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THE THERMAL DEGRADATION OF POLYSTYRENE

AND RELATED POLYMERS

A Thesis presented by Graeme Paton Kerr to the University of
St. Andrews in application for the degree of Doctor of Philosophy.



Tr 5510

DECLARATION

I hereby declare that this thesis is a record of experimental work carried out by me, except where due acknowledgement has been made in the text where the results of previous workers in the field have been used. This thesis is my own composition, and has not previously been presented in application for a higher degree.

The investigation was carried out under the supervision of Dr. G.G. Cameron in the Chemistry Research Laboratories of St. Salvator's College , St. Andrews from October 1964 to September 1966, and of Aberdeen University from September 1966 to September 1967.

A paper relating to this work has been published in the European Polymer Journal.

CERTIFICATE

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

UNIVERSITY CAREER

I matriculated in the University of St. Andrews in October 1960, and graduated B.Sc. with Upper Second Class Honours in Chemistry in June 1964.

I was admitted as a Research Student to the Department of Chemistry, St. Salvators College in October 1964. The work described in this thesis was carried out during the period October 1964 to June 1967.

ACKNOWLEDGEMENTS

I would like to take this opportunity to record my thanks to the Science Research Council for a Scholarship, during the tenure of which the investigations described in this thesis were carried out. In addition, my thanks are due to Professor J.I.G. Cadogan and Professor G.M. Burnett of the Departments of Chemistry in St. Andrews and Aberdeen Universities respectively for making available laboratory and technical facilities. Finally in this context, I wish to thank Dr. Cameron for his constant guidance, encouragement and friendship during the studies described in this thesis.

Reference is made in this thesis to polymers which were kindly given to me by other workers in this field. For this invaluable assistance, I am indebted to Drs. W.J. Bryce and G. M^cGibbon of the Department of Chemistry in Aberdeen University,

Professor H. Hopff of the Swiss Federal Institute of Technology, Zurich and Professor K. Chikanishi of Kyoto University, Japan. The computer programmes and part of the mathematical treatment described in Chapter III of Part I of this thesis were the responsibility of Dr. A.R. Gourlay of the Department of Applied Mathematics in St. Andrews University, for whose assistance I am very grateful. Finally, I would like to thank fellow students and members of staff with whom I have had many interesting discussions.

In conclusion, I wish to thank the technical staff of the Departments of Chemistry in St. Andrews and Aberdeen Universities.

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PART I.

THE THERMAL DEGRADATION OF POLYSTYRENE.

CHAPTER I.INTRODUCTION

It is a curious fact that the thermal degradation of polystyrene - the first synthetic addition polymer to be examined in this way - should be one of the most controversial topics in polymer chemistry today, despite the very considerable volume of work expended on it. Although most of the individual steps in the reaction mechanism have been identified, the relative importance of these reactions is currently a matter of some conjecture. A review of the theories on the thermal degradation of polystyrene provides an excellent illustration of the development of the understanding of polymer degradation mechanisms over the past three decades, and it is from this viewpoint that the previous work on this topic is surveyed.

(I) The Early Investigations

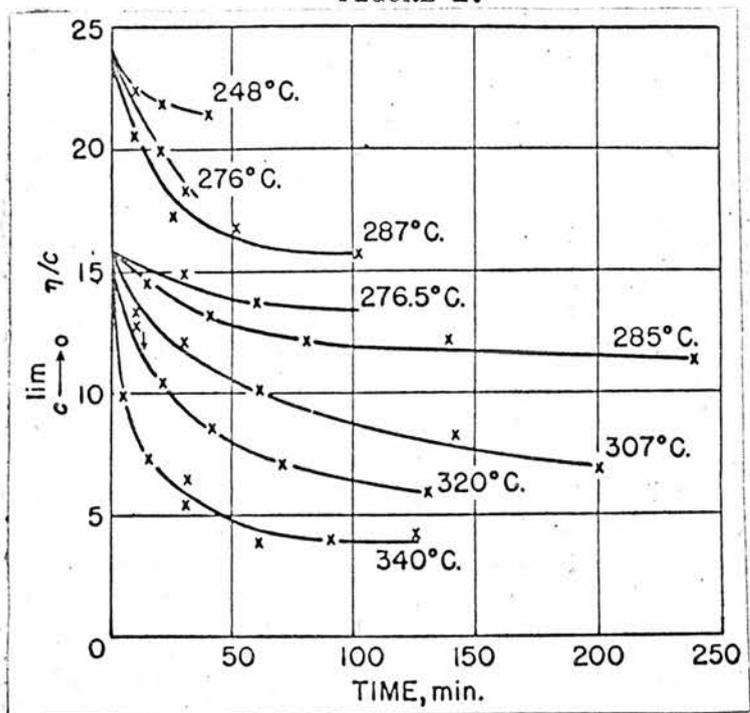
Some hundred years ago it was known that styrene on heating or exposure to the atmosphere produces a glassy solid, from which the monomer can be recovered by destructive distillation. The structure of this glass was not known then, but during the early 20th century scientists began to appreciate that such glassy solids are composed of very large molecules, rather than aggregates of small molecules. Staudinger and Steinhofer^I hastened the acceptance of this idea by postulating - on the basis of an analysis of the pyrolysis products from polystyrene - that polymeric materials are

composed of very large molecules consisting of monomer units head - to - tail. Furthermore, these investigators suggested that the degradation mechanism comprises simple random chain scission, a postulate which was based on the theory proposed by Meyer, Hopff and Mark², Kuhn^{3,4} and Freudenberg⁵ to account for the hydrolytic degradation of polysaccharides. Subsequently, Votinov, Kobeko and Marei⁶ claimed good agreement between their results for the thermal degradation of polystyrene and poly (methyl methacrylate) and Kuhn's theory⁴. In these experiments both Staudinger and Votinov ignored the anomalous production of large amounts of monomer early in the reaction. Simha⁷ modified Kuhn's theory⁴, but still could not obtain quantitative agreement between theory and experiment. Moreover, it was becoming increasingly obvious from the accumulating data on polymer degradations that no simple random theory could account for the experimental results, and chemists, influenced by the evidence presented by the decomposition of hydrocarbons of low molecular weight⁸, began to think of polymer degradations as free-radical chain processes consisting of initiation, propagation, termination and, probably, transfer steps. At the same time the appreciation of the free-radical nature of polymerisation contributed to the reappraisal of degradation reactions.

(2) The Investigations by Jellinek

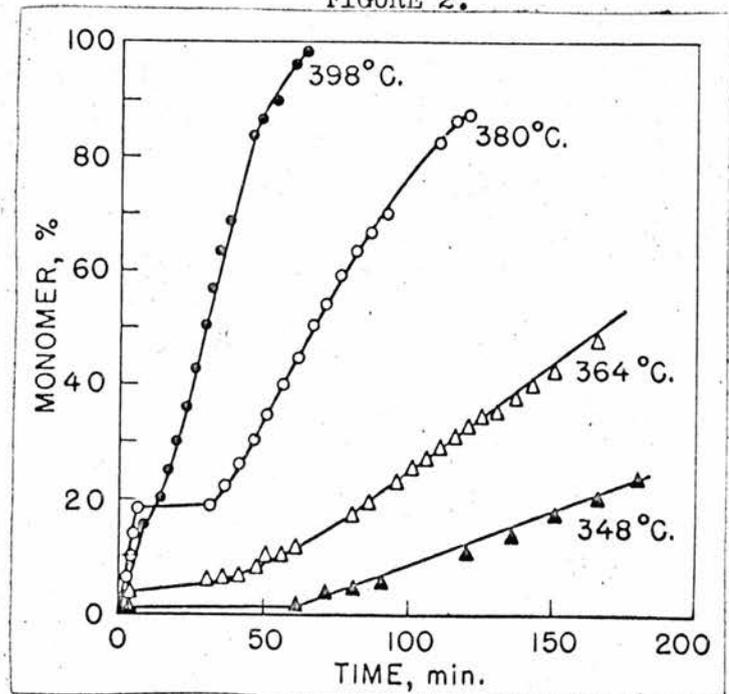
The first comprehensive study of the thermal degradation in vacuo of polystyrene was made by Jellinek⁹, who studied the rate

FIGURE 1.



Jellinek - Ref. 9.

FIGURE 2.



Jellinek - Ref. 9.

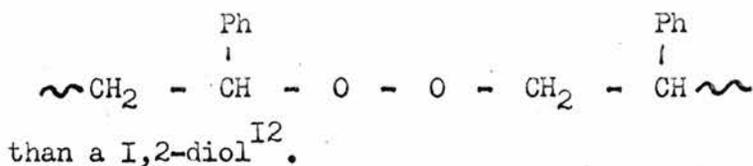
of volatile production and the molecular weight and molecular weight distribution changes in polymers degraded at temperatures between 240° and 340° C.. Figure 1 shows the limiting viscosity with time of degradation, and Figure 2 shows the formation of volatiles as a function of time for a polymer fraction.

Jellinek rejected the simple random theory for a number of reasons :-

- (a) the very large amount of monomer produced early in the reaction,
- (b) the Activation Energy, $44.7 \text{ kcal. mole.}^{-1}$, was lower than expected for a random reaction,
- (c) plots of $(\text{molecular weight})^{-1}$ against time, which should be linear for a simple random degradation, showed pronounced curvature, presumably because the initial rate of bond scission was not sustained, and
- (d) the molecular weight distributions were narrower than predicted for a random degradation.

Instead, Jellinek postulated that the degradation is initiated at a limited number of "weak bonds" randomly distributed along the polymer chain. These thermolabile structures can decompose with or without chain scission, in the first case to form unstable chain ends which subsequently initiate volatilisation and in the second case to introduce unsaturation into the chain. The high initial rate of volatilisation is a manifestation of depropagation initiated at labile end-groups formed by "weak link" scission, subsequent volatilisation being initiated at normal chain ends.

Jellinek suggested that "weak links" are the result of the incorporation of oxygen into the polymer as a 1,2-diol, and he suggested plausible mechanisms for the formation and decomposition of these structures. Achhammer^{I0}, however, examined the infra-red spectra of polystyrenes and found no evidence of oxygenated groups, but Madorsky and Straus^{II} did find small amounts of carbon monoxide in the volatiles from the pyrolysis of polystyrene, presumably from oxygenated groups present in the polymer. However, if oxygen is incorporated into the polymer it is far more likely to copolymerise with styrene to form a polyperoxide



The reaction scheme proposed by Jellinek does not account for the production of non-monomeric volatiles, and also requires that the depropagation reaction initiated by "weak link" scission proceed through a diradical, a most improbable mechanism. The observed inflection in the volatilisation versus time curves (Figure 2), explained by Jellinek as an induction period, has been attributed by critics^{I3,I4} to experimental deficiencies, a view contested by Jellinek^{I5}.

Subsequently, Jellinek and coworkers^{I6,I7} investigated the degradation of polystyrene in solution in naphthalene and tetralin. The degradation in the former solvent was substantially similar to

the bulk degradation, but in the latter solvent volatilisation was totally inhibited, although the typical drop in molecular weight was observed. A chain-transfer reaction between the radicals formed by "weak link" scission and tetralin was suggested to account for the absence of monomer.

The importance of Jellinek's work lies in the postulate that "weak bonds" may be incorporated into polymers during synthesis. Furthermore, his systematic investigations set an example for later investigators.

(3) The Investigations at The National Bureau of Standards, Washington
(1948 - 1958)

In 1948 Madorsky and Straus^{II} published an account of the vacuum pyrolysis of polystyrene at 350 - 420°C.. The degradation products were divided into four fractions, and the composition and average molecular weights of these fractions were determined. The important conclusions drawn from these experiments were :-

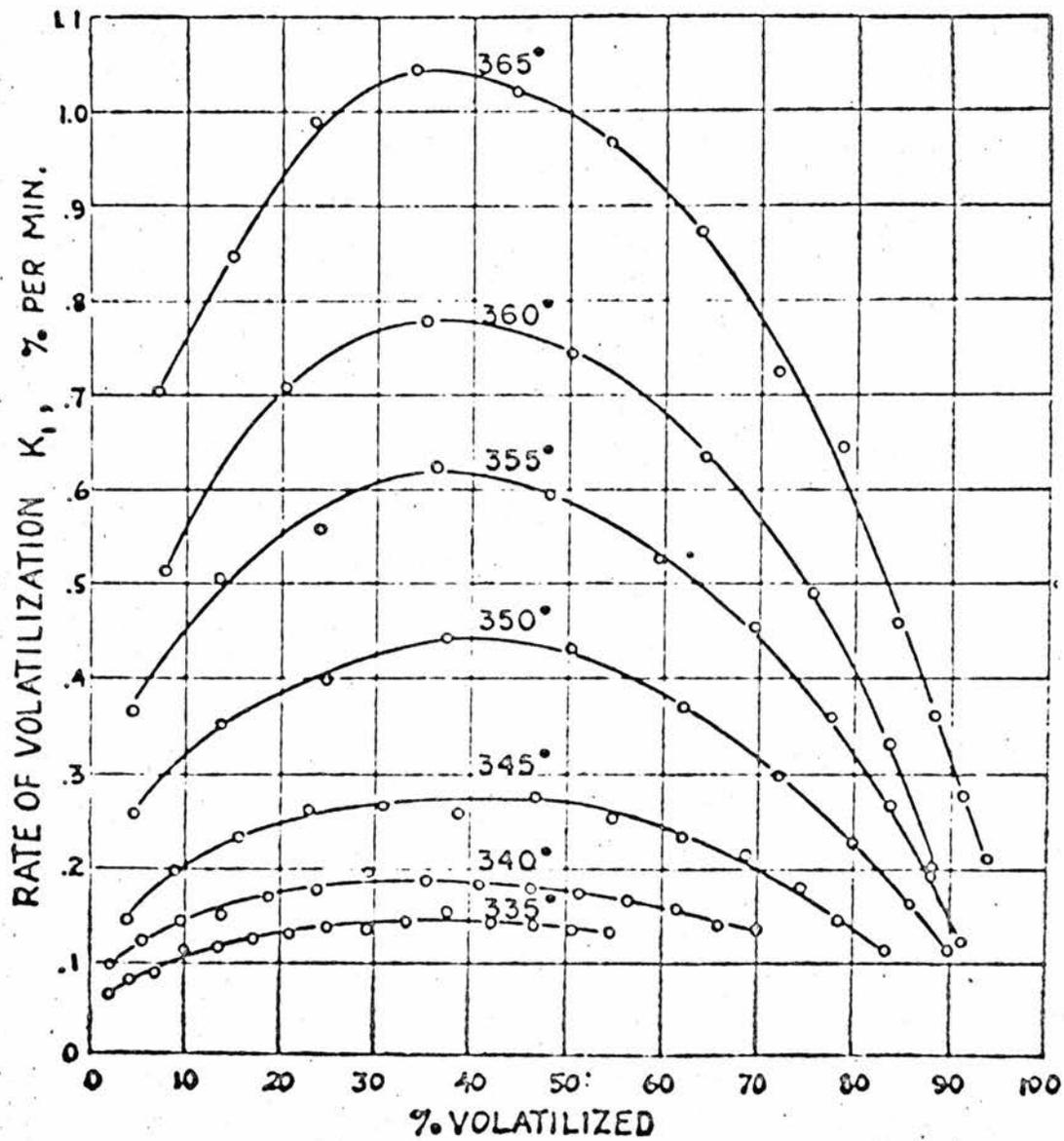
(I) the composition of all fractions is independent of the time and temperature of pyrolysis, and of the original sample of polystyrene, (2) a maximum yield of 42% by weight of styrene is obtained at 420°C. and (3) the wax-like fraction II consists of dimer, trimer and a little tetramer. The fact that no larger fragments were detected suggested that molecules larger than the tetramer remain in the melt and are decomposed into smaller fragments which then volatilise.

Shortly afterwards Wall^{I8} published the results of an

examination, by Mass Spectroscopy, of the volatiles produced from the pyrolyses of polyethylene, polyisobutylene and polystyrene. His results for the latter polymer agree well with Madorsky's^{II} data. Wall also speculated on the nature of the depolymerisation of vinyl polymers, suggesting a simplified scheme consisting of random initiation, reverse polymerisation, intermolecular hydrogen transfer and termination by combination or disproportionation. The mechanism was essentially the reverse of polymerisation. Furthermore, he pointed out that, since most addition polymers are formed from mono - or asymmetrically di - substituted monomers, chain scission produces two types of radical, one which is reactive and abstracts hydrogen and the other which is unreactive and tends to depolymerise to monomer. The importance of this distinction has been generally overlooked by later workers, especially in theoretical studies.

Having analysed the volatiles^{II} produced by the pyrolysis of polystyrene, Madorsky^{I9} extended his investigations to include a study of the rates of volatilisation from 335° to 365° C. using a tungsten spring balance. A limited amount of molecular weight measurements were made. The rates of volatilisation per unit weight of original sample (R_T) all showed maximum at 35 - 40% conversion, (Figure 3), and these curves indicated that the reaction order is between zero and first, with an Activation Energy of 58 kcal. mole⁻¹. The experimental molecular weight versus conversion curves showed a rapid fall in molecular weight, with subsequent levelling off.

FIGURE 3.

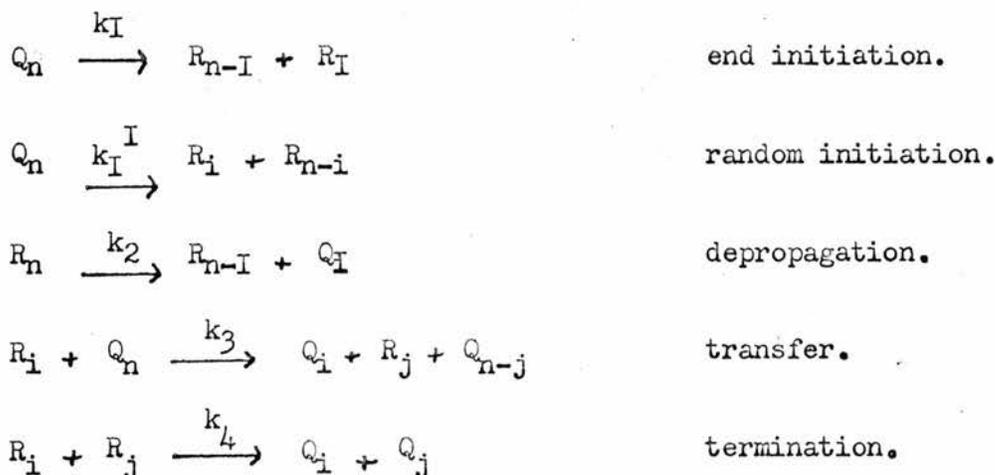


Madorsky - Ref. 19.

The mechanism proposed by Madorsky to account for these characteristics consists of chain-end initiated volatilisation, with a superimposed random component to produce non-monomeric fragments and the rapid fall in molecular weight.

The next fundamental advance in the field of polymer degradation reactions came not from experimental studies but from a theoretical approach by Simha, Wall and collaborators^{20,21,22}.

The radical chain reaction assumed by these investigators consists of the following steps :-



where R_n and Q_n represent a radical and inactive polymer molecule respectively containing n monomer units. The treatment was applied to monodisperse samples in open systems so that allowance had to be made for the loss of volatile fragments. Three important variable parameters were introduced :-

$$\text{(I) transfer constant, } \sigma = \frac{\text{probability of transfer}}{\text{probability of initiation}}$$

$$= \frac{k_3 R}{k_t}$$

(2) kinetic chain length, $\frac{I}{\epsilon}$

where $\frac{I}{\epsilon} = \frac{\text{probability of depropagation} + \text{transfer} + \text{termination}}{\text{probability of transfer} + \text{termination}}$.

(3) L - the number of monomer units in the smallest chain which does not evaporate.

Two separate sets of equations expressing rate of volatilisation and molecular weight as functions of conversion were constructed for end and random initiation respectively, and the effects of varying I/ϵ and L were studied in an attempt to duplicate the experimental results for poly(methyl methacrylate)²³ and polystyrene¹⁹. For random initiation the theory invariably produced a maximum in the theoretical rate versus conversion curve at or below 26% conversion, whereas Madorsky¹⁹ had found an experimental rate maximum for polystyrene at 40% volatilisation. Simha and Wall²² tentatively suggested that the observed rate maximum may be due to the superposition of two rate curves, as found by Oakes and Richards²⁴ for polyethylene.

Later work by Simha, Wall and Bram²⁵, using a computer to handle the expressions previously derived, gave calculated rate maxima below 26% conversion. Increasing the transfer parameter shifted the maxima towards, but never beyond, 26% conversion, the position

characteristic of a simple random breakdown.

Transfer reactions were now widely accepted as components of polymer degradation mechanisms, and, although the exact sites of hydrogen abstraction had not been experimentally demonstrated, tertiary hydrogen atoms seemed the likely locus. Wall, Brown and Hart²⁶ demonstrated that this supposition was indeed correct when they found that substitution of the α - hydrogen atom in polystyrene by deuterium increased the monomer yield to 70%, whereas β - substitution had no effect. In addition the molecular weight decrease in poly(α - deuterostyrene) was less than the decrease in polystyrene. These differences in behaviour are explicable in terms of the slower rate of abstraction of deuterium from the α - carbon atom, thus favouring the depropagation reaction. Therefore, intermolecular transfer appears to be a more likely cause of the initial fall in molecular weight than labile structural abnormalities.

In summary, the researches at the National Bureau of Standards up to 1958 led Wall and his colleagues to describe the thermal decomposition of polystyrene as a free-radical chain reaction consisting of random scission, depropagation, intermolecular and intramolecular transfer, and termination by disproportionation. The existence of "weak links" was disputed by this group who suggested that the main chain breaking process is intermolecular transfer. Dimer, trimer and other short chain fragments were assumed to be formed by transfer, and the depropagation reaction was deduced to

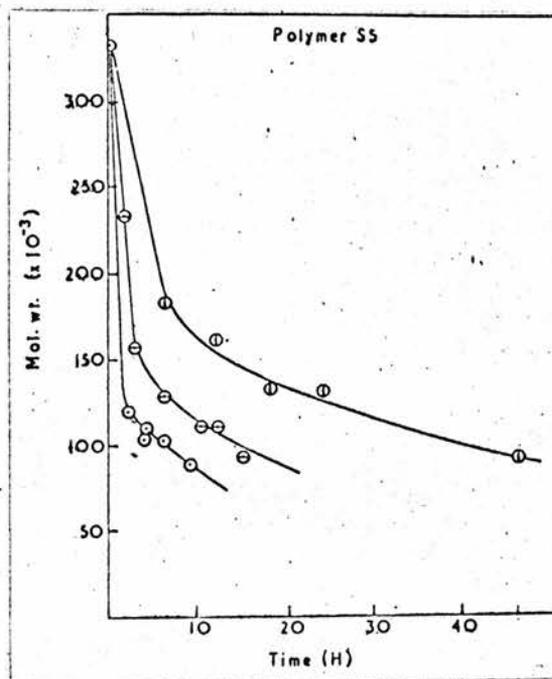
have a kinetic chain length of about three monomer units. The reaction scheme is qualitatively plausible but, unfortunately their mathematical treatment of it predicted rate versus conversion curves with maxima at 26% rather than at the observed 40%.

(4) The Experiments by Grassie and coworkers

Having noted the general lack of conformity in the data of previous investigators, Grassie set out to resolve the controversy, especially in the sphere of molecular weight measurements where most workers had used viscometry. Degradations were carried out in a molecular still²³ at 320°, 330° and 338°C., and rates of volatilisation were measured at 360°C. using a Pirani gauge.

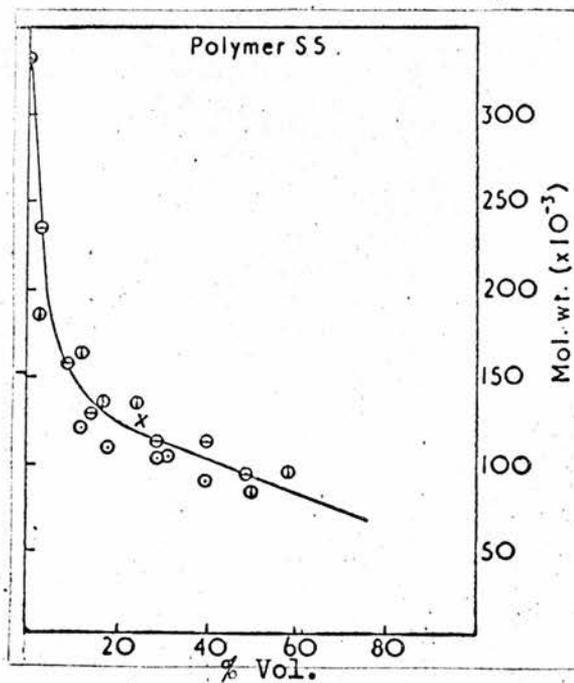
Grassie and Kerr²⁷ found a qualitative similarity between their plots and Jellinek's data⁹ for molecular weight against time, (Figure 4) but also demonstrated that if the molecular weights were plotted as functions of conversion, rather than time, the curves are superposable (Figure 5). From these graphs Grassie and Kerr deduced that there are "weak links" in polystyrene which decompose early in the reaction, always with chain scission. After this phase the molecular weight curves are almost linear with conversion and appear to run between the horizontal and the diagonal running to zero molecular weight (Figure 6). By analogy with the degradation behaviour of poly(methyl methacrylate)²³ they concluded that decomposition in this second phase of the reaction is initiated at chain ends, and that the kinetic chain length, including intramolecular transfer,

FIGURE 4.



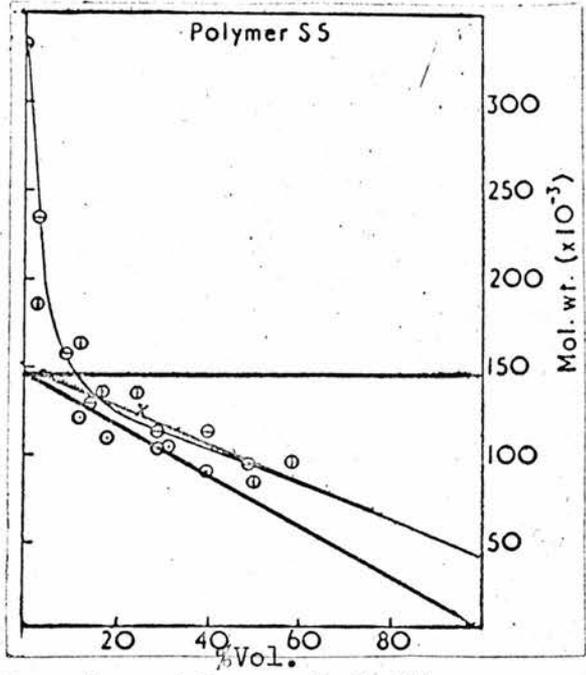
Grassie and Kerr - Ref. 27.

FIGURE 5.



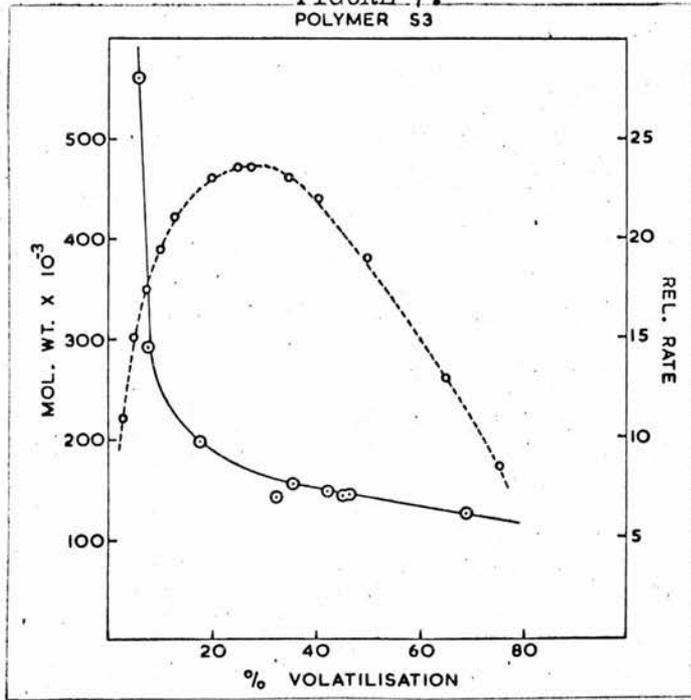
Grassie and Kerr - Ref. 27.

FIGURE 6.



Grassie and Kerr - Ref. 27.

FIGURE 7.
POLYMER S3



Kerr - Ref. 28.

is of the same order as the molecular chain length, i.e. about 1,000. Because the ratio of monomer to non-monomer was found to be constant throughout the degradation, Grassie and Kerr suggested that the only transfer reaction occurs intramolecularly. Furthermore, they pointed out that the rate against conversion curves show an initial low rate which means that the "weak link" scission reaction must result in stable chain ends, not radicals, and a "cage" reaction was suggested as an explanation. In support of their theory of chain-end initiated volatilisation, Grassie and Kerr²⁸ suggested that the rate of this reaction will be a maximum when the number of chain ends, i.e. the molecular population, is at its greatest value. This condition obtains when the "weak link" scission phase is just complete, namely at about 30% volatilisation, and their observed rate maxima at c.30% conversion must be regarded as satisfactory proof of the postulate of chain-end activated volatilisation. (Figure 7).

Detailed studies of polystyrenes prepared under a variety of free-radical conditions²⁹ led to the suggestion that the labile bonds are formed by abnormal propagation steps during polymerisation, and do not involve oxygen. Possible structures considered, included head to head links and double bonds introduced by propagation through one of the canonical forms of the growing polymer radical. Head to head bonds were eliminated³⁰ when it was found that copolymers of styrene with stilbene did not have a significantly increased concentration of "weak links". The ozonisation of polystyrenes in solution³¹,

however, was found to reduce the molecular weight to about the same value as found in thermal degradation, which was strong evidence that the labile structures contain double bonds. On this basis a reaction scheme which explained all the important features of "weak link" scission was drawn up.

To complete this investigation, Cameron and Grassie³² studied the degradation of polystyrene in solution in naphthalene and tetralin. They found - as had Jellinek -^{16,17} that the degradations in bulk and in naphthalene are essentially similar, that in tetralin volatilisation is inhibited, but that in all three media the initial rapid fall in molecular weight occurs at approximately the same rate and to the same extent. This data strengthened the theory that the initial fall in molecular weight and the depolymerisation reaction are two separate processes. Therefore, in contradiction to Wall's²⁶ conclusion, intermolecular transfer cannot be important in reducing the chain length.

Grassie and Kerr³³ also found by osmometry that the solution properties of degraded polystyrenes showed significant differences from those of undegraded polymer, and tentatively suggested that the effect might be due to the disappearance of structural abnormalities on heating. More recently, however, Cameron³⁴ showed that this effect was due simply to diffusion of low polymer through the membrane.

(5) The Theoretical Treatment by Gordon

The experimental results of Grassie²⁷ and Madorsky¹⁹ were

used by Gordon³⁵ in a simple kinetic treatment to illustrate that volatiles are formed by initiation at chain ends in polystyrene. In order to achieve satisfactory curve fitting Gordon found it necessary to assume first order termination for Grassie and Kerr's data²⁷ and a second order termination for Madorsky's results¹⁹. More importantly, Gordon also found that he had to superimpose a random scission component on the chain-end activated depropagation to obtain satisfactory agreement with the experimental results, but his treatment was insufficiently sensitive to determine the nature of this random component, although he did suggest that "weak links" are an unnecessary complication.

(6) Some Recent Investigations on the Thermal Degradation of Polystyrene

Anderson and Freeman³⁶ have studied the degradation by dynamic thermogravimetry, using the method of Freeman and Carroll³⁷ to interpret their results. They found that the reaction appeared to occur in two stages - a low temperature stage representing approximately 10% volatilisation up to 370^o C., and a subsequent high temperature reaction covering from 15 - 95% of the degradation. The low temperature phase appeared to obey zero order kinetics with an Activation Energy of 46 kcal. mole.⁻¹, whereas the high temperature reaction appeared to be first order with an Activation Energy of 60 kcal. mole.⁻¹. These results, the authors suggest, explain the discrepancy between Jellinek's reported zero order kinetics⁹ and Madorsky's first order kinetics¹⁹, because Jellinek used temperatures below 340^o C. and Madorsky used temperatures greater than 340^o C.. Two different mechanisms seem to be

operative, the low temperature reaction appearing to represent the splitting off of monomer.

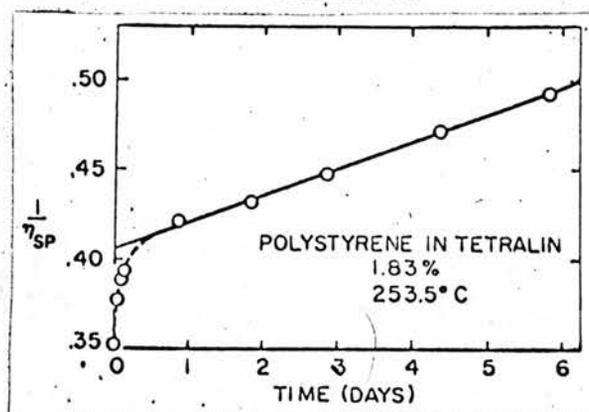
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At the same time Delava³⁸ studied the degradation of isotactic and atactic polystyrenes by thermogravimetry and found an overall zero order reaction with an Activation Energy from 50 - 58 kcal. mole⁻¹. No significant differences were found between the samples under the prevailing experimental conditions, therefore, stereoregularity does not appear to influence the reaction.

Flynn³⁹ re-investigated the thermal degradation of polystyrene in solution in tetralin at lower temperatures than previously used in an effort to slow down the initial fall in molecular weight and make the effect more readily observable. His results are shown in Figure 8. The number of scissions represented by the initial rapid fall in molecular weight is a factor of 10^3 less than the number of "weak links" found by Cameron and Grassie³² in a similar polymer. The reason for the initial rapid chain scission was not elucidated, but structural "weak bonds" could be involved.

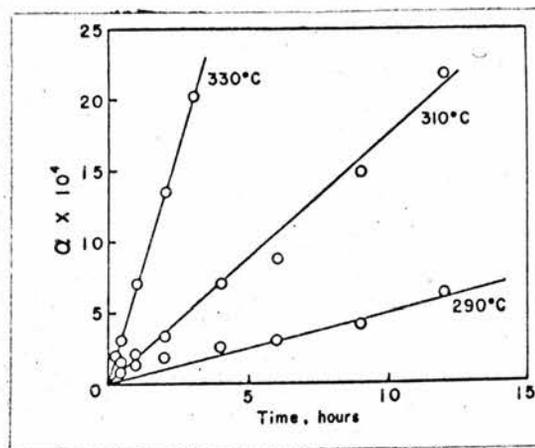
MacCallum⁴⁰ has reviewed the vinyl polymers in which there appear to be bonds more thermally labile than normal, i.e. polystyrene^{9,27}, polyethylene²⁴ and polypropylene⁴¹. Using a simple kinetic treatment he showed that all these polymers appear to contain "weak links". In addition the concentration of these thermolabile bonds was found to be a function of the degradation temperature - a conclusion which detracts from the validity of the "weak link" theory. His approach

FIGURE 8.



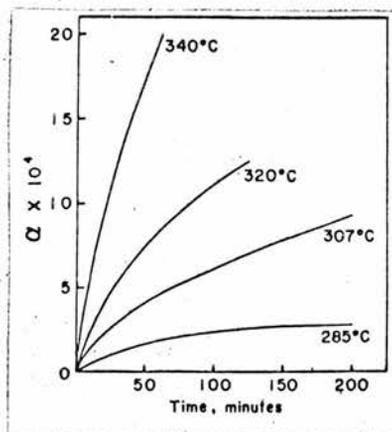
Flynn - Ref. 39.

FIGURE 9.



Nakajima et al. - Ref. 43.

FIGURE 10.



Nakajima et al. - Ref. 43.

however, is only strictly correct when the polymer samples suffer no volatilisation, and its application to the above degradations, where this condition did not obtain, renders the treatment rather qualitative. MacCallum concluded that the "weak link" concept may require revision.

Boon and Challa⁴² have recently studied, by melt viscometry at 265° - 320°C. under nitrogen, the kinetics of the thermal degradation of isotactic polystyrenes prepared by Ziegler - Natta catalysis. The sample volatilisation was less than 0.5%, indicating that no depropagation occurs under these experimental conditions. The melt viscosity, and therefore the molecular weight, was found to decrease continuously with time, and Boon and Challa explained this behaviour in terms of the cleavage of polymer chains by random scission in a zero order reaction with an Activation Energy of 39 kcal. mole.⁻¹. No evidence was found of "weak links". These authors suggest that subsequent depolymerisation is initiated at chain ends to produce monomer by unzipping, oligomers by intramolecular transfer and larger fragments by intermolecular transfer. In view of the anionic nature of the polymerisation it was considered improbable that the quinonoid "weak links", proposed by Grassie and Kerr²⁷ for atactic polystyrenes, can exist in isotactic polymers.

Nakajima, Hamada and Shimizu⁴³ have also studied the thermal degradation of isotactic polystyrene but under high vacuum in a closed system. For temperatures between 290° and 330°C. volatilisation

was very low. Good agreement was obtained between experimental and theoretical molecular weight distributions for degraded polymers, assuming random scission. The rate of degradation at various temperatures was followed by observing the dependence on time of α , the fractional number of bonds broken. For a simple random degradation α versus time is linear passing through zero at t_0 , and this relationship was obeyed in this work. (Figure 9). They also reworked Jellinek's molecular weight data⁹ for atactic polystyrene into the form of an α versus t plot, and found a short, initial high rate period followed by a linear dependence of α on t . (Figure 10). The Activation Energies for isotactic and atactic polystyrenes were found to be identical within experimental error (~ 40 kcal. mole⁻¹), and the initial high rate period in atactic polystyrene was explained by "weak link" scission. Although application of this theory to their own work is correct, application to Jellinek's data is invalid because of the high volatilisation of samples in his experiments. These results are in good agreement with Boon and Challa's⁴², and together prove conclusively that isotactic polystyrenes prepared by Ziegler - Natta catalysts do not contain measurable concentrations of "weak bonds".

In 1966 Wall⁴⁴ and coworkers completed a sophisticated computer survey of the relative importance of the experimental parameters operative during the thermal degradation of polystyrene. In the programme the effect of the following variables was studied :-

N - Initial Number Average \overline{DP} .

L - Number of Monomer units in the largest vaporisable molecule

(= 9 for polystyrene).

$$\mu = \frac{k_I}{k_I} \quad \text{where } k_I - \text{rate constant for random initiation.}$$

k_I - rate constant for end initiation.

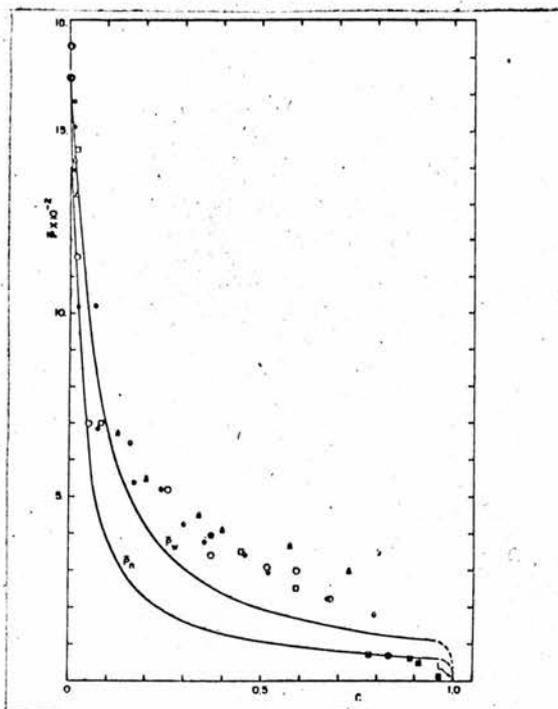
σ - Intermolecular transfer constant

$$Z = \frac{I}{\epsilon} \quad -I - \text{kinetic chain length}$$

(= 5 for polystyrene)

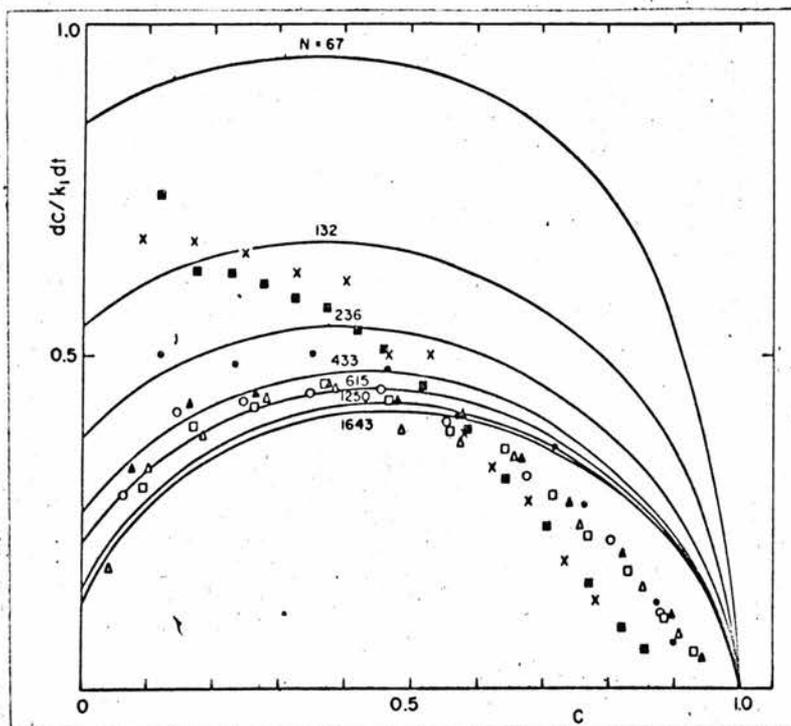
The reaction scheme and kinetic derivations were similar to those in previous work^{20,21,22} but the computer was capable of handling larger numbers and more parameters. To obtain rate of volatilisation maxima at 40% conversion it was found necessary to have $\mu = 0$, i.e. no random initiation, and σ equal to a positive number. For the same values of these parameters molecular weight against conversion plots were obtained. "Weak links" were claimed to be absent, although the authors concede that a small amount of random scission - which would be more important at high molecular weights - may improve the agreement between theoretical and experimental data. In fact the published diagrams (Figures II and I2) show a rather poor correlation between experimental and theoretical results, especially in the rate curves for low molecular weight polymers at all conversions, and for all polymers at high conversions. In view of this poor agreement, it is

FIGURE 11.



Wall et al. - Ref. 44.

FIGURE 12.



Wall et al. Ref. 44.

difficult to agree with the authors' confidence in their theory.

Cameron⁴⁵ has recently drawn up a simple kinetic scheme which, when applied to the literature data, showed that chain-end initiation of volatilisation occurs to the exclusion of random initiation, a finding in agreement with Grassie and Kerr's²⁷ conclusions. Cameron suggested that random initiation of depolymerisation is inhibited by "cage" disproportionation reactions which are enhanced by the low diffusivity of large macroradicals in the polymer melt. This treatment also showed that termination of active radicals is apparently a first order process, a finding which is at variance with most previous theoretical approaches^{23,25,44}. A possible reaction scheme involving intramolecular transfer and the volatilisation of a small radical is suggested as an explanation.

In a new approach to decide whether "weak links" or intermolecular transfer is responsible for the rapid fall in molecular weight of polystyrene, Richards and Salter⁴⁶ induced the degradation by decomposing other polymers in polystyrene at temperatures where the latter is stable. Firstly, the degradation of polystyrene was studied by decomposing poly (α - methylstyrene) between 260° and 290° C. in a mixture of the two polymers. An Activation Energy of 65 kcal. mole.⁻¹ was found for the polystyrene degradation. In a second series of experiments polystyrene, prepared by "living" anionic synthesis to contain a few head to head bonds, was found to be more thermolabile than normal anionically prepared polystyrenes. This "weak bond"

polystyrene was decomposed at various dilutions in normal polystyrene, and the nature of the termination reaction investigated. This reaction was found to be predominantly bimolecular at high "weak link" concentrations but unimolecular at low concentrations of the labile bonds. Consideration of the nature of these "weak bonds" led to the conclusion that they were head to head links, a view rejected earlier by Cameron and Grassie³⁰. In a third approach Richards and Salter investigated the extent of the intermolecular chain transfer reaction by decomposing "weak link" polystyrene in β -¹⁴C labelled polystyrene. From the amount of radioactive styrene in the volatiles they concluded that intermolecular transfer occurs in the degradation to a considerably greater extent than previously postulated⁴⁴. They also suggested that the lower thermal stability of free-radically prepared polystyrenes compared to anionically synthesised polymers may be due to "weak links" whose incorporation into the polymer is favoured by the higher polymerisation temperatures of the former polymers.

(7) Scope of the present work

The foregoing review shows that from the outset the mechanism of polystyrene pyrolysis has been the subject of considerable controversy. General agreement on the nature of the various steps in the degradation is obtained from most investigators, but the relative amounts of chain transfer, the order of the termination reaction and the kinetic chain length have not been incontrovertibly established. The main point of contention, however, as has been stressed in this

chapter, is the presence or otherwise of abnormal thermolabile structures in the polymer, and there are no results in the literature which prove or disprove beyond doubt their existence in free-radically prepared polymers. At present the weight of evidence appears to be against the "weak link" theory, but this hypothesis has never been shown to be completely untenable except in the case of anionic polystyrenes^{42,43} prepared by Ziegler - Natta catalysis.

It seems that most of the controversy stems from the difficulty in interpreting molecular weight data when both chain scission and depropagation reactions occur together. Consequently an approach to this problem under conditions where the depropagation reaction is negligible should provide unambiguous data on the initiation or chain scission reaction, and should demonstrate the presence, or absence, of thermolabile structures.

A simple way to achieve this experimental separation is to lower the degradation temperature, and support for this approach comes from the investigations by Boon and Challa⁴² and Nakajima and collaborators⁴³. However, these authors confined their studies to Ziegler - Natta polystyrenes in which they found no evidence for "weak links", whereas most of the controversy has arisen from work using free-radically prepared polystyrenes^{9,19,27,35}. Consequently it was considered vital to study the degradation of the latter polymers under the same conditions of low volatilisation. Anionic polystyrenes, prepared in "living" systems, were studied for comparison since their

mode of synthesis would also seem to preclude structural abnormalities. The first part of this thesis is concerned with the degradation of these types of polystyrenes.

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CHAPTER II.

APPARATUS and EXPERIMENTAL TECHNIQUESA. The Synthesis of PolymersI. Thermally Polymerised Styrene Homopolymers and Styrene-Stilbene
Copolymersa) The Purification of Styrene monomer.

Styrene monomer (B.D.H.) was washed three times with dilute sodium hydroxide solution to remove inhibitor, three times with distilled water to remove alkali, then dried overnight over magnesium sulphate. In the next stage of the purification, the monomer was distilled under reduced pressure with a nitrogen leak, through a four foot column packed with Fenske helices, the first and last 20% of the distillate being discarded. The middle fraction, boiling at $52-3^{\circ}\text{C}$. at 28-30 mm. mercury, was collected and immediately distilled on the high vacuum line into a reservoir tube from where it could be distilled when required into calibrated tubes, and then into dilatometers. Both reservoir and calibrated tubes contained activated Type 4A Molecular Sieves to dry the monomer, and glass-coated hammers to break the surface film which formed during distillation of the styrene.

b) The Purification of Trans-Stilbene

Trans-stilbene (Koch-Light.) was recrystallised three times from ethanol; dried under high vacuum. M.pt. $125.5 - 126.0^{\circ}\text{C}$.
(Lit. m. pt. 125°C .)

c) The Filling of Dilatometers.

Since the rate of polymerisation was not being studied, the stems of the dilatometers were constructed of 5mm. diameter Viridia tubing which provided sufficient accuracy for the determination of conversion of monomer to polymer without calibration. Before use, the dilatometers were checked for leaks, thoroughly cleaned and dried, then attached to the vacuum line and pumped out for at least 24 hours at high vacuum, with intermittent flaming. Evacuation was achieved by means of a mercury diffusion pump backed by a rotary oil pump, to give a vacuum better than 10^{-5} mm. mercury.

Styrene was distilled from the reservoir to the calibrated tubes, where it was degassed four times. Measured amounts were distilled into the dilatometers, degassed four times, and the dilatometers sealed off under high vacuum.

When a styrene-stilbene copolymer was being prepared, a weighed amount of stilbene was added to the dilatometer and washed down with a little dry Analar acetone. The acetone was removed by pumping, with the dilatometer cooled in liquid nitrogen to prevent loss of stilbene by sublimation. As before, a measured amount of styrene was distilled into the dilatometer, degassed, and the dilatometer sealed under high vacuum.

d) Polymerisation

Polymerisations at 45°C . and 60°C . were carried out in a water-bath controlled by a mercury-toluene regulator and a Sunvic relay. Temperature control was estimated at better than $\pm 0.1^{\circ}\text{C}$.

Polymerisations at 90°C. and 120°C. were undertaken in a Dewar vessel, silvered as usual except for a vertical strip which allowed observations to be made on the dilatometers within the vessel. The Dewar was filled with liquid paraffin, and the temperature controlled by a Contact Thermometer and a Sunvic relay to an accuracy better than $\pm 0.2^\circ\text{C}.$

Conversion of monomer to polymer was estimated from the contraction in volume of the polymerising liquid, the data of Melville and Valentine^I being used to relate volume contraction and conversion to polymer. In the case of the styrene-stilbene copolymers, only small amounts of stilbene enter the growing polymer chains, so that the polymerisation was treated as if the stilbene plays no part in the change in volume.

e) The Precipitation and Purification of Polymers

On completion of polymerisation, the dilatometers were opened, the contents dissolved in the minimum volume of Analar toluene, and the polymer was precipitated by adding the toluene solution to vigorously stirred methanol. The polymer was filtered off and dried at the water pump overnight. Finally the polymer was dissolved in enough Analar toluene to make a 0.5% w./v. solution, and the solution was filtered before being added slowly to a rapidly stirred volume of methanol (10 times the volume of the solution). The polymer was filtered off, and dried to constant weight in a vacuum oven, initially at room temperature and finally at 60°C.. In this way the polymer was obtained as a fine powder.

II. Anionically Polymerised Polystyrenes

These polymers were obtained from W.J. Bryce and G. M^cGibbon² of the Department of Chemistry in Aberdeen University. They were prepared in tetrahydrofuran at -20°C . using cumyl-potassium as initiator. The low molecular weight, polymeric fraction, formed during polymerisation by this initiator, was removed by fractional precipitation.

B. The Bulk Degradation of Polymers

I. Degradations in the Molecular Still

Bulk degradations of polymer samples were carried out in a molecular still of the type pioneered by Grassie and Melville³. This method has advantages in that it allows degradations to be carried out at accurately known and controlled temperatures while the evacuation of the still prevents oxidation and permits the rapid escape of volatiles from the reaction zone, hence reducing complicating side reactions. In some cases, e.g. poly(methylacrylate)⁴, the copper used in the construction of the degradation trays and as a powder covering the polymer to reduce temperature gradients, exerts a catalytic influence on the degradation, but this has not been found with polystyrene^{5,6}.

a) The Glass Apparatus

Degradations were carried out in the apparatus shown in Figure I. The molecular still was a heavy glass cylinder, 18 cms. deep and 10 cms. in diameter, rounded off at one end and closed at

FIGURE 1
BULK DEGRADATION APPARATUS
MOLECULAR STILL

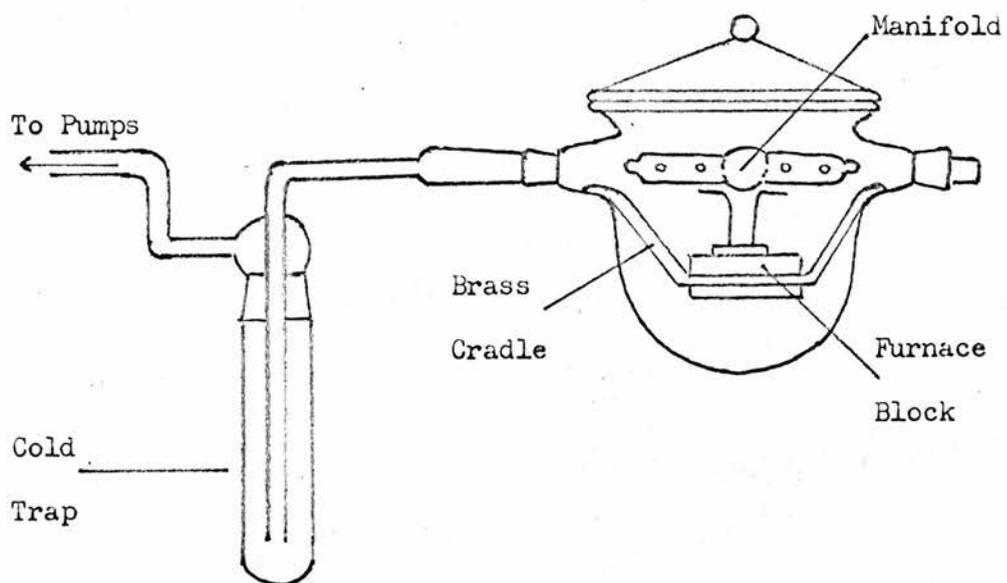


FIGURE 2

COPPER TRAY and FURNACE BLOCK

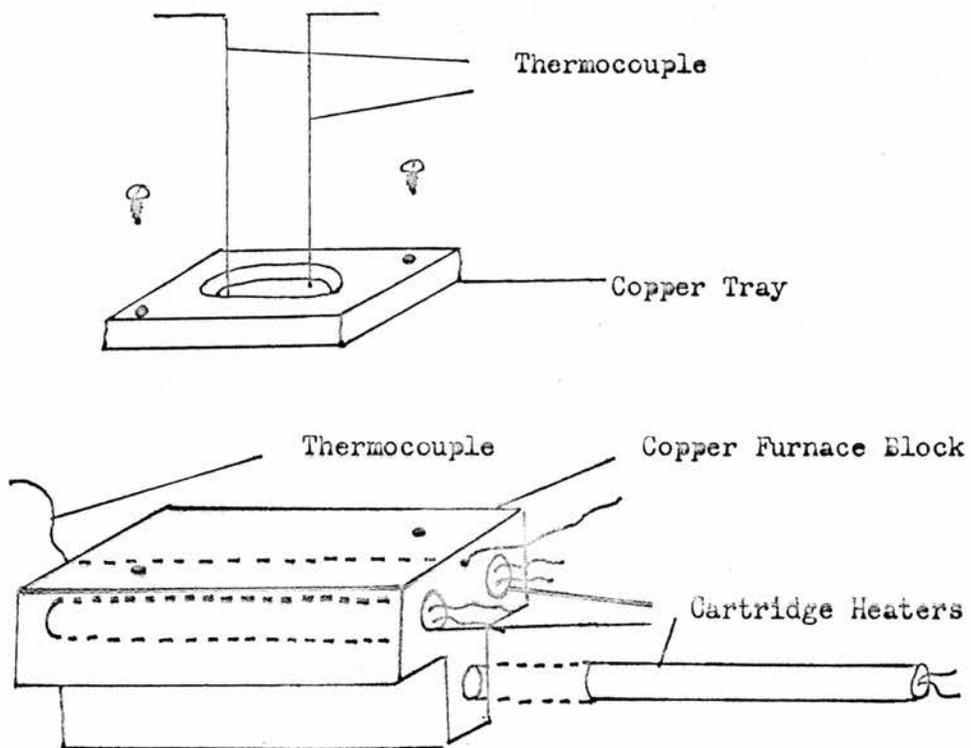
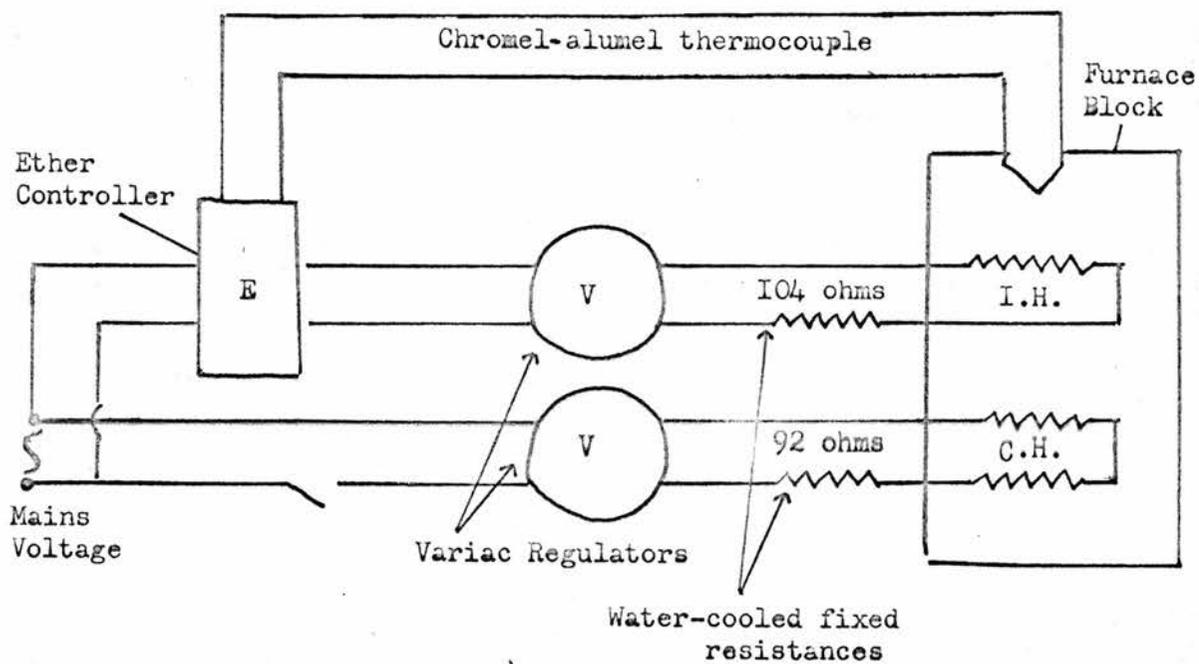


FIGURE 3
HEATER CIRCUITS



I.H. Intermittent Heater

C.H. Constant Heaters

the other by a desiccator-type lid with a ground-glass flange. Four B.24. sockets were arranged symmetrically, and perpendicular to the wall of the cylinder. This part of the still was specially constructed by Quickfit and Quartz, Ltd..

A glass manifold - carrying two thermocouple and two heater circuits into the still - fitted into one of the sockets, while another socket led directly to a cold trap and from there to the pumping system. Vacuum-tight seals in the manifold were effected with "Picien" wax. A rigid brass cradle, which supported the heating block, was suspended between the other two sockets, and fixed in place with "Araldite" resin. These sockets were sealed with stoppers. Evacuation to 10^{-5} mm. was effected by a mercury diffusion pump backed by a rotary oil pump.

b) The Heating Block

The copper heating block is shown in Figure 2. Three cartridge heaters (50 watts, 24 volts. Hedin Ltd.) and a chromel-alumel thermocouple were fitted into holes which had been drilled through the block. During a degradation the upper heaters, which were in series, were supplied with a constant predetermined voltage not quite sufficient to maintain the required temperature. The lower heater operated intermittently under the control of an "Ether Transitrol" controller, actuated by the thermocouple to maintain the degradation temperature. Variac transformers (Cressall Manufacturing Company Ltd.) reduced the output to both

sets of heaters from the mains voltage to the values required to maintain the degradation temperature. Each heater circuit contained a fixed water-cooled resistance in series so that full scale on the Variac gave the maximum permissible output across the corresponding heaters i.e. 48 volts across the constant heaters, 24 volts across the intermediate heater. This modification gave excellent control of the voltages supplied to the heaters, thus providing temperature control better than $\pm 1^{\circ}\text{C}$. The heater circuits are shown in Figure 3.

c) The Degradation Tray

The trays, (Fig.2), were copper blocks, 40 mm. square and 9 mm. deep, in which a depression, 33 mm. in diameter and 7 mm. in depth, was cut out from the centre. A copper-constantan thermocouple was silver-soldered to the surface of the cavity, and connected to the rest of the thermocouple circuit outside the still via the manifold. The output of the thermocouple circuit was measured by a Pye Portable Potentiometer. Two holes were drilled in opposite corners of the tray and in corresponding positions in the block so that tray and block could be screwed tightly together to ensure good thermal contact. All four trays used, weighed about 45 grams, and therefore possessed equal heat capacities.

d) The Copper Powder

In all bulk degradations, polymer was weighed into the tray

and covered with a layer of copper powder to reduce both sputtering and temperature gradients in the molten polymer. Oxide-free copper powder of regular particle size (60 - 80 mesh) was supplied by Hopkin and Williams, Ltd.. Previous work by Grassie et als.^{5,6} had shown that this powder has no effect on the degradation of polystyrene. The same quantity of powder - 10 grams - was used in all degradations.

e) The Degradation Procedure

The same weights of polymer and copper powder were used in all but a few experiments, viz. 9 mg. of polymer, and 10 g. of copper powder. In the exceptions, 25 mg. of polymer were used. The polymer was weighed directly into the tray and covered with copper powder, after which, the tray was screwed firmly to the heating block and the still pumped out to a sticking vacuum. When this condition was obtained, heating was commenced by setting the Constant Heater Variac to its maximum output while maintaining the Intermittent Heater Variac at its controlling value. At 35°C. below the required temperature, the Constant Heater Variac was reduced to its controlling value, and timing of the degradation was begun. A little experimentation was required to determine these controlling voltages. The interval between the start of heating and the attainment of the degradation temperature was of the order of 12 minutes. When the required degradation time had elapsed, the power to both sets of heaters was switched off. The temperature

fell quite rapidly to about 200°C., then dropped more slowly to room temperature at which point the tray was removed.

Errors due to neglect of the time required for the sample to reach degradation temperature and to fall afterwards to a temperature where degradation ceases, are inherent in the method, but are considered small except where very short degradation times are involved.

II. The Degradation of Polymers by Thermogravimetric Analysis

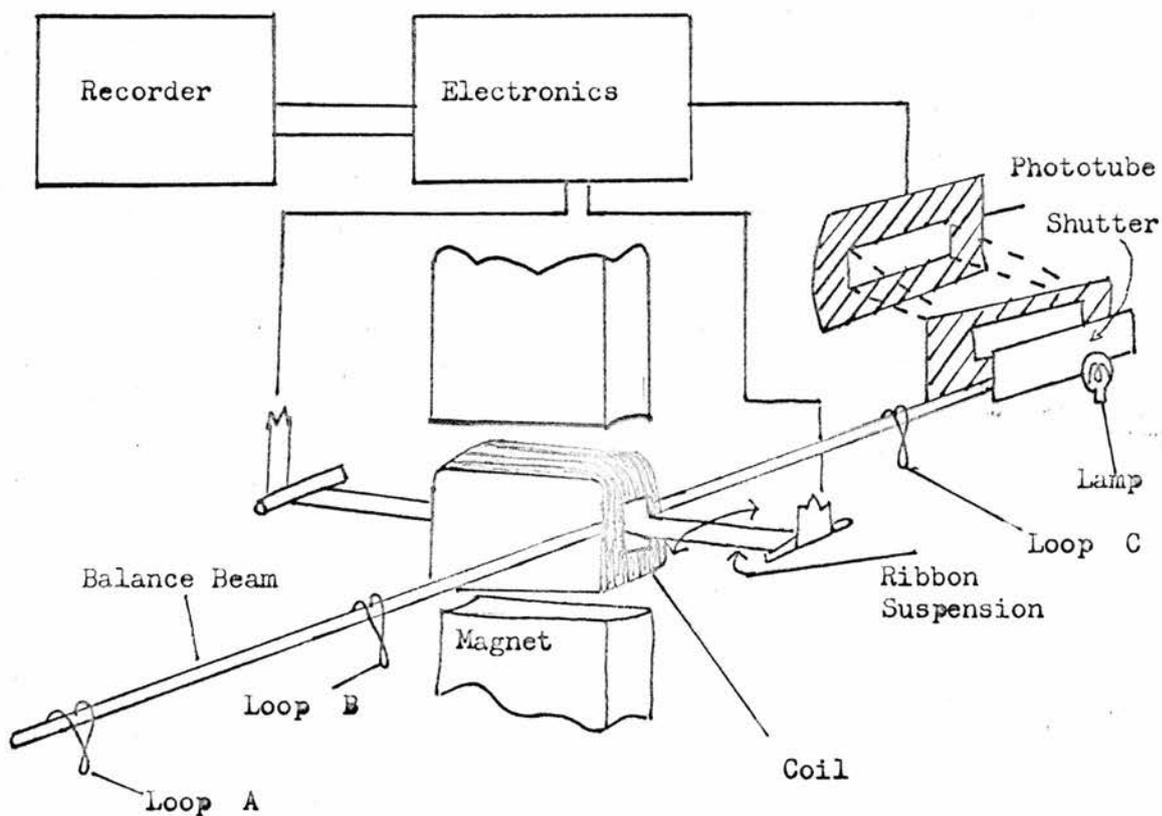
Thermogravimetric analysis (TGA.) is the specialised science of recording the weight - either continuously or intermittently - of a decomposing substance while it is being heated. Although the first Thermobalance was built in 1915, it is only within the last twenty years that this type of instrument has been used in the study of polymer degradation.

a) The Thermobalance

The thermobalance used in this investigation was a Cahn R. G. Automatic Electrobalance^{7,8} (shown schematically in Fig. 4), which utilises the null-deflection principle. As the weight of the sample changes, the displacement of the shutter attached to the balance beam increases or decreases the intensity of the light falling on the phototube. The resultant change in the magnitude of the current from the phototube is amplified by a two-stage servo amplifier and applied to the coil attached to the centre of the beam. Because this coil is in the magnetic field of

FIGURE 4

SCHEMATIC DIAGRAM of CAHN R.G. ELECTROBALANCE



the fixed magnet, the passage of current through it exerts a moment on the beam, restoring it to its null position. This coil current is, therefore, proportional to the change in weight. The voltage across the coil is measured continuously and can be related directly to the change in weight of the sample by means of a series of calibrations carried out before the start of a degradation. During a run, the weight of the sample can be recorded either intermittently by balancing a potentiometer in the electronics module which records the voltage across the coil, or continuously by feeding the voltage directly from the module to a 1 mV. chart recorder (Leeds and Northrup Ltd.). A Cahn Time Derivative Computer is available for electronically differentiating the weight vs. time/temperature curves. The outstanding merits of this electrobalance are the accuracy of the null-deflection principle and the very quick response to changes in weight.

