DEGRADATION STUDIES OF COPOLYMERS
OF STYRENE AND ACRYLONITRILE

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by

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SUMMARY

The thermal degradation of copolymers of styrene and acrylonitrile containing up to 50 moles per cent acrylonitrile has been studied in vacuo in the temperature range 240-330°C.

As in polystyrene, "weak links" occur in the copolymers. The increase in the rate of "normal" chain scission over that of polystyrene is proportional to the concentration of acrylonitrile, at temperatures above 262°C. Below this temperature the relationship is not obeyed.

The increase in the rate of production of volatiles over that of polystyrene is also proportional to the concentration of acrylonitrile, indicating the close relationship between chain scission and the production of volatiles. A small decrease in the amount of volatiles produced per chain scission, in copolymers of high acrylonitrile concentration, is explained by an increase in termination at pairs of acrylonitrile units.

The products of degradation are shown to be hydrogen cyanide, acrylonitrile, benzene, toluene, styrene and a variety of chain fragments, some containing acrylonitrile. One in two acrylonitrile units is released as monomer giving a measure of the blocking effect of the acrylonitrile units. The increase in the chain fragment to monomer ratio with increasing acrylonitrile concentration indicates that intramolecular transfer producing chain fragments occurs at the second acrylonitrile unit. The chain fragments were examined using the LKB 9000

Gas Chromatograph - Mass Spectrometer and structures are suggested for the various compounds.

Sequence distribution calculations show that even in copolymers containing up to 50 per cent acrylonitrile, the bulk of the acrylonitrile is present as single units. Therefore the coloration reaction arising from conjugation of sequences of nitrile groups, the characteristic reaction in polyacrylonitrile, is inhibited by the styrene units.

The copolymers were also examined by the thermoanalytical techniques of TVA and TGA.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

The term degradation, when applied to polymers, may be defined as any process which modifies the chemical or physical properties of the material. It is hardly surprising therefore that the literature on polymer degradation is both formidable and diverse. Degradation reactions may be broadly classified according to the agencies which bring about the degradation, the most common being heat, light and oxygen, alone or in combination.

Early studies in polymer degradation were carried out in order to determine the chemical structure of the polymer, for example the pyrolysis of natural rubber in 1860,[1] and the thermal degradation of polystyrene by Staudinger in 1935.[2] However as polymeric materials became increasingly important commercially, the various types of degradative processes were studied with a view to stabilising and thus extending the areas of application of these materials. Attention was inevitably focussed on the detailed chemistry of the degradation processes and a number of monographs have appeared on the subject.[3,4,5,6]

Increased industrial growth in the field of copolymers and grafted polymers of increasing complexity has led to a corresponding interest in the degradation of such systems. The addition of small amounts of comonomer has long been used industrially as a method of stabilising polymers, without much attention being paid to the mechanism of stabilisation. Grassie and Farish have studied copolymers of styrene and methyl methacrylate,[7] and methyl methacrylate and acrylonitrile[8] in an attempt to elucidate effects attributable to each type of monomer unit in the copolymers, since the homopolymers derived from the three monomers each have different mechanisms of thermal degradation. Poly(methyl methacrylate unzips to form monomer; polystyrene exhibits a chain scission reaction accompanied by the formation of volatile products; and the principal feature of polyacrylonitrile degradation is a colouration reaction.

The styrene/acrylonitrile system merits study for several reasons:-

1) It is a constituent of the commercially important terpolymer acrylonitrile/butadiene/styrene (ABS).

2) The growing importance of copolymers generally, for example styrene/butadiene rubber.

3) To complete the study of the thermal degradation of the trio of copolymers obtained from styrene, methyl methacrylate and acrylonitrile, and thus enable a comparison of the behaviour of the monomer units in different environments to be made.

4) The homopolymers derived from styrene and acrylonitrile have been extensively studied.

Before discussing the copolymer, it is appropriate to discuss briefly the thermal degradation of the homopolymers, polystyrene and polyacrylonitrile, and also to review the current state of knowledge of the degradation of copolymers. As thermal degradation only is being studied in the present work, discussion will be restricted to thermal degradation of the related systems.

1.2 The Thermal Degradation of Polystyrene

(a) Introduction

Despite the considerable amount of attention which has been devoted to this polymer, its thermal degradation is still the subject of considerable controversy.

The salient features of the degradation are:-

1) A rapid initial fall in molecular weight followed by a slower drop after 30 per cent volatilisation.

2) The production of volatiles consisting of monomer, dimer, trimer and tetramer in decreasing amounts.

Early theories on the degradation of polymers generally were somewhat clarified by the work of Rice and Herzfield[9] on the degradation of low molecular weight hydrocarbons. From this it was shown that polymer degradation might be considered as a free radical reaction, the reverse of polymerisation, and having initiation, propagation, termination and transfer steps.

(b) Investigation by Jellinek

The thermal degradation of polystyrene under high vacuum was first studied by Jellinek.[10] Jellinek rejected the theory that the reaction could be explained by a random scission mechanism for several reasons:-

1) The large amount of monomer produced early in the reaction.

2) The activation energy of 44.7 kcal./mole was lower than expected for random scission.

3) Plots of (molecular weight)$^{-1}$ against time which should be linear for random scission, showed pronounced curvature.

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

Jellinek explained the rapid initial drop in molecular weight as arising from scission at a number of "weak links" randomly distributed along the polymer chain. He also demonstrated the radical nature of the monomer production by studying the degradation in tetralin and naphthalene.[11] Jellinek's "weak link" theory has been the source of much of the subsequent investigation and resultant controversy.

(c) Investigation by Madorsky and Co-workers at N.B.S.

Madorsky[12] and Wall[13] studied the degradation products of polystyrene and showed that:-

1) The composition of the products was independent of the time and temperature of degradation.

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

3) The wax-like fraction obtained consisted of dimer, trimer and tetramer in decreasing amounts.

Madorsky[14,15] extended his work to a detailed study of the rate of degradation in the temperature range 335 - 365°C using a tungsten spring balance. A rate maximum was found to occur in the production of volatiles around 30 - 40 per cent volatilisation. The rapid initial drop in molecular weight was also observed.

Theoretical aspects of the degradation were considered by Simha, Wall and collaborators.[16,17,18] Using a kinetic scheme involving end and random initiation, depropagation, transfer and termination, they predicted a rate maximum at or below 26 per cent conversion, which was at variance with Madorsky's experimentally observed value of 30 - 40 per cent. Increasing the transfer parameter increased the maximum towards but never beyond 26 per cent. Wall[19] demonstrated that transfer was indeed occurring, the transfer site being the α-hydrogen atom. Degradation of α-deuterostyrene produced 70 per cent monomer, but β-deuteration had no effect on the monomer production. This reaction was explained by the slower abstraction of the deuterium from the α site, thus favouring depropagation to monomer.

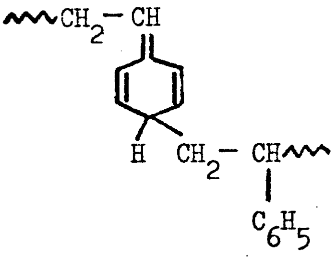
Wall and the N.B.S. group concluded that the degradation of polystyrene was a free radical chain reaction involving random scission, depropagation, inter and intramolecular transfer, and termination by disproportionation. Most important was the fact that they disputed the "weak link" theory and suggested intermolecular transfer as being responsible for main chain scission. However, their mathematical treatment based on this scheme has shown poor agreement with experimental results.

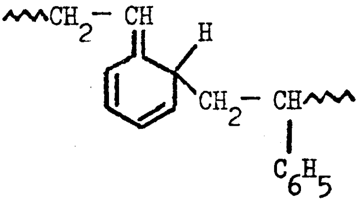
(d) Investigation of Grassie and Co-workers

Grassie and Kerr[20,21] concluded from their experiments, in agreement with Jellinek, that chain scission occurred at "weak links". They also postulated that after the "weak links" had been broken, volatiles were produced by initiation at chain ends, as in poly(methyl methacrylate).[3] The initial low rate of production of volatiles, rising to a maximum at 35 per cent degradation, was ascribed to "weak link" scission followed by disproportionation in a " cage". This would result in an increase in the number of unsaturated chain ends which are the initiation sites for the production of volatiles. Further work by Grassie and Kerr[22] suggested that the labile structures were incorporated in the chain during polymerisation.

The nature of the "weak links" were investigated by Grassie and Cameron. Head-to-head linkages were eliminated by a study of the degradation of styrene/stilbene copolymers.[23] Degradation studies in naphthalene and tetralin[24] showed that a molecular weight drop occurred in the absence of volatilisation. Therefore chain scission and depolymerisation were two separate processes. This was in contradiction to Wall's argument that intermolecular transfer was reducing the chain length.

Since the stability of the polystyryl radical was attributed to resonance with the benzene ring, Grassie and Cameron[25] suggested the transfer of the active site to the benzene nucleus and addition of monomer to give the structures:-





The evidence in favour of associating "weak links" with main chain unsaturation such as is introduced by the above propagation step came from a comparison of thermal and ozone degradation. It was found that the molecular weight obtained by ozonolysis followed by treatment with zinc and acetic acid to break the ozonide resulted in a molecular weight similar to that obtained by thermal degradation.

(e) Miscellaneous Investigations

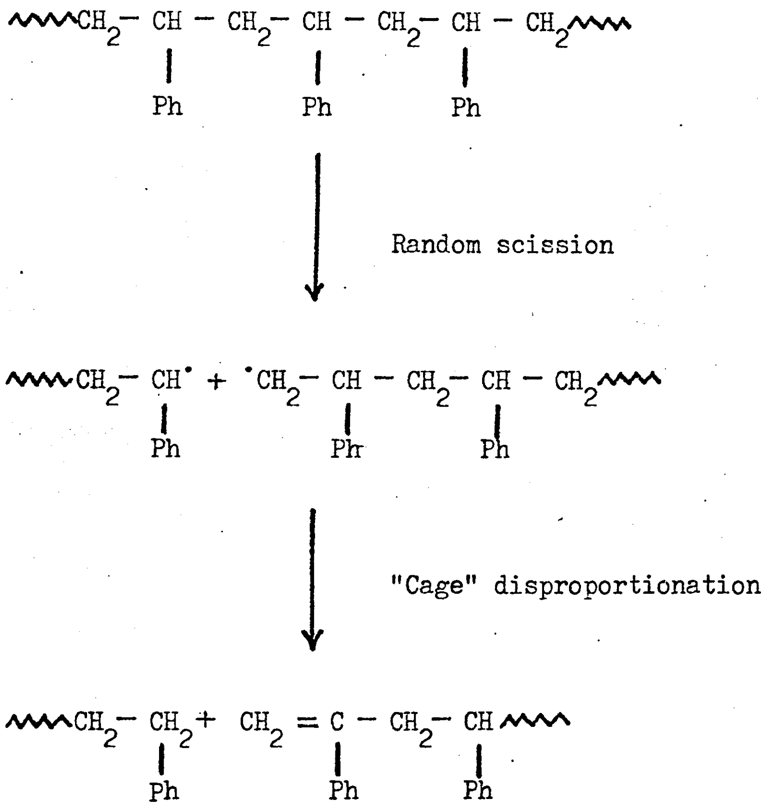
The results of Grassie and Kerr[20,22] and Madorsky[14,15] were examined by Gordon[26] in a kinetic treatment to show that volatiles were produced by initiation at chain ends. To achieve satisfactory agreement with experimental results, a random scission component had to be superimposed on the chain end initiated depropagation. The nature of the random scission component was not defined but Gordon did suggest that "weak links" were an unnecessary complication.

MacCallum[27] has made a survey of vinyl polymers which appear to contain thermolabile structures, namely polystyrene,[10] polyethylene[28] and polypropylene.[29] He applied a theoretical treatment to the results of the other workers to obtain the concentration of weak bonds in the polymer molecule. A disturbing feature of this study was the increase in the number of weak links with increasing temperature of degradation. This coupled with the fact that evidence could be found for "weak links" in many vinyl polymers, even poly(methyl methacrylate), must cast some doubt on the "weak link" theory. This treatment however is only strictly correct when no volatilisation occurs, a condition not always maintained in the results considered.

Boon and Challa[30] studied polystyrene prepared using Zeigler-Natta catalysts and obtained an activation energy of 39 kcal./mole for random scission, in a zero order reaction. No evidence was found for "weak links", and they concluded that volatile products and chain fragments were formed by initiation at chain ends to give unzipping and intramolecular transfer.

Nakajima and others[31] studied the vacuum degradation of isotactic polystyrenes and their work agreed with the findings of Boon and Challa. However Wall[32] in a computer-based study of polystyrene degradation, ignoring "weak link" scission, but allowing simple random scission, inter and intramolecular transfer, obtained poor agreement between theory and experimental results for this scheme.

Cameron[33] in a kinetic treatment of data from the literature on polystyrene degradation, showed that chain end initiation of the production of volatiles occurred to the exclusion of random initiation. The termination reaction in the polymerisation of methyl methacrylate is a mixture of combination and disproportionation accounting for the unsaturated chain ends. In polystyrene termination by combination predominates. This means that in polystyrene the terminal structures are saturated initiator fragments. However after a few random scission reactions followed by "cage" disproportionation have occurred thus:-



$$\sim\!\sim\mathrm{CH_2}-\underset{\mathrm{Ph}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}\sim\!\sim$$

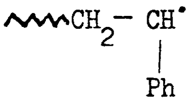
$$\Big\downarrow \;\text{Random scission}$$

$$\sim\!\sim\mathrm{CH_2}-\underset{\mathrm{Ph}}{\underset{|}{\mathrm{CH}^{\bullet}}} + {}^{\bullet}\mathrm{CH_2}-\underset{\mathrm{Ph}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}\sim\!\sim$$

$$\Big\downarrow \;\text{"Cage" disproportionation}$$

$$\sim\!\sim\mathrm{CH_2}-\underset{\mathrm{Ph}}{\underset{|}{\mathrm{CH_2}}} + \mathrm{CH_2}=\underset{\mathrm{Ph}}{\underset{|}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\underset{|}{\mathrm{CH}}}\sim\!\sim$$

unsaturated structures would build up. Scission then occurs β to the double bond to give the radical:-



$$\sim\!\sim\mathrm{CH_2}-\underset{\mathrm{Ph}}{\underset{|}{\mathrm{CH}^{\bullet}}}$$

which depropagates.

(f) Investigations of the Chain Scission Reaction

In a survey of the current state of knowledge of polystyrene degradation, Kerr[34] decided that the production of volatiles was an unnecessary complication to the investigation of the chain scission reaction, the main point of controversy in the study of the polymer. Accordingly he studied the degradation in the temperature range 280-300°C where volatilisation was minimal. A theoretical treatment of Wall and Flynn[35] was applied to the results of this work. The amount of abnormal scission was measured by the ordinate intercept obtained from plots of α, the fraction of bonds broken, against time and $(\text{molecular weight})^{-1}$ against time, both of which give the rate of chain scission. For a simple random scission process, the expected intercepts would be at $\alpha = 0$ and at $(M_o)^{-1}$. In polystyrenes synthesised using free radical initiation, substantial α-ordinate intercepts were obtained and the $(\text{molecular weight})^{-1}$ intercept was greater than $(M_o)^{-1}$. "Living" polystyrenes prepared by ionic techniques however, showed the theoretically predicted intercepts, indicating the absence of "weak links". A value of 67 kcal./mole was found for the activation energy of chain scission in "living" polystyrenes. This compared well with the calculated value of scission of the carbon-carbon bond in polystyrene (64 kcal./mole). The rate of chain scission in these polymers was found to be an increasing non-linear function of molecular weight. The activation energy for scission in thermally initiated polystyrenes was found to be 49 kcal./mole, considerably lower than the anionic value. It would appear that the "normal" chain scission in thermally initiated polystyrene also takes place at bonds which are weaker than the normal C - C bonds.

In an investigation of the unsaturation occurring in polystyrenes, McNeill and Makhdumi[36] have shown the existence of main chain unsaturation in thermally initiated polystyrenes. Polystyrene prepared by a cationic mechanism contained only terminal unsaturation.[37] Scission of carbon bonds β to a C - C double bond occurs with an activation energy of about 17 kcal./mole less than the normal aliphatic C - C scission.[38] Kerr has suggested that the "normal" scission in thermally initiated polystyrenes is β to C - C double bonds and this would account for the difference in activation energy observed for the two polystyrenes.

Further work on styrene/stilbene copolymers in the absence of volatilisation showed that head-to-head linkages do indeed cause a decrease in thermal stability, but this is observed as an increase in the rate of "normal" scission. Head-to-head linkages are not responsible for the very rapid drop in molecular weight at the beginning of the degradation.

Two important conclusions were reached in Kerr's work:-

1) "Weak links" were responsible for the rapid initial drop in molecular

weight of thermally initiated polystyrenes. Such thermolabile structures were not observed in polystyrenes prepared by Zeigler-Natta catalysis and ionic techniques. The "weak links" were attributed to oxygenated structures incorporated into the polymer chain during free radical polymerisation. The more rigidly controlled polymerisation mechanism occurring in ionic systems precluded the formation of such structures.

2) The "normal" chain scission in free radical polystyrenes also took place at a lower temperature and proceeded with a lower activation energy than the corresponding phase in the anionic polystyrenes. This second type of thermolabile structure was attributed to scission of a carbon bond β to a C - C double bond.

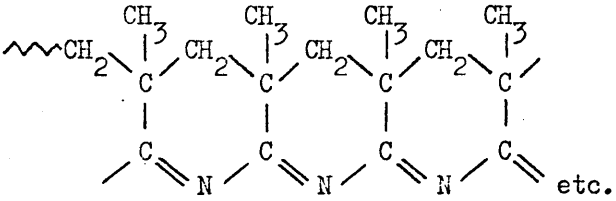
(g) Conclusion

It is clear from this brief review of polystyrene degradation that general agreement has not been reached on the mechanism of degradation. If, as has been suggested by Kerr[34] oxygen is responsible for the weak links, one might have expected an even greater discrepancy between the results in various laboratories. As well as the effect of oxygen on the polymerisation, the effects of other impurities such as water will have to be considered.

1.3 Degradation of Polyacrylonitrile

In spite of the greater commercial importance of polyacrylonitrile, significant progress in explaining the coloration reaction, which is the principal feature of the degradation of polyacrylonitrile, was made by studies on the degradation of polymethacrylonitrile.[39,40] This was mainly due to the more favourable physical properties of this polymer, for example solubility, and also the result of a less complicated reaction.

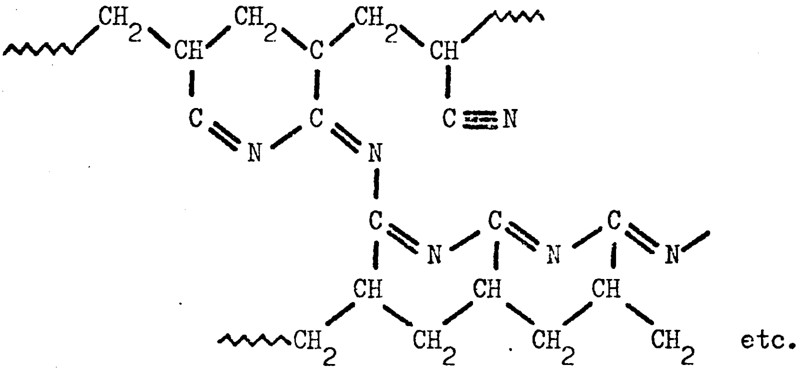
It was shown by Grassie and McNeill that coloration was due to the conjugation of nitrile groups, initiated by nucleophilic reagents to give the structure:-



This was supported by the work of Skoda and Shurz.[41]

The coloration reaction in polyacrylonitrile was studied by Grassie and Hay.[42,43] As in polymethacrylonitrile, the reaction is initiated by nucleophilic reagents, but unlike polymethacrylonitrile, there was substantial self initiation of the colour reaction. This suggested that the coloration is the property of the polymer molecule rather than an impurity effect.

Insolubility was found to occur very early in the thermal degradation reaction of polyacrylonitrile, a feature not exhibited by polymethacrylonitrile. This was attributed to "propagation cross-linking" due to the more intimate packing of the polyacrylonitrile chain. The reaction may be represented thus:-



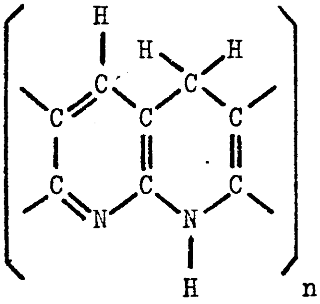
Copolymerisation with small quantities of styrene or methyl methacrylate inhibited coloration and crosslinking by blocking the nitrile conjugation and sterically inhibiting the "propagation cross-linking" reaction. Products formed in the degradation of polyacrylonitrile have been studied by Kern and Fernow,[44] Burlant and Parsons,[45] Nagas,[46] Takayama,[47] Strauss and Madorsky[48,49] and most recently by Monahan.[50] Sixteen products were identified by a variety of spectroscopic techniques, cyanogen, hydrogen cyanide, acetonitrile, acrylonitrile and vinylacetonitrile being the major components. The distribution of these components at various temperatures of degradation is shown in the following table.

Table 1.1

Product Analysis for Pyrolysis of Polyacrylonitrile[50]

Product	Mole % after 30 minutes pyrolysis 286°C	327°C	379°C	450°C
Cyanogen	0.01	0.02	0.01	0.40
Hydrogen Cyanide	0.03	1.54	0.49	20.97
Acetonitrile	5.23	5.86	1.02	2.42
Acrylonitrile	94.73	90.90	59.28	3.85
Vinylacetonitrile	0.01	1.68	39.20	72.30

A poly-1, 4,4-trihydronaphthyridine was suggested as the structure of the residue, from elemental analysis and infra-red spectroscopy, thus:-



The extensive degradation of polyacrylonitrile to produce carbon fibres has recently assumed some importance in the search for new materials which are resistant to high temperatures, as well as being light and having strengths comparable with metals.

1.4 The Thermal Degradation of Copolymers

(a) Introduction

Although copolymerisation has been widely used as a method of polymer stabilisation and in order to combine the favourable properties of two different polymeric materials to give a more versatile product, for example styrene/butadiene rubber, there is a serious lack of basic chemical information about the degradation of these materials. The increasing accumulation of data on the homopolymers provides a good basis for a study of many copolymers. In certain cases study of the copolymers may shed new light on the degradation of the homopolymers. A number of systems have been studied[51] and those relevant to the styrene/acrylonitrile system are reviewed here.

(b) Thermal Degradation of Styrene/Methyl Methacrylate Copolymers

Thermal degradation studies of styrene/methyl methacrylate copolymers were carried out by Grassie and Farish.[7] It was found that the number of "weak links" increased linearly with the styrene content of the copolymer. Sequence distribution calculations showed that a large proportion of the styrene units existed in isolation; therefore the "weak link" must be a property of a single styrene unit in the chain. The nature of this link is still speculative however. Methyl methacrylate lost from the copolymer could be quantitatively accounted for as monomer, indicating that chain fragments did not contain methyl methacrylate. The amount of methyl methacrylate monomer produced increased with increasing methacrylate content of the polymer, indicating inhibition of the transfer reaction which produces chain fragments in polystyrene. The differing volatilisation behaviour exhibited by poly(methyl methacrylate) and polystyrene is seen in the styrene rich and methacrylate rich copolymers in Fig. 1.1.

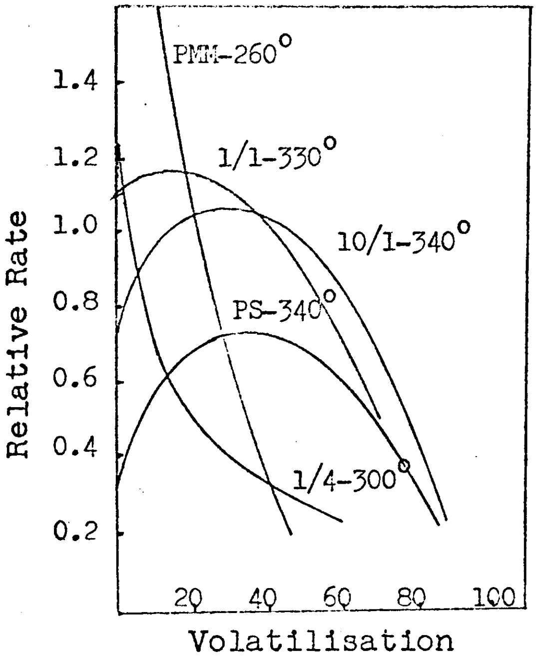


Fig. 1.1 Rates of Volatilisation of Homopolymers and Copolymers of Styrene and Methyl Methacrylate[7]

The styrene rich copolymers exhibit the characteristic maximum associated with polystyrene, the latter showing the initial high rate falling off as the reaction proceeds, characteristic of poly(methyl methacrylate).

The large increase in the thermal stability as measured by the rate of volatilisation could be accounted for by a decrease in the chain end unsaturation normally found in poly(methyl methacrylate), due to the presence of the styrene. As little as 17 per cent styrene reduces the disproportionation termination in the polymerisation to 8 per cent of the total.

(c) Thermal Degradation of Methyl Methacrylate/Acrylonitrile Copolymers

In the investigation of the coloration of polyacrylonitrile, Grassie and Hay[42] found that the addition of small amounts of methyl methacrylate inhibited the coloration reaction by blocking the conjugation of the nitrile groups. Addition of small quantities of acrylonitrile to methyl methacrylate was found to give an induction period in the production of monomer from the copolymer.[52]

Clarification of the thermal degradation of poly(methyl methacrylate) led Grassie and Farish[8] to re-examine the degradation of copolymers of methyl methacrylate and acrylonitrile, varying the composition over a much wider range.[8,52]

It was found that the rate of chain scission decreased with increasing acrylonitrile content. This was at variance with the initial investigations by Grassie and Melville,[52] who suggested that scission was associated with acrylonitrile units. Volatile material could be accounted for as monomer but the acrylonitrile to methyl methacrylate ratio was less in the volatiles than in the corresponding copolymer.

The appearance of an inhibition period in the 220°C degradations followed by a maximum rate of volatilisation was attributed to unzipping not passing through the first acrylonitrile unit encountered, thus halting the production of monomer. This was followed by termination of the radical. A random scission process produces radicals which undergo "cage" termination, some by disproportionation giving molecules with unsaturated chain ends. These are subsequently re-initiated and depolymerise to produce monomer. The rate maximum occurs when the populatation of chain ends capable of degradation reaches a maximum. A similar situation exists in polystyrene.

When the degradation temperature is raised to 280°C, random scission is rapid, producing radicals which immediately depropagate to give monomer. Hence no rate maximum was observed at this temperature. At higher temperatures also, the unzipping reaction can pass through acrylonitrile units in the copolymer, accounting for acrylonitrile monomer among the products of degradation.

The one experimental observation which could not be readily accounted for was the decrease in chain scission with increasing acrylonitrile content of the copolymers. This could be due to decreased flexibility of the chain because of the acrylonitrile units, which would favour "cage" recombination or decrease the probability of achieving the correct conformation for monomer production.

(d) The Thermal Degradation of Styrene/α-Chloroacrylonitrile Copolymers

In this copolymer system, the effect of introducing a monomer unit which degrades at a much lower temperature than its comonomer is discussed. Poly(α-chloroacrylonitrile) was shown by Grassie and Grant[53] to degrade at 135°C producing hydrogen chloride and unsaturation in the main chain. Since unsaturation has been suggested as a source of "weak links" in the polystyrene chain,[54] the effect of controlled concentrated unsaturation on the degradation behaviour of the polymer is of interest.

The degradation of copolymers of styrene and α-chloroacrylonitrile was studied by Grassie and Grant.[55] Chain scission can be conveniently studied at 155°C, well below the temperature at which styrene produces volatile material. The α-chloroacrylonitrile was found to constitute "weak links" in the polymer backbone.

Significant effects were also observed at higher temperatures. The rate maximum associated with polystyrene degradation was completely obscured by the very rapid chain scission, induced by the α-chloroacrylonitrile units. The relative stabilities may be seen from the fact that in one hour at 322°C polystyrene produces 2.7 per cent volatiles compared with 42.8 per cent from a copolymer of 2.4 per cent α-chloroacrylonitrile.

(e) The Thermal Degradation of Methyl Methacrylate/Methyl Acrylate Copolymers

The degradation of copolymers of methyl methacrylate and methyl acrylate has been studied by Grassie and Torrance.[56] Thermal volatilisation analysis (T.V.A.) studies described by McNeill,[57] showed that the rate of production of monomer from poly(methyl methacrylate) was suppressed by the presence of the methyl acrylate units in the chain. The depropagation reaction could pass through methyl acrylate units to some extent however, since one methyl acrylate unit in four was found in the volatile products. This may be taken as a measure of the blocking effect of methyl acrylate.

The volatile products consisted of carbon dioxide, methyl methacrylate, chain fragments, small quantities of methyl acrylate and traces of permanent gases. The production of chain fragments formed in transfer reactions, methyl acrylate monomer and permanent gases all increased with increasing methyl acrylate in the copolymer. The coloration which is due to the development of unsaturation in the chain backbone was also shown to be associated with permanent gas production. The absence of methanol, a product of degradation of poly(methyl acrylate) indicated that sequences of acrylates longer than two were necessary for its production.

It was clearly demonstrated that one molecule of carbon dioxide is formed per chain scission. The amount of volatilisation produced per chain scission was also shown to be constant for a particular copolymer. The zip length decreased with increasing amounts of methyl acrylate in the copolymer. A comprehensive reaction scheme was presented which accounted for all the important features of the reaction.

(f) Conclusion

In the light of the previous work on copolymers it is clear that effects such as enhanced chain scission, unsaturation and stabilisation by inhibition of volatile production occur in copolymers depending on the individual characteristics of the comonomers. The influence of temperature of degradation and also the distribution of monomer units in the copolymer chain are points worthy of consideration in the study of the mechanism of degradation.[8,56]

CHAPTER 2

EXPERIMENTAL TECHNIQUES AND APPARATUS

2.1 Preparation of Copolymers

(a) Purification of Styrene

Styrene (Forth Chemicals Ltd.) was washed three times with 5M sodium hydroxide to remove the inhibitor, p-tertiary butyl catechol, and three times with distilled water to remove traces of alkali. The purified monomer was dried for 24 hours over calcium chloride followed by 24 hours over freshly dried calcium hydride. Finally the monomer was filtered into a reservoir containing some calcium hydride. A magnetic stirrer was used to break the polymer film which formed on the surface of the styrene and reduced the rate of distillation. The reservoir was then attached to a vacuum system and degassed several times by the usual freezing and thawing method. The first 10 per cent was distilled off and discarded, after which the required quantity was distilled into a calibrated reservoir and finally into the dilatometer.

(b) Purification of Acrylonitrile

Acrylonitrile (Hopkins and Williams Ltd.) was washed once with 5M sodium hydroxide and several times with distilled water. The purified monomer was then dried for 24 hours over calcium chloride followed by 24 hours over calcium hydride. This treatment was reported to give a material of standard purity as indicated by G.L.C. and I.R. analysis.[42] The monomer was filtered into a reservoir containing a little calcium hydride and degassed several times. It was then distilled into a calibrated reservoir and finally into the dilatometer.

The purity of both monomers was checked by G.L.C. analysis using 1 per cent SE 30 (silicone gum) and 10 per cent dinonyl phthalate columns. Single products only were detected using a flame ionisation detector at high sensitivity settings.

(c) Purification of Initiator

2-2' Azobisisobutyronitrile (Kodak Ltd.) was purified by recrystallisation from methanol.

The initiator was introduced into the dilatometer as a freshly prepared solution in Analar toluene, the solvent being removed by a water pump and finally on the vacuum line. The dilatometer was then pumped for several hours under high vacuum, light being excluded to prevent decomposition of the initiator.

(d) Preparation of Dilatometers

Pyrex glass dilatometers of approximately 100 ml., with a 5 ml. graduated stem were washed with cleaning solution, distilled water and finally Analar acetone and attached to the vacuum line. The dilatometers were then flamed intermittently for several hours prior to the addition of the initiator solution.

