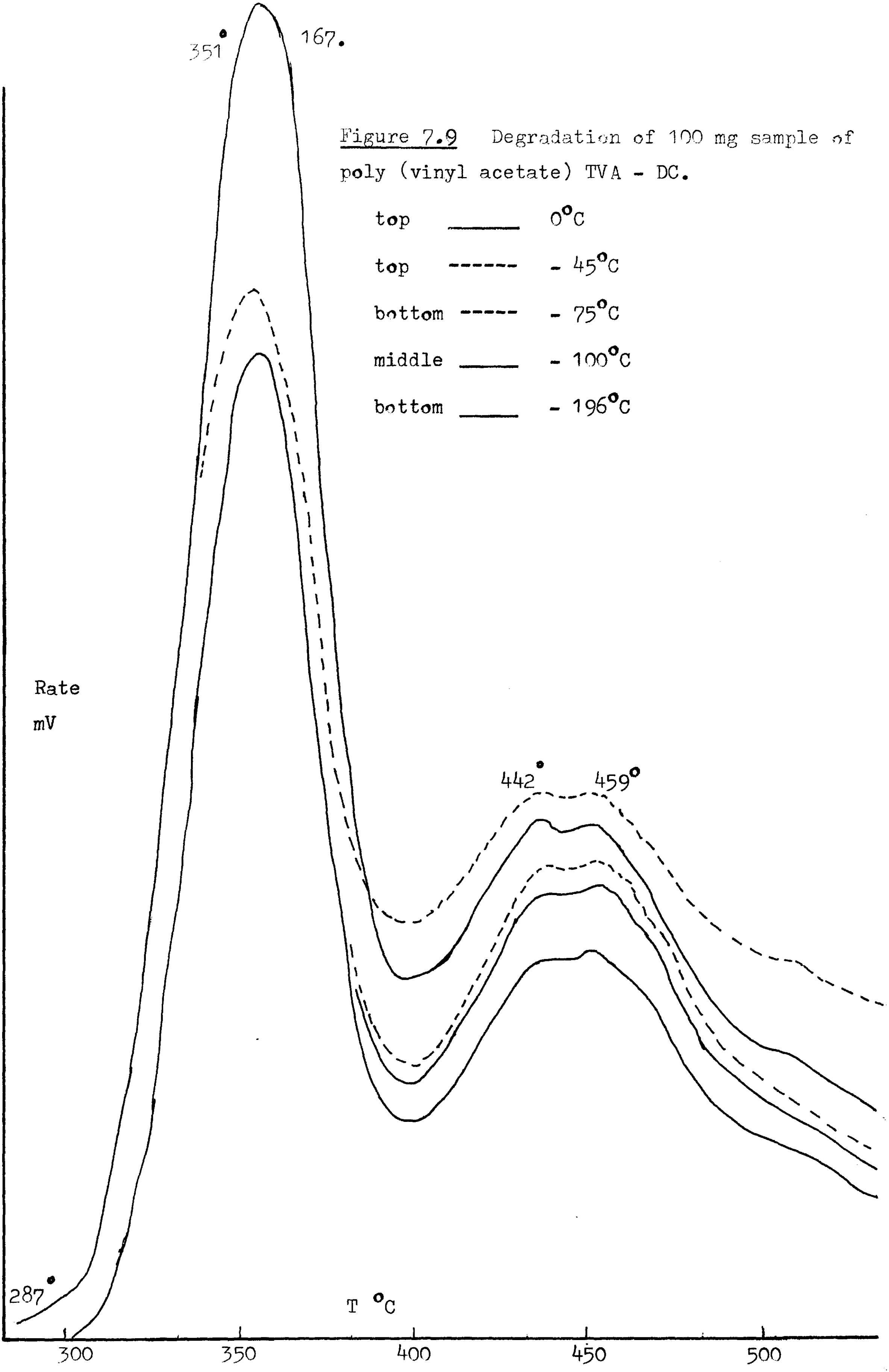
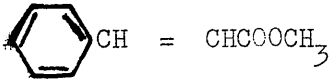


Figure 7.9 Degradation of 100 mg sample of poly (vinyl acetate) TVA - DC.