The balance beam possesses three loops, loops A and B being sample loops, while loop C is a taring loop. The maximum sample weight on loop A is 1 g., with a maximum weight change of 200 mg., while loop B has a maximum sample weight of 2.5 g., with a maximum weight change of 1,000 mg.. The sensitivity at the longer radius is 5 times that at the shorter radius, so that in these experiments the former was always used. The constant part of the sample weight, i.e. the sample pan, can be counterweighted on loop C with tare weights, so that the electromagnetic system works

only on the change in sample weight. In practice, approximately 10 mg. samples were used, and the electrobalance calibration adjusted to give 10 mg. as full scale deflection on the recorder. Accordingly the sample weight was read directly from the recorder chart.

b) The Electrobalance Installation and Vacuum System

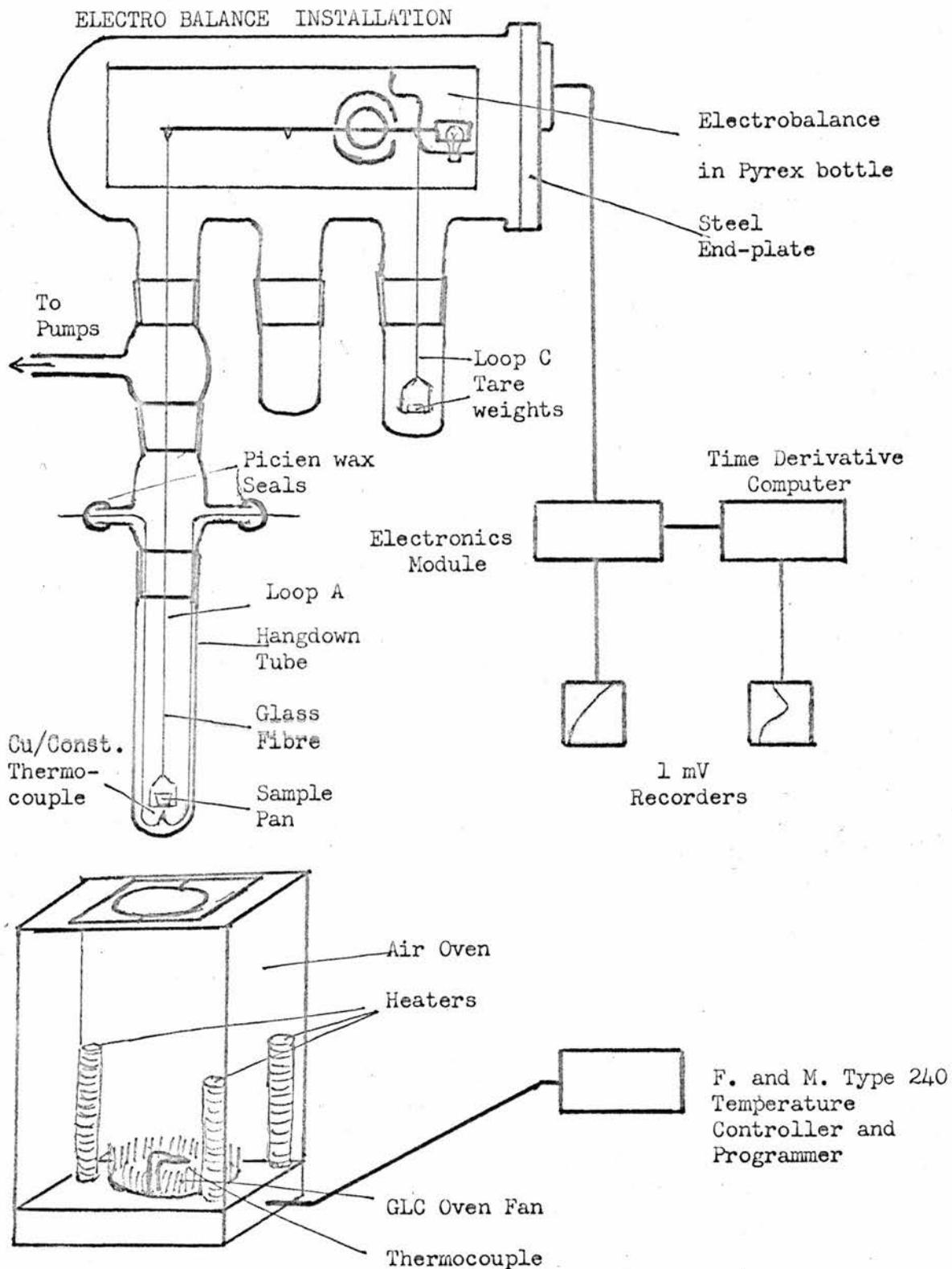
The electrobalance installation and vacuum system are shown in Figure 5. The balance was mounted in a Pyrex bottle, with electrical connections made through a steel end-plate. Two copper-constantan thermocouples were brought into the hangdown tube through Picien wax-filled inlets. One thermocouple was held rigidly by glass sleeves, in a position 2 - 3 mm. below the sample pan, while the second was constructed of finer gauge wire and was used as described later in temperature calibrations. A small stirrup, on which the platinum sample pan was placed, was suspended from a long, thin glass fibre. In the experiments the total weight of the stirrup, pan and sample was so low that it failed to keep the finest possible nichrome wire absolutely straight, thus necessitating the use of a rigid glass fibre.

Evacuation was achieved by a mercury diffusion pump backed by a rotary oil pump, and was of the order of 10^{-4} to 10^{-5} mm. mercury.

c) The Furnace and Temperature Controller

Initial experiments with a wire wound iron pot as furnace

FIGURE 5



were unsuccessful because of a considerable temperature gradient up the pot. Accordingly an air oven was constructed which utilised a Perkin-Elmer GLC. oven fan with three heaters arranged symmetrically about it. An iron-constantan thermocouple was mounted directly over the fan. Temperature gradients up the oven were found to be of the order of $3^{\circ}\text{C}.$

Temperature control was achieved by an F. and M. Type 240 temperature controller and programmer, actuated by the thermocouple in the furnace. This instrument is capable of both isothermal and temperature - programmed operations up to a maximum temperature of $550^{\circ}\text{C}.$ and heating rates from $0.5^{\circ}\text{C}.$ to $30^{\circ}\text{C}.$ per minute.

d) The Sample Size

Atherton⁹ has criticised early work by Jellinek¹⁰ on the grounds that the weight of sample employed (20 mg.) gave rise to a considerable amount of spattering, and Madorsky¹¹ found that smaller samples, 6 - 7 mg., reduced this effect to a minimum. With this earlier work in mind, 9 - 10 mg. of polymer were employed in this study.

e) The Temperature Calibrations

In many reported TGA. experiments^{10,11,12,13,14} the accuracy of the temperature measurements is doubtful because the temperature of the sample has been assumed to be the same as that of a thermocouple placed directly below the sample pan. Since, in

vacuum thermogravimetry all the energy is supplied by radiation, the rate of energy absorption by a body will depend on the area and nature of the surface, and the rate of temperature increase will depend to some extent on the heat capacity of the body. Because these factors were very different for the thermocouple and sample used in these experiments, there was a considerable divergence in the temperatures of these two objects, especially in temperature programmed operations.

Therefore, it was considered necessary to have a more accurate estimate of the temperature inside the sample pan. Direct measurement of the temperature inside the pan could not be made during actual TGA. experiments because a thermocouple touching the inside of the pan affected the weight of the pan in an unreproducible way. Accordingly the temperature calibration was constructed in blank runs, using a fine thermocouple embedded in a little silicone vacuum grease in the pan. The temperatures measured by the thermocouples in the air oven, in the sample pan, and below the sample pan were recorded simultaneously for both isothermal and temperature - programmed runs. In these experiments it was found that the tray thermocouple attained equilibrium more rapidly than the tube thermocouple and gave a higher temperature reading, the difference between the two thermocouple readings increasing with temperature. Calibration graphs were constructed, as shown in Figure 6, to allow the estimation of the sample temperature during

FIGURE 6a.

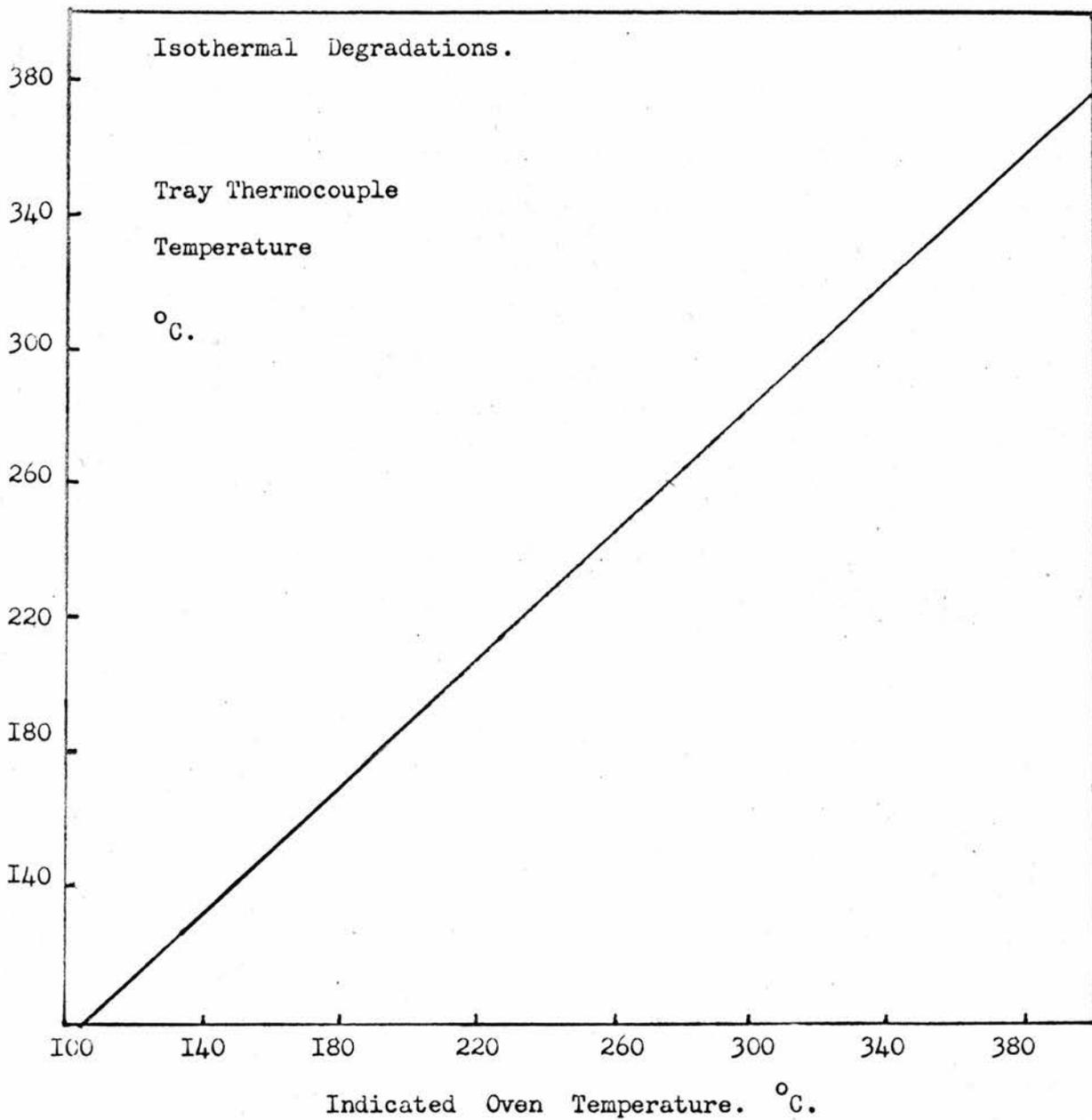


FIGURE 6b.

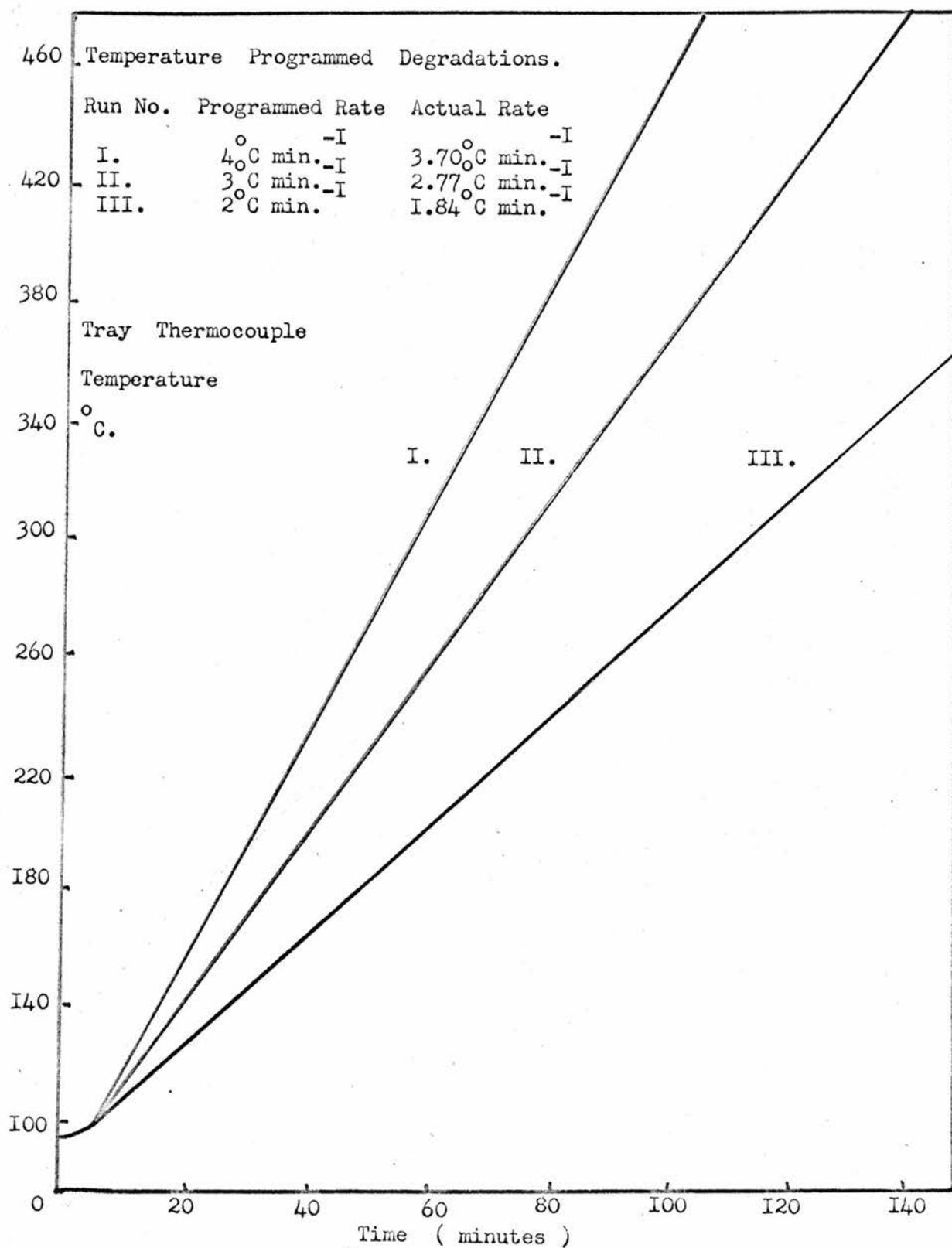
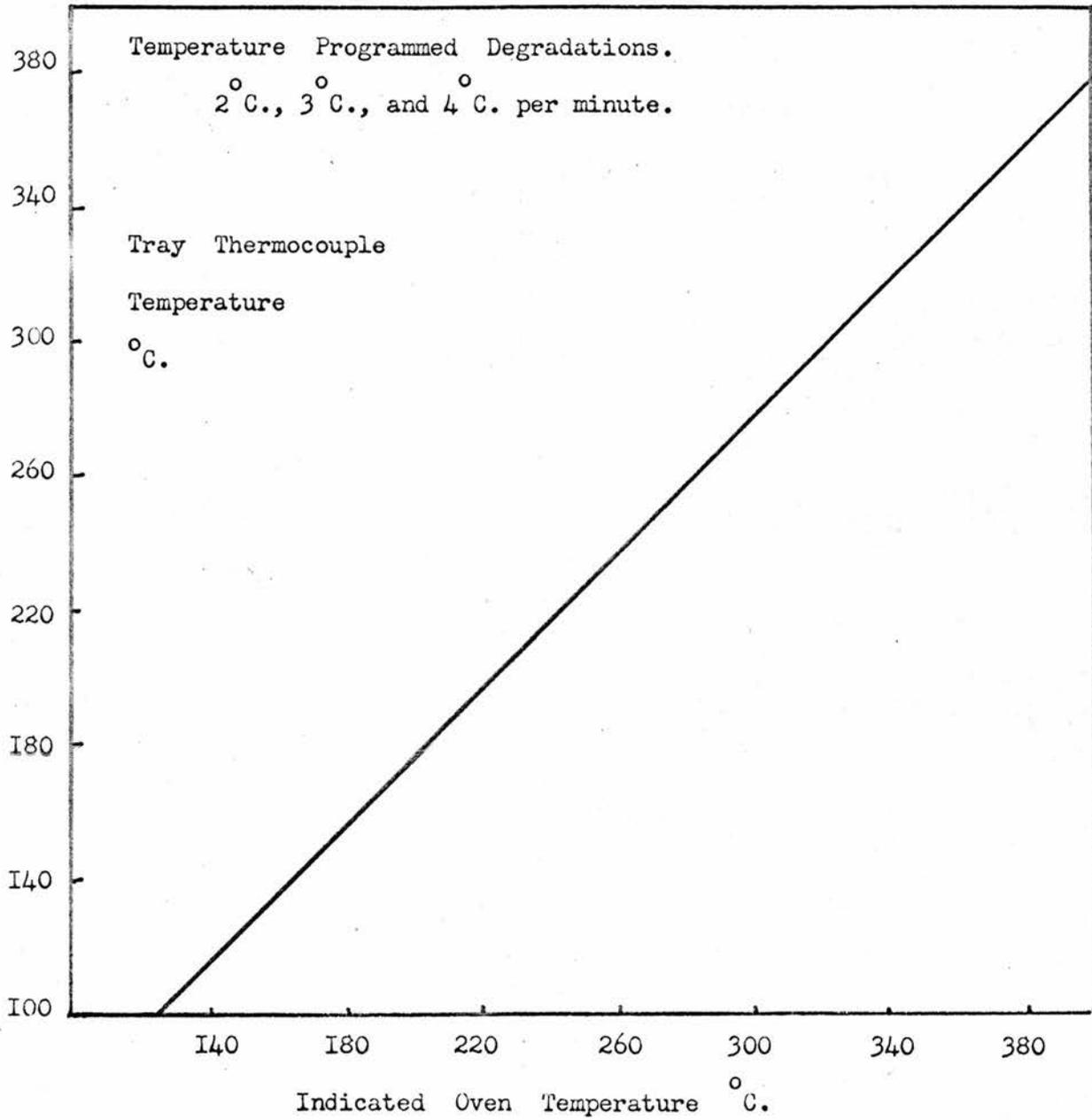


FIGURE 6c.



a degradation from the measurement of the oven or tube temperatures. In this way, while the problem of accurate temperature measurement was never fully overcome, a far better estimate of the temperature in the polymer melt was obtained.

f) The Experimental Procedure

In degradation experiments, 10 mg. of polymer were weighed into a small platinum crucible, the hangdown tube replaced, and the system evacuated. On attainment of a good vacuum, the sample was preheated to constant weight at 100°C.. Degradation was commenced by setting the temperature controller to the required isothermal temperature or programmed rate of heating. Because of the low heat capacity of the air oven and hangdown tube, the isothermal degradation temperatures were reached within five minutes of resetting the temperature controller and there was very little lag in temperature during programmed runs.

This method of initiating degradation was found to be better than the alternative procedure of raising the preheated oven because the latter often gave rise to oscillations in the glass fibre which took some time to damp out, meanwhile causing vibrations in the recorder trace. Degradations were stopped by lowering the oven away from the hangdown tube.

III. The Investigation Of Polymer Melting Points by Differential

Thermal Analysis

The instrument used in this study was a Du Pont 900 Differential Thermal Analyser. This apparatus is designed on a modular interchangeable cell basis, and offers a variety of options. Three cell assemblies are available with temperature ranges of -100° to 500° C., ambient to 850° C., and ambient to $1,200^{\circ}$ C. respectively. The first cell was used in the present study. Heating rates of 0 to 30° C./min. are continuously available. The programmed temperature control can be set to heat, hold at a preset temperature or cycle between preset limits. The atmosphere may be controlled with either static or flowing gas, or it can be operated under vacuum. In the present experiments, nitrogen was used as the inert gas. Data presentation is temperature as the X axis, ΔT as the Y axis on an X - Y recorder with variable scales ranging from ΔT of about 0.1 to 10° C./in., T approximately 10 to 200° C./in. The stated sensitivity is ΔT 0.025° C. or 10^{-3} cal. with precision for T of 0.2° C., provided temperature readings from the thermocouples are corrected for deviations from linearity

In the present investigations, the polymer was compacted in a press, and ground before use. Imm. silica microtubes were used to contain the sample, and the polymer - together with a few glass beads to increase the thermal response of the sample - was pressed firmly into the bottom of the tube, where the sample thermocouple was embedded firmly in it.

C. The Characterisation of Polymers

The determination of the molecular weights - and in some cases the molecular weight distributions - of both undergraded and degraded polymer samples formed a very important part of this study. Since the molecules produced in both polymerisation and degradation reactions cover a range of molecular weights, any measured value of molecular weight is of necessity an average, which depends on the experimental method employed.

The three most important average molecular weights are defined as follows :

$$\begin{array}{l} \text{Number Average} \\ \text{Molecular Weight} \end{array} \quad \bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

$$\begin{array}{l} \text{Weight Average} \\ \text{Molecular Weight} \end{array} \quad \bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$\begin{array}{l} \text{Viscosity Average} \\ \text{Molecular Weight} \end{array} \quad \bar{M}_v = \left(\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right)^{\frac{1}{a}}$$

where 'a' is the exponent in the Mark - Houwink¹⁵ Equation $[\eta] = K \bar{M}_v^a$

By the nature of these definitions $\bar{M}_w \geq \bar{M}_v \geq \bar{M}_n$, equality occurring only in a perfectly monodisperse polymer. Consequently the ratios \bar{M}_w/\bar{M}_n or \bar{M}_v/\bar{M}_n can be used as a measure of the polydispersity of a polymer.

During the present study, the change in the number of polymer molecules during degradation was the most important parameter to be measured. Consequently, Number Average Molecular Weights had to be obtained, but direct measurements of \bar{M}_n by osmometry on degraded polymer samples were found to be unsuitable because difficulty was experienced in obtaining reproducible results. This may have been the result of some diffusion of low polymer through the membrane, a problem which is encountered even with modern high-speed instruments, such as the Mechrolab Model 50I osmometer. For this reason it was decided to measure most of the average molecular weights by viscometry and to convert these to number averages using the theory and computer programme discussed in Chapter III. This programme, which gives the ratio \bar{M}_v/\bar{M}_n and α (the degree of degradation) directly for a known initial molecular weight distribution, is based on the assumptions that the polymer breaks down in an essentially random manner, and that the degradation occurs in a closed system. For polystyrene the first assumption is justified, while the degradation system used approximates closely to a closed system because there is very little weight loss in the degraded samples.

All undegraded polymers were characterised by the determination of \bar{M}_n - and, in some cases, \bar{M}_w - as well as \bar{M}_v , so that an experimental estimate of molecular weight distribution was available.

Degraded polymer samples were removed from the copper trays

by solution in Analar benzene or toluene, and the solutions were filtered before being made up in standard flasks. The concentrations of these solutions were determined by adding a known volume to a weighing bottle and evaporating off the solvent to constant weight, firstly in an air oven at 110 C. and latterly in a vacuum oven at 90 C.. Although Grassie¹⁶ has pointed out that small amounts of volatiles occluded in some polymers may cause errors as great as 10% in concentrations, Kerr¹⁷ found satisfactory results from a less rigorous removal of solvent from polystyrenes than used in these experiments.

I. Viscometry

The Limiting Viscosity Number, $[\eta]$, of a polymer solution is related to the molecular weight of the polymer by the Mark - Houwink Equation¹⁵

$$[\eta] = K \bar{M}^a$$

where 'K' is a constant depending on the polymer, solvent and temperature employed;

and 'a' is a constant depending on the shape of the molecules in solution.

All viscometric measurements were made in an Ubbelohde suspended level dilution viscometer, using either benzene at 25 C. or toluene at 30 C. as solvent. The viscometer was suspended in a thermostatted water bath controlled to ± 0.05 C. by a mercury-toluene regulator

and an Ether relay. Flow times were determined at six dilutions with a stop watch reading to 0.01 second. The viscometer design was such that kinetic energy corrections were unnecessary.

The Specific Viscosity, η_{sp} , was calculated from the flow times of the pure solvent (t_0) and the solution (t) by the relationship

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0}$$

Values of η_{sp}/C were plotted against the concentration (C) for the various dilutions, and by means of the Huggins Equation¹⁸

$$\eta_{sp}/C = [\eta] + k [\eta]^2 C$$

$[\eta]$ was obtained by extrapolation to infinite dilution.

The values 'k' and 'a' were taken from the literature and were as follows :

benzene / 25°C. ¹⁹	$k = 1.12 \times 10^{-4}$	toluene / 30°C. ²⁰	$k = 1.04 \times 10^{-4}$
	$a = 0.73$		$a = 0.733$

The values of 'k' and 'a' are determined experimentally by measuring the L.V.N., $[\eta]$, of certain narrow fractions of polymers of different molecular weights, and relating this value to \bar{M}_n or \bar{M}_w determined by Osmometry or Light Scattering respectively. Therefore, for other monodisperse samples of the same polymer, \bar{M}_n or \bar{M}_w may be determined from the appropriate Mark - Houwink Equation, but for polydisperse samples this equation gives a Viscosity Average

Molecular Weight which is intermediate between \bar{M}_n and \bar{M}_w and from which \bar{M}_n and \bar{M}_w cannot be calculated unless the molecular weight distribution of the polydisperse sample is known.

II. Osmometry

The Osmotic Pressure (π) of dilute solutions is given by Van't Hoff's Equation

$$\lim_{c \rightarrow 0} \frac{\pi}{C_2} = \frac{RT}{\bar{M}_2}$$

where \bar{M}_2 = Number Average Molecular Weight of Solute.

C_2 = Concentration of solute in grams / 100 ml.

R = Gas Constant.

T = Absolute Temperature.

π = Osmotic Pressure in cms. of toluene.

Hence \bar{M}_n can be determined by plotting $\frac{\pi}{C}$ against C for various values of C and extrapolating the line through the points to $C = 0$. For measurements in toluene at $37^\circ \text{C}.$,

$$\bar{M}_n = \lim_{c \rightarrow 0} \frac{RT}{\pi/c} = \frac{3.028 \times 10^4}{\lim_{c \rightarrow 0} \pi/c}$$

This relationship is valid at low concentrations, e.g. ≤ 10 grams / litre, but at higher concentrations considerable curvature develops in the $\frac{\pi}{C}$ vs. C plot, and extrapolation to zero concentration is very inaccurate.

The explanation for this is readily seen from consideration of the two most promising theoretical approaches to the solution

properties of polymers. The lattice theory of Huggins²¹ and Flory²² gives the following relationship

$$\frac{\bar{\pi}}{C_2} = \frac{RT}{\bar{M}_2} + \frac{RT}{V_1 \rho_2^2} \left(\frac{1}{2} - \chi \right) C_2 + \frac{RT}{3 V_1 \rho_2^3} C_2^2 \quad \text{--- (I)}$$

while the dilute solution theory developed by Flory and Krigbaum²³ predicts that

$$\frac{\bar{\pi}}{C_2} = \frac{RT}{\bar{M}_2} \left[1 + \Gamma_2 C_2 + g \Gamma_2^2 C_2^2 \right] \quad (2)$$

Both these equations show that curvature is to be expected as C_2 , and hence C_2^2 , increase.

Since concentrations of ≤ 20 grams / litre must be used with high molecular weight polymers in order to obtain sufficiently large osmotic pressures, the $\frac{\bar{\pi}}{C}$ vs. c. plot is useless here. Considering equation (2), it is found for most good solvents that $g = \frac{1}{4}$.

Therefore

$$\begin{aligned} \frac{\bar{\pi}}{C_2} &= \frac{RT}{\bar{M}_2} \left[1 + \Gamma_2 C_2 + \frac{1}{4} \Gamma_2^2 C_2^2 \right] \\ &= \frac{RT}{\bar{M}_2} \left[1 + \frac{1}{2} \Gamma_2 C_2 \right]^2 \\ \left(\frac{\bar{\pi}}{C_2} \right)^{\frac{1}{2}} &= \left(\frac{RT}{\bar{M}_2} \right)^{\frac{1}{2}} \left[1 + \frac{1}{2} \Gamma_2 C_2 \right] \end{aligned}$$

Therefore a plot of $\left(\frac{\bar{\pi}}{C} \right)^{\frac{1}{2}}$ vs. C should give a straight line, and is generally found to do so. Accordingly this plot is used for high concentrations.

Osmotic pressure measurements were carried out on a Mechrolab Model 50I High Speed Membrane Osmometer using Ultracella-filter "allerfeinst" cellulose membranes. The temperature was 37°C. and toluene was used as solvent.

III. Light Scattering

Weight Average Molecular Weights, \bar{M}_w , were obtained from light scattering measurements using a Sofica Photo Genie Diffusometer Model 42000. The instrument was calibrated by comparing the 90° scattering intensity of a cylindrical glass standard against that of pure benzene, and a value of $16.3 \times 10^{-6} \text{ cm}^{-1}$ was taken as the Rayleigh ratio for pure benzene.

The green mercury line, 5461 \AA (unpolarised), was used, and measurements were made at room temperature in benzene solutions of different polymer concentrations and at nine angles between 30° and 150° . Zimm plots of $Kc / R_{(\theta)}$ against $(\sin^2 \frac{\theta}{2} + Ac)$ were constructed when the dissymmetry was high, but when the scattering intensities did not show dissymmetry $Kc / R_{(90^\circ)}$ was plotted as a function of c .

Solutions were prepared individually and clarified by nitrogen pressure through millipore filters (0.45μ). Solutions were filtered directly into the optical cells.

IV. Gel Permeation Chromatography

Until recently the measurement of polymer molecular weight distributions was a long and tedious process involving fractionation and characterisation, or turbidimetry. However, within the last three years, the development of the Gel Permeation Chromatography (GPC.) technique by Moore and others^{24,25} has enabled differential molecular weight distribution curves to be obtained within a few hours,

and a commercial instrument utilising this principle is now in production by Waters Associates, Inc..

In brief, the instrument operates by elution of a polymer solution by solvent flowing at a constant rate through a series of columns, each packed with a polystyrene gel of different limiting molecular weight permeability. Fractionation according to molecular size is obtained in the columns, because molecules larger than the maximum pore size pass through in the interstitial volume, whereas smaller molecules permeate the gel and are separated according to size. The smallest molecules enter furthest into the gel and require the largest volume for elution. A highly sensitive differential refractometer detects the eluted sample by comparing the refractive index of the sample stream with that of the pure solvent stream.

In this study a Waters Associates Gel Permeation Chromatograph unit Model 200 instrument was used. Toluene was used throughout as solvent, at a temperature of 80°C. and a flow rate of 1 ml./min.. The instrument was calibrated by plotting elution volume against molecular weight for a series of monodisperse polystyrenes of known molecular weight. The calculation of \bar{M}_n and \bar{M}_w from a GPC. curve is outlined in Waters Associates publications, but in practice was subject to error because of base-line drift, so that only a qualitative estimate of polydispersity was obtained.

D. Molecular Weights of Polymers available for Degradative Studies.(i) Thermally Prepared Styrene Homopolymers and Styrene - Stilbene

Copolymers.

Polymer	Temp. of Polym ⁿ .	Conv. %	\bar{M}_n $\times 10^{-6}$	\bar{M}_v $\times 10^{-6}$	\bar{M}_w $\times 10^{-6}$	$\frac{\bar{M}_v}{\bar{M}_n}$	Copolymers.	
							Moles styrene.	Moles stilbene.
TPS/1	45 °C	12.5	1.712	2.382	-	1.391	-	-
TPS/2	60 °C	12.5	1.490	2.183	-	1.465	-	-
TPS/3	60 °C	12.5	1.044	1.496	-	1.433	-	-
TPS/4	90 °C	12.5	0.515	0.735	-	1.431	-	-
TPS/5	120 °C	12.5	0.233	0.408	0.430	1.747	-	-
TPS/6	120 °C	60.0	0.263	0.415	0.440	1.578	-	-
TPSS/1	60 °C	12.5	0.918	1.406	-	1.532	-	157
TPSS/2	60 °C	12.5	0.736	1.045	-	1.420	-	71
TPSS/3	60 °C	12.5	1.000	1.419	-	1.419	-	116
TPSS/4	60 °C	12.5	1.010	1.432	-	1.418	-	96
TPSS/5	60 °C	12.5	0.977	1.384	-	1.416	-	72

(ii) Anionically Prepared Polystyrenes.

Polymer	Temp. of Polym ⁿ .	Conv. %	\bar{M}_n $\times 10^{-6}$	\bar{M}_v $\times 10^{-6}$	\bar{M}_w $\times 10^{-6}$	$\frac{\bar{M}_v}{\bar{M}_n}$	Initiator and Solvent.
APS/1L	- 20 °C	100	0.229	0.233	0.255	1.018	Cumyl -
APS/2L	- 20 °C	100	0.420	0.468	-	1.114	Potassium;
APS/3L	- 20 °C	100	0.530	0.593	0.584	1.119	THF.

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CHAPTER IIITHE DERIVATION of NUMBER AVERAGE MOLECULAR WEIGHTS from the
LIMITING VISCOSITY NUMBER

As mentioned in Chapter II, number average molecular weights are most meaningful in this study where we are concerned with the changes in numbers of molecules on degradation. However, because of difficulties in obtaining accurate and reproducible results from osmometry, it was decided to adopt viscometry as the main method of molecular weight measurement. Since the molecular weight distribution may change during degradation, viscosity average molecular weights, by nature of their definition, do not always give a completely accurate picture of the changes in numbers of polymer molecules. Nevertheless, methods can be devised for converting viscosity average into number average molecular weights and, by using a computer to perform the calculations, the conversion can be made very rapidly. The derivation of the method used to effect this conversion is outlined in this chapter.

The ensuing theoretical treatment stems from the work of Montroll and Simha^I and Montroll² concerning the molecular weight distributions resulting from the degradation of long chain molecules of known initial distribution. Initially this theory was derived to account for the hydrolytic degradation of cellulose, but it is equally applicable to other cases of random degradations in closed systems, provided these occur without depropagation. This treatment,

therefore, can be applied to the particular case of polystyrene degraded at sub-volatilisation temperatures, since it is well established that chain scission, whether by "weak links"^{3,4} or by intermolecular transfer⁵, occurs at random. The equations express the distribution of molecular sizes in a depolymerised system as a function of the initial chain length and the average number of bonds split per molecule.

Three basic assumptions are made:-

- (1) the initial molecular weight can be expressed in terms of a distribution function,
- (2) the accessibility to reaction of a bond in a given chain is independent of its position in the chain and independent of the length of the parent chain,
- (3) all chains in the polymer are equally accessible to reaction.

Fundamental units in a long chain molecule will be called monomeric elements, and t monomeric elements linked by $(t-1)$ bonds will be defined as a t -mer.

$$\begin{aligned}
 \text{Let } \alpha &= \text{degree of depolymerisation (degradation)} \\
 &= \frac{\text{total number of inter-element bonds cut}}{\text{total number of inter-element bonds in the system}} \\
 &= \text{average fraction of inter-element bonds cut per} \\
 &\hspace{15em} \text{molecule} \\
 &= \frac{r_0}{p} \quad \text{in a homogeneous polymer}
 \end{aligned}$$

where r_0 = number of bonds cut, and

p = number of inter-element bonds.

The average fraction of monomeric elements existing as components of t -mers in a system originally composed of $N(p+1)$ -mers after degree of depolymerisation, α , is

$$F_t(p, \alpha) = \frac{\alpha^t (1-\alpha)^{t-1}}{(p+1)} [2 + (p-t)\alpha], \quad t \leq p$$

$$F_{p+1}(p, \alpha) = (1-\alpha)^p \quad (1)$$

Since the total number of t -mers, $N_t(p, \alpha)$, is given by

$$N_t(p, \alpha) = N F_t(p, \alpha) (1+p) / t$$

it follows from Equation (1) that

$$N_t(p, \alpha) = N \alpha (1-\alpha)^{t-1} [2 + (p-t)\alpha], \quad t \leq p$$

$$N_{p+1}(p, \alpha) = N (1-\alpha)^p \quad (2)$$

Now consider the depolymerisation of a system which initially consisted of N polymers distributed into Nn_1 monomers, Nn_2 dimers, ---, Nn_p p -mers, ---, in such a way that the basic assumptions remain valid. In this system the total number of t -mers $N_t(\alpha)$, when the degree of degradation is α , is the totality of t -mers generated from each of the original molecular species composed of t or more monomers. Thus

$$N_t(\alpha) = \sum_{p+1=t}^{\infty} N_t(p, \alpha)$$

$$= Nn_t (1-\alpha)^{t-1} + N \sum_{p+1=t+1}^{\infty} n_{p+1} \alpha (1-\alpha)^{t-1} [2 + (p-t)\alpha] \quad (3)$$

where n_t and n_{p+I} are number fraction distributions for the original polymer. The two terms arise thus:-

1st term = number of t-mers left uncut after degree of depolymerisation α ,
 2nd term = number of t-mers produced by scission of all chains $\geq (t+I)$.

To apply Equation (3) to practical systems, suitable distribution functions must be substituted for n_t and n_{p+I} . The polystyrenes used in this study were prepared by "living" anionic synthesis and by thermal polymerisation in bulk without initiator. In the first case a monodisperse polymer is obtained, i.e. $\bar{M}_v / \bar{M}_n = 1$. In the second example a "coupling" distribution almost certainly results, since, despite early theories that thermal initiation was diradical in nature⁶, it is now fairly certain that initiation occurs by monoradicals⁷, although the mechanism remains obscure. Furthermore, it has been unquestionably shown by Bamford and Jenkins⁸ and Bevington and collaborators⁹, that termination is almost exclusively by combination. This being the case, the assumption of a "coupling" distribution for thermally polymerised polystyrene is correct. As a check on this assumption, however, the ratio of \bar{M}_v / \bar{M}_n for all the thermally polymerised polymers used in this work were measured. In all the polymers, except those prepared at high temperatures, this ratio was found to be approximately 1.44, the theoretical value for a polymer possessing a "coupling" distribution. (See later).

(I) The Coupling Distribution

For this distribution the number fraction of t-mers, n_t ,

is given by¹⁴

$$n_t = \frac{4t}{\bar{r}^2} \exp\left(\frac{-2t}{\bar{r}}\right) \quad \text{where } \bar{r} \text{ is the number average degree of polymerisation.}$$

From Equation (3), the total number of t-mers formed after degree of depolymerisation α in a polymer with an initial coupling distribution is

$$N_t(\alpha) = N \frac{4t}{\bar{r}^2} (1-\alpha)^{t-1} \exp\left(\frac{-2t}{\bar{r}}\right) + N \sum_{p=t}^{\infty} \frac{4(p+1)}{\bar{r}^2} \alpha (1-\alpha)^{t-1} [2+(p-t)\alpha] \exp\left(\frac{-2(p+1)}{\bar{r}}\right) \quad (4)$$

Replacing the summations by integrals, because p and t are large and the summation is virtually continuous, gives

$$N_t(\alpha) = N \frac{4t}{\bar{r}^2} (1-\alpha)^{t-1} \exp\left(\frac{-2t}{\bar{r}}\right) + \frac{4\alpha}{\bar{r}^2} (1-\alpha)^{t-1} N \int_{p=t}^{\infty} [2+(p-t)\alpha] (p+1) \exp\left(\frac{-2(p+1)}{\bar{r}}\right) dp \quad (5)$$

Integration by parts of Equation (5) (Appendix I) results in

$$N_t(\alpha) = \frac{4N}{\bar{r}^2} (1-\alpha)^{t-1} \exp\left(\frac{-2t}{\bar{r}}\right) \left\{ t + \alpha \bar{r} \exp\left(\frac{-2}{\bar{r}}\right) \left[t \left(1 + \frac{\alpha \bar{r}}{4}\right) + \frac{\alpha \bar{r}^2}{4} + \frac{(\alpha+2)\bar{r}}{4} + 1 \right] \right\} \quad (6)$$

Equation (6) may be written in the form

$$N_t(\alpha) = K_I (K_2 t + K_3) (1-\alpha)^{t-1} \exp\left(\frac{-2t}{\bar{r}}\right)$$

where $K_1 = \frac{4N}{\bar{r}^2}$

$$K_2 = 1 + \alpha \bar{r} \left(1 + \frac{\alpha \bar{r}}{4} \right) \exp\left(\frac{-2}{\bar{r}}\right)$$

$$\text{and } K_3 = \alpha \bar{r} \left[1 + \frac{(\alpha+2)\bar{r}}{4} + \frac{\alpha \bar{r}^2}{4} \right] \exp\left(\frac{-2}{\bar{r}}\right)$$

We now have an expression for the molecular weight distribution after degree of depolymerisation α in a polymer with an initial coupling distribution.

As degradation proceeds, the parameter measurable with time is the Limiting Viscosity Number, $[\eta]$. For any polydisperse polymer it can be shown that

$$[\eta] = \frac{\sum_t t N_t f(M_0 t)}{\sum_t t N_t} \quad (7)$$

where N_t is the number of each species t present

and M_0 is the monomer molecular weight.

Suppose $f(M_0 t)$ is of the Mark - Houwink type,

$$\text{i.e. } f(M_0 t) = K (M_0 t)^a \quad (8)$$

where K and a are constants for a given polymer-solvent system

at a fixed temperature, then the Limiting Viscosity Number, $[\eta]$

is given by

$$[\eta] = \frac{\sum_t t N_t K (M_0 t)^a}{\sum_t t N_t} \quad (9)$$

$$= \frac{K M_0^a \sum_t t^{I+a} N_t}{\sum_t t N_t} \quad (10)$$

For high molecular weight polymers t is very large. The summation is therefore virtually continuous and is commonly replaced by an integral. Substituting $N_t(\alpha)$ for N_t and integrals for summations in Equation (10) gives

$$[\eta] = \frac{K M_0^a \int_0^\infty t^{I+a} N_t(\alpha) dt}{\int_0^\infty t N_t(\alpha) dt} \quad (11)$$

Substituting into Equation (11) the value for $N_t(\alpha)$ from Equation (6), and integrating by parts (Appendix 2) gives

$$[\eta] = \frac{K M_0^a \Gamma(a+2) \left\{ K_2 (a+2) + K_3 [2/\bar{r} - \ln(I-\alpha)] \right\}}{[2/\bar{r} - \ln(I-\alpha)]^a \left\{ 2K_2 + K_3 [2/\bar{r} - \ln(I-\alpha)] \right\}} \quad (12)$$

where K_2 and K_3 have the same significance as before, and Γ is the "gamma function" which simplifies the analytical integration of complicated functions^{II}. Thus, the insertion of known values of \bar{r} , M_0 , K and a into Equation (12) permits the calculation of the Limiting Viscosity Number for any degree of depolymerisation α ; conversely α can be calculated from any value of $[\eta]$.

The validity of Equation (12) can be readily checked.

Set $\alpha = 0$, then $K_2 = I$

and $K_3 = 0$

Equation (I2) simplifies to the form

$$\begin{aligned} [\eta] &= \frac{K M_o^a \Gamma(a+2) \Gamma(a+2)}{2 (2/\bar{r})^a} \\ &= \frac{K (M_o \bar{r})^a \Gamma(a+3)}{2^{a+1}} \end{aligned} \quad (I3)$$

which is the correct relationship between $[\eta]$ and \bar{r} for a polymer with a "coupling" distribution. The numerical value of the ratio \bar{r}_v / \bar{r} , where \bar{r}_v is the viscosity average degree of polymerisation, can be easily evaluated. From Equation (I3)

$$\begin{aligned} [\eta] &= \frac{K (M_o \bar{r})^a \Gamma(a+3)}{2^{1+a}} \\ &= K (M_o \bar{r}_v)^a \quad \text{from the Mark - Houwink Equation} \end{aligned}$$

Therefore,

$$\frac{\bar{r}_v}{\bar{r}} = \left(\frac{\Gamma(a+3)}{2^{1+a}} \right)^{\frac{1}{a}}$$

In the Mark - Houwink Equation used for polystyrene^{I2}, $a = 0.73$, which gives

$$\frac{\bar{r}_v}{\bar{r}} = 1.436 \quad \text{for the "coupling" distribution.}$$

Equation (I2) in its present form relates the degree of depolymerisation, α , with the corresponding Limiting Viscosity Number. Number average molecular weights are easily obtained from this equation, however, as is the ratio \bar{M}_v / \bar{M}_n . This follows from the relationship for simple random degradation.

Consider a simple random degradation in a closed system.

$$\frac{I}{\bar{r}_t} - \frac{I}{\bar{r}_0} = \alpha, \quad \alpha \ll I \quad (\text{I4})$$

where \bar{r}_0 is the initial number average degree of polymerisation and \bar{r}_t is the number average DP. after degree of degradation α , i.e. after time of degradation t .

From Equation (I4) it follows that

$$\frac{I}{\bar{M}_n_t} - \frac{I}{\bar{M}_n_0} = \frac{\alpha}{M_0} \quad (\text{I5})$$

where \bar{M}_n_0 and \bar{M}_n_t are the number average molecular weights corresponding to \bar{r}_0 and \bar{r}_t respectively, and M_0 is the monomer molecular weight (as before).

Rearranging Equation (I5) gives

$$\begin{aligned} \frac{I}{\bar{M}_n_t} &= \frac{\alpha}{M_0} + \frac{I}{\bar{M}_n_0} \\ &= \frac{\alpha}{M_0} + \frac{I}{M_0 \bar{r}_0} \\ &= \frac{\alpha \bar{r}_0 + I}{M_0 \bar{r}_0} \end{aligned} \quad (\text{I6})$$

From the Mark - Houwink Equation,

$$[\eta] = K \bar{M}_v^a$$

$$\therefore \bar{M}_v = \left(\frac{[\eta]}{K} \right)^{\frac{1}{a}} \quad (I7)$$

After time of degradation t , Equation (I7) gives

$$\bar{M}_{v_t} = \left(\frac{[\eta]}{K} \right)^{\frac{1}{a}} \quad (I8)$$

Combining Equations (I6) and (I8) leads to Equation (I9),

$$\frac{\bar{M}_{v_t}}{\bar{M}_{n_t}} = \left(\frac{[\eta]}{K} \right)^{\frac{1}{a}} \times \frac{1 + \alpha \bar{r}_0}{M_0 \bar{r}_0} \quad (I9)$$

Thus, for any value of the Limiting Viscosity Number, the degree of depolymerisation can be calculated from Equation (I2), the number average molecular weight from Equation (I6), and the ratio \bar{M}_v / \bar{M}_n from Equation (I9).

Computer programmes were run for polystyrenes with a series of arbitrary initial degrees of polymerisation. The input to the computer consisted of the following parameters.

$$\left. \begin{aligned} K &= 1.12 \times 10^{-4} \\ a &= 0.73 \end{aligned} \right\} \quad \text{From the Mark - Houwink Equation } I2$$

$$M_0 = 10^4$$

$$\bar{r}_0 = 500; 1,000; 5,000; 100,000.$$

The computer output comprised the degree of depolymerisation, α , the corresponding Limiting Viscosity Number and the ratio \bar{M}_v / \bar{M}_n . Figures (I) and (2) show plots of Limiting Viscosity Number and the ratio \bar{M}_v / \bar{M}_n , respectively, as functions of α for the various initial

FIGURE 1 COUPLING DISTRIBUTION

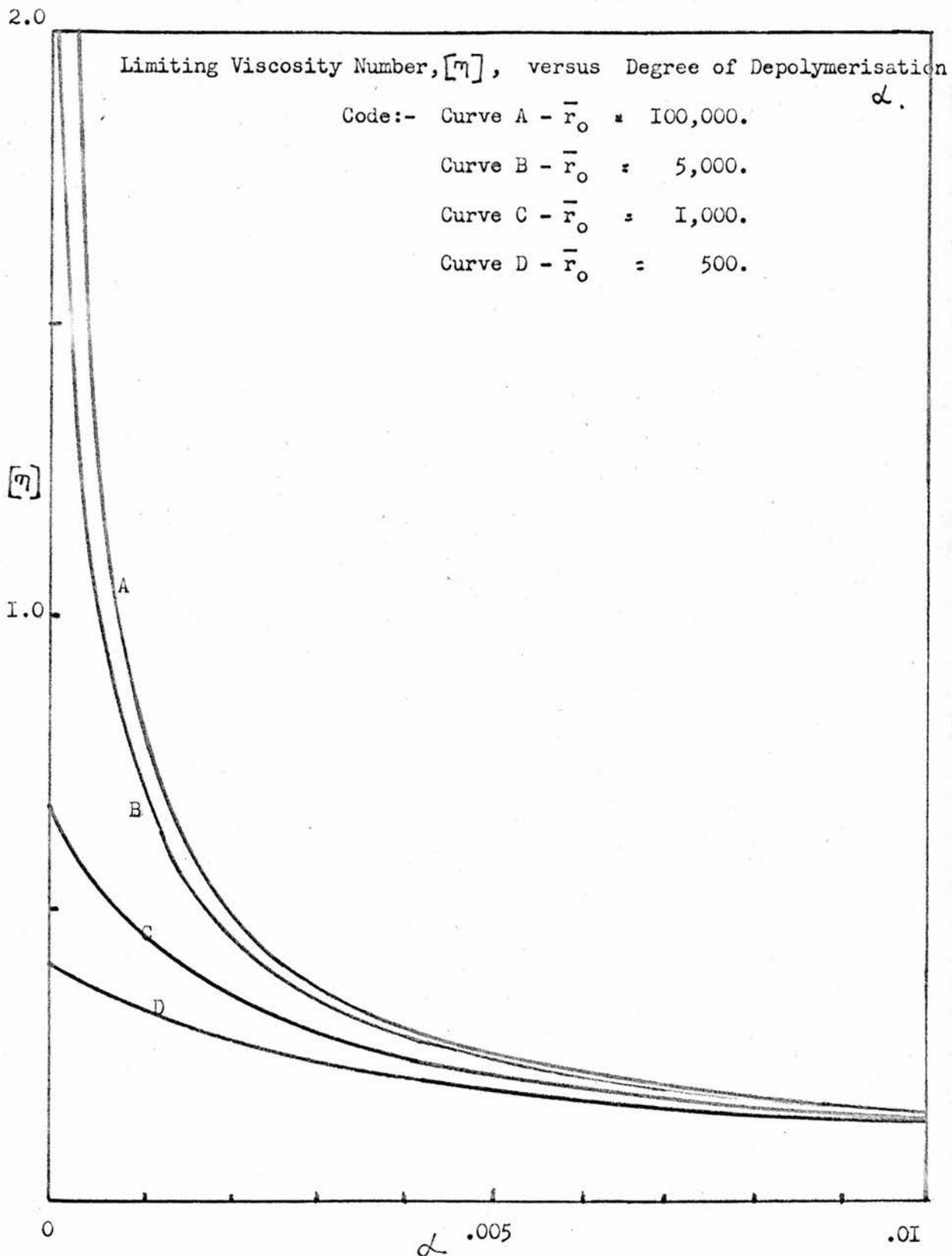
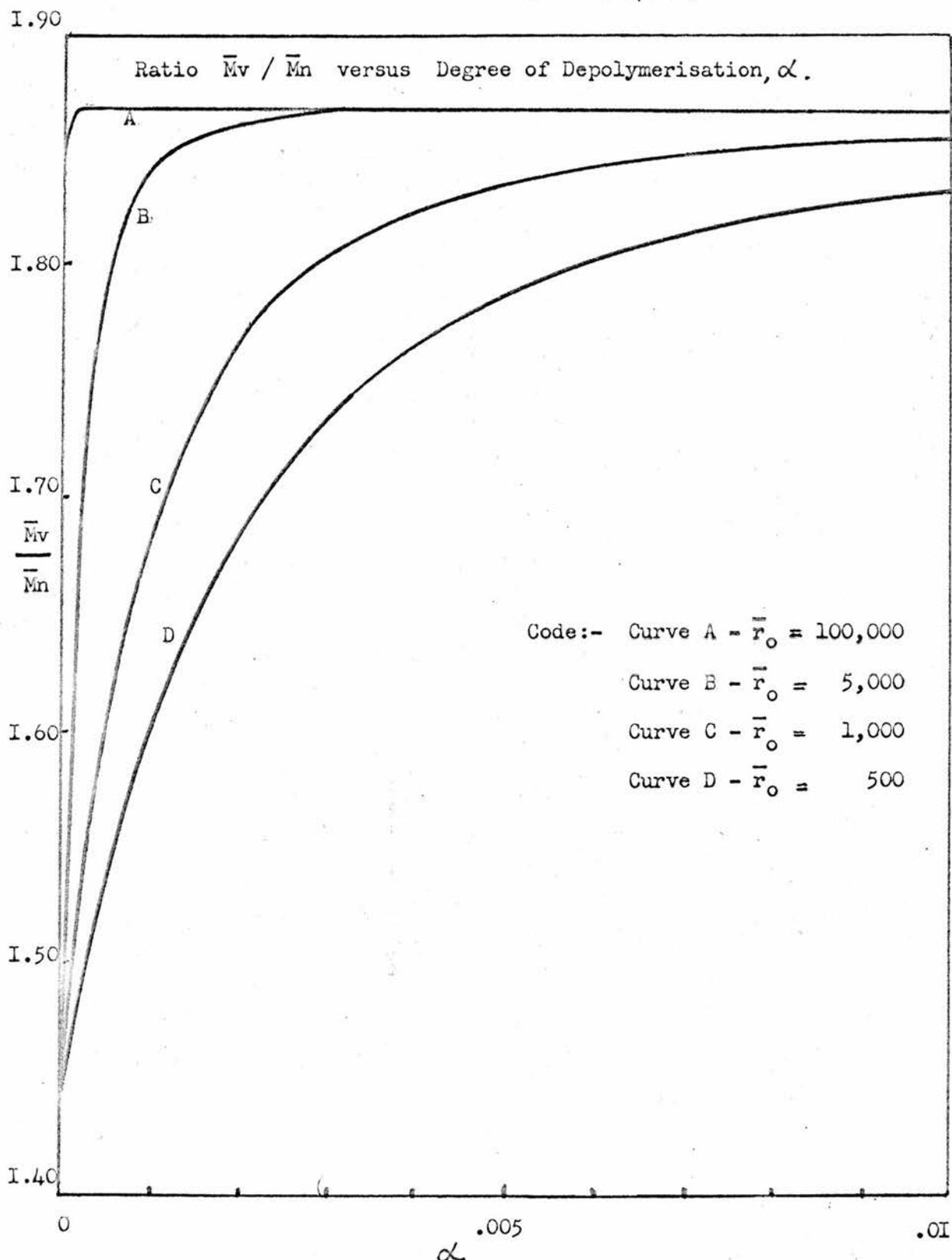


FIGURE 2 COUPLING DISTRIBUTION



degrees of polymerisation. Four important features are immediately apparent from these graphs. These are

- (1) the Limiting Viscosity Numbers all tend to the same value at high values of α ,
- (2) all polymers, regardless of initial molecular weight, tend to a limiting value of the ratio \bar{M}_v / \bar{M}_n with degradation,
- (3) the higher the initial molecular weight, the faster is the attainment of the limiting value of \bar{M}_v / \bar{M}_n ,
- (4) the limiting value of \bar{M}_v / \bar{M}_n is 1.88, which is the value required of polystyrenes with the most probable distribution. It has been shown^{I3} that polymers attain this distribution on degradation.

The fact that the present theoretical considerations lead to the same conclusion is further evidence that the treatment derived in this chapter is fundamentally correct. At high degrees of depolymerisation, the ratio \bar{M}_v / \bar{M}_n tends to decrease, but this occurs because the condition ($\alpha \ll 1$) inherent in Equation (I4) is no longer met.

The effect of using the fundamentally less correct integrals instead of summations in the theoretical derivations was checked by comparing the computer data from identical programmes using either summations or integrals. No detectable difference in the data was found. Since one complete computer run using integrals takes I2 minutes, compared to 30 minutes for one value of α using summations, integrals were used throughout this work.

Programmes were also run for the polystyrenes used in the experimental studies described in the ensuing chapter.

(2) The Monodisperse System

After a degree of depolymerisation α in a system originally comprising N $(p+1)$ -mers,

$$N_{p+1}(p, \alpha) = N (1-\alpha)^p \quad (2)$$

$$N_t(p, \alpha) = N (1-\alpha)^{t-1} [2 + (p-t)\alpha] \quad t \leq p$$

Therefore, after a degree of degradation α , the total number of $(p+1)$ -mers uncut is given by

$$N_{p+1}(p, \alpha) = N (1-\alpha)^p$$

and the totality of t -mers generated by scission of $(p+1)$ -mers is

$$N_t(\alpha) = N \sum_0^{p+1} n_{p+1} \alpha (1-\alpha)^{t-1} [2 + (p-t)\alpha] \quad (20)$$

The number fraction of $(p+1)$ -mers initially is unity. Substituting this value for n_{p+1} into Equation (20), and replacing the summation by an integration gives

$$N_t(\alpha) = N \int_0^{p+1} \alpha (1-\alpha)^{t-1} [2 + (p-t)\alpha] dt \quad (21)$$

In the case of a monodisperse system, the replacement of summations by integrals is fundamentally less correct, than in the example of a "coupling" distribution, because it assumes a continuous sum. This condition only applies at relatively large values of α where there is a spectrum of molecular sizes between zero and $(p+1)$. For practical purposes the values of α used seem to be large enough to justify the use of integrals. (See later).

The total number of molecules in the system after degree of depolymerisation α in a monodisperse system of N $(p+1)$ -mers is

$$N_{\text{total}}(\alpha) = N (1-\alpha)^p + N \int_0^{p+1} \alpha (1-\alpha)^{t-1} [2 + (p-t)\alpha] dt \quad (22)$$

As mentioned previously, the Limiting Viscosity Number, $[\eta]$ of a polydisperse system is given by

$$[\eta] = \frac{K M_0^a \int_0^{\infty} t^{1+a} N_t(\alpha) dt}{\int_0^{\infty} t N_t(\alpha) dt} \quad (II)$$

In this case the upper limit of molecular size is $(p+1)$, not ∞ , so that Equation (II) is modified to read

$$[\eta] = \frac{K M_0^a \int_0^{p+1} t^{1+a} N_t(\alpha) dt}{\int_0^{p+1} t N_t(\alpha) dt} \quad (23)$$

In Equation (23) $\int_0^{p+1} t^{1+a} N_t(\alpha) dt$ expresses the sum of the products $(t^{1+a} N_t)$ for all t -mers from 0 to $(p+1)$ in the degraded system. It can be split into contributions from the undegraded polymer and the products of degradation of the original polymer, that is to say

$$\int_0^{p+1} t^{1+a} N_t(\alpha) dt = (p+1)^{1+a} N (1-\alpha)^p + N \int_0^{p+1} t^{1+a} \alpha (1-\alpha)^{t-1} [2 + (p-t)\alpha] dt \quad (24)$$

Also, since degradation occurs in a closed system,

$$\int_0^{p+1} t N_t (\alpha) dt = N (p+1) \quad (25)$$

Substituting the above expressions (24) and (25) into Equation (23)

leads to

$$\begin{aligned} [\eta] &= \frac{K M_0^a \int_0^{p+1} t^{I+a} N_t (\alpha) dt}{\int_0^{p+1} t N_t (\alpha) dt} \\ &= \frac{K M_0^a \left\{ (p+1)^{I+a} N (1-\alpha)^p + N \int_0^{p+1} t^{I+a} \alpha (1-\alpha)^{t-1} [2 + (p-t)\alpha] dt \right\}}{N (p+1)} \\ &= \frac{K M_0^a}{(p+1)} \left\{ (p+1)^{I+a} (1-\alpha)^p + \int_0^{p+1} t^{I+a} \alpha (1-\alpha)^{t-1} [2 + (p-t)\alpha] dt \right\} \quad (26) \end{aligned}$$

Evaluating the integral (Appendix 3) in Equation (26) gives

$$[\eta] = \frac{K M_0^a}{(p+1)} \left\{ (p+1)^{I+a} (1-\alpha)^p + \frac{\alpha}{(1-\alpha) [\log \frac{1}{1-\alpha}]^{a+1}} \left[(2+p\alpha) \log \frac{1}{1-\alpha} \gamma [a+2, \theta] - \alpha \gamma [a+3, \theta] \right] \right\} \quad (27)$$

$$\text{where } \theta = (p+1) \log \frac{1}{1-\alpha}$$

and the integrals $\gamma [\beta, \theta]$ are incomplete "Gamma Functions" which allow the analytical integration of complicated functions to finite limits.