(e) Filling the Dilatometers

The arrangement of glassware on the vacuum line is shown in Fig. 2.1. This system was particularly useful for dealing with copolymers since the second monomer could be prepared and degassed while the first was distilling.

When the required quantities of monomer had been added, the contents of the dilatometer were finally degassed and sealed off at a pressure of less than 10^{-5} torr.

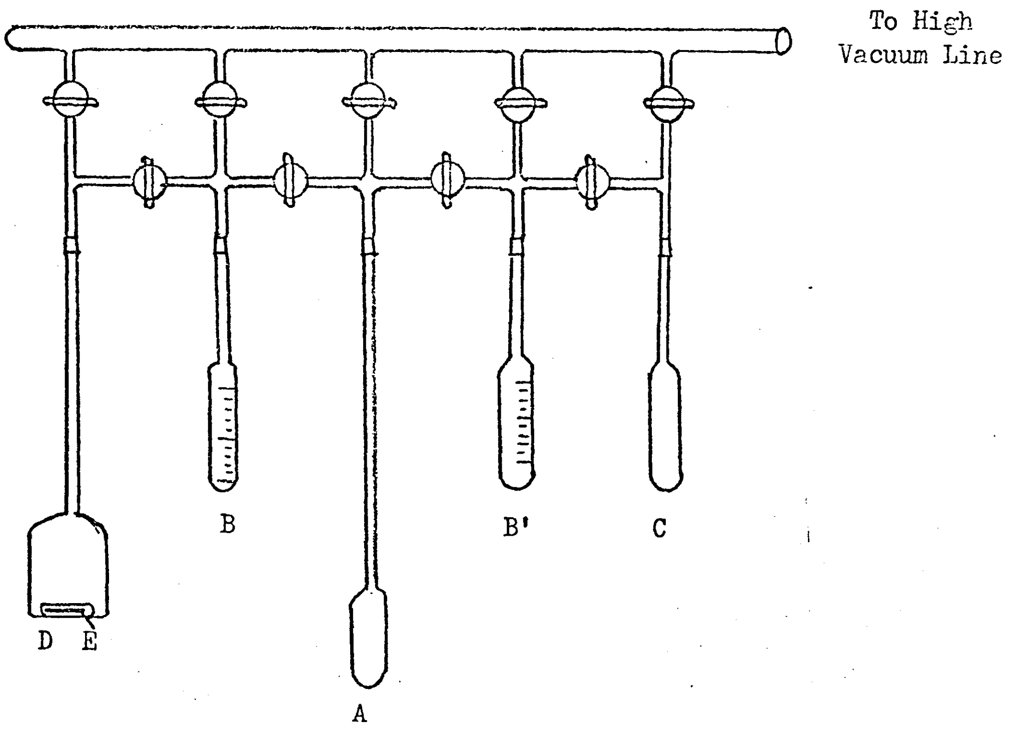
(f) Polymerisation

All polymerisations were carried out at 60°C ± 0.1°C. Polymerisation was never carried beyond 10 per cent conversion which could be estimated with sufficient accuracy by observing the liquid level in the calibrated stem and making use of the contraction data presented in the following table.

Table 2.1

Calculated Volume Contraction for 100% Polymerisation at 60°C

Monomer	% Volume Contraction	Ref.
Acrylonitrile	26.7	58
Styrene	15.0	59



A	Dilatometer
BB'	Calibrated Reservoirs
C.	Acrylonitrile Container
D	Styrene Container
E	Glass Covered Magnet

Fig. 2.1 Vacuum Line for Filling Dilatometers

(g) Copolymer Recovery and Purification

In all cases the copolymers formed (0.25-50 per cent acrylonitrile) were soluble in the monomer mixture.

All copolymers except the one containing 50 per cent acrylonitrile (SA9) were recovered by dissolving the contents of the dilatometer in 300-400 ml. Analar toluene. Precipitation was carried out by slowly running the solution into 5 litres of Analar methanol with constant stirring. This proceedure was repeated a second time but for the final precipitation Analar dioxan was used as the solvent, since this was found to give a polymer which could be more readily ground.

The copolymer containing 50 per cent acrylonitrile was, like polyacrylonitrile, insoluble in toluene. It was precipitated from solution in Analar acetone, with methanol as precipitant.

After the final precipitation, the copolymers were placed in a vacuum oven, initially at room temperature and finally at 50°C for 48 hours, with frequent crushing to facilitate solvent removal. They were then passed through a 40-60 mesh sieve, the smallest usable because of the highly electrostatic nature of the material. The ground copolymers were then replaced in the vacuum oven for a further 24 hours at 50°C to ensure complete removal of the solvent.

(h) Calculation of Monomer Feed Composition

The molar ratio of monomers necessary to produce a copolymer of the required composition was calculated using the copolymer composition equation:-[60,61,62,63]

$$\frac{(P_1)}{(P_2)} = \frac{(M_1)}{(M_2)} \cdot \frac{r_1(M_1) + (M_2)}{(M_1) + r_2(M_2)}$$

where $(P_1)/(P_2)$ is the ratio of the molar concentrations of the two monomers in the copolymer, and (M_1) and (M_2) are the molar concentrations of the monomers in the feed. This relationship applies if the conversion is sufficiently low for the monomer concentrations to remain unchanged. Values of reactivity ratios from the literature were used:-[64]

$$r_{\text{styrene}} = 0.41 \pm 0.08 \,, \quad r_{\text{acrylonitrile}} = 0.04 \pm 0.04$$

Data for the copolymers used in this work are shown in Table 2.2.

Table 2.2

Copolymer Composition Data

Code No.	% Styrene	% Acrylonitrile	Molecular Weight	% W/W Initiator
SA2	99	1	370,000	0.03
SA3	91.7	8.3	411,000	0.03
SA4	99.75	0.25	347,000	0.03
SA5	75.1	24.9	650,000	0.03
SA6	84.5	15.5	470,000	0.03
SA7	95.3	4.7	857,000	0.03
SA8	95.3	4.7	331,000	0.06
SA9	50	50	not determined	0.06
SA10	66.6	33.4	366,000	0.06
PS3	100	0	470,000	0.03

2.2 The Degradation Apparatus

(a) Introduction

The variables which may influence the course of a thermal degradation reaction are numerous and complex. Important variables include temperature of degradation, heating rate, rate of removal of volatile products from the reaction zone, softening and melting point of the polymer, melt viscosity, sample size and dimensions, adsorbed or occluded impurities, the initiator used, and the termination mechanism in the polymerisation. Working with highly purified polymers as films or fine powders under a specified set of conditions eliminates many of the problems associated with this type of work, but it is often difficult to obtain reliable kinetic data unaccompanied by diffusion effects when using samples large enough to allow the molecular weights of the residue to be determined, or the volatile products to be analysed.

(b) The Molecular Still Apparatus

1) The Molecular Still

For studies of the change in molecular weight or rate of volatilisation under isothermal conditions, the dynamic molecular still, similar in principle to that of Grassie and Melville,[52] but incorporating certain modifications, was used.

The still and associated equipment is shown in Fig. 2.2. The sample of powdered polymer (100 mg.) was contained in the circular depression (33 mm. diameter x 7 mm. deep) in the copper tray (40 mm. x 40 mm. x 9 mm.) which is shown along with the heating block in Fig. 2.3. Two copper-constantin thermocouples were hard soldered to the base of the tray. One thermocouple was connected to a Doran precision potentiometer so that the temperature could be continuously measured to 0.1°C. The other thermocouple

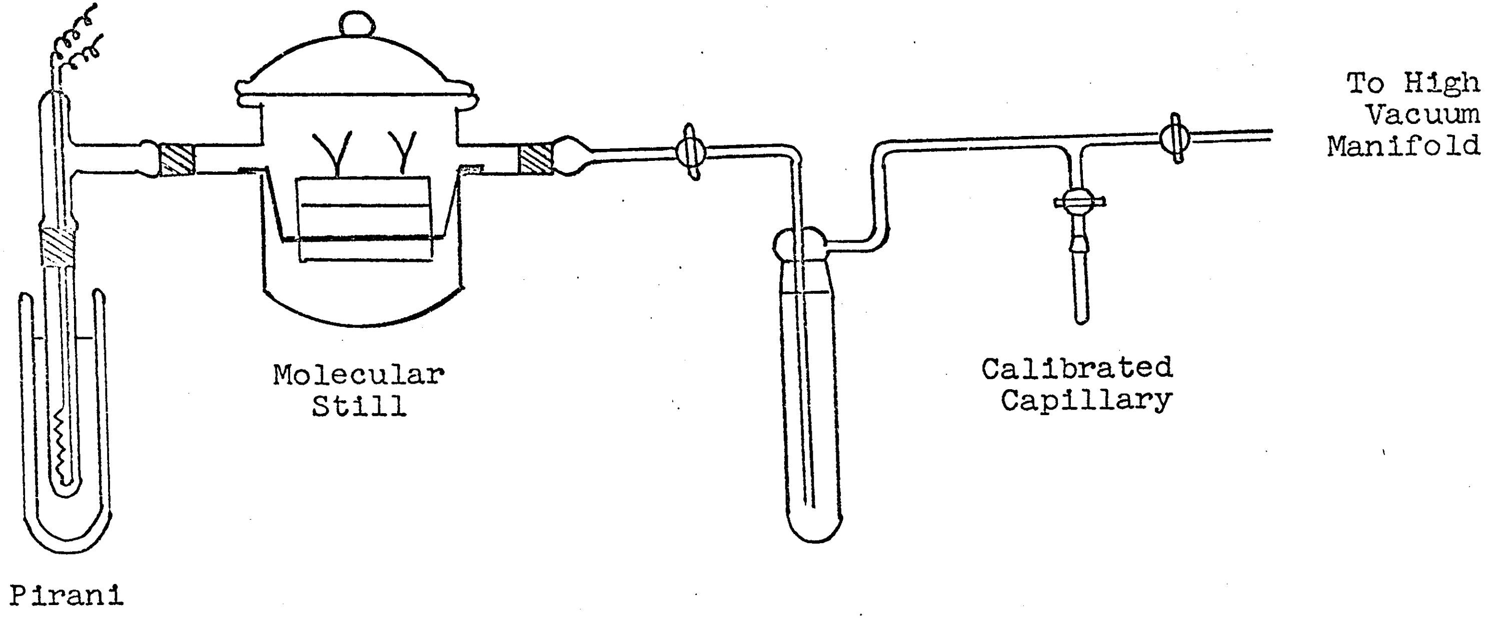


Fig. 2.2 Molecular Still Apparatus

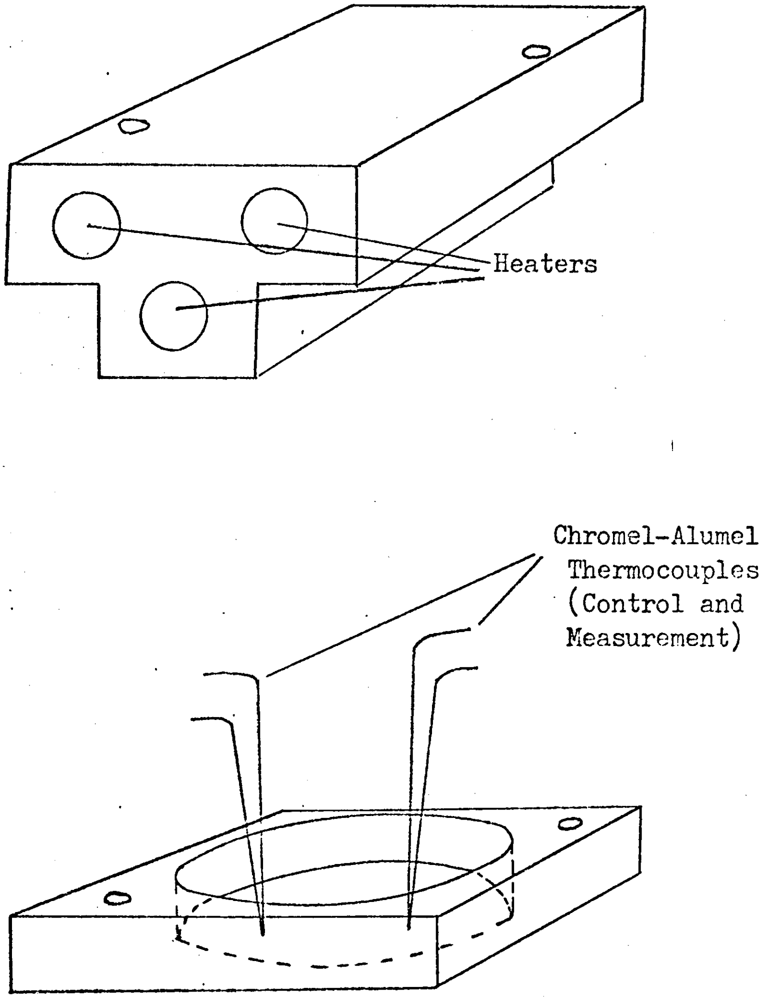


Fig. 2.3 Molecular Still Heating Block and Degradation Tray

activated the proportional temperature controller described in section 2.2 (b) 2). Temperature could be maintained to ± 1°C for many hours with little or no attention.

Heating was effected by 3 cartridge heaters (24 V., 50 watt, Hedin Ltd.) housed in the copper block shown in Fig. 2.3. The bottom of the tray was ground to give good contact with the heating block to which it was tightly secured by two screws. Connecting wires to the heaters and thermocouples were taken out through glass capillaries in two of the four B.24 joints, symmetrically spaced at right angles around the body of the still. The wires were sealed into the capillaries with Picien wax.

To maintain isothermal conditions throughout the sample, and to prevent loss of sample by sputtering, the polymer was covered with a layer of copper powder (60-80 mesh Hopkins and Williams).

The two main disadvantages of this type of apparatus are its heating and cooling periods, and the loss of chain fragments, which remain coated on the walls of the still. The former problem is a function of the system but is more than compensated for by advantages of accurate degradation conditions for large samples. Where 100 per cent product collection was desirable the sealed tube technique was used.

2) <u>The Heater Controller</u>

The heating of the molecular still has previously been effected by a system of Variac transformers coupled to an Ether "on-off" controller. This system was found to be unsatisfactory as large temperature fluctuations accompanied changes in the mains voltage. With the development of transistorised proportional controllers, it seemed desirable to employ such a system.

The following characteristics were necessary in the temperature controller:-

(1) A rapid attainment of temperature of degradation.

(2) Control to better than ± 1°C for long operating periods.

(3) Minimum attention during the course of the degradation.

(4) Ability to be used with the existing block and cartridge heaters in the molecular still.

Commercial proportional controllers such as the West Viscount (West Instruments Ltd.) were available, but their cost and the fact that modifications would have to be made to accomodate the start-up made them undesirable. Accordingly a controller was developed which has proved satisfactory over a large number of experiments.

Circuit diagrams for the controller, and associated wiring to the transformers and heaters are shown in Fig. 2.4 (a),(b) and (c). The controller can be operated in three characteristic modes as shown in Fig. 2.5 depending on the requirements of the system.

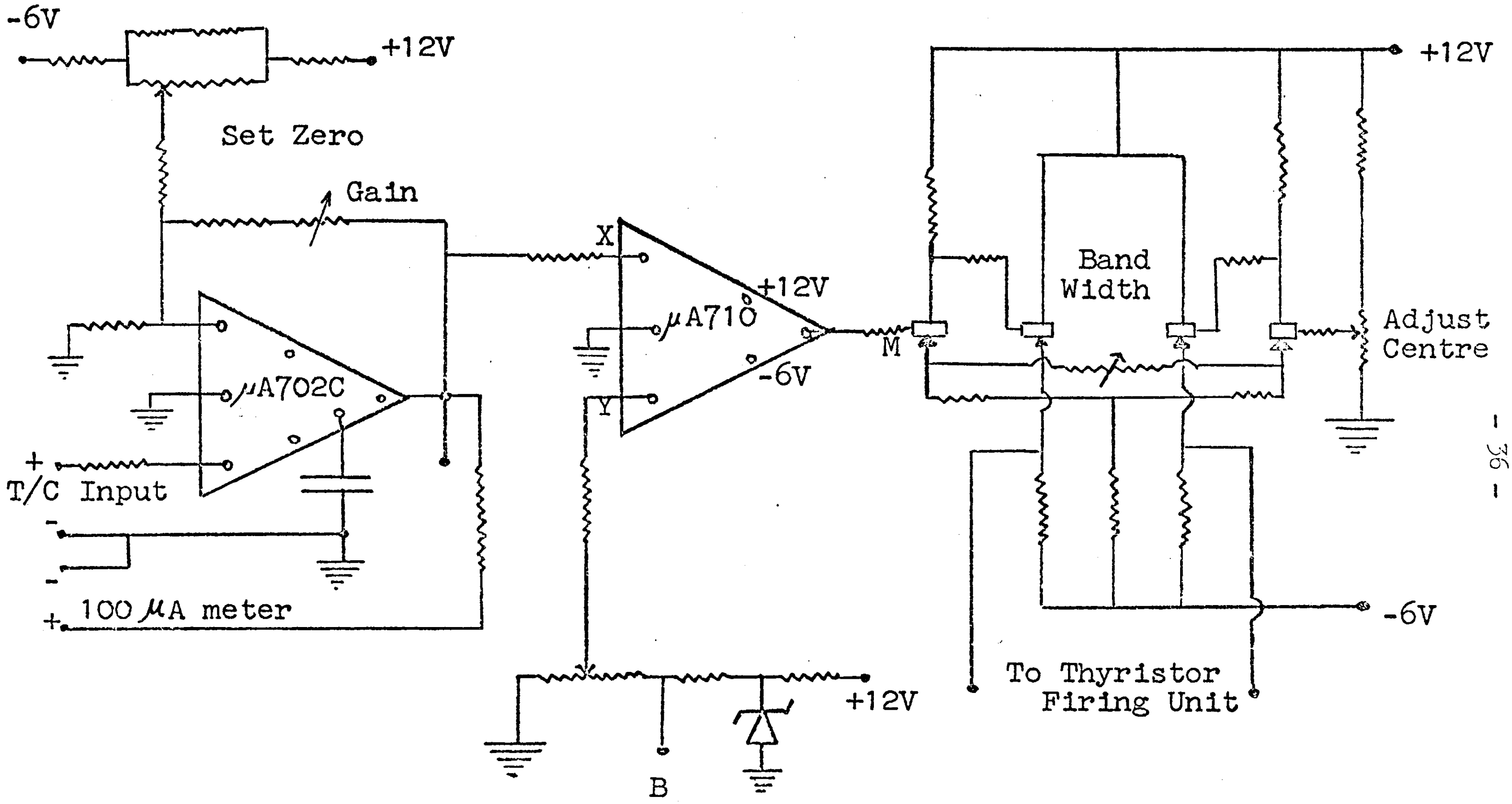


Fig. 2.4(a) Temperature Control Module

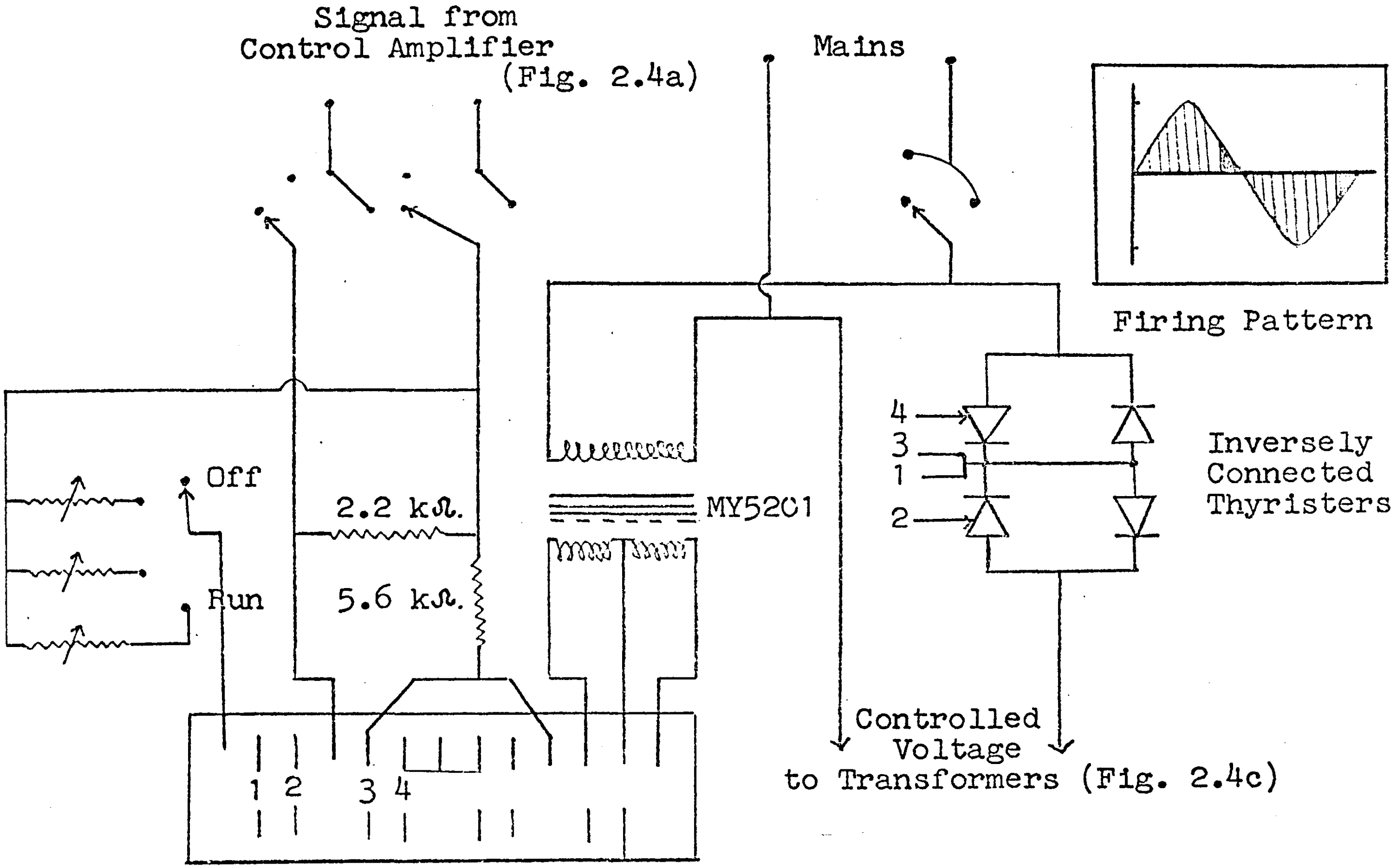


Fig. 2.4(b) Firing Unit and Output to Transformers

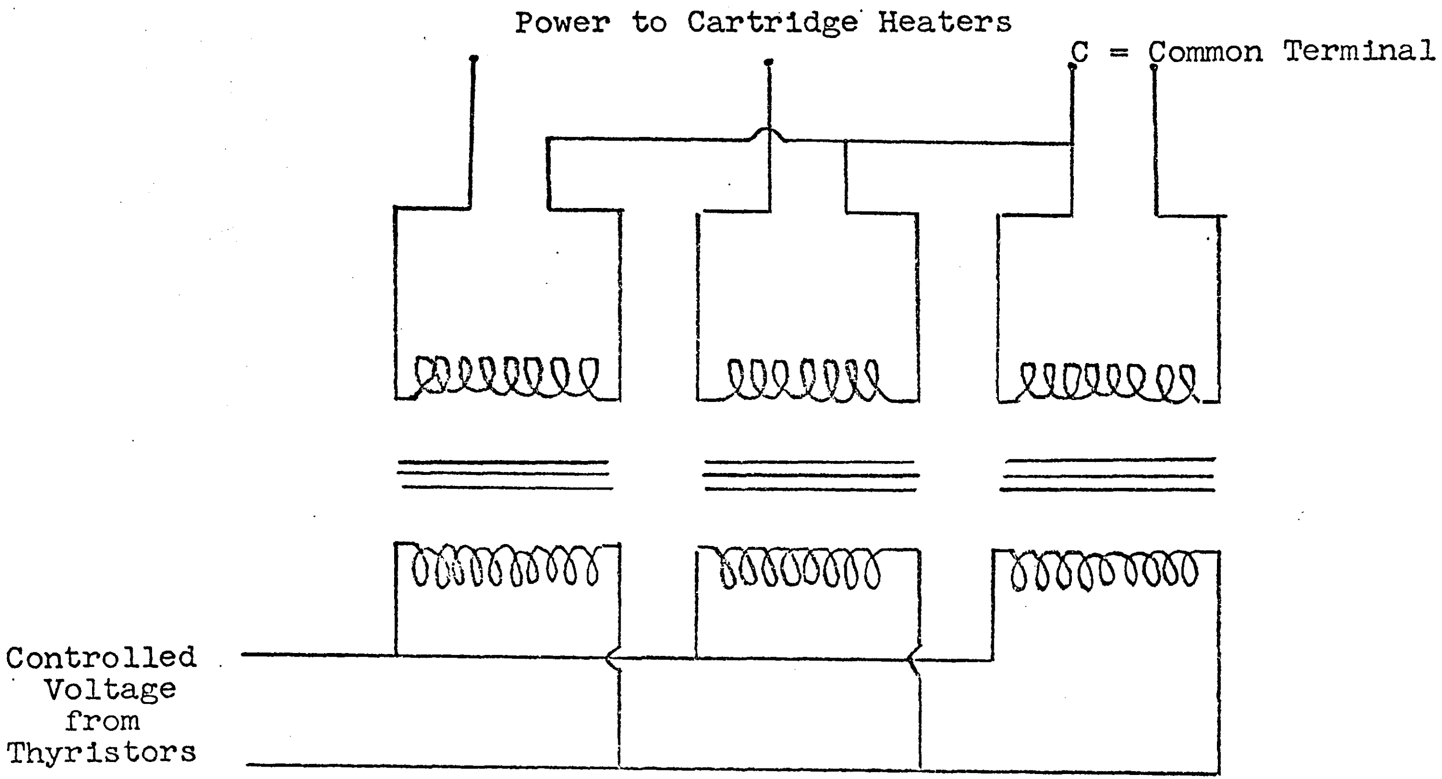
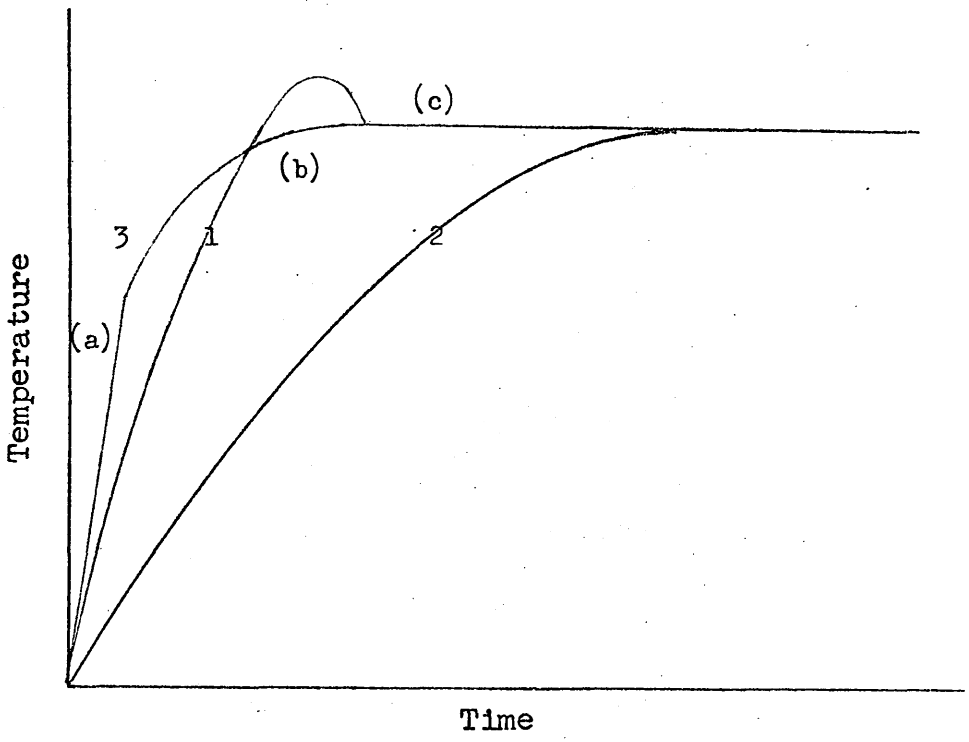


Fig. 2.4(c) Circuit Diagram of Transformers and Connections to the Cartridge Heaters



1. Run mode only - temperature overshoot

2. Run up mode - too slow

3. Multiple mode

   (a) Full power

   (b) Reduced power - run up without overshoot

   (c) Set at run power

Fig. 2.5 Temperature Controller Characteristics

(1) Run Mode

If the controller is set at the power value required to maintain a certain temperature, an overshoot will arise as a consequence of the temperature gradient between the block and the thermocouples on the tray.

(2) Run-up Mode

Setting the controller at this value gives no overshoot but the time to reach operating temperature is too long.

(3) Multiple Mode

This is found to give the desired characteristics. In section (a) of Fig. 2.5 power is full on and a rapid rise occurs. At a fixed temperature, power is reduced to the run-up value, (b), and the degradation temperature is attained without overshoot. At this stage the controller is set to "run" (c), and the temperature is maintained at the desired value, in the proportional band which accomodates any fluctuations in temperature or power.

Although the controller is "blind" in that operating conditions at a particular temperature have to be established prior to degradation, the inconvenience caused is minimal since several runs are usually carried out at the same temperature and once established, a desired temperature can be attained at any time. The fine control has enough latitude to allow a useful range of temperatures (approximately 30°C) to be obtained, enough to enable activation energies to be measured, without altering the run-up settings.

The voltage from the controlling thermocouple is fed into the unit at the T/C input shown in Fig. 2.4 (a), to an amplifier (μA702C). The amplifier signal is fed to a second amplifier (μA710) which operates in a small proportional band as well as in an "on-off" manner.

When the potential difference between the points X and Y (Fig. 2.4 (a)) is zero, the thermocouple supplies the output preset at B, and the amplifier produces 1.5 volts. This is fed to a third amplifier circuit at M. This is balanced by the third pre-set amplifier and zero voltage is fed to the thyristor firing unit. However any fluctuation in temperature changes the thermocouple output and unbalances the amplifier, μA710. This results in a voltage (positive or negative) being fed to the third amplifier and subsequently to the firing unit which decreases or increases the power input to the heaters, depending on the voltage change. The inversely connected thyristors control the power to the heaters. The thyristors fire 50 times per second and the magnitude of the power delivered, which has the effect on the heaters of a continuous voltage, is determined by the position of firing. This effect is shown in the inset to Fig. 2.4 (b). If firing occurs early in the half cycle, the power will be on for the long shaded period, the "full-on" mode. If, however, firing occurs late in the cycle, as shown by the small darker sections, much less power is delivered. This occurs in the proportional band. The amount of power produced depends on the demands of the system, that is the variation in output from the controlling thermocouple.

3) The Pirani Gauge

The volatiles produced can be monitored by following the pressure inside the molecular still as the reaction proceeds. If a single component is evolved in the reaction, previous calibration allows quantitative kinetic data to be obtained using a Pirani gauge to measure pressure changes. This system was used by Grassie and Melville to study the decomposition of poly(methyl methacrylate).[52]

With the styrene/acrylonitrile copolymers, the complex mixture of products formed makes it impossible to obtain exact kinetic data using this method. The Pirani gauge was therefore not used quantitatively but as a guide to the course of the reaction.