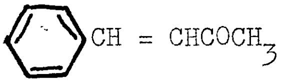
7.4 Product Analysis:

This was carried out mainly by I.R. spectroscopy. The cold ring fractions (formed on the upper region of the degradation tube) from both the E/VA and the S/VA degradations were examined and it was found that the cold ring from E/VA contained no acetate whereas the cold ring from S/VA copolymer did contain acetate.

In the case of E/VA copolymer the only product detected in the - 75°C trap was acetic acid but in the case of S/VA copolymer the - 75°C trap contained styrene and acetic acid. Also detected in the I.R. spectra of these products from S/VA were shoulders on the acetic acid carbonyl peak at 1760 cm^{-1} and 1675 cm^{-1} which could be due to



and



respectively.

The volatile products from the E/VA degradation which were not condensable at - 75°C were collected and examined in a closed system and found to be methane, CO_2, CO, ethylene and possibly ketene. The presence of ketene was verified using an open system (as shown in fig. 7.1) to remove carbon monoxide which was pumped off.

The non-condensable products from S/VA were CH_4, CO_2, $CH_2 = CH_2$ and CO but no ketene was detected.

7.5 Investigation of Molecular weight:

When partial degradations were carried out to the same extent on polystyrene and S/VA copolymer of approximately the same molecular weight, the following results were obtained.

	Polystyrene	5% S/VA
Initial Mol. Wt.	44,600	35,200
Mol. wt. after partial degradation	37,600	21,400
Drop in Mol. wt.	7,000	13,800

7.6 Discussion of Results:

From the shift in values of the initiation of break down toward lower temperatures and the similar shift in values of T_{max} with increasing acetate content, it would appear that the acetate units were the weak links in the S/VA copolymer chain. This can also be inferred from fall in molecular weight of partially degraded samples.

There was no change in T_{max} values for E/VA copolymers of various acetate contents.

The fact that ketene is produced in a significant quantity from the E/VA copolymer degradation and none is detected from the S/VA copolymer degradation seems to contradict Grassie's hypothesis that ketene is a result of the pyrolysis of acetic acid, since acetic acid is produced in both these degradations. Also a large quantity of CO is detected in the degradation products from E/VA copolymer which suggests CO and ketene may come from the same source.

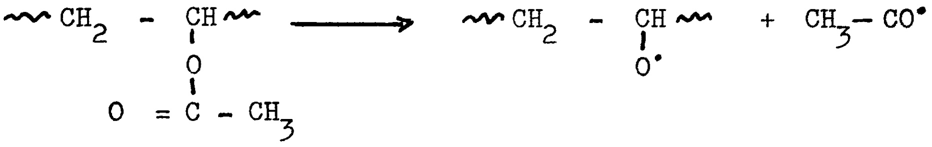
The presence of methane, and CO_2 can be accounted for by being attributed to the pyrolysis of acetic acid.

$$CH_3COOH \longrightarrow CH_4 + CO_2$$

Since there is acetate in the cold ring from the degradation of S/VA copolymers it would appear that the polymer chain can be broken down initially at both acetate and phenyl group sites although scission at acetate sites is probably favoured. These copolymers contain between 80% and 95% styrene units and since the degradation of polystyrene occurs by a free radical process (see Introduction in Chapter One), it is very likely that free radicals are present in this degradation.

In the cold ring from E/VA no acetate was detected which indicates that the initial degradation process occurs entirely at acetate sites.

The presence of ketene and CO in fairly large amounts in the products of the E/VA degradation could be explained by the following type of reaction.



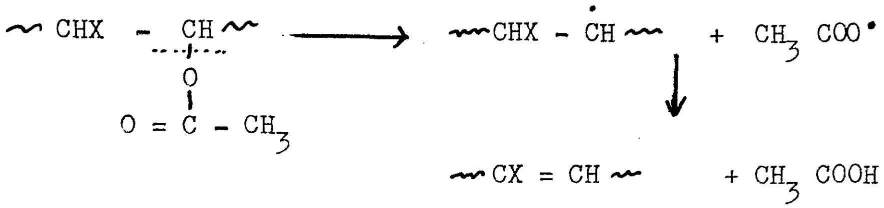
$$\sim CH_2 - \underset{\underset{O = C - CH_3}{|}}{\overset{}{CH}} \sim \;\longrightarrow\; \sim CH_2 - \underset{O^\bullet}{CH} \sim \; + \; CH_3 - CO^\bullet$$