As a check of Equation (27), set α equal to zero. In this special case

FIGURE 3 MONODISPERSE SYSTEM

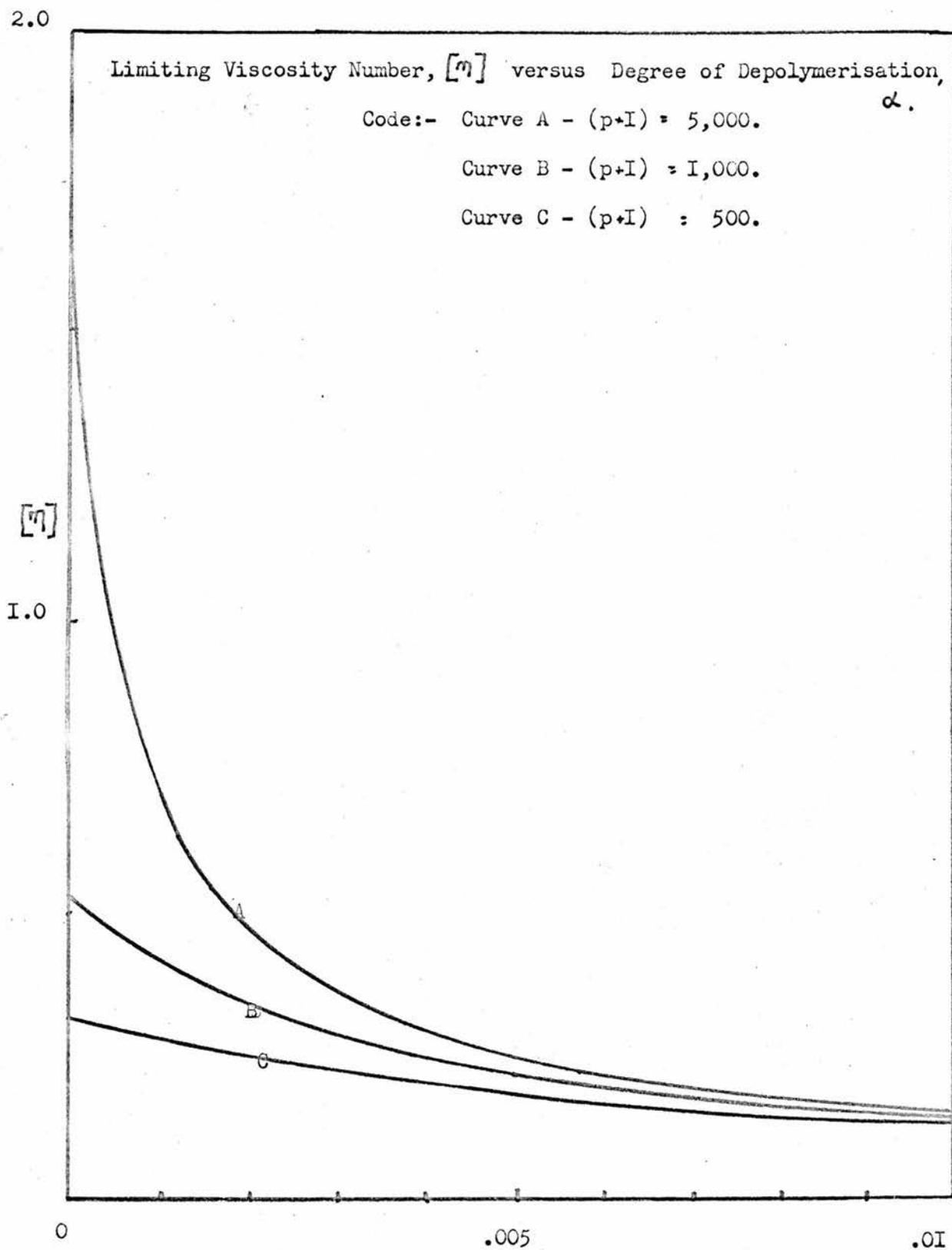
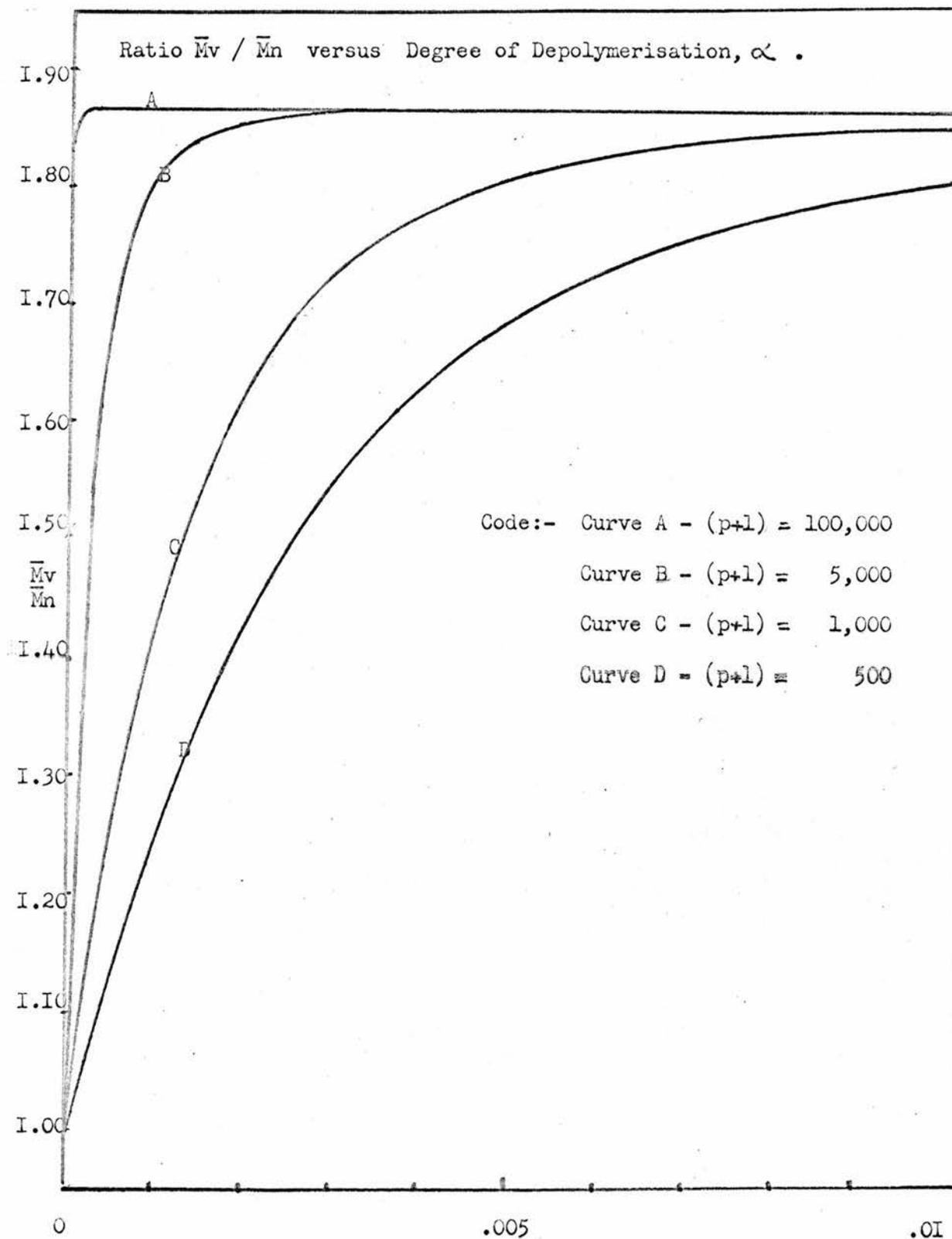


FIGURE 4 MONODISPERSE SYSTEM



$$[\eta] = \frac{K M_0^a (p+1)^{a+1}}{(p+1)}$$

$$= K M_0^a (p+1)^a$$

which is the correct relationship for a monodisperse polymer of $(p+1)$ monomeric elements.

As in the case of the "coupling" distribution, we are primarily interested in determining number average molecular weights from these theoretical expressions. Thus, again we use the relationship,

$$\frac{\bar{M}v_t}{\bar{M}n_t} = \left(\frac{[\eta]}{K} \right)^{\frac{1}{a}} \cdot \frac{1 + \alpha \bar{r}_0}{M_0 \bar{r}_0} \quad (19)$$

and can determine the value of $[\eta]$ and the ratio $\bar{M}v_t / \bar{M}n_t$ for a given degree of depolymerisation α in a homodisperse polymer of known initial number average degree of polymerisation.

Computer programmes were run for a spread of arbitrary values of the number average \overline{DP} ., feeding in the same parameters and printing out results for $[\eta]$, α and $\bar{M}v_t / \bar{M}n_t$ in exactly the same way as was done previously with the "coupling" distribution.

Figures (3) and (4) show plots of Limiting Viscosity Number and the ratio $\bar{M}v / \bar{M}n$, respectively, as functions of α for the various initial degrees of polymerisation. These graphs show exactly the same behaviour as was found for polymers with the "coupling" distribution. Again, the regular nature of these curves justifies the simplifying substitution of integrals for summations in Equation (21).

Programmes were also run for the polystyrenes used in the experimental studies described in the next chapter.

(3) The Most Probable Distribution

The most common molecular weight distribution found in free-radically prepared polymers is the exponential or "most probable" distribution, which results from polymerisation initiated by monoradicals and terminated by disproportionation. This case has not been treated here because it was not encountered in the experimental study.

However, \bar{M}_n can be readily evaluated from \bar{M}_v because the "most probable" distribution has been shown to be invariant with degradation ^{I3}.

Theoretical considerations ^{I4} of the possible molecular weight distributions resulting from free-radical polymerisation show that for an exponential distribution

$$\frac{\bar{r}_v}{\bar{r}} = \left\{ \int (2+a) \right\}^{\frac{1}{a}}$$

where \bar{r}_v , \bar{r} and a have their usual significance. For polystyrene where $a = 0.73$,

$$\frac{\bar{r}_v}{\bar{r}} = 1.88.$$

Thus, for a polystyrene with an initial "most probable" molecular weight distribution, \bar{M}_n can be calculated directly from \bar{M}_v at any degree of degradation by use of the above relationship.

(4) Computer Programmes

The programmes for both monodisperse and "coupling"

distribution polymers were written in "Fortran" and run on an IBM I620 computer. The programmes are given in Appendix 4.

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CHAPTER IV

THE CHAIN SCISSION REACTIONS IN THERMALLY AND ANIONICALLYSYNTHESISED POLYSTYRENES.

I

Jellinek was the first investigator to postulate the existence of "weak bonds" in polystyrene, formulating this hypothesis on the basis of molecular weight measurements of degraded polymers. Such thermolabile structures, he suggested, are less stable than the normal carbon - carbon backbone bonds, and are probably composed of 1, 2 - diols. Degradation is initiated at these "weak links", subsequent volatilisation being initiated at the chain ends resulting from "weak link" scission.

Grassie and Kerr² studied the molecular weight changes in a number of polystyrenes prepared free-radically with different initiators under conditions of rigorous exclusion of oxygen. They, too, postulated the existence of thermolabile structures in polystyrenes, but could only find a correlation between the concentration of "weak links" and the temperature of polymerisation. Oxygenated structures were excluded from the list of possibilities. Subsequently Cameron and Grassie³ postulated that the "weak links" were C - C single bonds β to double bonds incorporated in the polymer by an abnormal propagation step during polymerisation. Strangely, polystyrenes prepared by cationic⁴ and anionic⁵ initiators showed concentrations of "weak links" of the same order found in free-radical polymers.

Concurrently, Wall and collaborators⁶⁻¹⁰ were persistently

maintaining that "weak links" were an unnecessary complication to explain an effect which could readily be interpreted by intermolecular transfer. Gordon^{II} also considered the postulate of "weak bonds" superfluous to a viable explanation of the degradation characteristics of polystyrene.

Most of the controversy over these two conflicting theories stems from the difficulty in relating various aspects of the observed degradation characteristics to individual reactions within the overall reaction mechanism. The depropagation reaction, especially, tends to obscure the molecular weight changes due to scission of the macromolecules. Consequently, in this investigation, the molecular weight changes in polystyrenes, degraded at temperatures where depropagation is negligible, were studied, with the aim of isolating the changes due solely to the initial scission reactions. Since it is fairly well established that the initial scission reaction in polystyrene occurs at random in the macromolecule, a very simple theoretical treatment^{I2} applicable to simple random degradations was employed to interpret the molecular weight data.

(I) Theoretical Treatment of Simple Random Degradations in Closed Systems

For a simple random scission reaction without loss of polymer

$$\overline{DP}_n = \frac{\overline{DP}_0}{n+1} \quad (I)$$

where \overline{DP}_n = number average degree of polymerisation
after n breaks per molecule,

and \overline{DP}_0 = initial number average degree of polymerisation.

The fraction of initial bonds ruptured, α , is given by

$$\alpha = \frac{n}{\overline{DP}_0 - I} \quad (2)$$

$$= I - \exp. (-k_I t) \quad (3)$$

where k_I = a first order velocity constant for the scission
of identical bonds,

and t = time.

Combining Equations (1), (2) and (3) gives

$$\frac{\overline{DP}_n - I}{\overline{DP}_n} = \frac{\overline{DP}_0 - I}{\overline{DP}_0} \exp. (-k_I t) \quad (4)$$

$$\therefore -\ln \left(\frac{\overline{DP}_n - I}{\overline{DP}_n} \right) = -\ln \left(\frac{\overline{DP}_0 - I}{\overline{DP}_0} \right) + k_I t \quad (5)$$

where I/\overline{DP} is very small, i.e. the molecular weight is
very high, Equation (5) simplifies to

$$\frac{I}{\overline{DP}_n} - \frac{I}{\overline{DP}_0} = k_I t \quad (6)$$

$$= \alpha$$

$$\therefore \alpha = k_I t \quad \text{where } \alpha \ll I \quad (7)$$

Multiplying both sides of Equation (6) by I/m , where m = molecular
weight of styrene, gives

$$\frac{I}{\bar{Mn}_t} - \frac{I}{\bar{Mn}_0} = \frac{k_I t}{m} \quad (8)$$

where \bar{Mn}_t = number average molecular weight after n breaks per molecule,

and \bar{Mn}_0 = initial number average molecular weight.

Where average degrees of polymerisation other than number average are measured, Equation (6) becomes

$$\frac{I}{\overline{DP}_x} - \frac{I}{\overline{DP}_0} = \frac{k_I t}{a} \quad (9)$$

where a = the ratio of the x - average \overline{DP} to the number average \overline{DP} for the particular molecular weight distribution of the polymer.

Since degraded polymers rapidly attain the most probable distribution ^{II}, $a = 1.88$ for polystyrene - except in the very early stages of the degradation - where viscosity average molecular weights are measured in benzene at 25°C. (See Chapter III). Thus, the velocity constant k_I will depend on the molecular weight distribution in the degraded polymer at the time when I/\overline{DP}_x is determined, and a linear dependence of I/\overline{DP}_x on time will not be obtained while the molecular weight distribution is changing. However, the theoretical treatment described in Chapter III provides number average molecular weights from intrinsic viscosity data, and in so doing takes into account the changing molecular weight distribution. Thus, plots of α and I/\overline{DP}_n calculated by this theoretical treatment from viscosity measurements will exhibit a linear

dependence on time, provided the concentration of frangible bonds remain constant.

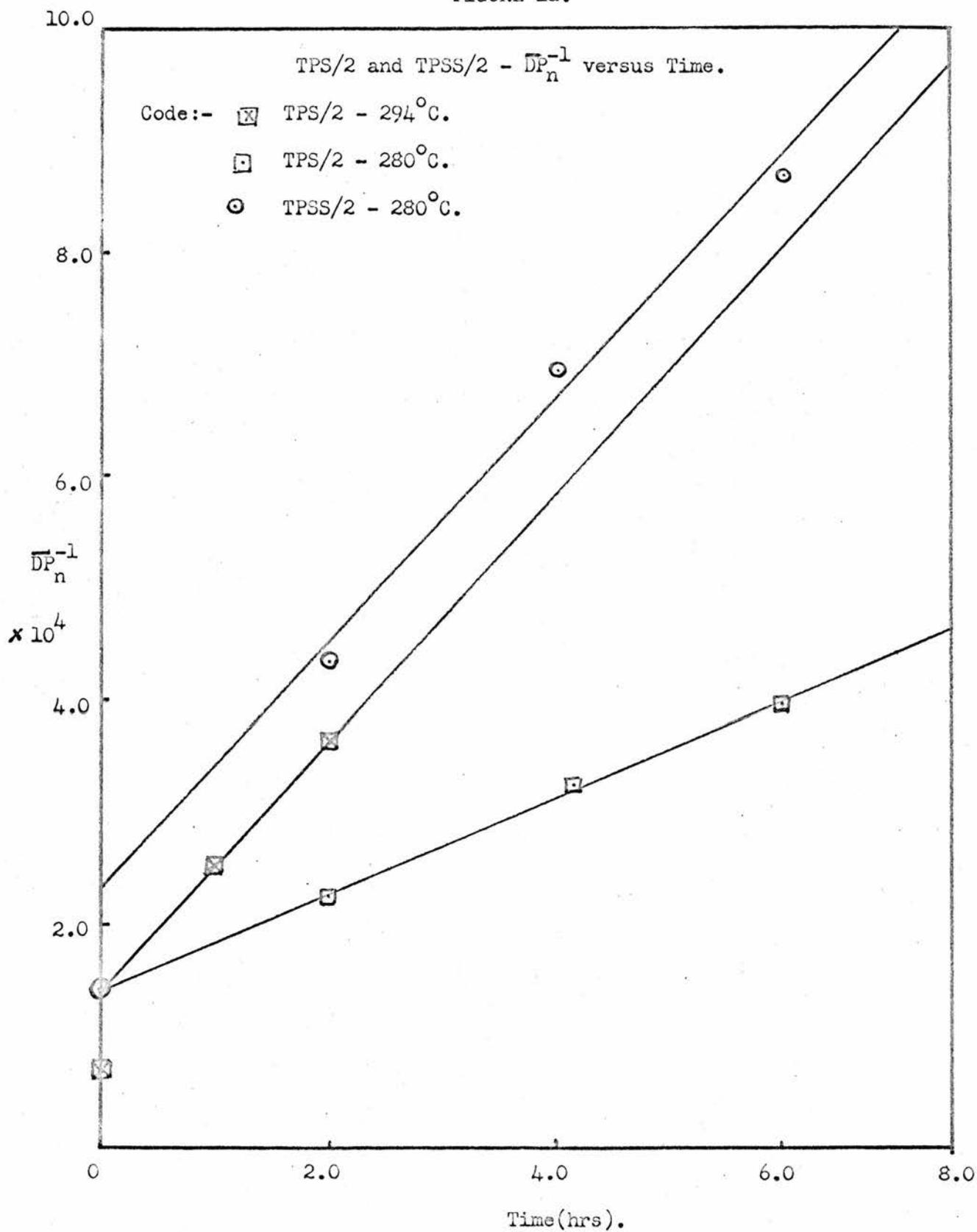
Equation (7) predicts that, for a simple random degradation in a closed system, α versus time should be linear through $\alpha = 0$ at $t = 0$, with a slope equal to k_I . Plots of reciprocal \bar{M}_n as a function of time should also be linear with a slope of k_I / m and an intercept of $1/\bar{M}_{n_0}$. Both types of plot are utilised in this study.

(2) Preliminary Investigations of the Molecular Weight Changes in Thermally Polymerised Styrene Homopolymer TPS/2 and Styrene - Stilbene Copolymer TPSS/2.

Homopolymer TPS/2 was degraded at 280° and 294° C. in the molecular still, and molecular weights measured by osmometry. The relevant data is tabulated in Table I, and plotted in Figures Ia and Ib.

TABLE I. Polymer	Temperature °C.	Time of Degradation (hrs.)	\bar{M}_n $\times 10^{-6}$	\bar{DP}_n $\times 10^{-4}$	\bar{DP}_n^{-1} $\times 10^4$	α .
TPS/2	-----	-----	1.490	1.433	0.698	0
	280	2.00	0.462	0.444	2.252	0.000155
	280	4.15	0.319	0.307	3.257	0.000256
	280	6.00	0.261	0.251	3.984	0.000329
	294	1.00	0.410	0.394	2.538	0.000184
	294	2.00	0.285	0.274	3.651	0.000295
TPSS/2	-----	-----	0.736	0.708	1.412	0
	280	2.00	0.239	0.230	4.348	0.000294
	280	4.00	0.150	0.144	6.944	0.000553
	280	6.00	0.120	0.115	8.696	0.000728

FIGURE 1a.



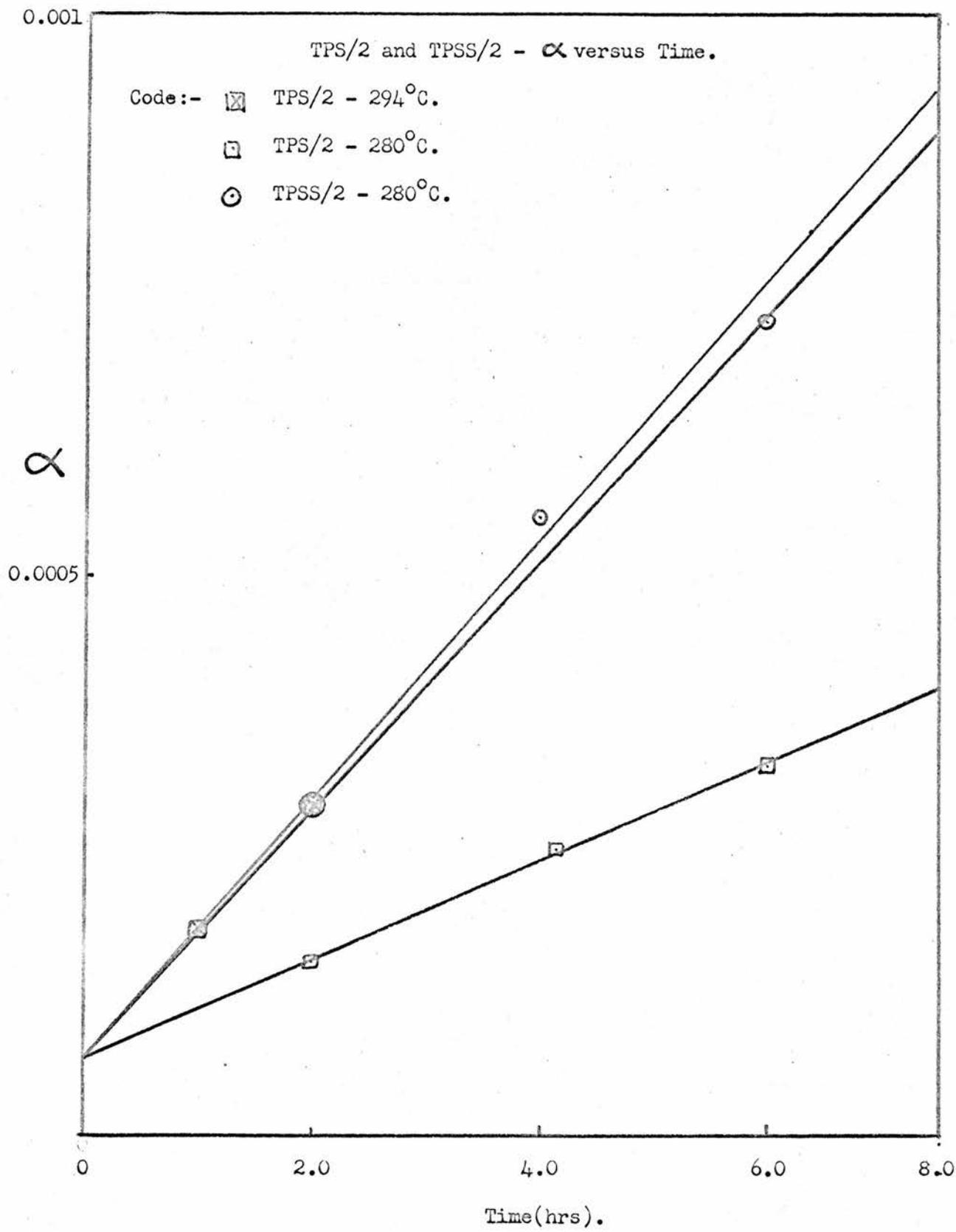


Figure Ia demonstrates that the plot of reciprocal \overline{DP} as a function of time appears to be linear, but does not pass through $1/\overline{DP}_0$. Similarly, the α versus time plot (Figure Ib) shows a substantial ordinate intercept. Similar experiments conducted on the copolymer TPSS/2 give substantially similar results. (Figures Ia, Ib; Table I.)

Because some difficulty was experienced with diffusion of low polymer through the membrane in the osmometer, the molecular weight data tabulated in Table I are slightly suspect, although any error in molecular weights due to diffusion would give a negative, rather than the observed positive, intercept. Therefore, a programme of degradations of polystyrenes was initiated in which molecular weights were measured by viscometry, and converted to number averages by reference to the relevant computer programme, as discussed in Chapter III.

(3) The Molecular Weight Changes in Polystyrenes Prepared Thermally at 60°C. in Bulk.

Homopolymer TPS/2 was degraded at 280, 287, 294 and 300°C. The relevant data are tabulated in Table 2, and plotted in Figures 2a, b, c, d and e.

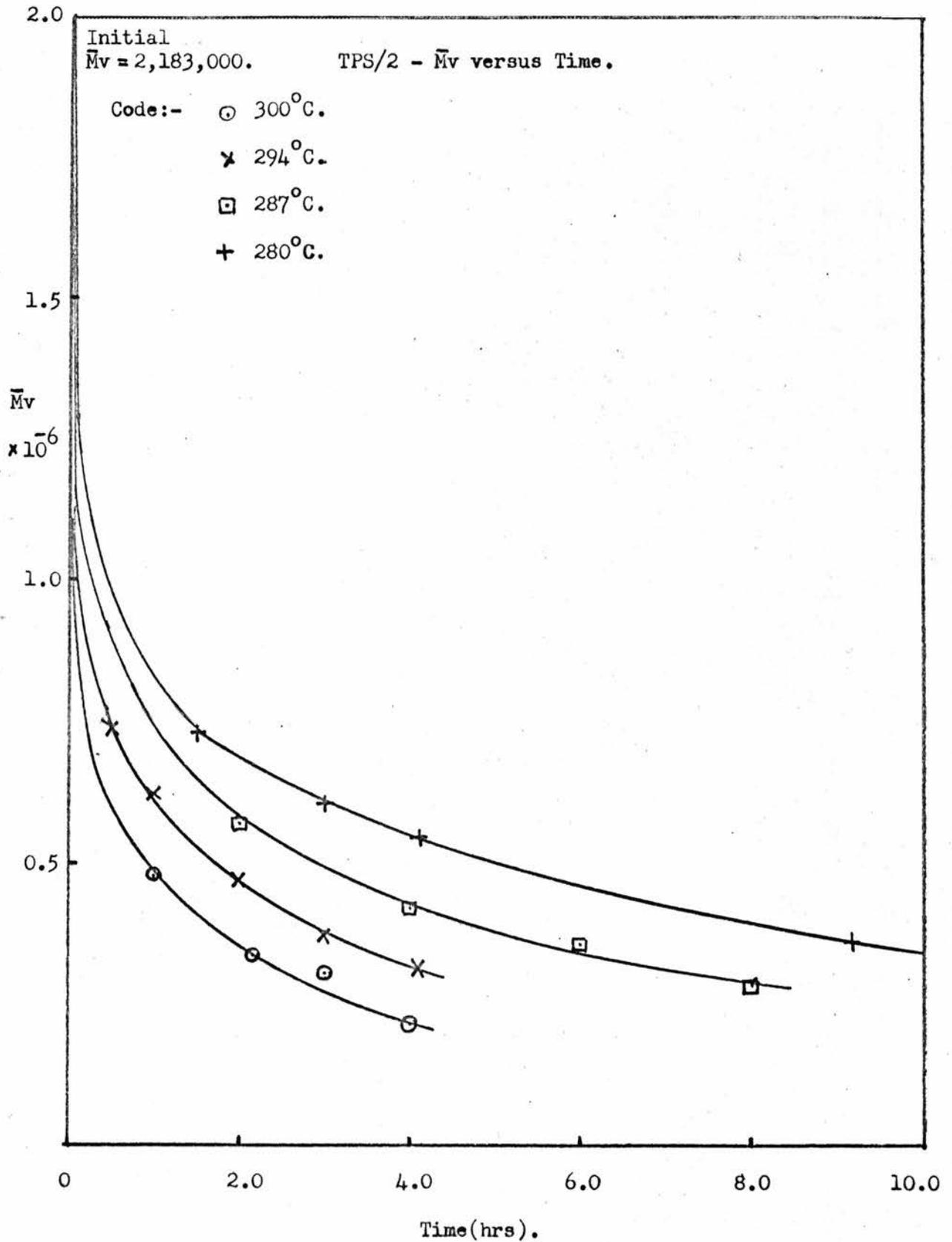
Figures 2a and 2b indicate the magnitude of the rapid fall in molecular weight, as measured by viscosity and number average molecular weights respectively. Both graphs show a large initial drop in molecular weight, followed by a more gradual decline. The magnitude of the initial molecular weight fall is a function of the

TABLE 2.

Thermal Degradation of TPS/2.

Molecular Weight Data.

Temp. °C.	Time. (hrs)	$[\eta]$	\bar{M}_v $\times 10^{-6}$	\bar{M}_v^{-1} $\times 10^6$	\bar{M}_n $\times 10^{-6}$	\bar{M}_n^{-1} $\times 10^6$	$\frac{\bar{M}_v}{\bar{M}_n}$	α
-	-	4.74	2.183	0.458	1.520	0.658	1.436	0
300	1.00	1.57	0.479	2.089	0.260	3.843	1.839	0.000331
300	2.17	1.21	0.334	2.992	0.180	5.553	1.856	0.000506
300	3.00	1.13	0.304	3.288	0.164	6.112	1.859	0.000564
300	4.00	0.88	0.216	4.637	0.116	8.621	1.866	0.000826
294	0.50	2.15	0.735	1.361	0.409	2.446	1.796	0.000185
294	1.00	1.90	0.622	1.607	0.342	2.925	1.820	0.000235
294	2.00	1.54	0.467	2.143	0.254	3.942	1.840	0.000342
294	3.00	1.30	0.367	2.723	0.198	5.046	1.854	0.000451
294	4.10	1.15	0.313	3.199	0.168	5.945	1.858	0.000550
287	2.00	1.79	0.572	1.753	0.312	3.202	1.830	0.000260
287	4.00	1.43	0.421	2.377	0.228	4.389	1.847	0.000387
287	6.00	1.27	0.357	2.805	0.192	5.200	1.854	0.000470
287	8.00	1.07	0.283	3.540	0.152	6.589	1.861	0.000614
280	1.50	2.14	0.731	1.368	0.406	2.463	1.801	0.000187
280	3.00	1.86	0.604	1.655	0.332	3.014	1.820	0.000244
280	4.09	1.73	0.547	1.828	0.299	3.347	1.830	0.000271
280	9.17	1.27	0.359	2.786	0.194	5.165	1.854	0.000470



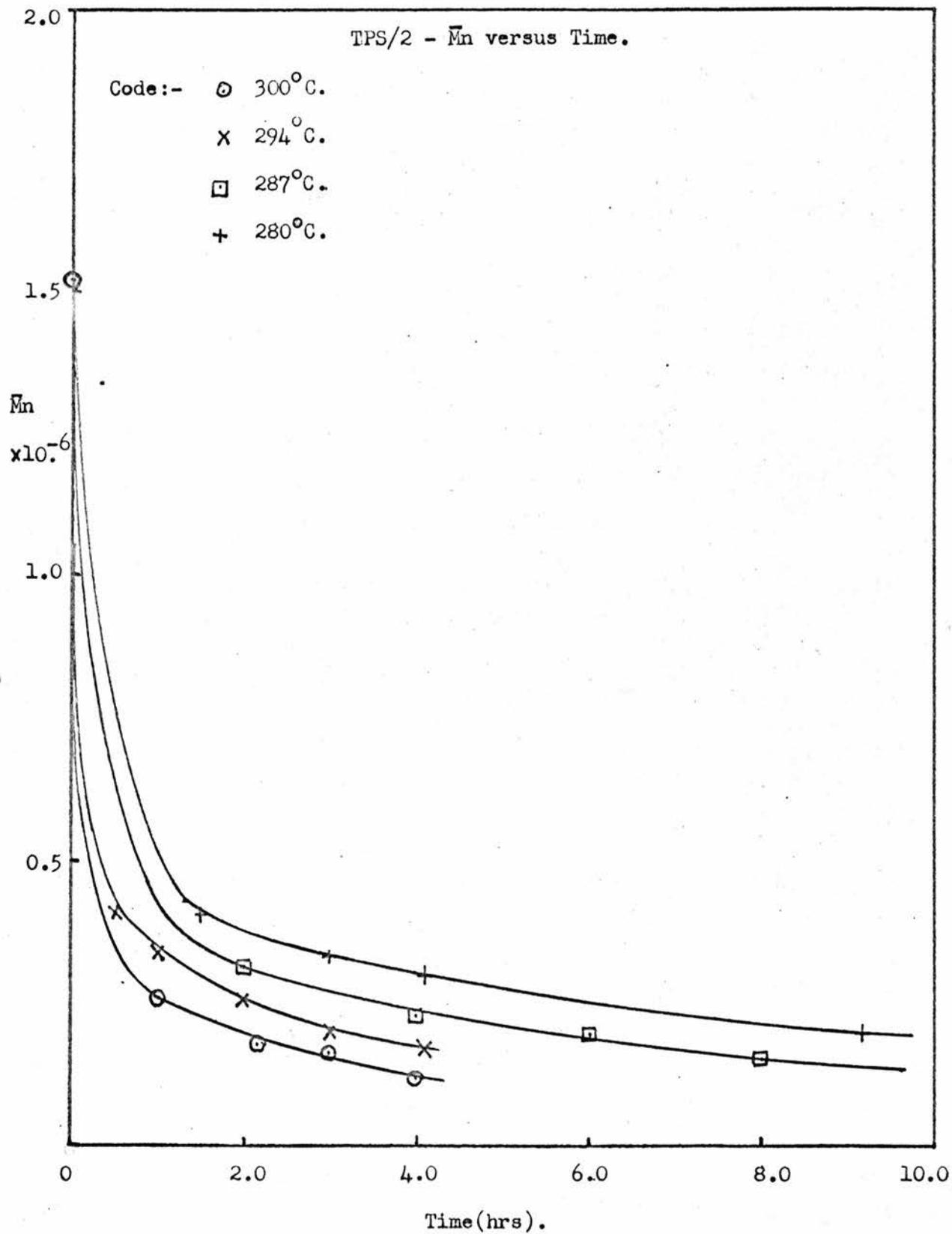


FIGURE 2c.

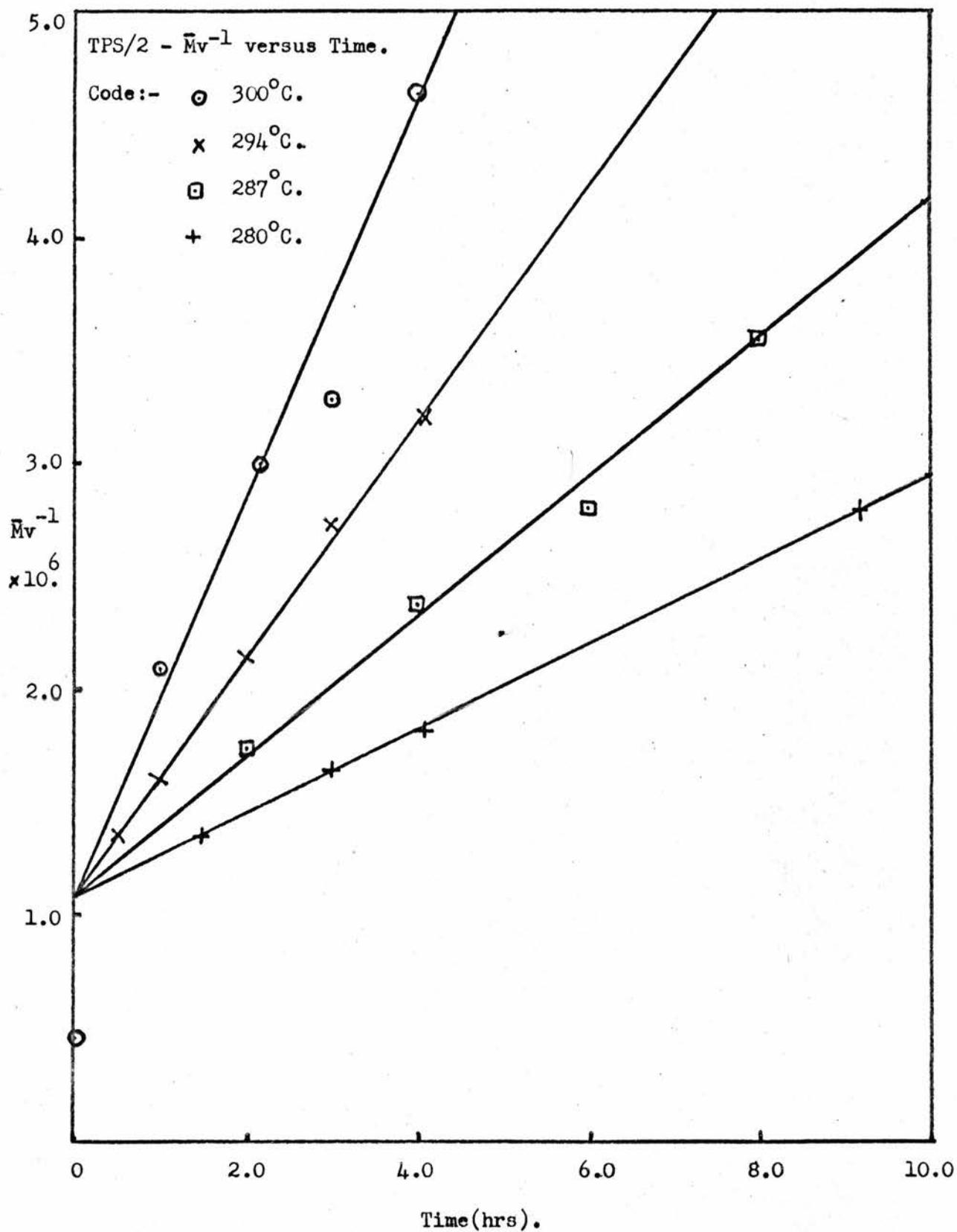


FIGURE 2d.

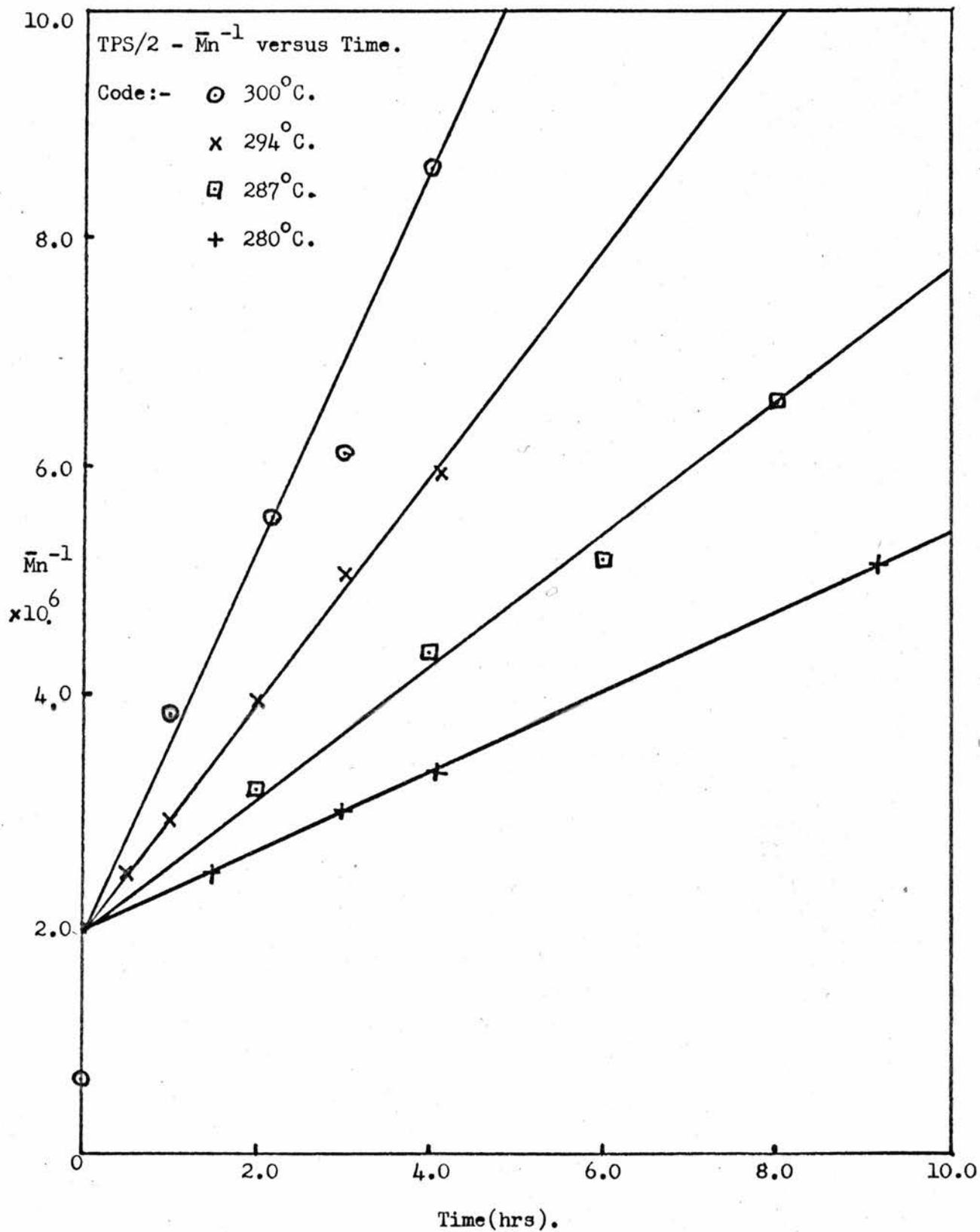
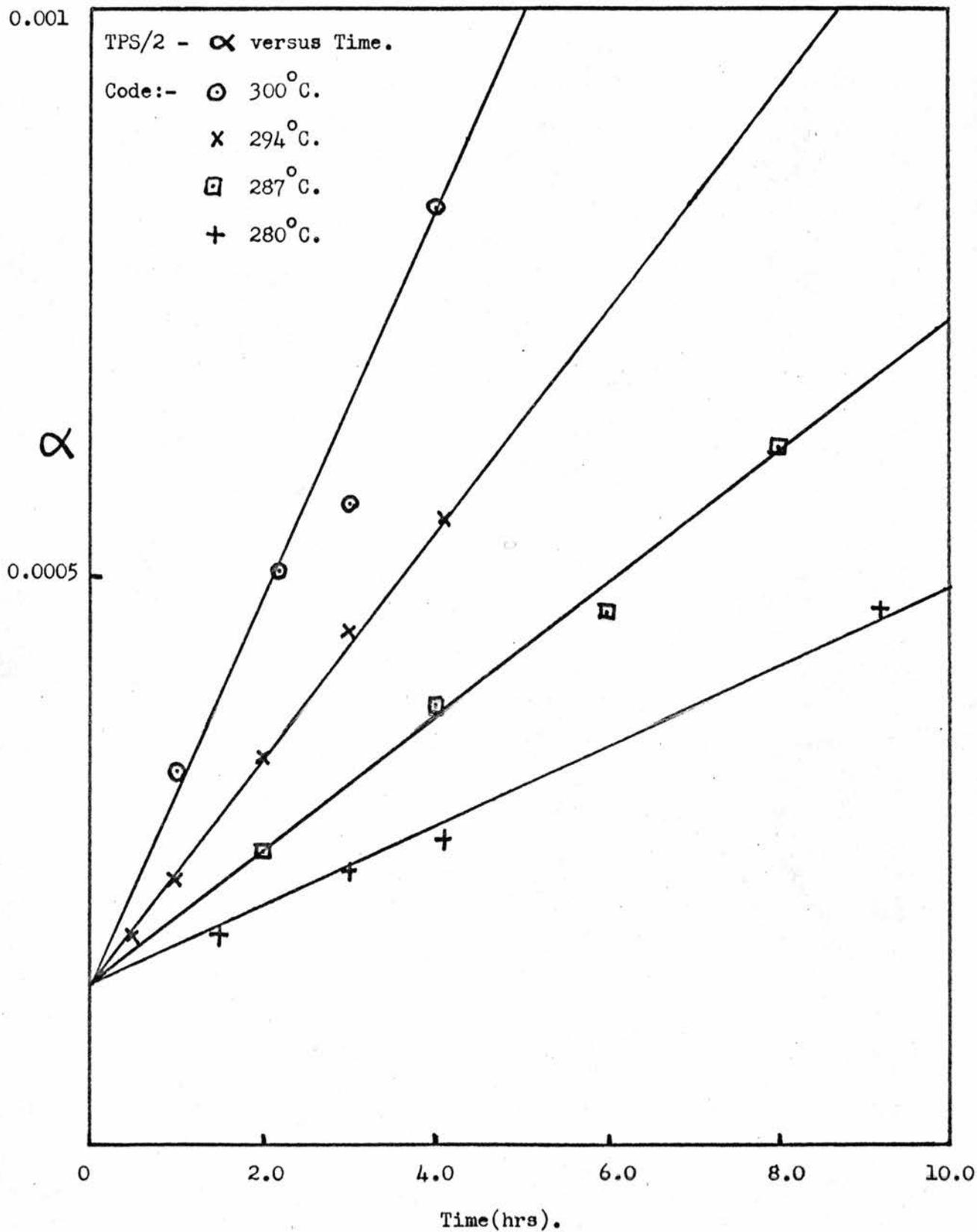


FIGURE 2e.



degradation temperature, as was found by Jellinek^I for degradations at temperatures where volatilisation was considerable.

Figures 2c and 2d indicate that plots of reciprocal \bar{M}_v and \bar{M}_n respectively as functions of time are linear, but do not pass through the corresponding $\bar{M}_{v_0}^{-1}$ or $\bar{M}_{n_0}^{-1}$, showing instead positive intercepts on the ordinate axis. Similarly, plots of α versus time (Figure 2e) for the four temperatures are linear and show an ordinate intercept. It is interesting that in these three plots (Figures 2c, d and e) the ordinate intercept appears to be independent of the degradation temperature, and there is no evidence of curvature in any of the lines. Attempts to degrade the polymer for longer times in an effort to detect any departure from linearity were unsuccessful because of the excessively high volatilisation.

Equation (6) predicts that the slope of the reciprocal \bar{DP} versus time curves for the different degradation temperatures is equal to the velocity constant of chain scission, k_I , for the corresponding temperature. Values of k_I were calculated from Figures 2c and 2d, and Arrhenius plots were constructed. (Table 3a and 3b; Figure 3). Activation Energies of 51.2 and 49.2 kcal.mole⁻¹ were found from viscosity and number average molecular weights respectively. Thus, the use of different average molecular weights does not appear to affect the magnitude of the Activation Energy, at least in this case. This value of Activation Energy is in close agreement with literature values for the same process.^{13, 14, 15}

TABLE 3a.

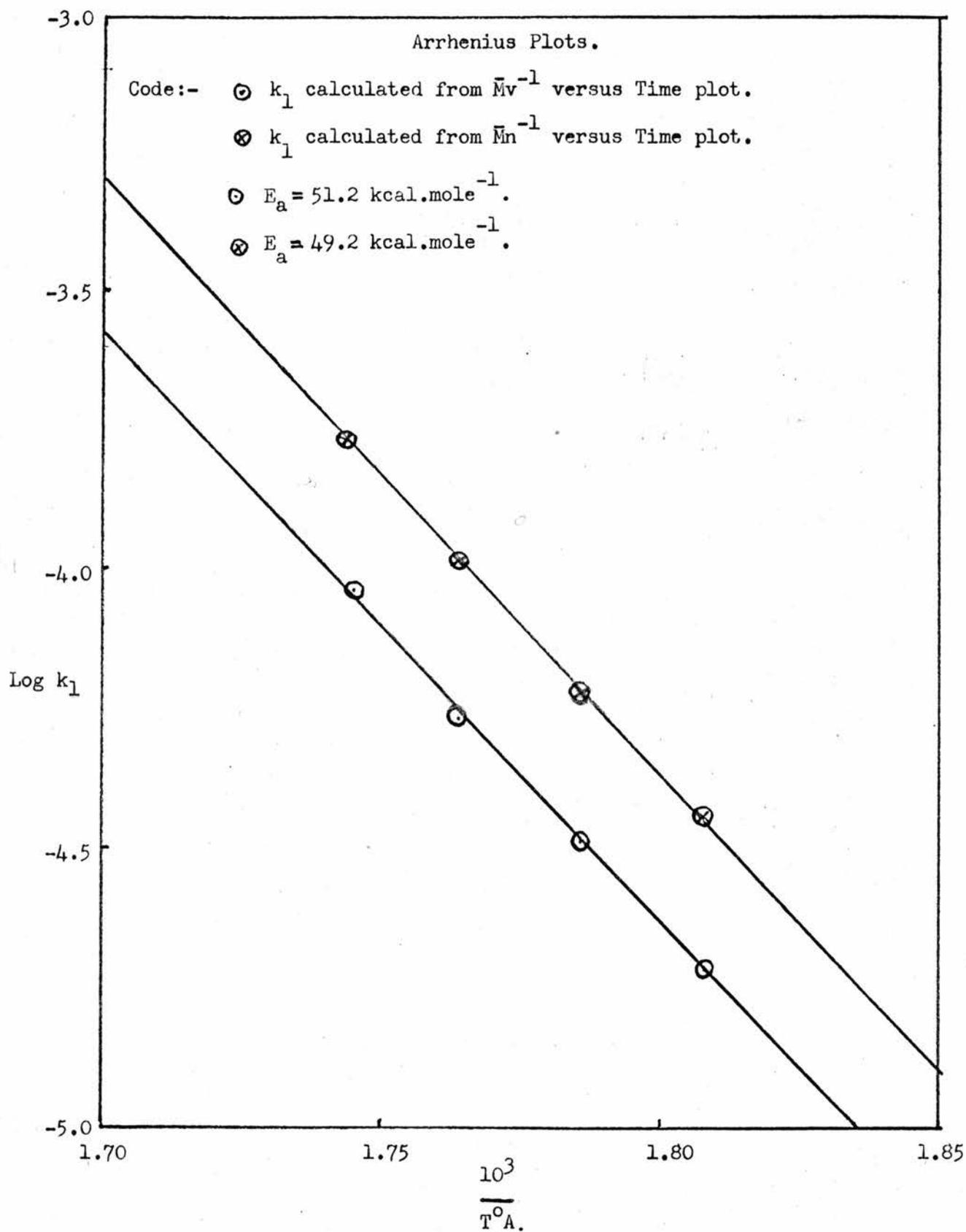
Data for Arrhenius Plot:- from $1/\bar{M}_v$ versus Time plot(Figure 2c).

Temp. T ^o C.	Temp. T ^o A.	$\frac{10^3}{T^o A.}$	$k_1 \times 10^4.$ (hr. ⁻¹)	log. $k_1.$
300	573	1.745	0.918	- 4.0373
294	567	1.764	0.548	- 4.2612
287	560	1.786	0.328	- 4.4870
280	553	1.808	0.193	- 4.7135

TABLE 3b.

Data for Arrhenius Plot:- from $1/\bar{M}_n$ versus Time plot(Figure 2d).

Temp. T ^o C.	Temp. T ^o A.	$\frac{10^3}{T^o A.}$	$k_1 \times 10^4.$ (hr. ⁻¹)	log. $k_1.$
300	573	1.745	1.730	- 3.7621
294	567	1.764	0.964	- 3.9839
287	560	1.786	0.604	- 4.2188
280	553	1.808	0.367	- 4.4389



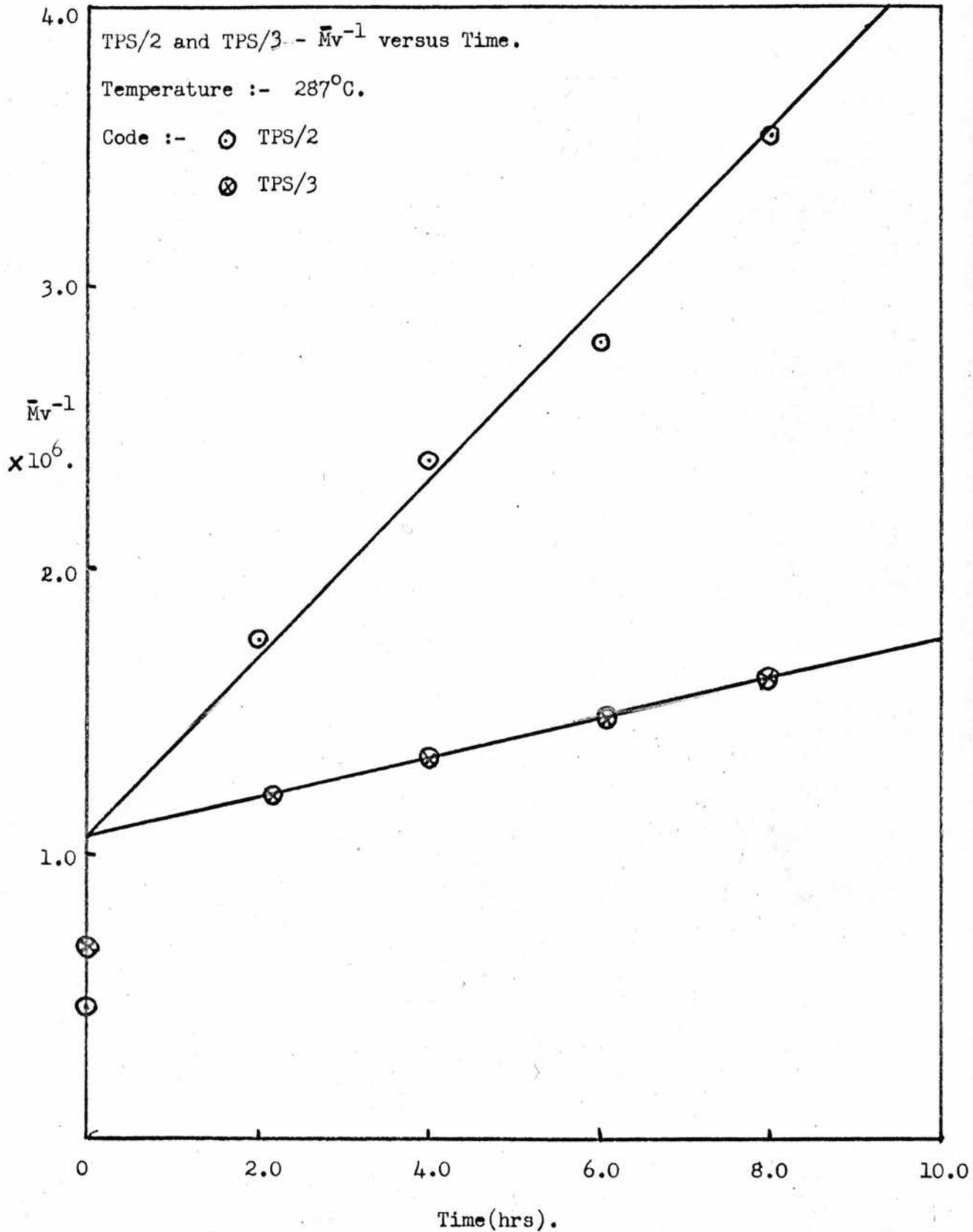
Before speculating on the nature of the reactions occurring during the degradation of homopolymer TPS/2, it is essential to prove that the observed characteristics are typical of all polystyrenes prepared under similar conditions, and are not restricted to the one polymer studied so far. This check is doubly important because thermal polymerisation is notoriously susceptible to impurities, especially oxygen¹⁶. Homopolymer TPS/3 was therefore similarly prepared at 60°C without initiator, and degraded at 287°C. The molecular weight data are tabulated in Table 4 and plotted in Figures 4a, b and c, with the corresponding data for TPS/2 for comparison.

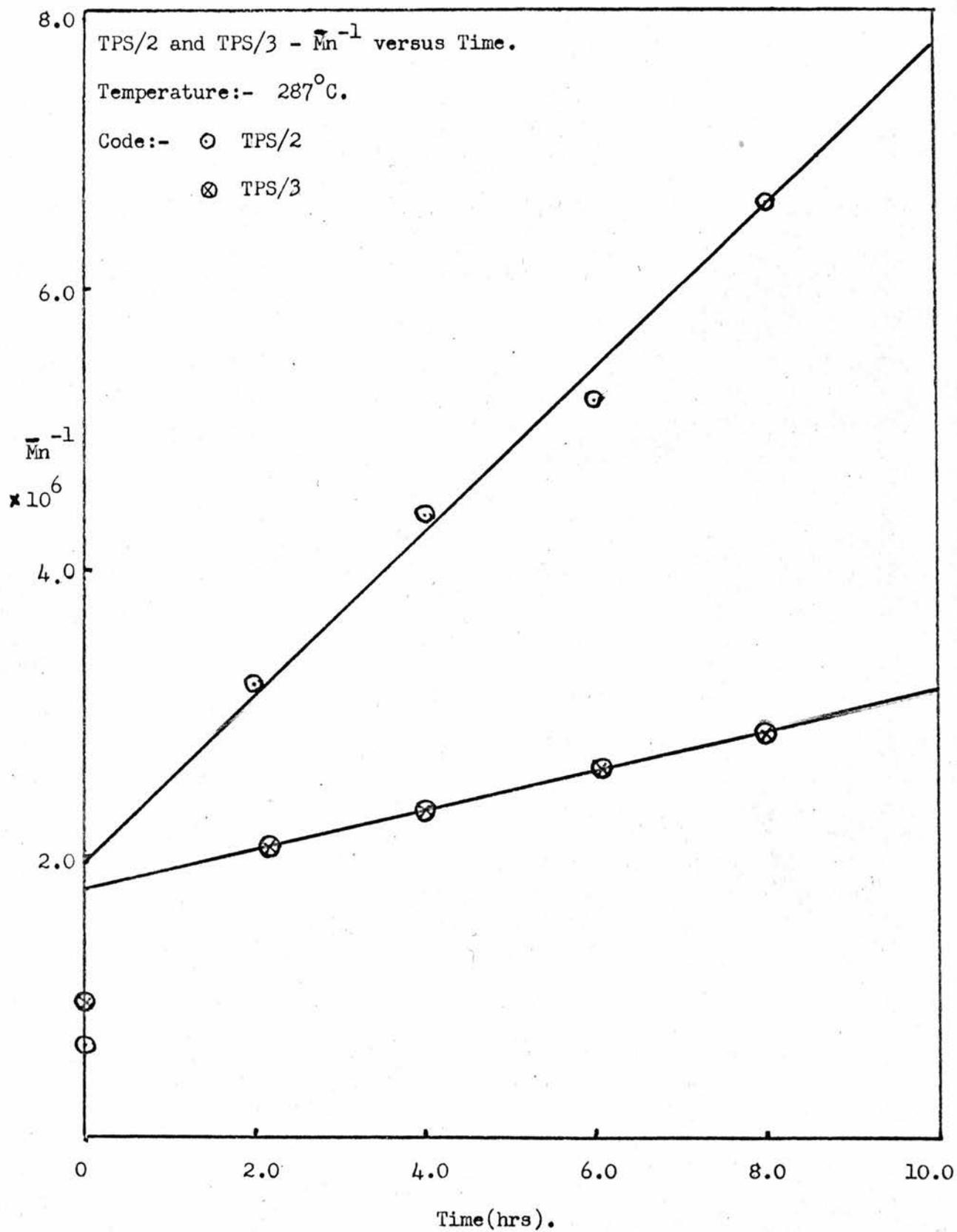
TABLE 4.

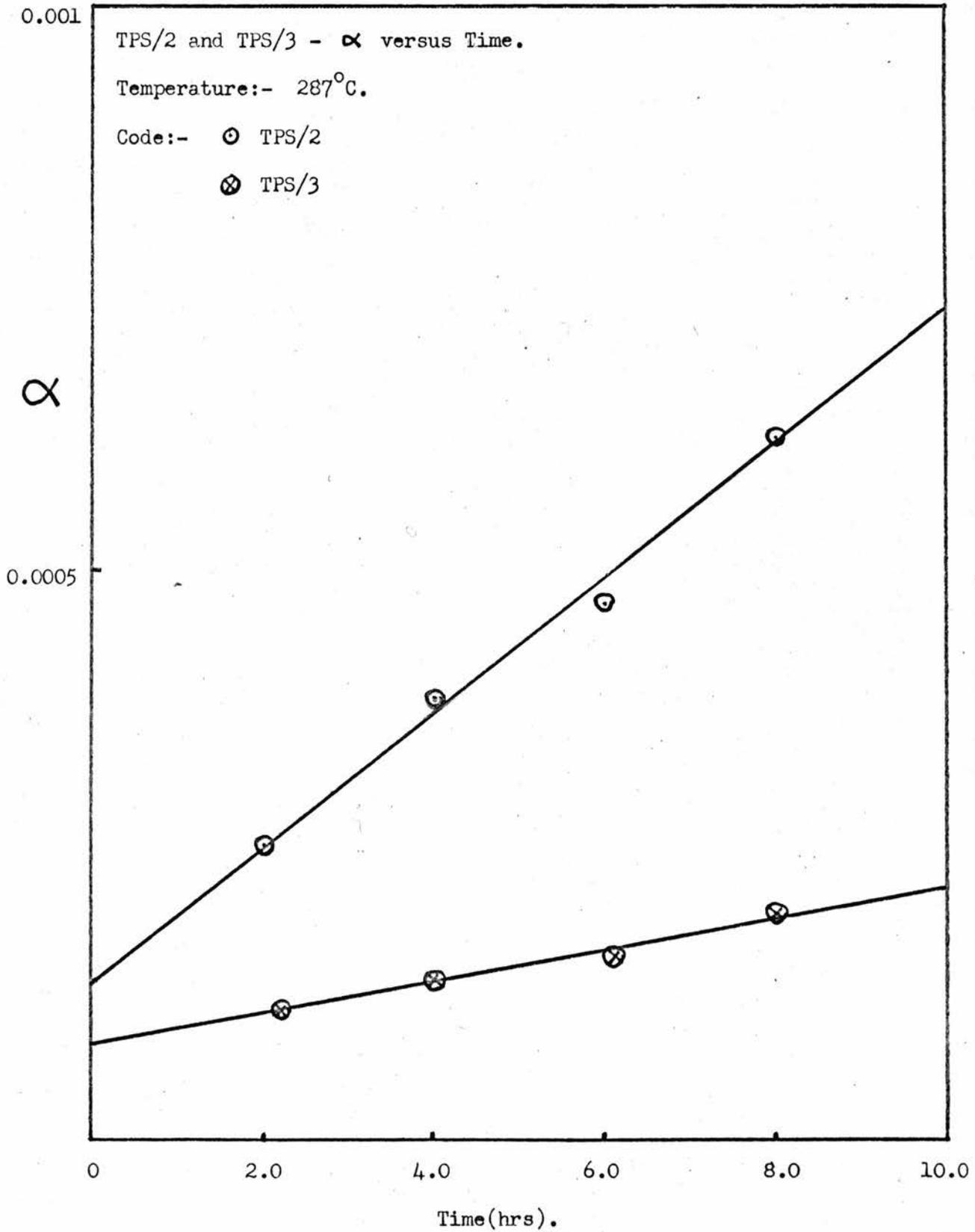
Thermal Degradation of TPS/2 and TPS/3 at 287°C.

Molecular Weight Data.

Polymer	Time. (hrs)	$[\eta]$	\bar{M}_v $\times 10^{-6}$	\bar{M}_v^{-1} $\times 10^6$	\bar{M}_n $\times 10^{-6}$	\bar{M}_n^{-1} $\times 10^6$	$\frac{\bar{M}_v}{\bar{M}_n}$	α
TPS/2.	-	4.74	2.183	0.458	1.520	0.658	1.436	0
	2.00	1.79	0.572	1.753	0.312	3.202	1.830	0.000260
	4.00	1.43	0.421	2.377	0.228	4.389	1.847	0.000387
	6.00	1.27	0.357	2.805	0.192	5.200	1.854	0.000470
	8.00	1.07	0.283	3.540	0.152	6.589	1.861	0.000614
TPS/3.	-	3.60	1.496	0.668	1.042	0.960	1.436	0
	2.20	2.34	0.830	1.207	0.488	2.051	1.703	0.000114
	4.00	2.17	0.745	1.343	0.431	2.320	1.728	0.000141
	6.10	2.02	0.676	1.479	0.386	2.594	1.750	0.000160
	8.00	1.90	0.622	1.607	0.352	2.838	1.766	0.000196







It is immediately apparent from these figures that the two homopolymers behave in an essentially similar manner, although there are differences in detail. Both show linear plots of α versus time, and both exhibit positive ordinate intercepts in this plot. The differences concern the size of the intercept and the rate of chain scission, homopolymer TPS/2 exhibiting both a larger intercept and a higher rate of scission (Figure 4c). The reason for these dissimilarities is not immediately apparent, although TPS/2 has a higher molecular weight, and polymerised more quickly, than TPS/3. The higher rate of chain scission in TPS/2 may be due in part to the greater molecular weight, a similar effect having been found recently in the degradation of Ziegler - Natta polystyrenes¹³. The differences between TPS/2 and TPS/3 will be discussed in more detail in the succeeding chapter.