The Pirani gauge consists of a tungsten filament (50 ohms) suspended between copper supports (Fig. 2.6). The filament forms one arm of a Wheatstone Bridge circuit which is shown in Fig. 2.7. A voltage, V_o, is applied to the filament, and the bridge is balanced by means of the "zero" control, when a sticking vacuum is obtained in the still. This is taken as zero pressure. To prevent thermal fluctuations, the side arm containing

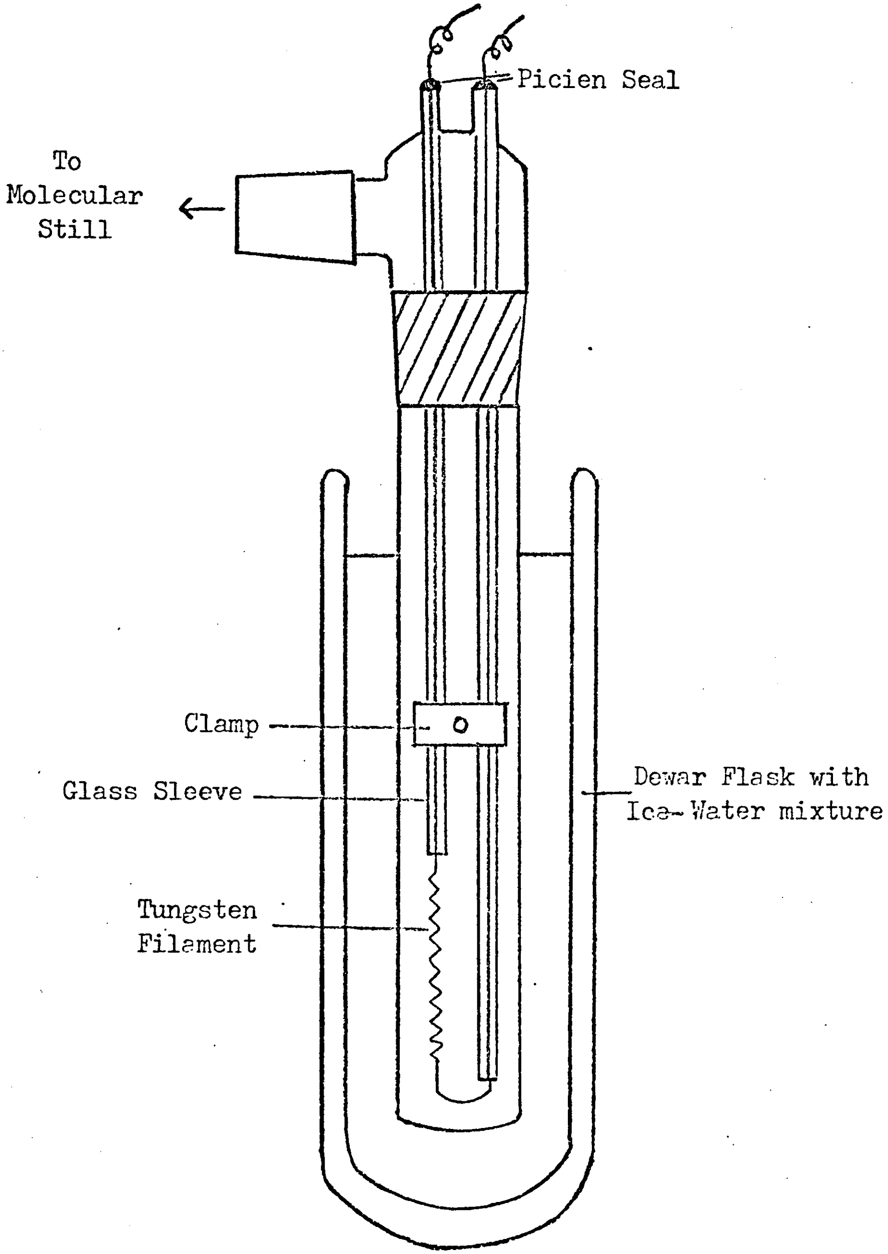
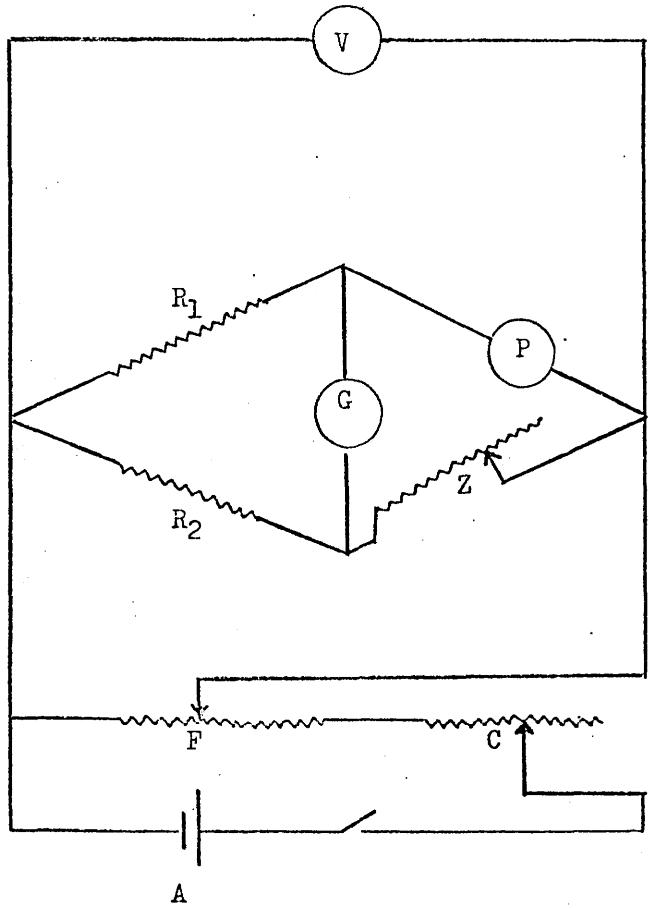


Fig. 2.6 The Pirani Gauge



A	Accumulator
C	Coarse Potentiometer 0-250 ohms
F	Fine Potentiometer 0-10 ohms
R_1R_2	Fixed Resistors
G	Galvanometer
P	Pirani Filament (50 ohms)
Z	Zero Control
V	Voltmeter

Fig. 2.7 The Pirani Control Unit

the Pirani gauge is thermostatted in an ice bath.

The temperature and hence the resistance of the filament depend on the thermal conductivity of the surrounding medium. Therefore any change in pressure changes the resistance of the wire. This unbalances the bridge circuit and the voltage has to be increased to a new value V to re-balance it. At low pressures, the expression $\frac{V^2 - V_o^2}{V_o^2}$ is proportional to the pressure. This relationship is linear over a limited range of pressure.[52]

4) Collection of Products

Volatile products from the reaction were collected in the cold trap (Fig. 2.2) during the course of the degradation. When the reaction was complete, the appropriate section of the vacuum line was isolated and the products distilled at room temperature into a calibrated capillary tube, for measurement and subsequent analysis. In this system the bulk of the chain fragments remained on the walls of the still. The second distillation however ensured that the liquid collected in the capillary was the highly volatile monomer fraction only. It was therefore possible to obtain the weight of monomer from density data and, since the total weight loss from the tray could be determined accurately, it was possible to measure the chain fragment to monomer ratio.

(c) The Sealed Tube Technique

To facilitate total analysis of the products, a sealed tube of the type shown in Fig. 2.8 was used. The polymer sample was introduced into the tube, which had been cleaned and flamed, in powder form through the B.14 cone. The tube was then attached to the vacuum line, pumped for several hours under high vacuum, and sealed off.

The end of the tube containing the polymer sample was inserted into a furnace, the temperature of which was controlled to $\pm 2^{o}C$. The capillary end was cooled in liquid nitrogen. The short distance between the hot zone and the cooled limb was such that products distilled rapidly away from the degrading sample, minimising recombination or further reaction. At the end of the degradation the tube was withdrawn from the furnace and cooled rapidly.

Gas analysis was carried out by attaching the tube directly to the inlet of a mass spectrometer (MS10, A.E.I. Ltd.). Where necessary the mass spectrum was scanned with cold traps of various temperatures ($-178^{o}C$ to $0^{o}C$) around the capillary limb of the tube. This considerably reduced the complexity of the spectrum by reducing the number of components volatile at any one time.

In the degradation of styrene/acrylonitrile copolymers, fractionation into residue, chain fragments and volatiles was effected by cutting the tube at the appropriate points. Once separated, the fractions were then analysed by the various techniques available.

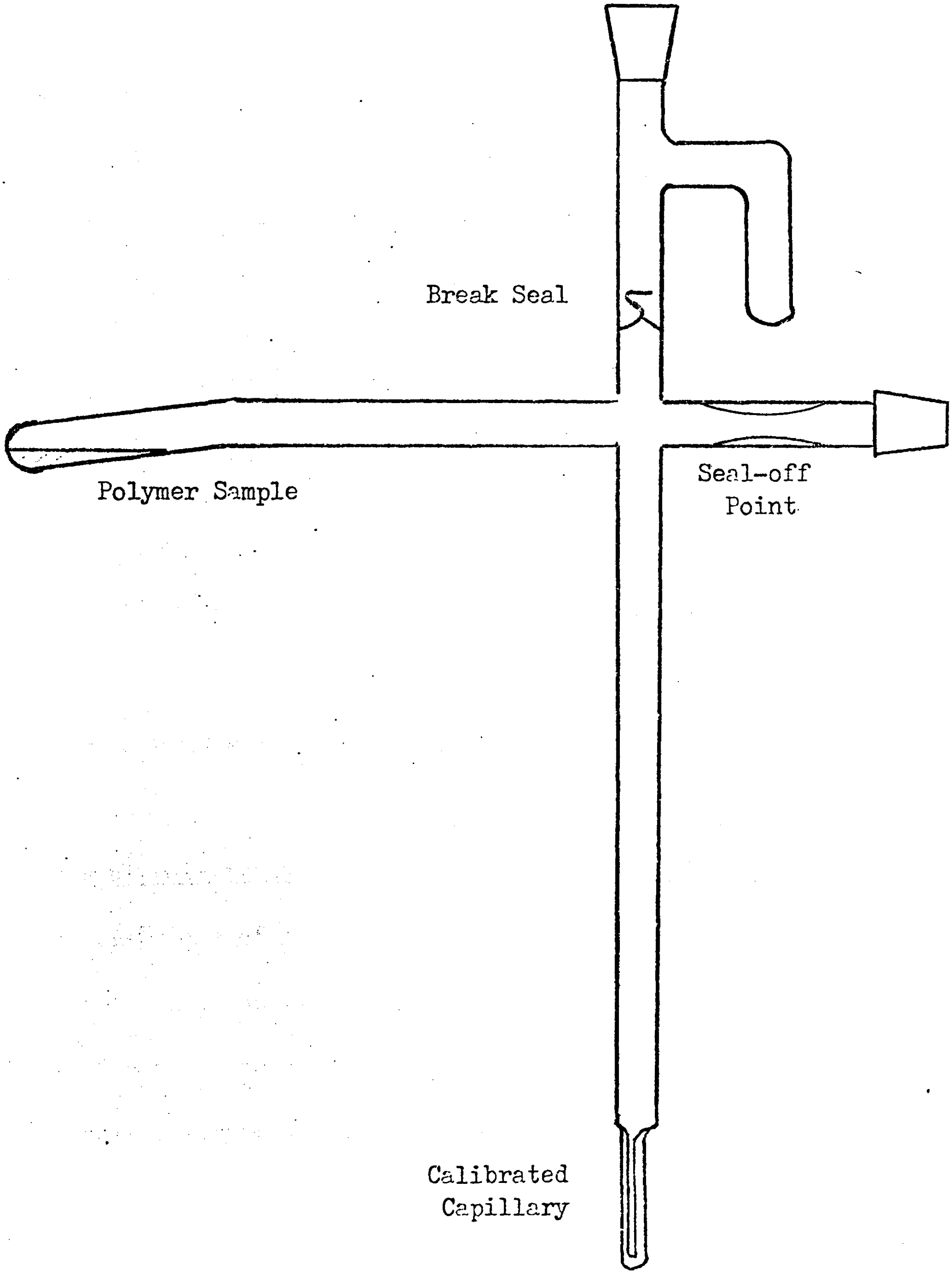


Fig. 2.8 The Sealed Tube

2.3 Thermal Methods of Analysis

(a) Introduction

Thermoanalytical techniques have been applied to the study of inorganic compounds for many years but it is only recently that such methods have been applied to studies of polymer degradation. The rapid advances in the application of these techniques are reflected by the increasing amount of literature on the subject.[65,66] The increasing importance of high temperature polymers, which are generally insoluble and therefore cannot be investigated by traditional techniques, such as solution properties, has largely contributed to the growth of thermoanalytical techniques as a convenient method of characterisation.[67] The techniques of DTA and TGA can equally well be applied to the study of conventional polymers to investigate further the properties of these materials.

(b) Thermal Volatilisation Analysis (TVA)

The technique of TVA has been described by McNeill.[68] The pressure which exists in a continuously pumped system between the hot decomposing sample and a cold trap is continuously monitored as the sample temperature is raised in a linear manner. The system has been further extended to incorporate differential condensation.[69] Four cold traps at temperatures of -100, -75, -45, and 0°C are mounted in parallel between the reaction vessel and the cold trap at -178°C. The system is shown in Fig. 2.9. The pressure in the vicinity of each cold trap is continuously monitored by a Pirani gauge (Edwards High Vacuum Ltd.). The output from the Pirani gauges is fed to a 12 channel recorder (Leeds and Northrup). A typical thermogram obtained from a styrene/acrylonitrile copolymer is shown in Fig. 2.10.

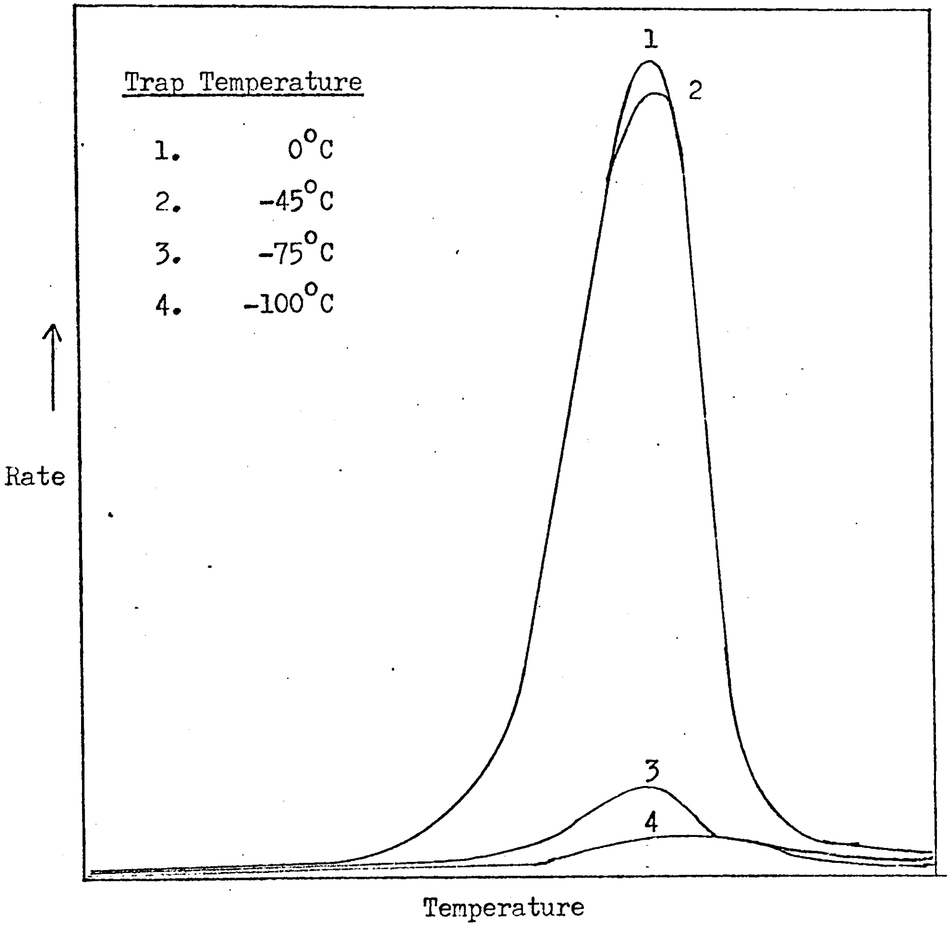


Fig. 2.10 Differential Condensation TVA of a 20/1 Styrene Acrylonitrile Copolymer

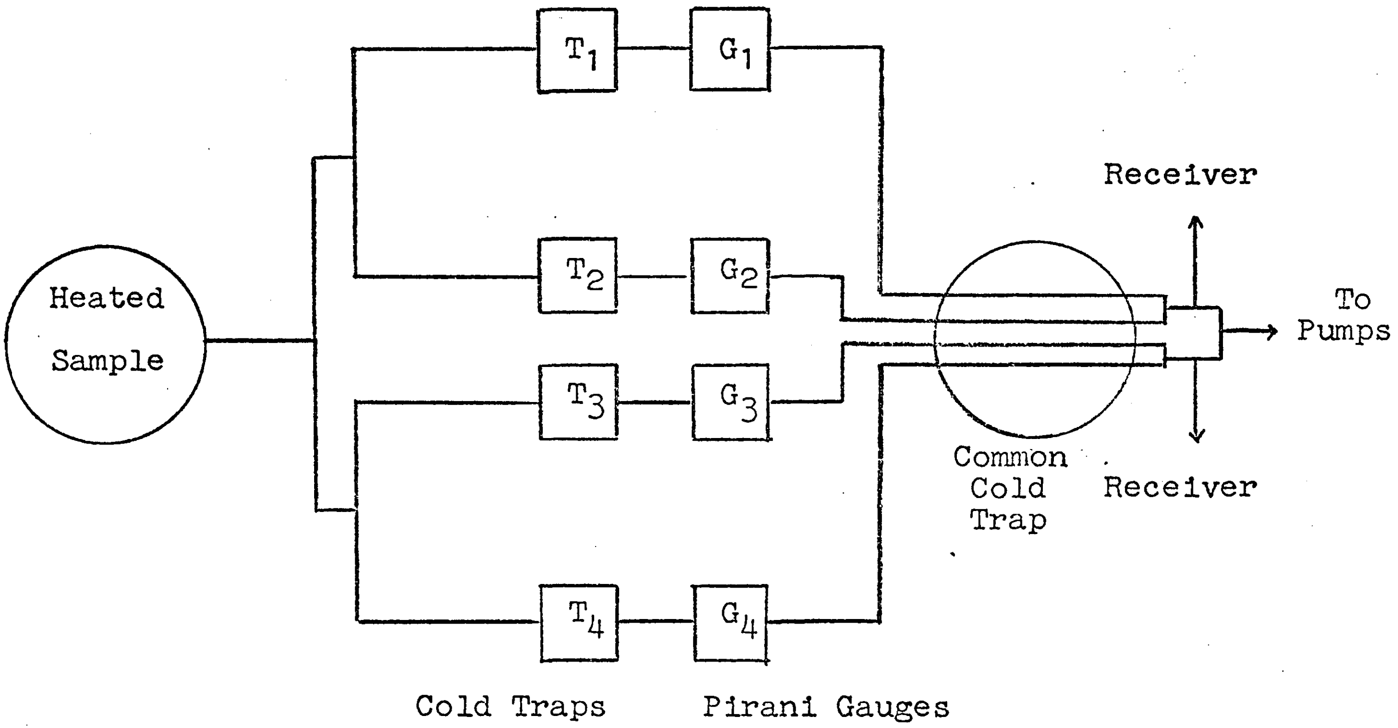


Fig. 2.9 Differential Condensation TVA

The thermogram provides information about the volatility of the products and is invaluable as a guide to the type of study appropriate at the various temperatures.

(c) Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the copolymers was carried out using a Du Pont 950 Thermogravimetric Analyser. This instrument operates on the null balance principle. The beam is maintained in the reference position by an optically activated servo loop. The balance can be operated up to 1200°C either isothermally or by programming at a heating rate of 0.5°C to 30°C per minute. Small samples are used which minimise heat transfer problems, and an accurate temperature sensing device allows high heating rates to be used. The sample can be accurately weighed on the balance.

The main disadvantage with this particular instrument is that it cannot be used under high vacuum conditions. This is generally desirable in polymer degradation where rapid removal of products from the viscous melt is considered important in preventing secondary reactions.

Samples were degraded in an atmosphere of very pure nitrogen (British Oxygen "White Spot") and it was possible to compare the degradation of a series of copolymers under carefully controlled conditions. Typical thermograms for temperature programmed and isothermal runs are shown in

Fig. 2.11 (a) and (b).

TGA has been extensively used to derive kinetic parameters but there is considerable disagreement about fundamental principles between the various workers in the field. Physical effects have been shown to influence the results considerably. The effects of aerodynamic drag and momentum transfer have been discussed by Friedman.[67] Since the balance could not be operated under high vacuum conditions and because of the complexity of the degradation, a complete kinetic analysis was not attempted. The copolymers were degraded in flowing nitrogen to find if such a method would yield some simple parameters for characterising the copolymers according to their acrylonitrile content.

2.4 Molecular Weight Measurement

(a) Introduction

The study of changes in molecular weight which occur during the degradation of many polymers and copolymers, must normally form an important part of any investigation. The osmotic pressure method, leading directly to number average molecular weights has been particularly valuable in degradation investigations. This technique has been extensively reviewed by Hookway.[70] Modern developments in osmometers have made it possible to measure molecular weights rapidly and with high precision. The speedy attainment of equilibrium greatly reduces the diffusion problem

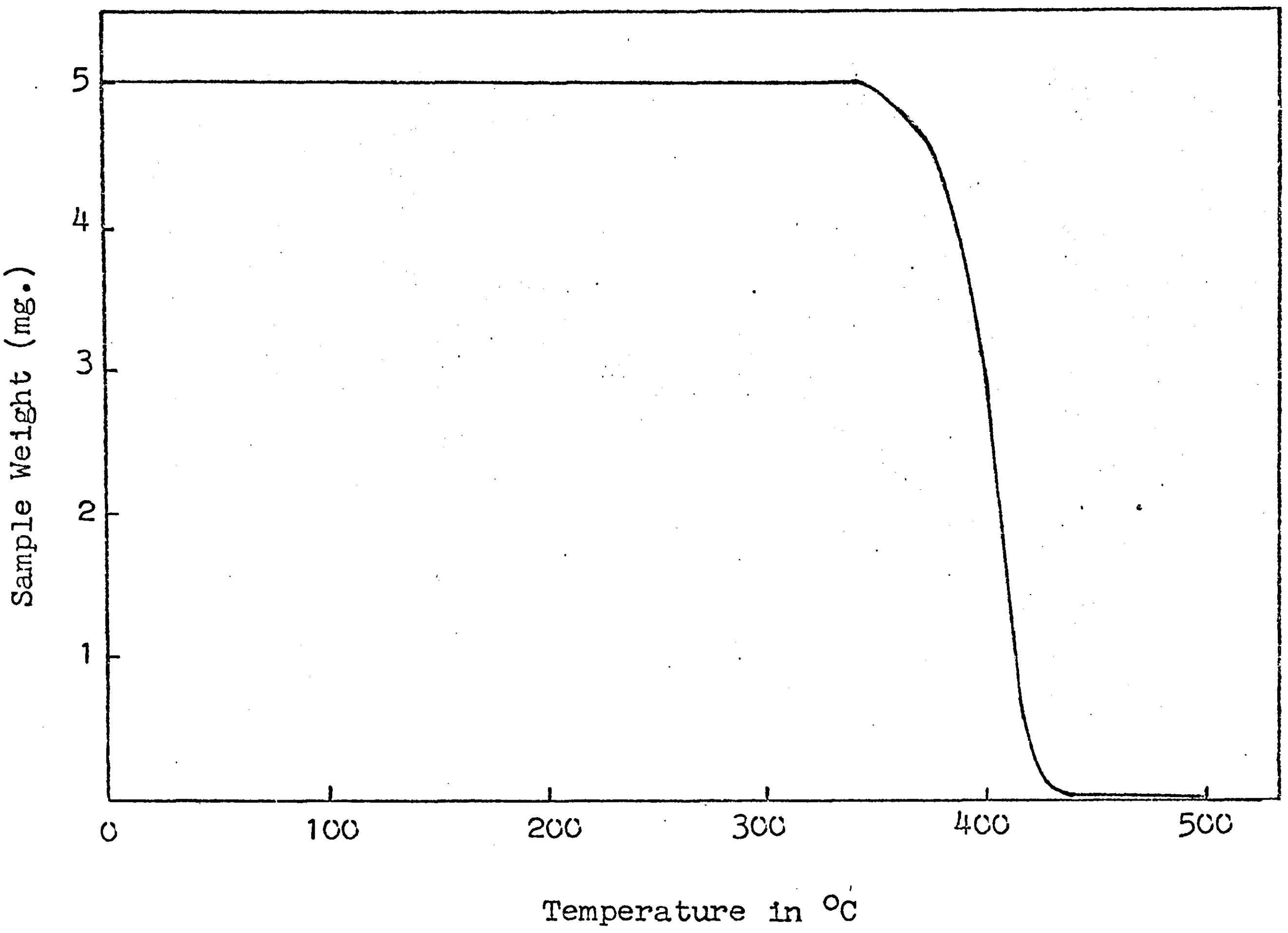


Fig. 2.11(a) Temperature Programmed TGA of Copolymer SA6

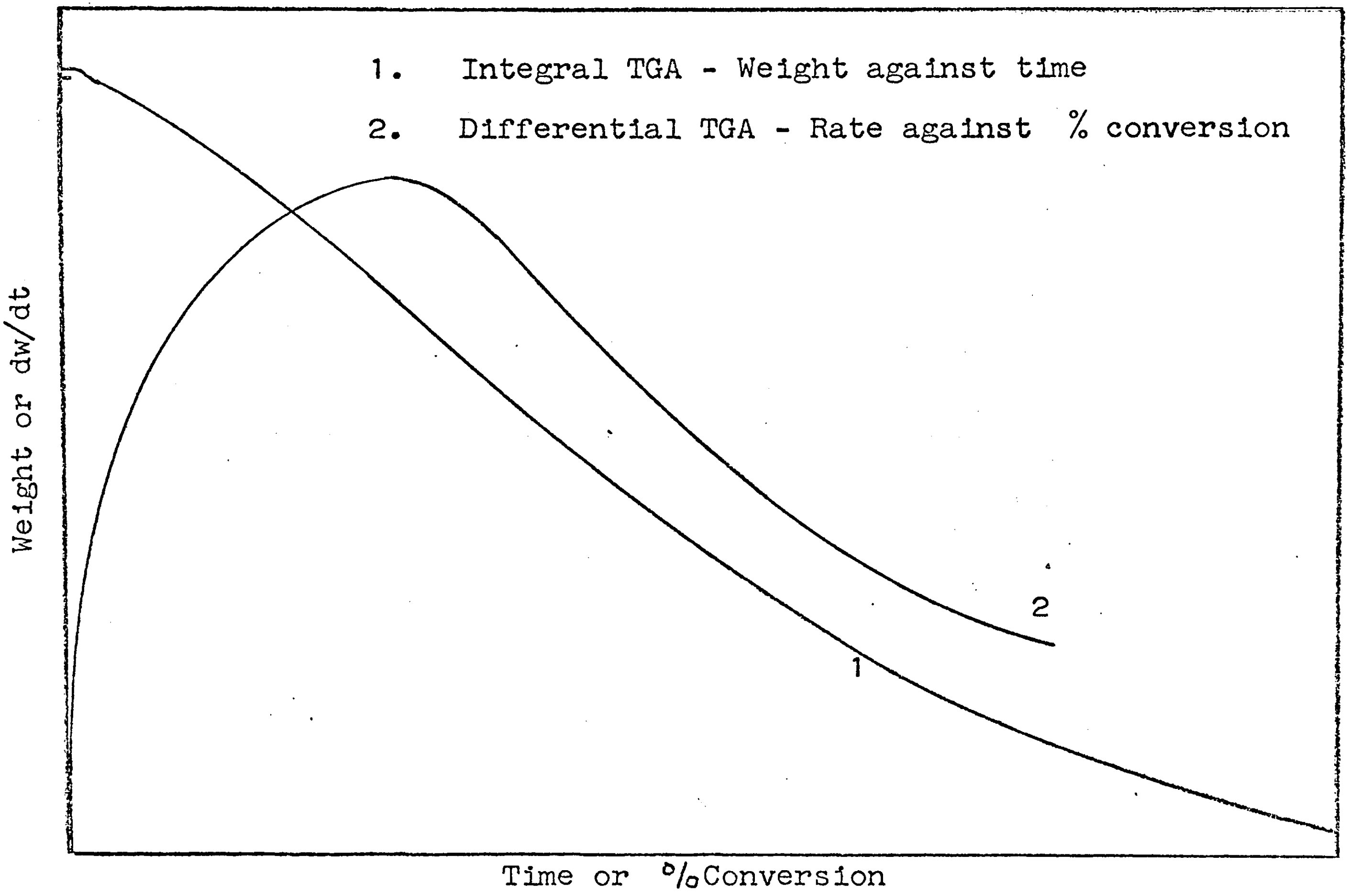


Fig. 2.11(b) Integral and Differential Isothermal Thermograms of SA6 at 340°C in Flowing Nitrogen

which could be troublesome in the older type of osmometer.

(b) The Mechrolab High Speed Osmometer

The Mechrolab 501 High Speed Osmometer was used in this work.[71] The instrument is shown in Fig. 2.12. Cellophan 300 membranes were used with toluene as solvent. The osmometer was thermostatted at 25°C. Solution concentrations of 0.5 to 1 gm. per 100 gm. of solution were used. Concentrations were determined by evaporating one ml. portions of the solution to constant weight in an air oven at 110°C (usually 4-6 hours). No further weight loss was obtained by heating in a vacuum oven at the same temperature. The small quantity of polymer required for molecular weight measurement by this method is an important consideration in dealing with degradation residues. Typical plots of osmometer data are shown in Fig. 2.13 (a) and (b), the molecular weight being calculated from $(\pi/c)_0$, which is the extrapolated value of (π/c) at zero concentration, using the equation $(\pi/c)_0 = RT/M$.