$$CH_3 - CO^\bullet \longrightarrow CH_3^\bullet + CO$$

$$CH_3^\bullet + CH_3\,CO^\bullet \longrightarrow CH_4 + CH_2 = C = O$$

If the radical $CH_3\,CO^\bullet$ is produced in the E/VA degradation there is no reason why it should not be produced in the S/VA degradation. The absence of ketene and the small quantity of CO may be explained however, by probability of a reaction between $CH_3\,CO^\bullet$ and the free radicals produced due to the unzipping of the polystyrene part of the copolymer chain.

The acetic acid produced in both degradations is probably produced as follows; as shown in Chapter One;



$$\sim CHX - \underset{\underset{O=C-CH_3}{|}}{\overset{}{\underset{O}{CH}}}\sim \longrightarrow \sim CHX - \overset{\bullet}{C}H\sim + CH_3COO^{\bullet}$$

$$\downarrow$$

$$\sim CX = CH\sim + CH_3COOH$$

Where X = H or Ph.

The fact that acetic acid is produced in the S/VA degradation process seems to contradict the reasoning for the absence of ketene and the minute quantity of CO i.e. there is no reason why the $CH_3COO^{\bullet}$ radical should not also be used up in reaction with free radicals produced by the unzipping of the polystyrene part of the copolymer chain.

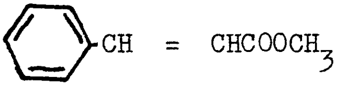
However, the radical $CH_3COO^{\bullet}$ is more stable than $CH_3CO^{\bullet}$ due to resonance stabilisation and also probably far more abundant, hence some $CH_3COO^{\bullet}$ radicals could react with the radicals produced by the unzipping of the polystyrene part of the copolymer chain and other $CH_3COO^{\bullet}$ radicals could abstract a hydrogen atom from the chain to give acetic acid, which is indicated by the drop in molecular weight of E/VA more rapidly than polystyrene.

This radical could also explain the presence of CO_2:

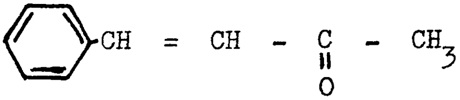
$$CH_3COO^{\circ} \longrightarrow CH_3^{\circ} + CO_2$$

These postulates seem to be borne out by the fact that in the I.R. spectra of products condensed in the - 75°C trap the carbonyl peak due to acetic acid has various shoulders.

The shoulder at 1760 cm^{-1} could be due to an ester having the **structure:**



and the shoulder at 1675 cm^{-1} could be due to a ketone having the structure;



These products suggest that the radicals $CH_3\,CO^{\bullet}$ and $CH_3\,COO^{\bullet}$ have combined with the radicals produced by the unzipping of the polystyrene part of the molecule.

Appendix:

List of Polystyrene samples used in this work:

Polymer	$\bar{M}_n$	History of the polymer
PS	140,000	0.4% Benzoyl peroxide (BZ_2O_2) at 60°C. Polymerised to 7.4% conversion.
PS,ST.11.	130,200	0.3% (BZ_2O_2) at 30°C to 15% conversion.
PS,ST.8	60,000	1% (BZ_2O_2) Initiated by U.V. light.
PS,ST.2	605,000	Thermal at 90°C in vacuum to 15% conversion
PS,ST.7	421,000	Thermal at 120°C.
PS,	184,000	0.06% (BZ_2O_2) at 80°C
PS	75,000	0.3% azobisisobutyronitrile as initiator, at 60°C by D. Bain.
PS	228,000	0.1% azobisisobutyronitrile as initiator, at 60°C by I. Cooke.
PS	4,000	Both polymers were prepared by an ionic polymerisation origin unknown.
PS	2,000	
PS,L13	48,000	narrow prepared by an anionic polymerisation by J.P. Pannell.
PS,L2	44,600	± 1000
PS,NBS,705	175,000	narrow, $M_w/M_n = 1.07$ (anionic)

Polymer	$\bar{M}_n$	History of the polymer
PS,NBS.706	136,000	M_w/M_n = 2.1 Thermal at 140°C to 37% conversion NBS, National Bureau of Standards.
PS	108,000	(Cationic) prepared by S. Haider at (- 78°) using 0.75 ml stannic chloride as a catalyst.