So far in this study, only thermally initiated polystyrenes have been investigated under degradative conditions of low volatilisation, but it is important to discover if polymers prepared under different conditions show similar characteristics. Studies by Nakajima and collaborators¹⁴ and Boon and Challa¹³ on the thermal degradation of polystyrenes prepared by Ziegler - Natta catalysis have shown that these polymers do not give an intercept on the α versus time curve. Therefore, the features present in thermally polymerised polystyrenes which are responsible for the ordinate intercept are absent from the anionically prepared polystyrenes. For direct comparison with the polymers already used in the present

study, three polystyrenes prepared by "living" anionic initiation were degraded to low volatilisation in the molecular still. The results are presented in the following section.

(4) The Molecular Weight Changes in Anionically Polymerised

Polystyrene.

(a) The Thermal Degradation of APS/1L and APS/3L.

These polymers were degraded at temperatures between 280°C and 320°C; the relevant temperature and molecular weight data are tabulated in Tables 5 and 6, and plotted in Figures 5a, b and c, and 6a, b and c.

The figures 5c and 6c show linear plots of α versus time passing through $\alpha = 0$ at $t = 0$ for both polymers. The absence of a positive ordinate intercept in these plots for polystyrenes prepared anionically is in marked contrast to the behaviour of thermally synthesised polymers. Calculations show that, if the intercept in the α versus time plots for thermal polystyrenes represents the fraction of "weak bonds" in these polymers, the existence of a similar concentration in the anionically prepared polymers would be readily detected in the present experiments, despite the lower molecular weights of the A P S series. The α versus time plots obtained in this study for anionically synthesised polymers are similar in character to those obtained under comparable conditions for polystyrenes prepared by Ziegler - Natta catalysis^{13,14}.

Both of these types of anionic polystyrenes, therefore, do not undergo the reaction responsible for the ordinate intercept in similar plots

TABLE 5.

Thermal Degradation of APS/LL.

Molecular Weight Data.

Temp. T°C.	Time. (hrs)	$[\eta]$	\bar{M}_v $\times 10^{-6}$	\bar{M}_v^{-1} $\times 10^6$	\bar{M}_n $\times 10^{-6}$	\bar{M}_n^{-1} $\times 10^6$	$\frac{\bar{M}_v}{\bar{M}_n}$	α
-	-	0.93	0.233	4.287	0.233	4.287	1.000	.0
320	1.00	0.82	0.196	5.110	0.156	6.418	1.417	0.000224
320	2.00	0.74	0.170	5.875	0.120	8.326	1.573	0.000420
320	3.00	0.64	0.140	7.128	0.089	11.210	1.693	0.000718
320	3.75	0.53	0.113	10.740	0.066	15.050	1.758	0.001120
310	1.00	0.88	0.216	4.623	0.194	5.167	1.118	0.000090
310	2.00	0.82	0.198	5.046	0.158	6.317	1.252	0.000217
310	3.00	0.79	0.187	5.359	0.141	7.072	1.320	0.000290
310	4.00	0.76	0.176	5.676	0.127	7.862	1.386	0.000395
300	3.00	0.88	0.216	4.623	0.191	5.233	1.129	0.000099
300	6.00	0.82	0.207	4.842	0.163	6.131	1.266	0.000230
300	6.00	0.82	0.196	5.110	0.156	6.418	1.260	0.000223
300	9.00	0.79	0.188	5.322	0.143	6.978	1.311	0.000282
287	2.00	0.93	0.230	4.346	0.225	4.426	1.014	0.000009
287	4.00	0.92	0.226	4.426	0.220	4.537	1.025	0.000018
287	6.00	0.90	0.224	4.472	0.208	4.817	1.081	0.000055
287	8.00	0.92	0.226	4.426	0.220	4.537	1.025	0.000018

FIGURE 5a.

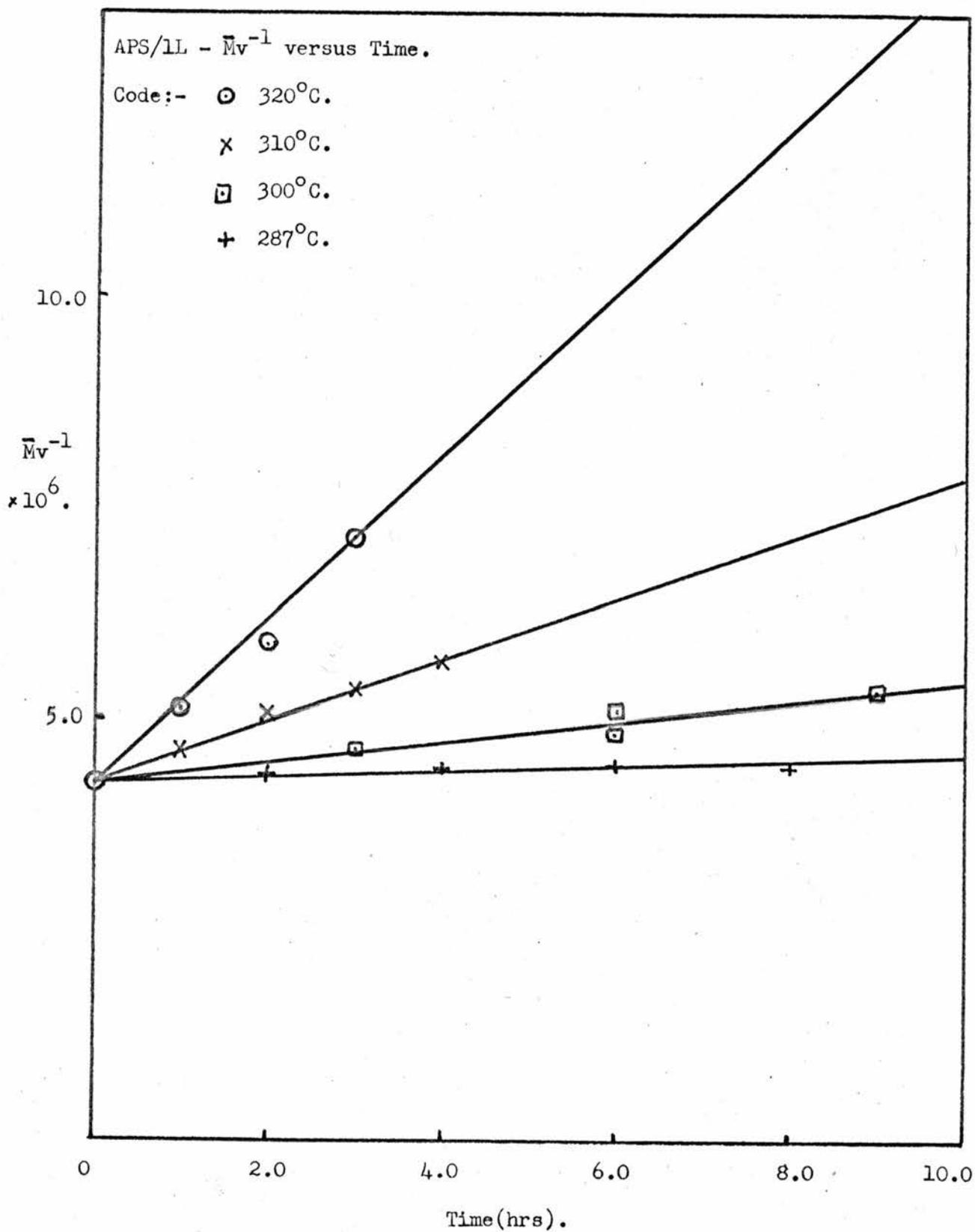


FIGURE 5b.

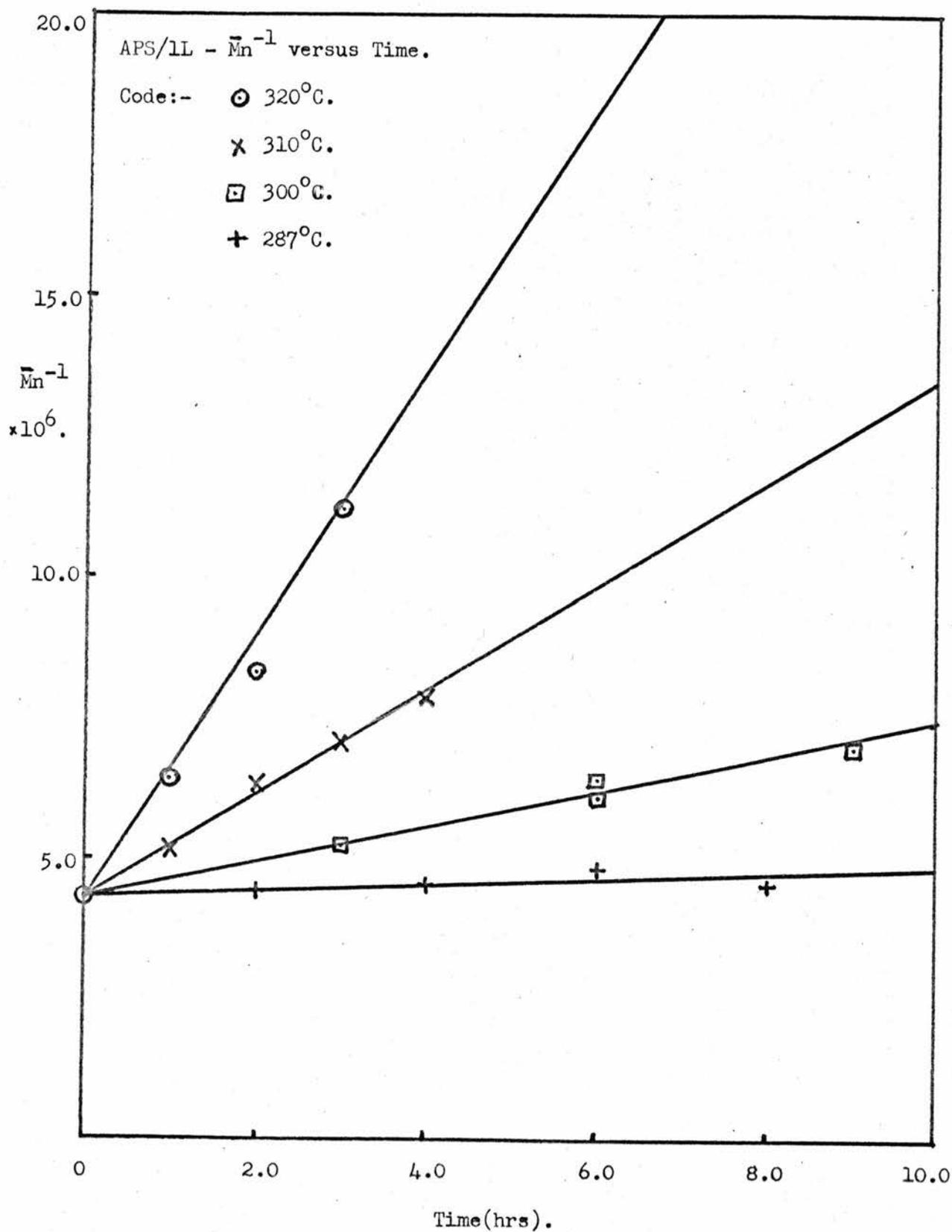


FIGURE 5c.

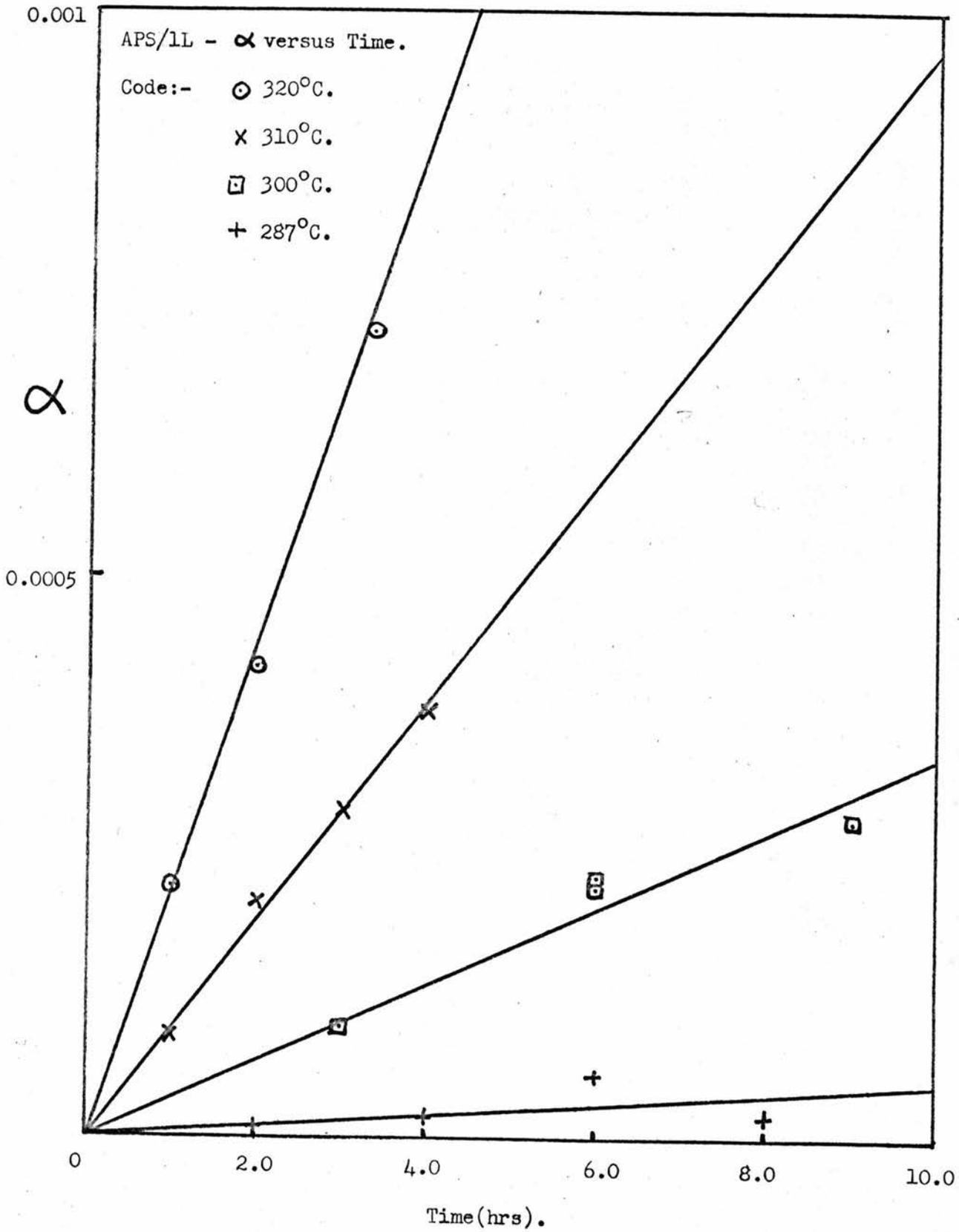


TABLE 6.

Thermal Degradation of APS/3L.

Molecular Weight Data.

Temp. T°C.	Time. (hrs)	$[\eta]$	\bar{M}_v $\times 10^{-6}$	\bar{M}_v^{-1} $\times 10^6$	\bar{M}_n $\times 10^{-6}$	\bar{M}_n^{-1} $\times 10^6$	$\frac{\bar{M}_v}{\bar{M}_n}$	α
-	-	1.84	0.593	1.686	0.593	1.686	1.000	0
313	1.00	1.29	0.366	2.736	0.235	4.250	1.556	0.000267
313	2.00	1.04	0.271	3.690	0.158	6.317	1.712	0.000478
313	3.00	0.87	0.213	4.699	0.119	8.383	1.784	0.000687
310	1.00	1.39	0.404	2.477	0.274	3.650	1.477	0.000207
310	1.75	1.19	0.327	3.061	0.201	4.975	1.626	0.000341
310	2.50	1.03	0.268	3.752	0.156	6.410	1.718	0.000491
310	5.00	0.74	0.171	5.835	0.094	10.640	1.820	0.000926
303	1.00	1.59	0.489	2.046	0.380	2.635	1.288	0.000100
303	3.05	1.13	0.306	3.266	0.184	5.435	1.664	0.000392
303	5.10	0.94	0.237	4.217	0.135	7.413	1.757	0.000593
293	2.33	1.63	0.505	1.981	0.406	2.462	1.243	0.000080
293	5.00	1.37	0.396	2.523	0.267	3.745	1.482	0.000208
293	7.00	1.20	0.332	3.013	0.205	4.880	1.620	0.000333
280	2.00	1.73	0.547	1.828	0.483	2.072	1.133	0.000040
280	5.00	1.70	0.535	1.871	0.459	2.178	1.165	0.000052
280	8.00	1.54	0.465	2.157	0.348	2.878	1.328	0.000123

FIGURE 6a.

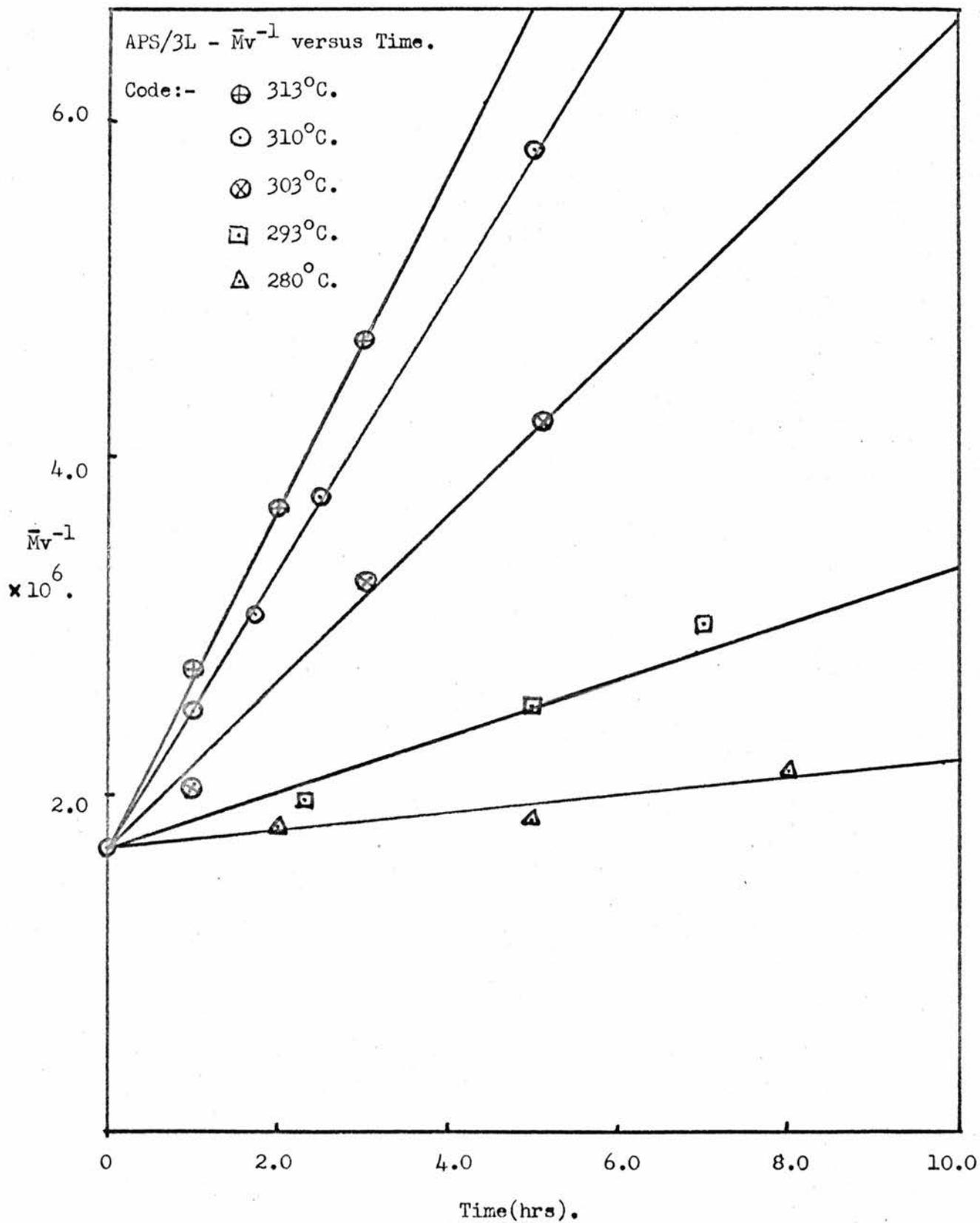


FIGURE 6b.

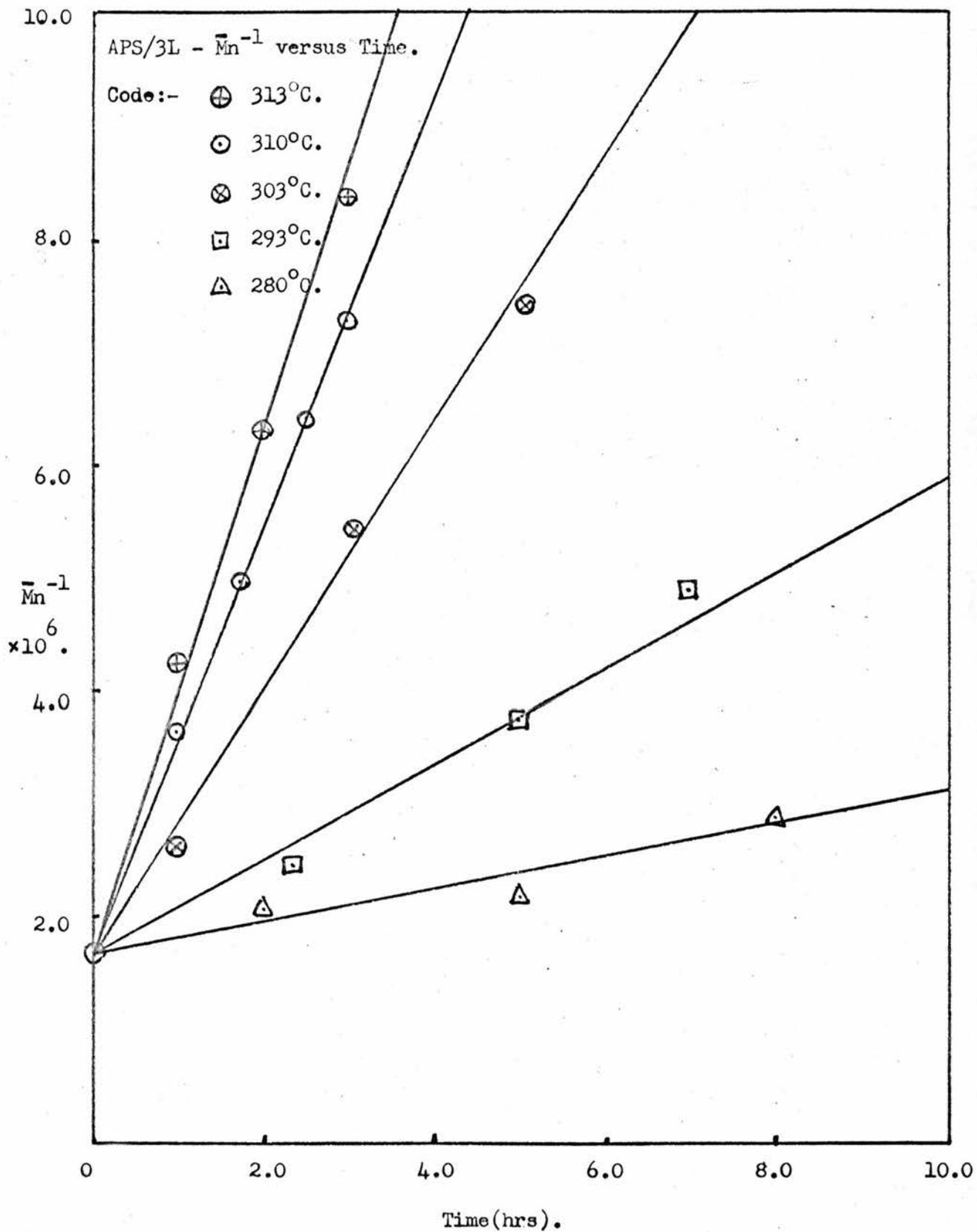
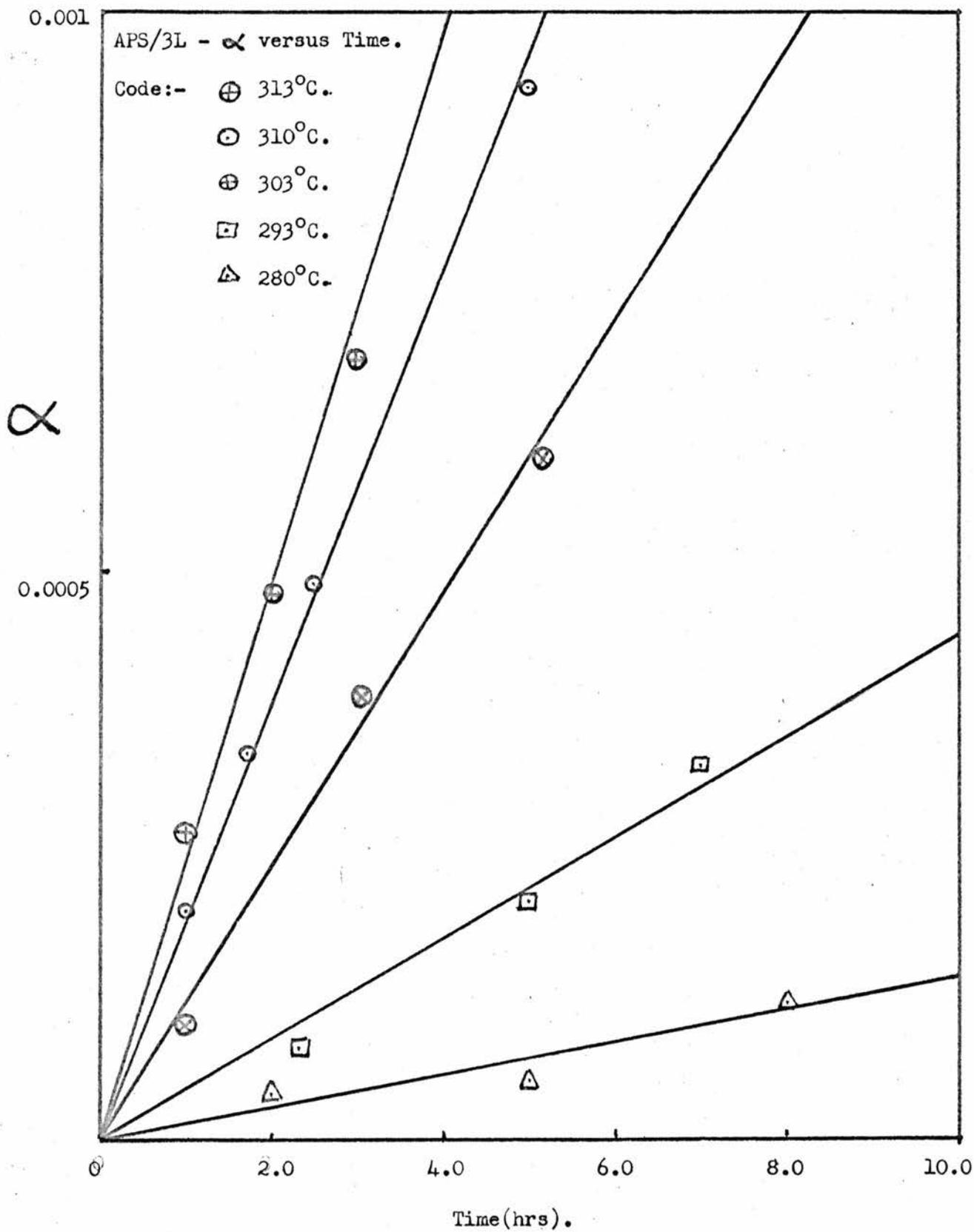


FIGURE 6c.



for thermally prepared polymers.

The velocity constants, k_I , for the various degradation temperatures, were calculated from the slopes of the α versus time plots for APS/IL and APS/3L. (Figures 5c and 6c respectively). Arrhenius plots were constructed for both polymers. (Figure 7; Table 7).

Activation Energies of 73 and 60 kcal. mole.⁻¹ were obtained for APS/IL and APS/3L respectively, values greatly exceeding that found for the thermally synthesised homopolymer TPS/2. The difference in Energy of Activation between the two anionic polymers is well outside experimental error, and might appear to indicate an inverse dependence of Activation Energy on molecular weight under the experimental conditions employed, but there is no evidence in the literature to support this hypothesis. Further discussion of this question is postponed until later in this chapter.

As was found in the comparison of the rates of chain scission of thermal homopolymers TPS/2 and TPS/3, there appears to be a direct relationship between the rate of chain scission and the molecular weight in the anionic homopolymers APS/IL and APS/3L. To further illustrate this dependence, another anionic polymer APS/2L, of molecular weight intermediate between the first two polymers, was degraded at 310°C., and the rate of chain scission compared with those for APS/IL and APS/3L.

TABLE 7.

Data for Arrhenius Plots.

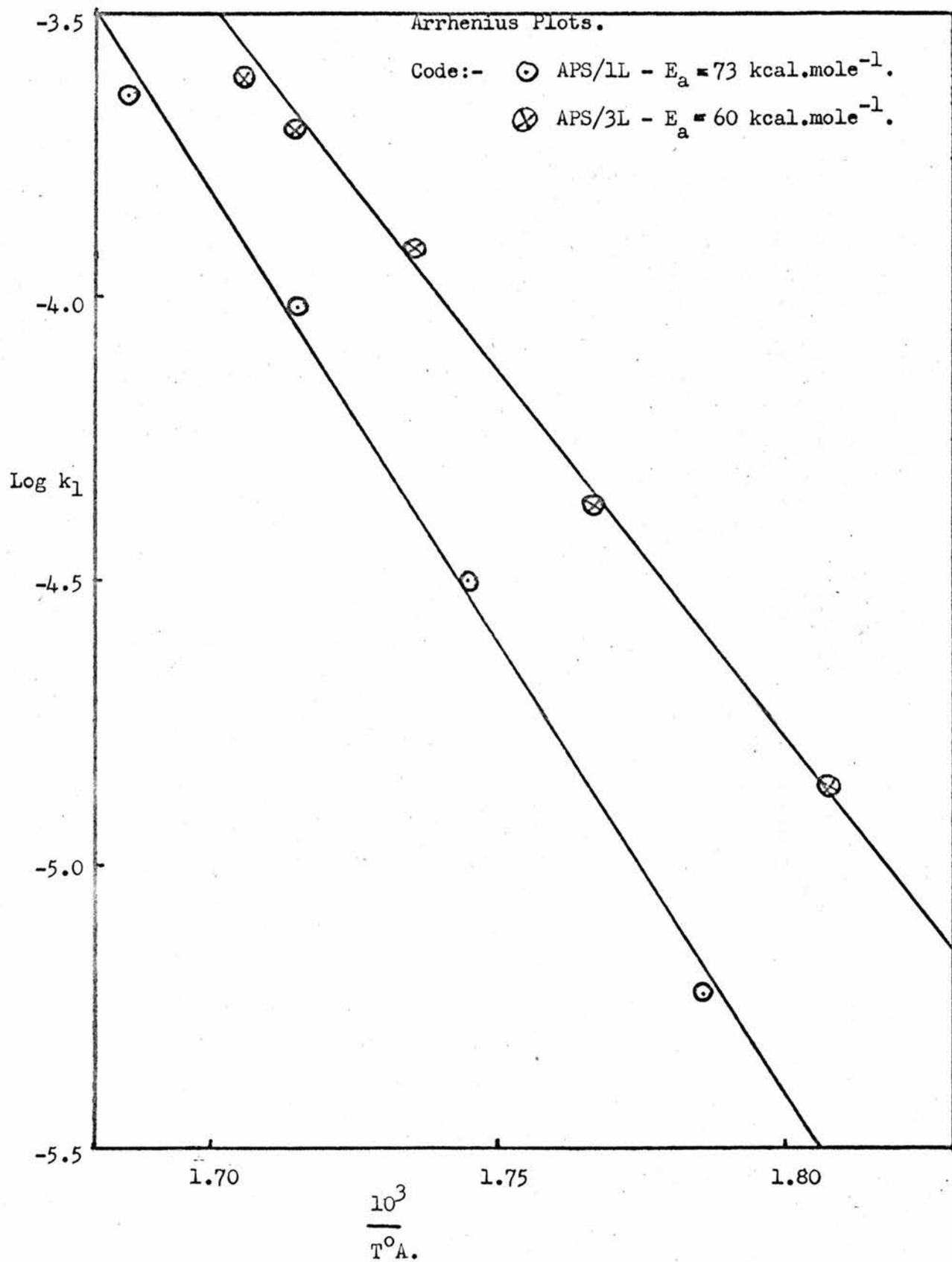
APS/1L.

Temp. T°C.	Temp. T°A.	$\frac{10^3}{T^\circ A.}$	$k_1 \times 10^4.$ (hr. ⁻¹)	log. $k_1.$
320	593	1.686	2.273	- 3.6435
310	583	1.715	0.960	- 4.0178
300	573	1.745	0.314	- 4.5030
287	560	1.786	0.059	- 5.2271

APS/3L.

Temp. T°C.	Temp. T°A.	$\frac{10^3}{T^\circ A.}$	$k_1 \times 10^4.$ (hr. ⁻¹)	log. $k_1.$
313	586	1.706	2.411	- 3.6178
310	583	1.715	1.946	- 3.7109
303	576	1.736	1.210	- 3.9172
293	566	1.767	0.427	- 4.3696
280	553	1.808	0.136	- 4.8665

FIGURE 7.



(b) A Comparison of the Rates of Chain Scission of Anionically Synthesised Polystyrenes of Different Molecular Weights.

The relevant molecular weight data for the three anionically prepared polystyrenes are tabulated in Table 8, and plotted in Figures 8a,b and c. From these diagrams it is clear that the rate of chain scission is a function of the molecular weight of the polymer. A plot. (Figure 9; Table 9) of the velocity constant k_I against molecular weight indicates that k_I is an increasing, non-linear function of the initial molecular weight of the polymer. A similar dependence of k_I on molecular weight has not previously been reported in the thermal degradation of polymers.

(5) Discussion

The results presented in this Chapter have indicated some important differences between the degradation behaviours of thermally and anionically prepared polystyrenes. These may be summarised as follows:-

- (1) Anionically polymerised polystyrenes show a linear dependence of the degree of degradation, α , on time. For these polymers there is no ordinate intercept, i.e. $\alpha = 0$ at $t = 0$. Thermally prepared polymers, on the other hand, show a linear dependence of α on time, but also exhibit a positive ordinate intercept.
- (2) Thermally prepared polymers are less stable than anionic samples at a given temperature, and the Activation Energy for chain scission of the former polymers is some $11 - 24$ kcal. mole.⁻¹

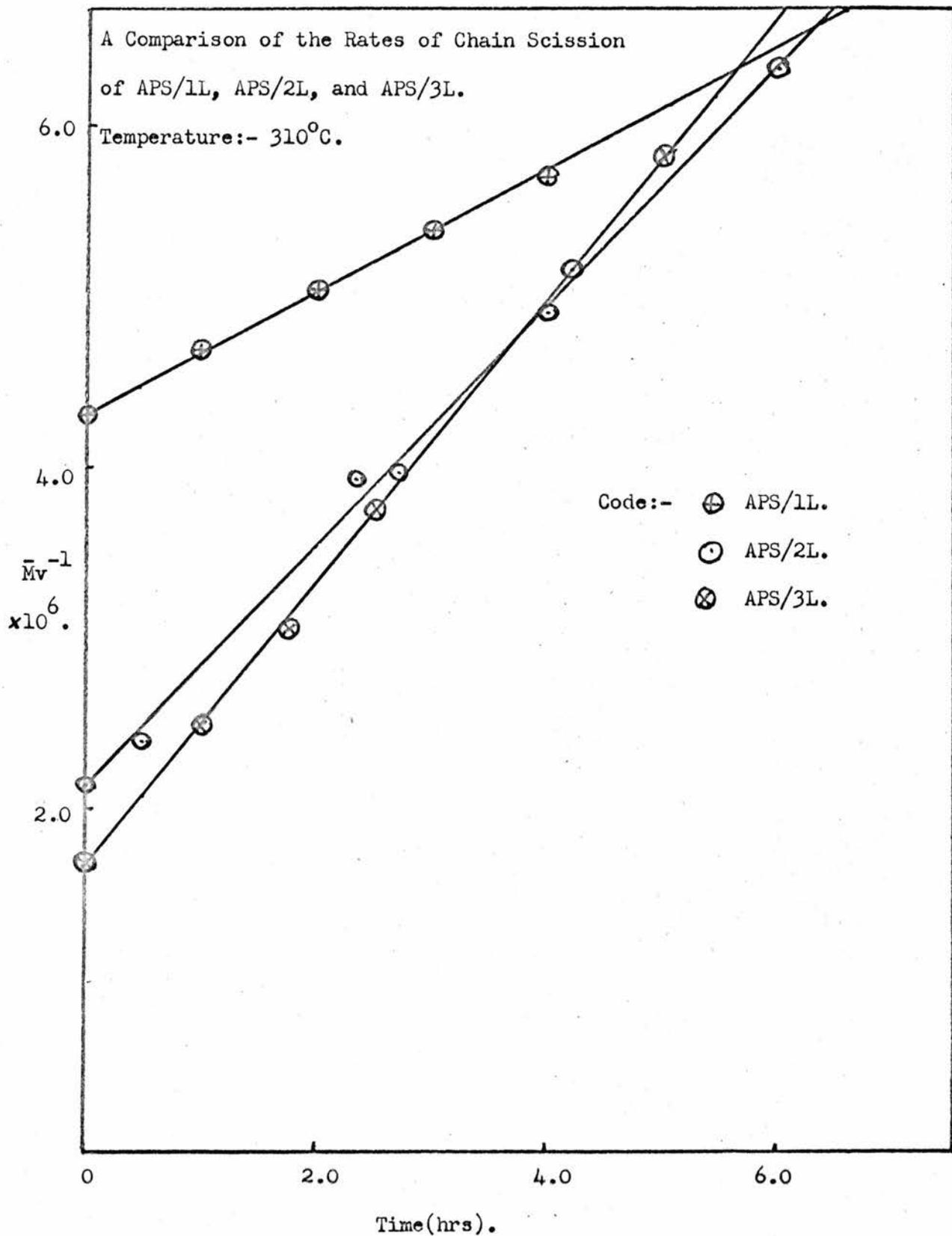
TABLE 8.

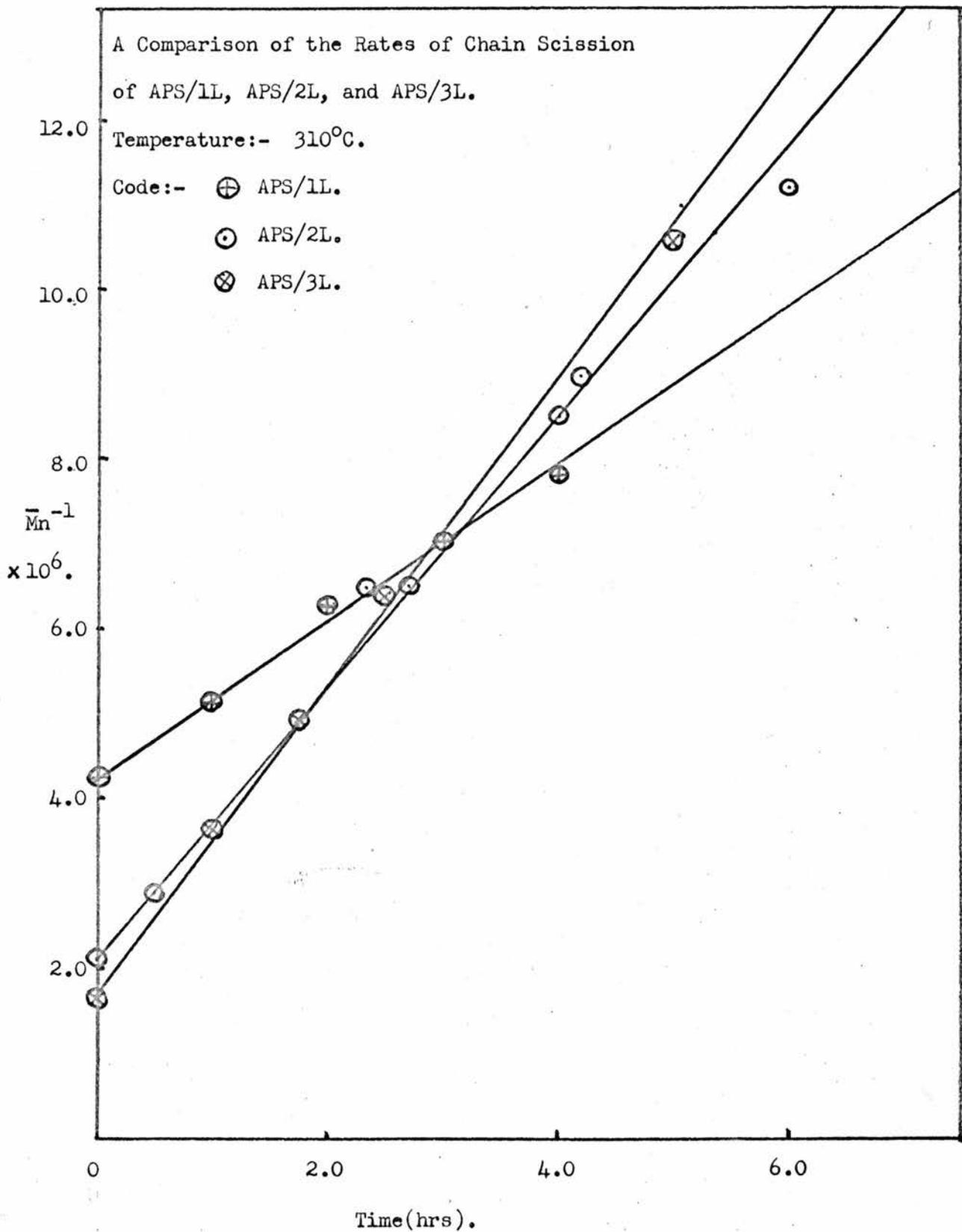
Thermal Degradation of APS/1L, APS/2L and APS/3L.

Molecular Weight Data.

Temperature:- 320°C.

Polymer.	Time. (hrs)	$[\eta]$	\bar{M}_v $\times 10^{-6}$	\bar{M}_v^{-1} $\times 10^6$	\bar{M}_n $\times 10^{-6}$	\bar{M}_n^{-1} $\times 10^6$	$\frac{\bar{M}_v}{\bar{M}_n}$	α
APS/1L.	-	0.93	0.233	4.287	0.233	4.287	1.000	0
	1.00	0.88	0.216	4.623	0.194	5.167	1.118	0.000090
	2.00	0.82	0.198	5.046	0.158	6.317	1.257	0.000217
	3.00	0.79	0.187	5.359	0.141	7.072	1.320	0.000290
	4.00	0.76	0.176	5.676	0.127	7.862	1.386	0.000375
APS/2L.	-	1.54	0.468	2.143	0.468	2.143	1.000	0
	0.50	1.42	0.416	2.405	0.351	2.851	1.186	0.000075
	2.33	0.99	0.255	3.926	0.154	6.494	1.634	0.000444
	2.70	0.98	0.252	3.972	0.153	6.519	1.640	0.000455
	4.00	0.84	0.204	4.909	0.117	8.534	1.732	0.000644
	4.20	0.81	0.193	5.176	0.111	9.009	1.747	0.000706
	6.00	0.70	0.158	6.325	0.089	11.300	1.795	0.000955
APS/3L.	-	1.84	0.593	1.686	0.593	1.686	1.000	0
	1.00	1.39	0.404	2.477	0.274	3.650	1.477	0.000207
	1.75	1.19	0.327	3.061	0.201	4.975	1.626	0.000341
	2.50	1.03	0.268	3.752	0.156	6.410	1.718	0.000491
	5.00	0.74	0.171	5.835	0.094	10.640	1.820	0.000926





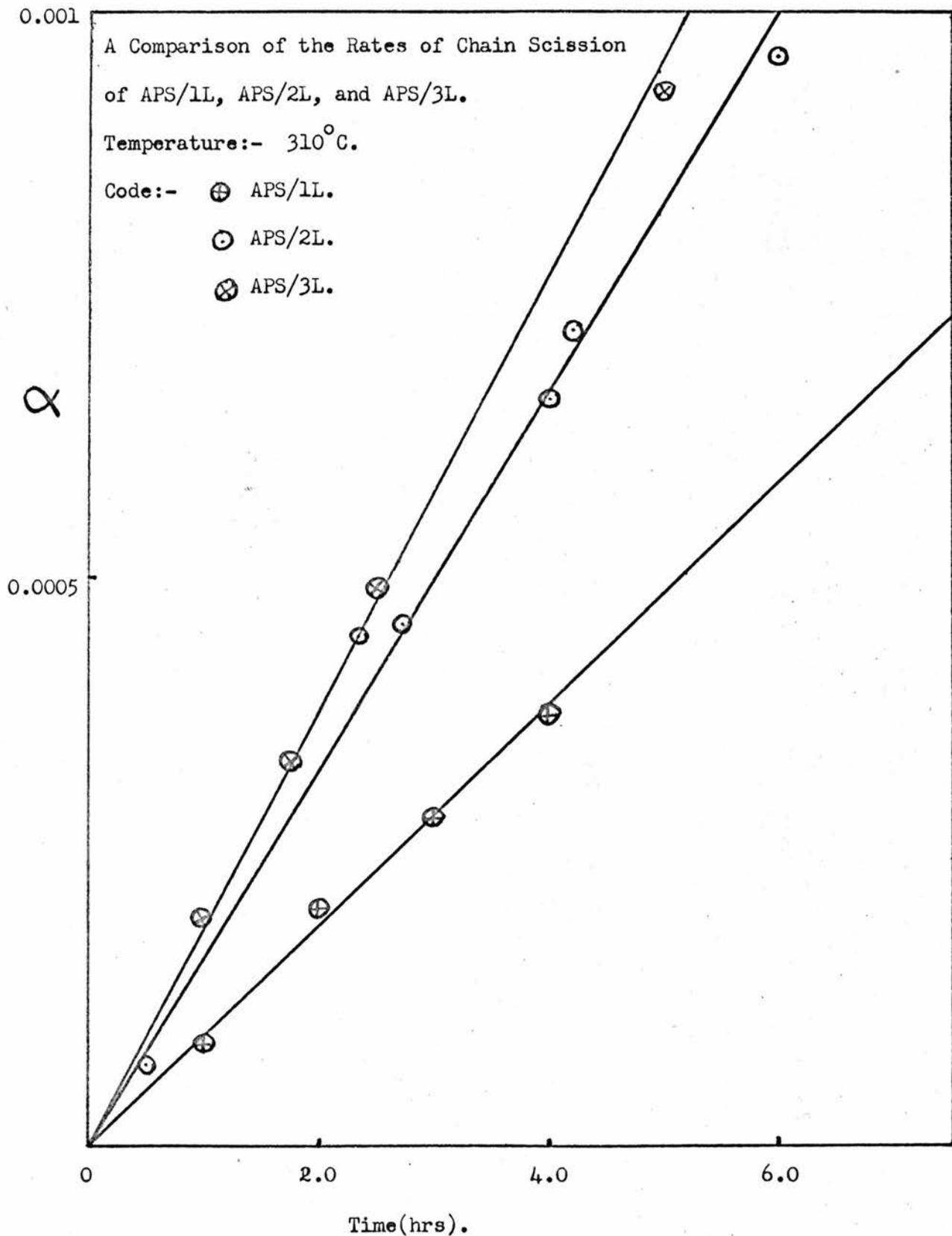
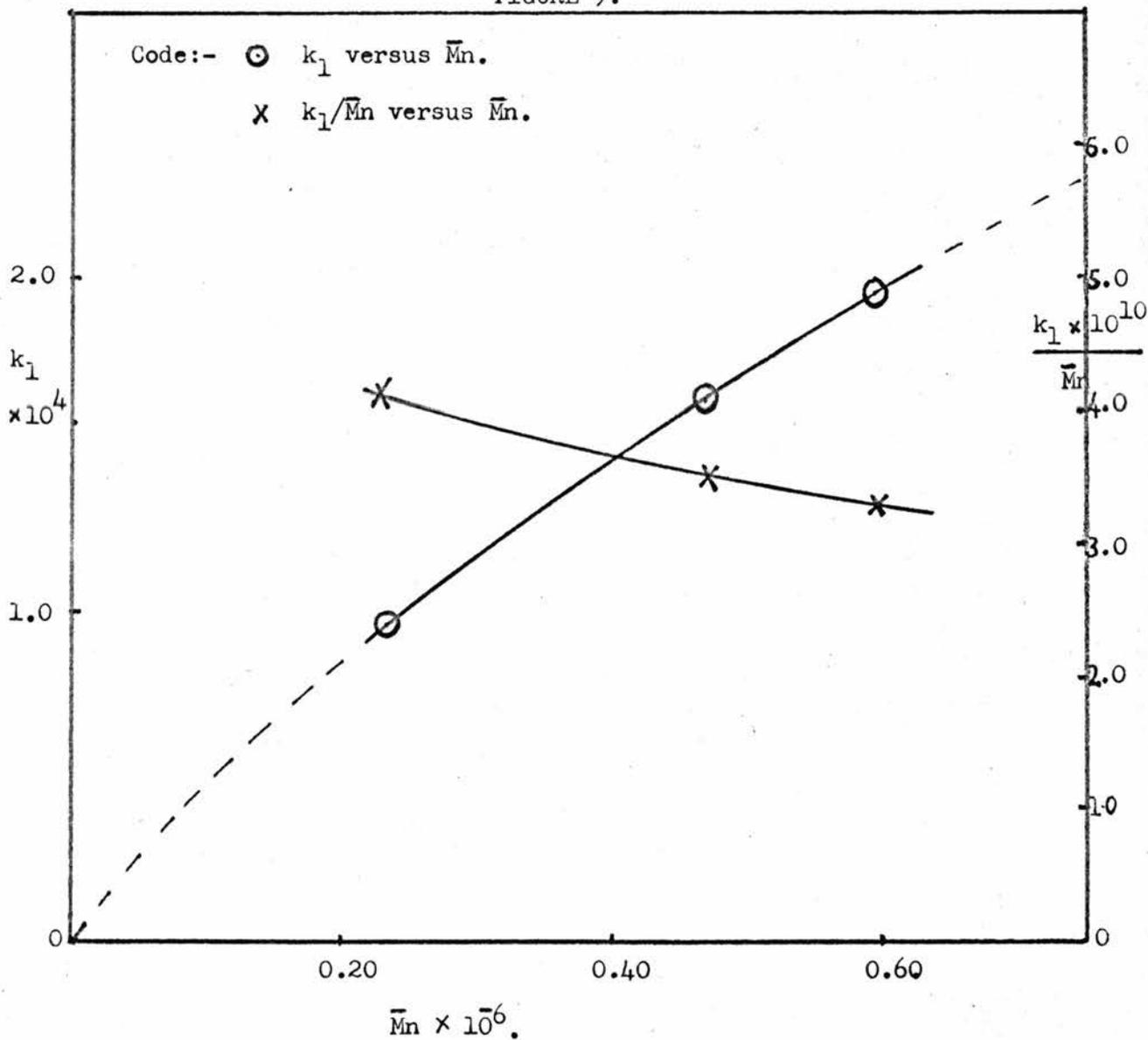


TABLE 9.

k_1 and the corresponding \bar{M}_n for the APS polymers.

Polymer.	$k_1 \times 10^4$. (hr ⁻¹).	Molecular Weight. \bar{M}_n .	$\frac{k_1 \times 10^{10}}{\bar{M}_n}$.
APS/1L.	0.960	233,000	4.120
APS/1L.	1.636	468,000	3.496
APS/3L.	1.946	593,000	3.281

FIGURE 9.



lower than for the latter.

The simple linear plot of α versus time for the A P S series of polymers shows that simple random cleavage of the polymer chains occurs. Furthermore, over the range of degradations studied in this work, there is no evidence in the α versus time plots of more than one type of bond rupture. However, the discrepancy between the two values of the Activation Energy of chain scission obtained for APS/IL and APS/3L is somewhat puzzling. Boon and Challa^{I3} have studied the degradation at sub-volatilisation temperatures of Ziegler - Natta polystyrenes of molecular weights between 340,000 and 600,000. For chain scission they found an Activation Energy of 39 kcal. mole.⁻¹, apparently invariant with molecular weight. Similarly Nakajima and collaborators^{I4} found an Activation Energy of 42 kcal. mole.⁻¹ for chain scission in a Ziegler - Natta polystyrene of molecular weight 364,000. The agreement between these two sets of data is very good. In the present work, under similar experimental conditions to those used by the above investigators, Activation Energies of 73 and 60 kcal. mole.⁻¹ have been found for anionic polystyrenes of molecular weights 233,000 and 593,000 respectively. Although an inverse dependence of the Activation Energy on molecular weight might be postulated from the experimental results described in the present study, it is impossible on this basis to explain the difference in Activation Energies between the A P S polymers and the anionic polystyrenes used by previous investigators^{I3,I4}, since both series

of polymers have comparable molecular weights and would, therefore, be expected to degrade with similar Activation Energies. The observed difference would appear to be due to differences in chemical structure between the "living" and the Ziegler - Natta anionic polystyrenes. This problem will be further discussed in the succeeding chapter.

At least part of the discrepancy found in the present study of the Activation Energies of chain scission in anionically prepared polymers, may be due to the incomplete removal of catalyst residues (potassium methoxide) formed by termination of the "living" anionic polymerisation with methanol, since Boon and Challa^{I3} have observed an increase of 3 kcal. mole⁻¹ in the Activation Energy of a polymer after reprecipitation from n - butanol. Accordingly, some catalyst may still be present in APS/3L and may be responsible for its lower Activation Energy of chain scission, although the magnitude of the difference in Activation Energy renders this explanation doubtful. The problem is made more obscure by the apparent dependence of the rate of chain scission on the molecular weight of the polymer. A similar increase in k_I with increasing molecular weight was found by Boon and Challa^{I3}, but they also showed that there was no dependence of Activation Energy on molecular weight. At present there is insufficient evidence to draw any hard and fast conclusions about this problem, but a simple dependence of the Activation Energy for chain scission on the molecular weight of the polymer seems improbable.

The average value for the Activation Energy of bond scission

in the anionic polystyrenes is approximately $67 \text{ kcal. mole}^{-1}$. This value is very close to the estimated dissociation energy of polystyrene backbone bonds ($64 \text{ kcal. mole}^{-1}$),^{I7} and is comparable to the strength of the analogous bond in the model compound ethyl benzene, $\text{PhCH}_2 - \text{CH}_3$.^{I8} Although no definite assertions can be made on this topic because of the difference in Activation Energy between the anionic homopolymers, it seems probable that the bonds rupturing in these polymers are the normal C - C backbone bonds in polystyrene. Accordingly, despite the complications of the obscure molecular weight effect, the data on the A P S polymers suggest that the initiation process occurs at random in the chain backbone. Further support for this postulate comes from a consideration of the mode of synthesis - "living" anionic polymerisation terminated by methanol - which precludes the formation of unstable chain ends. Indeed, it seems quite possible that a random initiation reaction followed by immediate mutual deactivation, possibly in a "cage"^{I9}, is responsible for the bond scissions observed during degradation. At this point, it is not possible to distinguish between pure random initiation and random initiation followed by transfer, since in both cases a similar plot of α versus time passing through the origin would result.

For the two thermally prepared polymers, the most striking feature of the degradation behaviour is the appearance of a substantial ordinate intercept in the α versus time plot. As this effect is

in clear contrast to the characteristic behaviour of the A P S polymers, it is vital to examine it closely in order to arrive at a sound interpretation. Possible sources of the intercept are:-

- (1) poor viscometry techniques or the wrong choice of Mark - Houwink equation,
 - (2) changes in the molecular weight distribution during degradation,
 - (3) intermolecular transfer,
- or (4) the scission of thermolabile structures in the polymer.

The first two effects can be immediately discounted because preliminary experiments using osmometry to obtain number average molecular weights directly also showed the same effect. Furthermore, although the A P S series of polymers may be more tactic than the T P S series, stereoregularity has been shown to have no effect on the validity of the Mark - Houwink equation ²⁰. Secondly, the theoretical treatment used for calculating α from viscosity data takes into account the changes in molecular weight distribution during degradation, and tests have shown that the values of \bar{M}_n obtained from this treatment correspond closely to the values of \bar{M}_n obtained directly by osmometry. Moreover, any molecular weight distribution effect occurring during degradation should be more prominent in the A P S series than in the T P S series, since the change in distribution is far greater in the former than in the latter. The possibility that the intercept results in some way from intermolecular transfer seems equally improbable since

both anionic and thermal polystyrenes, although probably differing in stereoregularity, contain equal concentrations of the tertiary hydrogen atoms known to be reactive in transfer reactions²¹.

Finally, therefore, there remains the possibility that, unlike the A P S polymers, the thermally initiated polystyrenes contain "weak links" which break down very rapidly in the early stages of the degradation. Strong evidence supporting this conclusion is the observed independence of the magnitude of the ordinate intercept on the temperature of degradation. This postulate of "weak links" supports the theories of Jellinek¹ and Grassie². However, the present method of detecting weak structures is much more sensitive and experimentally more rigorous than the procedures used by these authors, since Grassie would have concluded by his criterion (the initial sharp fall in molecular weight) that there were "weak bonds" in the anionic polymers investigated in the present study.

The results obtained for the thermal polymers in this work are closely in line with those of Flynn¹⁵ for the slow thermal degradation of polystyrene in tetralin at 253.5°C. Flynn discovered that at the onset of degradation there is a rapid decrease in viscosity, followed by a more gradual, linear decay over a period of days. The resultant plot of reciprocal Specific Viscosity versus time is very similar to Figure 4b for TPS/2 and TPS/3. As a possible explanation of the initial rapid bond scission phase, Flynn suggested the rupture of "weak links" present in the polymer at a concentration

of 0.11 per molecule. Thus, it seems that free-radically prepared polystyrenes contain minute concentrations of "weak bonds", whereas these highly thermolabile structures are absent from polymers prepared anionically by "living" and Ziegler-Natta catalysis.

The Energy of Activation of 49 kcal. mole⁻¹. for bond scission in the thermally prepared polystyrenes is markedly lower than found for the anionic polymers, but is in close agreement with the values obtained by Flynn¹⁵, Boon and Challa¹³ and Nakajima and coworkers¹⁴. It is, however, some 15 kcal. mole⁻¹. lower than estimated¹⁷ for the bond dissociation energy of the C - C backbone bonds in polystyrene. The effect of this lower Activation Energy is apparent in the reduced thermal stability of the thermally prepared polymers investigated in this study, and a similar observation has recently been made by Richards and Salter²². M^cNeill²³ has recently observed that a small shoulder appears at ~ 273°C. in the Thermal Volatilisation Analysis curves for free-radically prepared polystyrenes, whereas anionic and cationic polymers only exhibit the main volatilisation peak at ~ 410°C. This is evidence that the free-radically synthesised polymers undergo a low temperature degradation phase, which is not exhibited in any other type of polystyrene.

From the data currently available, therefore, thermally prepared polystyrenes appear to be less thermo-stable than anionic polymers on two counts. Firstly, they exhibit an initial, very

rapid chain scission phase which is completed before the subsequent normal chain rupture begins. It has been shown in the above discussion that this initial phase is most probably due to "weak link" scission. Secondly, the subsequent "normal" chain scission reaction occurs with an Activation Energy which is some 15 kcal.mole⁻¹. lower than the estimated bond dissociation energy of C - C backbone bonds in polystyrene. This information, together with other qualitative observations, tends to suggest that other "weak bonds" of unknown type are breaking during the second stage of the degradation of thermal polystyrene. These conclusions, however, are based on rather tenuous evidence, which in turn is confused by the undefined molecular weight dependence of the rate of chain scission.

Since it is apparent that thermally prepared polystyrene contains at least one type of "weak link", further investigations must now be directed at elucidating the chemical structure of these bonds. With this aim, various abnormal structures were introduced into thermal polystyrenes, and their effect on the characteristic α versus time plot was studied. This work is described in the next chapter.

Chapter IVReferences

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CHAPTER VINVESTIGATIONS INTO THE NATURE OF THE "WEAK LINKS" IN THERMALLY
POLYMERISED POLYSTYRENES.

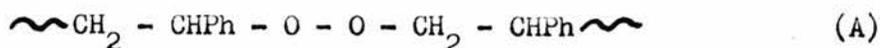
The investigations described in Chapter IV have established the existence of at least one type of "weak link" in thermal polystyrenes, but have produced no evidence on the specific nature of these thermolabile bonds. It seems most probable that the "weak links" are incorporated into the polymer by abnormal propagation steps, whose frequency will be enhanced by the relatively high temperatures employed in thermal polymerisation. Indeed, this type of dependence has previously been observed by Grassie and Kerr^I. It is now necessary to discuss the possible types of abnormal propagation step, and the effect of polymerisation variables on their concentration.

(I) Possible Abnormal Propagation Steps and the Structures

resulting from them.

(a) Incorporation of Oxygen.

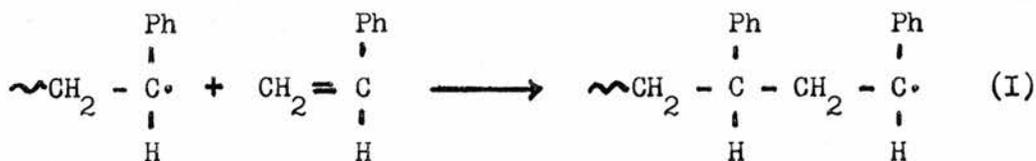
Oxygen is known to accelerate the polymerisation of styrene², but its entry into the polymer has not been established, although small amounts of carbon monoxide, presumably from oxygenated structures, have been found in the volatiles produced by pyrolysis of the polymer³. If oxygen does enter into the polymer, it seems most probable that it will copolymerise with styrene to form a polyperoxide⁴, A,



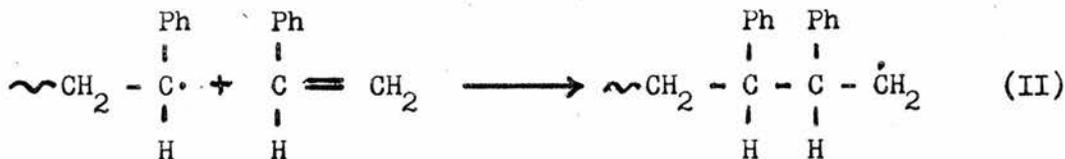
The central - O - O - bond will decompose readily on heating. Unfortunately, there is no indication available in the literature concerning the effect of the temperature of polymerisation on the amount of oxygen copolymerised into the polymer. Several investigators^{1,5,6} have found no significant differences in the degradation characteristics of polymers prepared in air and in vacuum, but these experiments were conducted at high volatilisation where any effect of an increased concentration of "weak bonds" may be obscured by subsequent depropagation reactions.

(b) Head to Head Bonds in the Polymer.