2.5 Product Analysis

(a) Introduction

On degradation, the majority of polymers give a complex mixture of products, any one of which may hold the key to the degradation mechanism. In the work under consideration, it was possible to separate the products by chromatography. Identification and estimation were then carried out by

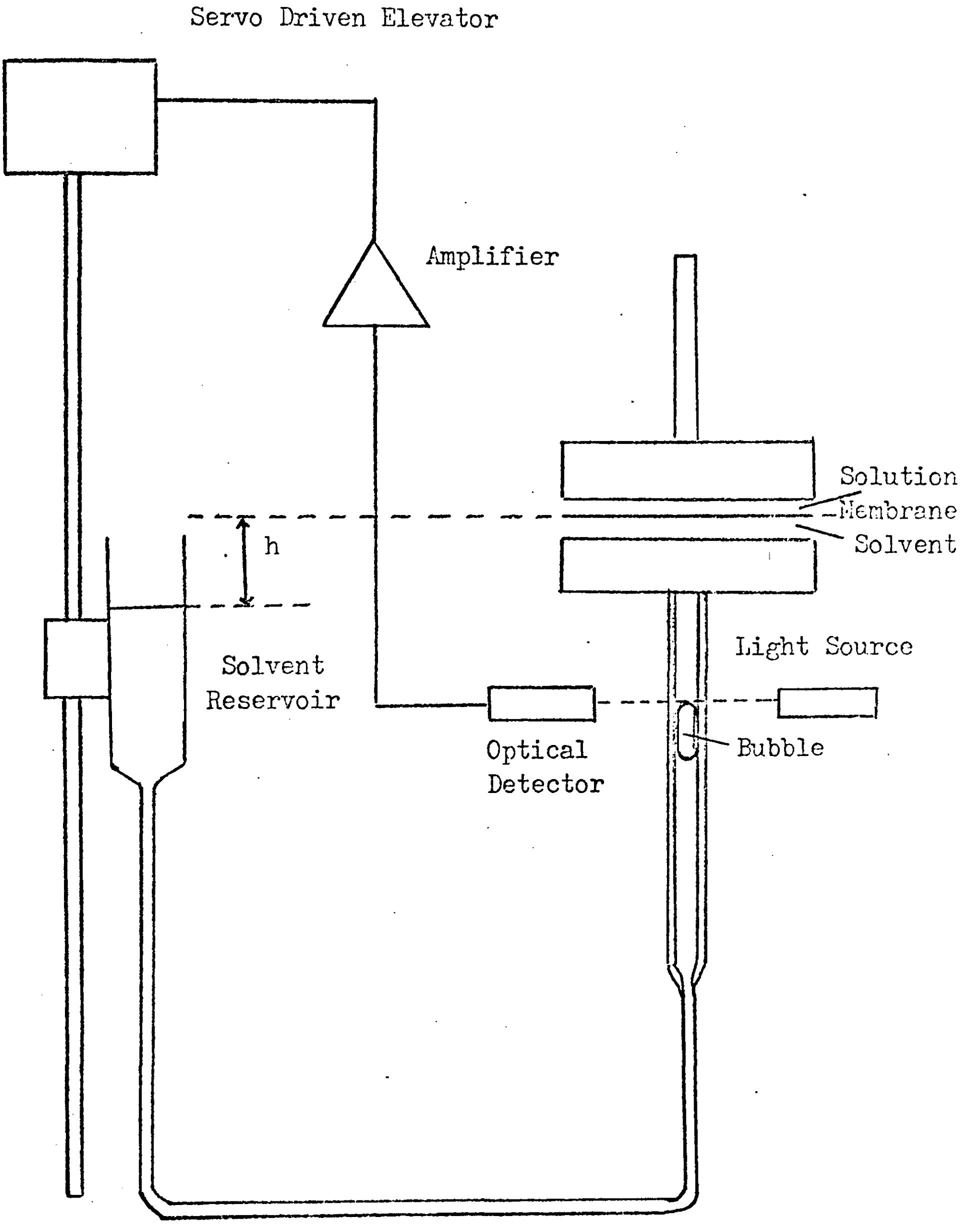


Fig. 2.12 The Mechrolab High Speed Membrane Osmometer - Schematic Representation

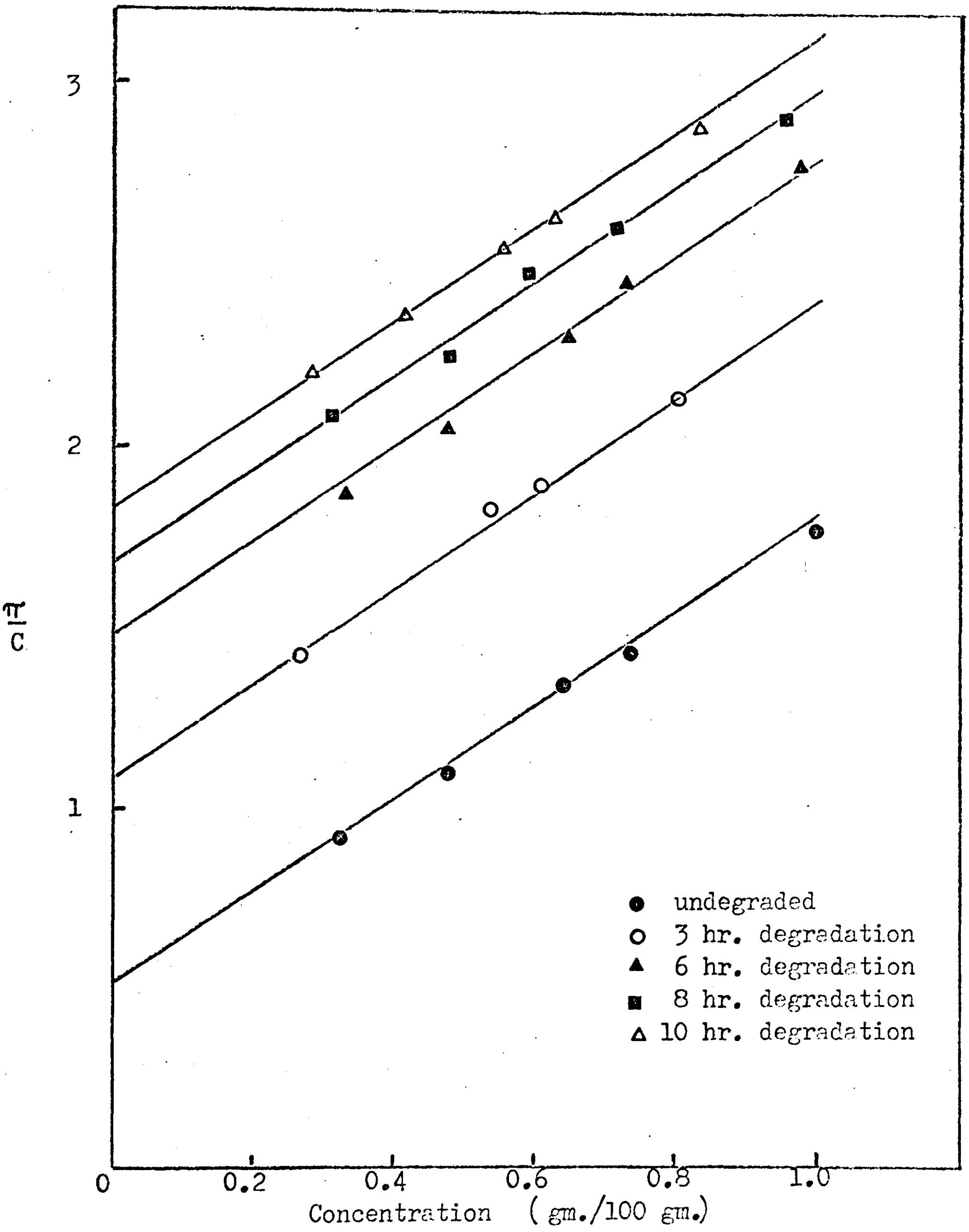


Fig. 2.13(a) Osmotic Pressure Plot for SA6 (Undegraded and Degraded for Various Times at 252°C)

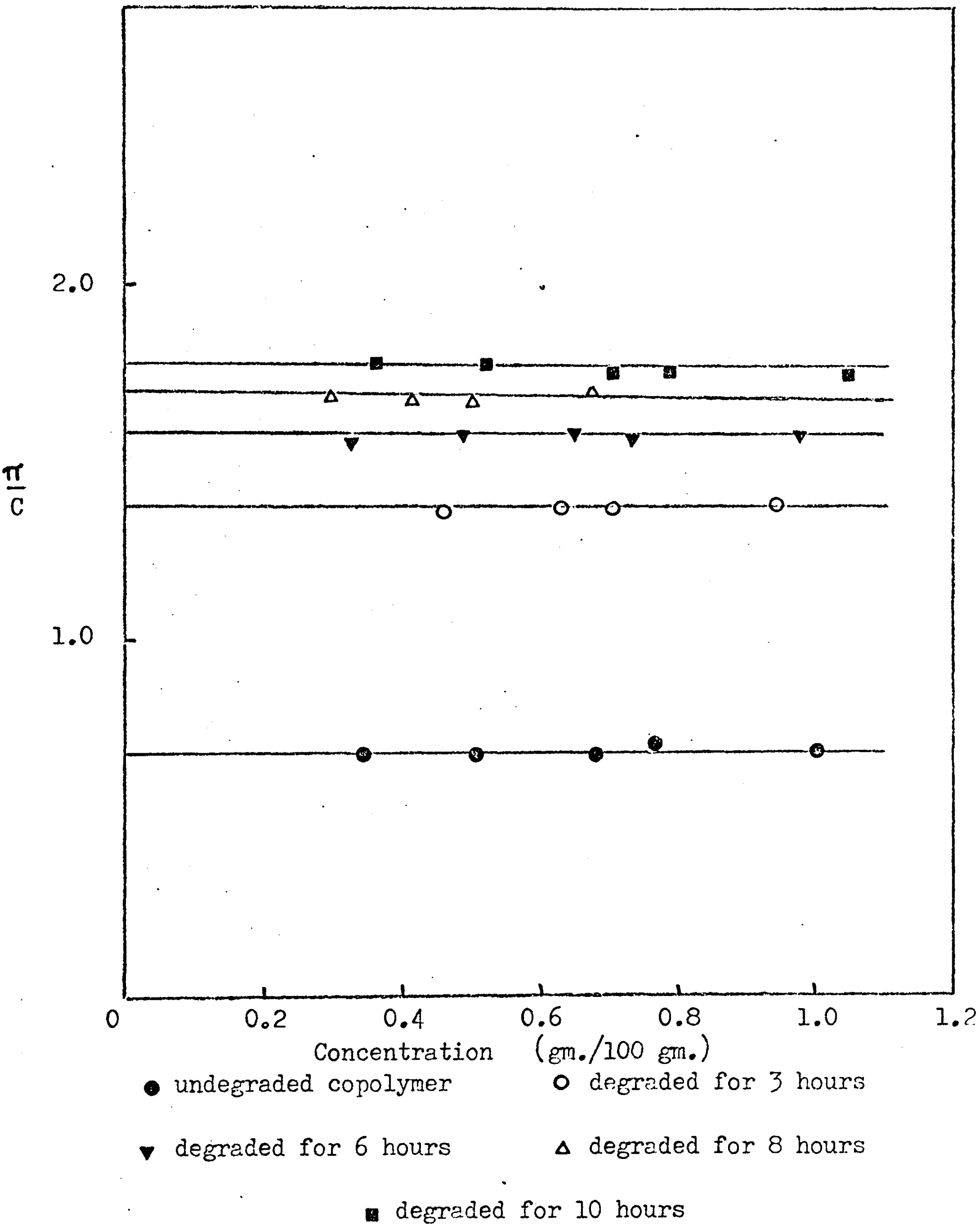


Fig. 2.13(b) Osmotic Pressure Plot for SA10 (Undegraded and Degraded for Various Times at 252°C)

a variety of spectroscopic techniques.

(b) Gas-Liquid Chromatography (GLC)

GLC analysis was carried out using a "Microtek 2000 R" gas chromatograph equipped with dual columns, flame ionisation detector and a linear temperature programmer.

One of the problems of separating products of polymer degradation by GLC is the range of boiling points and polarities of the components. It is not usually possible to find a column giving good separation over the wide range of components obtained. In the case of styrene/acrylonitrile copolymers, efficient fractionation in the sealed tube meant that the highly volatile products and the chain fragments could be examined separately without further fractionation. Two columns proved to be most useful.

1) 10 per cent dinonyl phthalate (DNP), a polar column, which gave good separation of the highly volatile fraction. (The limit of operation is 120°C).

2) 1 per cent SE30 (or commercial variation), a silicone gum column which could be used up to 300°C and was suitable for chain fragment separation.

Once these columns had been shown to give effective separation, they were used in the later gas chromatograph - mass spectrometer analysis.

Attempts to measure the styrene/acrylonitrile ratio in the volatile products by GLC analysis were abandoned in favour of a more convenient and accurate infra-red technique. The high styrene/acrylonitrile ratio, coupled with the unfavourable response of the flame ionisation detector to acrylonitrile, made the technique inaccurate. A 1/1 molar mixture of styrene and acrylonitrile gave a peak area ratio of 4/1.

(c) The Combined Gas Chromatograph - Mass Spectrometer

Until very recently, the standard method of analysing complex organic mixtures has been to separate the components by chromatography, to collect each product and analyse it by the normal techniques of IR and NMR to supplement the retention time data from the gas chromatograph. The small samples which could be used for degradation very often meant that products from several runs had to be combined to give enough of a single component for analysis. The combination of gas chromatography with mass spectrometry has eliminated much of the tedious separation and collection of the components.

The instrument used was an LKB 9000 (LKB-Produkter, Stockholm) and a block diagram is shown in Fig. 2.14. The chromatographic system consists of a heated inlet and a coiled glass column in an oven which can be operated isothermally or temperature programmed from 1°C to 15°C per minute up to a temperature of 300°C.

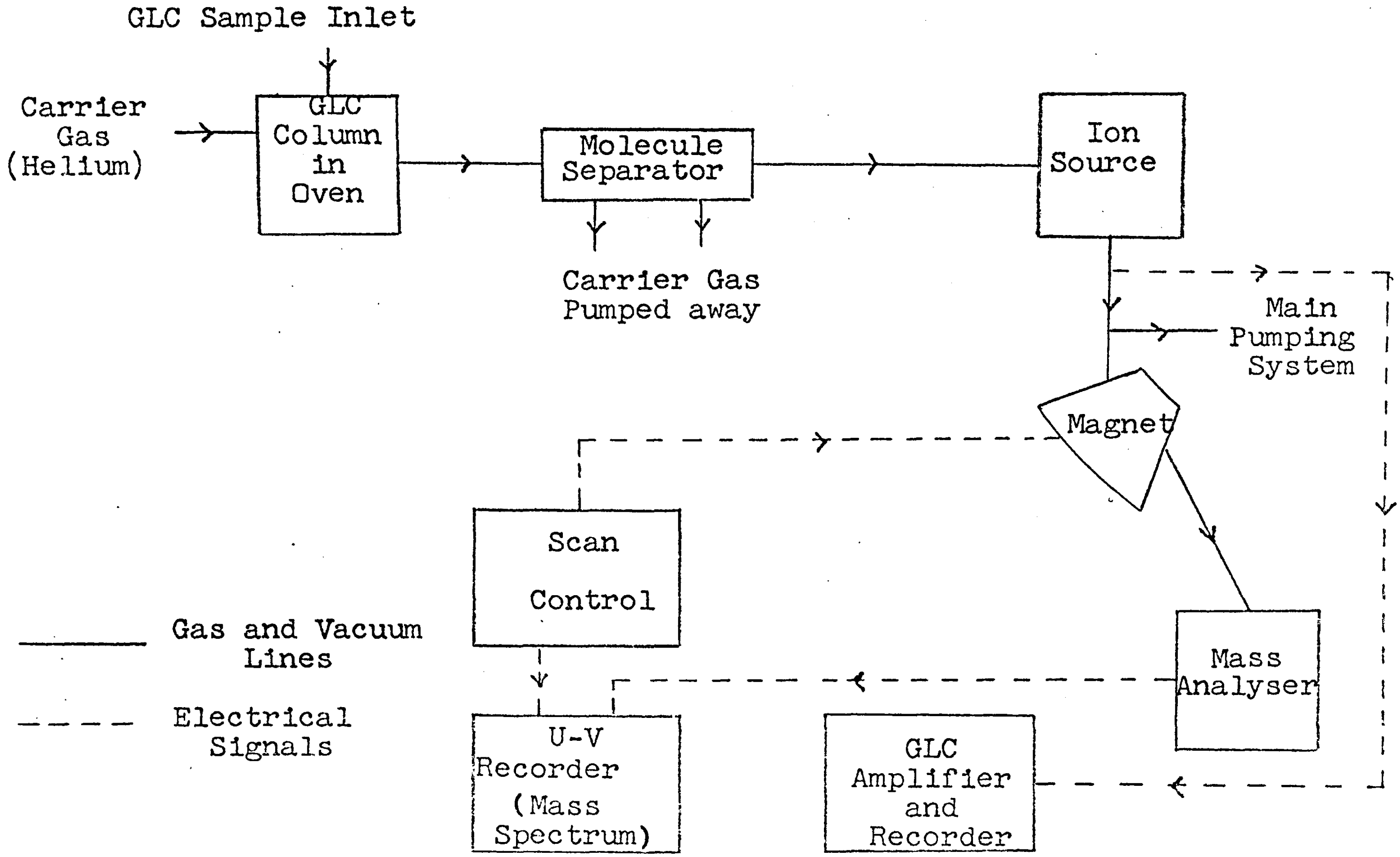


Fig. 2.14 LKB 9000 Gas Chromatograph - Mass Spectrometer

Block Diagram of Main Components

The principal feature of incompatibility between a gas chromatograph and a mass spectrometer is that whereas the former operates at atmospheric pressure or above, the latter requires a pressure of 10^{-6} torr. Some method has to be devised whereby the carrier gas is removed and the sample allowed to pass into the ionisation chamber of the spectrometer. In this instrument, a Becker-Ryhage jet separator (Fig. 2.15) is used. The helium is pumped away in two stages by a rotary pump and an oil diffusion pump, while 50-75 per cent of the sample passes into the mass spectrometer.

At all times other than when the mass spectrum is being scanned, the instrument operates with an electron beam energy of 20 eV. This is below the ionisation potential of helium (24.8 eV) but high enough to ionise any organic matter coming off the column. The total ion current is measured by an electrometer in the ion source and this is fed through an amplifier to the GLC recorder. A typical chromatogram is shown in Fig. 2.16.

The mass spectrometer is a single focusing instrument with a fast scanning speed (48-1000 in 3.6 sec. $M/\Delta M \simeq 1000$) and the sample required is less than 0.1 μg. from a packed column. When a component is observed on the GLC recorder, pressing the scan button automatically increases the ionisation voltage to 70 eV, and a mass spectrum over the desired range is obtained from the fast U-V recorder.

Provided that suitable columns are available to separate the

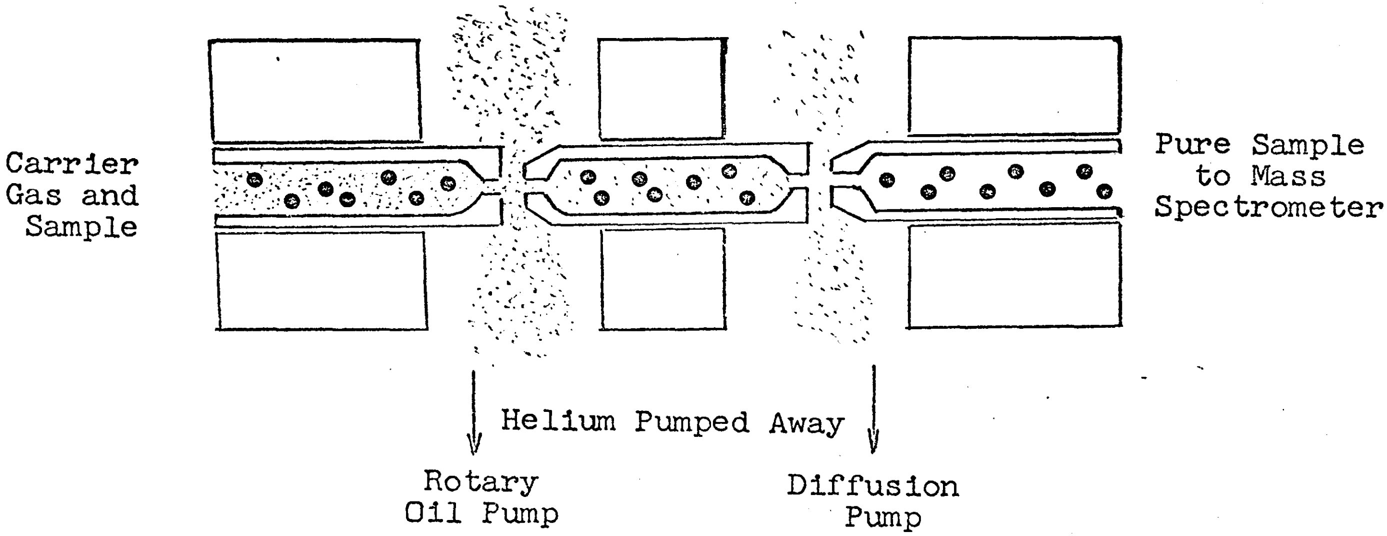


Fig. 2.15 Becker-Ryhage Jet Separators in LKB 9000 GC-MS

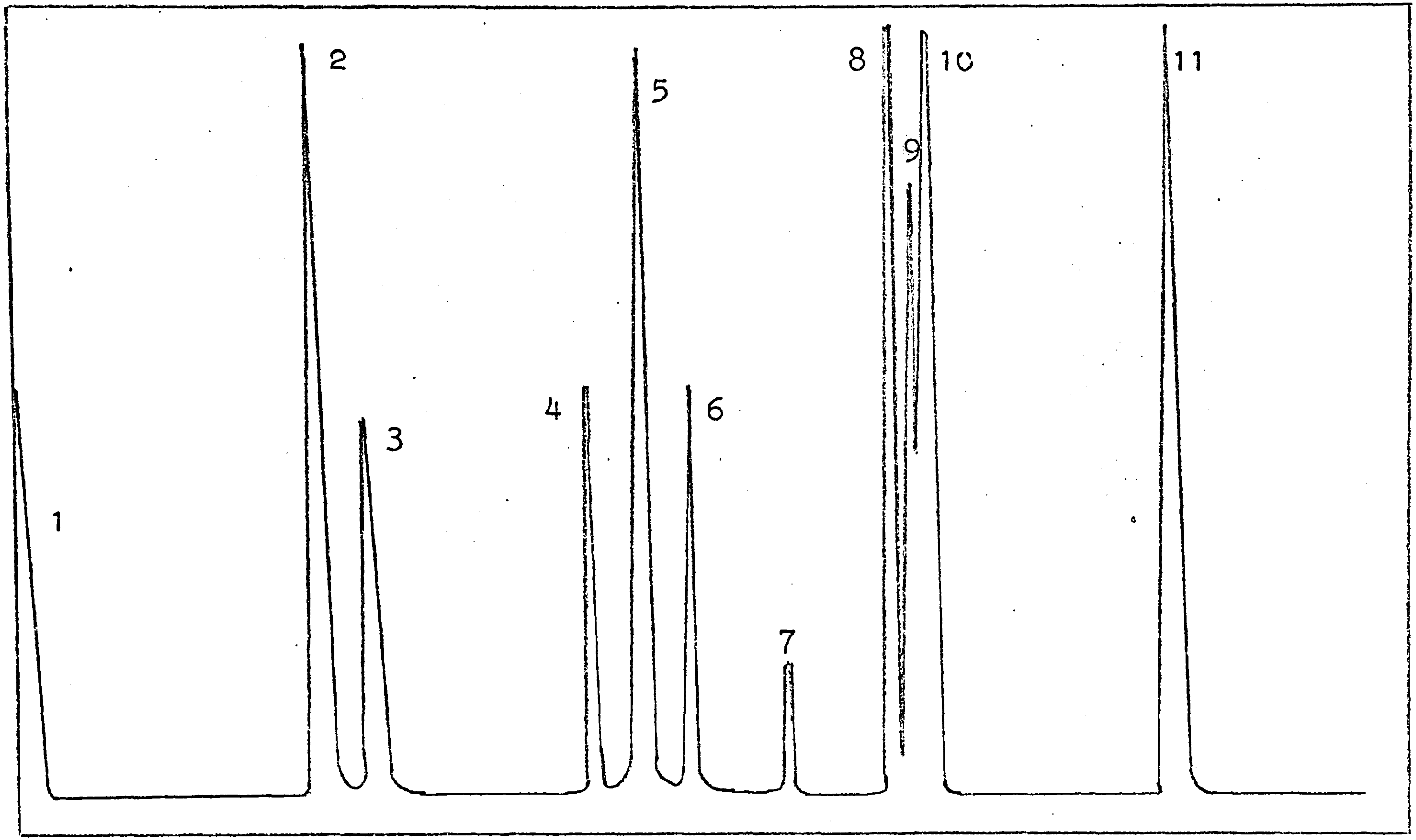


Fig. 2.16 GC-MS Chromatogram of Chain Fragments from a 3/1 Styrene/Acrylonitrile Copolymer (1% SE30. 10ft., 60 250°C at 5°C/min.)

degradation products, this instrument has great potential in polymer degradation. Previous techniques of feeding a complex mixture into the mass spectrometer gave a spectrum which in many cases defied analysis. With the LKB, the spectrum obtained for a single component can very often lead to positive identification of the component. This can be confirmed by other spectroscopic techniques if necessary.

Problems can arise in this technique if the components under investigation come off the column very close together. In the normal chromatographic detector the material leaving the column is either consumed in the flame, or swept rapidly through the small volume of the katherometer. With the GC - MS, the chromatographic detector is inside the analyser tube of the mass spectrometer, and the rate of removal of each component depends on the efficiency of the spectrometer's pumping system. In the case of the chain fragments, a single peak is often obtained for the various molecular weight groups instead of a resolved chromatogram as in Fig. 2.16. Sharp peaks can also result in anomalous m/e intensities as the pressure of the component in the analyser is changing rapidly while the spectrum is being recorded.

(d) Direct Pyrolysis inside the Mass Spectrometer

The pyrolysis of polymers in the ion source of a mass spectrometer has been used by Hummel[72] as a method of polymer characterisation. To avoid the normally complex spectra obtained from mixtures of products, a field ionisation source was used. With this type of source, fragmentation of the parent ion is small and almost every peak in the spectrum is due to a primary ion. The minimum information one obtains is the molecular weight of the components.

In dealing with a copolymer system producing a variety of chain fragments, this technique offers an extension of the previous work. In the absence of a field ionisation source, an ionisation of 20 eV is used with the electron bombardment source. This reduces the cracking pattern and simplifies the spectrum.

Preliminary runs were carried out on the MS12 Mass Spectrometer (A.E.I.). This instrument has a solid sample probe which can be heated to 350°C. A sample of approximately 0.1 mg. of the copolymer was inserted into the probe, and the temperature gradually raised. The appearance of a peak at $m/e = 91$ at approximately 290°C indicated that degradation was taking place. However, even at 340°C, it was impossible to identify any products other than styrene. Unlike flash pyrolysis the sample was degrading slowly at the temperatures used and this combined with the small sample size meant that pressure of any component in the analyser tube was too small to obtain a spectrum. Increasing the sensitivity by raising the ionisation voltage to 70 eV did not improve the situation. No attempt was made to develop this technique due to the limited availability of the mass spectrometer. The method is potentially useful if the surface area of the probe can be increased to handle a larger sample. Linear programmed heating of the probe to 500°C would also be an advantage.

(e) Quantitative Infra-Red Analysis

Because of the inaccuracy of the GLC analysis for acrylonitrile in the volatiles, other methods were sought. The linearity of the optical density of the nitrile peak at 2230 cm^{-1} with increasing nitrile concentration appeared to be potentially useful. Standard styrene/acrylonitrile mixtures were prepared and run on a Unicam SP100 double beam infra-red spectrometer. A microcell (0.1 mm. path length, volume approximately 10 μl., R.I.I.C. Ltd.) was used because of the small amount of volatiles which would be available from the degradation experiments. A plot of optical density against the molar percentage of acrylonitrile in the mixture is shown in Fig. 2.17, from which it is clear that the molar percentage of acrylonitrile in an unknown mixture can readily be found from the optical density of the nitrile peak. Although the method suffers certain inaccuracies inherent in the spectrometer, it was found to be much superior to chromatography. From styrene/toluene standards it was also possible to estimate the toluene concentration in the volatiles. Benzene was present in the degradation products in amounts less than 1 per cent.

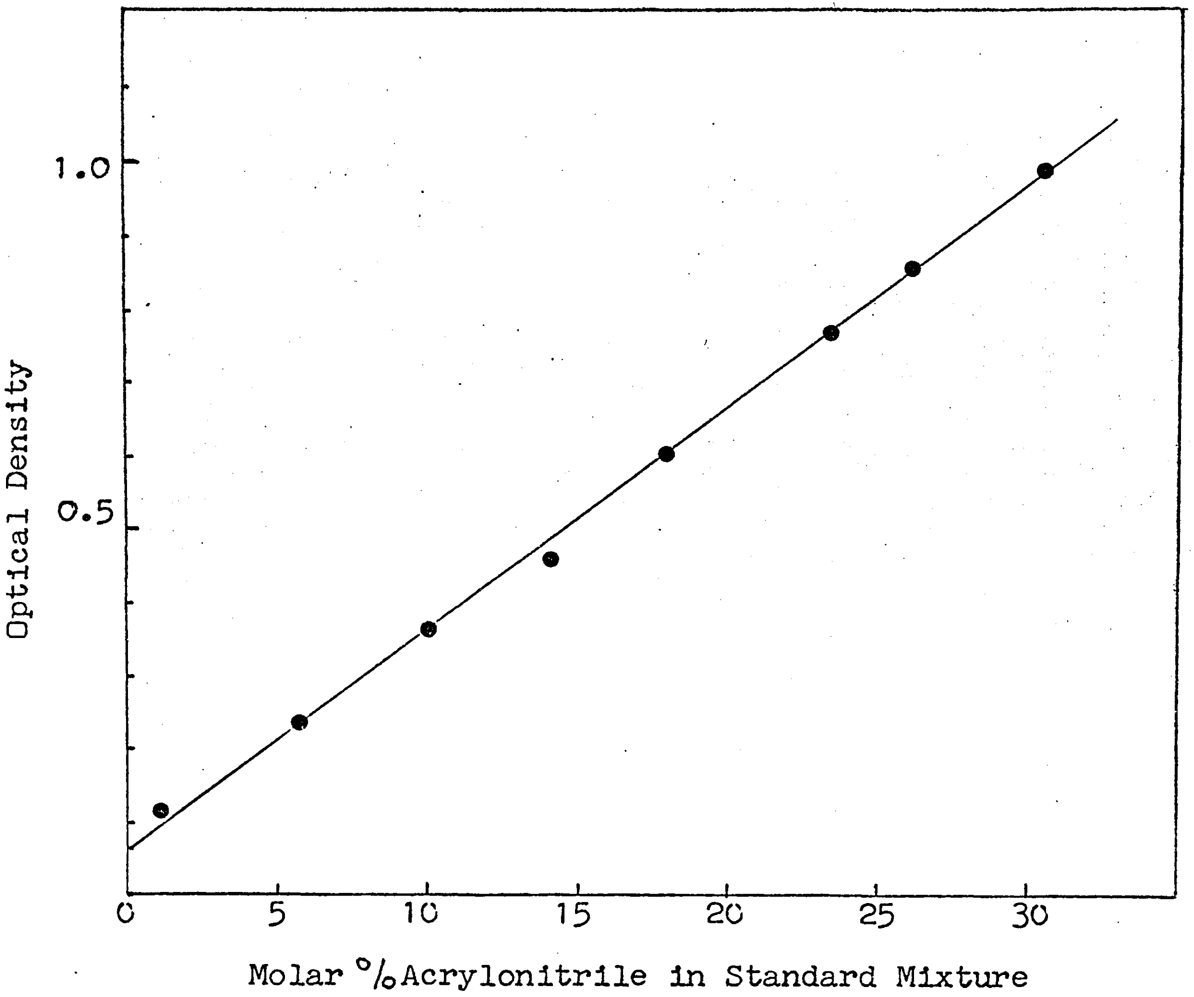


Fig. 2.17 Calibration Graph for Infra-Red Analysis of the Acrylonitrile Concentration in the Volatiles

200 mg. samples of the copolymers were degraded at 330 ± 2°C for 5 hours in sealed tubes described in section 2.2(c). The volatile products were distilled into capillary tubes and analysed immediately.

(f) Miscellaneous Spectroscopic Analysis

(1) U-V Analysis of the Residue

U-V analysis was carried out in Analar chloroform on a Unicam SP 800 U-V spectrophotometer. 2 mm. quartz cells were used with a solution concentration of approximately one mg./ml.

(2) Infra-Red Analysis of Copolymers and Residue

IR spectra were obtained using Perkin-Elmer 225 and 257 spectrometers. The residue was run as a film deposited on a sodium chloride disc from chloroform solution. Chloroform was removed by evaporation, initially at room temperature and finally in a vacuum oven at 50°C.

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CHAPTER 3

MOLECULAR WEIGHT CHANGES AND THE PRODUCTION OF VOLATILES IN STYRENE/ ACRYLONITRILE COPOLYMERS

3.1 Introduction

Much of the information reported by Grassie and others concerning the thermal degradation of polystyrene has been obtained by a study of changes in molecular weight and the rate of production of volatiles as the reaction proceeds.[54] Similar investigations should therefore prove useful in the initial examination of styrene/acrylonitrile copolymers. The effects of small quantities of acrylonitrile on the molecular weight changes and production of volatiles from polystyrene was considered to be a useful starting point in a systematic study.