List of Poly (methyl methacrylate) samples used in this work:

PMMA IC.	134,000	Azobisisobutyronitrile at 60°C by (I. Cooke).	to less than 10% conversion.
PMMA F.R.I.	1,580,000	(Bisto) at 60°C	
PMMA D.N.	206,000	(Anionic), 0.024 equivalent of phenyl magnesium chloride was used. The reaction was carried out at 0°C prepared by D. Neil.	
PMMA D 6	300,000	1.5% (Bisto) at 60°	Prepared by I.C. McNeill purified by reprecipitation in methanol from $CHCl_3$.
D10	50,000	1% (Bisto) at 80° in Benzene	
D12	24,000	4% (Bisto) at 80°C	
PMMA A_1	28,200	4% Bisto at 80°C (by J. Mohammed.) to 30% conversion.	

Poly (methyl acrylate) was prepared at 60°C, by A.W. McAllister, from 20% solution of the monomer in n-propyl acetate using 0.1% W/V of azobisisobutyronitrile as initiator. $\bar{M}_n$ = 684,000

Poly (tert. Butyl Methacrylate) was prepared by free radical mechanism using 0.025% Benzoyl peroxide as initiator and U.V. light, by N. Grassie.[63]

Poly methacrylonitrile was polymerised at 30°C and the reaction was initiated by photodecomposition of benzoyl peroxide , $\bar{M}_n$ = 18,000.

Polymer	$\bar{M}_n$	History of Polymer
Poly (α- methyl styrene)	97,400	(Cationic) at - 78° prepared by J. Pang.
Poly (P - methyl styrene)	138,000	Bulk polymerisation at 60°C using azobisisobutyronitrile.
Poly (m-methyl styrene)	246,000	
Poly isobutene, IV.	100,000	Polymerised at (- 78°C) using stannic chloride, by R. McGuchan.[48]
Polypropylene		I.C.I. Propathene MF20, purified by reprecipitation.
Polybutadiene		Industrial samples kindly supplied by the India Tyre and Rubber Co. Both were purified.
Cis-polyisoprene		
Butyl Rubber MD501		High unsaturation, supplied by Esso Co.

The last three polymers were purified by reprecipitation twice in excess methanol from dilute solutions in benzene.

Poly (vinyl chloride) PVC Geon 101, British Geon polymers, additive-free sample, $\bar{M}_n$ was 16,000.

Poly (vinyl acetate), B.D.H. sample, $\bar{M}_n$ was 36,400.

Poly (vinyl alcohol), Shawinigan (Gelvatol O - 90 G) with 0.3% residual poly (vinyl acetate) content.

Poly (methyl methacrylate) A_1, was prepared as follows:

Methyl methacrylate monomer (I.C.I. Ltd.) was washed with 2N sodium hydroxide to remove inhibitor, then several times with distilled water, and dried using Calcium hydride or calcium chloride. It was distilled three times in vacuo, only the middle fraction being retained from each distillation.

4% Azobisisobutyronitrile was introduced into the dilatometer dissolved in 4 ml of benzene. The benzene was removed from the dilatometer by distillation under vacuum. The monomer was then distilled into the dilatometer which was then sealed under vacuum. The dilatometer was surrounded with a net of wire gauze to prevent the shattering of glass in case of an explosion. It was then placed in a water bath which was kept at 80°C. The reaction began very rapidly and the dilatometer was removed after 3-4 minutes and placed in liquid nitrogen.

The polymer was reprecipitated three times in excess volume of methanol from benzene solution.

It was then washed with methanol and dried under vacuum at room temperature for several days.

The $\bar{M}_n$ was determined by using Machrolab Model 501 Membrane Osmometer, at 25°C. Sylvania 300 grade cellophane membrane in toluene, $\bar{M}_n$ was 28,200.

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