The normal addition of monomer to the growing polystyryl radical (or anion) occurs by a head to tail mechanism,⁷ i.e.



because of the very high resonance stabilisation of the radical end (I). An abnormal propagation step to form a head to head bond thus,

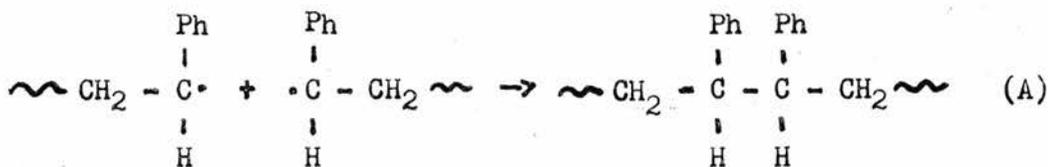


results in a macroradical (II) in which the possibility of delocalising the free electron no longer exists. Flory⁸ has pointed out, from a study of the bond strengths in similar model

compounds, that a benzyl radical of type (I) has a resonance stabilisation energy some 20-25 kcal. mole⁻¹. greater than the methyl type (II), and consequently, although the resonance energies in the transition state will be considerably less than in the product, an energy difference of some 10 kcal. mole⁻¹. favouring head to tail addition is expected.

Since an energy difference of this kind exists, it can readily be proved that an increase in the temperature of polymerisation favours the head to head addition of monomer at the expense of head to tail addition, although the latter reaction still greatly predominates. Because the concentration of head to head links in free - radical polystyrene appears to be very low, the probability of their formation in anionic polymers prepared at - 20°C. is virtually zero.

The free - radical polymerisation of styrene is known to be terminated by a bimolecular combination reaction, A,^{9,10,11}



so that at least one head to head link per molecule must be formed. This kind of termination step does not occur in the anionic polymerisation of styrene initiated by cumyl potassium.

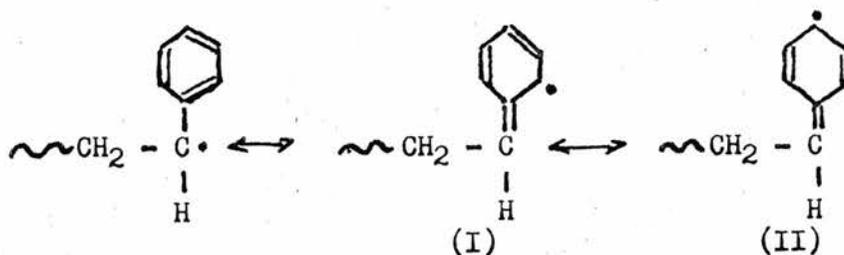
(c) Branching.

Branch points incorporated in polystyrene during

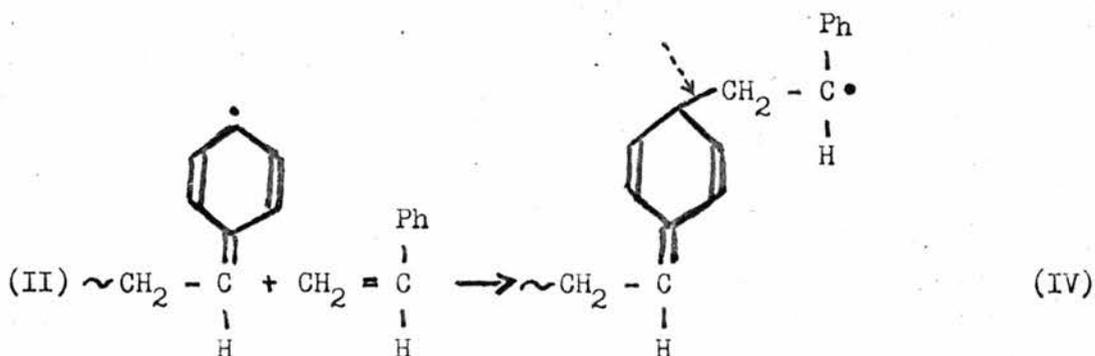
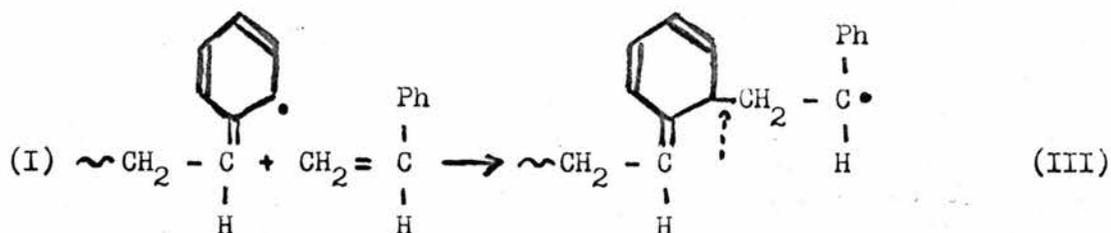
polymerisation may constitute reactive centres in the polymer by the creation of quaternary carbon atoms which have reduced bond strengths. However, Bevington, Guzman and Melville^{I2}, and Wall and Brown^{I3} have shown that the extent of branching in polystyrenes prepared by free - radical initiation at elevated temperatures is negligible. Branching during polymerisation of styrene occurs by transfer to polymer, a reaction which appears to have a slightly higher energy of activation (7.0 kcal. mole⁻¹)^{I2} than the competitive normal propagation step (6.3 kcal. mole⁻¹)^{I4,I5}, so that the former reaction is favoured by increased temperatures of polymerisation. Furthermore, branching increases rapidly with conversion to polymer, as has been shown in a simple theoretical treatment by Flory^{I6}.

(d) Internal Double Bonds.

Grassie and McNeill^{I7} have suggested that the ketene - imine unsaturation in poly (methacrylonitrile) is the result of polymerisation through an alternative, relatively uncommon, resonance form of the growing macroradical. Similarly, Cameron and Grassie^{I8} proposed that the polystyryl radical is capable of resonating into the canonical forms (I) and (II).



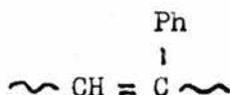
Subsequent addition of monomer to the macroradicals (I) and (II) results in the macroradicals (III) and (IV),



which contain backbone double bonds. Termination of the radicals (III) and (IV) produces polymer molecules which contain chain unsaturation. The single bonds indicated in structures (III) and (IV) are expected to be less stable than other C - C single bonds in the backbone of the polymer molecule because they are in a position β to two double bonds¹⁹. Cameron and Grassie¹⁸ have shown that the molecular weight of a free-radically prepared polystyrene, after ozonolysis, approximates very closely to the value associated with the completion of "weak link" scission in the same polymer degraded thermally at 335°C. From this result, it appeared that each backbone double bond was associated with a

thermolabile link, as required by the polymerisation mechanism discussed above.

Cameron and Grassie¹⁸ also considered the possible existence of the structure,



which may exist in polystyrene chains as a consequence of transfer between the polystyryl radical and the tertiary hydrogen atoms of inert polystyrene molecules. The radical formed by hydrogen abstraction may throw off a hydrogen atom from a main chain carbon atom to form a double bond. Since the rate of formation of the latter structures will depend upon the concentration of polymer in the polymerising system, their concentration in polymer chains should increase with conversion. The amount of "weak links" in polystyrene has not been found to have this dependence^I.

The probability of propagation through the other canonical forms of the polystyryl radical - to give double bonds in the chain backbone - will again depend directly on the temperature of polymerisation. Consequently, these structural abnormalities are not expected to exist in polystyrenes prepared by anionic synthesis.

Throughout this discussion, it has been stressed that high temperatures of polymerisation favour all abnormal types of propagation reaction. Anionically synthesised polymers, because of the low temperature of polymerisation, and the rigorous purity of

the reactants, seem unlikely to undergo these reactions, but thermally prepared polystyrenes may well contain appreciable concentrations of abnormal bonds because of the high polymerisation temperatures employed. The effect of the temperature of polymerisation on the chain scission of thermally synthesised polystyrenes will now be described.

(2) The Molecular Weight Changes in Polystyrenes prepared by Thermal Initiation at various temperatures.

Five polymers, prepared to 12.5% conversion at 45, 60, 60, 90 and 120°C. respectively, were available for investigation. A sixth, prepared to 60% conversion at 120°C. was also studied. The coding and characterisation of these polymers are given in Chapter II, Section D. All polymers were degraded at 287°C.; the relevant experimental data are listed in Table 1, and plotted in Figures 1a, b and c.

The effect of the temperature of polymerisation is shown most strikingly in Figure 1c, in which the size of the ordinate intercept increases with increasing temperature of polymerisation. If it is assumed that this intercept represents the fraction of "weak bonds" in the polymer, then clearly this fraction increases with increasing polymerisation temperature. The fraction of "weak links" in the polymers is tabulated in Table 2, and plotted as a function of the polymerisation temperature in Figure 2. A linear relationship appears to obtain, which is strong evidence in favour of the

TABLE 1.

Molecular Weight Changes in TPS Homopolymers Degraded at 287°C.

Polymer.	Time. (hrs)	$[\eta]$	\bar{M}_v $\times 10^{-6}$	\bar{M}_v^{-1} $\times 10^6$	\bar{M}_n $\times 10^{-6}$	\bar{M}_n^{-1} $\times 10^6$	$\frac{\bar{M}_v}{\bar{M}_n}$	α
TPS/1.	-	5.05	2.382	0.420	1.659	0.603	1.436	0
	1.33	3.44	1.406	0.711	0.836	1.199	1.682	0.000062
	1.50	3.38	1.374	0.728	0.814	1.229	1.689	0.000065
	2.00	2.93	1.122	0.891	0.645	1.551	1.740	0.000092
	3.00	2.86	1.094	0.914	0.612	1.634	1.747	0.000116
	5.00	2.64	0.975	1.026	0.551	1.814	1.769	0.000125
	6.00	2.38	0.845	1.183	0.472	2.120	1.793	0.000157
	8.00	2.19	0.757	1.322	0.418	2.391	1.810	0.000185
TPS/2.	-	4.74	2.183	0.458	1.520	0.658	1.436	0
	2.00	1.79	0.571	1.753	0.312	3.202	1.830	0.000260
	4.00	1.43	0.421	2.377	0.228	4.389	1.847	0.000386
	6.00	1.27	0.357	2.805	0.192	5.200	1.854	0.000470
	8.00	1.07	0.283	3.540	0.152	6.589	1.861	0.000614
TPS/3.	-	3.60	1.496	0.668	1.042	0.960	1.436	0
	2.17	2.34	0.830	1.207	0.488	2.051	1.703	0.000113
	4.00	2.17	0.745	1.343	0.431	2.320	1.728	0.000140
	6.08	2.022	0.676	1.479	0.386	2.594	1.750	0.000170
	8.00	1.90	0.622	1.607	0.352	2.838	1.766	0.000195

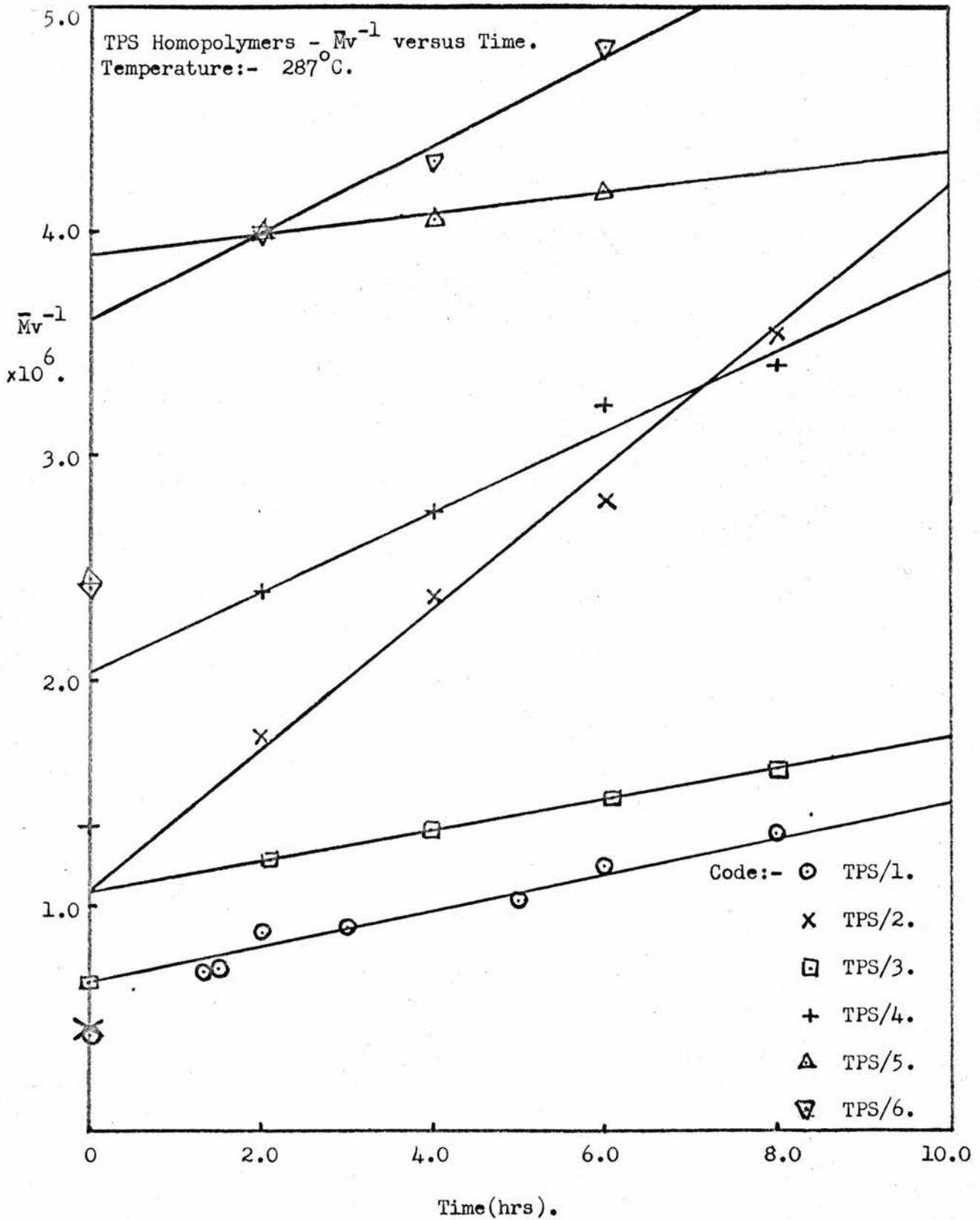
(Continued.)

TABLE 1 (Continued).

Polymer.	Time. (hrs)	$[\eta]$	\bar{M}_v $\times 10^{-6}$	\bar{M}_v^{-1} $\times 10^6$	\bar{M}_n $\times 10^{-6}$	\bar{M}_n^{-1} $\times 10^6$	$\frac{\bar{M}_v}{\bar{M}_n}$	α
TPS/4.	-	2.08	0.735	1.361	0.515	1.942	1.430	0
	2.00	1.37	0.417	2.399	0.280	3.567	1.490	0.000169
	4.00	1.24	0.363	2.756	0.233	4.294	1.552	0.000244
	6.00	1.10	0.311	3.220	0.192	5.220	1.621	0.000340
	8.00	1.06	0.294	3.397	0.174	5.747	1.691	0.000386
TPS/5.	-	1.35	0.408	2.449	0.233	4.292	1.750	0
	2.00	0.94	0.250	4.000	0.173	5.780	1.445	0.000155
	4.00	0.93	0.246	4.065	0.164	6.112	1.538	0.000188
	6.00	0.91	0.238	4.188	0.156	6.406	1.531	0.000221
TPS/6.	-	1.37	0.415	2.410	0.254	3.941	1.640	0
	2.00	0.94	0.250	4.000	0.168	5.945	1.486	0.000210
	4.00	0.89	0.231	4.333	0.141	7.103	1.642	0.000328
	6.00	0.82	0.207	4.831	0.128	7.831	1.620	0.000403
	8.00	0.78	0.193	5.176	0.112	8.951	1.728	0.000520

N.B. In this table number average molecular weights for degraded samples of homopolymers TPS/1, TPS/2 and TPS/3 were obtained from Intrinsic Viscosities by the relationship previously discussed. (Chapter III). Number average molecular weights for TPS/4, TPS/5 and TPS/6 were measured by osmometry.

FIGURE 1a.



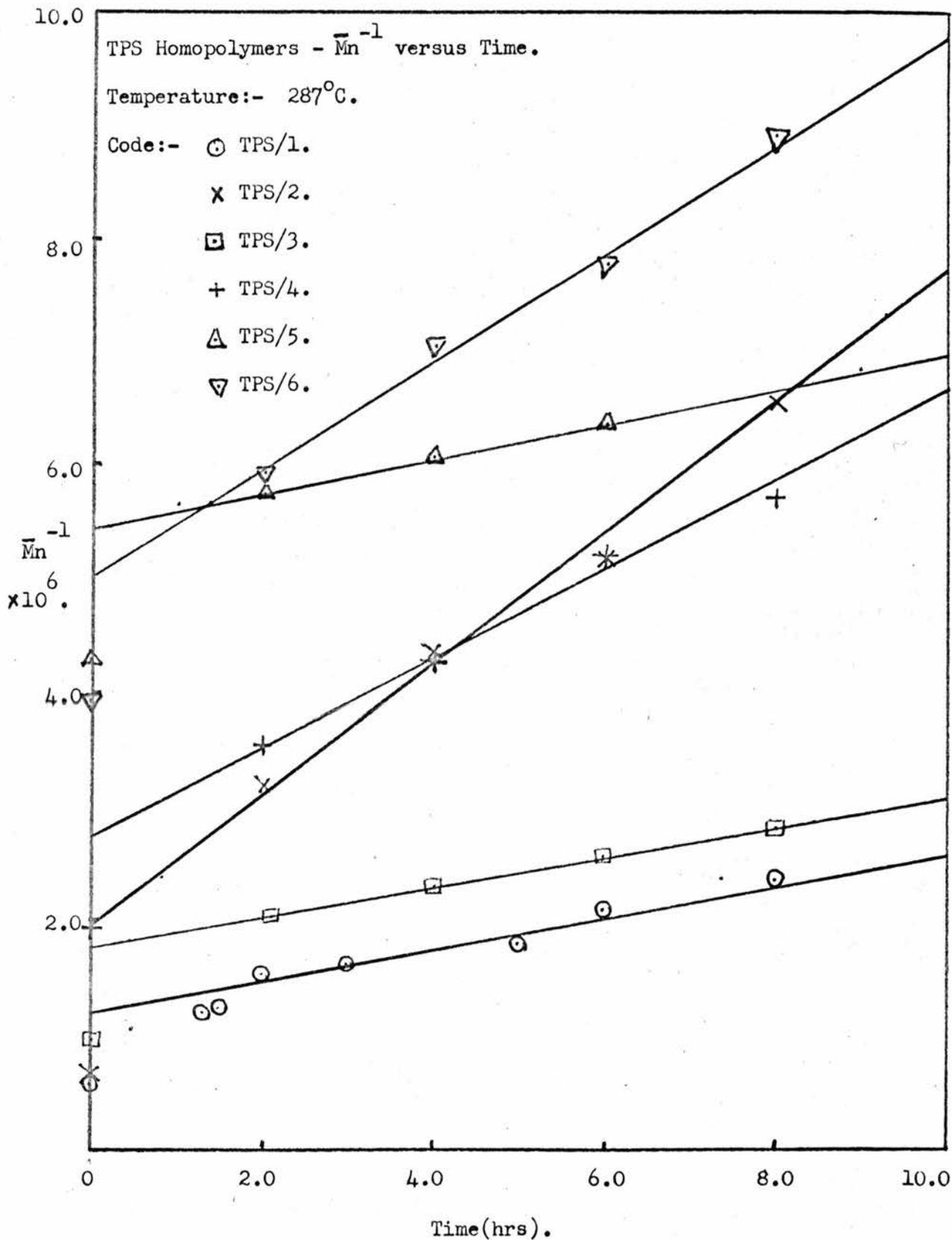
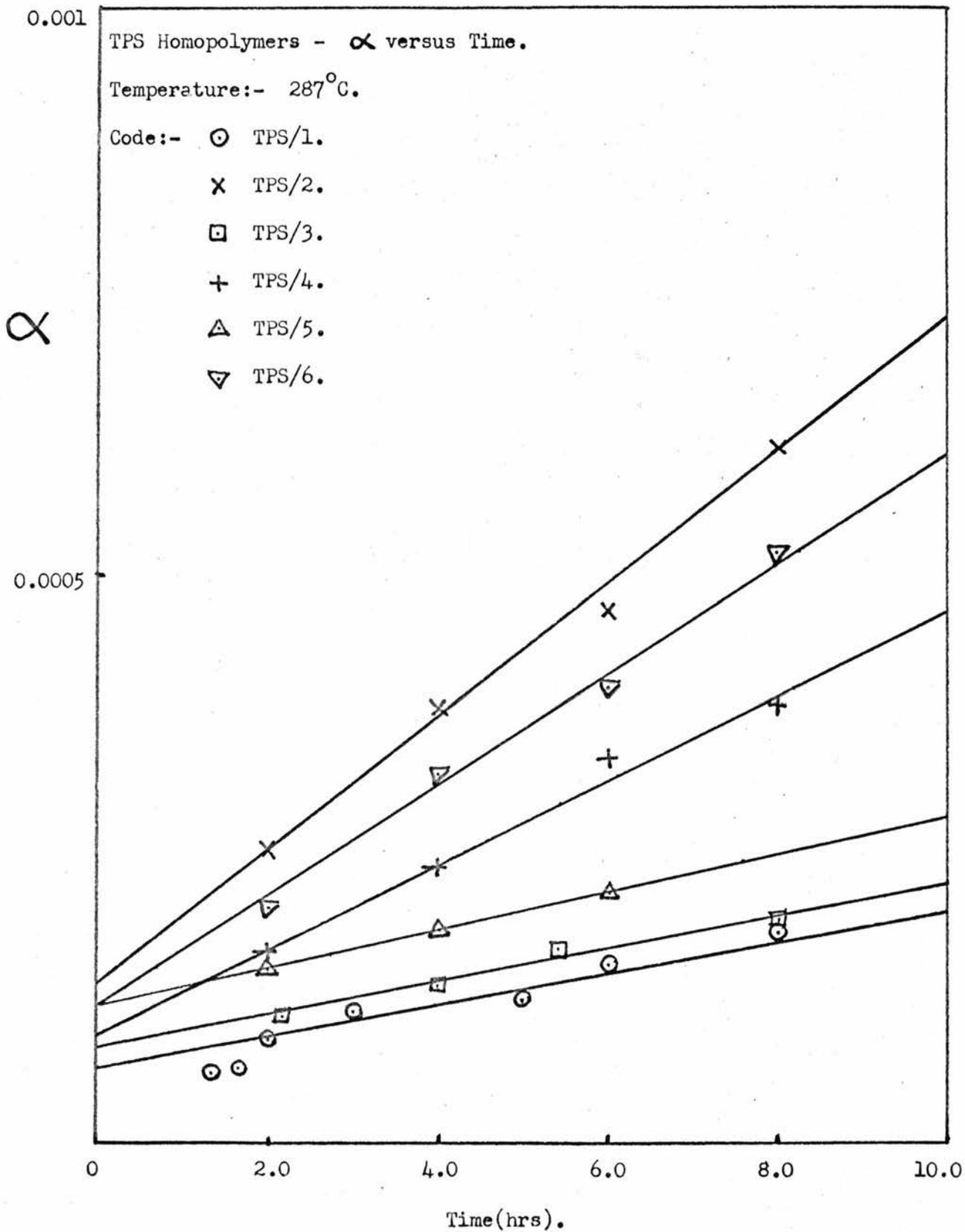


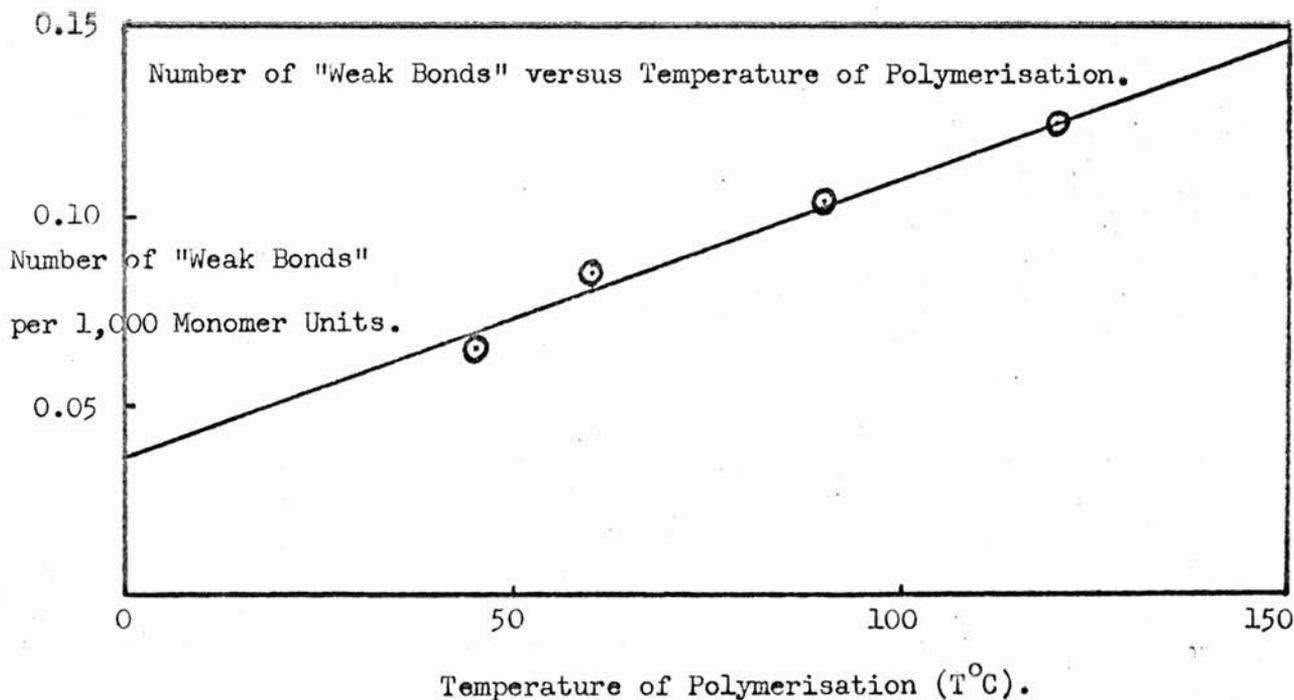
FIGURE 1c.



The Concentrations of "Weak Bonds" in the TPS Homopolymers.

Polymer.	Temp. of Polym ⁿ . T°C.	Fraction of "Weak Bonds" per molecule.	Number of "Weak Bonds" per molecule.	Number of "Weak Bonds" per 1,000 monomer units	$k_1 \times 10^4$ hr ⁻¹ .
TPS/1.	45	0.000068	1.0848	0.068	0.148
TPS/2.	60	0.000143	2.0890	0.143	0.586
TPS/3.	60	0.000085	0.8515	0.085	0.148
TPS/4.	90	0.000103	0.5100	0.103	0.362
TPS/5.	120 (12% conv.)	0.000122	0.2734	0.122	0.165
TPS/6.	120 (60% conv.)	0.000122	0.2980	0.122	0.486

FIGURE 2.



validity of the assumption . Homopolymer TPS/2 appears to be an exception to this rule but reference to the rates of polymerisation of polymers TPS/2 and TPS/3 and various copolymers at 60°C. indicates that the rate of polymerisation of TPS/2 was abnormally high. Further comparison with similar polymerisation data obtained by Mayo²⁰ reinforces this conclusion, and provides a plausible explanation for the anomalous pyrolysis behaviour (see later).

Homopolymers TPS/5 and TPS/6 were prepared at 120°C. to 12.5 and 60% conversion respectively. Flory¹⁶ has shown that the probability of branching in a polymer increases greatly with increasing conversion, yet both polymers appear to contain the same fraction of "weak links". Obviously, branch points are not the highly thermolabile structures in the polymers.

The slopes of the α versus time plots in Figure 1c bear no obvious relationship to the temperature of polymerisation, at first sight. However, these slopes have been shown in the previous chapter to depend directly on the molecular weight of the polymer, and, as the molecular weights of the thermal polymers decrease with increasing temperature of polymerisation, the rates of chain scission should decrease with increasing polymerisation temperature if only a molecular weight effect is active. As Table 2 indicates, the rate of bond scission increases with temperature despite the molecular weight effect. Accordingly, this tendency implies that increased amounts of a second thermolabile structure are incorporated

into the polymer by increased polymerisation temperatures. These structures are more thermostable than the links whose rupture constitutes the first phase of chain scission, but are less thermostable than the normal backbone bonds. The alternative explanation that the bond dissociation energy of normal backbone bonds depends on the temperature of polymerisation is untenable on thermodynamical considerations. Unfortunately, the molecular weight dependence of the rate of chain scission in thermal polystyrenes is inadequately characterised to allow a more explicit definition of the relationship between the rate of bond rupture and the temperature of polymerisation.

It is relevant at this juncture to compare the rates of bond scission in TPS/5 and TPS/4 which are similar in respect of molecular weight to the anionic homopolymers APS/1L and APS/3L respectively. These data are tabulated in Table 2a.

TABLE 2a.

Comparison of the Rates of Bond Scission in Thermal and Anionic Polystyrenes of similar Molecular Weights.

Temperature :-	Polymer.	$\bar{M}_n \times 10^{-6}$	$k_p \times 10^4$
287°C.	TPS/5	0.233	0.165
	APS/1L	0.233	0.046
	TPS/4	0.515	0.362
	APS/3L	0.593	0.251

In both of these comparisons, the thermal polymer degrades faster

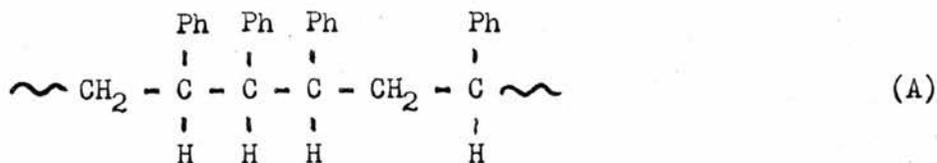
than the comparable anionic polystyrene. The data is rather scant, but is the only direct comparison available of the rates of chain scission in the two types of polystyrene.

Homopolymer TPS/6, prepared to 60% conversion, exhibits a faster rate of bond scission than TPS/5 which was prepared to 12.5% conversion, although both polymers have very similar molecular weights. As indicated in Section Ic of this chapter, the extent of branching in polystyrene increases greatly in polymers prepared to high conversion, so that TPS/6 should contain many more branches than TPS/5. On this basis, branch points might be responsible, at least in part, for the variations in the rate constant, k_T , for bond scission among the T P S polymers. However, it seems unlikely that there are sufficient of these abnormalities in polymers prepared at 60°C. to low conversion^{12,13} to account for the low Activation Energy of chain scission in polystyrenes prepared by thermal initiation. Accordingly, other possible structures such as head to head links or double bonds must now be considered.

(3) The Molecular Weight Changes in Styrene - Stilbene Copolymers.

21

Cameron and Grassie have studied the effect on the molecular weight fall in polystyrene of small amounts of stilbene copolymerised into the polymer. Incorporation of Stilbene into the polystyrene probably provides units of the type A,



which are analogous to the structures B,



formed in polystyrene by a head to head polymerisation step. If head to head links are thermolabile, copolymers of styrene and stilbene should show a dependence of the molecular weight fall on the amounts of stilbene copolymerised into the polymer. Under conditions of high volatilisation, Cameron and Grassie found no such dependence, and concluded that head to head links are not weak. However, under their reaction conditions, unzipping, distillation of small fragments, and transfer reactions, if the latter occur, could mask the effect of any initial "weak link" scission on the molecular weights of degraded polymers. Accordingly, it was considered important to reinvestigate this feature, especially since thermally prepared polystyrenes should contain at least one head to head link from termination by combination during polymerisation.

(a) The Thermal Degradation of Copolymer TPSS/I.

TPSS/I was degraded at several temperatures between 270° and 294° C.. The relevant data are tabulated in Table 3 and plotted in Figures 3a,b and c.

As with the thermally prepared polystyrenes, a linear dependence of α and reciprocal \bar{M}_v and \bar{M}_n on time is found. In addition, positive intercepts are again found. However, comparison

TABLE 3.

Thermal Degradation of TPSS/1.

Molecular Weight Data.

Temp. T°C.	Time. (hrs)	$[\eta]$	\bar{M}_v $\times 10^{-6}$	\bar{M}_v^{-1} $\times 10^6$	\bar{M}_n $\times 10^{-6}$	\bar{M}_n^{-1} $\times 10^6$	$\frac{\bar{M}_v}{\bar{M}_n}$	α
-	-	3.44	1.406	0.711	0.979	1.021	1.436	0
294	0.50	1.73	0.547	1.828	0.308	3.247	1.776	0.000232
294	1.03	1.41	0.413	2.421	0.228	4.395	1.815	0.000351
294	1.50	1.01	0.263	3.802	0.142	7.027	1.848	0.000630
294	2.00	0.93	0.234	4.276	0.126	7.924	1.853	0.000720
294	2.50	0.83	0.200	5.000	0.108	9.269	1.858	0.000863
294	3.00	0.77	0.181	5.535	0.097	10.300	1.861	0.000970
287	1.00	1.64	0.509	1.966	0.285	3.513	1.789	0.000260
287	2.00	1.23	0.343	2.917	0.187	5.345	1.832	0.000450
287	3.00	1.08	0.286	3.519	0.155	6.448	1.843	0.000563
287	4.00	0.91	0.228	4.386	0.123	8.130	1.854	0.000746
280	1.50	1.88	0.611	1.637	0.347	2.879	1.759	0.000192
280	1.50	1.97	0.655	1.528	0.376	2.663	1.743	0.000171
280	3.10	1.41	0.412	2.426	0.227	4.407	1.816	0.000351
280	5.00	1.18	0.322	3.105	0.175	5.701	1.836	0.000484
280	7.10	1.02	0.266	3.767	0.144	6.958	1.847	0.000620
280	9.00	0.88	0.216	4.623	0.117	8.575	1.855	0.000787
275	2.50	1.78	0.566	1.761	0.319	3.130	1.772	0.000218
275	5.00	1.44	0.425	2.355	0.235	4.265	1.811	0.000338
275	7.50	1.12	0.302	3.311	0.164	6.094	1.840	0.000530
275	9.50	1.06	0.281	3.577	0.152	6.579	1.845	0.000582

TABLE 3 (Continued).

Temp. T°C.	Time. (hrs)	$[\eta]$	\bar{M}_v $\times 10^{-6}$	\bar{M}_v^{-1} $\times 10^6$	\bar{M}_n $\times 10^{-6}$	\bar{M}_n^{-1} $\times 10^6$	$\frac{\bar{M}_v}{\bar{M}_n}$	α
270	2.00	2.26	0.785	1.274	0.462	2.164	1.699	0.000113
270	3.00	2.06	0.693	1.442	0.401	2.496	1.731	0.000154
270	4.00	1.81	0.579	1.726	0.328	3.067	1.767	0.000210
270	6.00	1.69	0.533	1.875	0.299	3.340	1.781	0.000244
270	7.00	1.59	0.486	2.056	0.271	3.689	1.794	0.000276
270	7.00	1.50	0.450	2.231	0.249	4.013	1.805	0.000312
270	9.00	1.42	0.417	2.399	0.230	4.348	1.813	0.000346

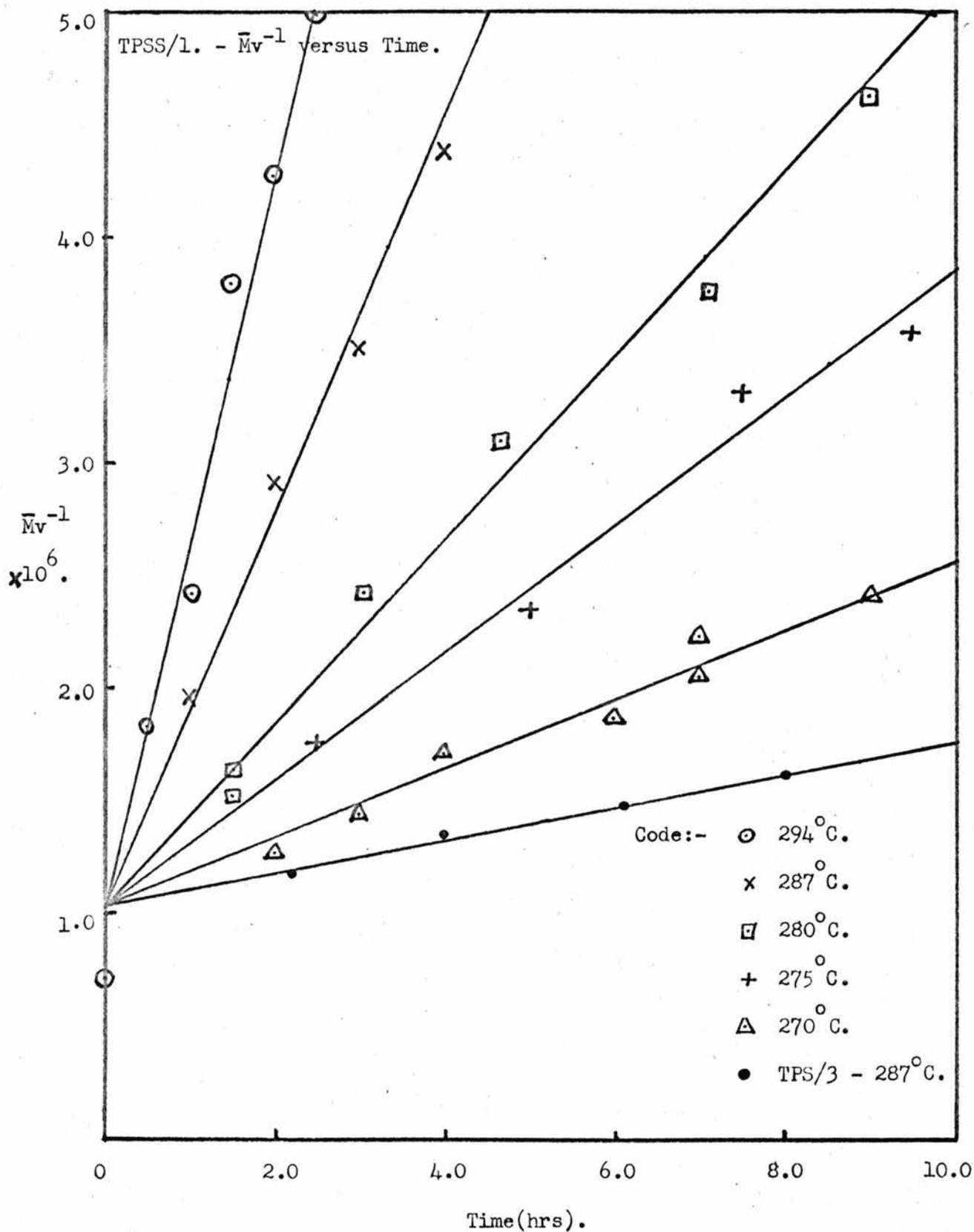
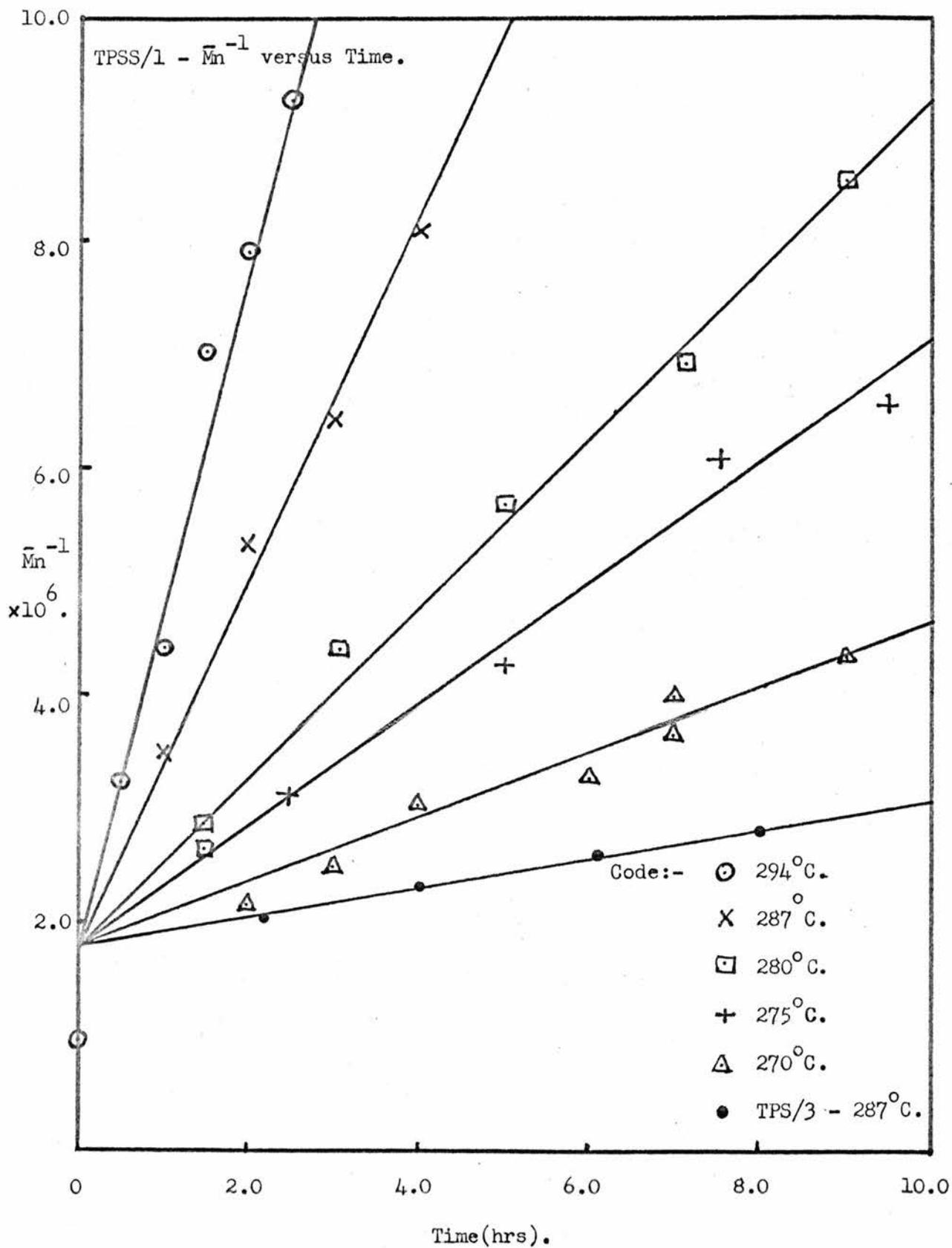
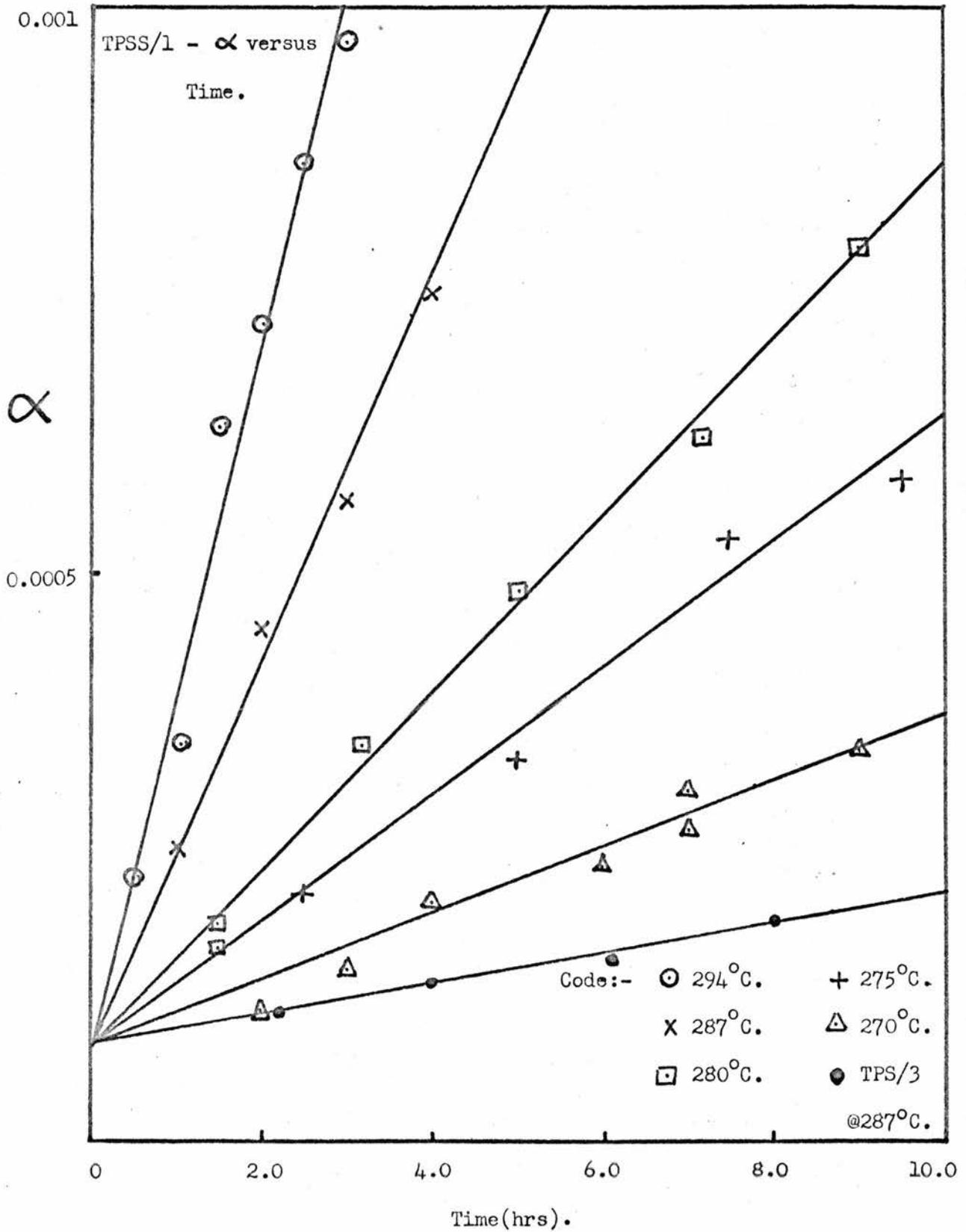
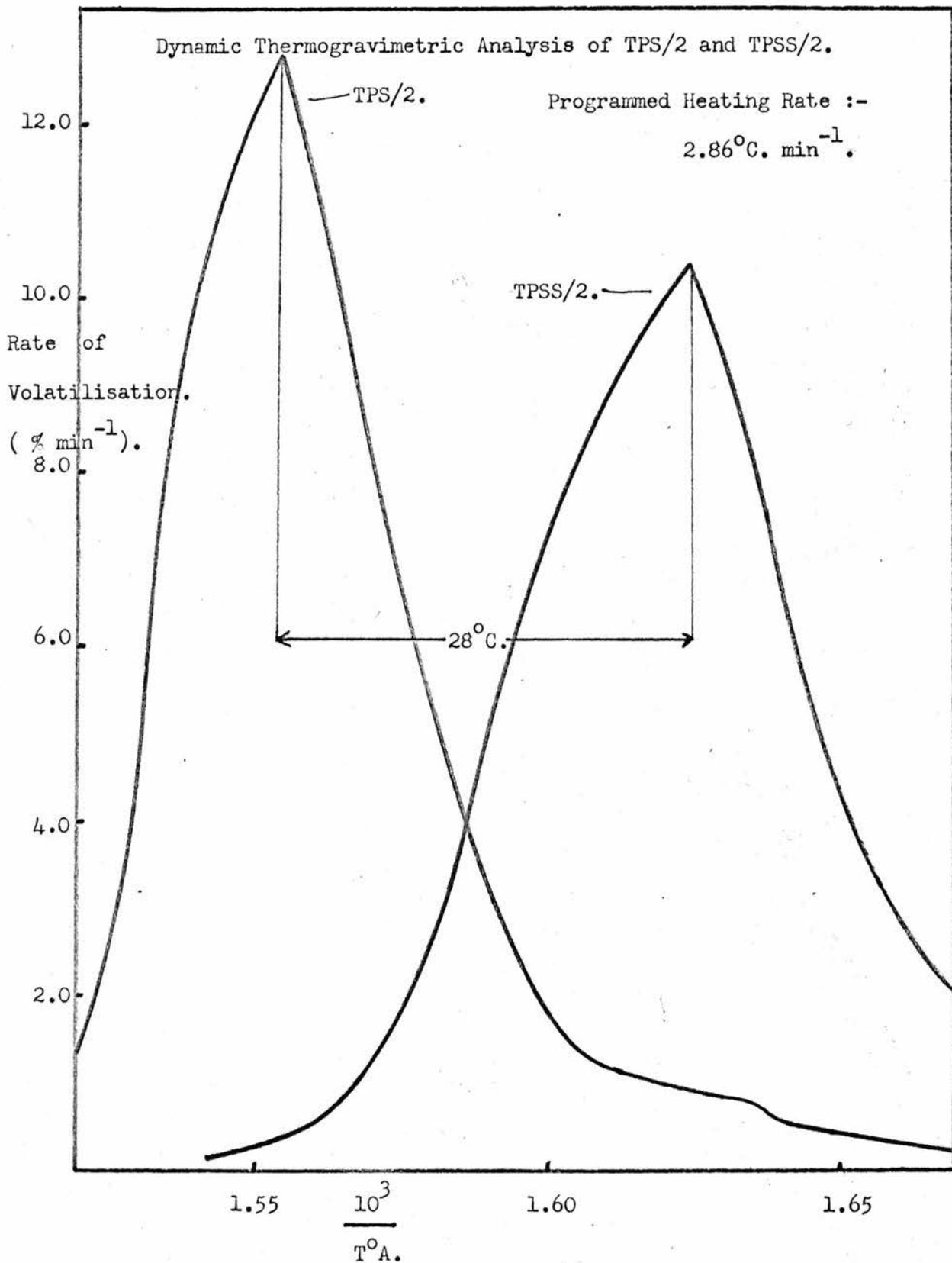


FIGURE 3b.







of the α versus time plot (Figure 3c) for TPSS/I with that of homopolymer TPS/3, of similar molecular weight and likewise prepared at 60°C., shows that both polymers give the same intercept at $t = 0$. This is incontrovertible evidence that head to head bonds are not responsible for the intercept on the α against time plots for polystyrenes. However, comparison of the rate of chain scission at 287°C. of TPS/3 and TPSS/I indicates that the copolymer degrades some ten times more rapidly than the homopolymer. Programmed temperature degradations on the Thermobalance confirm this increased thermal instability of the copolymers. Figure 3d indicates that TPSS/I begins to degrade some 28°C. lower than another comparable homopolymer TPS/2. Richards and Salter²² have also observed that head to head bonds, introduced into polystyrenes prepared by "living" anionic synthesis, reduced the thermal stability of the polymer. Therefore, it appears that head to head links in polystyrenes do not affect the intercept on the α against time plot, but do increase the rate of chain scission. To test this hypothesis, degradations were effected on three copolymers, TPSS/I, TPSS/3 and TPSS/5, of increasing stilbene content, and a dependence was sought between the rate of chain scission and the stilbene content of the copolymer.

(b) The Thermal Degradation of Copolymers TPSS/I, TPSS/3 and TPSS/5.

Degradations were effected at 280°C., and the relevant data is tabulated in Table 4 and plotted in Figures 4a,b and c.

Figure 4c clearly indicates that the ordinate intercept

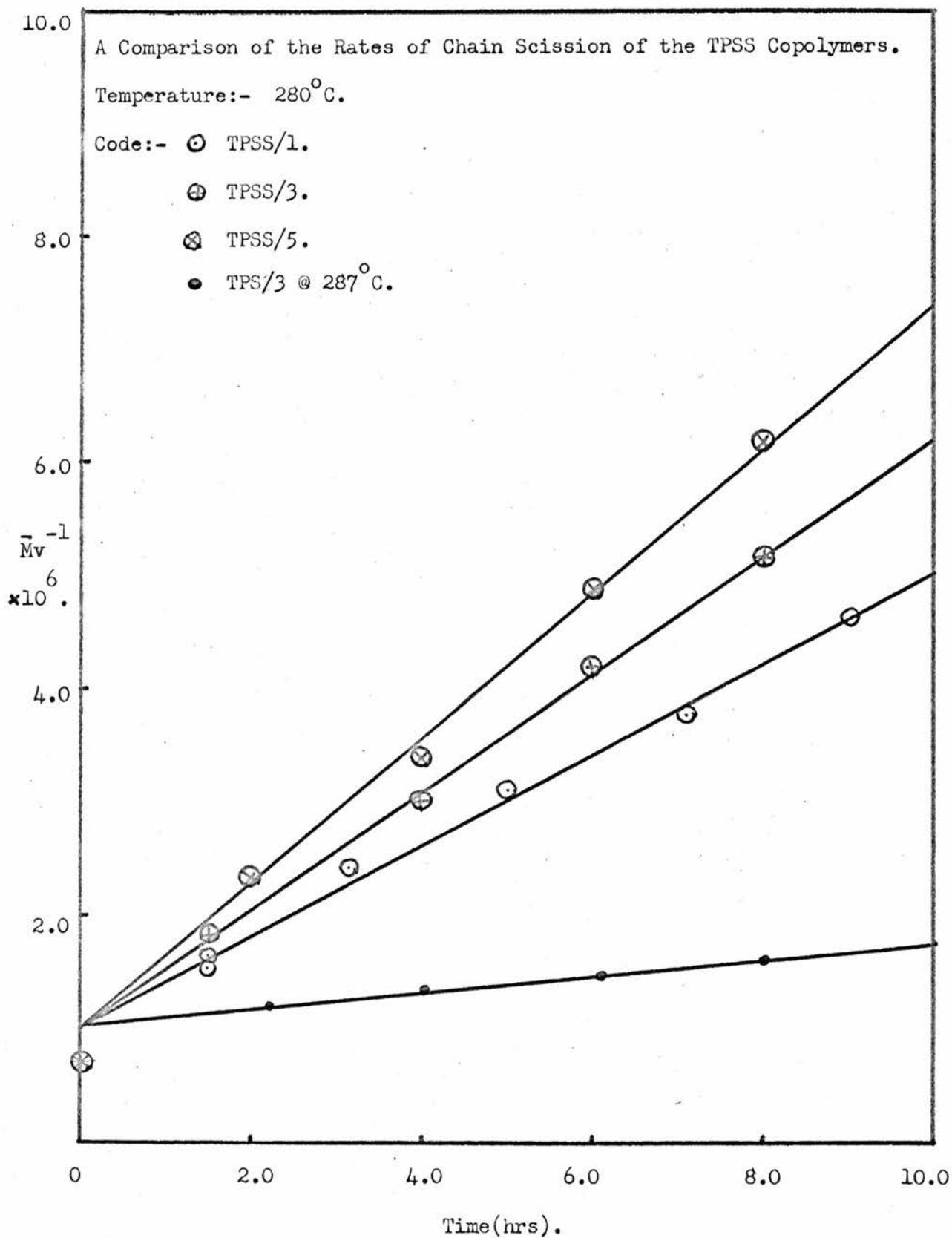
TABLE 4.

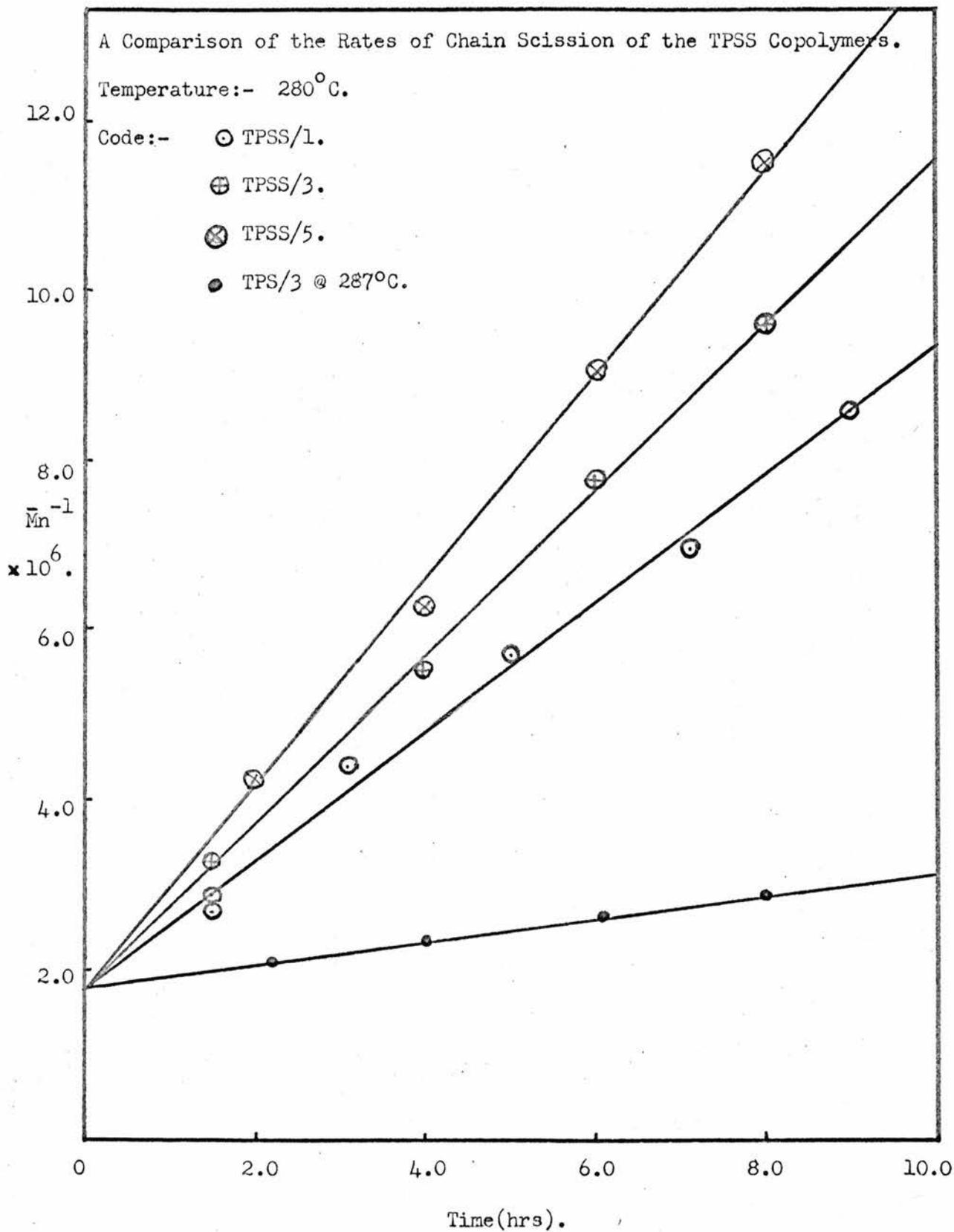
Thermal Degradation of Copolymers TPSS/1, TPSS/3 and TPSS/5.

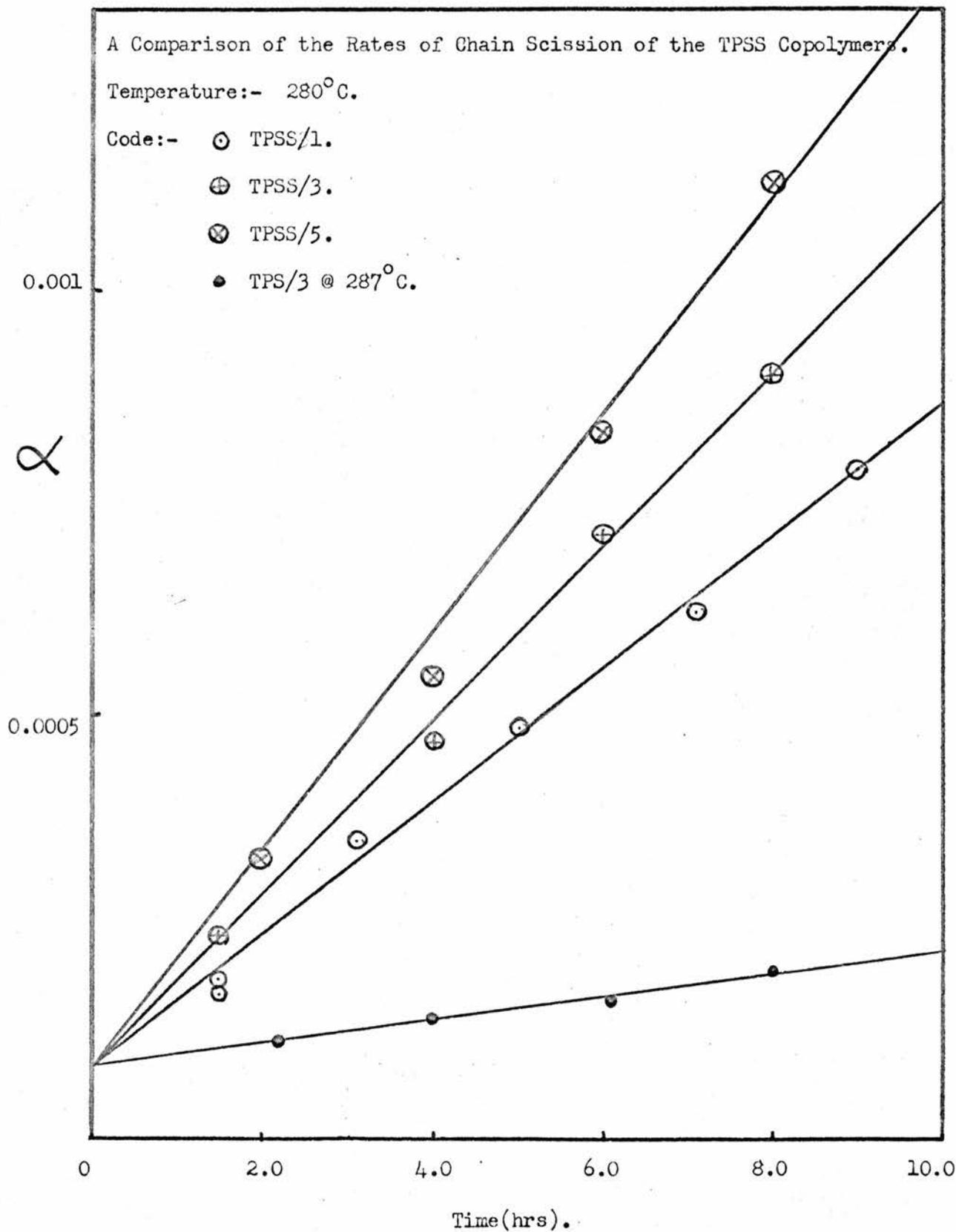
Temperature:- 280°C.

Polymer.	Time. (hrs)	$[\eta]$	\bar{M}_v $\times 10^{-6}$	\bar{M}_v^{-1} $\times 10^6$	\bar{M}_n $\times 10^{-6}$	\bar{M}_n^{-1} $\times 10^6$	$\frac{\bar{M}_v}{\bar{M}_n}$	α
TPSS/1.	-	3.44	1.406	0.711	0.979	1.021	1.436	0
	1.50	1.88	0.611	1.637	0.347	2.879	1.759	0.000192
	1.50	1.97	0.655	1.528	0.376	2.663	1.743	0.000171
	3.10	1.41	0.412	2.426	0.227	4.407	1.816	0.000351
	5.00	1.18	0.322	3.105	0.175	5.701	1.836	0.000484
	7.10	1.02	0.266	3.767	0.144	6.958	1.847	0.000620
	9.00	0.88	0.216	4.623	0.117	8.575	1.855	0.000787
TPSS/3.	-	3.46	1.419	0.705	0.988	1.012	1.436	0
	1.50	1.74	0.543	1.842	0.305	3.279	1.780	0.000241
	4.00	1.20	0.332	3.015	0.181	5.525	1.836	0.000468
	6.00	0.94	0.239	4.190	0.129	7.752	1.853	0.000712
	8.00	0.81	0.194	5.155	0.104	9.615	1.860	0.000900
TPSS/5.	-	3.40	1.384	0.723	0.964	1.037	1.436	0
	2.00	1.45	0.428	2.339	0.236	4.230	1.809	0.000330
	4.00	1.10	0.294	3.397	0.160	6.253	1.841	0.000544
	6.00	0.85	0.206	4.864	0.111	9.035	1.857	0.000830
	8.00	0.71	0.161	6.196	0.087	11.550	1.863	0.001096

FIGURE 4a.







is independent of the concentration of stilbene in the copolymer, which further emphasises that head to head links are not highly thermolabile, whereas the rate of chain scission is directly dependent on the amount of stilbene present. The relationships between the velocity constants, k_1 , for the three copolymers and the amount of stilbene in the copolymer is shown in Figure 5, the relevant data being tabulated in Table 5. From these figures, it appears that the rate of bond scission increases with increasing concentration of stilbene in the copolymer, although the dependence is not linear.