3.2 Preliminary Investigations of Low Acrylonitrile Copolymers

(a) Introduction

The two copolymers containing 0.25 per cent and 1 per cent acrylonitrile along with a polystyrene "standard" were synthesised under identical conditions, as described in Chapter 2. Details are given in Table 3.1.

Table 3.1 Copolymer Data

Code	% Acrylonitrile	Molecular Weight
PS3	0	470,000
SA4	0.25	347,000
SA2	1.0	370,000

To establish suitable temperatures for degradation the copolymers were examined in the early form of the TVA apparatus.[68] A typical thermogram is shown in Fig. 3.1.

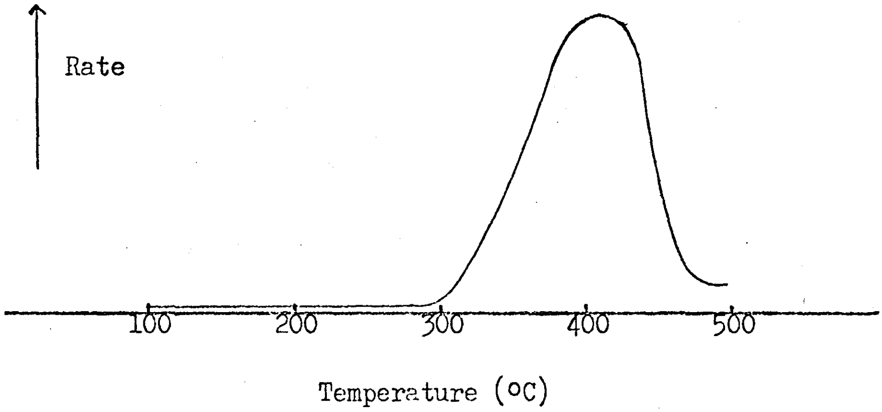


Fig. 3.1 TVA Thermogram of Copolymer SA2

The absence of a peak at low temperatures demonstrated that no significant quantities of occluded volatiles such as solvent or precipitant used in the copolymer preparation were present. This was confirmed by heating the copolymer at 200°C in the degradation tray of the molecular still. Weight loss for all polymers was less than 0.5 per cent and no correction was necessary during the molecular still degradations. Volatilisation was seen to commence at 300°C, rising to a maximum at 390-410°C. From this evidence it was decided that a temperature of approximately 290°C was suitable for studying the relationships between molecular weight changes and volatilisation. Where a more rapid degradation was desirable for the collection and analysis of products, 330°C was chosen as the degradation temperature. The 290-330°C region is also particularly useful as much of the data on polystyrene degradation has been collected around these temperatures.

(b) Molecular Still Degradations at 292°C

100 mg. samples of the powdered copolymers were degraded under standard conditions as described in Chapter 2. The weight of material lost by volatilisation was obtained by weighing the copper tray before and after degradation. The residue was dissolved in toluene for molecular weight measurement. Results are presented in Table 3.2 and illustrated in Fig. 3.2, 3.3, and 3.4.

The plot of percentage volatilisation against degradation time, Fig. 3.2, shows that the addition of small quantities of acrylonitrile does not increase the rate of production of volatiles. No drastic drop in molecular weight occurs as a result of addition of one unit of acrylonitrile to 100 styrene units. The molecular weight of all three copolymers falls to a common value.

In Fig. 3.4, the molecular weight change occurring during volatilisation is independent of the composition of the copolymer, within the limits of

Table 3.2

Degradations of Copolymers of Low Acrylonitrile Content at 292°C

Copolymer Identification	Degradation Time (hours)	% Volatilisation	Mn x 10^{-5}	Mn as % of Original
PS3	0	0	4.70	100
	1	2.15	1.495	31.8
	3	3.27	1.22	26
	4	4.5	1.02	21.8
	6	7.64	0.865	18.5
	10	13.8	0.567	12.1
	12	15.3	0.617	13.2
SA4	0	0	3.47	100
	1	1.92	1.49	43.2
	3	4.17	1.09	31.4
	4	4.7	0.95	27.4
	6	8.0	0.70	20.2
	10	13.9	0.552	15.9
	12	18.1	0.520	15.0
	16	20.2	0.426	8.2
SA2	0	0	3.70	100
	1	1.85	1.39	37.6
	3	3.77	0.88	23.8
	4	5.68	0.88	23.8
	6	6.7	0.76	20.5
	10	11.8	0.607	16.3
	12	18.9	0.51	13.8
	16	20.3	0.40	9.30

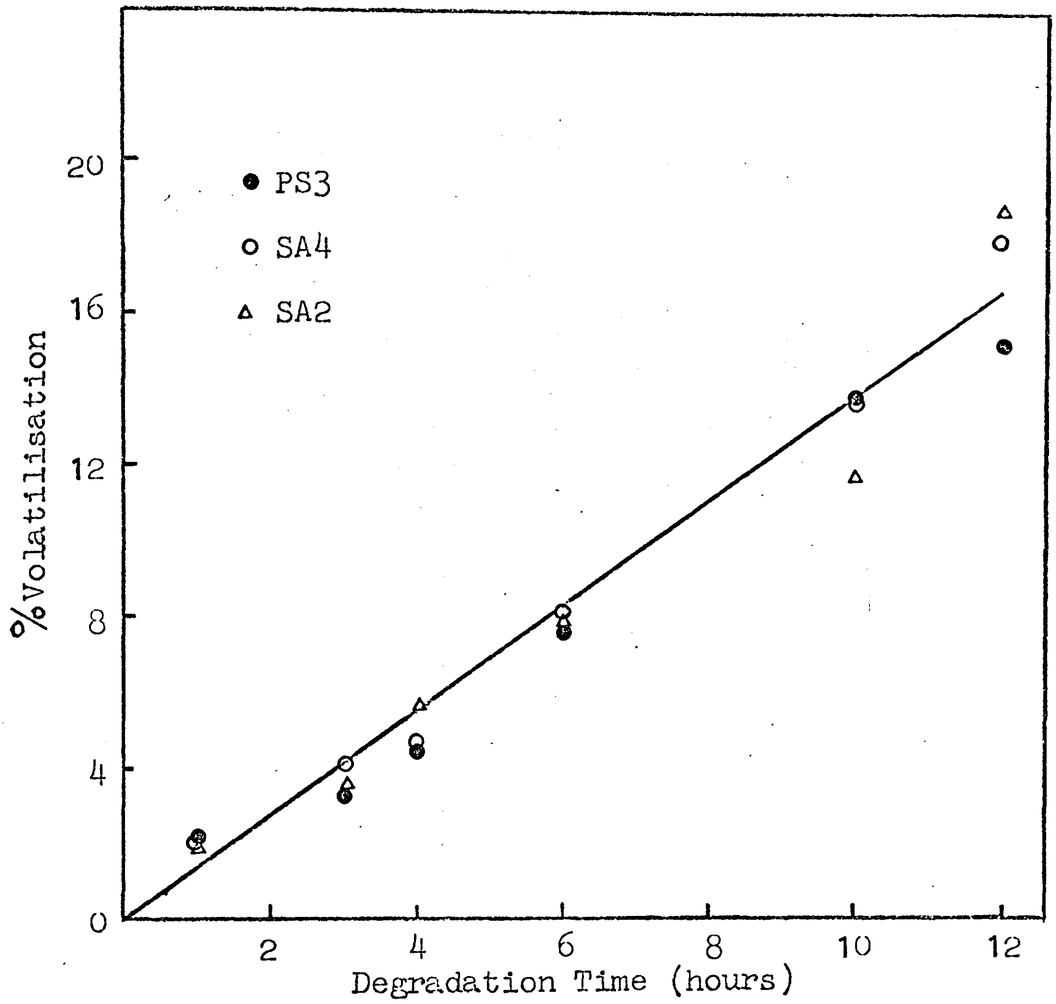


Fig. 3.2 % Volatilisation at 292°C of Copolymers of low Acrylonitrile Concentration as a Function of Time of Degradation

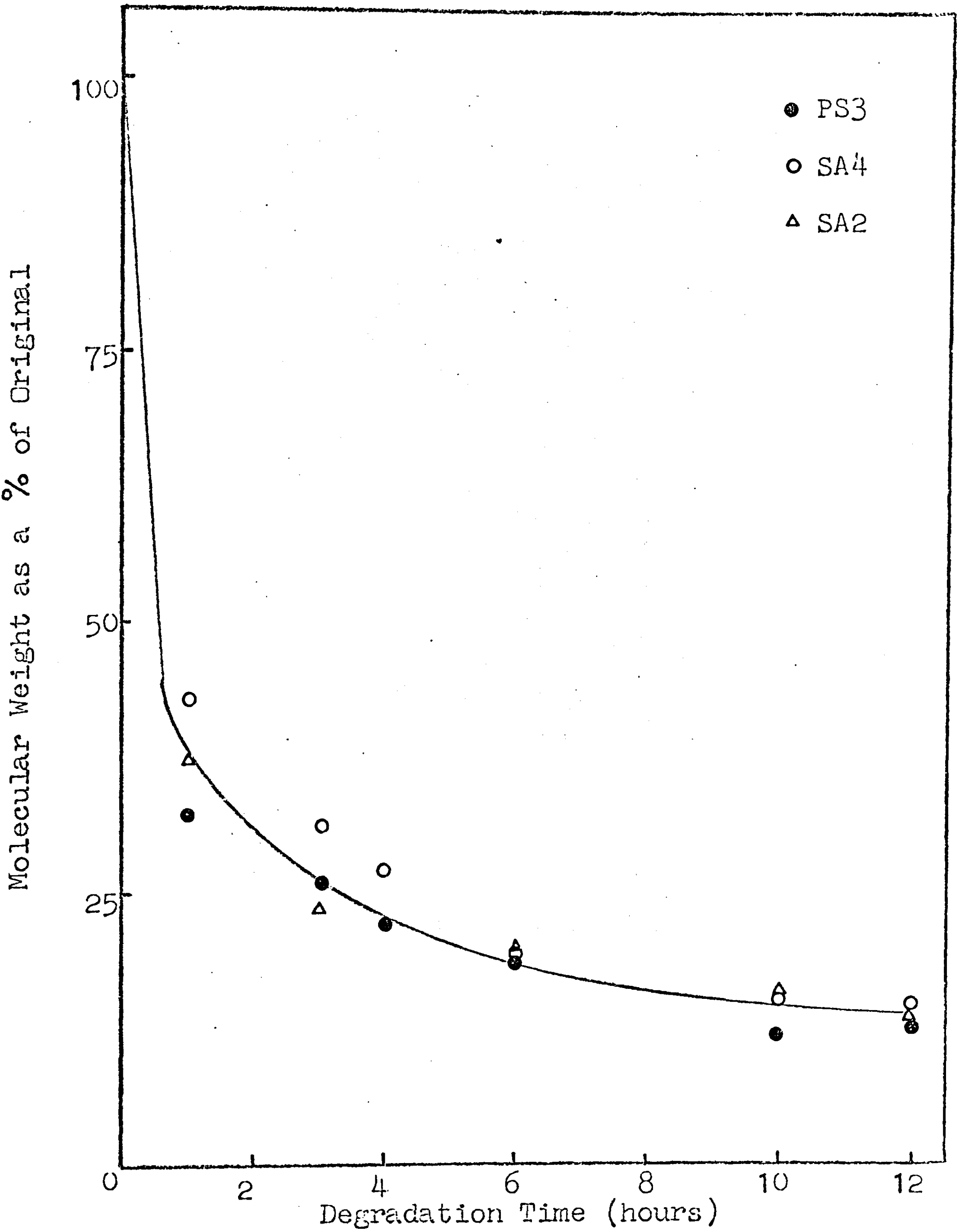


Fig. 3.3 Changes in Molecular Weight with Time of Degradation at 292oC

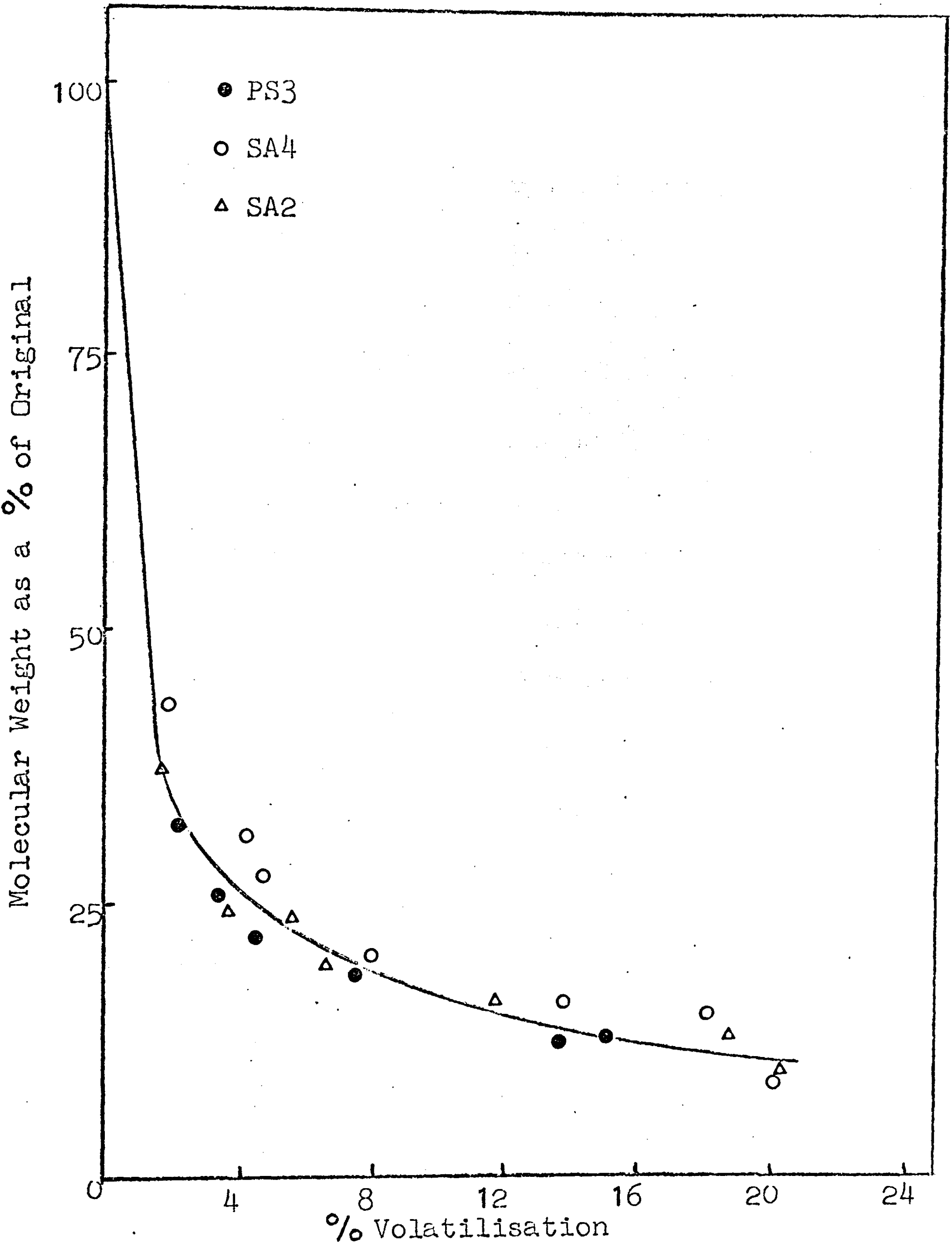


Fig. 3.4 Changes in Molecular Weight with Volatilisation at 292°C

experimental error. This implies that a constant amount of volatile material is produced per chain scission.

It would seem therefore that the addition of small quantities (up to 1 per cent) of acrylonitrile has little or no effect on the thermal degradation characteristics of the copolymer. The investigation was therefore extended to copolymers of higher acrylonitrile content.

3.3 Degradation of Copolymers Containing up to 50 per cent Acrylonitrile

(a) Production of Volatiles

Copolymers containing a higher percentage of acrylonitrile were prepared by the methods described in Chapter 2. The initiator concentration was regulated to give comparable molecular weights. Details of the copolymers are shown in Table 3.3.

Table 3.3 Copolymer Data

Code	% Acrylonitrile	Molecular Weight
SA8	4.7	331,000
SA3	8.4	411,000
SA6	15.5	470,000
SA5	24.9	650,000
SA10	33.4	366,000
SA9	50	unknown

TVA thermograms were run as before, and the degradation patterns were the same as for the series of polymers with a low concentration of acrylonitrile. A similar degradation programme was carried out at 292°C and the results are shown in Table 3.4. The rate of volatilisation and molecular weight drop in SA10 were such that reproducibility was poor. It was therefore not included in the series. SA9 (50 per cent acrylonitrile) showed marked similarity to polyacrylonitrile including insolubility in toluene, the most suitable solvent for molecular weight measurement. For reasons of experimental convenience it too was excluded from this series but both SA9 and SA10 were used in other aspects of the investigation.

A plot of percentage volatilisation against time is shown in Fig. 3.5. The slopes of the lines give the rates of production of volatiles. When these are plotted against the acrylonitrile content of the copolymer as in Fig. 3.6, a linear relationship is observed, indicating that the increase in the rate of volatilisation over that of polystyrene is proportional to the acrylonitrile content of the copolymer.

The molecular weight data in Table 3.4 and also that for polystyrene (Table 3.2) is shown in Fig. 3.7 and 3.8. From the plot of molecular weight against time (Fig. 3.7) it would appear that acrylonitrile units are causing an increased rate of chain scission in the copolymer. After one hour the molecular weight of copolymer SA5 (24.9 per cent acrylonitrile)

Table 3.4

% Volatilisation and Molecular Weight Changes for a Series of Styrene/ Acrylonitrile Copolymers at 292°C

Copolymer Identification	Degradation Time (hours)	% Volatilisation	Residue Mn × 10^{-5}	Mn as % of Original
SA8	0	0	3.31	100
	2	3.9	0.92	27.8
	4	7.45	0.64	19.3
	6	10.1	0.52	15.7
	8	16.2	0.38	11.5
SA3	0	0	4.11	100
	1	3.14	1.02	24.8
	3	7.13	0.53	12.9
	4	11.22	0.51	12.4
	6	16.7	0.38	9.25
	10.25	29.0	0.327	7.95
SA6	0	0	4.70	100
	1	6.6	0.924	19.7
	2	8.25	0.445	9.45
	3	13.9	0.362	7.70
	4	17.0	0.298	6.35
	6	24.5	0.247	5.25
	7	34.7	0.196	4.20
	9.5	45.0	0.170	3.62
	12	53.0	0.180	3.84
SA5	0	0	6.50	100
	1	7.37	0.645	9.85
	3	20.3	0.330	5.09
	4	25.8	0.330	5.09
	6	43.2	0.215	3.3
	10	69.4	0.160	2.5

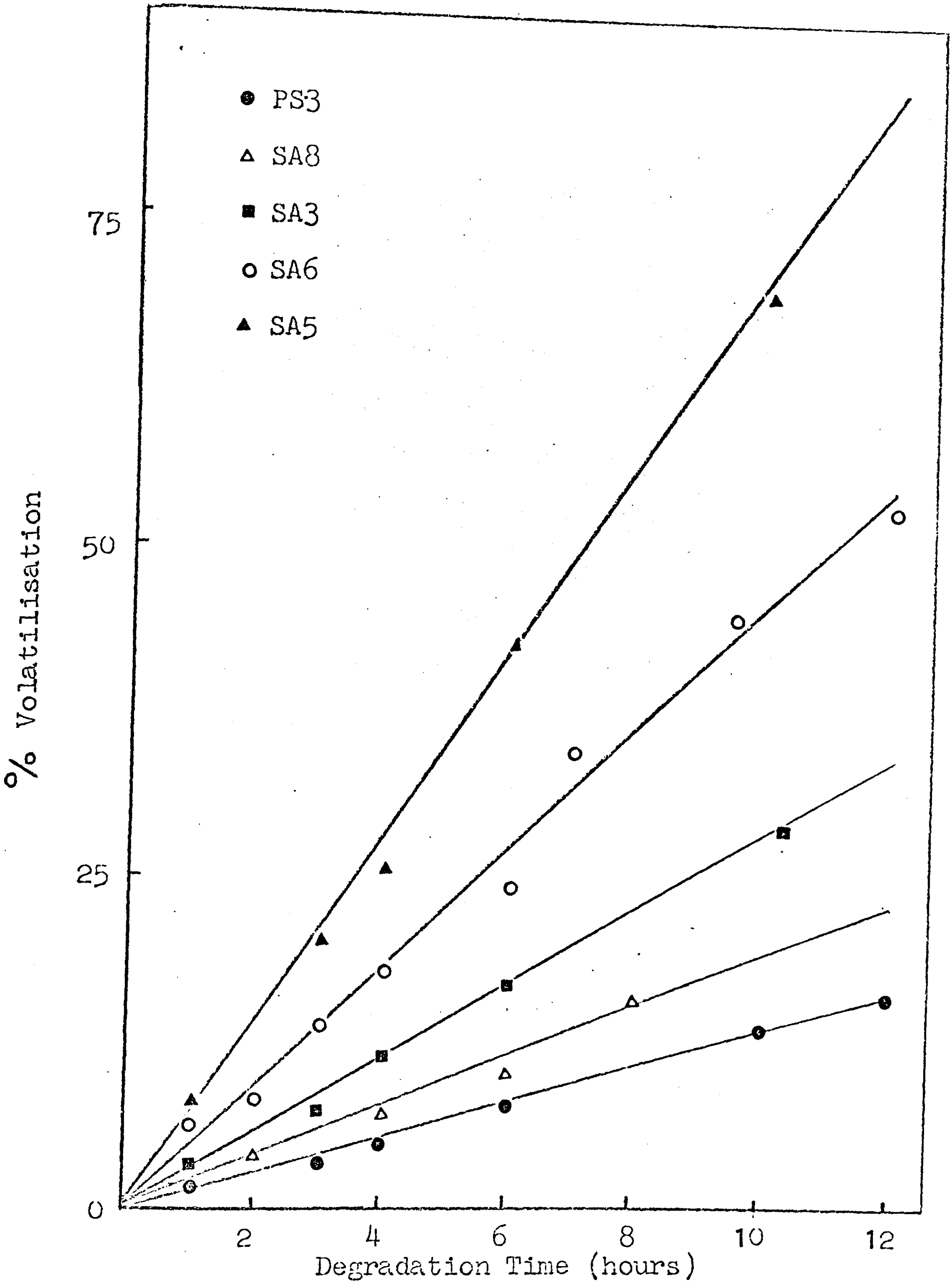


Fig. 3.5 Production of Volatiles at 292°C as a Function of Time of Degradation

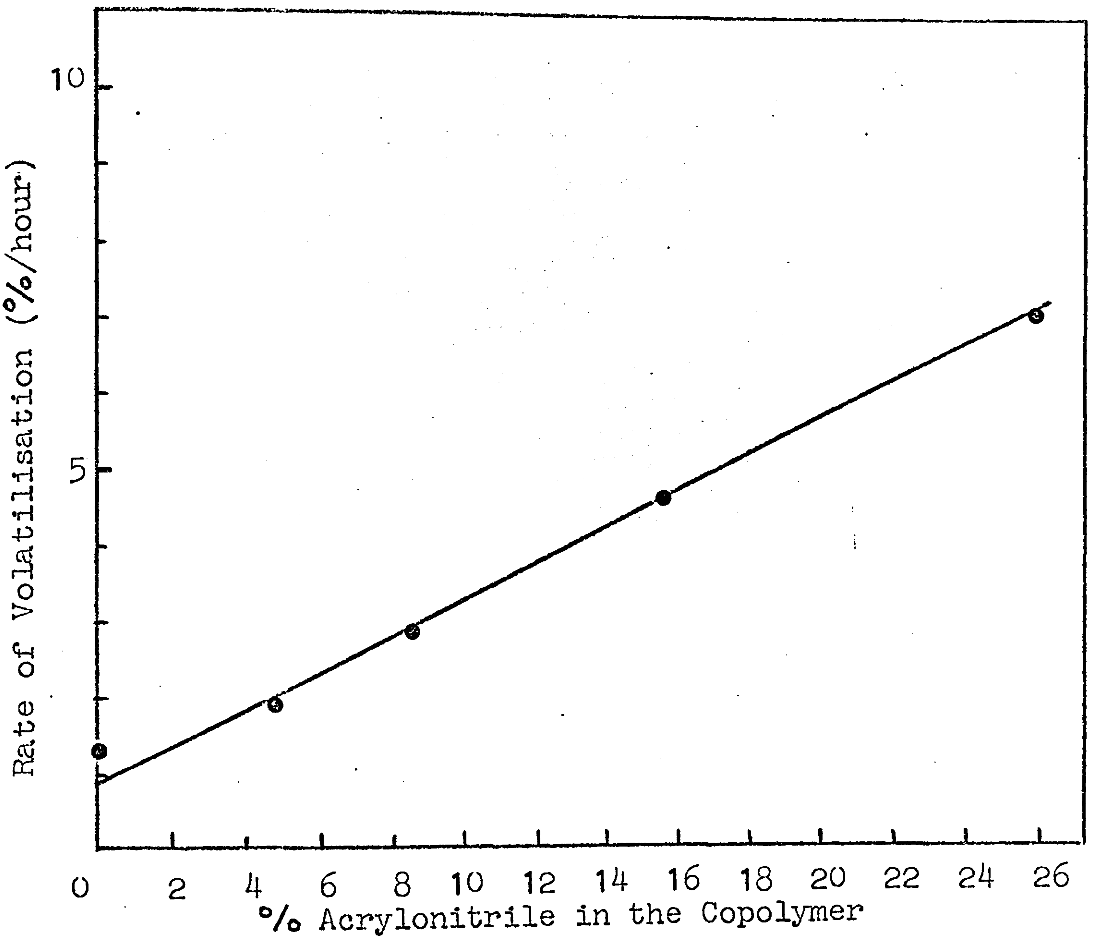


Fig. 3.6 Rate of Volatilisation at 292°C as a Function of the Acrylonitrile Concentration of the Copolymers

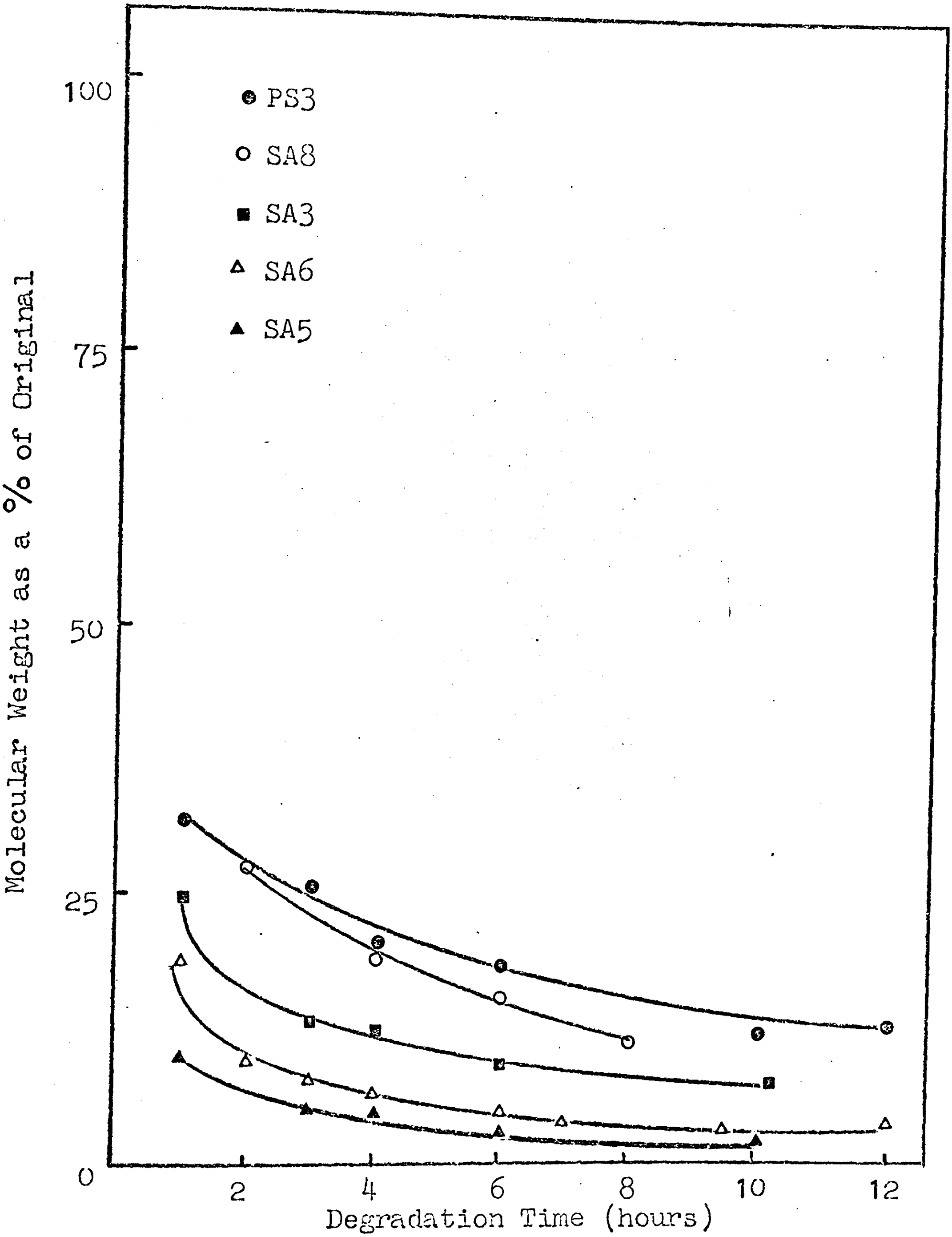


Fig. 3.7 Changes in Molecular Weight with Time of Degradation at 292°C

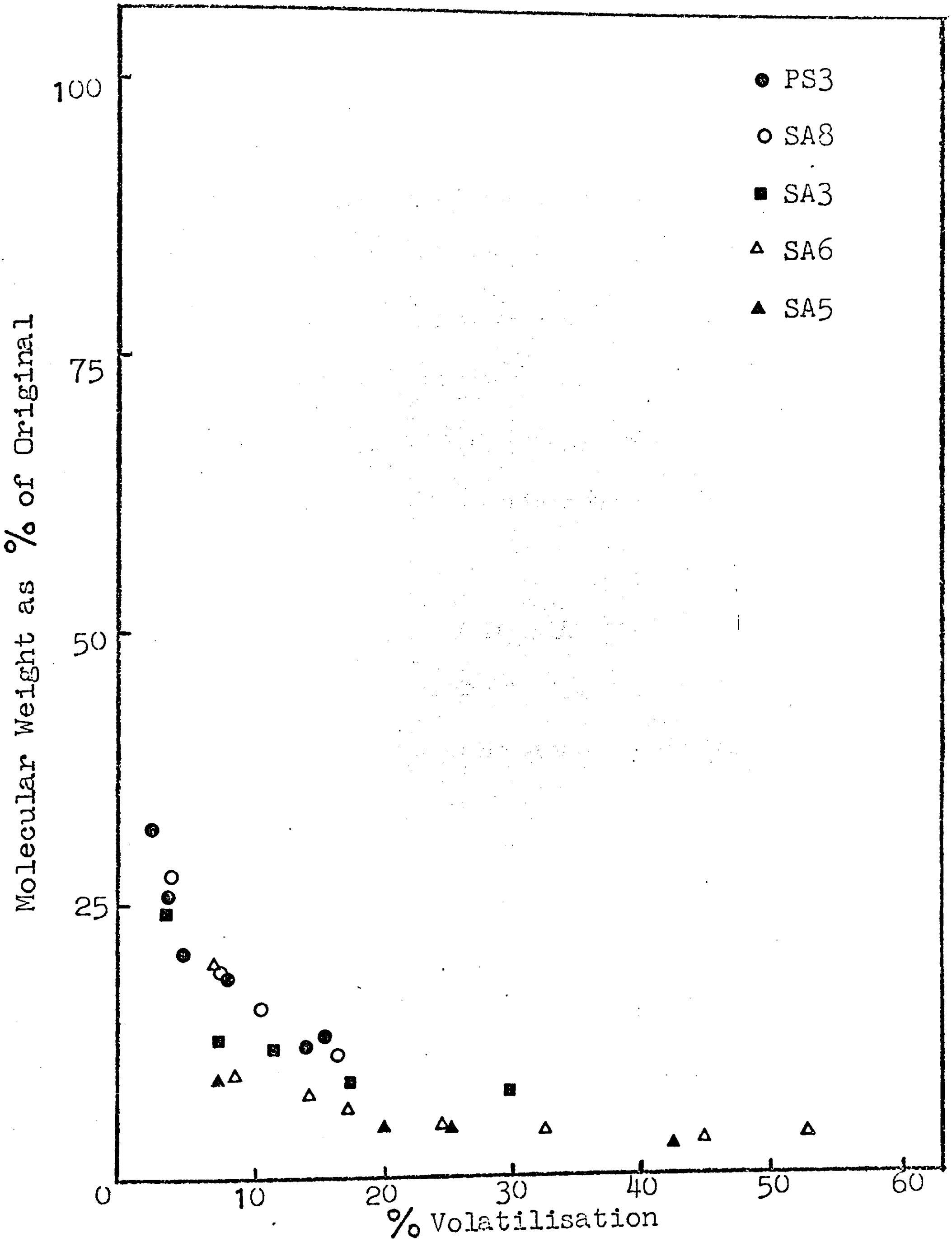


Fig. 3.8 Changes in Molecular Weight with Volatilisation at 292 °C

has fallen to less than 10 per cent of its original value compared with 35 per cent for polystyrene. The concept of acrylonitrile as "weak links" in the copolymer chain will be dealt with in greater detail in Chapter 5.

The changes in molecular weight occurring with volatilisation are illustrated in Fig. 3.8. From this it is evident that the amount of monomer per chain scission is decreasing slightly with increasing acrylonitrile content of the copolymer. The mechanistic significance of this will be dealt with in greater detail together with other data later in this chapter.

(b) Calculation of Chain Scission in the Presence of Volatilisation

If N is the number of bonds broken at random in a polymer molecule of chain length CL_0, and CL is the chain length after N breaks, then,

$$N = \frac{CL_0}{CL} - 1 \qquad (1)$$

provided that no material is lost by volatilisation. If a fraction x is lost by degradation producing volatile products, but assuming that no complete polymer molecules are lost by unzipping,

$$N = \frac{(1 - x)CL_0}{CL} - 1 \qquad (2)$$

To compare polymers of different molecular weights, it is convenient to express chain scission in terms of scissions per monomer unit. Therefore,

$$N = nCL_0 \qquad (3)$$

where n = number of scissions per monomer unit. Substituting this value of N in equation (2) we get,

$$n = \frac{(1 - x)}{CL} - \frac{1}{CL_o} \qquad (4)$$

Values of n are calculated from the data in Tables 3.2 and 3.4, and the results are presented in Table 3.5. A plot of n against time is shown in Fig. 3.9. Quantitative analysis of the rate of chain scission is valueless due to the rapid curvature of the majority of the lines. Equation (4) is only valid when no molecules are being lost by complete unzipping. The increasing amount of scission at acrylonitrile units in the copolymers means that this condition is no longer obeyed. The very fast initial chain scission in polystyrene PS3 and copolymer SA8 (4.7 per cent acrylonitrile), followed by a diminished rate, after the first hour of degradation, suggests the influence of "weak links". This effect is not observed in the copolymers containing a higher concentration of acrylonitrile at this temperature because of the high rate of scission associated with the acrylonitrile units.

(c) The Relationship between the Production of Volatiles and Chain Scission

Using equation (2), the number of chain scissions, N, per polymer molecule can be calculated, taking into account the material lost by volatilisation. The values of N along with other relevant data are shown in Table 3.6 (calculated from data in Table 3.5). The amount of volatiles

Table 3.5

Data for Calculation of n, the Number of Chain Scissions (from equation 4)

Copolymer Code	Degradation Time (hours)	$\bar{M}n \times 10^{-5}$	$CL \times 10^{-3}$	% Volatilisation	$n \times 10^{3}$
PS3	0	4.70	4.5	0	0
	1	1.49	1.43	2.15	0.463
	3	1.22	1.18	3.27	0.603
	4	1.02	0.98	4.15	0.758
	6	0.865	0.83	7.64	0.888
	10	0.567	0.55	13.8	1.318
	12	0.617	0.59	15.3	1.208
SA8	0	3.31	3.27	0	0
	2	0.92	0.908	3.9	0.75
	4	0.64	0.631	7.45	1.16
	6	0.52	0.513	10.1	1.45
	8	0.38	0.375	16.2	1.93
SA3	0	4.11	4.11	0	0
	1	1.02	1.02	3.14	0.707
	3	0.53	0.53	7.13	1.517
	4	0.51	0.51	11.22	1.515
	6	0.38	0.38	16.70	1.950
	10.25	0.327	0.327	29.00	1.930
SA6	0	4.7	4.87	0	0
	2	0.445	0.461	8.25	1.78
	4	0.298	0.308	17.0	2.48
	6	0.247	0.256	24.5	2.66
	7	0.196	0.203	34.7	2.99
	9.5	0.170	0.176	45.0	2.92
	12	0.180	0.187	53.0	2.29
SA5	0	6.50	7.0	0	0
	1	0.645	0.695	7.6	1.17
	3	0.33	0.355	20.3	2.10
	4	0.332	0.355	25.8	1.94
	6	0.215	0.231	43.2	2.22
	10	0.159	0.171	69.4	1.60

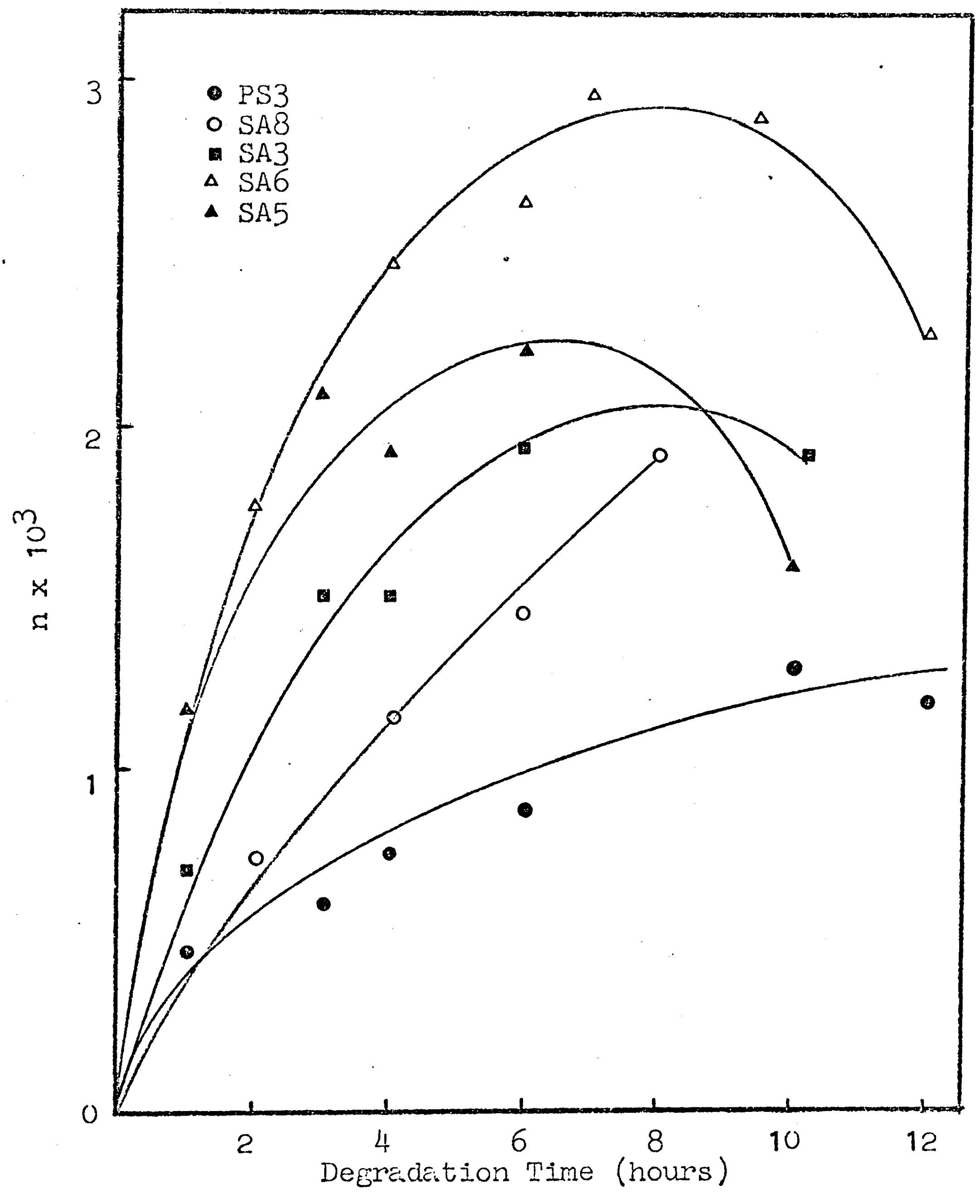


Fig. 3.9 Chain Scissions occurring per Monomer Unit as a Function of Time

Table 3.6

Number of Chain Scissions (N) per Polymer Molecule at 292°C

Copolymer Code	Degradation Time (hours)	% Volatilisation	N
PS3	0	0	0
	1	2.15	2.08
	3	3.27	2.73
	4	4.15	3.38
	6	7.64	4.0
	10	13.80	6.15
	12	15.30	5.44
SA8	0	0	0
	2	3.9	2.6
	4	7.45	4.2
	6	10.1	5.37
	8	16.2	7.7
SA3	0	0	0
	1	3.14	2.92
	3	7.13	6.20
	4	11.20	6.15
	6	16.7	8.0
	10.25	29	7.85
SA6	0	0	0
	1	6.6	3.7
	2	8.25	9.0
	3	13.9	10.2
	4	17.0	12.1
	6	24.5	13.0
	7	34.7	14.6
	9.5	45.0	14.2
	12	53.0	11.2
SA5	0	0	0
	1	7.6	8.3
	3	20.3	14.7
	4	25.8	13.6
	6	43.2	16.0
	10	69.7	11.2

produced per chain scission is illustrated in Fig. 3.10. This data must be interpreted in accordance with the restrictions placed on the foregoing theoretical treatment. Loss of complete molecules from the reaction will give an anomalously high value of the volatiles produced per chain scission. This effect is clearly visible at high conversion as is shown in Fig. 3.10. Taking the best linear regions where this effect is minimal, an estimate can be made of zip length which produces volatile products. These results are shown in Table 3.7.

Table 3.7

Calculation of Zip Length

Copolymer	Slope (Fig. 3.10)	M_o	M.Wt. lost per Scission	Average Monomer Wt.	Zip Length
PS3	2	470,000	9400	104	90
SA8	2	331,000	6620	101.4	65
SA3	2	411,000	8220	100	82.2
SA6	1.47	470,000	6900	96.5	71.5
SA5	1.0	650,000	6500	93	69.5

The inability to separate the data for PS3, SA8 and SA3 results in an anomalous molecular weight effect on the zip length, but comparing SA6 and PS3 which have the same molecular weights, it is quite clear that the zip length is reduced by increasing acrylonitrile in the copolymer.

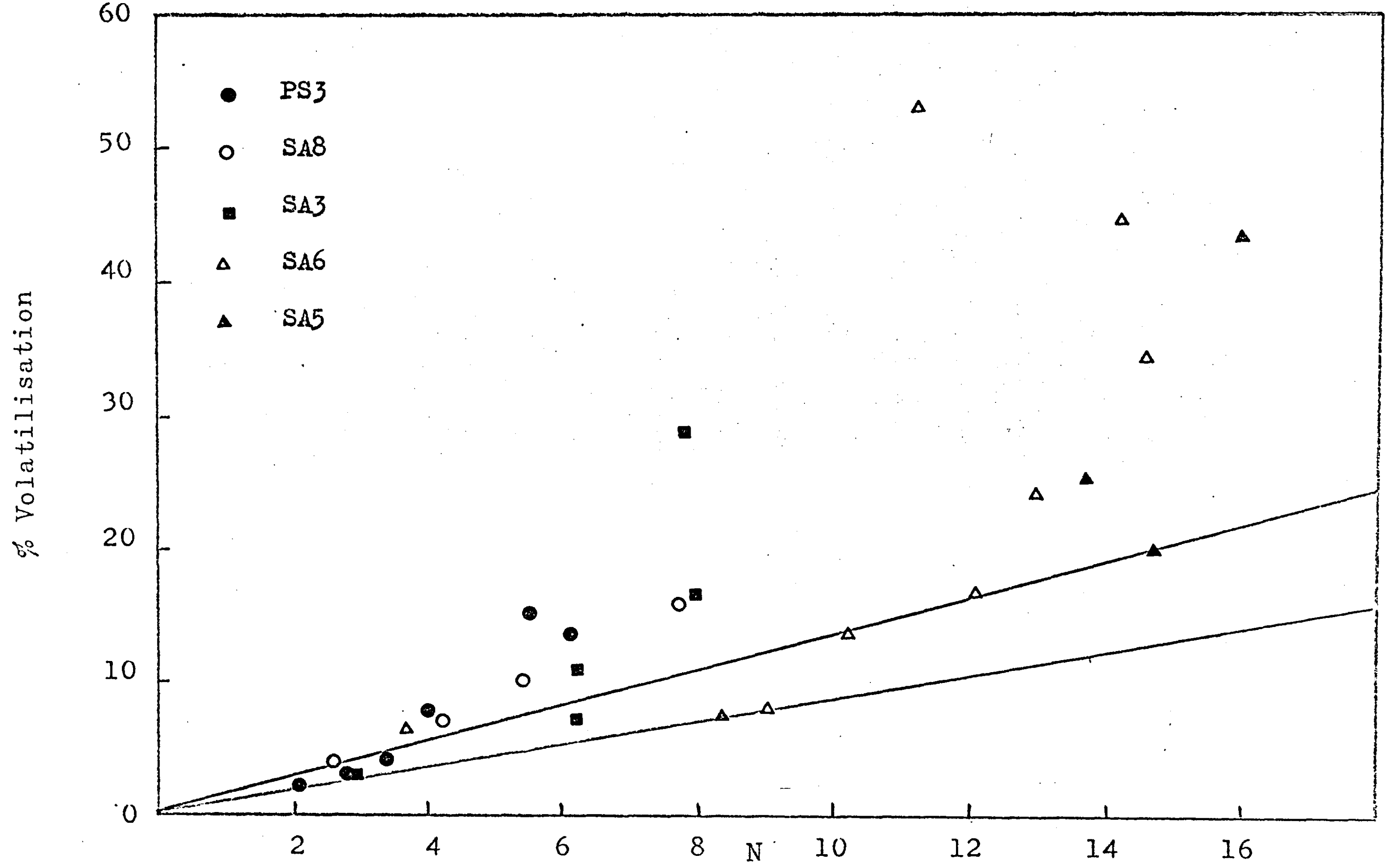
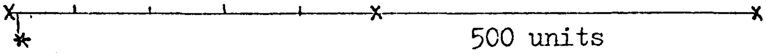


Fig. 3.10 % Volatilisation at 292°C as a Function of the Number of Scissions per Polymer Molecule.

In view of the fact that it has been clearly established that the rate of production of volatiles increases with increasing acrylonitrile concentration, some explanation of the decreased zip length is necessary.

Shortening of the zip length must imply that termination of the depropagation reaction is increasing. The increase in the amount of chain fragments produced as opposed to monomer (discussed later in this chapter) indicates that the intramolecular transfer reaction producing chain fragments occurs very easily and does not readily account for the increased termination. However both depropagation to monomer and intramolecular transfer will be much less favourable if two or more acrylonitrile units occur together. From the sequence distribution calculations[73] shown in Table 3.8, it can be seen that approximately 0.2 per cent of the bonds in SA5 are between two acrylonitrile units. This means that in every 1000 units there are two pairs of adjacent acrylonitrile units.



Assuming initial scission at * , immediately after a double acrylonitrile unit, and a zip length of approximately 100 units then after four more scissions, the next double unit will be reached. This will undoubtedly result in termination. Depending on the point of initial scission and initiation of volatilisation, a decrease of up to 20 per cent in the

Table 3.8

Sequence Distribution Calculations[73]

Copolymer Code	% Sx	% Ax	% S	% A	Run No.	% S-A	% SS	% A-A
SA2	99.6	0.4	99.0	1	1.92	1.92	98.08	0
SA8	97.9	2.1	95.3	4.7	9.47	9.48	90.52	0
SA3	96.1	3.9	91.7	8.3	16.53	16.54	83.45	0.01
SA6	91.6	8.4	84.5	15.5	30.90	30.90	69.05	0.05
SA5	83.2	16.8	75.1	24.9	49.53	49.53	50.29	0.18
SA10	71.5	28.5	66.6	33.4	65.72	65.72	33.76	0.52
SA9	23.7	76.3	50	50	88.69	88.69	5.65	5.65

Sx and Ax are the molar percentages of styrene and acrylonitrile in the monomer mixture.

S and A are the molar percentages of styrene and acrylonitrile in the copolymers.

S-A = styrene to acrylonitrile bonds

S-S = styrene to styrene bonds

A-A = acrylonitrile to acrylonitrile bonds average amount of monomer produced may be expected. A similar effect is observed for SA6 although it has less pairs of acrylonitrile units. In spite of the small increase in termination however, the overall rate of volatilisation increases because of the very high rate of chain scission at acrylonitrile units, and subsequent increase in the number of chain ends capable of re-initiation and depropagation.

Intermolecular transfer is not considered important as a source of chain scission in styrene/acrylonitrile copolymers because of the very large molecular weight drop occurring with negligible volatilisation. It has already been eliminated as a source of "normal" chain scission in polystyrene by the use of the inhibitor 1,4-diamino-anthraquinone(DAA).[34] The increasing quantity of chain fragments produced with increasing acrylonitrile concentration suggests that the result of the blocking effect on the production of monomer is intramolecular transfer. The fact that the zip length is very much longer than the distance between adjacent acrylonitrile units also suggests that intermolecular transfer does not occur to any great extent.

(d) Relative Rate Measurements by Pirani Gauge

A detailed analysis of the relative rate of volatilisation as a function of conversion was not undertaken using the Pirani gauge. This can be obtained much more readily by differentiating the isothermal TGA thermograms as discussed in Chapter 6. It was however observed that whereas polystyrene showed a maximum at the accepted 30-40 per cent conversion, the maximum rate of volatilisation occurred very much earlier in the copolymers. This is in keeping with the increased rate of chain scission associated with acrylonitrile units, producing the maximum number of chain ends capable of degradation much earlier in the reaction.

3.4 Degradations at 330°C in the Molecular Still

(a) Rate Studies

To obtain suitable quantities of products for analysis, degradation at 330°C was used. As it was not impossible for the overall characteristics of the reaction to change with temperature, it was desirable to check this factor. A polystyrene "standard" and two copolymers were degraded at 330°C and the rate of volatilisation measured. A plot of percentage volatilisation against time is shown in Fig. 3.11. This shows that, as at 292°C, the rate increases with increasing acrylonitrile in the copolymer.

(b) The Chain Fragment to Monomer Ratio

On thermal degradation, polystyrene was shown by the earliest workers to produce monomer by a reverse depolymerisation, and chain fragments (dimer, trimer, etc.) by an intramolecular mechanism.[2] In a study of styrene/ethyl acrylate copolymers, Jones and Reynolds showed that the amount of styrene monomer produced decreased with increasing ethyl acrylate in the copolymer.[74]

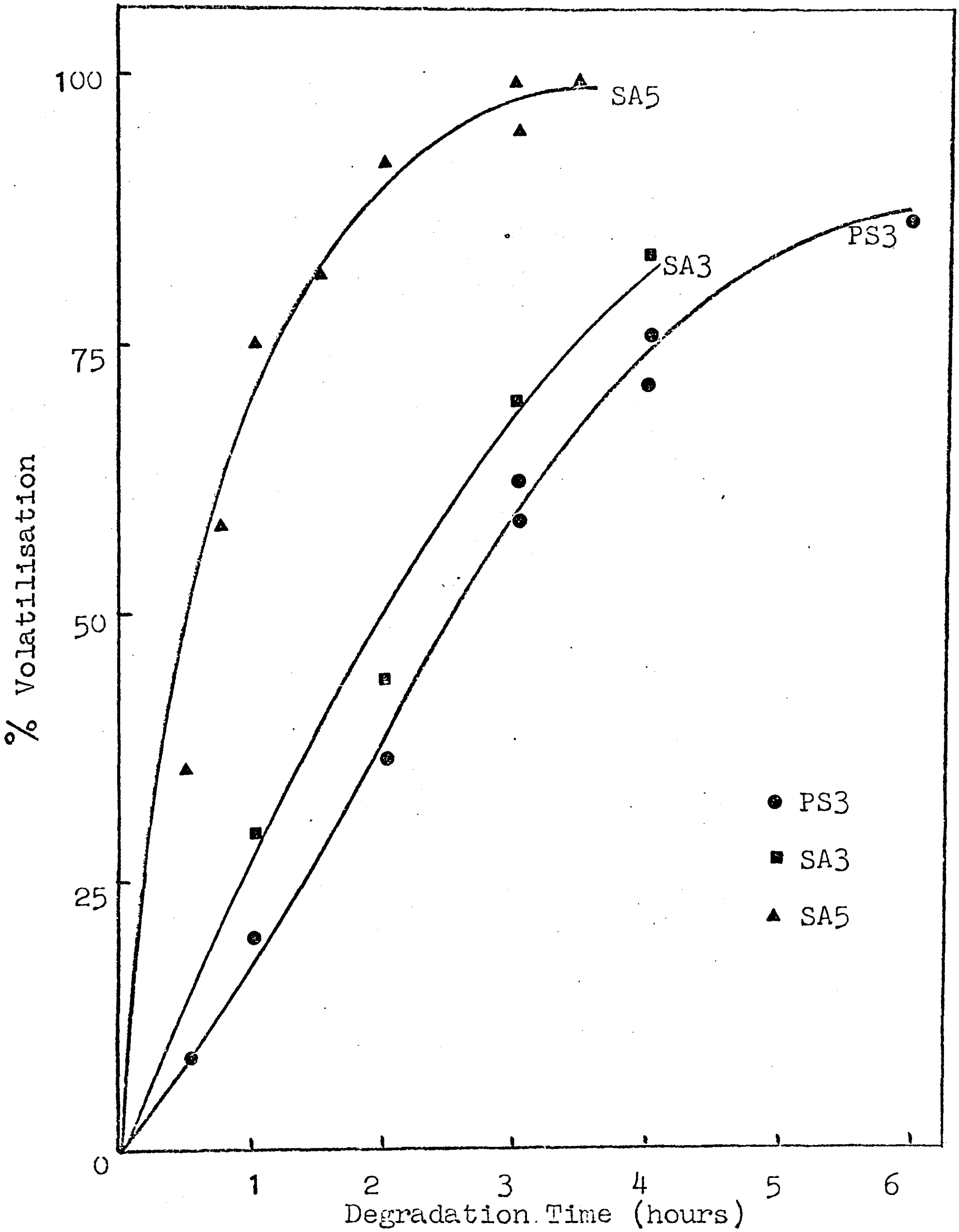


Fig. 3.11 % Volatilisation against Time at 330°C

In the present work, the monomer and chain fragments were separated and estimated as follows. Material distilling from the continuously pumped molecular still was collected in the cold trap (Fig. 2.2) which was immersed in liquid nitrogen. At the end of the degradation, the relevant section of the vacuum system shown in Fig. 2.2 was isolated and the material in the cold trap allowed to distil at room temperature into the calibrated capillary tube. This left behind any material which might have distilled into the cold trap at the reaction temperature. The weight of monomer was obtained from density data (taken as 0.9 gm./cc. because the liquid is mainly styrene). Thus from this figure and the total weight loss from the degradation tray, the weight of chain fragments was calculated. Most of the chain fragment to monomer values were obtained at 330°C but a few measured from the 292°C degradation to high conversion indicated no difference in the values (within the limits of experimental error). The results are shown in Table 3.9.

Table 3.9 The Chain Fragment to Monomer Ratio

Copolymer Code	$\frac{\text{Chain Fragment}}{\text{Monomer}}$
PS3	1.0
SA2	1.0
SA4	1.0
SA3	1.5
SA6	2.0
SA5	2.5

Although the experimental error in these determinations is fairly high, probably 10-15 per cent, the trend towards increasing chain fragments with increasing concentration of acrylonitrile in the copolymers is quite unmistakable. Degradation in sealed tubes showed the same trend and results for SA10 (33 per cent acrylonitrile) suggest a value of chain fragments to monomer of 4/1. This technique however also has its disadvantages because of the difficulty of measuring accurately the total amount of degradation.

3.5 Conclusions

From the foregoing series of degradations the following features emerge:-

(1) Small amounts of acrylonitrile, up to one per cent, have little or no effect on the thermal degradation of the polymer.

(2) The increase in the rate of volatilisation over that of polystyrene is proportional to the acrylonitrile concentration of the copolymer.

(3) The rate of chain scission appears to increase with increasing acrylonitrile content.

(4) The amount of volatiles produced per chain scission shows a small decrease for copolymers containing a high concentration of acrylonitrile. This decrease is explained by a small increase in termination at pairs of acrylonitrile units, consistent with sequence distribution calculations.

(5) The chain fragment to monomer ratio increases with increasing

concentration of acrylonitrile in the copolymers. This is in agreement with the theoretical calculations of Shibasaki[75] discussed in Chapter 4.

CHAPTER 4

THE PRODUCTS OF DEGRADATION

4.1 Introduction

The analysis of the products of degradation forms an important part of any investigation of polymer degradation. The nature of the products, the quantity in which they are produced, and the temperature at which they appear supplement the kinetic data necessary to elucidate the degradation mechanism. In copolymer studies the products are particularly important because they indicate the influence of one monomer on the other. For example in the degradation of copolymers of methyl methacrylate and methyl acrylate,[56] the acrylate units inhibit the production of monomer, so characteristic of the degradation of poly(methyl methacrylate). Methanol, one of the main products obtained in the degradation of poly(methyl acrylate), is absent even from copolymers containing 30 per cent methyl acrylate. The analysis of degradation products is extensively utilised in determining the sequence distribution in copolymers.[73,76] Bombaugh, Cook and Clampitt[77] have used the monomer production in ethylene/methyl acrylate copolymers to differentiate between random and block copolymers of which only the latter produce methanol.

Analysis of the products of degradation from styrene/acrylonitrile copolymers is somewhat simplified by the extensive analysis which has been carried out on the homopolymers.[2,5,50] In the light of previous observations on copolymers,[7,8] of obvious interest is the effect of acrylonitrile on the production of monomer, and also the ratio of the monomers in the volatile fraction compared with the copolymer composition. In defining the products of degradation, it is important to specify the conditions under which the degradations are carried out. Reported differences in the products of degradation of a particular polymer can usually be attributed to differences in temperature of degradation, sample size, atmosphere or some other physical effect.[5,67]

4.2 The Volatile Products

(a) Introduction

The volatile products were obtained from degradations in the molecular still and in sealed tubes, described in Chapter 2. Because of the initial high vacuum and the short distance between the degrading sample and the limb cooled in liquid nitrogen, the latter approximated to a pumped system. No measurable differences were observed between the two systems, for example in the styrene/acrylonitrile ratio in the volatiles.

From degradations in the differential condensation TVA apparatus (Chapters 2 and 6) material was seen to be passing through the cold trap at -100°C. The vapour pressures of the various products suggested that this was hydrogen cyanide or acrylonitrile. By attaching the sealed tube to an MS10 mass spectrometer (A.E.I.) both compounds were identified.

The liquid products were analysed by the LKB gas chromatograph-mass spectrometer (GC-MS) and shown to be acrylonitrile, benzene, toluene and styrene, all predictable from degradation of the homopolymers.

(b) Quantitative Analysis of the Styrene/Acrylonitrile Ratio in the Monomer Fraction

Because of the "blocking" effect of certain comonomers in thermal or photochemical depolymerisations, for example acrylates in the depolymerisation of poly(methyl methacrylate),[56] it is necessary to measure the styrene/acrylonitrile ratio in the volatiles. Comparison with the copolymer composition gives a measure of the blocking effect of the acrylonitrile unit.

As already discussed in Chapter 2, infra-red analysis was found to be the most satisfactory technique, and the calibration graph in Fig. 2.17 was obtained from standard mixtures of styrene and acrylonitrile. Using the same sample cell, the redistilled volatiles were examined, and from the optical density of the nitrile peak at 2230 cm^{-1} and the calibration graph (Fig. 2.17), the concentration of acrylonitrile in the volatiles was obtained. The products of several degradations for each copolymer were examined. The results are presented in Table 4.1 and illustrated in Fig.4.1. If the copolymer had undergone reverse depolymerisation to produce monomer,

Table 4.1

Quantitative Infra-Red Analysis of Acrylonitrile in the Volatile Products

(5 Hour Degradation at 330 ± 2°C)

Sample No.	% Acrylonitrile in Copolymer	% Acrylonitrile in Volatiles
SA7/2	4.7	1.9
SA8/1	4.7	2.7
SA8/7	4.7	2.0
SA3/24	8.3	3.7
SA3/28	8.3	3.4
SA6/36	15.5	6.0
SA6/37	15.5	6.2
SA5/39	24.9	9.4
SA5/48	24.9	11.0
SA10/29	33.4	16.3
SA9/4	50	22.0
SA9/5	50	22.6

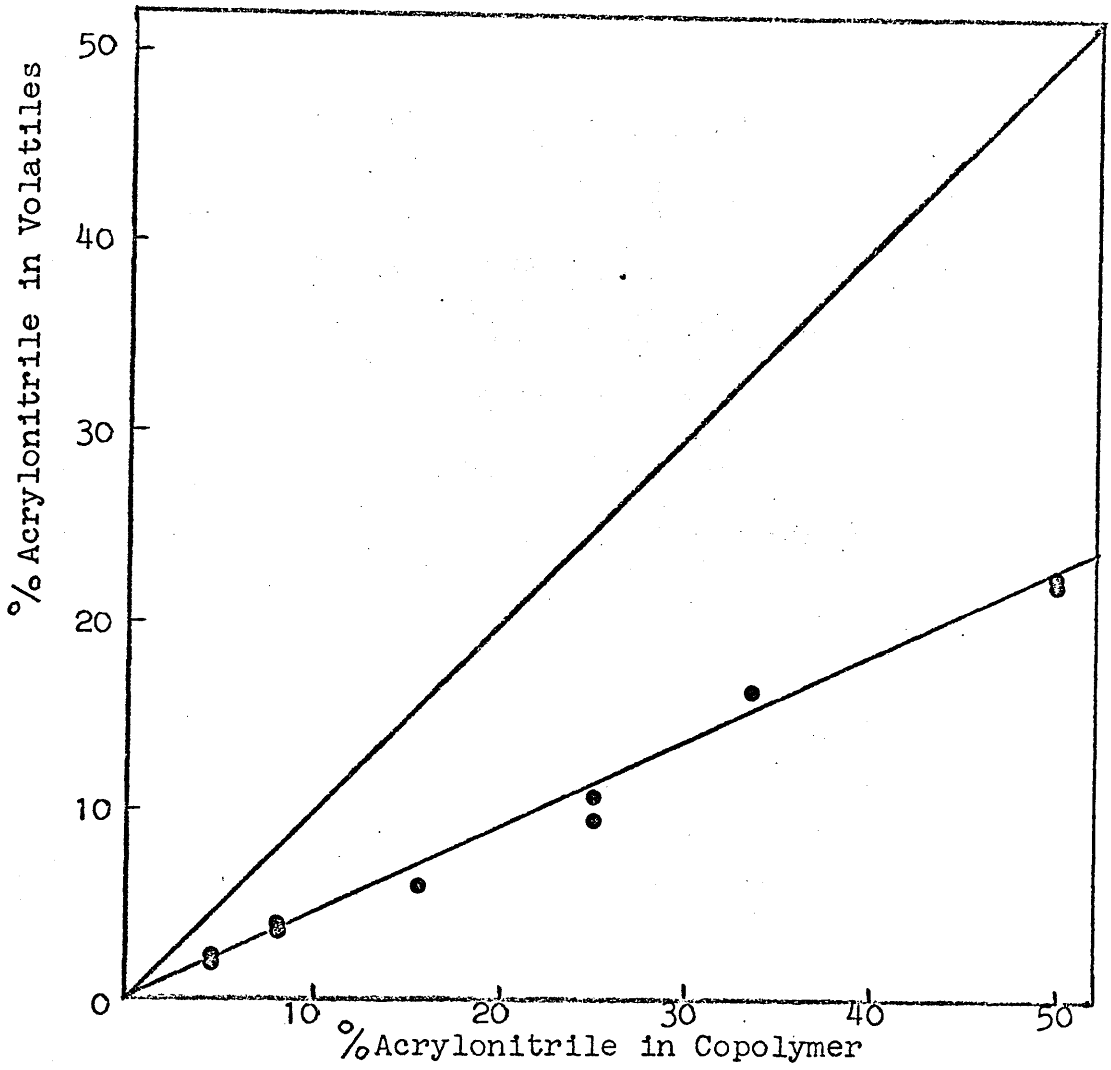
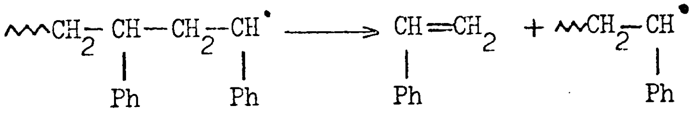


Fig. 4.1 . The Relationship between the amount of Acrylonitrile found in the Volatile Products, and the Acrylonitrile Concentration of the Copolymers

quantitative release of acrylonitrile would have occurred to give the diagonal in Fig. 4.1. The experimental points lie on a line which, within the limits of experimental error, has a slope half that of the diagonal, indicating that one in two acrylonitrile units is released as monomer. In a study of the sequence distribution of monomer units in copolymers, Harwood has developed a method whereby the amount of each type of linkage in the copolymer may be calculated from the copolymerisation data and the copolymer composition.[73] The data in Table 3.9 were obtained by this method. The occurrence of two acrylonitrile units is almost negligible up to 33.3 per cent acrylonitrile so the "blocking" effect observed must be due to a single acrylonitrile unit. The increase in the chain fragment to monomer ratio observed (Chapter 3) indicates that this second encounter results in intramolecular transfer producing chain fragments, and chain fragments containing acrylonitrile may be taken as added evidence of this.