The inference may be drawn from the results described in this section that the stilbene units form thermolabile structures in the copolymers, but are not as unstable as the bonds whose scission results in the intercept in the α versus time plot. However, the increased rates of bond rupture in the copolymers, relative to the homopolymer of comparable molecular weight, TPS/3, are far less than would be expected from the ratios of head to head or similar structures in the two different types of polymer. Consequently, it appears that head to head links are responsible only to a very slight degree, if at all, for the increased rate of chain scission and lower Activation Energy of the thermally prepared polystyrene, relative to the anionic polymers.

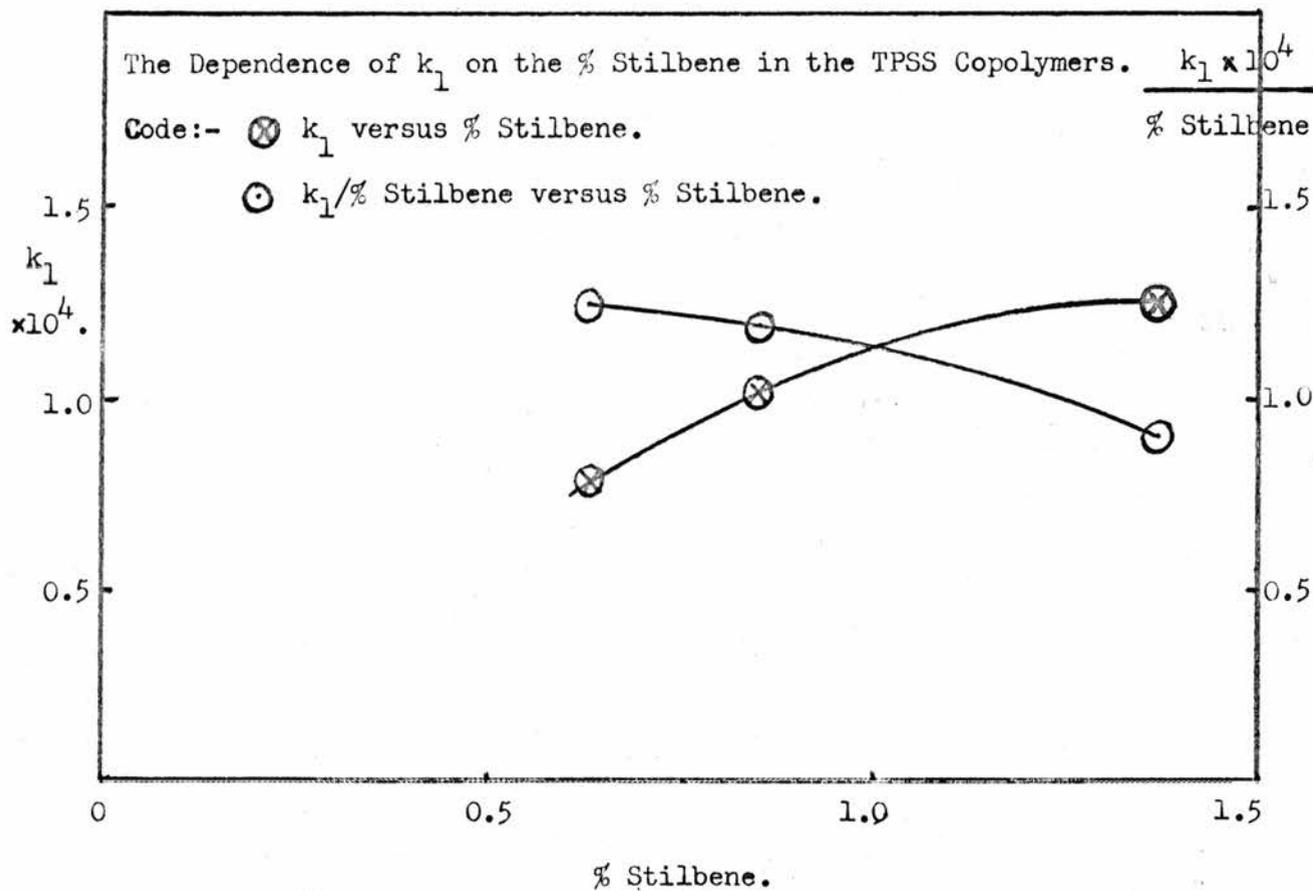
The velocity constants measured from the α versus time plots in Figures 3c and 4c are composite values, consisting of contributions from the scission of head to head bonds introduced by the stilbene, and the rupture of normal C - C bonds in the polystyrene.

TABLE 5.

The Dependence of k_1 on the % Stilbene in the TPSS Copolymers.

Polymer.	% Stilbene.	$k_1 \times 10^4$. (hr ⁻¹).	$\frac{k_1 \times 10^4}{\% \text{ Stilbene.}}$
TPSS/1	0.63	0.783	1.243
TPSS/3	0.85	1.015	1.194
TPSS/5	1.37	1.248	0.911

FIGURE 5.



However, it is possible to resolve these two effects, and the theory on which the resolution is based will now be derived.

(c) Theoretical Treatment of the Chain Scission Reactions in Polymers containing "Weak Links".

Consider w grams of a polymer in which the monomer repeat unit molecular weight is M . Let there be a small fraction x of the interunit bonds less stable than normal, that is

$$\text{fraction of "weak bonds"} = x$$

$$\text{Therefore fraction of normal bonds} = 1 - x$$

Accordingly, the number of "weak bonds" in w g. of polymer

$$= \frac{w x}{M}$$

and the number of normal bonds in w g. of polymer

$$= \frac{w (1 - x)}{M}$$

Consider the random rupture of both kinds of bonds.

Let n "weak bonds" per molecule break in time t ,

and m normal bonds per molecule break in time t .

Therefore, the number of new molecules formed per molecule

$$= (m + n + 1)$$

and the number of new molecules formed per w g.

$$(m + n + 1) \frac{w}{\overline{DP}_0 M}$$

Accordingly, the degree of polymerisation at time t , \overline{DP}_t , is given by

$$\overline{DP}_t = \frac{\overline{DP}_0}{(m + n + 1)}$$

and the total number of "weak bonds" broken per w g. = $\frac{n w}{\overline{DP}_0 M}$

Similarly, the total number of normal bonds broken per w g.

$$= \frac{m w}{\overline{DP}_0 M}$$

Now consider the scission of both types of bond to be a first order reaction.

(i) For "Weak Bonds!"

$$\ln \frac{\frac{w x}{M}}{\frac{w x}{M} - \frac{n w}{\overline{DP}_0 M}} = k_1^l t$$

$$\therefore \ln \frac{x}{n - \frac{x}{\overline{DP}_0}} = k_1^l t$$

$$\therefore \ln \frac{1}{1 - \frac{n}{x \overline{DP}_0}} = k_1^l t$$

$$\therefore n / x \overline{DP}_0 = k_1^l t$$

$$\therefore n = x \overline{DP}_0 k_1^l t$$

(ii) For Normal Bonds.

$$\ln \frac{\frac{w(1-x)}{M}}{\frac{w(1-x)}{M} - \frac{mw}{\overline{DP}_0 M}} = k_1 t$$

$$\therefore \ln \frac{(1-x)}{(1-x) - \frac{m}{\overline{DP}_0}} = k_1 t$$

$$\therefore \ln \frac{1}{1 - \frac{m}{(1-x)\overline{DP}_0}} = k_1 t$$

$$\therefore \frac{m}{(1-x)\overline{DP}_0} = k_1 t$$

$$\therefore m = (1-x)\overline{DP}_0 k_1 t$$

$$\therefore m+n = t\overline{DP}_0 [xk_1 + (1-x)k_1]$$

$$\therefore \frac{m+n+1}{\overline{DP}_0} = t [xk_1 + (1-x)k_1] + \frac{1}{\overline{DP}_0}$$

$$\therefore \frac{1}{\overline{DP}_t} - \frac{1}{\overline{DP}_0} = t [xk_1 + (1-x)k_1]$$

For styrene homopolymer, $x = 0$

$$\therefore \frac{1}{\overline{DP}_t} - \frac{1}{\overline{DP}_0} = k_1 t$$

For styrene - stilbene copolymers, $x > 0$, but $(1 - x) \rightarrow 1$ since x is very small.

$$\frac{1}{\overline{DP}_t} - \frac{1}{\overline{DP}_0} = t \left[xk_1^1 + k_1^1 \right]$$

If the assumption is made that the backbone C - C bonds in polystyrene constitute normal bonds, whereas each new bond in the copolymer caused by incorporation of stilbene is a "weak link", then it is possible to calculate k_1^1 from the rate of bond scission in styrene homopolymer, and $(k_1^1 + xk_1^1)$ from the rate of bond scission in a styrene - stilbene copolymer of the same molecular weight. Consequently, if x is known, then k_1^1 can be determined. In the present example, x has been assumed equal to the fraction of stilbene units in the copolymer. Alternatively, xk_1^1 may be employed directly in Arrhenius plots.

Homopolymer TPS/3 and copolymer TPSS/1 were compared because they are of similar molecular weight. Only one value of k_1^1 is known for TPS/3, but if the assumption is made that this polymer also degrades with the established Activation Energy of 49 kcal. mole⁻¹., then k_1^1 may be calculated for other temperatures. Arrhenius plots of $\log k_1^1$ and $\log k_1^1$ versus reciprocal absolute temperature were constructed. The relevant data is tabulated in Tables 6a and 6b, and plotted in Figures 6a and 6b.

The Activation Energy for the scission of the "weak links"

TABLE 6a.

Data for Arrhenius Plots.

TPSS/l.

Temp. T ^o C.	Temp. T ^o A.	$\frac{10^3}{T^{\circ}A.}$	$k_1 \times 10^4$ (hr ⁻¹)	log. k_1 .
294	567	1.764	3.0992	- 3.5087
287	560	1.786	1.6869	- 3.7729
280	553	1.808	0.7852	- 4.1050
275	548	1.825	0.5595	- 4.2522
270	543	1.842	0.3006	- 4.5221

TABLE 6b.

Data for the Arrhenius Plot of $\log. k_1$ versus $\frac{10^3}{T^{\circ}A.}$

$\frac{10^3}{T^{\circ}A.}$	$\log.(xk_1 + k_1)$	$(xk_1 + k_1)$ $\times 10^2$ (hr ⁻¹)	log. k_1	k_1 $\times 10^4$ (hr ⁻¹)	xk_1 $\times 10^3$	log. k_1 .
1.70	- 2.692	0.2032	- 3.993	1.016	1.930	- 0.697
1.72	- 2.948	0.1130	- 4.158	0.695	1.058	- 0.958
1.74	- 3.200	0.0631	- 4.371	0.426	0.588	- 1.213
1.76	- 3.454	0.0352	- 4.588	0.258	0.326	- 1.470
1.78	- 3.710	0.0195	- 4.803	0.157	0.179	- 1.729
1.80	- 3.963	0.0109	- 5.018	0.096	0.099	- 1.986
1.82	- 4.218	0.0060	- 5.232	0.059	0.055	- 2.246
1.84	- 4.471	0.0034	- 5.448	0.036	0.030	- 2.503

FIGURE 6a.

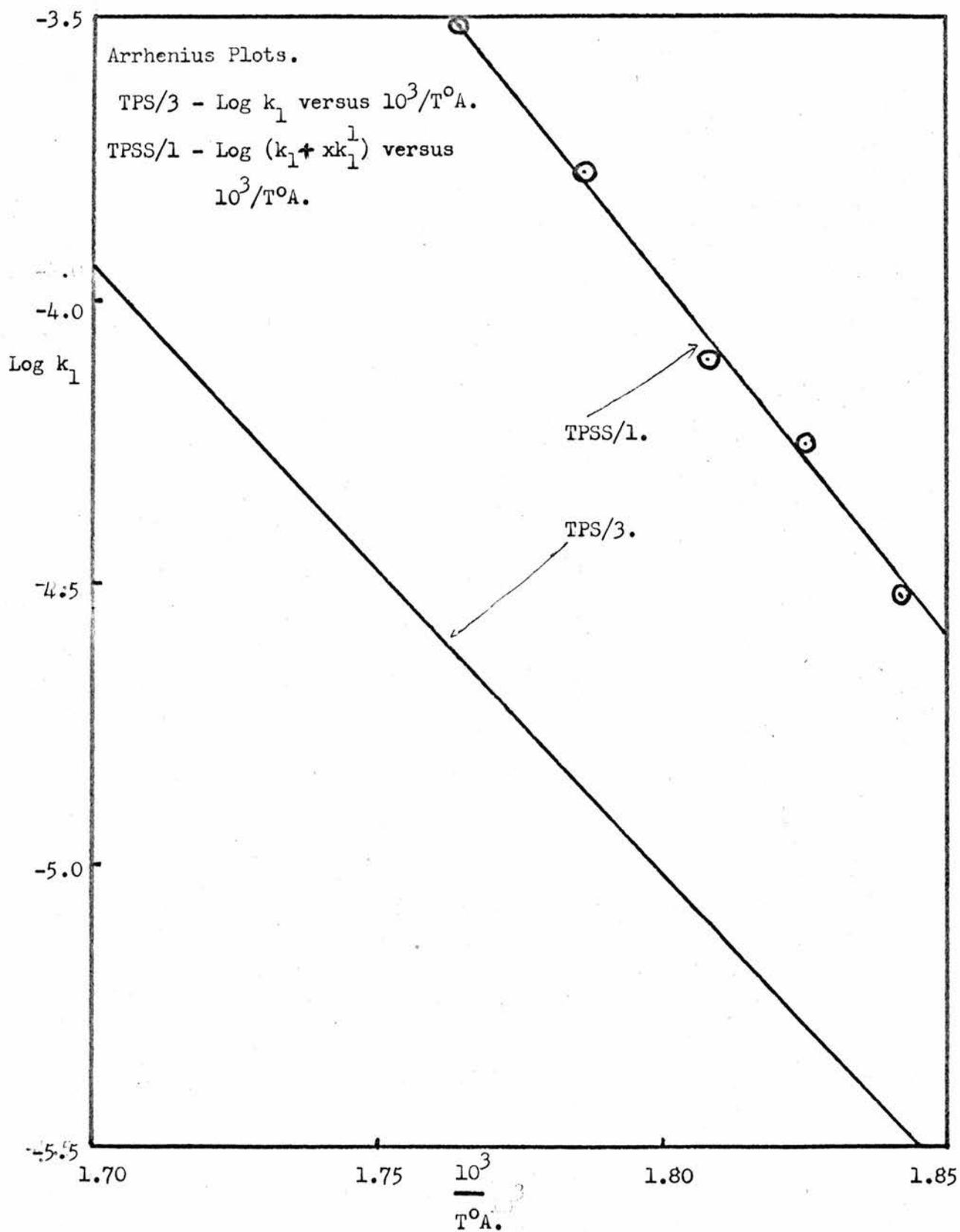
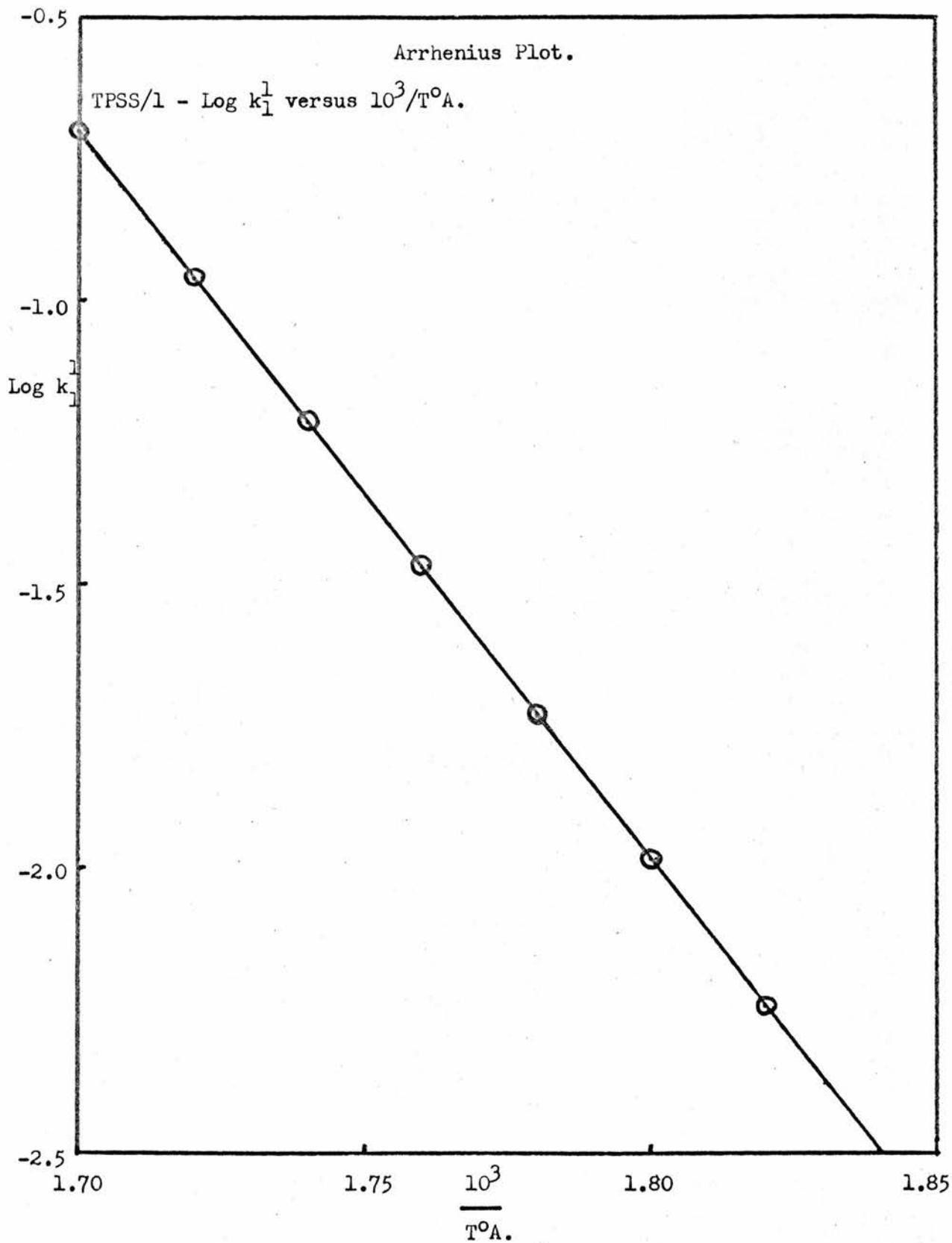


FIGURE 6b.



formed by stilbene units is $57.6 \text{ kcal. mole}^{-1}$, compared with $49.0 \text{ kcal. mole}^{-1}$ for the scission of normal bonds in styrene homopolymer. The greatly increased rate of chain scission in the copolymers is accounted for by the considerably larger A value in the expression for velocity constants, namely

$$k = A \exp.(-E / RT).$$

A for the scission of stilbene units is found to be $5.86 \times 10^{-5} \text{ sec}^{-1}$, whereas A for the rupture of normal C - C bonds in polystyrene is $3.33 \times 10^{-8} \text{ sec}^{-1}$.

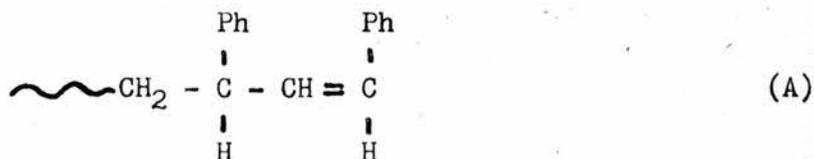
The relative magnitude of the two Activation Energies is surprising because studies of the bond dissociation energies of the respective model compounds, dibenzyl $\text{PhCH}_2 - \text{CH}_2\text{Ph}$ and ethyl benzene $\text{PhCH}_2 - \text{CH}_3$, give values of 47 and 63 kcal. mole^{-1} respectively²³. It is difficult to explain this apparent reversal in behaviour, but part of the explanation may lie in the fact that very little is known about the distribution of stilbene units in the copolymers. Trans - stilbene is known not to homopolymerise²⁴, and Cameron and Grassie²¹ have shown that it has little tendency to enter into copolymers with styrene. They found that the reactivity ratio $r_1 = k_{aa} / k_{ab} = 11.2$ where a and b refer to styrene and stilbene respectively. Since stilbene does not homopolymerise, i.e. $k_{bb} = 0$, it would be predicted that stilbene units will enter the copolymer singly and at random. Recently Bevington and Johnson²⁵ have found that the velocity constant for the addition of the benzoyloxy radical to trans - stilbene is

some five times greater than the corresponding constant for the addition to styrene. This difference in reactivity has been ascribed in part to polar factors, which are unlikely to be operative in uncatalysed thermal polymerisations. In the absence of further information concerning the distribution of stilbene units in the copolymers with styrene, the only conclusion which may be drawn about their effect on the thermostability of polystyrene is that they lower the resistance of the polymer to thermal degradation, but do not constitute the most thermolabile bonds in the polymer.

With reference to the surprising value obtained for the Activation Energy of chain scission of the supposedly "weak links", Davis, Tobias and Peterli²⁶ applied a similar treatment to the degradation of polypropylene to obtain an estimate of the bond strength of "weak links" in this polymer. They, too, found from the Activation Energies that the "weak" bonds were stronger than the normal bonds by some 8 kcal. mole⁻¹.

It has been concluded in Chapter IV that the ordinate intercept in α versus time plots for thermally prepared polystyrenes is not due to intermolecular transfer, since a similar effect would also be expected from anionically synthesised polystyrenes. In the present chapter, this intercept has been found proportional to the temperature of polymerisation. Although several investigators^{9,10,11} have found that termination in the free - radical polymerisation of styrene is exclusively by combination, it is conceivable that a

very small fraction of the macroradicals terminate by disproportionation, a reaction which would also be favoured by increased temperatures of polymerisation. Disproportionation will result in the formation of unsaturated chain ends, A



which, by analogy with similar end - groups in poly (methyl methacrylate)²⁷, are expected to be thermolabile. Decomposition of these end - groups at temperatures where normal C - C backbone bonds are stable, and subsequent intermolecular transfer, will result in a rapid decrease in molecular weight before main - chain scission reactions have begun. However, the intermolecular transfer reaction is expected to be sensitive to free - radical catchers, and should be at least partially inhibited by their presence. Degradations in the presence of a known inhibitor were therefore studied in the next part of this investigation.

(4) The Molecular Weight Changes in Polystyrenes degraded in the presence of 1,4 - diaminoanthraquinone (DAA):

If the ordinate intercept found in the α versus time plots for thermally polymerised polystyrenes is a manifestation of intermolecular transfer reactions of the radicals formed either by random or, more probably, by chain - end initiation, this reaction should be affected by inhibitors. 1,4 - diaminoanthraquinone (DAA)

has been used previously^{27,28} in polymer degradation systems, and has been shown to inhibit free - radical decomposition reactions. Accordingly, DAA introduced into the degradation system should react with the primary decomposition radicals and prevent their subsequent transfer reactions, thus inhibiting the molecular weight fall. If, on the other hand, the ordinate intercept is a sign of "weak link" scission followed by deactivation of the radicals, DAA will have no effect on this latter reaction, and no difference in the intercept for inhibited and uninhibited degradations is expected.

The results of the degradations of homopolymers TPS/2 and TPS/3 and copolymer TPSS/1 are tabulated in Table 7 and plotted in Figures 7a, b and c. From these plots it is apparent that DAA does not affect either the size of the ordinate intercept or the slope of the α versus time plots. Consequently, neither feature can be caused by intermolecular transfer reactions occurring during degradation. Thus, it appears that the ordinate intercept represents the rupture of internal "weak links" in the polymer, and not inter - molecular transfer following chain - end initiation, and also that the "normal" chain breaking process does not involve transfer reactions.

These conclusions require one possible qualification since there is no absolute certainty that DAA and the polystyrene have reacted at all. It is difficult to make films containing both reactants since each is insoluble in solvents in which the other is soluble. In the present experiments, polystyrene powder was mixed

TABLE 7.

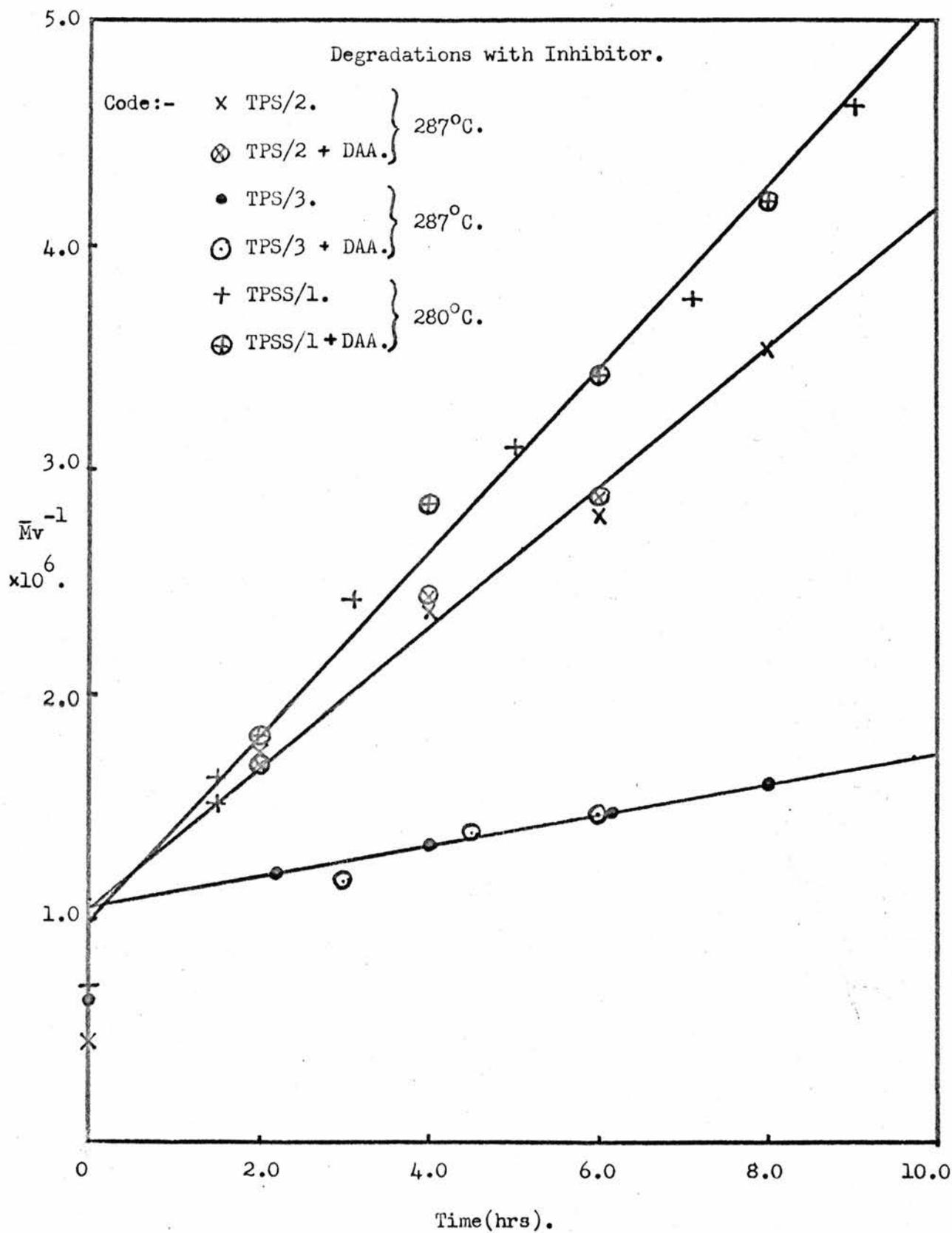
Degradations with Inhibitor.

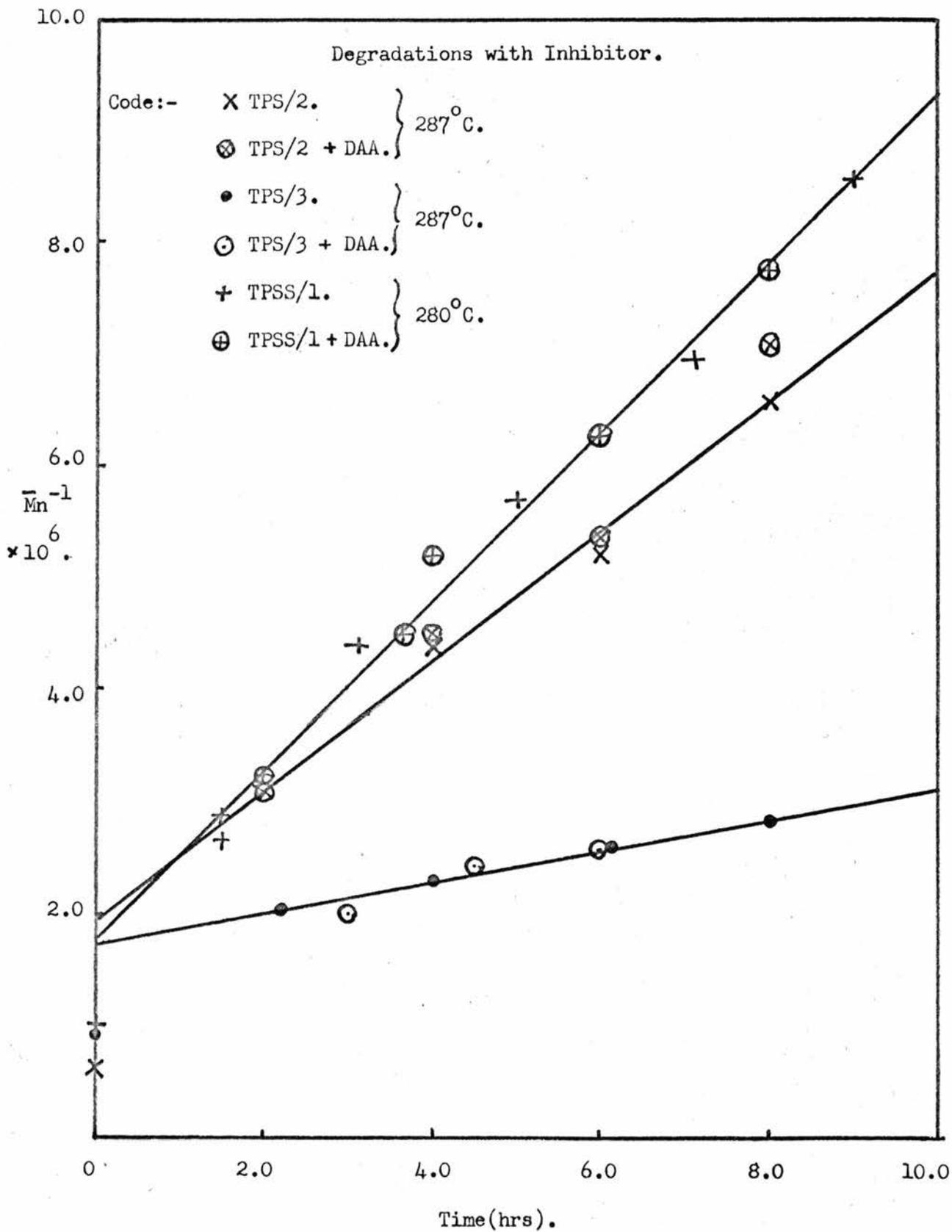
Polymer and Temp. °C.	Time. (hrs)	$[\eta]$	\bar{M}_v $\times 10^{-6}$	\bar{M}_v^{-1} $\times 10^6$	\bar{M}_n $\times 10^{-6}$	\bar{M}_n^{-1} $\times 10^6$	$\frac{\bar{M}_v}{\bar{M}_n}$	α
TPS/2.	-	4.74	2.183	0.458	1.520	0.658	1.436	0
287°C.	2.00	1.79	0.572	1.753	0.312	3.202	1.830	0.000260
	4.00	1.43	0.421	2.377	0.228	4.389	1.847	0.000387
	6.00	1.27	0.357	2.805	0.192	5.200	1.854	0.000470
	8.00	1.07	0.283	3.540	0.152	6.589	1.861	0.000614
TPS/2.	2.00	1.85	0.588	1.701	0.323	3.096	1.822	0.000248
+DAA.	4.00	1.41	0.411	2.435	0.223	4.484	1.847	0.000392
287°C.	6.00	1.24	0.347	2.884	0.187	5.348	1.855	0.000490
	8.00	1.01	0.262	3.811	0.141	7.092	1.863	0.000679
TPS/3.	-	3.60	1.496	0.668	1.042	0.960	1.436	0
287°C.	2.20	2.34	0.830	1.207	0.488	2.051	1.703	0.000114
	4.00	2.17	0.745	1.343	0.431	2.320	1.728	0.000141
	6.10	2.02	0.676	1.479	0.386	2.594	1.750	0.000160
	8.00	1.90	0.622	1.607	0.352	2.838	1.766	0.000196
TPS/3.	3.00	2.37	0.845	1.183	0.498	2.008	1.697	0.000111
+DAA.	4.50	2.11	0.718	1.394	0.414	2.415	1.736	0.000152
287°C.	6.00	2.04	0.683	1.465	0.391	2.558	1.747	0.000165

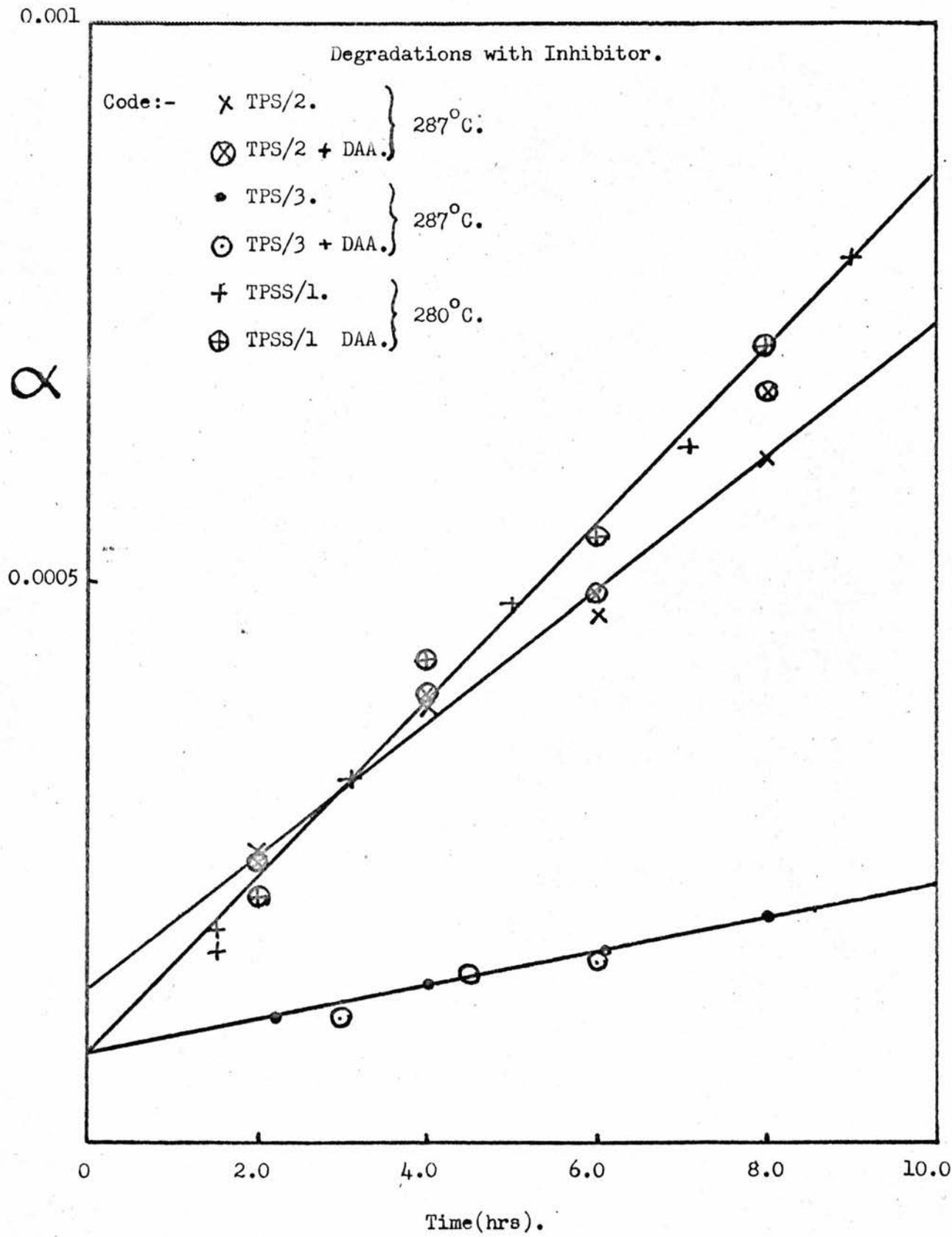
TABLE 7 (Continued).

Polymer. and Temp. °C.	Time. (hrs)	$[\eta]$	\bar{M}_v $\times 10^{-6}$	\bar{M}_v^{-1} $\times 10^6$	\bar{M}_n $\times 10^{-6}$	\bar{M}_n^{-1} $\times 10^6$	$\frac{\bar{M}_v}{\bar{M}_n}$	α
TPSS/l.	-	3.44	1.406	0.711	0.979	1.021	1.436	0
280°C.	1.50	1.88	0.611	1.637	0.347	2.879	1.759	0.000192
	1.50	1.97	0.655	1.528	0.376	2.663	1.743	0.000171
	3.10	1.41	0.412	2.426	0.227	4.407	1.816	0.000351
	5.00	1.18	0.322	3.105	0.175	5.701	1.836	0.000484
	7.10	1.02	0.266	3.767	0.144	6.958	1.847	0.000620
	9.00	0.88	0.216	4.623	0.117	8.575	1.855	0.000787
TPSS/l.	2.00	1.76	0.549	1.821	0.309	3.236	1.774	0.000222
+DAA.	4.00	1.26	0.352	2.857	0.192	5.208	1.829	0.000430
280°C.	6.00	1.11	0.292	3.420	0.159	6.289	1.841	0.000538
	8.00	0.94	0.238	4.200	0.129	7.752	1.852	0.000702

FIGURE 7a.







with a very considerable molar excess of DAA. in the degradation tray. Since polystyrene is molten at temperatures above 240°C .²⁹ and DAA melts at 268°C .³⁰, both compounds are fluid at the degradation temperatures employed. After degradation the polymer melt was coloured purple throughout, and there did not appear to be a macroscopic two - phase system. It is just possible, however, that a two - phase system did exist, as apparently happens with poly (α -methylstyrene) in polystyrene³¹, and that there was no real contact between the polymer and DAA. This possibility seems rather remote because, even if a true solution of DAA in polymer was not formed, the DAA had such a high surface area that one would expect it to react with at least a proportion of the macroradicals formed. The same qualification could probably be made about DAA and other polymers, yet it has been proved that DAA does inhibit free - radical reactions in polymer degradations.^{27,28}

(5) Summary of Results.

Several important features of the chain scission reactions in thermally prepared polystyrenes have been elucidated. It is convenient to summarise them at this stage as follows:-

- (i) The magnitude of the ordinate intercept on the α versus time curve is directly proportional to the temperature of polymerisation,
- (ii) the magnitude of the intercept does not depend on the amount of branching or head to head bonds in the polymer,
- (iii) the intercept increased in size for a polystyrene which

polymerised abnormally quickly,

(iv) the intercept is not caused by intermolecular transfer following the scission of thermolabile chain ends,

(v) the slope of the α versus time plot, i.e. the rate of "normal" chain scission, appears to depend directly on the temperature of polymerisation as well as on the molecular weight of the polymer;

(vi) the rate of "normal" bond scission increases with branching, and

(vii) the rate of chain scission increases with increasing concentration of head to head bonds.

These experimental findings mentioned above have all been discussed previously in this chapter, and it is not intended to dwell on them further at this point. It is sufficient to stress that neither branching nor head to head bonds affect the magnitude of the ordinate intercept on the α versus time plot, although both appear to increase the rate of chain scission in the second phase of the reaction. Since head to head links appear to have a higher Activation Energy for their scission, such groupings cannot explain the low Activation Energy for the thermal breakdown of free - radical polystyrenes. Branching might be partly responsible for this low value, but the concentration of branch points in low conversion polymers is almost certainly too low to make this explanation convincing.

The magnitude of the ordinate intercept has been found

to be a function of the temperature of polymerisation. This feature, together with the anomalously high "weak bond" concentration in TPS/2 which was noted to polymerise abnormally rapidly, is suggestive that the "weak links" present in thermal polystyrenes are oxygenated structures, since this explanation is the only one which fits all the experimental facts available at present. On this basis, a mechanism for the breakdown of polystyrene is discussed in the next section.

(6) A Possible Degradation Mechanism for Polystyrene.

On the basis of the linear α versus time plots and the high Activation Energy for bond scission, the polystyrenes prepared by "living" anionic synthesis appear to degrade by a simple random scission. This type of scission reaction is expected from these polymers since their method of synthesis precludes the formation of labile chain ends and structures resulting from abnormal propagation steps. Furthermore, the very high purity of the reactants greatly reduces the possibility of the incorporation of impurities, such as oxygen, into the polymer. On consideration of the very high bulk viscosity of the polymer melt at the degradation temperatures, it seems probable that the macroradicals formed by random scission deactivate mutually in a "cage" reaction, and little diffusion of the radicals away from the site of rupture occurs. This explanation is consistent with the experiments involving DAA. As was indicated previously, the average Activation Energy for bond scission in the

anionic polymers approximates closely to that expected for the rupture of backbone bonds in polystyrene. However, the observed dependence of the rate of chain scission on the molecular weight of the polymer, and the possible, although improbable, inverse dependence of the Activation Energy on molecular weight renders this hypothesis rather tentative.

In Chapter IV it was shown that the most probable explanation of the intercept in the α versus time plots for thermal polystyrenes is the scission of thermolabile bonds in the polymer. Subsequently in Chapter V it has been proved that these "weak bonds" are not associated with branch points or head to head links in the polymer, although it has been shown that the concentration of "weak links" is a linear function of the temperature of polymerisation. McNeill³² has recently found backbone unsaturation in free - radical polystyrene, but the concentration of the thermolabile points found in the present polymers is some ten times smaller than would be expected if these "weak bonds" were associated with backbone unsaturation.

The clues to the possible nature of the "weak bonds" come from two sources. Firstly, anionic polymers do not contain these thermolabile structures, and secondly homopolymer TPS/2, which contains an abnormally high concentration of "weak bonds", was also noted to polymerise far more quickly than other polymers similarly prepared at 60°C. Oxygen is a known accelerator of the free - radical

polymerisation of styrene², and although no evidence exists in the literature concerning its copolymerisation with styrene, small amounts of carbon monoxide, presumably from oxygenated structures, have been found in the pyrolysis products from polystyrene³. It would appear very probable, therefore, that the "weak links" in polystyrene are the result of the incorporation of oxygen into the polymer, probably as a polyperoxide⁴. Support for this hypothesis comes from the absence of "weak links" in anionic polymers where the more stringent purity of the reactants in this type of polymerisation greatly reduces the possibility of oxygen in the polymerisation system. By exactly the same arguments, small traces of water vapour could be present during the thermal polymerisation, but it is less probable that water could be incorporated into the polymer. Obviously, a degradative study of polystyrenes prepared free - radically under conditions of rigorous exclusion of oxygen is necessary to confirm this theory. Further experiments using polymers prepared in the presence of known concentrations of oxygen and water would also help to clarify the chemical nature of the "weak links".

It has been indicated previously that the onset of the chain scission reaction, which manifests itself as a linear dependence of α on time, occurs at lower temperatures in thermal polystyrenes than in anionic polymers, and the rate of scission in thermal polystyrenes is greater than the corresponding rate in anionic polymers of the same molecular weight. Furthermore, the

Activation Energy for chain scission in the thermal polymers is $\sim 49 \text{ kcal. mole}^{-1}$, compared with $60 - 73 \text{ kcal. mole}^{-1}$ found for anionic polymers. It has also been indicated in section (2) of this chapter that the rate of chain scission increases with increasing temperature of polymerisation. This behaviour is highly suggestive that thermal polystyrenes contain appreciable quantities of a second type of thermolabile bond which, however, is more stable than the polyperoxides previously discussed. Once again, these unstable bonds appear to be incorporated into the polymer during synthesis, presumably by an abnormal propagation step. Both branch points and head to head links have been shown in the present study to increase the thermal instability of thermally prepared polystyrene. However, the former structures are considered to exist in too small amounts¹² to be responsible for more than a very small part of the observed instability of polystyrenes, while the latter appear to rupture with a higher Activation Energy than the normal bonds in polystyrene, and so cannot be considered responsible for the decreased thermal stability of free - radically prepared polymers.

In this context, it is important to consider the postulate of Cameron and Grassie¹⁸ that the "weak bonds" in polystyrene are caused by backbone unsaturation. This conclusion has been regarded with suspicion, primarily because of the method of determining "weak link" concentrations from the molecular weight data. Recently, McNeill³² has found considerable unsaturation in free - radically

synthesised polystyrenes, thus supporting Cameron's evidence for backbone unsaturation. M^CNeill, however, concludes that the double bonds in free - radically prepared polystyrenes are not associated with "weak links" since both thermal and cationic polystyrenes give similar molecular weight versus conversion curves. However, Grassie's method¹ of estimating "weak link" concentrations from the above curves is very insensitive, and would predict the existence of thermolabile bonds in any polymer which degrades by a random mechanism. The present method described in this work is far more sensitive, and appears to be capable of differentiating between "weak" and normal bond scission.

Further evidence that the bond rupture in thermal polystyrenes differs from the scission in anionic polymers comes from a comparison of the bond dissociation energies in model compounds. Carbon - carbon bonds β to a double bond are some 17 kcal. mole⁻¹ less stable than normal aliphatic C - C bonds²³. Accordingly, the bond dissociation energy of backbone bonds β to double bonds in polystyrene would be reduced from their normal value³³ of 64 kcal. mole⁻¹ to about 47 kcal. mole⁻¹, a value in close agreement with that found in the present study.

On the basis of the above experimental observations, it seems probable that the bonds in thermal polystyrenes whose rate of scission is linear with time are C - C bonds β to double bonds incorporated into the polymer during synthesis. A plausible

mechanism for the formation of the double bonds is that proposed by Cameron and Grassie¹⁸, and illustrated in Section (1d) of this chapter. This mechanism involves the propagation of the polystyryl macroradical through a quinonoid resonance form.

The tentative nature of the postulates discussed above must again be emphasised, especially since the rates of chain scission are complicated by the molecular weight dependence. In the absence of more experimental data, no more definite conclusions can be drawn from the present results. It is important to stress, however, that the degradation appears to be thermal, not mechanical, in nature since experimental measurements of the molecular weight distributions indicate that an exponential distribution is quickly obtained after the onset of degradation.

It is difficult to interpret the low Activation Energies for bond scission found for Ziegler - Natta polystyrenes on the basis of the postulate that the "weak links" in polystyrene are associated with backbone unsaturation. No investigations have been made of unsaturation in these polymers, although it has been postulated that chain end unsaturation results from possible termination steps.³⁴ Obviously, direct investigations of possible unsaturation, and branching, in Ziegler - Natta polystyrenes are required.

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CHAPTER VITHE PROBLEM REVIEWED

The thermal degradation of polystyrene at sub - volatilisation temperatures has been studied. Initiation of degradation in polymers prepared by "living" anionic synthesis has been shown to occur at random in the polymer chain, and the Activation Energy for bond rupture is consistent with this postulate. The macroradicals formed by scission most probably deactivate in a "cage" reaction.

Polystyrenes prepared by thermal initiation appear to degrade in a more complex manner. The initial chain scission reaction occurs at a small fraction of highly thermolabile "weak links" in the polymer, and the concentration of these structures has been shown to increase with increasing temperature of polymerisation. These "weak bonds" have been proved not to be due to branching or head to head links in the polymer, and an inhibitor does not affect their rupture. It seems most probable, on the basis of the evidence available, that these "weak links" are oxygenated groups, probably polyperoxides, incorporated into the polymer during polymerisation.

The second phase of chain scission in thermal polystyrenes has been shown to start at lower temperatures and to proceed with a lower Activation Energy than the corresponding phase in the degradation of the anionic polymers. Furthermore, the rate of

chain scission does appear to be an increasing function of the temperature of polymerisation. Branching and head to head links have been shown to increase the rate of chain scission, but neither structure is considered responsible for the reduced thermal stability, relative to anionic polymers, of polystyrenes prepared thermally at low temperatures ($\sim 60^{\circ}\text{C}.$) to low conversions. Inhibitor does not affect this phase of chain scission. Accordingly, it is suggested that a second type of thermolabile bond is present in the thermal polymers, and it is further suggested that this bond is a backbone C - C single bond β to a double bond incorporated into the polymer chain. Evidence has been presented in the literature that free-radically synthesised polystyrenes contain backbone unsaturation, thus substantiating the postulate made above. Again, it seems probable that the two types of scission reaction occurring in thermal polystyrenes are terminated in a "cage" because of the high bulk viscosity of the polymer melt.

Throughout the present study, a direct dependence of the rate of chain scission on molecular weight has been found, but it has been shown that the degradation is thermal, and not mechanical, in nature. This dependence has obscured in part the effect of the temperature of polymerisation on the rate of chain scission in thermal polystyrenes, and has led to the possible, but improbable, postulate that the Activation Energy for chain scission is an inverse function of molecular weight.

Future investigations must include the degradation of polystyrenes prepared by the thermal initiation of very pure styrene, and, conversely, of polymers prepared under an atmosphere of oxygen. The amount of oxygen copolymerised into the polystyrenes could be determined by radiochemical investigations using O^{18} , and the concentration of oxygen in the polymer related to the "weak bond" concentration obtained by the degradative method described in the present work. Further evidence is also required of the amount of unsaturation in a range of polystyrenes prepared thermally at various temperatures. It might be possible to introduce controlled amounts of unsaturation into polystyrene by copolymerising styrene with phenylacetylene, probably by employing anionic synthesis to reduce the possibility of branching reactions. More work must also be done to characterise the observed dependence of the rate of chain scission on the molecular weight of the polymer.

In conclusion, this study has demonstrated conclusively for the first time that there are "weak links" in free - radically prepared polystyrenes, and has also verified the conclusions of previous investigators that polystyrenes prepared by anionic initiation do not contain these very thermolabile structures. It is also suggested from the present study that free - radical polystyrenes contain a second type of "weak link" which is probably due to backbone unsaturation in the polymer.

PART II.

THE THERMAL DEGRADATION OF

POLY (METHYL α - PHENYLACRYLATE).

CHAPTER IINTRODUCTION

The thermal degradation of poly (methyl α -phenylacrylate), P M A, has not been studied to date, yet this depolymerisation reaction is intrinsically interesting in its own right, and in comparison with the degradation characteristics of analogous polymers. Until recently such a study could not be attempted because methyl α -phenylacrylate, in common with most other α -alkyl and α -aryl acrylates^I (except the methacrylates), does not polymerise to high polymer with free-radical initiators. However, these monomers have been found to polymerise to high molecular weight with the anionic initiators discovered some twelve years ago by Szwarc², and their polymerisation^{3,4} and copolymerisation^{5,6} have recently been examined. Thus, P M A suitable for degradative studies can now be prepared. Furthermore, it has been found that the use of different solvent / initiator systems in the anionic polymerisation of the α -alkyl and α -aryl acrylates^I permits a measure of variation in the stereoregularity³ of the resultant polymer. Similar observations have previously been made on the anionic polymerisation of methyl methacrylate⁷⁻¹⁰. Thus, it appears that a judicious choice of solvent and initiator, and probably temperature, should permit control of the tacticity in P M A.

The thermal degradation of P M A was considered worthy of investigation for several reasons. Firstly P M A provides an important structural link between the poly (alkyl methacrylate esters) whose

degradation is well understood^{II}, and the styrene polymers where there is still some controversy over the degradation mechanism, especially that of polystyrene^{I2,I3}. The various aspects of the thermal depolymerisation of polystyrene which are still disputed have been reviewed in Chapter I of the first part of this thesis, special emphasis having been placed on the questionable existence of "weak links". The existence and possible nature of these thermolabile structures have been directly investigated in Part I of this thesis. Further information on this subject may be obtained by examining the decomposition of polymers with related structures, and correlating differences in degradation characteristics with changes in molecular structure. With this objective, degradative studies have already been made on poly (α -methylstyrene)^{I4}, poly (α -deuterostyrene)^{I5} and poly (β -deuterostyrene)^{I5}, which work has emphasised the importance of hydrogen transfer reactions in the thermal breakdown of polystyrene, especially with regard to the molecular weight changes. The proposed examination of the depolymerisation of P M A is an extension of this approach.

Secondly, the degradation of P M A is of interest in its own right. If P M A breaks down by chain scission - as seems highly probable - one of the macroradicals formed, A,



will be more highly resonance stabilised than any other radical known to occur in polymer degradation systems. The free-radical copolymerisation behaviour of methyl α -phenylacrylate is apparently abnormal in some respects^{5,16}, possibly because of the high resonance stabilisation of the above radical A (which is the propagating species), and it is of interest to determine if the degradation behaviour in any way reflects this stabilisation.

Finally, P M A is a convenient polymer in which to investigate the effect, if any, of stereoregularity on the degradation characteristics, since stereoregularity in the polymer can be controlled by the use of various solvent / initiator systems. Such studies have received scant attention to date.

Any investigation of the thermal degradation of P M A will inevitably seek to draw comparisons of the characteristics found with the known behaviour of structurally similar polymers other than polystyrene, primarily poly (α -methylstyrene) and poly (methyl methacrylate). At this juncture, therefore, it is convenient to review the thermal degradation of these polymers, and brief synopses now follow.

(I) The Thermal Degradation of Poly (α -methyl styrene).

Early experiments soon proved that poly (α -methylstyrene), P M S , degrades completely to monomer¹⁷, but the first study of the rates of volatilisation and molecular weight changes during the depolymerisation of P M S was not carried out until 1958, about which

time anionically synthesised polymers became available. Brown and Wall¹⁴ investigated the degradation of a series of fractions of P M S with molecular weights ranging from 80,000 to 1,120,000. From their study, the investigators concluded that the decomposition mechanism comprised random initiation, depropagation to monomer and termination by disproportionation. Intermolecular transfer did not appear to be important in the system, and the zip length was estimated at approximately 1,300 monomer units at 272.5°C. The Activation Energy (65 kcal. mole⁻¹.) was found to be invariant with temperature. Subsequent investigations of the depolymerisation in solution^{18,19,20} confirmed this general mechanism.

Braun and Heufer²¹ have recently found that highly syndiotactic P M S, prepared by cationic polymerisation, degrades at a substantially slower rate than the almost atactic polymers prepared by anionic synthesis. More data, however, is necessary for the unqualified acceptance of this observation.

(2) The Thermal Degradation of Poly (methyl methacrylate).

Most of the investigations^{22,23,24} of the thermal degradation of poly (methyl methacrylate), P M M A, have been concerned with polymers prepared by free - radical initiation. These polymers generally contain double - bond chain ends at which degradation is initiated at fairly low temperatures (< 270°C.). Recently, however, Jellinek²⁵ has studied the thermal degradation at 300 - 400°C. of isotactic and syndiotactic P M M A, prepared

by ionic catalysis, which contain no double - bond chain ends. From a kinetic analysis of his data, Jellinek has shown that degradation proceeds by random initiation, followed by depropagation to monomer with a large zip length and termination by disproportionation. An overall Activation Energy of $68 - 62 \text{ kcal. mole}^{-1}$, depending on conversion, was found for both polymers, despite the fact that the molecular chain length of the isotactic polymer was greater than the zip length, whereas the molecular chain length of the syndiotactic polymer was of the same order as the zip length.

These data agree well with the results from the solution depolymerisation of anionically prepared P M M A investigated by Bywater and collaborators^{20,26}. These authors concluded that degradation was initiated at random, the zip length was of the order of 1,000 - 2,000 monomer units at $290 - 324^{\circ}\text{C.}$, and the overall Activation Energy was $62 - 64 \text{ kcal. mole}^{-1}$. Thus, good agreement exists between the data from these sources concerning the degradation of ionically prepared P M M A.

From this brief review, it is apparent that the thermal degradations of P M S and P M M A prepared by ionic initiators show the same essential features. Since P M A is likewise polymerised anionically, similar degradation behaviour is anticipated.

(3) The Scope of the Present Investigations.

The principal aims of the investigations described

herein are twofold :- (i) a preliminary study of the thermal decomposition of P M A, with a special emphasis on the search for any characteristics attributable either to the high resonance stabilisation of the probable depolymerising macroradical or to the varying stereoregularity of the polymer samples, and (ii) a comparison, where valid, of the degradation behaviour of P M A with the known characteristics of structurally related polymers, with a particular view to clarifying the decomposition of polystyrene.

The investigations encompassed studies of the composition of the volatile pyrolysis products, the rates of degradation, determined mainly by thermogravimetry, and molecular weight measurements of the polymeric pyrolysis residues.

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CHAPTER II

APPARATUS and EXPERIMENTAL TECHNIQUESA. The Synthesis of Poly (methyl α - phenylacrylate).I. The Synthesis of methyl α - phenylacrylate

Esters of α - phenylacrylic acid may be synthesised by two main routes - either by preparations giving the free acid which is then esterified, or by syntheses which give the ester directly. In the first case, a multistep reaction, involving the hydrolysis of acetophenone cyanhydrin to atrolactic acid which on fusion gives α - phenylacrylic acid, results in low overall yields ^{I - 6}. The free acid may also be obtained from the reaction of a suitable Grignard reagent and carbon dioxide ⁷, with subsequent hydrolysis. The second route involves the reaction of phenylacetylene with nickel carbonyl ^{8,9}. Yields of ester are high in this synthesis, but nickel carbonyl is a highly toxic reagent, and consequently difficult to use. However, there exists in the literature a third and most promising route to the preparation of methyl α - phenylacrylate. Ames and Davey ¹⁰, using a modification of the method of Schinz and Hinder ^{II}, have prepared the ethyl ester, ethyl α - phenylacrylate, in high yields (88%) in a simple two-step reaction. Because of the apparent simplicity and good yields of this method, it was adopted and modified to produce methyl α - phenylacrylate.

Dimethyl oxalate (88.5g.; 0.75mole.) and methyl phenylacetate (150g.; 1.00mole.) were successively added to sodium

methoxide foam (from 17.4g.; 0.75g. atom of sodium) in 500ml. benzene, and the mixture vigorously stirred before being set aside overnight at room temperature. The solid mass of sodium salt which separated out was filtered, washed with dry ether, and acidified with hydrochloric acid. The aqueous solution was extracted with ether, and the ether removed by aspiration. To the resultant oxaloester, in 38% aqueous formaldehyde (90ml.; 1.1mole.) and water (300ml.) at 15°C., was added, over a period of 30 minutes, potassium carbonate (81g.; 0.60mole.) in water (150ml.), and the mixture was stirred for two hours. The aqueous solution was extracted with ether, and the ethereal solution dried overnight over magnesium sulphate. After removal of the ether by distillation, the product was distilled under reduced pressure. B. pt. 46-8°C./0.2mm.. Analysis of the product by Gas - Liquid Chromatography (GLC) on 5% Apiezon L and polyethyleneglycol succinate columns showed two components in the approximate molar ratio 4:1. Separation of the constituents by preparative GLC and analysis of them by Infra-Red and Nuclear Magnetic Resonance spectroscopy showed that the product was a mixture of methyl phenylacetate and methyl α -phenylacrylate in the molar ratio 4:1. Subsequent repetitions of the experiment incorporating various modifications in the method of preparation^{12,13,14} and hydrolysis of the oxaloester gave no improvement in the yield of methyl α -phenylacrylate. The similar boiling points and chromatographic behaviour of the two components offered no prospect of separating them.

Because of the inability to synthesise pure methyl α - phenylacrylate attempts were made to prepare pure ethyl α - phenylacrylate by duplicating exactly the method of Ames and Davey¹⁰. High yields ($\sim 70\%$) of product were obtained but again GLC analysis showed a mixture of two components, identified as ethyl α - phenylacrylate and ethyl phenylacetate in the approximate molar ratio 3:1. Distillation under nitrogen at 20mm. mercury through a 4 foot column packed with Fenske helices gave 10g. of ethyl α - phenylacrylate containing approximately 2% ethyl phenylacetate. This purity is inadequate for anionic polymerisation, and could not be increased in subsequent preparations incorporating various modifications.