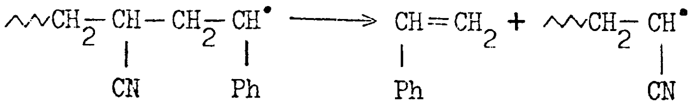
In a theoretical and experimental study of styrene/acrylonitrile copolymers using pyrolysis techniques, Shibasaki[75] has examined in detail the factors affecting the production of monomer from radical chain ends in copolymers. In the copolymers studied in this work three types of chain end producing monomer must be considered.

(1)



$$\sim CH_2-\underset{\substack{|\\ Ph}}{CH}-CH_2-\underset{\substack{|\\ Ph}}{CH^{\bullet}} \longrightarrow \underset{\substack{|\\ Ph}}{CH}=CH_2 + \sim CH_2-\underset{\substack{|\\ Ph}}{CH^{\bullet}}$$

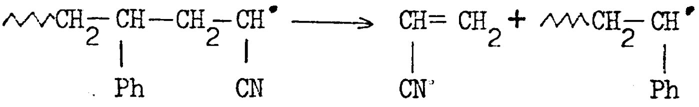
(2)



$$\sim\!\sim\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH}^{\bullet}}\longrightarrow\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH}}=\mathrm{CH_2}+\sim\!\sim\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{CH}^{\bullet}}$$

and since acrylonitrile appears as monomer,

(3)



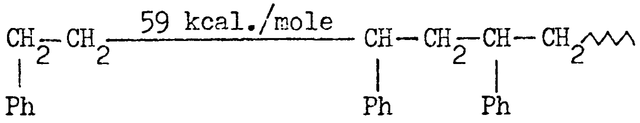
$$\sim\!\sim\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{CH}^{\bullet}}\longrightarrow\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{CH}}=\mathrm{CH_2}+\sim\!\sim\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH}^{\bullet}}$$

The results of theoretical calculations on monomer production from various types of chain ends are shown in Table 4.2.

Table 4.2

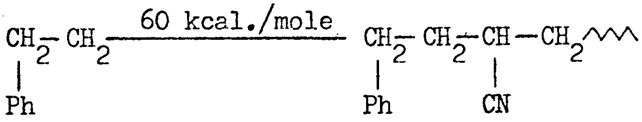
Bond Dissociation Energies at Chain Ends in Styrene/Acrylonitrile Copolymers

(1)



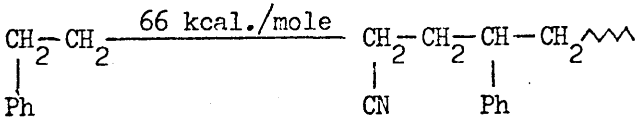
$$\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH_2}}-\mathrm{CH_2}\overset{\text{59 kcal./mole}}{\rule{3cm}{0.4pt}}\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH}}-\mathrm{CH_2}\sim\!\sim$$

(2)



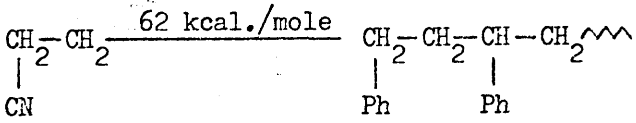
$$\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH_2}}-\mathrm{CH_2}\overset{\text{60 kcal./mole}}{\rule{3cm}{0.4pt}}\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH_2}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{CH}}-\mathrm{CH_2}\sim\!\sim$$

(3)



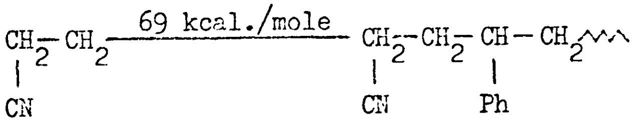
$$\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH_2}}-\mathrm{CH_2}\overset{\text{66 kcal./mole}}{\rule{3cm}{0.4pt}}\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{CH_2}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH}}-\mathrm{CH_2}\sim\!\sim$$

(4)



$$\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{CH_2}}-\mathrm{CH_2}\overset{\text{62 kcal./mole}}{\rule{3cm}{0.4pt}}\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH_2}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH}}-\mathrm{CH_2}\sim\!\sim$$

(5)



$$\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{CH_2}}-\mathrm{CH_2}\overset{\text{69 kcal./mole}}{\rule{3cm}{0.4pt}}\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{CH_2}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{CH}}-\mathrm{CH_2}\sim\!\sim$$

The values are calculated for saturated chain ends since precise values are not available for radical ends. The formation of a double bond in the monomer after cleavage β to the free radical reduces the energy of the β-bond by approximately 50 kcal./mole and this should be similar for both monomers.

From Table 4.2, reactions (1), (2) and (4) in that order are most favourably inclined to the production of monomer. Therefore the amount of monomer produced decreases as the amount of acrylonitrile in the copolymer increases. This is consistent with the increased chain fragment to monomer ratio (Chapter 3). Reaction (3) should lead to intramolecular transfer to produce chain fragments. Reaction (5) will be relatively unimportant because of the small number of adjacent acrylonitrile units.

(c) Estimation of Toluene in the Volatile Products

From the presence in the toluene spectrum of a single band at 738 cm.$^{-1}$ which is unaffected by the presence of styrene, acrylonitrile or benzene, an estimate of the amount of toluene in the volatile products was obtained. Comparison of the optical density of this peak with a calibration graph obtained from toluene/styrene mixtures, indicated that toluene was present to not more than 3 per cent in the volatile products. This was in agreement with a previous GLC estimate. A more accurate estimate was not considered important enough to merit the full scale investigation necessary. Benzene constituted less than one per cent of the volatiles.

4.3 Analysis of the Chain Fragments

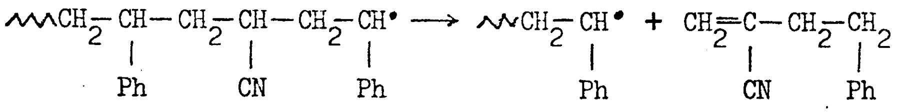
(a) Gas Chromatograph-Mass Spectrometer Analysis

In his early work on polystyrene, Staudinger[2] separated and identified the dimer and trimer formed during the degradation of polystyrene. Modern analytical instrumentation has simplified this process very much, and degradations can be carried out on much smaller samples with consequent improvement in control of the degradation conditions.

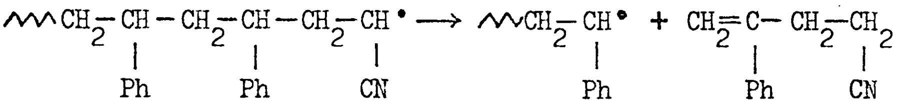
Chain fragments obtained from sealed tube degradations were found to separate on a one per cent SE30 column (10 ft.) by temperature programming to 250°C. Once separation conditions had been established, it was possible to examine the chain fragments on the LKB GC-MS described in Chapter 2.

The chromatogram obtained from a solution of the chain fragments of copolymer SA5 is shown in Fig. 2.16. A mass spectrum was obtained for each compound at 70 eV to give the full cracking pattern necessary for identification. Peaks at $m/e = 157, 208, 261$ and 312 indicated that not only were styrene dimer and trimer formed, but also chain fragments containing a single acrylonitrile unit. These were present as several isomeric species and the cracking patterns were examined in an attempt to elucidate the structure of some of these species.

Considering for example the styrene/acrylonitrile dimers, it is first necessary to examine the reactions leading to the different structures by intramolecular transfer.

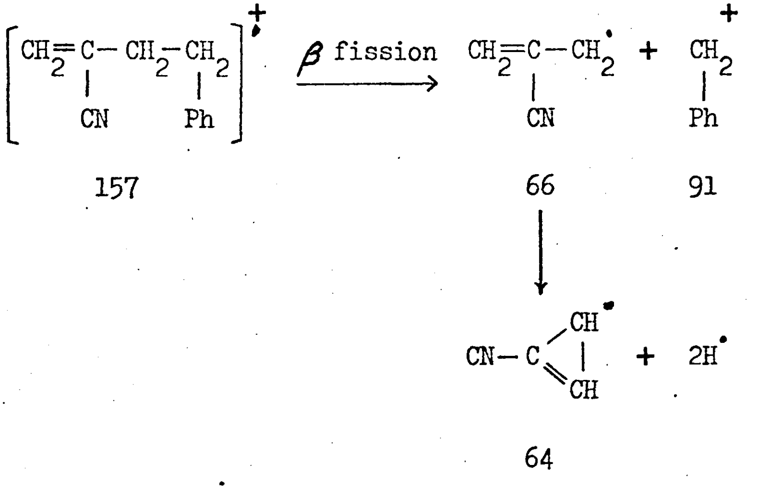
(1) 

$$\sim\!\sim CH_2-\underset{Ph}{\underset{|}{CH}}-CH_2-\underset{CN}{\underset{|}{CH}}-CH_2-\underset{Ph}{\underset{|}{CH^{\bullet}}} \longrightarrow \sim\!\sim CH_2-\underset{Ph}{\underset{|}{CH^{\bullet}}} + CH_2=\underset{CN}{\underset{|}{C}}-CH_2-\underset{Ph}{\underset{|}{CH_2}}$$

(2) 

$$\sim\!\sim CH_2-\underset{Ph}{\underset{|}{CH}}-CH_2-\underset{Ph}{\underset{|}{CH}}-CH_2-\underset{CN}{\underset{|}{CH^{\bullet}}} \longrightarrow \sim\!\sim CH_2-\underset{Ph}{\underset{|}{CH^{\bullet}}} + CH_2=\underset{Ph}{\underset{|}{C}}-CH_2-\underset{CN}{\underset{|}{CH_2}}$$

The fragmentation patterns which might reasonably be expected from these structures can be formulated and compared with the mass spectra obtained from the GC-MS.



This fragmentation is in agreement with the line diagram shown in Fig. 4.2, obtained from peak 2 in Fig. 2.16. The base peak at m/e = 91 is the stable tropylium ion formed by the rearrangement of $PhCH_2$. This arises as a result

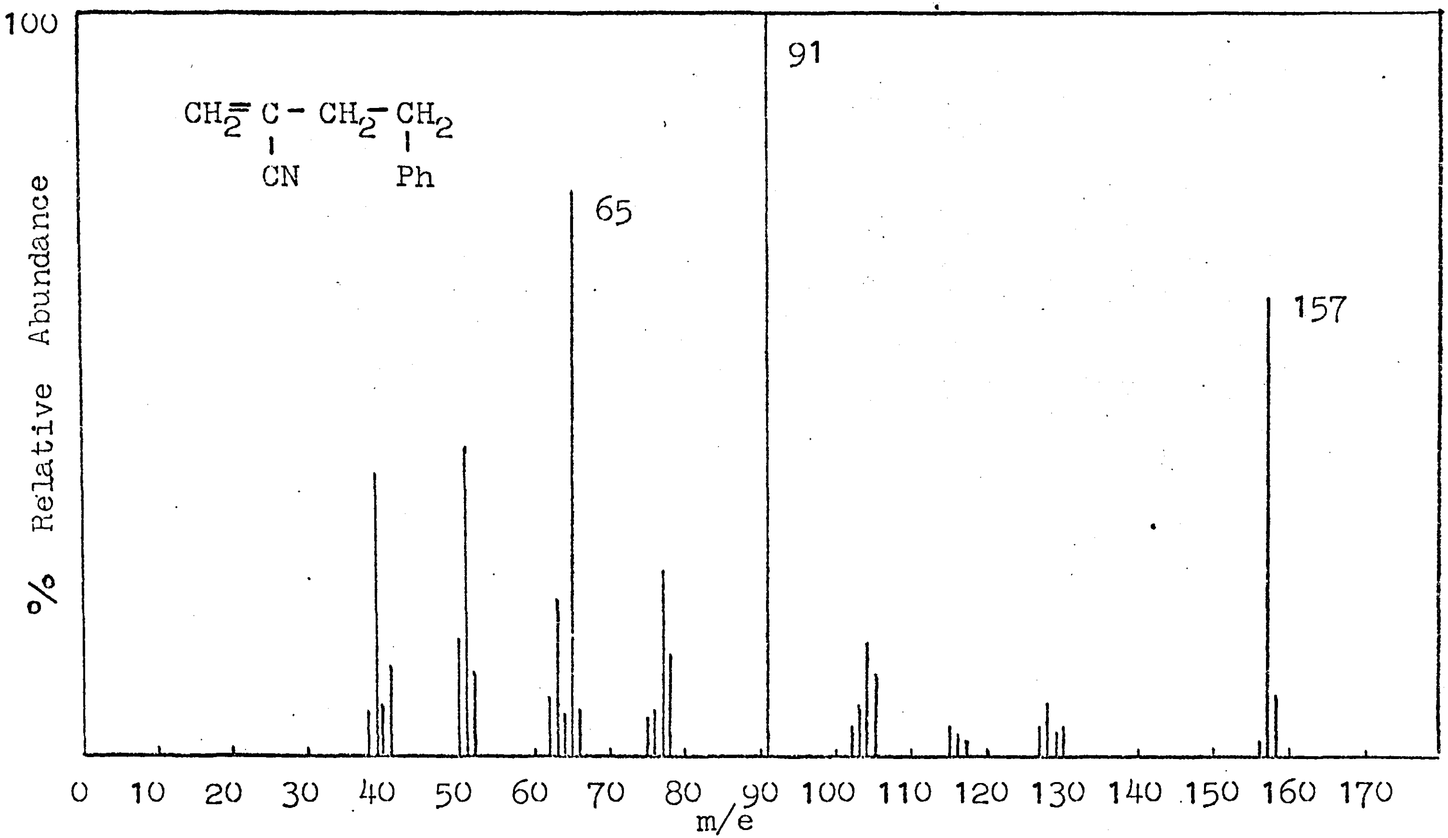
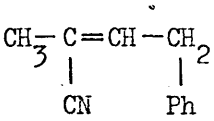


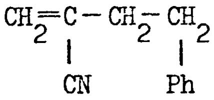
Fig. 4.2 Mass Spectrum of the Styrene-Acrylonitrile Dimer appearing as Peak 2 in Fig. 2.16 from the GC-MS

of fission β to the double bond, the favoured mode of fission. This is confirmed by the peaks at m/e = 66 and 64 corresponding to formation of the more stable cyclic radical. Peaks at m/e = 39, 50, 51, 52 and 65 are due to the benzene ring fragmentation.[78] The structure



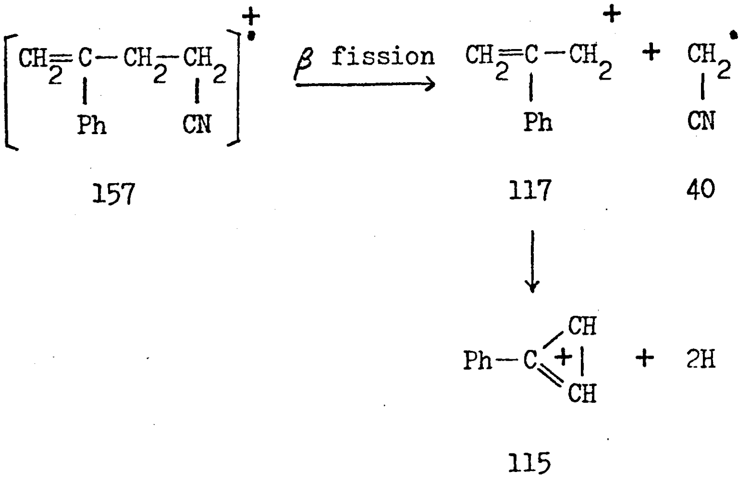
$$CH_3-\underset{CN}{\underset{|}{C}}=CH-\underset{Ph}{\underset{|}{CH_2}}$$

would also give the m/e = 91 peak, but the absence of a peak at m/e = 142 corresponding to loss of a methyl group suggests that this structure is not formed in the degradation or by isomerisation in the electron beam. The most abundant styrene/acrylonitrile dimer therefore has the structure

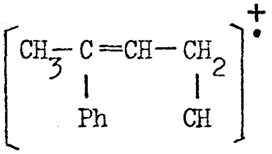


$$CH_2=\underset{CN}{\underset{|}{C}}-CH_2-\underset{Ph}{\underset{|}{CH_2}}$$

The fragmentation of the dimer obtained from reaction (2) is as follows:-



Comparing this fragmentation with the line diagram in Fig. 4.3, obtained from peak 3, Fig. 2.16, several points of similarity are observed. As in the previous case initial fission is β to the double bond. This results in the ion at m/e = 117. This however rearranges to the more stable substituted cyclopropenyl ion (m/e = 115) and the rearrangement is supported by a "metastable" ion at m/e = 113 and a peak at m/2e = 57.5, both indicative of the high stability of the cyclopropenyl ion. The peak at m/e = 91 is small compared with the parent ion indicating that it is not situated at a point in the molecule where fission is favourable. The appearance of an ion at m/e = 142 suggests the presence of the ion



$$\left[\begin{array}{cccc} CH_3- & C= & CH- & CH_2 \\ & | & & | \\ & Ph & & CH \end{array}\right]^{\overset{+}{\cdot}}$$

which loses the methyl group. This structure is thought to arise from isomerisation in the electron beam rather than as a product of the degradation. The fact that in the mass spectrum shown in Fig. 4.3, the m/e = 157 is the base peak suggests that this ion is more stable than the other isomer formed in reaction (1). This would favour some isomerisation before fragmentation had time to take place.

Obviously it is impossible to assign these structures with absolute certainty without the use of deuterated samples of the pure compounds to

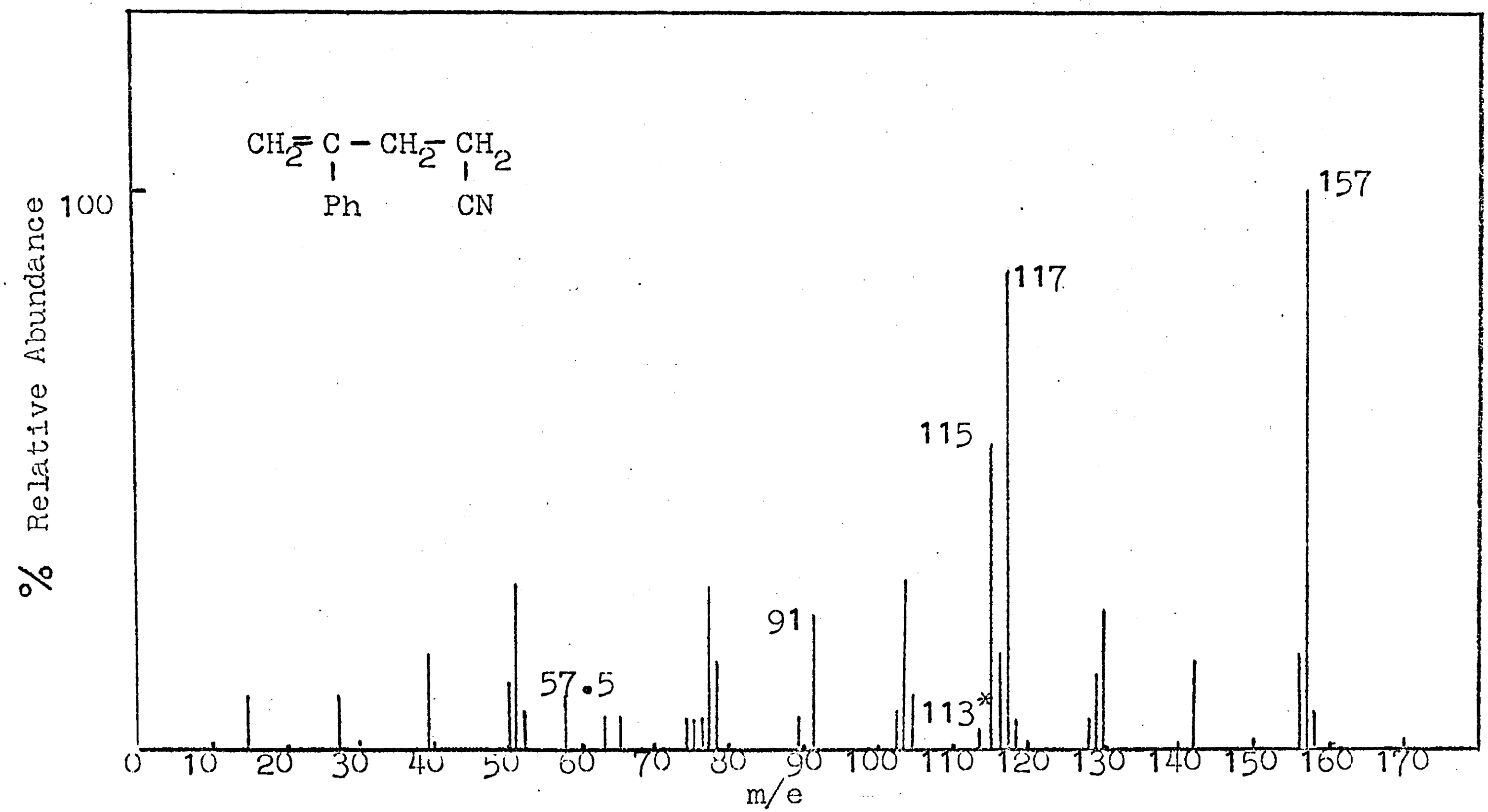
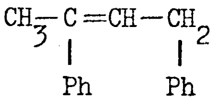


Fig. 4.3 Mass Spectrum of the Styrene-Acrylonitrile Dimer appearing as Peak 3 in Fig. 2.16 from the GC-MS

study hydrogen migration. Nevertheless the structures observed agree with those predicted by intramolecular transfer at the various types of radical chain ends, demonstrating the potential of the GC-MS technique. From a study of the cracking patterns, the structures shown in Table 4.3 are suggested for the chain fragments in Fig. 2.16. The mass spectra of the m/e = 261 peaks agree with the structures predictable from the various radical chain ends. The styrene dimer structures are less satisfactory in this respect, the largest dimer peak having the structure



$$CH_3-\underset{\underset{Ph}{|}}{C}=CH-\underset{\underset{Ph}{|}}{CH_2}$$

The shape of the chromatographic peak does not indicate isomerisation on the column. Since these products are being formed by extensive radical rearrangement, it is impossible to rationalise completely the formation of the products without extensive investigations on deuterated compounds.

(b) Other Spectroscopic Analysis

The chain fragments collected on the cold ring of the TVA apparatus were colourless. Infra-red analysis was carried out on liquid films between two sodium chloride plates. The 1500-1700 cm.$^{-1}$ region is shown in Fig. 4.4. A peak at 1625 cm.$^{-1}$ indicates ethylenic structures[79] in agreement with the mass spectrometric evidence.

Table 4.3

Structures of Chain Fragments from a 3/1 Styrene/Acrylonitrile Copolymer

(Peak numbers refer to the chromatogram in Fig. 2.16)

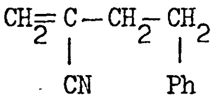
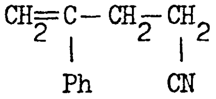
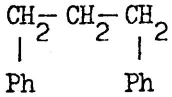
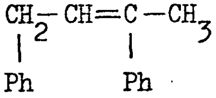
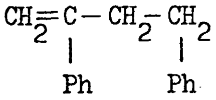
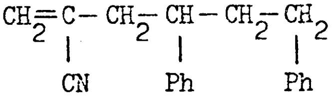
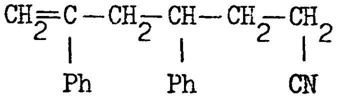
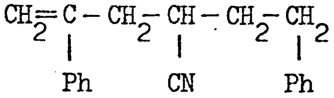
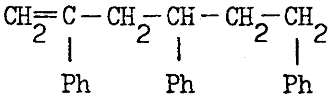
Peak No.	Molecular Weight	Structure
1	-	Tail of solvent peak (Chloroform)
2	157	 $CH_2{=}\underset{CN}{\underset{\vert}{C}}{-}CH_2{-}\underset{Ph}{\underset{\vert}{CH_2}}$
3	157	 $CH_2{=}\underset{Ph}{\underset{\vert}{C}}{-}CH_2{-}\underset{CN}{\underset{\vert}{CH_2}}$
4	196	 $\underset{Ph}{\underset{\vert}{CH_2}}{-}CH_2{-}\underset{Ph}{\underset{\vert}{CH_2}}$
5	208	 $\underset{Ph}{\underset{\vert}{CH_2}}{-}CH{=}\underset{Ph}{\underset{\vert}{C}}{-}CH_3$
6	208	 $CH_2{=}\underset{Ph}{\underset{\vert}{C}}{-}CH_2{-}\underset{Ph}{\underset{\vert}{CH_2}}$
7	239	unknown
8	261	 $CH_2{=}\underset{CN}{\underset{\vert}{C}}{-}CH_2{-}\underset{Ph}{\underset{\vert}{CH}}{-}CH_2{-}\underset{Ph}{\underset{\vert}{CH_2}}$

Table 4.3 (continued)

Peak No.	Molecular Weight	Structure
9	261	 $CH_2{=}\underset{\substack{\vert\\Ph}}{C}-CH_2-\underset{\substack{\vert\\Ph}}{CH}-CH_2-\underset{\substack{\vert\\CN}}{CH_2}$
10	261	 $CH_2{=}\underset{\substack{\vert\\Ph}}{C}-CH_2-\underset{\substack{\vert\\CN}}{CH}-CH_2-\underset{\substack{\vert\\Ph}}{CH_2}$
11	312	 $CH_2{=}\underset{\substack{\vert\\Ph}}{C}-CH_2-\underset{\substack{\vert\\Ph}}{CH}-CH_2-\underset{\substack{\vert\\Ph}}{CH_2}$

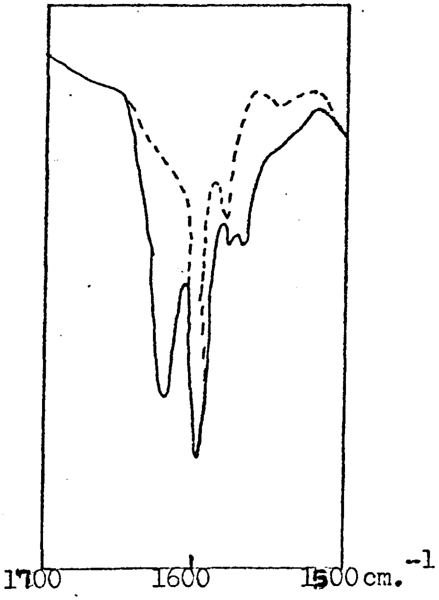


Fig. 4.4 Region of the Infra-Red Spectrum Showing Unsaturation in the Chain Fragments. (- - - SA9 undegraded, —— SA9 chain fragments)

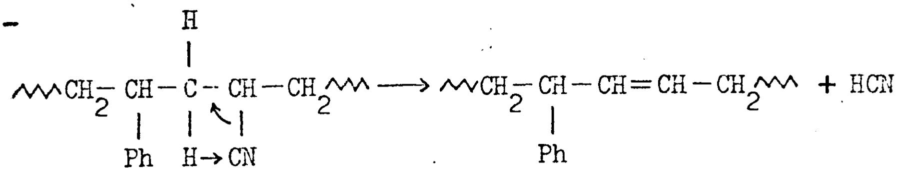
4.4 Examination of the Residue

(a) Molecular Weight Measurement

The most important property of the residue left after thermal degradation is the molecular weight and this is discussed in Chapters 3 and 5. Molecular weight measurement is facilitated by the ready solubility of all the degradation residues, except SA9, in toluene. The physical properties of the copolymers containing up to 33 per cent acrylonitrile resemble those of polystyrene. The 50 per cent copolymer (SA9) is more like polyacrylonitrile however, being insoluble in toluene.