The different solubilities^{1,15} of α - phenylacrylic and phenylacetic acids in water seemed to offer the only hope of obtaining pure methyl α - phenylacrylate from the above mixture of esters. Accordingly the esters were saponified with potassium hydroxide in ethanol. Removal of the ethanol after saponification, and acidification with dilute hydrochloric acid resulted in a crystalline precipitate. Fractional crystallisation in water gave α - phenylacrylic acid. Unfortunately the saponification resulted in a small amount of yellow oil which made recrystallisation difficult. Esterification with methanol saturated with gaseous hydrogen chloride gave methyl α - phenylacrylate, containing $\leq 0.5\%$ methyl phenylacetate. In all 20g. of monomer were available for polymerisation, and were stored over calcium hydride. IR and NMR spectra of methyl α - phenylacrylate

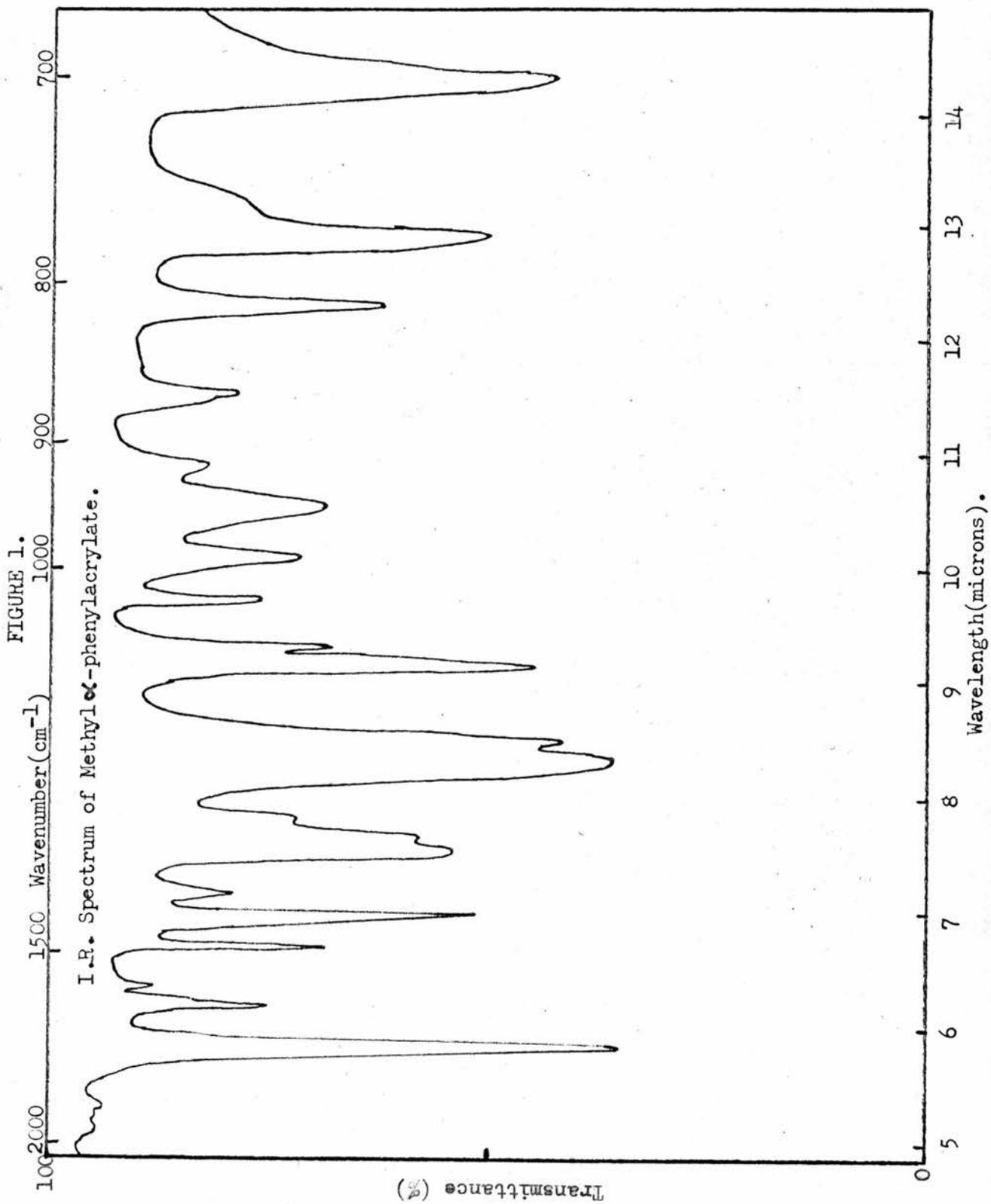
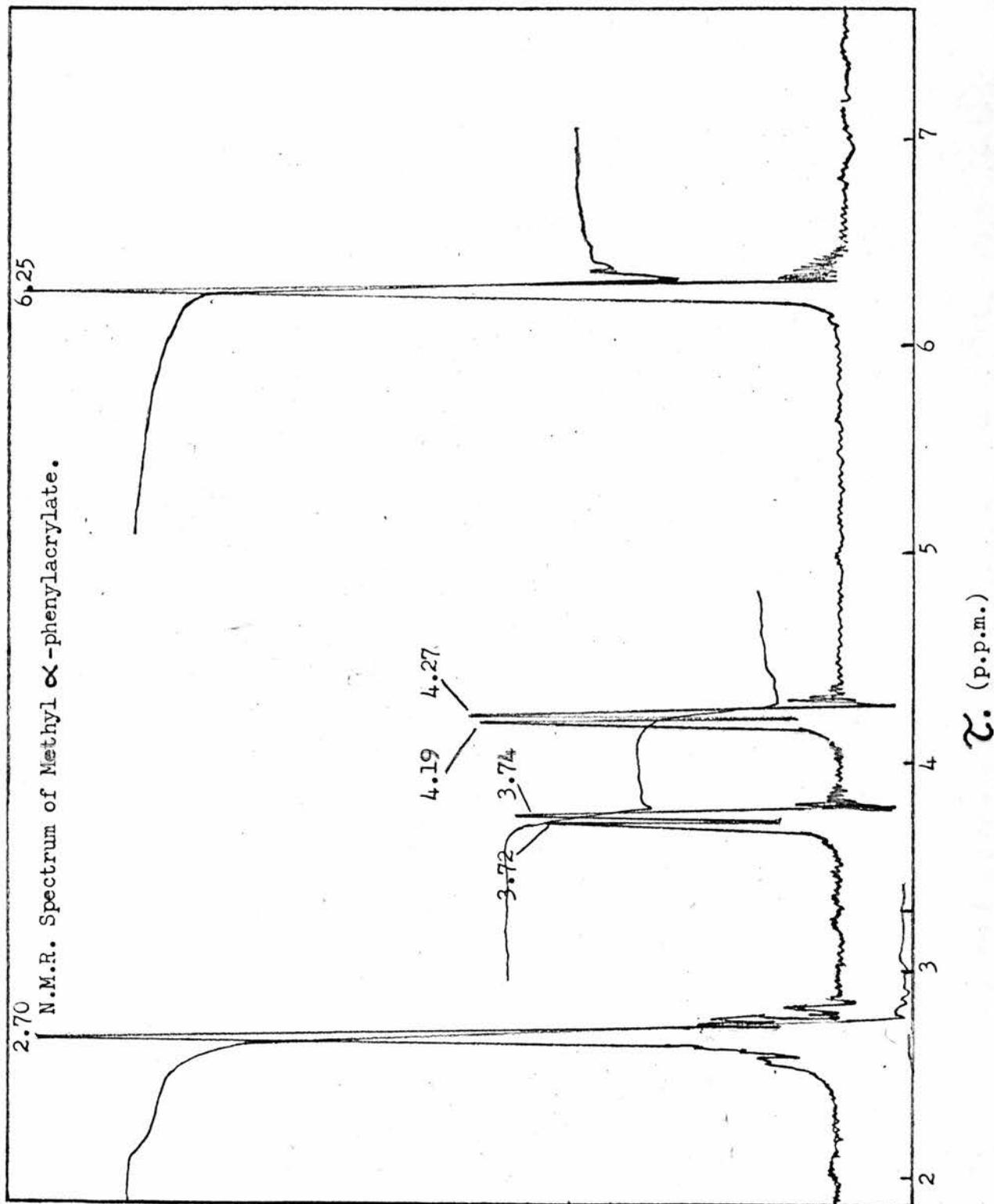


FIGURE 2.



II. The Polymerisation of Methyl α - phenylacrylate

The chosen anionic initiator was sodium naphthalenide, primarily because of its ease of preparation and handling.

Tetrahydrofuran (THF) was employed as solvent for the initiator and the polymerisation. All experiments were carried out under high vacuum to exclude traces of water vapour and oxygen which can terminate "living" polymerisations. The excellent paper by Morton and collaborators was consulted as a guide to experimental procedure. 18

(a) The Preparation of the Sodium - naphthalene Complex.

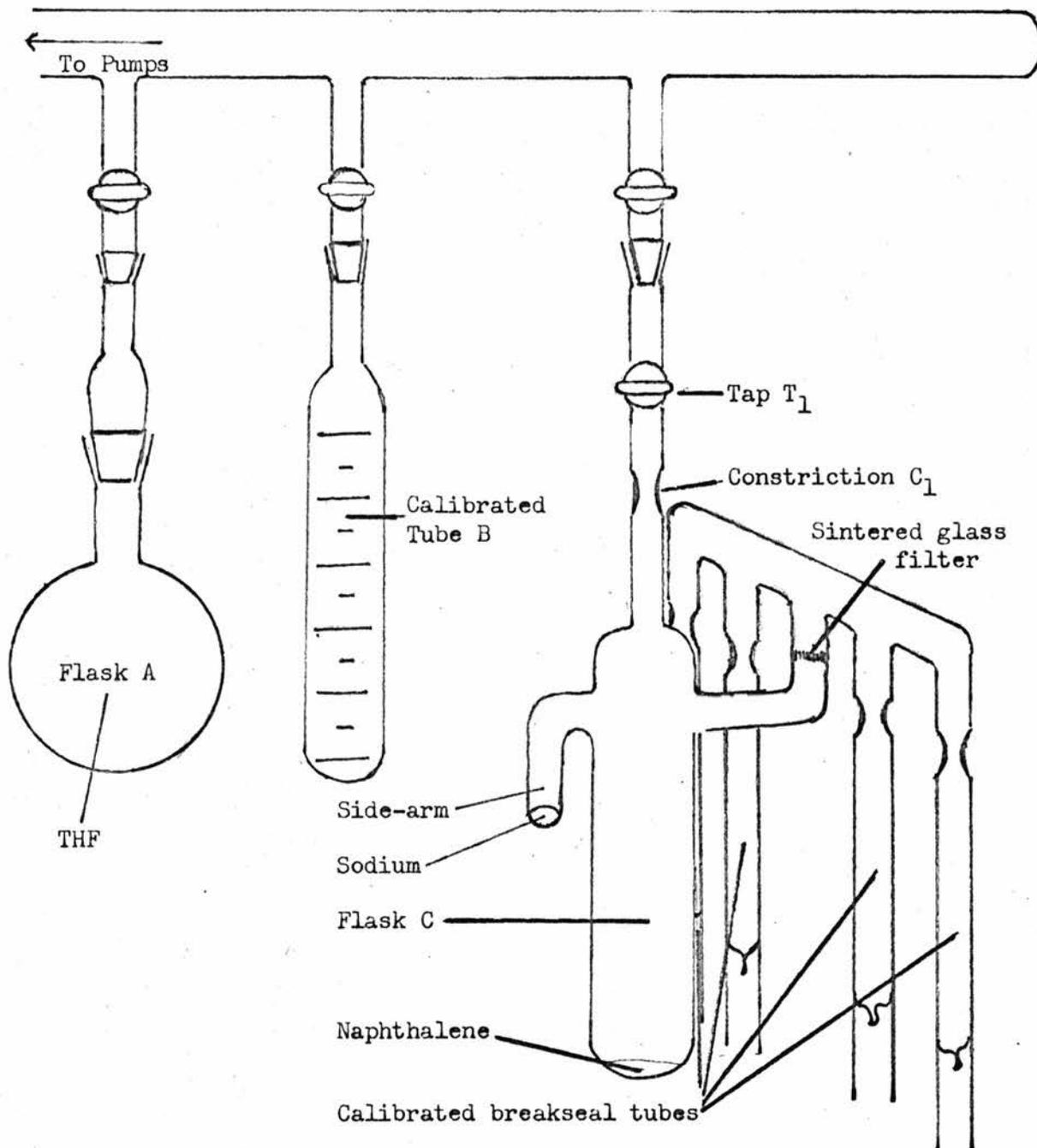
Naphthalene scales (B.D.H.) were recrystallised three times from ethanol and dried in a vacuum oven at 40°C . M.pt. $80 - 80.5^{\circ}\text{C}$. (Lit. m.pt. 80.5°C .).

Sodium lumps (B.D.H.) were thoroughly washed, firstly in dry petroleum ether and then in dry THF to remove all traces of liquid paraffin. The oxidised surface was pared off with a knife, and the freshly exposed pieces of sodium were cut into thin slivers and stored under sodium - dried THF.

THF was refluxed over sodium and distilled, the middle fraction being collected in a flask containing sodium wire and a little naphthalene. This flask (A in Figure 3) was attached to the vacuum line, frozen in liquid nitrogen, and degassed twice. The flask was kept on the vacuum line under high vacuum until required. The persistence of the intense green coloration in the solution indicated the efficiency of this method of excluding water from the THF.

FIGURE 3

APPARATUS FOR THE PREPARATION OF THE SODIUM-NAPHTHALENE COMPLEX.



Sodium naphthalenide solution was prepared in the apparatus C, (Figure 3). The glassware was thoroughly cleaned with chromic acid, washed with distilled water and acetone and dried at $110^{\circ}\text{C}.$ Immediately after removal from the oven, the apparatus was attached to the vacuum line and pumped out to a sticking vacuum for 24 hours. Evacuation to 10^{-5} mm. mercury was achieved by a mercury diffusion pump backed by a rotary oil pump.

The amounts of initiator and monomer used are related to the desired number average molecular weight of the polymer by the equation 19 found by Szwarc . This equation states that

$$\bar{M}_n = \frac{[\text{Monomer}]}{\frac{1}{2} [\text{Initiator}]} \quad \text{where } \bar{M}_n \text{ is the number average molecular weight}$$

5g. of monomer were used in each polymerisation, and the concentration of the catalyst to give the required molecular weight was controlled by the amount of naphthalene used. Accordingly, the necessary weight of naphthalene was weighed out accurately and dissolved in the minimum of THF. The flask C was removed from the vacuum line and an excess of sodium slivers introduced into the side-arm. The solution of naphthalene in THF was syringed into the flask C which was immediately re-attached to the vacuum line, and the THF removed by pumping, latterly with the flask immersed in liquid nitrogen to prevent sublimation of the naphthalene. After a sticking vacuum had been maintained for a few hours, the tap T_I was closed and the sodium in the side-arm warmed with a flame until it distilled into the

main tube where it formed a mirror. Tap T_I was opened after formation of the mirror.

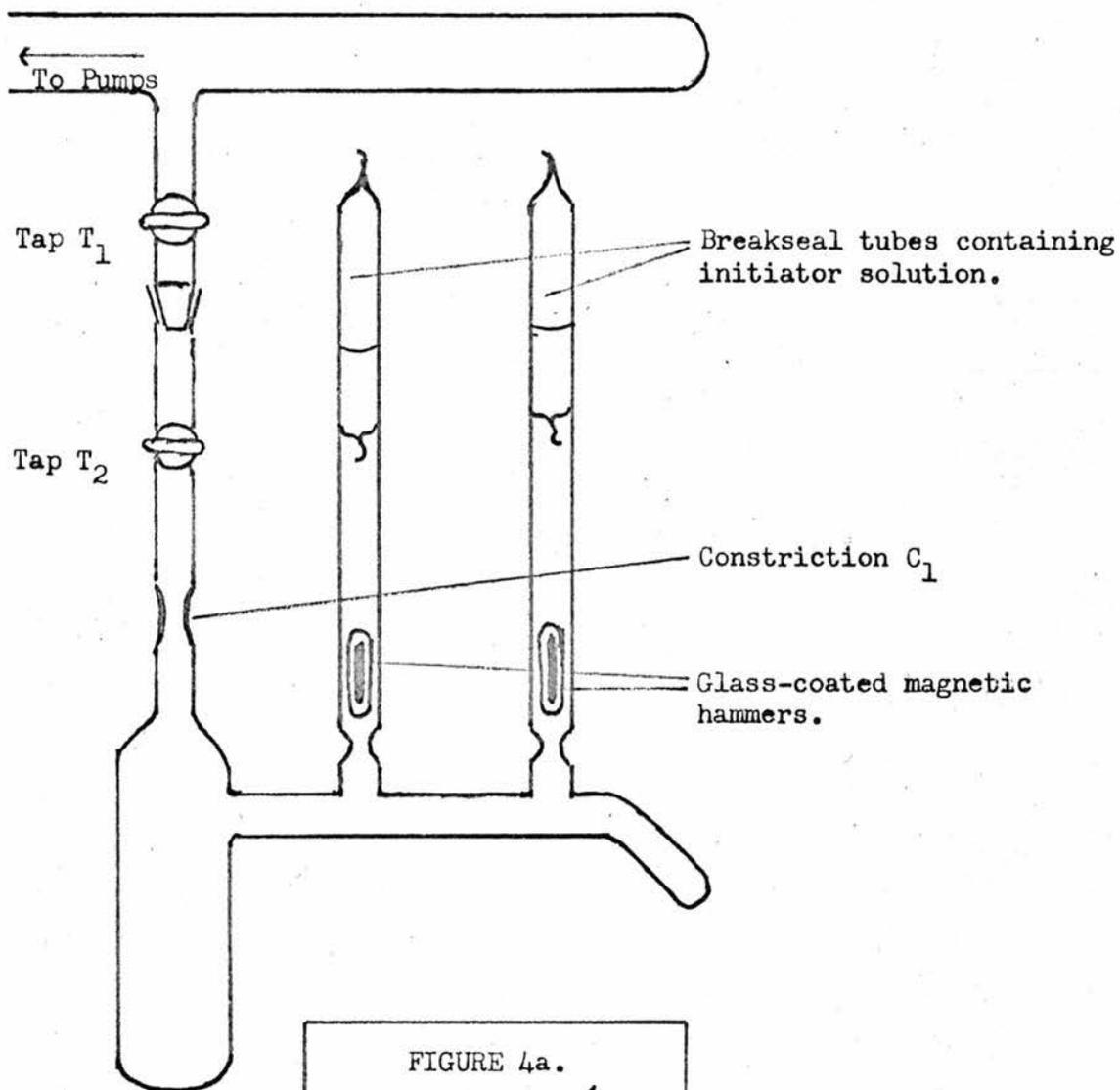
THF was distilled from Flask A into the calibrated tube B which also contained a sodium mirror as a precaution against moisture. After degassing, a measured amount of THF was distilled from B into Flask C where it was again degassed prior to being frozen in liquid nitrogen. When a sticking vacuum had been obtained Flask C was sealed at constriction C_I and removed from the line. On warming to room temperature the green colour of the sodium-naphthalene complex developed, and 24 hours were allowed for complete formation of the complex. Subsequently Flask C was tilted to allow the initiator solution to pass through the sintered glass filter into the calibrated breakseal tubes. The breakseal tubes were sealed off at the constrictions without recourse to freezing the solutions.

(b) The Preparation of Poly (methyl α - phenylacrylate)

Because of the high boiling point of methyl α - phenylacrylate, ($96-8^\circ\text{C./6mm.}^{20}$), it was impracticable to distil the monomer on the high vacuum line into the polymerisation vessel. Accordingly an alternative procedure, described below, was devised in which the monomer was syringed into the vessel under nitrogen in a "dry box". The method was tested using methyl methacrylate, and subsequent polymerisation gave a high yield of polymer.

The polymerisation vessel is shown in Figure 4. Two calibrated breakseal ampoules containing initiator solution were

FIGURE 4 POLYMERISATION APPARATUS



sealed on as indicated, and the apparatus was evacuated for at least 24 hours at a sticking vacuum. After this time Tap T_2 was closed and the vessel was removed from the vacuum line and put in the dry box which also contained monomer, syringes and a sintered glass filter. The dry box was flushed out overnight with dry nitrogen (B.O.C. White Spot). Subsequently the monomer was filtered, and the required volume syringed into the flask. Tap T_2 was closed again and the polymerisation vessel was removed from the dry box and attached to the vacuum line where Tap T_2 was opened and the monomer degassed three times. A measured amount of THF was distilled from the calibrated tube into the polymerisation vessel which was then sealed off at the constriction C_1 after degassing the solution twice.

The tube and end of the horizontal arm were both immersed in solid carbon dioxide / methanol baths (Figure 4a) at $-78^{\circ}\text{C}.$, and one of the breakseals opened with a glass coated hammer. Initiator solution ran into the side arm where it was cooled to $-78^{\circ}\text{C}.$ before being added slowly to the monomer solution. The time of polymerisation varied from 1 - 5 days at $-78^{\circ}\text{C}.$, and polymerisation was terminated by methanol. The second breakseal tube containing initiator was used as a stand by.

The polymers were dissolved in chloroform and precipitated by slow addition to methanol. After a second precipitation the polymers were dried in the vacuum oven, initially at room temperature and finally at $60^{\circ}\text{C}.$

B. The Thermal Degradation of Poly (methyl α - phenylacrylate.)

I. Analysis of the Volatiles produced by Pyrolysis.

Investigations of the volatiles produced from poly (methyl α - phenylacrylate), P M A, degraded in the molecular still were unsatisfactory because quantitative recovery of the products was never achieved. This was due to the high boiling point of the monomer and the distance between the still and the collecting capillary. Accordingly experiments in which the composition of the products was being investigated were carried out in the closed system apparatus shown in Figure 5. Complete recovery of the degradation products was effected in this system.

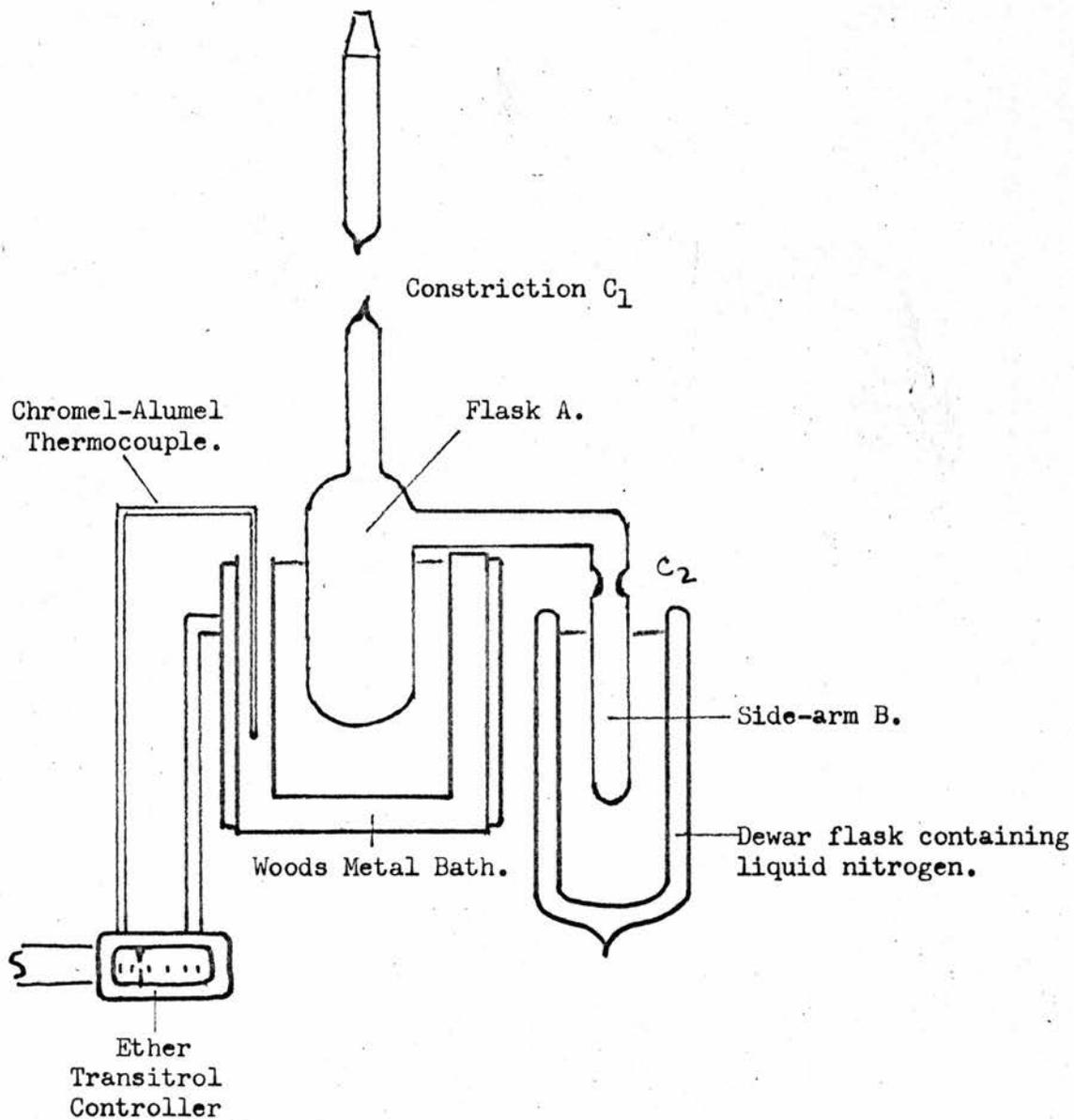
The degradation procedure was as follows. A known weight of polymer (0.22g.) was dissolved in the minimum of Analar benzene, and the solution was pipetted into the bulb A. The solvent was removed, firstly in an air oven and latterly by pumping to high vacuum on the vacuum line. On attainment of a sticking vacuum the apparatus was sealed at constriction C_1 . Degradation was effected with bulb A immersed in a Wood's metal bath and the side-arm B cooled in liquid nitrogen. The metal bath was controlled by an "Ether Transitrol" controller actuated by a chromel-alumel thermocouple sited in the wall of the bath. When degradation was complete the apparatus was divided into two parts by sealing at constriction C_2 . Both parts, A and B, were cleaned and weighed.

Part A was carefully cut open and weighed. The polymer

FIGURE 5

BULK DEGRADATION APPARATUS

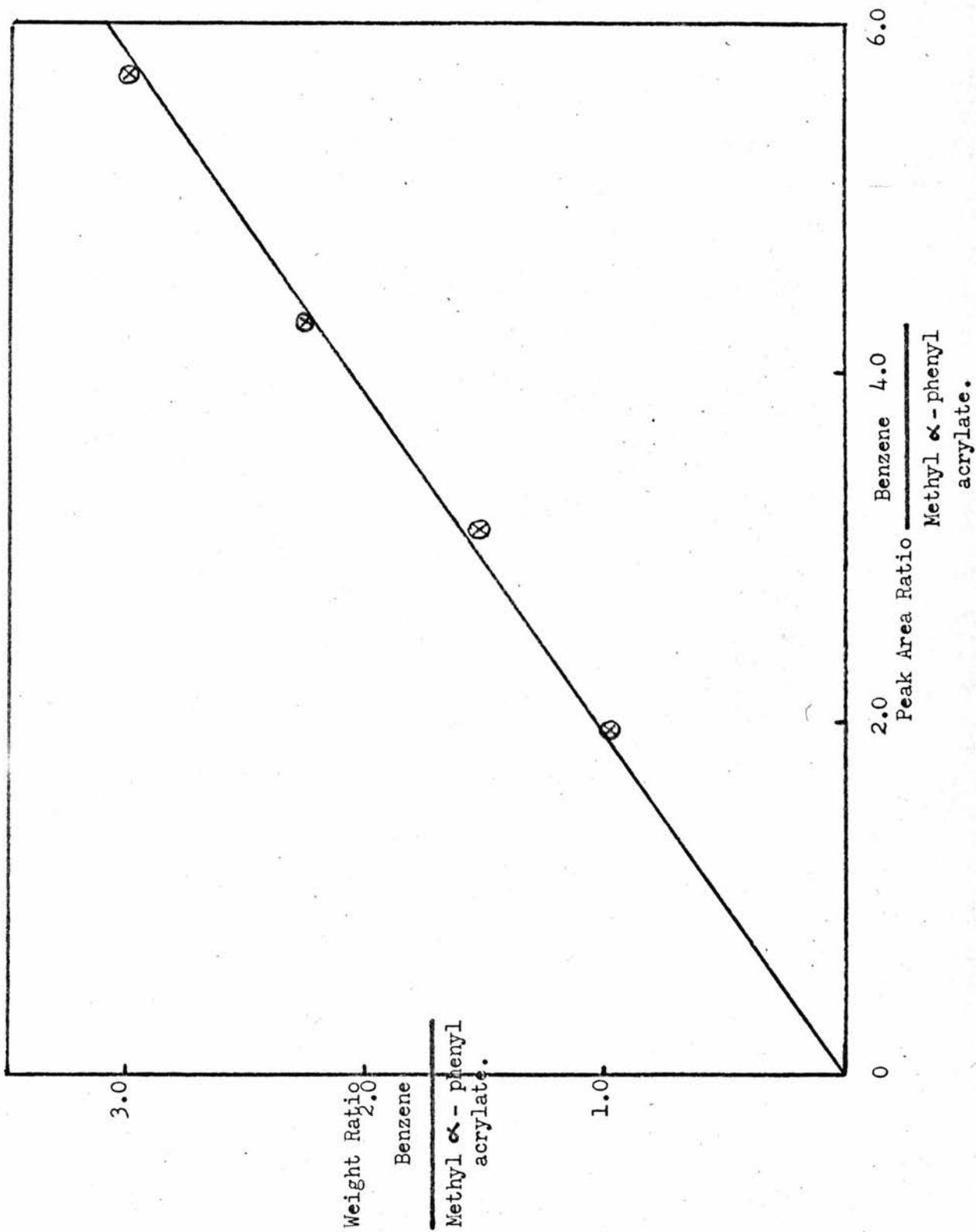
APPARATUS EMPLOYED TO COLLECT THE PYROLYSIS PRODUCTS FROM P M A.



residue was totally removed in solution in benzene, and the weight of part A re-determined after drying. An estimate of the weight of the residue was obtained from the difference between these two weighings. Confirmation of this estimate was obtained by evaporating the benzene solution of polymer to dryness at 90°C. in a vacuum oven, and good agreement was obtained between the two values.

Part B was cut open and the liquid contents removed in a syringe. Subsequently B was cleaned, dried and re-weighed. After applying a small correction to this second weighing to allow for the increased mass due to a small volume of air, the difference between the two weighings provides the mass of degradation products. Analysis of the liquid products of degradation by GLC on a 10% Apiezon / Celite column at 90°C. indicated two components, subsequently proved to be benzene and methyl α -phenylacrylate by comparison with the retention times of pure compounds. A calibration curve (Figure 6) was constructed of the ratio of GLC peak areas to the corresponding weight ratio for four mixtures of benzene and methyl α -phenylacrylate of known but different compositions. Using this graph, the ratio of the weights of the two components in the degradation products was obtained, and the absolute weights were calculated from the total weight of the liquid products. Usually some 6 - 7% of benzene was found in the products. Since the weight of monomer in all cases agrees well with the loss in weight of the polymer, the benzene is assumed to result from the incomplete removal

FIGURE 6.

GLC Calibration Plot for Mixtures of Benzene and Methyl α -phenylacrylate.

of solvent from the polymer after it was added to flask A.

No evidence was found of products volatile at room temperature since there was no observable decrease in mass on opening part B. However, the loss of very small amounts of gaseous volatiles would not be detected in this way.

II. Degradations in the Molecular Still

The procedure employed was exactly the same as described in Part I, Chapter II, Section B I of this thesis.

III. The Degradation of Polymers by Thermogravimetric Analysis

The procedure used was identical to that described in Part I, Chapter II, Section B II of this thesis.

C. The Characterisation of Polymers

The molecular weights of all undegraded samples were measured both by viscometry and osmometry to give an estimate of the polydispersity of the polymer. All samples dissolved readily in benzene and toluene at room temperature. Some difficulty was experienced in measuring osmotic pressures because of diffusion of small polymer molecules through the membrane, so that some of the number average molecular weights must be regarded as approximate.

Degraded polymers were found to be only partially soluble in cold benzene or toluene, almost certainly because crystallinity develops during the slow cooling from the degradation temperature to room temperature. The residues, however, were soluble in cold chloroform. Accordingly they were dissolved from the tray in this

solvent. The chloroform was then removed by distillation under reduced pressure, and the polymer dissolved in boiling benzene. There was no evidence of precipitation of polymer from solution on cooling to room temperature. Concentrations of solutions were determined, as previously, by evaporating the solvent from a known volume of solution, and determining the weight of polymer.

Because of the low molecular weights of degraded polymers, only viscosity average molecular weights were obtained for these residues, since osmotic pressure measurements were subject to large errors because of diffusion through the membrane.

I. Viscometry

The Mark-Houwink Equation found by Hopff, Lüssi and Borla²¹ for poly (methyl α - phenylacrylate) in benzene at 24.5°C. was employed in this work. This relationship is

$$[\eta] = K M^a$$

$$\text{where } K = 2.9 \times 10^{-4}$$

$$a = 0.593.$$

All viscosity measurements were made in an Ubbelohde suspended level dilution viscometer, suspended in a thermostatted water-bath controlled at 24.5 \pm 0.05°C. by a mercury-toluene regulator and an Ether relay.

II. Osmometry

Osmotic pressure measurements were made at 37°C. in a Mechrolab Model 50I High Speed Membrane Osmometer using Ultracella - filter "allerfeinst" membranes and toluene as solvent. Under these

experimental conditions the number average molecular weight, \bar{M}_n , is given by

$$\bar{M}_n = \frac{3.028 \times 10^4}{\lim_{c \rightarrow 0} \frac{\pi}{c}}$$

Attempts were made to restrict the diffusion of small polymer molecules through the membranes by employing Ultrafeinfilter "allerfeinst" membranes. These membranes, normally used in aqueous systems, have recently been shown by Feist²² to greatly reduce diffusion and permit accurate determinations of polymer molecular weights as low as 5,000 with toluene as solvent. However, consistent solvent osmotic pressure heads could not be determined with these membranes, despite lengthy periods of conditioning, and their use was discontinued.

D. Molecular Weights of Polymers available for Degradative Studies.

Polymer.	Temp. of Polym ⁿ .	Initiator and Solvent.	Prepared by *	\bar{M}_n $\times 10^{-6}$	\bar{M}_v $\times 10^{-6}$	$\frac{\bar{M}_v}{\bar{M}_n}$
PMA(1)	- 78°C	Na / Naph THF	K	0.029	0.474	16.34
PMA(2)	- 78°C	Na / Naph THF	K	0.017	0.017	1.00
PMA(3)	- 78°C	Na / Naph THF	H,L,B.	0.013	0.050	3.85
PMA(4)	- 78°C	BuLi Tol	C,T	0.012	0.047	3.92
PMA(5)	- 78°C	CaZnEt ₄ THF	C,T	0.120	0.366	3.05

* K - Kerr.

H,L,B. - Hopff, Lussi and Borla²¹.

C,T - Chikanishi and Tsuruta¹⁶.

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CHAPTER III

THE THERMAL DEGRADATION OF POLY (METHYL α - PHENYLACRYLATE)

In any study of the thermal degradation of a hitherto uninvestigated polymer, research along three major lines provides most of the evidence of the type of decomposition reaction involved.

These three main routes are

- (1) a study of the products of the degradation,
- (2) a study of the molecular weight changes in the polymer during degradation,

and (3) a study of the rates of volatilisation.

The thermal decomposition of poly (methyl α - phenylacrylate) was investigated along these three lines.

(I) The Products of the Thermal Degradation of P M A.

PMA(3) was degraded in the apparatus described in Chapter II, B, I. The relevant data concerning the weights of the products is tabulated in Table I.

TABLE I.

Analyses of the Products of the Thermal Degradation of PMA(3).

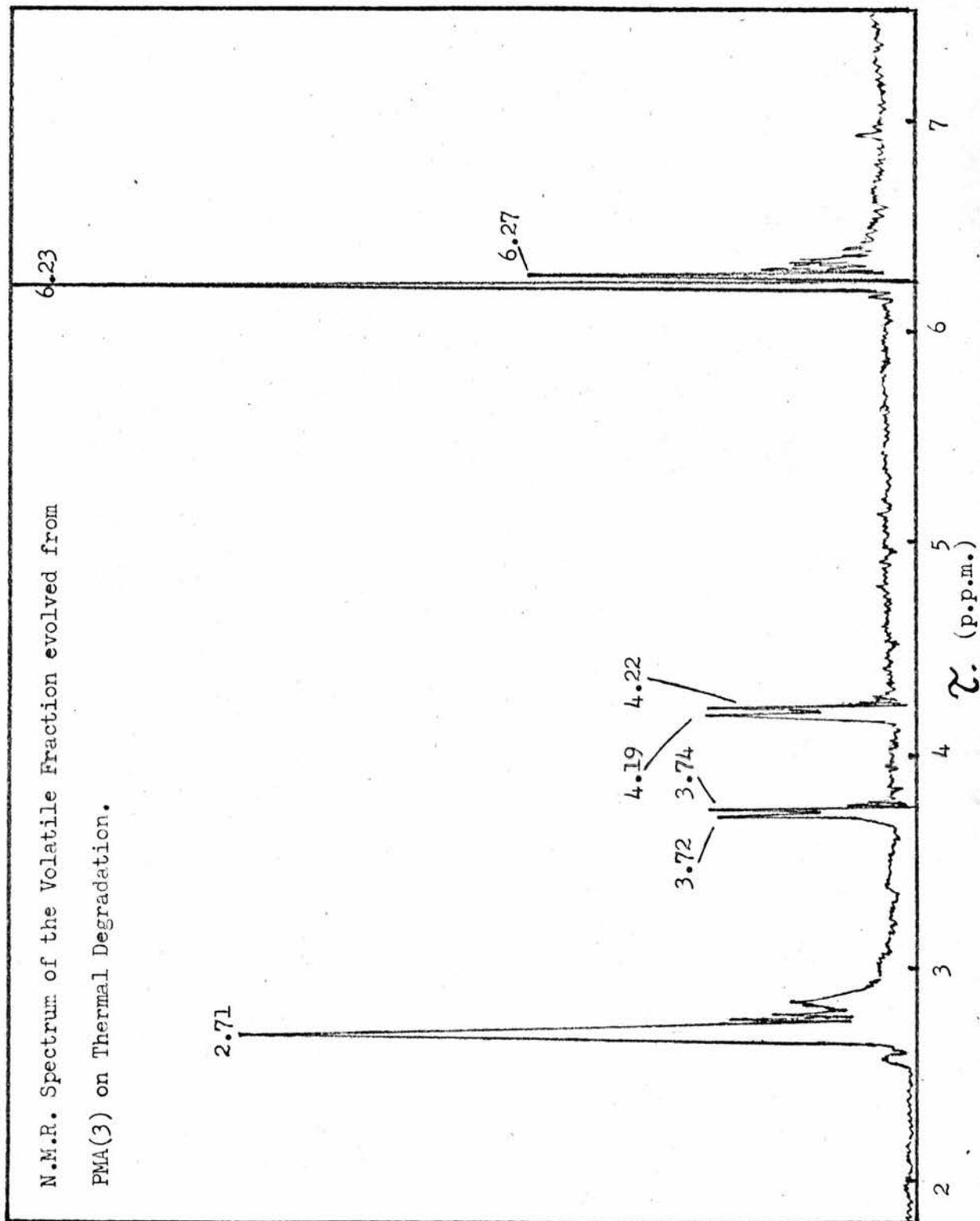
Temperature:- 250°C.

Run No.	Wt. of Polymer. (g)	Wt. of Residue. (g)	Wt. of Products. (g)	Wt. of Benzene in Products. (g)	Wt. of MA in Products. (g)	Wt. of MA + Residue. (g)
1	0.2297	0.0247	0.2182	0.0109	0.2073	0.2320
2	0.2218	0.1238	0.1094	0.0065	0.1029	0.2267
3	0.2332	0.0232	0.2312	0.0164	0.2158	0.2390

From Table I it is apparent that the sum of the weights of monomer and residue is equal to the initial weight of polymer. The benzene, therefore, originates from traces of this solvent remaining behind when the polymer film was formed, and is not the result of the decomposition of the aryl side-group. There was no evidence of low molecular weight material such as dimer, trimer etc., although very small amounts of these substances might not have been noticed. Nuclear Magnetic Resonance spectra of the volatile products (Figure I) showed no broadening of any of the peaks, and were in every way identical to the spectra of pure methyl α - phenylacrylate, thus further confirming the absence of oligomeric material in the degradation products.

Although these investigations are not completely exhaustive, the evidence available leads to the conclusion that monomer is the sole product of the thermal degradation of P M A. In this respect, P M A behaves very similarly to poly (methyl methacrylate)^{I-3} and poly (α - methylstyrene)⁴, and the tentative suggestion may be made that P M A, like the above mentioned polymers, exhibits a very long kinetic chain length on degradation. Such behaviour will be promoted by the absence of tertiary C - H bonds in the polymer, since such bonds are known sites of hydrogen abstraction in transfer⁵ reactions . The absence of dimer, trimer and larger fragments from the volatiles contrasts with the known products of the degradation of polystyrene^{6,7} where 60% of the products consist of these fragments.

FIGURE 1.



Thus, the effect on the monomer yield of the substitution of the reactive tertiary hydrogen atoms is again demonstrated, and the importance of these atoms in transfer reactions is emphasised.

(2) The Molecular Weights of Degraded Samples of P M A.

PMA(5) was chosen for this study because it possessed a reasonably high molecular weight. Samples were degraded at 210° and 220° C. in the molecular still, and the molecular weights of the residues were measured by viscometry. (Table 2, and Figures 2a,b and c).

Figure 2a indicates that the volatilisation starts at a high initial rate, and slowly decays with time. More will be said about this feature later.

The molecular weight versus time curves (Figure 2b) show a considerable initial fall in molecular weight, the drop being greater at the higher temperature. The molecular weight versus conversion curves, however, are far more informative as to the nature of the degradation mechanism. In Figure 2c it is immediately apparent that the points for degradations at 220° C. approximate closely to a diagonal between $\bar{M}_v = 367,000$ at 0% conversion and $\bar{M}_v = 0$ at 100% conversion, whereas the corresponding data for 210° C. lie on a gentle curve just below the diagonal. Such behaviour contrasts with the known characteristics of polystyrene, for which polymer the molecular weight falls far more rapidly over the first 10% volatilisation, and the molecular weight versus conversion curves appear to be independent of temperature over a considerable range.

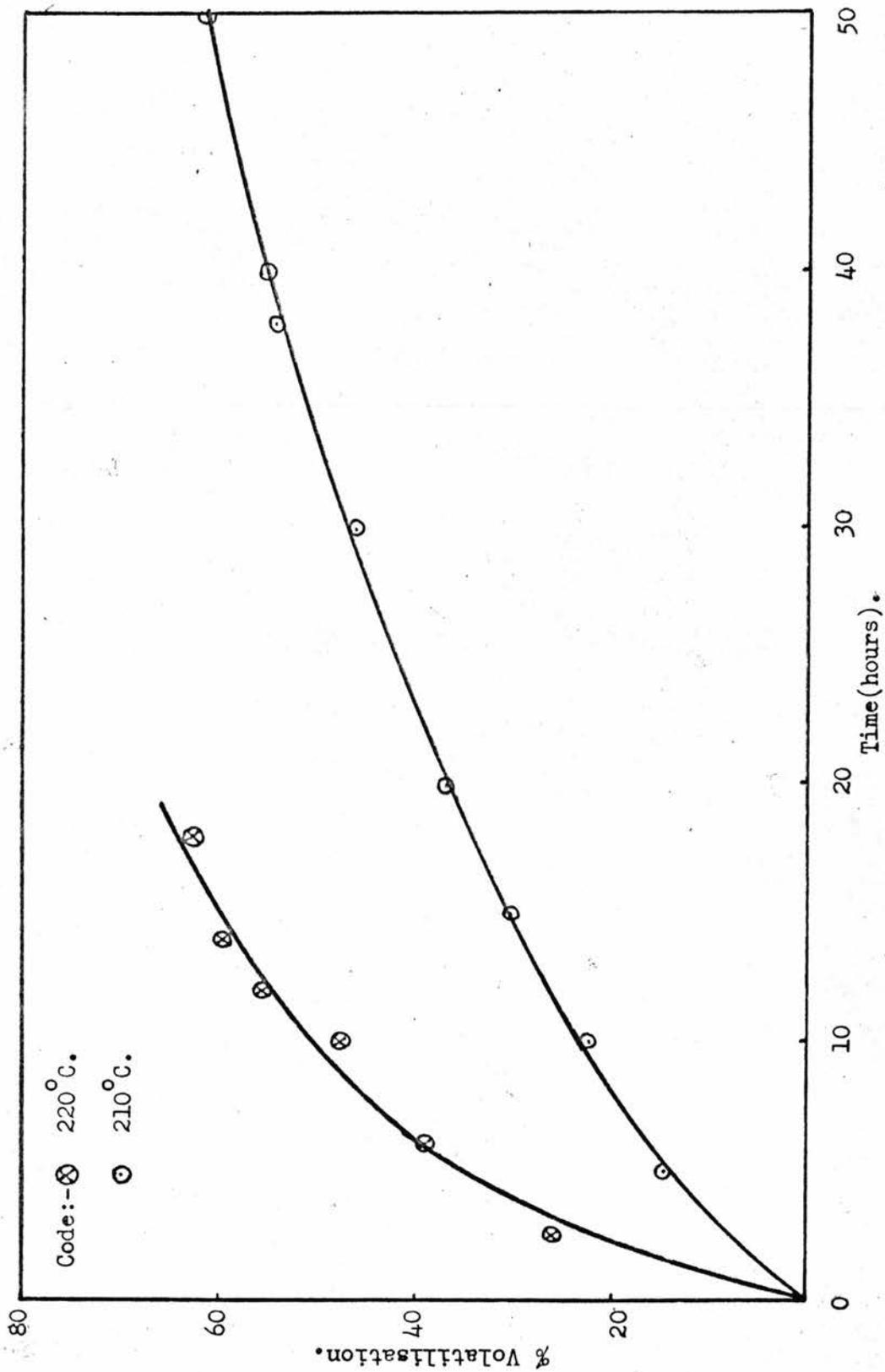
TABLE 2.

Thermal Degradation of PMA(5).

Molecular Weight Changes with Time and Temperature of Degradation.

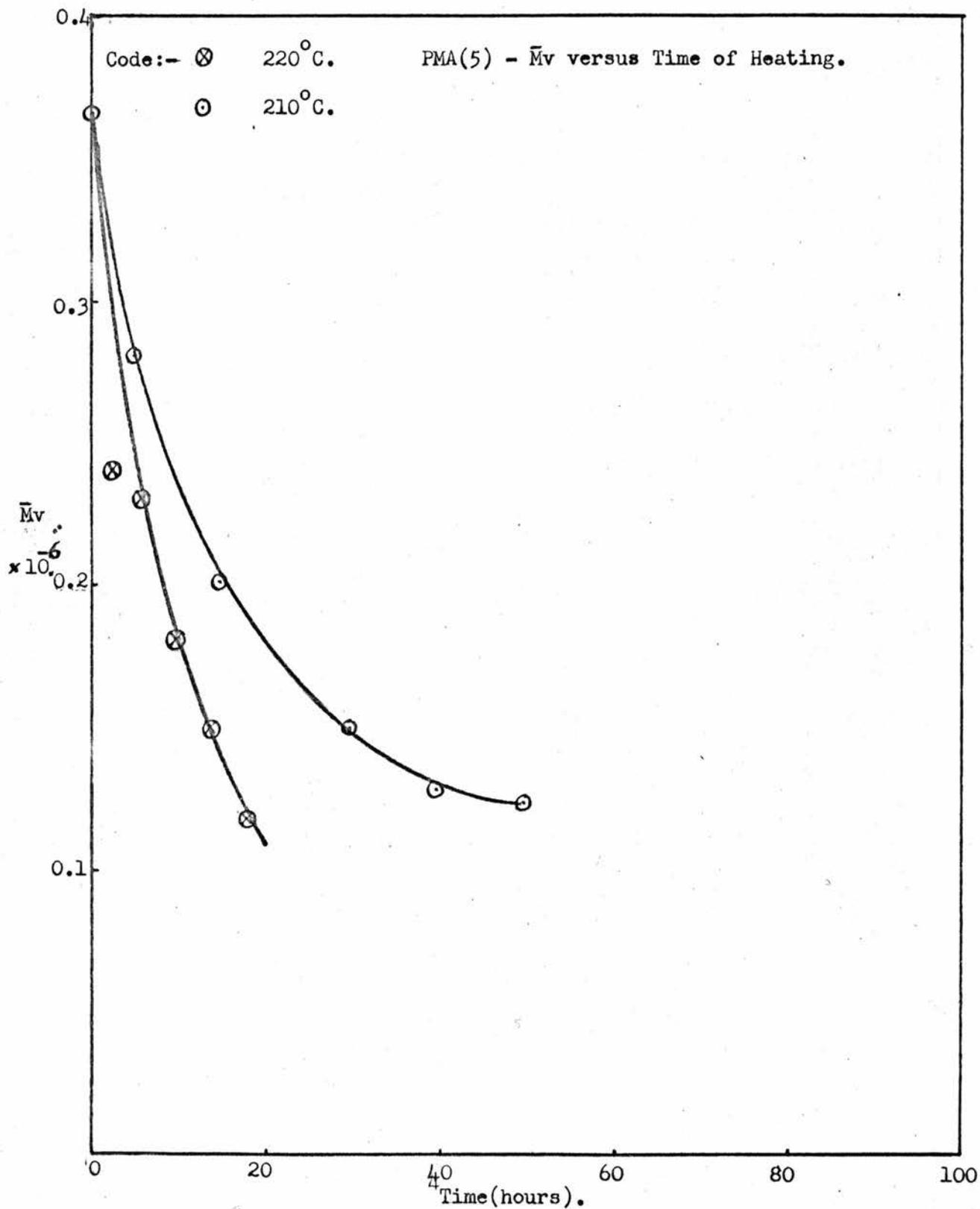
Temperature of Degradation. $T^{\circ}\text{C.}$	Time. (hr.)	Volatilisation (%)	$[\eta]$	\bar{M}_v_t $\times 10^{-6}$	$\frac{1-x}{\bar{M}_v_t}$ $\times 10^{+6}$	$\frac{1-x}{\bar{M}_v_t} - \frac{1}{\bar{M}_v_0}$ $\times 10^{+6}$
-	-	-	0.58	0.366	2.732	0
210	5.00	14.20	0.49	0.281	3.054	0.322
210	10.00	22.10	-	-	-	-
210	15.00	30.16	0.41	0.201	3.473	0.741
210	20.00	36.71	-	-	-	-
210	30.00	46.00	0.34	0.150	3.599	0.867
210	38.00	54.32	-	-	-	-
210	40.00	55.31	0.31	0.128	3.493	0.761
210	50.00	61.41	0.30	0.123	3.138	0.406
220	2.50	25.80	0.46	0.241	2.738	0.006
220	6.00	38.82	0.44	0.231	2.745	0.012
220	10.00	47.18	0.38	0.181	2.750	0.018
220	12.00	55.44	-	-	-	-
220	14.00	59.44	0.34	0.150	2.744	0.012
220	18.00	62.50	0.29	0.118	2.737	0.005

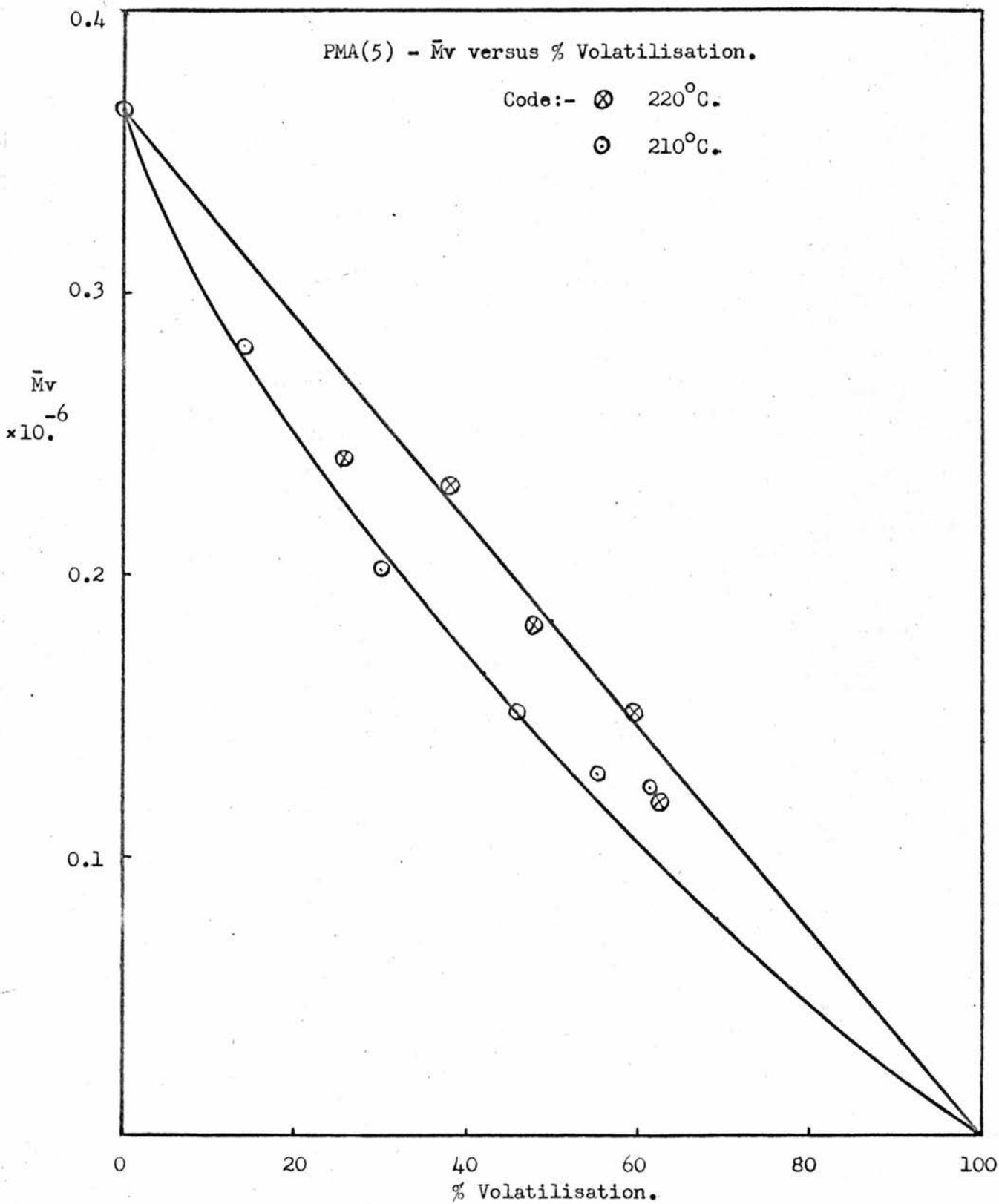
FIGURE 2a.



PMA(5) - %Volatilisation versus Time of Heating.

FIGURE 2b.





An explanation of these features comes from consideration of the simple representation introduced by Grassie and Melville^I of the effects of random and end initiation, with large and small zip lengths, on molecular weight versus conversion curves. These investigators have shown that a fall in molecular weight below the diagonal signifies a random scission reaction. Apparently, therefore, P M A degrades by a random scission process since the plot of molecular weight as a function of conversion for degradations at 210°C. lies below the diagonal; no change in mechanism is expected in the degradations at 220°C.. The difference in character between the 210°C and 220°C. curves must depend on the relative magnitude of the initiation, depropagation and termination steps at the two temperatures. Of these three steps, the amount of depropagation, i.e. the kinetic chain length (KCL), will probably be most affected by an increase in temperature. From the shape of the curves in Figure 2c it appears that the temperature range 210 - 220°C. represents a transition from the lower temperature where the $KCL < \overline{DP}$ and the upper temperature where $KCL \approx \overline{DP}$. Support for this theory comes from theoretical computations by Simha, Wall and Bram⁸, and experimental data obtained by Brown and Wall⁹ for the degradation of poly (α - methylstyrene).

The mechanism of initiation cannot be assigned by molecular weight measurements alone. Although the relatively rapid fall in molecular below the diagonal in Figure 2c is generally indicative of random scission, it can conceivably be a sign of random or chain-end

initiation followed by extensive intermolecular transfer, as is considered to occur in polystyrene ^{IO} during degradation. However, two factors militate against this possibility. Firstly, P M A prepared by "living" anionic synthesis does not contain the double-bond chain ends ^{II} normally associated with end initiation in vinyl addition polymers e.g. poly (methyl methacrylate) ^I. Secondly, there is no evidence, either in the experiments described in section (I) of this chapter or in the present investigations, that transfer reactions occur. Usually these reactions are associated with oligomeric products which are volatile at the degradation temperature but involatile at room temperature ^{6,7}. Furthermore, the absence of tertiary hydrogen atoms in P M A negates the tentative postulate that transfer reactions are responsible for the molecular weight change.

For a simple random degradation with no volatilisation ^{I2},

$$\frac{\bar{M}v_t}{\bar{M}v_0} - \frac{I}{M_0 a} = \frac{\alpha}{M_0 a} \quad (I)$$

where $\bar{M}v_t$ = viscosity average molecular weight at time t,

$\bar{M}v_0$ = viscosity average molecular weight of undegraded polymer,

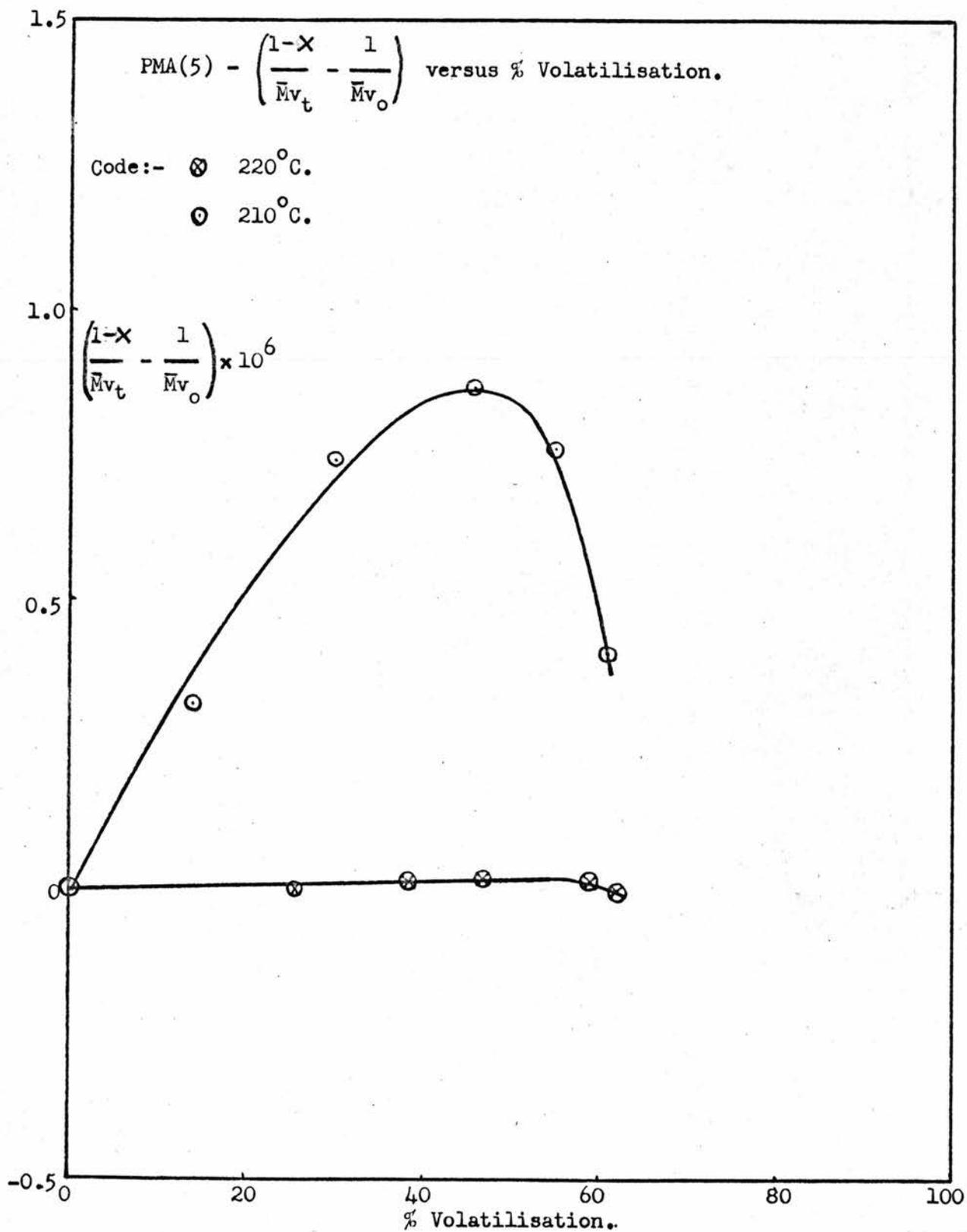
M_0 = monomer molecular weight,

a = ratio of viscosity to number average molecular weight,

and α = fraction of bonds broken.

In a system where volatilisation occurs Equation (I) becomes

FIGURE 2d.



$$\frac{I - x}{\bar{M}v_t} - \frac{I}{\bar{M}v_0} = \frac{\alpha}{M_0 a} \quad (2)$$

where x = fractional conversion.

A plot (Figure 2d) of $\left(\frac{I - x}{\bar{M}v_t} - \frac{I}{\bar{M}v_0} \right)$ as a function of conversion exhibits a maximum at $\sim 45\%$ conversion for the 210°C . curve, but is poorly defined for the 220°C . curve. A maximum in this plot signifies a maximum in the number of molecules present in the degraded polymer. If degradation were initiated at chain ends then there should be a corresponding maximum at $\sim 45\%$ conversion in the rate of volatilisation versus conversion curves, but no such dependence is found. (Figures 2a, 3a). Consequently, it seems probable that initiation of degradation in P M A occurs at random, that there is little, if any, transfer and the kinetic chain length is fairly long. It is possible from Figure 2d to estimate the kinetic chain length, since the molecular population begins to decrease beyond 45% conversion at 210°C ., i.e. macroradicals once initiated completely unzip. Therefore, the kinetic chain length at 210°C . is equal to the \bar{DP} at 45% conversion, which is approximately 1,000 monomer units.

(3) The Rates of Volatilisation of P M A.

As mentioned in section (2) of this chapter, volatilisation versus time curves were constructed for the degradations on PMA(5) carried out in the molecular still, although these experiments were

primarily concerned with providing molecular weight data. The initial rate of volatilisation percent of original weight (R_I) was obtained by drawing tangents to the volatilisation versus time curves at zero time. Subsequent rates were calculated by use of a numerical method of differentiation^{I3} employing the equation

$$f_t^I = \frac{I}{h} \left[\Delta^I f_t - \frac{I}{2} \Delta^2 f_t + \frac{I}{3} \Delta^3 f_t - \dots + \frac{(-I)^m \Delta^m f_t}{m} \right]$$

where f_t - percentage volatilised at time t ,

f_t^I = the rate of volatilisation (R_I) at time t ,

Δ^n = the n^{th} difference from f_t ,

and h = the time interval.

A computer programme showed that the scatter of the points increased so greatly for differences greater than unity that accuracy was lost by using more than one difference. Consequently, only one difference was employed, and the time interval h was made very small in order to increase the accuracy of the rate values. Rates of volatilisation as percent of original weight per hour (R_I) and percent of residual weight per hour (R_2) as functions of conversion are shown in Figures 3a and 3b respectively, and the relevant data is tabulated in Table 3.

Both R_I and R_2 curves show rates which decay with time in a non-linear manner. Qualitatively these curves resemble those

TABLE 3.

Thermal Degradation of PMA(5).

Rates of Volatilisation with Time and %Volatilised.

220°C.				210°C			
Vol. ⁿ (%)	Time. (hr.)	Rate.R ₁ % hr. ⁻¹	Rate.R ₂ % hr. ⁻¹	Vol. ⁿ (%)	Time. (hr.)	Rate.R ₁ % hr. ⁻¹	Rate.R ₂ % hr. ⁻¹
0	0	12.20	12.20	0	0	3.64	3.64
5	0.40	10.40	10.95	5	1.40	3.02	3.18
10	0.90	9.80	9.89	10	3.50	2.48	2.76
15	1.50	7.50	8.82	15	5.55	1.98	2.33
20	2.20	6.10	7.63	20	8.35	1.66	2.08
25	3.00	5.60	7.47	25	11.60	1.52	2.03
30	3.90	4.90	7.00	30	15.00	1.30	1.86
35	5.10	3.70	5.69	35	18.95	1.22	1.88
40	6.40	3.00	5.00	40	25.85	1.04	1.73
45	7.05	2.90	5.27	45	28.30	0.96	1.75
50	9.85	2.50	5.00	50	33.65	0.90	1.80
55	11.80	2.20	4.89	55	39.70	0.82	1.82
60	14.30	1.90	4.75	60	46.50	0.74	1.85
65	17.40	1.60	4.57	65	54.40	0.60	1.71

FIGURE 3a.

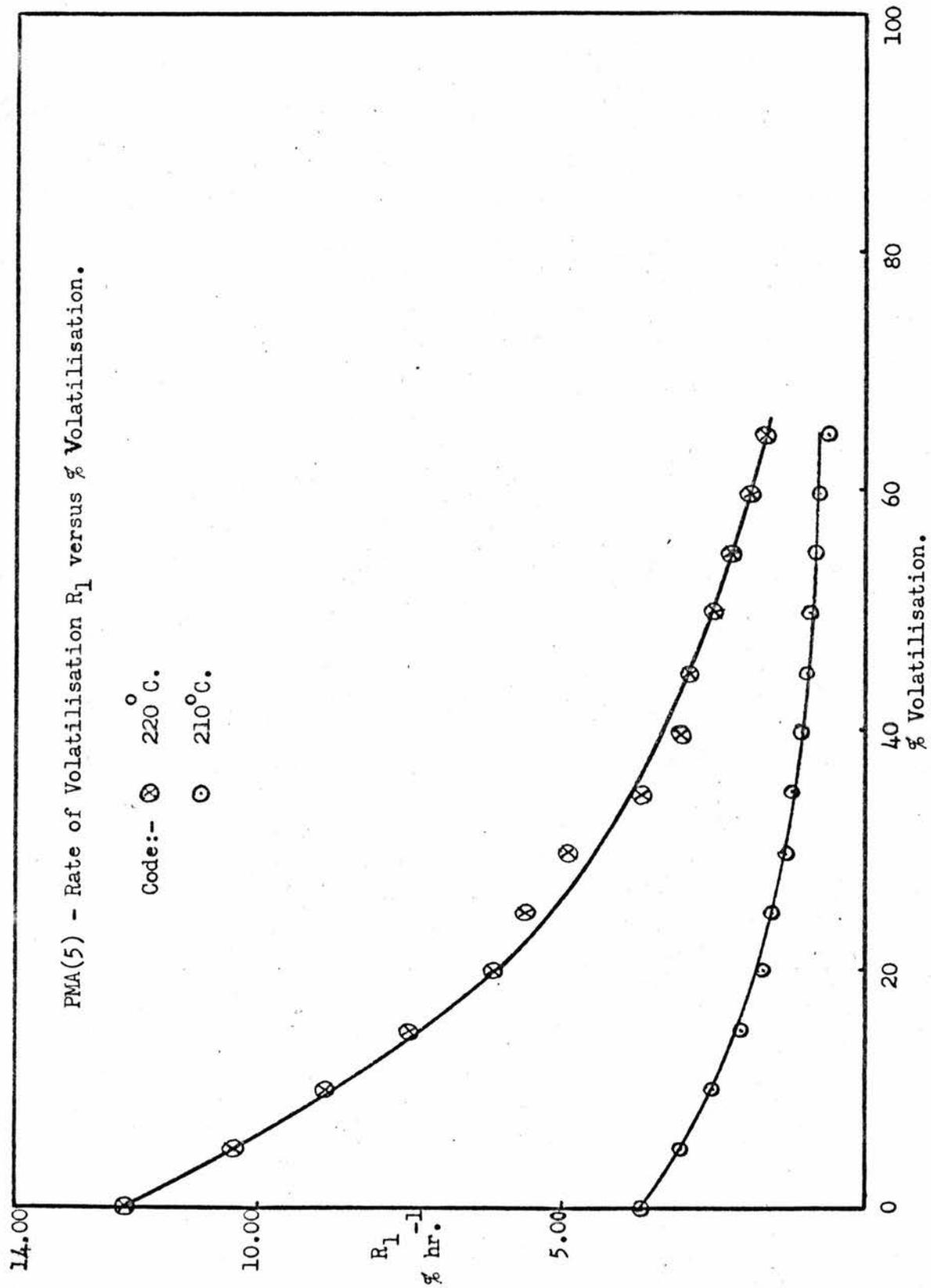
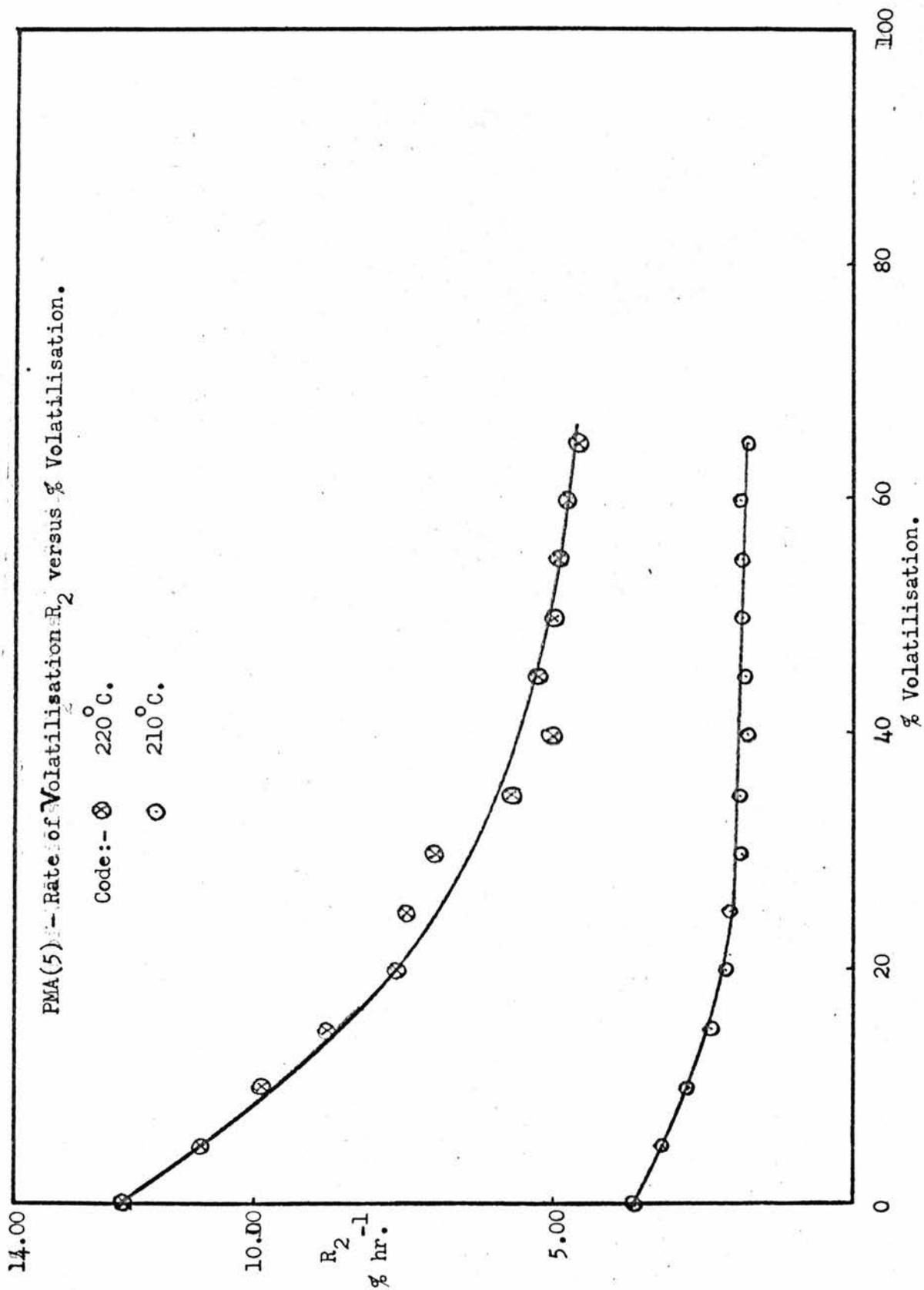


FIGURE 3b.



found previously for poly (α -methylstyrene)⁹ and poly (methyl methacrylate)^{3,14,15}, and are in no way similar to the rate curves for polystyrene^{2,10,16} which exhibit a maximum at 35 - 40% conversion. From the initial rates of degradation at 210° and 220°C. an approximate value of 57 kcal. mole⁻¹ was assigned to the overall Activation Energy for the thermal degradation of PMA(5). Further discussion of the rates of degradation of P M A will be postponed until consideration of the data from isothermal thermogravimetric analysis.

(4) Thermogravimetric Analysis of P M A

Both isothermal and temperature programmed methods were used in this study, and will be considered in this order.

(a) Isothermal (Static) Thermogravimetric Analysis of P M A

All five samples of P M A were investigated at four temperatures. Once again the initial rates were obtained by drawing tangents to the % volatilisation versus time curves, and subsequent rates were calculated by first differences using the method previously described¹³. Rate versus conversion curves for the polymers are shown in Figures 4a,b,c,d and e, and each figure shows an insert of the Arrhenius plot of log (initial rate) versus $1/T^{\circ}A$.

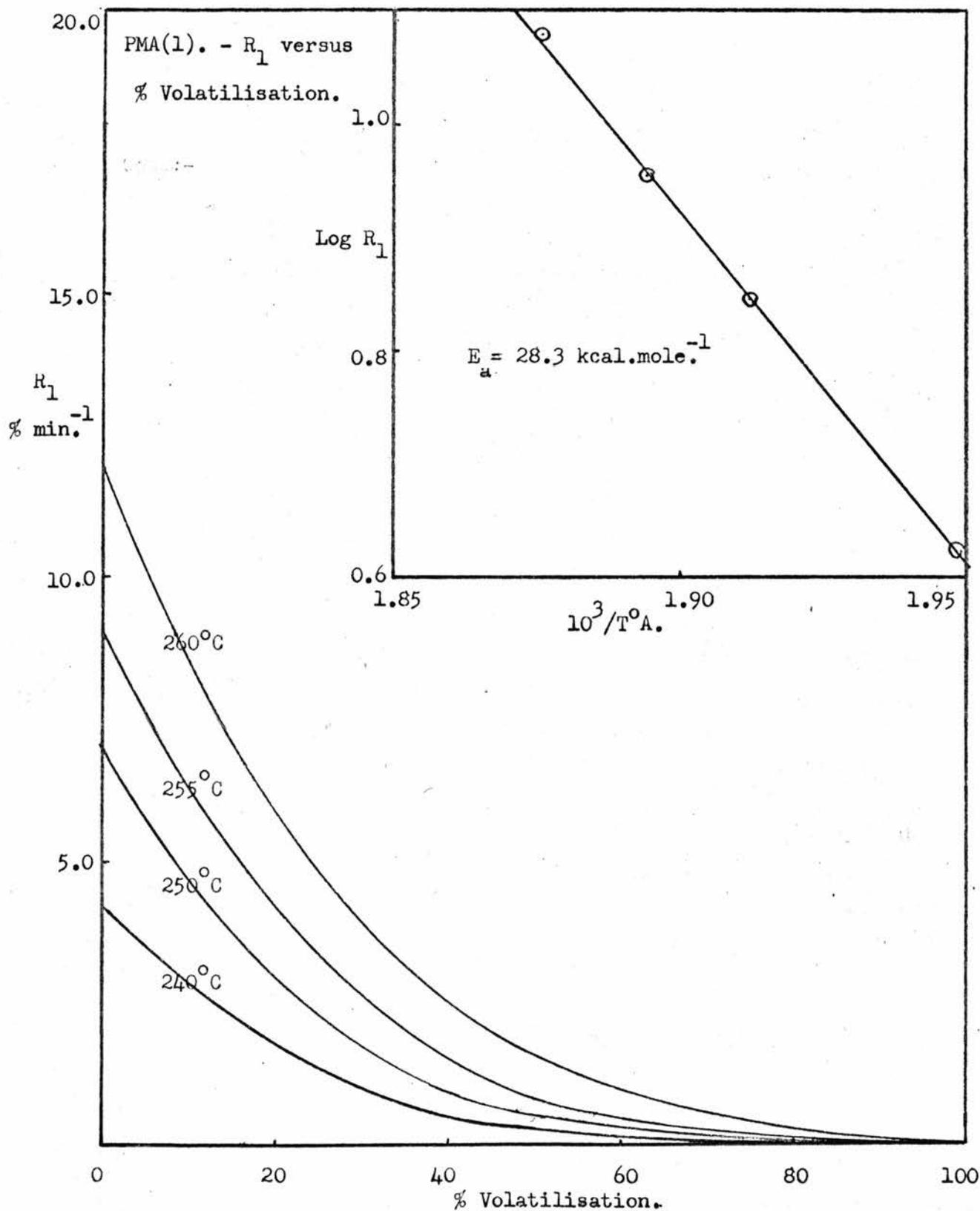
The rate curves are essentially similar to the R_T curves obtained previously for PMA(5) degraded in the molecular still, thus indicating that all five polymers degrade by a similar mechanism.

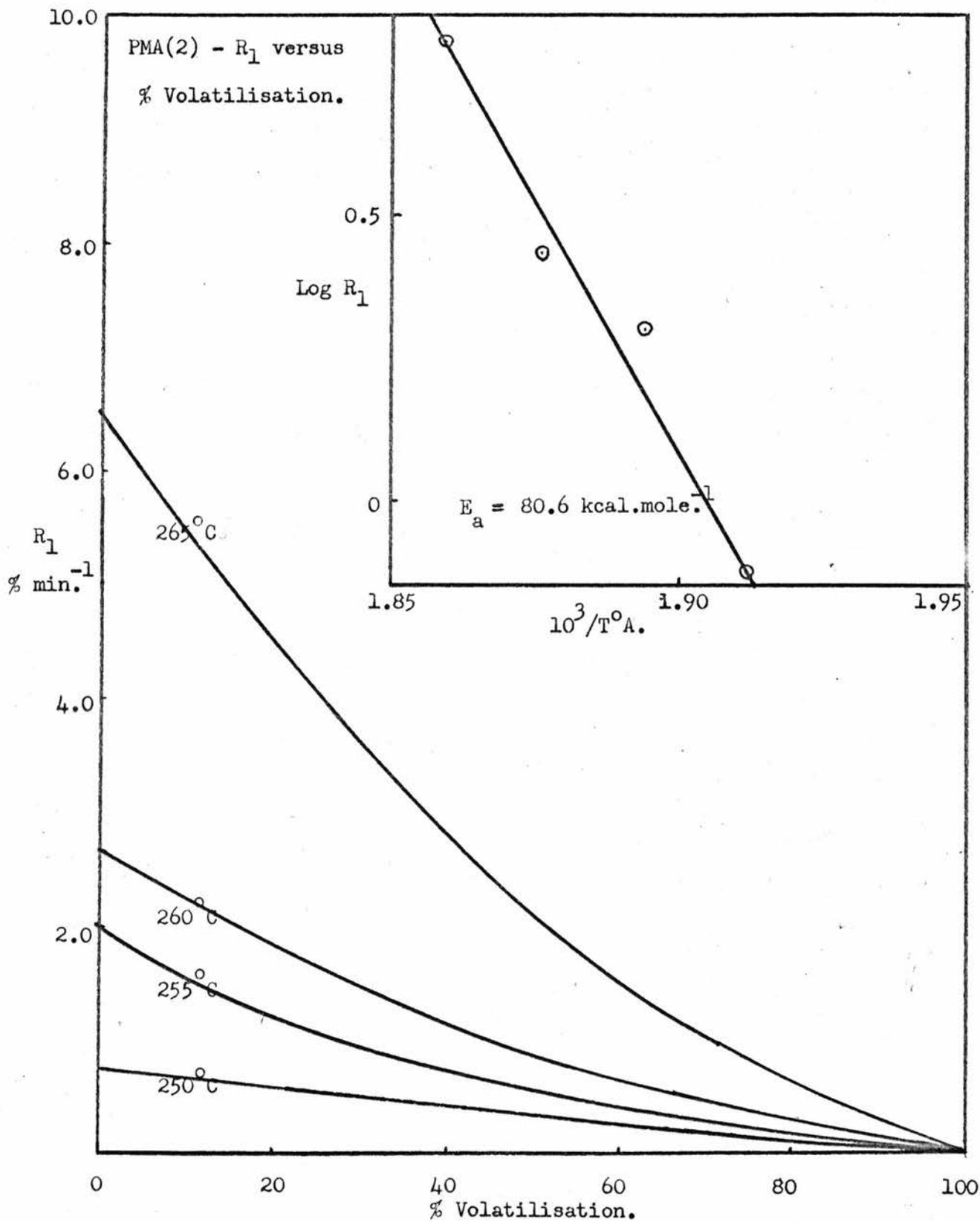
TABLE 4.

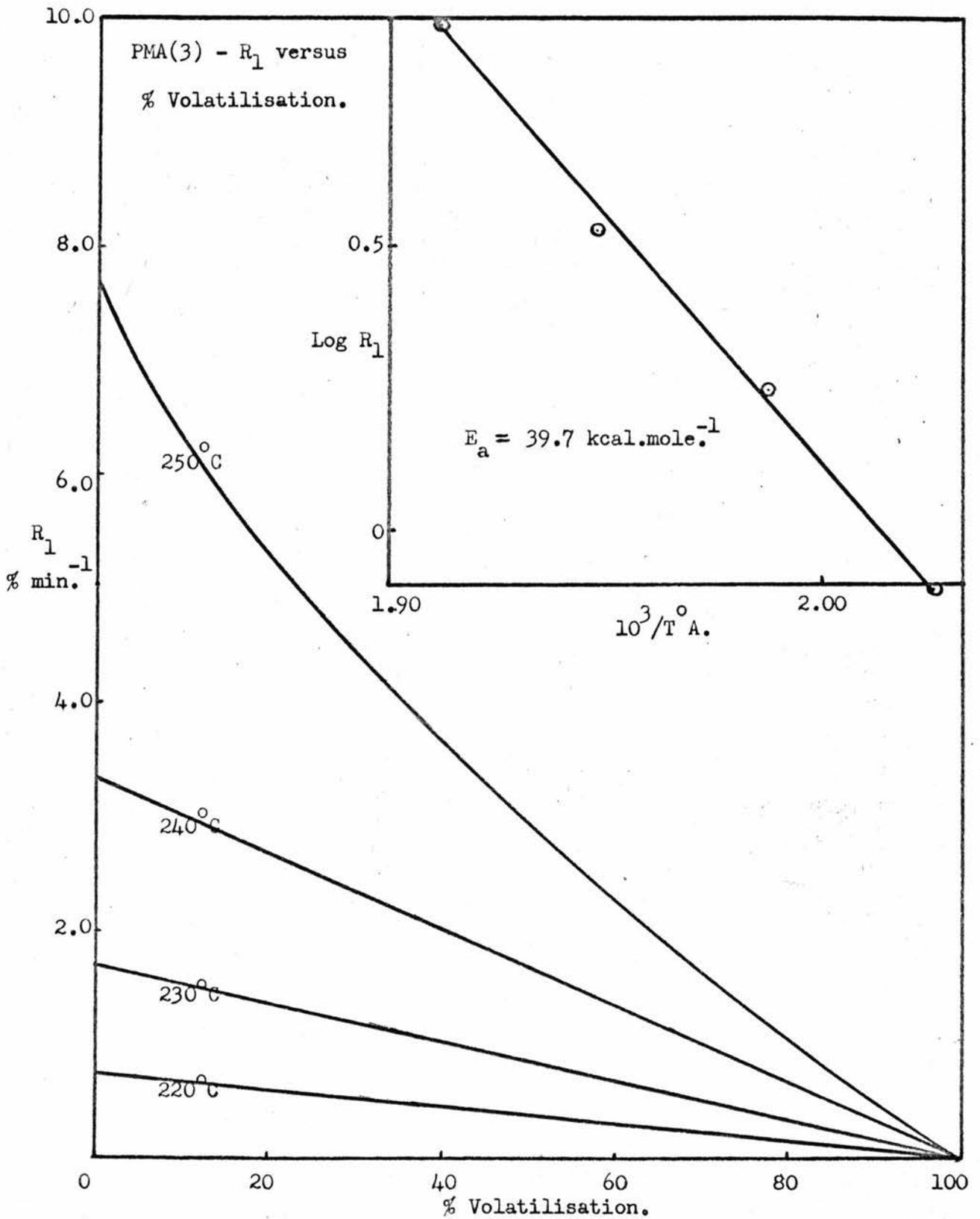
Isothermal Thermogravimetry of PMA.

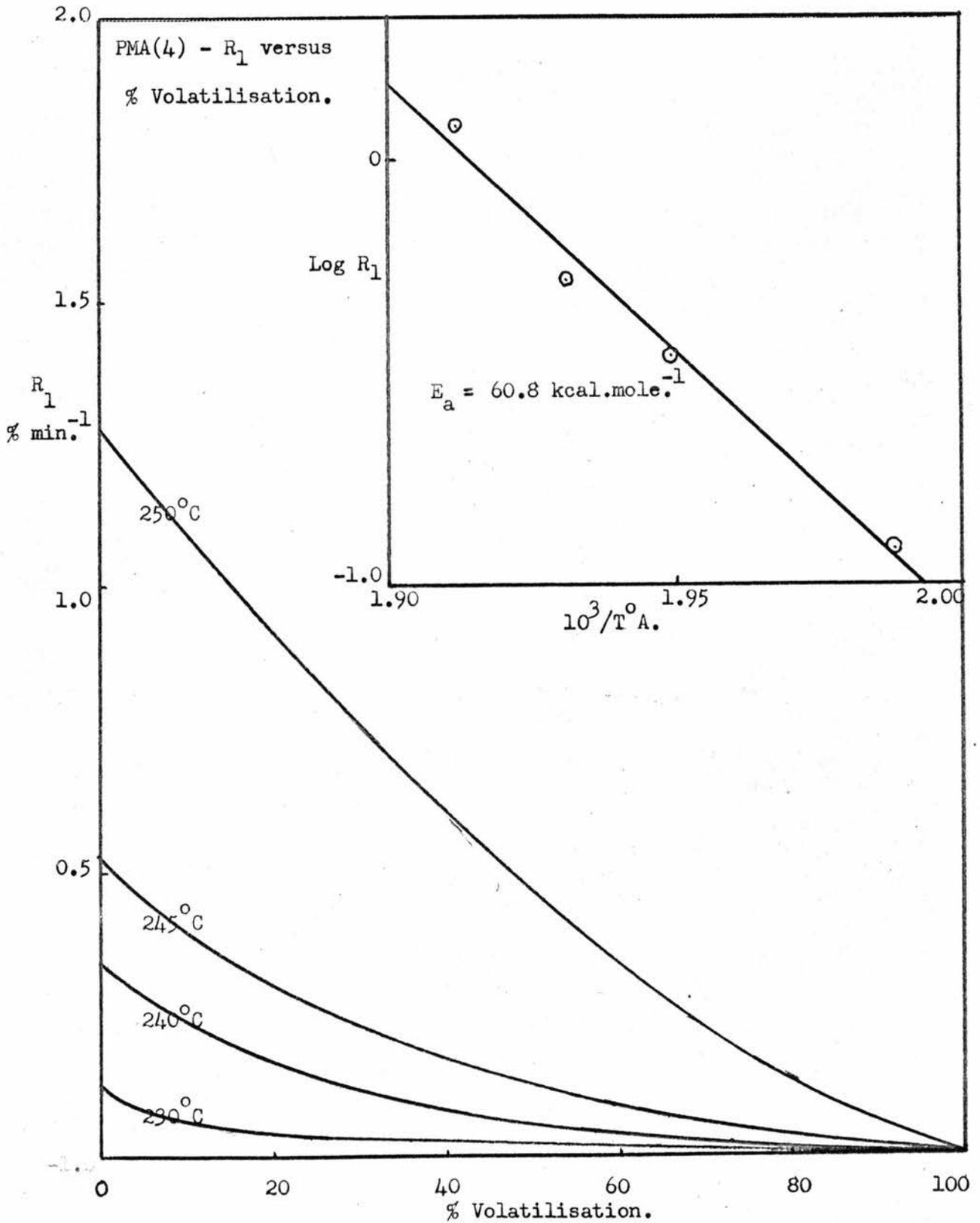
Initial Rates of Volatilisation and Activation Energies.

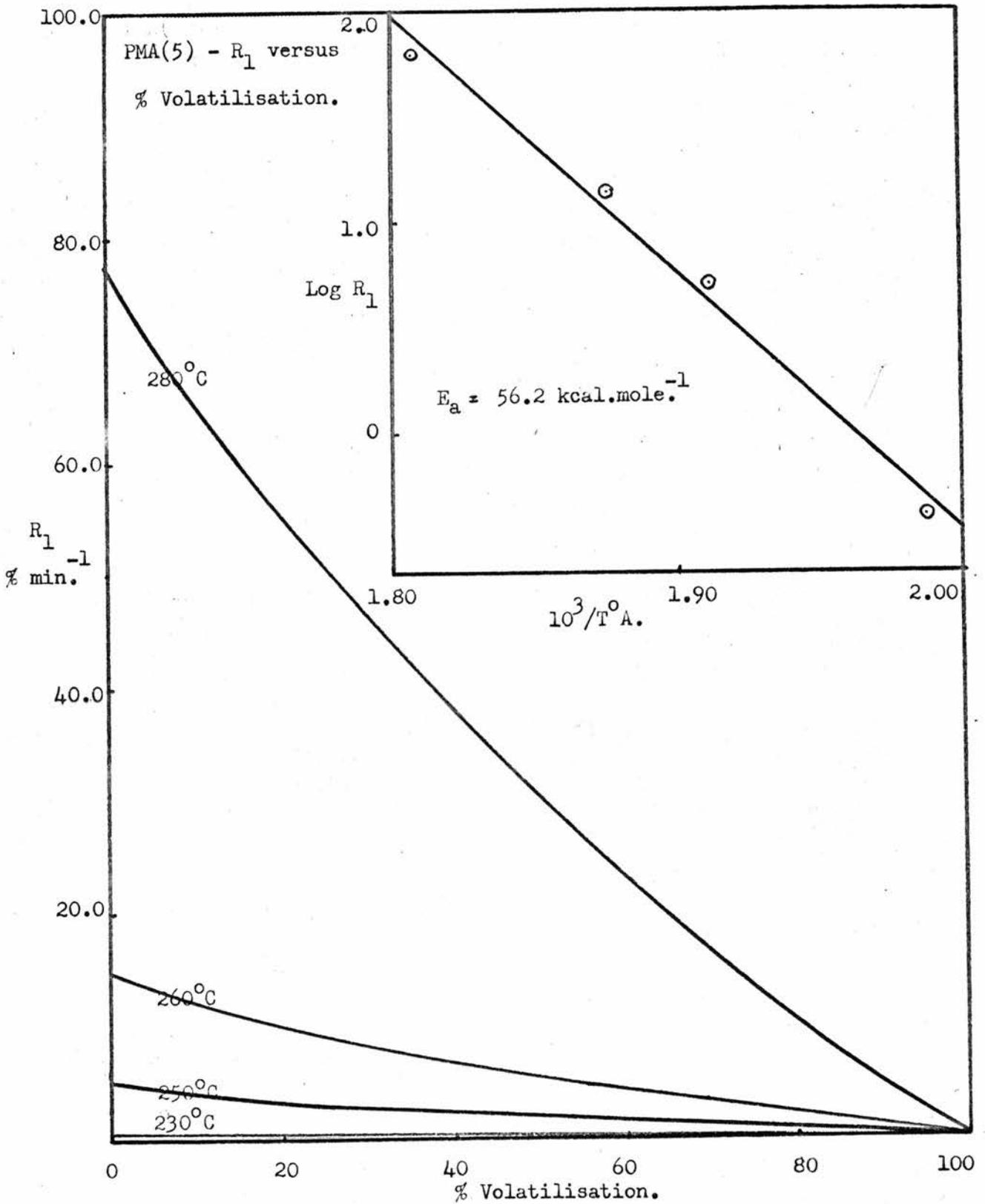
Polymer.	T °C.	$\frac{10^3}{T^\circ A}$	Rate. R ₁ % min. ⁻¹	Log ₁₀ Rate.	Activation Energy. kcal. mole. ⁻¹
PMA(1).	260	1.876	12.00	1.0792	28.3
	255	1.894	9.00	0.9542	
	250	1.912	7.00	0.8451	
	240	1.948	4.20	0.6232	
PMA(2).	265	1.859	6.44	0.8089	80.6
	260	1.876	2.73	0.4362	
	255	1.894	2.00	0.3010	
	250	1.912	0.74	-0.1308	
PMA(3).	250	1.912	7.80	0.8921	39.7
	240	1.948	3.36	0.5263	
	230	1.988	1.75	0.2430	
	220	2.028	0.79	-0.1024	
PMA(4).	250	1.912	1.28	0.1072	60.8
	245	1.931	0.52	-0.2840	
	240	1.949	0.34	-0.4685	
	230	1.988	0.12	-0.9208	
PMA(5).	280	1.808	77.50	1.8893	56.2
	260	1.876	14.10	1.1492	
	250	1.912	5.00	0.6990	
	230	1.988	0.40	-0.3979	











There is a considerable variation in the Activation Energies of the samples and this will be discussed in a later section.

At this point it is possible to compare the rate curves obtained from the molecular still degradations of PMA(5) and the isothermal T G A of all five polymers. The high initial rates observed in the degradation of P M A is strongly indicative of a randomly initiated degradation with a considerable zip length, as has been found for poly (α -methylstyrene)⁹. Chain end initiated degradation can be eliminated since in Figure 2d a maximum in the number of molecules in the degrading system has been shown to occur at $\sim 45\%$ conversion. Thus, the concentration of chain-ends is greatest at this point, and the rate of volatilisation, if degradation is initiated at chain-ends, should exhibit a similar maximum¹⁶. This has not been found. Further proof that the degradation is randomly initiated stems from consideration of the theoretical treatment for random initiation derived by Simha, Wall and Bram⁸. These authors have shown that for random initiation where $I/\epsilon \gg N/2 \gg I$, the initial rate of volatilisation is given by

$$\frac{dc}{dt} \Bigg|_{t \rightarrow 0} = k_I(I + \sigma/2)N - k_I(I + \sigma/2)N^2 \epsilon/6 \dots \dots \dots (I)$$

where N = number of backbone carbon atoms in the polymer,

I/ϵ = kinetic chain length,

and σ = intermolecular chain transfer constant.

If $\sigma = 0$, as seems probable for P M A, Equation (I) simplifies to

$$\frac{dc}{dt} \Big|_{t \rightarrow 0} = k_I N - k_I N^2 \epsilon / 6 \quad \dots\dots \quad (2)$$

$$= k_I N (I - N \epsilon / 6 \quad \dots\dots) \quad (3)$$

Where N is small,

$$\frac{dc}{dt} \Big|_{t \rightarrow 0} = \frac{k_I N}{I} \quad (4)$$

i.e. the initial rate of volatilisation is proportional to the molecular chain length.

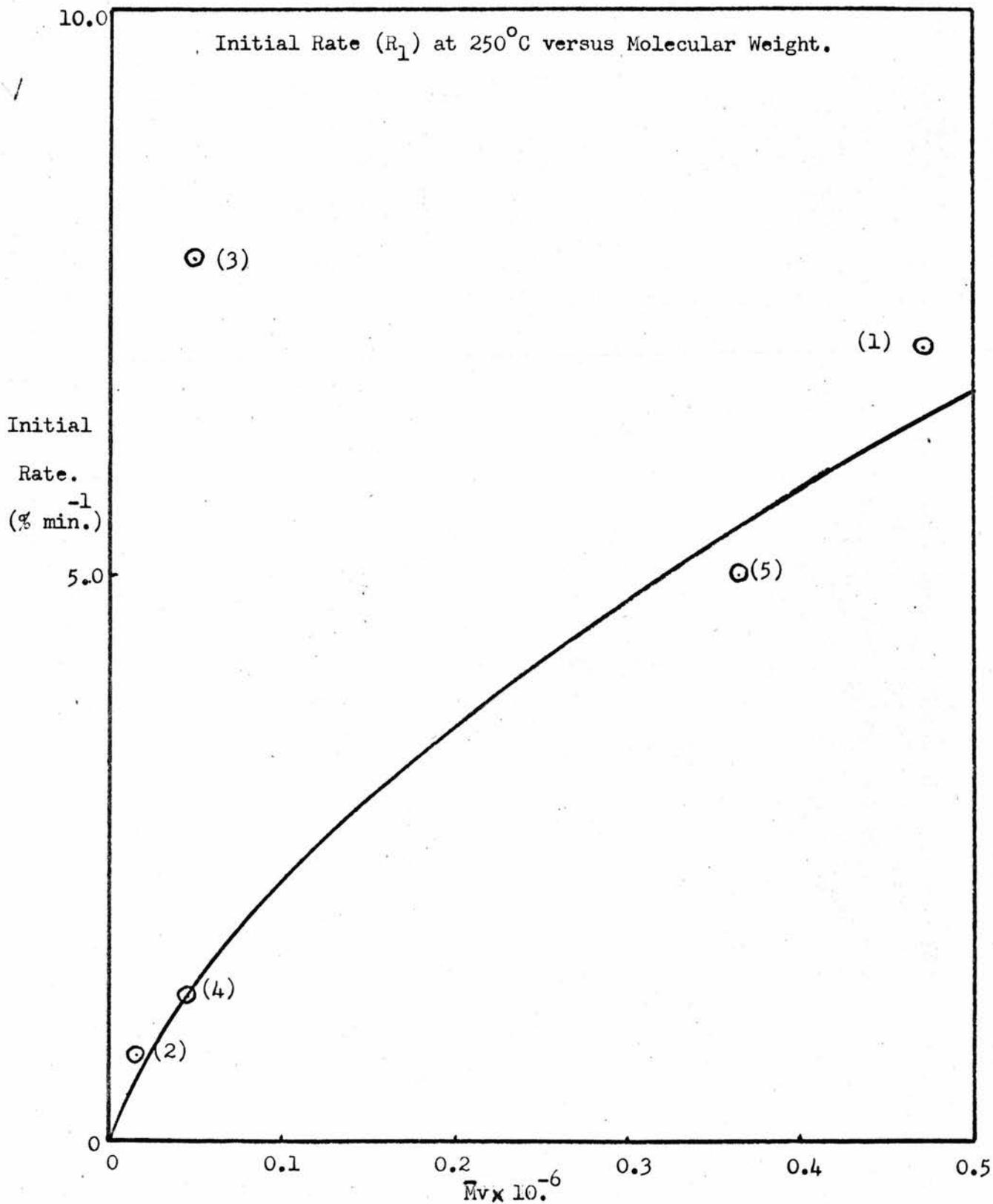
For random initiation where $N/2 \gg I/\epsilon \gg I$, the initial rate of volatilisation is given by

$$\frac{dc}{dt} \Big|_{t \rightarrow 0} = 4k_2 \left(\frac{k_I}{k_4} \right)^{\frac{1}{2}} \frac{I}{\left[2 (N - I) Q_{N-I} (0) \right]^{\frac{1}{2}}} \quad (5)$$

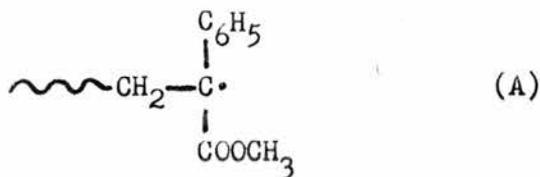
where the term $(N - I) Q_{N-I} (0)$ represents the initial concentration of bonds.

At very large values of N, therefore, dc/dt is independent of molecular weight.

This theoretical treatment indicates that for a range of polymers of increasing molecular weight, the initial rate of volatilisation (R_T) is proportional to the molecular weight of the polymer as long as $I/\epsilon \gg N/2$, but a transition occurs at the point where $I/\epsilon \approx N/2$ when the initial rate becomes independent of molecular weight. Figure 4f shows the initial rate of volatilisation at 250°C plotted against \bar{M}_v for the P M A samples studied in this investigation. PMA(3) shows an anomalously high initial rate, but



the other four polymers lie on a gentle curve of the type expected. In this aspect P M A correlates well with poly (α -methylstyrene)⁹ and poly (methyl methacrylate)¹⁷ prepared by ionic syntheses. An estimate of the kinetic chain length from this figure is theoretically possible, but impossible in practice because of the wide molecular weight distributions of the polymers and the inadequacy of the data available, but the indications are that the kinetic chain length at 250°C is about 3,000, compared with approximately 1,000 at 210°C. These estimates of the zip length of P M A are considerably larger than the published values of the kinetic chain lengths of poly (α - methylstyrene)⁹ and poly (methyl methacrylate)¹⁷. Obviously the increased resonance stabilisation of the radical end, A,



formed by chain scission, gives rise to the greater zip length by deactivating the macroradical in termination reactions.

Thus far, the thermal degradation of P M A has been described in terms of a mechanism comprising random initiation and a large kinetic chain length. The nature of the termination reaction has not been determined directly but is probably disproportionation. Certainly the molecular weight and rate versus conversion data compare well with theoretical curves⁸ assuming this termination step.

One feature of the results remains unexplained, namely the

variation in Activation Energies. To re - inforce the data available from isothermal TGA, temperature programmed runs were conducted on all five polymers.

(b) Temperature programmed (Dynamic) Thermogravimetric Analysis

of P M A.

Temperature programmed degradations were effected at a heating rate of $2.77^{\circ}\text{C}\cdot\text{min}^{-1}$, the initial starting temperature in all runs being 100°C . The difference - differential method of Freeman and Carroll^{18,19} was employed to determine Activation Energies and Orders of Reaction from the experimental volatilisation versus time curves. This method is based on the expression

$$\Delta \log (dW/dt) = n \Delta \log W_r - (\Delta E/2.303 R) \Delta (1/T) \quad (1)$$

where dW/dt is the rate of reaction,

n is the Order of Reaction,

ΔE is the Energy of Activation,

R is the Gas Constant,

and $W_r = \Delta W_c - \Delta W$ where ΔW is the weight loss at the point where dW/dt is taken, and ΔW_c is the total weight loss associated with a given reaction.

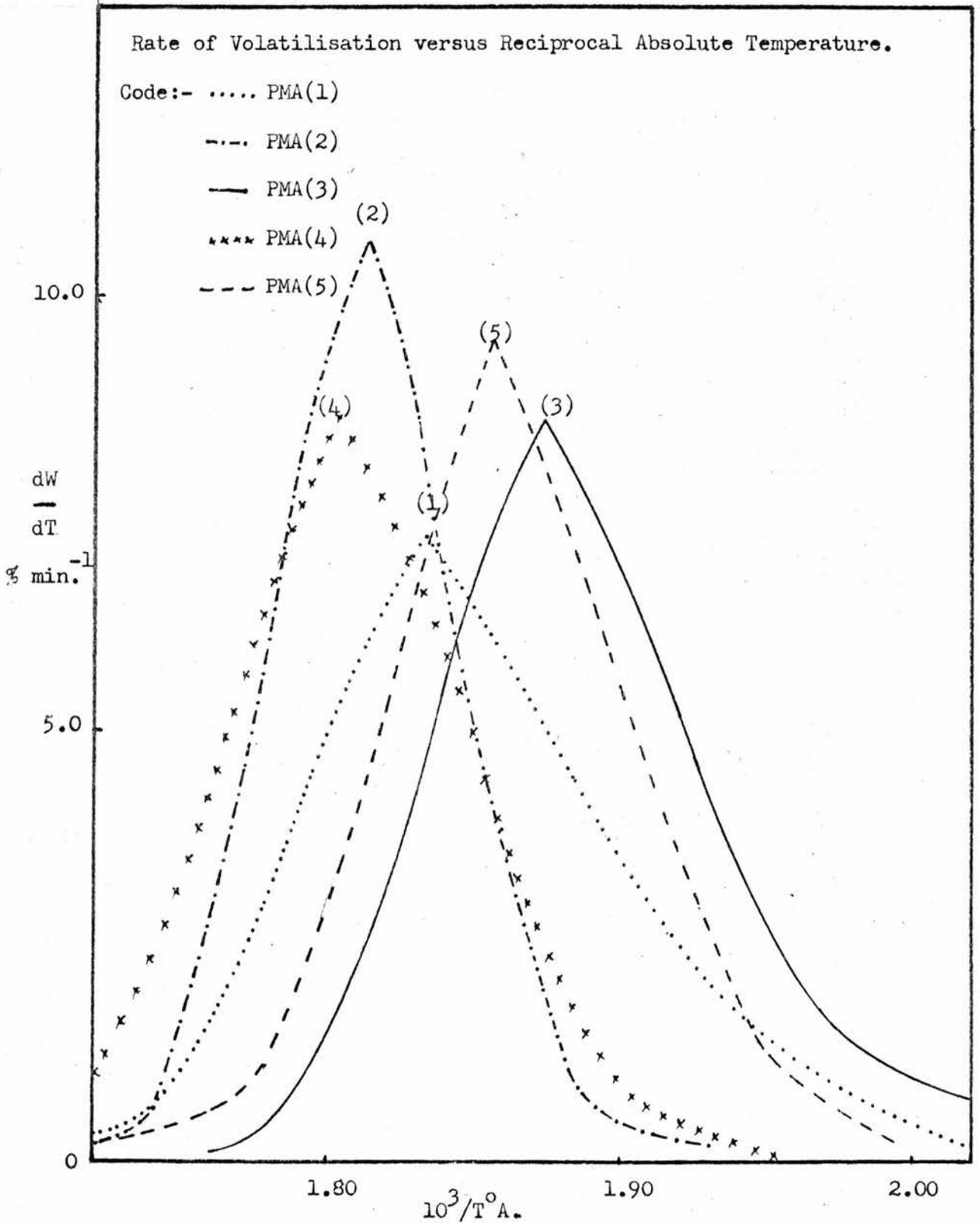
Wide use has previously been made of this method^{19,20,21,22} to analyse the kinetic data from dynamic thermogravimetric experiments. Consequently, it was adopted in this study.

To evaluate the constants in Equation (1), dW/dt and W_r were plotted as functions of reciprocal absolute temperature. The values of dW/dt and W_r at constant intervals of $1/T^{\circ}\text{A}$ were tabulated,

TABLE 5.

Comparison of the Activation Energies for the Thermal Degradation of PMA by Static and Dynamic Thermogravimetric Analysis.

Polymer.	\bar{M}_v	\bar{M}_n	E_a .Static. kcal.mole ⁻¹	E_a .Dynamic. kcal.mole ⁻¹	n.	E_a .Mol.Still. kcal.mole ⁻¹
PMA(1).	474,000	30,000	28.3	43.3	1.2	-
PMA(2).	17,000	17,000	80.6	79.3	1.6	-
PMA(3).	50,000	15,000	39.7	51.3	1.2	-
PMA(4).	47,000	12,000	60.8	68.4	1.8	-
PMA(5).	366,000	140,000	56.2	66.1	1.5	56.8



and plots of $\Delta \log dW/dt$ versus $\Delta \log W_r$ were constructed for the five polymers. From these diagrams, n is given by the slope, and the intercept is equal to $-(\Delta E/2.303 R)$. In this way n and ΔE were evaluated for all five polymers. A plot of dW/dt versus reciprocal absolute temperature is shown in Figure 5, to indicate the relative thermal stability of the polymers, and the values of n and ΔE are tabulated in Table 5.

In general, agreement between the Activation Energies obtained by static and dynamic TGA is rather poor, with the latter method appearing to give higher values. However, the general order of magnitude of the Activation Energies found by both methods is identical, namely,

$$\text{PMA}(1) < \text{PMA}(3) < \text{PMA}(5) < \text{PMA}(4) < \text{PMA}(2)$$

in increasing order of magnitude. From theoretical considerations¹², the Activation Energy for the degradation of any polymer has been shown to depend on the relative magnitudes of the \bar{DP} and the KCL.

For random initiation where $1/\epsilon \gg \bar{DP}$,

$$E_a = E_1$$

where E_a = overall Activation Energy,

and E_1 = Activation Energy for random scission.

E_1 for poly (methyl methacrylate) and poly (α -methylstyrene) has been estimated at 86 and 80 kcal.mole⁻¹. respectively. The experimental Activation Energy of ~ 80 kcal.mole⁻¹. found for PMA(2) would seem, therefore, to be E_1 for this polymer since

$\overline{DP} \ll KCL$ for this polymer. The decrease in Activation Energy for PMA(4), PMA(5), and PMA(3) presumably marks the onset of a termination step into the degradation process, since in the case where $\overline{DP} \gg 1/\epsilon$ the overall Activation Energy becomes¹²

$$E_a = E_1/2 + E_2 - E_4/2 \quad \text{where transfer is unimportant,}$$

and where E_2 = Activation Energy for depropagation,

and E_4 = Activation Energy for bimolecular termination.

The introduction of other energy terms into the expression for the overall Activation Energy has the effect of lowering the experimentally determined value. Thus, the gradation of Activation Energies found is a sign of increasing amounts of termination as the molecular weight of the polymer increases. However, the very low Activation Energy found for PMA(3) cannot be explained on a molecular weight basis since this polymer also has a very low molecular weight. A similar dependence of E_a on molecular weight has recently been found for poly (methyl methacrylate) by Jellinek and Luh²⁴. For the randomly initiated high temperature degradation of fractions of this polymer, they found a transition in E_a from 60 - 65 kcal.mole⁻¹. to 75 - 80 kcal.mole⁻¹. with decreasing molecular weight at degrees of polymerisation between 10^4 and 10^3 . The experimental verification of this dependence, which was initially predicted from theoretical considerations¹², is very important in view of the inability of previous investigators^{9,17} to find a similar relationship. However, the relatively high value of E_a obtained by Jellinek and Luh where

$1/\epsilon \gg \bar{DP}$ (60 - 65 kcal.mole⁻¹.) must be contrasted with the value of 28 kcal.mole⁻¹ found for PMA(1) in this work.

In connection with the relative validity of the values of the Activation Energies determined by TGA, it should be noted that both static and dynamic experiments were conducted in the same apparatus. Flynn and Wall²⁵ have recently been very critical of most of the methods used for the analysis of data available from dynamic TGA, so that the results from static TGA in the present study must be regarded as more accurate.

Because of the heterodispersity of the polymers, no effect of the mode of synthesis on the Activation Energy can be distinguished except, possibly, in the Activation Energies for PMA(3) and PMA(4) which differ by some 20 kcal.mole⁻¹, although both polymers are of similar molecular weight and molecular weight distribution. Reference to the work by Chikanishi and Tsuruta²⁶ on the anionic polymerisation of methyl α -phenylacrylate indicates that, whereas polymers prepared by sodium naphthalenide are totally soluble in boiling methyl ethyl ketone (MEK), polymers prepared by butyllithium in toluene are only 29% soluble. Since solubility in boiling MEK is a qualitative estimate of crystallinity - and, therefore, of stereoregularity - in a polymer, it seems that PMA(4) is far more stereoregular than PMA(3). Enhanced stereoregularity in a polymer such as P M A, where alternate backbone carbon atoms bear large substituent groups, can mean a considerable decrease in the free energy of the polymer molecule. From studies of the solution

degradation of poly (methyl methacrylate), Grant and Bywater²⁷ postulated that the normal C - C bond dissociation energy of 80 kcal.mole⁻¹. is reduced by some 10-15 kcal.mole⁻¹. because of steric strain. Thus, the overall Activation Energy, E_a , would be correspondingly reduced by 7.5 or 15.0 kcal.mole⁻¹. depending on whether $\overline{DP} \gg 1/\epsilon$ or $1/\epsilon \gg \overline{DP}$. Similarly, the overall Activation Energy for PMA(5) may be increased relative to that for PMA(1) since initiation of polymerisation by CaZnEt_4 in THF gives polymers which are 80% insoluble in boiling MEK. Obviously, however, the polydispersity of the polymers studied precludes any definite and quantitative estimate of the dependence of the Activation Energy on stereoregularity. Attempts to measure the heats of fusion from Differential Thermal Analysis, and thus obtain estimates of the amounts of stereoregularity in the polymers, were unsuccessful because the polymers did not exhibit crystalline melting points.

In summary, the thermal degradation of P M A can be described in terms of a free - radical chain reaction comprising random initiation, depropagation with a large kinetic chain length and termination by (probably) disproportionation. In these respects P M A behaves similarly to poly (α -methylstyrene) and poly (methyl methacrylate), and exhibits few similarities in behaviour to polystyrene. Thus, once again the extensive change in degradation behaviour brought about by the substitution of the active tertiary hydrogen atom is demonstrated,

Little evidence has been obtained concerning the effect of

stereoregularity on the Activation Energies of degradation. Obviously for such investigations monodisperse polymers are required, and initial experiments should be carried out on polymers where the DP is less than the kinetic chain length since the experimentally observed Activation Energy is equal to the Activation Energy of random scission. In this way the effect of stereoregularity on the C - C bond dissociation energy could be observed. However, the main effect of stereoregularity may lie in the Activation Energy for depropagation since the heat of polymerisation will be affected by stereoregularity, and in this case polymers with $\bar{DP} \gg KCL$ must be studied degradatively. It may be that such energy changes are too small to detect since Jellinek and Luh¹⁷ found identical Energies of Activation for the degradation of syndiotactic and isotactic poly (methyl methacrylates).

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APPENDICES.

Appendix 1

Evaluation of the Integral in

$$N_t(\alpha) = \frac{4N_t(1-\alpha)^{t-1}}{\bar{r}^2} \exp\left(\frac{-2t}{\bar{r}}\right) \\ + \frac{4\alpha}{\bar{r}^2}(1-\alpha)^{t-1} N \int_{p=t}^{\infty} [2 + (p-t)\alpha](p+1) \exp\left(\frac{-2(p+1)}{\bar{r}}\right) dp$$

$$\int u dv = uv - \int v du$$

$$\text{Let } \exp\left(\frac{-2p}{\bar{r}}\right) dp = dv$$

$$\therefore v = -\frac{\bar{r}}{2} \exp\left(\frac{-2p}{\bar{r}}\right)$$

$$\text{Integral } I_{(q)} = \int_t^{\infty} p^q \exp\left(\frac{-2p}{\bar{r}}\right) dp \\ = \left[p^q - \frac{\bar{r}}{2} \exp\left(\frac{-2p}{\bar{r}}\right) \right]_t^{\infty} - \int_t^{\infty} -\frac{\bar{r}}{2} \exp\left(\frac{-2p}{\bar{r}}\right) q p^{q-1} dp \\ = \frac{\bar{r}}{2} t^q \exp\left(\frac{-2t}{\bar{r}}\right) + \frac{\bar{r}}{2} I_{(q-1)}$$

$$\therefore I_{(0)} = \int_t^{\infty} \exp\left(\frac{-2p}{\bar{r}}\right) dp = \left[-\frac{\bar{r}}{2} \exp\left(\frac{-2p}{\bar{r}}\right) \right]_t^{\infty} \\ = \frac{\bar{r}}{2} \exp\left(\frac{-2t}{\bar{r}}\right)$$

Thus we obtain

$$\begin{aligned} I_{(1)} &= \frac{\bar{r}}{2} t \exp\left(-\frac{2t}{\bar{r}}\right) + \frac{\bar{r}}{2} I_{(0)} \\ &= \frac{\bar{r}}{2} t \exp\left(-\frac{2t}{\bar{r}}\right) + \frac{\bar{r}}{2} \cdot \frac{\bar{r}}{2} \exp\left(-\frac{2t}{\bar{r}}\right) \\ &= \frac{\bar{r}}{2} \exp\left(-\frac{2t}{\bar{r}}\right) \left[t + \frac{\bar{r}}{2}\right] \end{aligned}$$

$$\begin{aligned} \text{and } I_{(2)} &= \frac{\bar{r}}{2} t^2 \exp\left(-\frac{2t}{\bar{r}}\right) + \frac{\bar{r}}{2} 2 I_{(1)} \\ &= \frac{\bar{r}}{2} t^2 \exp\left(-\frac{2t}{\bar{r}}\right) + \bar{r} \cdot \frac{\bar{r}}{2} \exp\left(-\frac{2t}{\bar{r}}\right) \left[t + \frac{\bar{r}}{2}\right] \\ &= \frac{\bar{r}}{2} \exp\left(-\frac{2t}{\bar{r}}\right) \left[t^2 + \bar{r}t + \frac{1}{2} \bar{r}^2\right] \end{aligned}$$

$$\begin{aligned} \text{Now, } N_t(\alpha) &= \frac{4Nt}{\bar{r}^2} (1-\alpha)^{t-1} \exp\left(-\frac{2t}{\bar{r}}\right) \\ &\quad + \frac{4N\alpha}{\bar{r}^2} (1-\alpha)^{t-1} \exp\left(-\frac{2t}{\bar{r}}\right) \int_t^{\infty} (p+1) [2+(p-t)\alpha] \exp\left(-\frac{2p}{\bar{r}}\right) dp. \end{aligned}$$

$$\text{Let } \int_t^{\infty} (p+1) [2+(p-t)\alpha] \exp\left(-\frac{2p}{\bar{r}}\right) dp = G.$$

$$\therefore G = \int_t^{\infty} (p+1) (2+\alpha p - \alpha t) \exp\left(-\frac{2p}{\bar{r}}\right) dp.$$

(iii)

$$G = \int \exp.\left(\frac{-2p}{\bar{r}}\right) [2p + \alpha p^2 - \alpha p t + 2 + \alpha p - \alpha t] dp.$$

$$= \int \exp.\left(\frac{-2p}{\bar{r}}\right) [\alpha p^2 + p(2 + \alpha - \alpha t) + (2 - \alpha t)] dp.$$

$$\therefore G = \alpha I_{(2)} + [2 + \alpha(1-t)] I_{(1)} + (2 - \alpha t) I_{(0)}$$

$$= \alpha \frac{\bar{r}}{2} \exp.\left(\frac{-2t}{\bar{r}}\right) [t^2 + \bar{r}t + \frac{1}{2} \bar{r}^2]$$

$$+ [2 + \alpha(1-t)] \frac{\bar{r}}{2} \exp.\left(\frac{-2t}{\bar{r}}\right) [t + \frac{\bar{r}}{2}] + (2 - \alpha t) \frac{\bar{r}}{2} \exp.\left(\frac{-2t}{\bar{r}}\right)$$

$$= \frac{\bar{r}}{2} \exp.\left(\frac{-2t}{\bar{r}}\right) \left\{ \alpha (t^2 + \bar{r}t + \frac{1}{2} \bar{r}^2) + [2 + \alpha(1-t)] (t + \frac{\bar{r}}{2}) + (2 - \alpha t) \right\}$$

$$= \frac{\bar{r}}{2} \exp.\left(\frac{-2t}{\bar{r}}\right) \left\{ t \left(2 + \frac{\alpha \bar{r}}{2} \right) + \frac{\alpha}{2} \bar{r}^2 + \bar{r} \left(1 + \frac{\alpha}{2} \right) + 2 \right\}$$

$$= \bar{r} \exp.\left(\frac{-2t}{\bar{r}}\right) \left[t \left(1 + \frac{\alpha \bar{r}}{4} \right) + \frac{\alpha \bar{r}^2}{4} + \frac{(\alpha + 2) \bar{r}}{4} + 1 \right]$$

$$\therefore N_t(\alpha) = \frac{4N}{\bar{r}^2} (1-\alpha)^{t-1} \exp.\left(\frac{-2t}{\bar{r}}\right) \left[t + \alpha \bar{r} \exp.\left(\frac{-2t}{\bar{r}}\right) \left[t \left(1 + \frac{\alpha \bar{r}}{4} \right) + \frac{\alpha \bar{r}^2}{4} + \frac{(\alpha + 2) \bar{r}}{4} + 1 \right] \right]$$

which may be written in the form

$$N_t(\alpha) = K_1 (K_2 t + K_3) \exp.\left(\frac{-2t}{\bar{r}}\right) (1-\alpha)^{t-1}$$

(iv)

$$\text{where } K_1 = \frac{4N}{\bar{r}^2},$$

$$K_2 = 1 + \alpha \bar{r} \left(1 - \frac{\alpha \bar{r}}{4}\right) \exp\left(-\frac{2}{\bar{r}}\right)$$

$$\text{and } K_3 = \alpha \bar{r} \left[1 + \frac{(\alpha+2)\bar{r}}{4} + \frac{\alpha \bar{r}^2}{4}\right] \exp\left(-\frac{2}{\bar{r}}\right).$$

Appendix 2.

Integration by parts of

$$J_{(1)} = \int_0^{\infty} t N_t(\alpha) dt$$

and

$$J_{(1+q)} = \int_0^{\infty} t^{1+q} N_t(\alpha) dt.$$

Consider the integral

$$J_{(p)} = \int_0^{\infty} t^p (1-\alpha)^{t-1} e^{-kt} dt \quad \text{where } k = \frac{2}{T}$$

$$(1-\alpha)^{t-1} = \exp. [(t-1) \log_e (1-\alpha)]$$

$$\therefore J_{(p)} = e^{-\ln(1-\alpha)} \int_0^{\infty} t^p e^{-t[k - \ln(1-\alpha)]} dt.$$

$$\text{let } S = [k - \ln(1-\alpha)]t$$

$$\therefore dS = [k - \ln(1-\alpha)] dt$$

(vi)

$$\text{and } dt = \frac{ds}{[k - \ln(1-\alpha)]}$$

$$\therefore J(p) = e^{-\ln(1-\alpha)} \int_0^{\infty} \frac{s^p}{[k - \ln(1-\alpha)]^p} e^{-s} \frac{ds}{[k - \ln(1-\alpha)]}$$

$$= \frac{e^{-\ln(1-\alpha)}}{[k - \ln(1-\alpha)]^{p+1}} \int_0^{\infty} s^p e^{-s} ds$$

$$\text{BUT } \int_0^{\infty} s^p e^{-s} ds = \Gamma(p+1)$$

$$\text{and } e^{-\ln(1-\alpha)} = \frac{1}{1-\alpha}$$

$$\therefore J(p) = \frac{\Gamma(p+1)}{(1-\alpha) [k - \ln(1-\alpha)]^{p+1}}$$

$$\text{Firstly, } \int_0^{\infty} t N_t(\alpha) dt = \int_0^{\infty} K_1 (K_2 t^2 + K_3 t) (1-\alpha)^{t-1} \exp\left(-\frac{2t}{T}\right) dt$$

$$= K_1 K_2 J(2) + K_1 K_3 J(1)$$

$$= K_1 \left\{ \frac{2(K_2 \Gamma(2))}{(1-\alpha) \left[\frac{2}{\tau} - \ln(1-\alpha) \right]^3} + \frac{K_3 \Gamma(3)^{(vii)}}{(1-\alpha) \left[\frac{2}{\tau} - \ln(1-\alpha) \right]^2} \right\}$$

$$= \frac{K_1 \left\{ 2K_2 + K_3 \left[\frac{2}{\tau} - \ln(1-\alpha) \right] \right\}}{(1-\alpha) \left[\frac{2}{\tau} - \ln(1-\alpha) \right]^3}$$

Secondly, $\int_0^{\infty} t^{1+q} N_t(\alpha) dt$

$$= \int_0^{\infty} t^{1+q} K_1 (K_2 t^2 + K_3 t) (1-\alpha)^{t-1} \exp\left(-\frac{2t}{\tau}\right) dt$$

$$= K_1 K_2 J(2+q) + K_1 K_3 J(1+q)$$

$$= K_1 \left\{ \frac{K_2 \Gamma(a+3)}{(1-\alpha) [k - \ln(1-\alpha)]^{3+q}} + \frac{K_3 \Gamma(a+2)}{(1-\alpha) [k - \ln(1-\alpha)]^{2+q}} \right\}$$

$$= \frac{K_1 \left\{ K_2 \Gamma(a+3) + K_3 \Gamma(a+2) \left[\frac{2}{\tau} - \ln(1-\alpha) \right] \right\}}{(1-\alpha) \left[\frac{2}{\tau} - \ln(1-\alpha) \right]^{3+q}}$$

Therefore,

$$\begin{aligned}
 [\eta] &= \frac{KM_0^a \int_0^{\infty} t^{1+a} N_t(\alpha) dt}{\int_0^{\infty} t N_t(\alpha) dt} \\
 &= \frac{KM_0^a K_1 \Gamma(a+2) \left\{ K_2(2+a) + K_3 \left[\frac{2}{\tau} - \ln(1-\alpha) \right] \right\}}{(1-\alpha) \left[\frac{2}{\tau} - \ln(1-\alpha) \right]^{3+a}} \\
 &\quad \times \frac{(1-\alpha) \left[\frac{2}{\tau} - \ln(1-\alpha) \right]^3}{K_1 \left\{ 2K_2 + K_3 \left[\frac{2}{\tau} - \ln(1-\alpha) \right] \right\}} \\
 &= \frac{KM_0^a \Gamma(a+2) \left\{ K_2(2+a) + K_3 \left[\frac{2}{\tau} - \ln(1-\alpha) \right] \right\}}{\left[\frac{2}{\tau} - \ln(1-\alpha) \right]^a \left\{ 2K_2 + K_3 \left[\frac{2}{\tau} - \ln(1-\alpha) \right] \right\}}
 \end{aligned}$$

where K_2 and K_3 have the same significance as in Appendix 1.

Appendix 3.

Evaluation of the integral

$$J = \int_0^{p+1} t^{1+a} \alpha (1-\alpha)^{t-1} [2 + (p-t)\alpha] dt$$

$$\text{Let } J = \int_0^{p+1} t^{1+a} \alpha (1-\alpha)^{t-1} [2 + (p-t)\alpha] dt$$

$$= \int_0^{p+1} t^{1+a} \alpha e^{-(t-1) \log\left(\frac{1}{1-\alpha}\right)} [2 + (p-t)\alpha] dt$$

$$= \alpha e^{\log\left(\frac{1}{1-\alpha}\right)} \int_0^{p+1} t^{1+a} e^{-t \log\left(\frac{1}{1-\alpha}\right)} [2 + (p-t)\alpha] dt$$

$$\text{Let } Z = t \log\left(\frac{1}{1-\alpha}\right) \therefore dZ = dt \log\left(\frac{1}{1-\alpha}\right)$$

$$\therefore J = \frac{\alpha}{(1-\alpha)} \int_0^{(p+1) \log\left(\frac{1}{1-\alpha}\right)} \left[\frac{Z}{\log\left(\frac{1}{1-\alpha}\right)} \right]^{1+a} e^{-Z} \left[2 + \left(p - \frac{Z}{\log\left(\frac{1}{1-\alpha}\right)} \right) \alpha \right] \frac{dZ}{\log\left(\frac{1}{1-\alpha}\right)}$$

$$\text{Let } \theta = (p+1) \log \frac{1}{1-\alpha}$$

$$\text{and } \gamma[p, \theta] = \int_0^{\theta} z^{p-1} e^{-z} dz$$

Then

$$J = \frac{\alpha}{1-\alpha} \left\{ \frac{z+p\alpha}{\left[\log\left(\frac{1}{1-\alpha}\right)\right]^{2+a}} \int_0^{\theta} z^{1+a} e^{-z} dz - \frac{\alpha}{\left[\log\left(\frac{1}{1-\alpha}\right)\right]^{3+a}} \int_0^{\theta} z^{2+a} e^{-z} dz \right\}$$

$$= \frac{\alpha}{(1-\alpha) \left[\log\left(\frac{1}{1-\alpha}\right)\right]^{3+a}} \left\{ (2+p\alpha) \log\left(\frac{1}{1-\alpha}\right) \gamma[a+2, \theta] - \alpha \gamma[a+3, \theta] \right\}$$

APPENDIX 4.Computer Programme Instructions.(i) Coupling Distribution.

```

1      FORMAT(E14.8)
3      FORMAT(19xF8.5, 14xE14.8, 14xF12.8)
20     FORMAT(20x28H PARAMETERS FOR THIS RUN ARE/)
21     FORMAT(6x4H K = , E14.8,6H      M = ,E14.8,6H
           A = ,E14.8,6H      R = ,E14.8 1//)
23     FORMAT(20x6H ALPHA,20x5H NETA,20x4H RT /)
99     FORMAT(1H1)
C
           A = 0.73
           G = 1.582431
           AK = 1.12E-04
11     READ1,R,AM
           BM = AM**A
           Q = EXPF(+ 2./R)
           Q = 1./Q
131    PRINT99
130    PRINT20
           PRINT21, AK, AM, A, R
           PRINT23
           AL = 0.0
10     S = 2. /R-LOGF(1.-AL)

```

```
SS = S**A
AR = AL*R
AK2 = 1. + AR*(1. + AR/4.)* Q
AK3 = AR*(1. + (AL + 2.)*R/4. + AR*R/4.)* Q
B = 2.*AK2 + S*AK3
ANS = ANS/(SS*B)
RT = (ANS/AK)**(1./A)
RT = RT*(1. + AR)/(AM*R)
PRINT3, AL, ANS, RT
12 IF(AL-0.002)40, 41, 41
40 AL = AL + 0.00001
GO TO 10
50 CALL EXIT
END
```

(ii) Monodisperse System.

```

3      FORMAT(19xF8.5, 14xE14.8, 14xF12.8)
1      FORMAT(E14.8)
20     FORMAT(20x28H PARAMETERS FOR THIS RUN ARE/)
21     FORMAT(6x4H K = ,E14.8, 6H      M = ,E14.8,6H
A = ,E14.8, 6H AP1 = , E14.8 1//)
23     FORMAT(20x6H ALPHA, 20x5H NETA, 20x4H RT /)
99     FORMAT(1H1)
C
      A = 0.73
      CI = 10 * (A + 2.)
      AI = 1./0.73
      AK = 1.12E-04
31     READ1, AP1, AM
      AP = AP1 - 1
      BM = AM * * A
      PRINT99
      PRINT20
      PRINT21, AK, AM, A, AP1
      PRINT23
      AL = 0
      ANS = AK * BM * AP1 * * A
      GO TO 50
10     ALOG = LOGF(1./(1.-AL))
      BLOG = ALOG * * A

```

```

Q = (2. + AP * AL) * ALOG - AL * (2. + A)
TH = AP * ALOG
D = AGINGA(A + 2., TH)
DD1 = Q * D + AL
C2 = TH / C1
C3 = TH * .1
DD2 = DD1 * (EXPF(-C2) * C3) * C1
CLOG = 1. / ALOG
DD3 = AL * DD2 / ((1. - AL) * BLOG) * CLOG * CLOG * CLOG
ANS = (1. - AL) * AP * APL * (1. + A) + DD3
ANS = ANS * AK * BM / APL
50 RT = (ANS / AK) * AI
RT = RT * (1. + AL * APL) / (AM * APL)
PRINT3, AL, ANS, RT
IF(AL - 0.002)40, 41, 41
40 AL = AL + 0.00001
GO TO 10
41 IF(AL - 0.01)30, 31, 31
30 AL = AL + 0.0001
GO TO 10
211 CALL EXIT
END

```