(b) Spectroscopic Examination

The residues from the high acrylonitrile copolymers, particularly SA9, show signs of slight colouration. IR and U-V examinations indicate unsaturation in the main chain. The ethylenic peak at 1625 cm.$^{-1}$ present in the infra-red spectra of chain fragments is also observed in the residue. Only SA9 and SA10 show any significant absorption in the 275-400 mμ region of the ultra violet spectrum (Fig. 4.5), indicating that unsaturation is associated with the acrylonitrile units. The presence of hydrogen cyanide in the reaction products suggests that the following reaction may be taking place:-



$$\sim CH_2-\underset{Ph}{CH}-\overset{H}{\underset{H\rightarrow}{C}}-\underset{CN}{CH}-CH_2\sim \longrightarrow \sim CH_2-\underset{Ph}{CH}-CH=CH-CH_2\sim + HCN$$

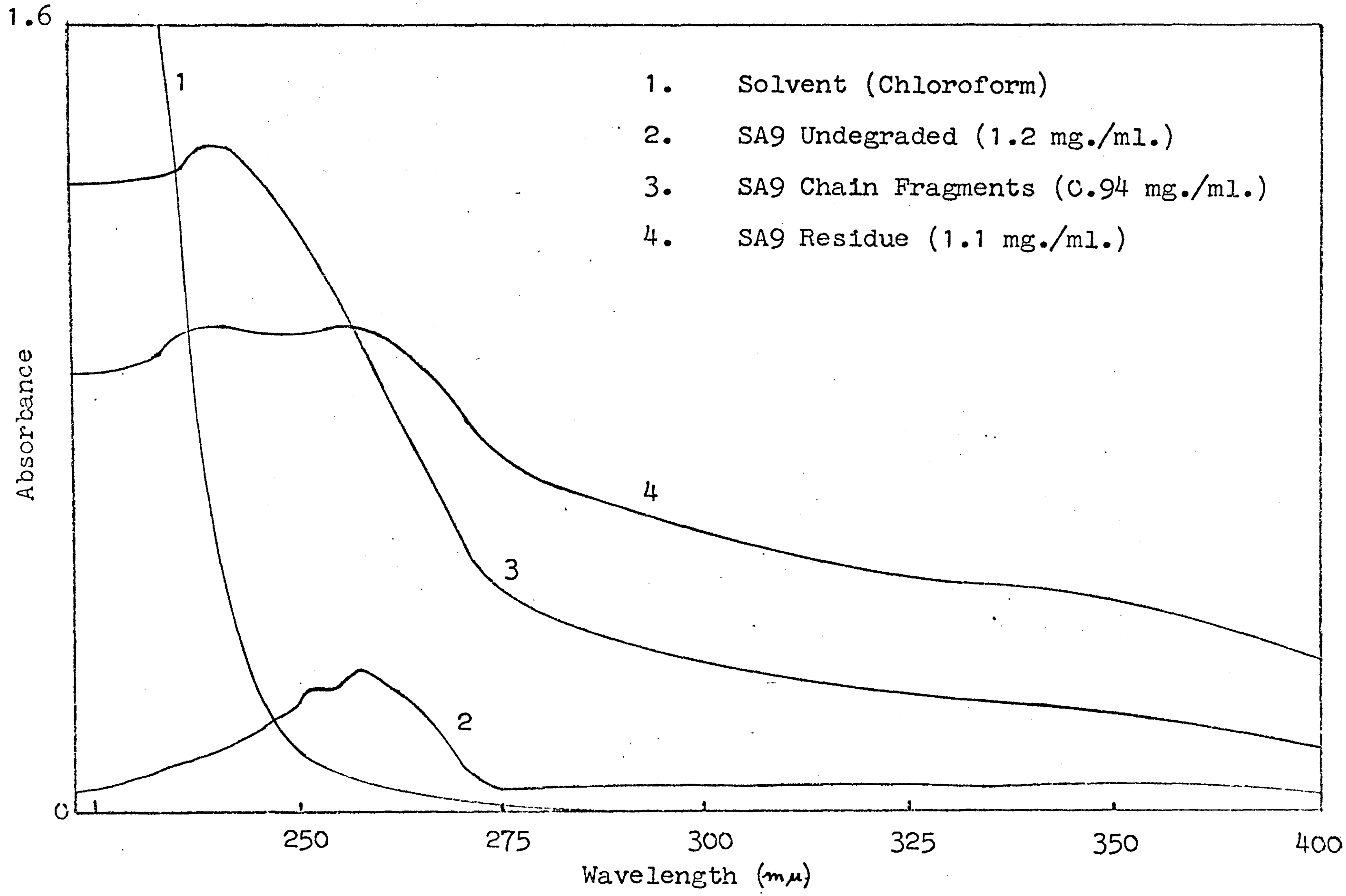


Fig. 4.5 UV Spectra of Undegraded SA9 and the Products of Degradation

This reaction will not lead to long sequences of unsaturation but in the case of SA9 (50 per cent acrylonitrile) can lead to 2 or 3 conjugated double bonds in the polymer backbone. The cyclisation of the nitrile units, so significant in the degradation of polyacrylonitrile, does not occur because of the separation of the acrylonitrile units by styrene. The blocking effect of styrene units in the colouration of polyacrylonitrile has been discussed by Grassie and Hay.[42]

4.5 Conclusions

The products of the degradation of styrene/acrylonitrile copolymers containing up to 50 per cent acrylonitrile can be explained by a mechanism involving depolymerisation and intramolecular transfer. The depropagation step can pass through one unit of acrylonitrile in every two, thus explaining the presence of acrylonitrile in the copolymers. This also gives some measure of the blocking effect of acrylonitrile units. The increase in the amount of chain fragments formed suggests that the second encounter results in intramolecular transfer.

The structures of the chain fragments are in keeping with the mechanism proposed for their formation, namely intramolecular transfer at radical chain ends. The presence of small quantities of hydrogen cyanide in the volatiles can account for the low unsaturation indicated by U-V spectroscopy. Nitrile conjugation and propagation cross linking do not occur because the acrylonitrile units are separated by styrene units.

CHAPTER 5

THE CHAIN SCISSION REACTION IN STYRENE/ACRYLONITRILE COPOLYMERS

5.1 Introduction

As in the case of polystyrene, attention inevitably focuses on the chain scission reaction as a vital controlling factor in the degradation. Results of degradations at 292°C (Chapter 3) show that the investigation of changes in molecular weight is considerably complicated by the production of volatiles. In a detailed study of the chain scission reaction in polystyrene, Kerr has collected information at temperatures which precluded the formation of volatiles.[34] This work is reviewed in Chapter 1. Kerr effectively demonstrated the presence of "weak links" in thermally initiated polystyrenes and also showed that the "normal" scission reaction proceeded with an activation energy of approximately 15 kcal./mole lower than the value calculated for carbon-carbon scission in polystyrene. In a study of polystyrenes prepared by free radical techniques, McNeill found unsaturation in the polymer backbone.[36] Kerr has suggested that the low activation energy observed for "normal" scission in polystyrenes prepared by free radical techniques is due to scission of bonds β to the carbon-carbon double bonds.[34] In a preliminary investigation of styrene/acrylonitrile copolymers, MacCallum suggested that if acrylonitrile units are incorporated in the polystyrene chain, they also cause "weak links".[80]

5.2 Theoretical Treatment of Random Scission in a Closed System

Since the degradations discussed in this section were carried out with negligible volatilisation, the theoretical approach initiated by Kuhn[81] and developed by others[3,35] may be applied to the chain scission in the copolymers.

If CL_o = initial chain length,

CL = chain length after degradation for time t,

N = number of bonds broken per polymer molecule after time t,

then
$$N = \frac{CL_o}{CL} - 1 \qquad (1)$$

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

$$\alpha = \frac{N}{CL_o - 1} \qquad (2)$$

$$= 1 - e^{-kt} \qquad (3)$$

where k is a first order rate constant for bond scission.

Combining equations (1), (2) and (3) we get,

$$\frac{CL - 1}{CL} = \frac{CL_o - 1}{CL_o} \cdot e^{-kt} \qquad (4)$$

therefore
$$-\ln\left[\frac{CL - 1}{CL}\right] = -\ln\left[\frac{CL_o - 1}{CL_o}\right] + kt \qquad (5)$$

When $(CL)^{-1}$ is small, that is molecular weight is high,

$$\frac{1}{CL} - \frac{1}{CL_o} = kt \qquad (6)$$

but $$\frac{1}{CL} - \frac{1}{CL_o} = \alpha, \quad \text{when} \quad \alpha < 1,$$

therefore $$\alpha = kt \qquad (7)$$

Multiplying both sides of (6) by $1/m$, where m is the average monomer unit weight,

$$\frac{1}{Mn_t} - \frac{1}{Mn_o} = \frac{kt}{m} \qquad (8)$$

where Mn_t, and Mn_o are the number average molecular weights of the degraded and undegraded polymers respectively.

From (7), a graph of α against time should be a straight line passing through the origin. In his work on polystyrenes, Kerr found that, whereas anionic polystyrenes obeyed this relationship, a positive α-ordinate intercept was obtained for thermally initiated polystyrenes.[34] This was taken as indicating "weak links" in polystyrenes prepared by a free radical mechanism. The value of the α-intercept has been suggested as a more sensitive method of measuring "weak links" than the extrapolation of the linear region of the molecular weight against percentage volatilisation graph used by Grassie and Kerr.[22] In view of the observations of Kerr[34] and the results of the present work at 292°C it seemed desirable to study the chain scission reaction by the methods discussed.

5.3 Degradation at 262°C

(a) Chain Scission in Copolymers of Different Compositions

Preliminary degradation in the molecular still showed that the region 240-265°C would be satisfactory for the investigation of chain scission. In this temperature range measurable molecular weight changes occur with little volatilisation.

100 mg. samples of the copolymers were degraded in the molecular still for periods of up to 10 hours. Attempts to degrade for longer resulted in appreciable volatilisation, a problem encountered particularly with copolymers of high acrylonitrile concentration. The results of a series of degradations at 262°C are shown in Table 5.1 and 5.2. Fig. 5.1 illustrates the change in molecular weight with degradation time. The rapid molecular weight drop at the beginning of the reaction, usually associated with "weak link" scission in polystyrene, is also observed in the copolymers at this temperature. Fig.5.2 and 5.3 show graphs of $(Mn_t)^{-1}$ against time and α against time. In Fig. 5.2 the intercepts obtained at $t = 0$ are not the various $(Mn_o)^{-1}$ values expected from random scission theory. Similarly the α against time graph shows positive ordinate

Table 5.1

Results of Degradation at 262^{o}C

Copolymer Code	Degradation Time(hr.)	% Volatilisation	Mn x 10^{-5}	Mn^{-1} x 10^{5}	Mn as % of Original
PS3	0	0	4.7	0.214	100
	3	0.3	2.14	0.467	45.6
	6	0.1	1.92	0.521	41.0
	8	0.5	1.85	0.541	39.5
	10	0.4	1.81	0.554	38.6
SA8	0	0	3.31	0.302	100
	3	0.7	1.63	0.615	49
	6	1.7	1.35	0.740	40.7
	8	2.0	1.31	0.763	39.4
	10	1.4	1.20	0.832	36.2
SA3	0	0	4.11	0.243	100
	3	0.8	1.68	0.597	40.8
	6	1.2	1.56	0.642	37.9
	8	1.6	1.21	0.826	29.4
	10	1.3	1.11	0.900	27.0
SA6	0	0	4.70	0.214	100
	1	1.8	1.73	0.578	37
	3	2.1	1.48	0.675	31.6
	6	3.0	1.10	0.910	23.5
	8	3.9	0.94	1.065	19.9
SA5	0	0	6.5	0.154	100
	3	1.4	1.42	0.705	21.9
	6	2.0	1.04	0.960	16
	8	3.0	0.80	1.24	12.3
	10	3.5	0.68	1.475	10.4
SA10	0	0	3.66	0.281	100
	1	1.25	1.45	0.690	39.6
	2	1.7	1.18	0.850	32.2
	3	2.1	1.22	0.820	33.4
	4	2.5	0.95	1.03	26
	6	3.15	0.77	1.30	21.0
	8	7.1	0.51	1.82	13.9

Table 5.2

Calculation of α from Degradations at 262°C

Copolymer Code	Degradation Time (hr.)	$\bar{M}n \times 10^{-5}$	$CL \times 10^{-3}$	$CL^{-1} \times 10^{3}$	$\alpha \times 10^{3}$
PS3	0	4.7	4.5	0.22	0
	3	2.14	2.06	0.49	0.27
	6	1.92	1.85	0.54	0.32
	8	1.85	1.78	0.56	0.34
	10	1.81	1.74	0.58	0.36
SA8	0	3.31	3.26	0.31	0
	3	1.63	1.61	0.63	0.32
	6	1.35	1.33	0.75	0.44
	8	1.31	1.29	0.78	0.47
	10	1.20	1.18	0.85	0.54
SA3	0	4.11	4.11	0.24	0
	3	1.68	1.68	0.60	0.36
	6	1.56	1.56	0.64	0.40
	8	1.21	1.21	0.83	0.59
	10	1.11	1.11	0.90	0.66
SA6	0	4.70	4.9	0.2	0
	1	1.73	1.8	0.56	0.36
	3	1.48	1.54	0.65	0.45
	6	1.10	1.15	0.87	0.67
	8	0.94	0.97	1.03	0.803
SA5	0	6.5	7.06	0.143	0
	3	1.42	1.55	0.645	0.502
	6	1.04	1.13	0.885	0.742
	8	0.80	0.87	1.15	1.00
	10	0.68	0.74	1.35	1.207
SA10	0	3.66	4.21	0.24	0
	1	1.45	1.67	0.60	0.36
	2	1.18	1.36	0.74	0.50
	3	1.22	1.4	0.72	0.48
	6	0.77	0.89	1.13	0.89
	8	0.51	0.59	1.70	1.46

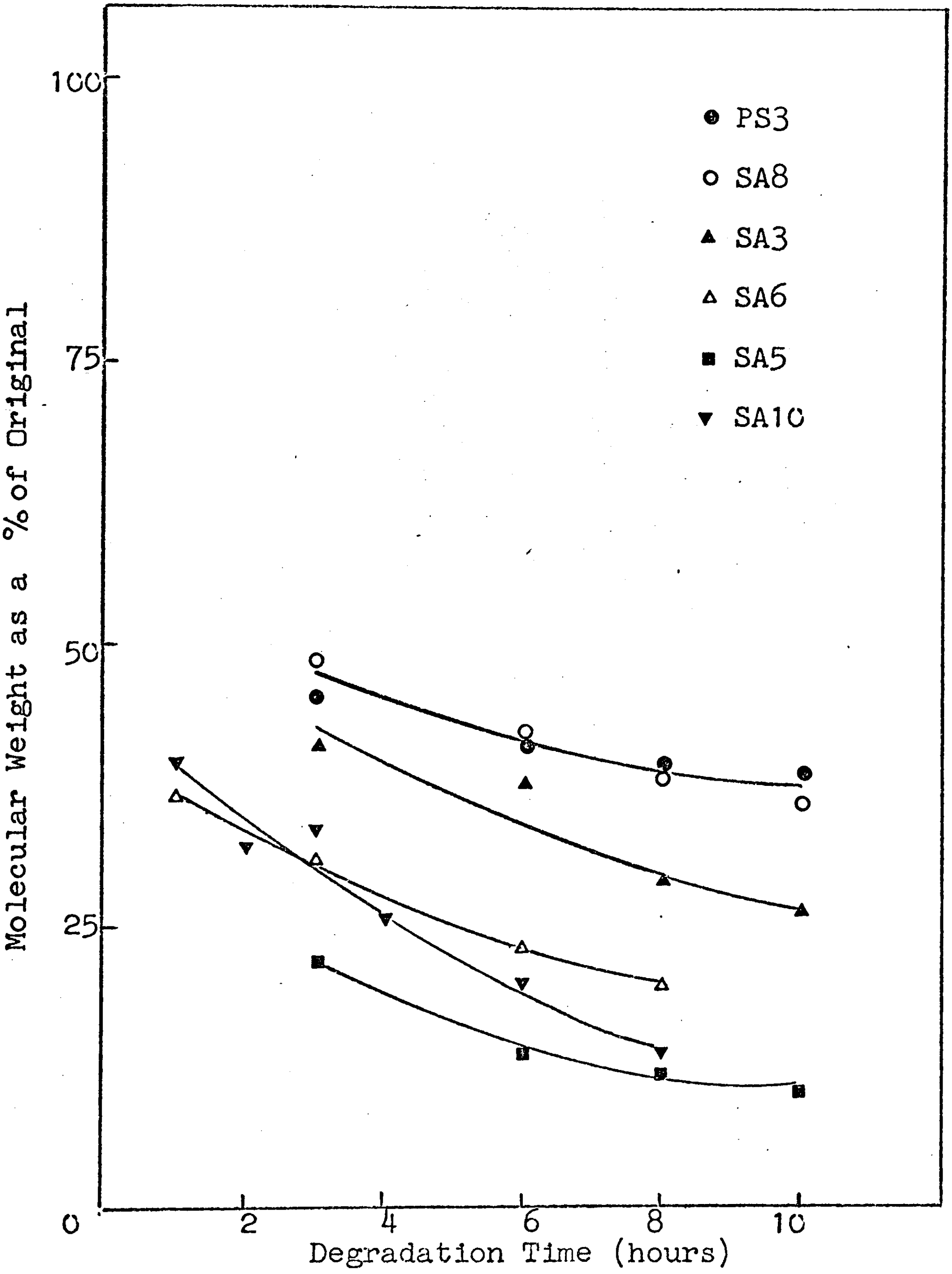


Fig. 5.1 Changes in Molecular Weight with Time of Degradation at 262°C

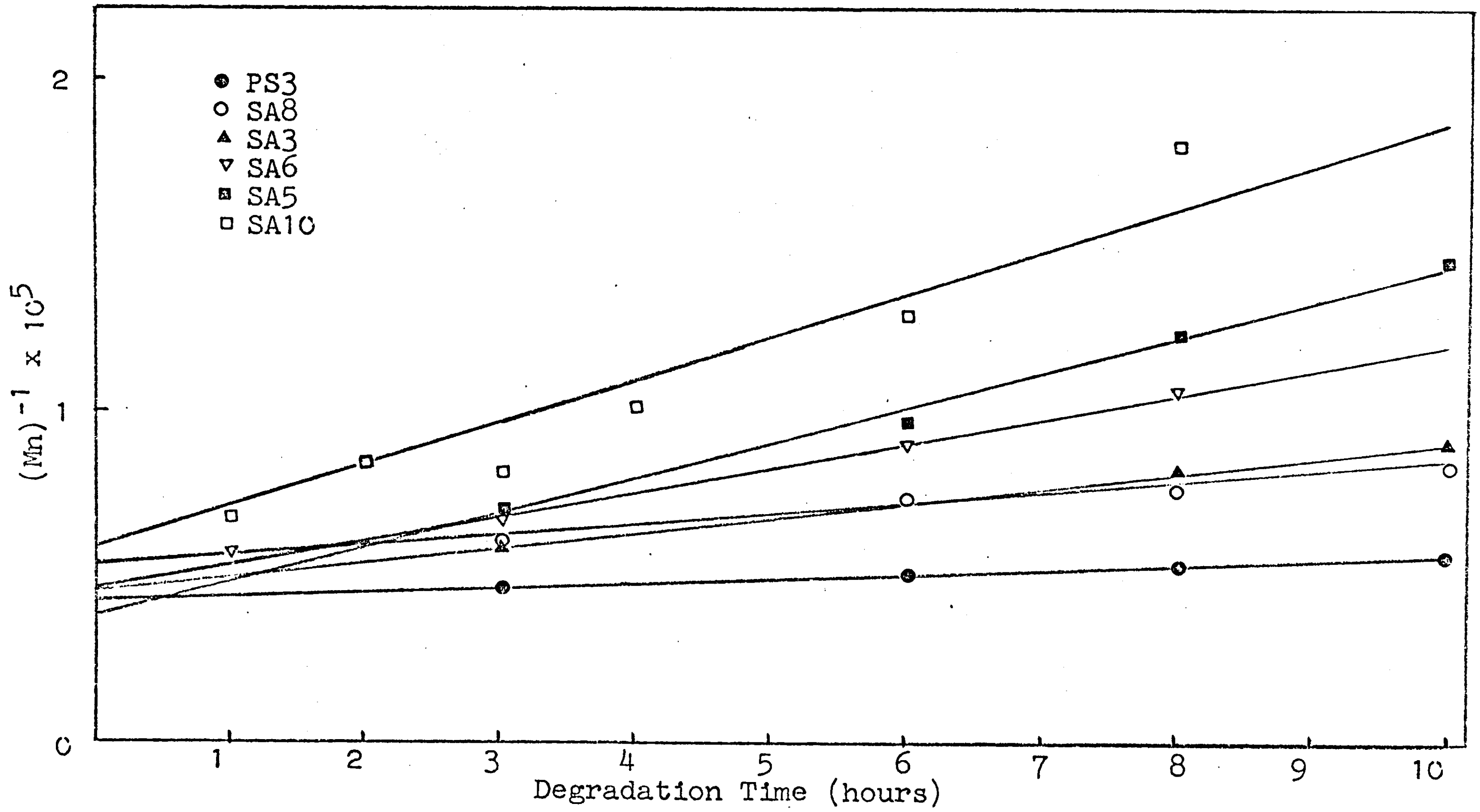


Fig. 5.2 $(Mn)^{-1}$ against Time of Degradation at 262°C

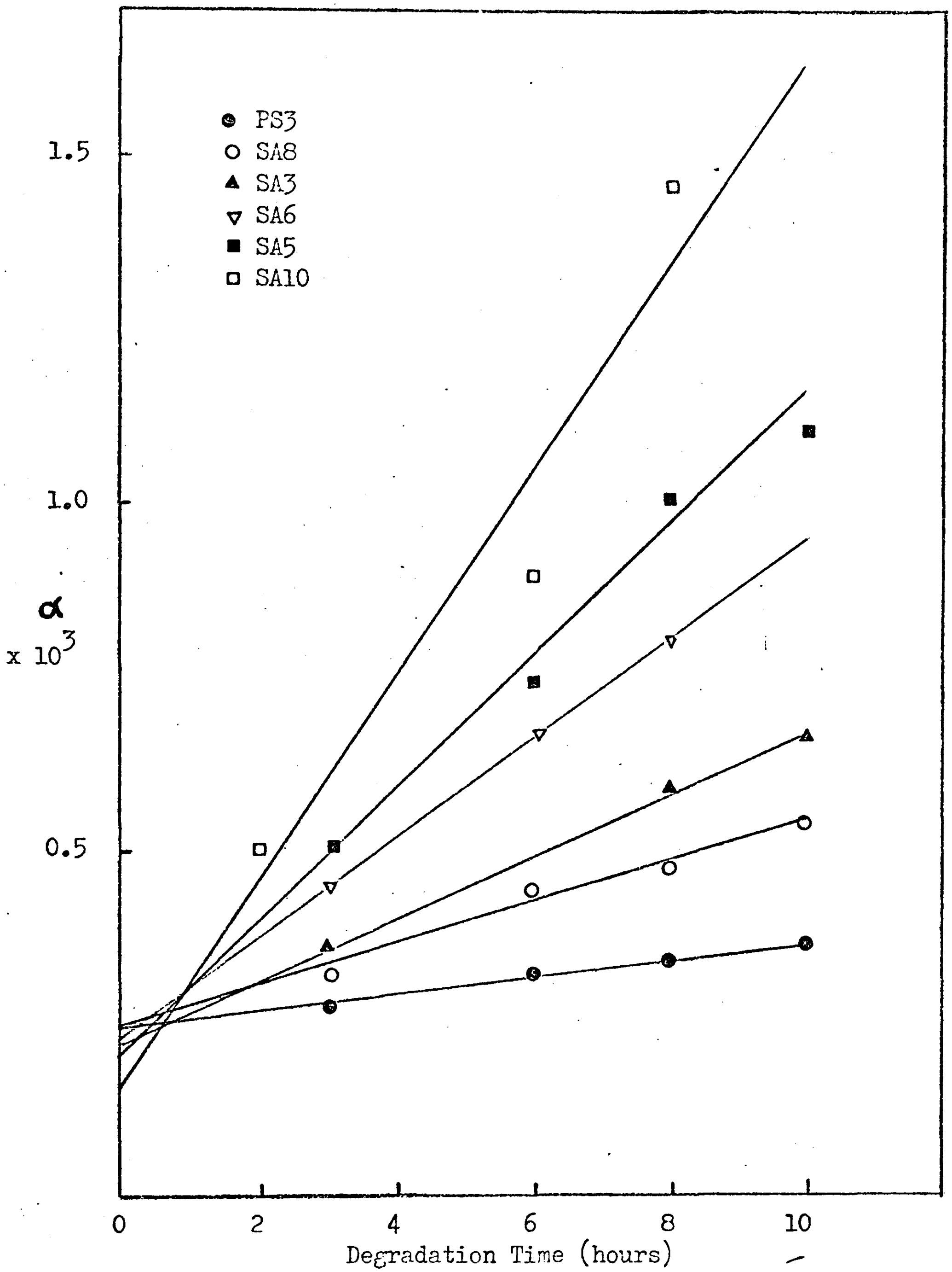


Fig. 5.3 Fraction of Original Bonds Broken against Degradation Time at 262°C

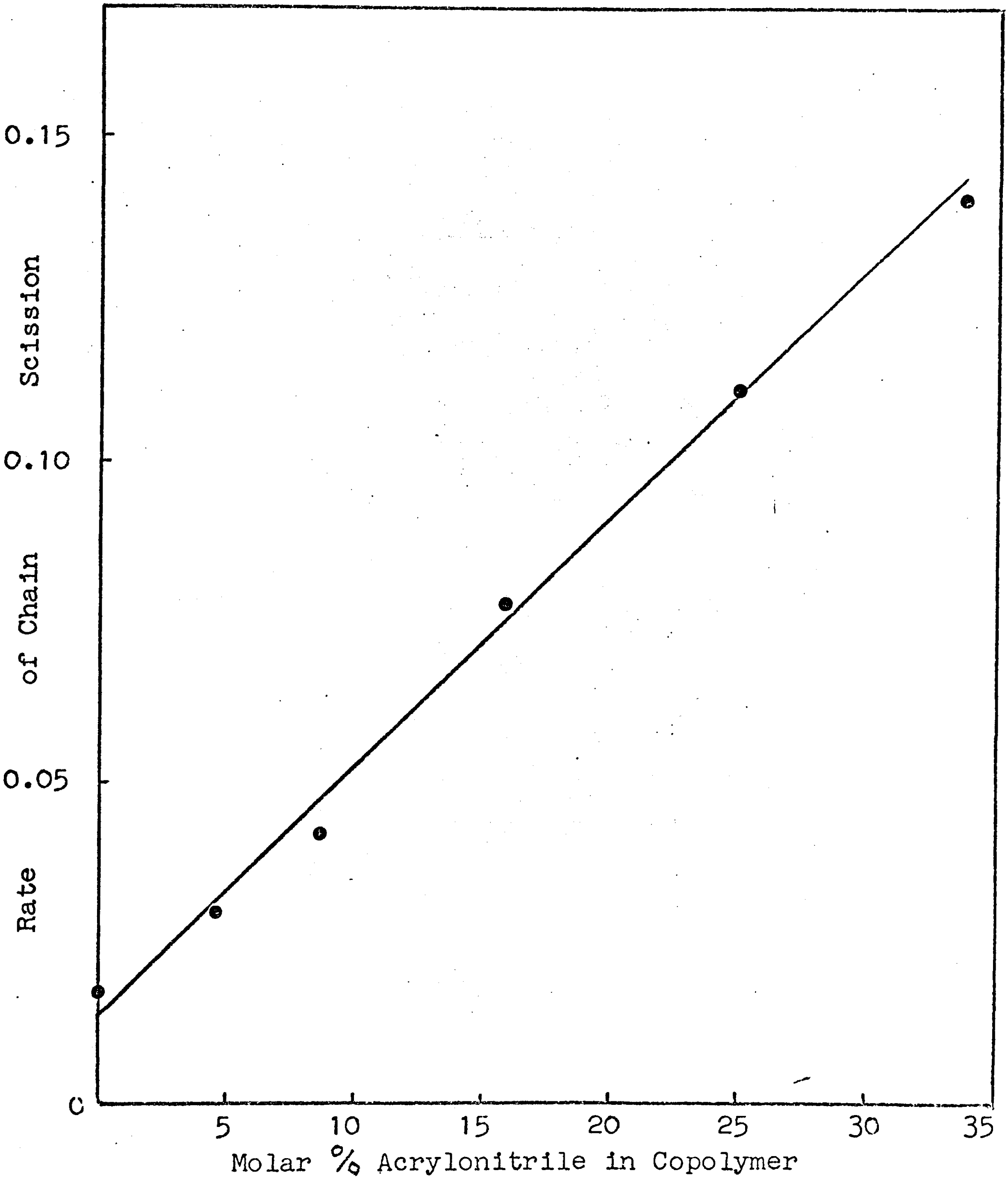


Fig. 5.4 Rate of Chain Scission at 262°C as a function of the Acrylonitrile Concentration of the Copolymers

intercepts. Both these effects are indicative of "weak links" in the chain. The gradients from Fig. 5.2 are shown in Table 5.3 and illustrated as a graph of rate of scission against molar percentage of acrylonitrile in the copolymer in Fig. 5.4.

Table 5.3

Rate of Chain Scission at 262°C

(from Fig. 5.2)

Copolymer Code	% Acrylonitrile in Copolymer	Rate of Scission
PS3	0	0.018
SA8	4.7	0.030
SA3	8.4	0.042
SA6	15.5	0.078
SA5	24.9	0.110
SA10	33.4	0.140

The graph shows that the increase in the rate of chain scission over that of polystyrene is proportional to the acrylonitrile concentration of the copolymer. Although polystyrene also undergoes chain scission at this temperature, a simple kinetic treatment allows the rate constant for scission at acrylonitrile units to be calculated.

$$\text{Rate of chain scission} = k_s(S) + k_a(A) \qquad (1)$$

where S = fraction of styrene in copolymer,

A = fraction of acrylonitrile in copolymer,

and k_s and k_a are rate constants for scissions associated with styrene and acrylonitrile respectively.

$$\text{But} \qquad S = (1 - A) \qquad (2)$$

$$\text{therefore} \qquad \text{Rate} = k_s(1 - A) + k_a(A) \qquad (3)$$

$$= k_s - k_s(A) + k_a(A) \qquad (4)$$

$$= k_s + A(k_a - k_s) \qquad (5)$$

Thus a graph of rate of scission against molar percentage of acrylonitrile in the copolymer should have an ordinate intercept equal to k_s, and a gradient equal to $(k_a - k_s)$. This is shown in Fig. 5.4. From this graph, at 262°C,

$$k_s = 0.018 \text{ hr.}^{-1}$$

$$k_a - k_s = 0.00374 \text{ hr.}^{-1}$$

$$\text{therefore} \qquad k_a = 0.02174 \text{ hr.}^{-1}$$

Using this method to calculate the rate constants for scission associated with acrylonitrile units, it should now be possible to obtain the activation energy for this type of scission. Before discussing this however, other aspects of the 262°C degradations are considered.

The data used to calculate α is presented in Table 5.2. From the α against time graph (Fig. 5.3), the α-ordinate intercepts are obtained and are shown in Table 5.4.

Table 5.4

Values of α Obtained from Degradation at 262°C for Copolymers of Different Acrylonitrile Content

Copolymer Code	α Intercept	% Acrylonitrile	Molecular Weight
PS3	0.25	0	469,000
SA8	0.27	4.7	331,000
SA3	0.225	8.3	411,000
SA6	0.23	15.5	469,000
SA5	0.20	24.9	650,000
SA10	0.14	33.4	366,000

The smallest intercepts are found for copolymers of highest acrylonitrile content, and if α is taken as a measure of the "weak links" it appears that "weak links" are a property of the styrene units in the copolymer.

Since the copolymers show slight differences in molecular weight it is possible that this could have some influence on the "weak link" concentration. This effect was therefore investigated.

(b) Influence of Molecular Weight on the Chain Scission Reaction

To establish the effect of molecular weight on the chain scission reaction, two copolymers with the same concentrations of acrylonitrile but different molecular weights were examined at 262°C. The results are shown in Table 5.5 and illustrated in Fig. 5.5, 5.6 and 5.7.

Table 5.5

The Effect, at 262°C, of Molecular Weight on the Chain Scission Reaction of Copolymers of the Same Acrylonitrile Concentration

Copolymer Code	Degradation Time	$\bar{M}n \times 10^{-5}$	$(\bar{M}n)^{-1} \times 10^{5}$	$CL \times 10^{-3}$	$(CL)^{-1} \times 10^{3}$	$\alpha \times 10^{3}$
SA7	0	8.57	0.117	8.45	0.12	-
	3	2.16	0.463	2.12	0.47	0.35
	6	1.82	0.550	1.80	0.57	0.45
	8	1.65	0.605	1.63	0.61	0.49
	10	1.57	0.637	1.55	0.65	0.53
SA8	0	3.31	0.302	3.26	0.31	-
	3	1.63	0.615	1.61	0.63	0.32
	6	1.35	0.740	1.33	0.75	0.44
	8	1.31	0.763	1.29	0.78	0.47
	10	1.20	0.832	1.18	0.85	0.54

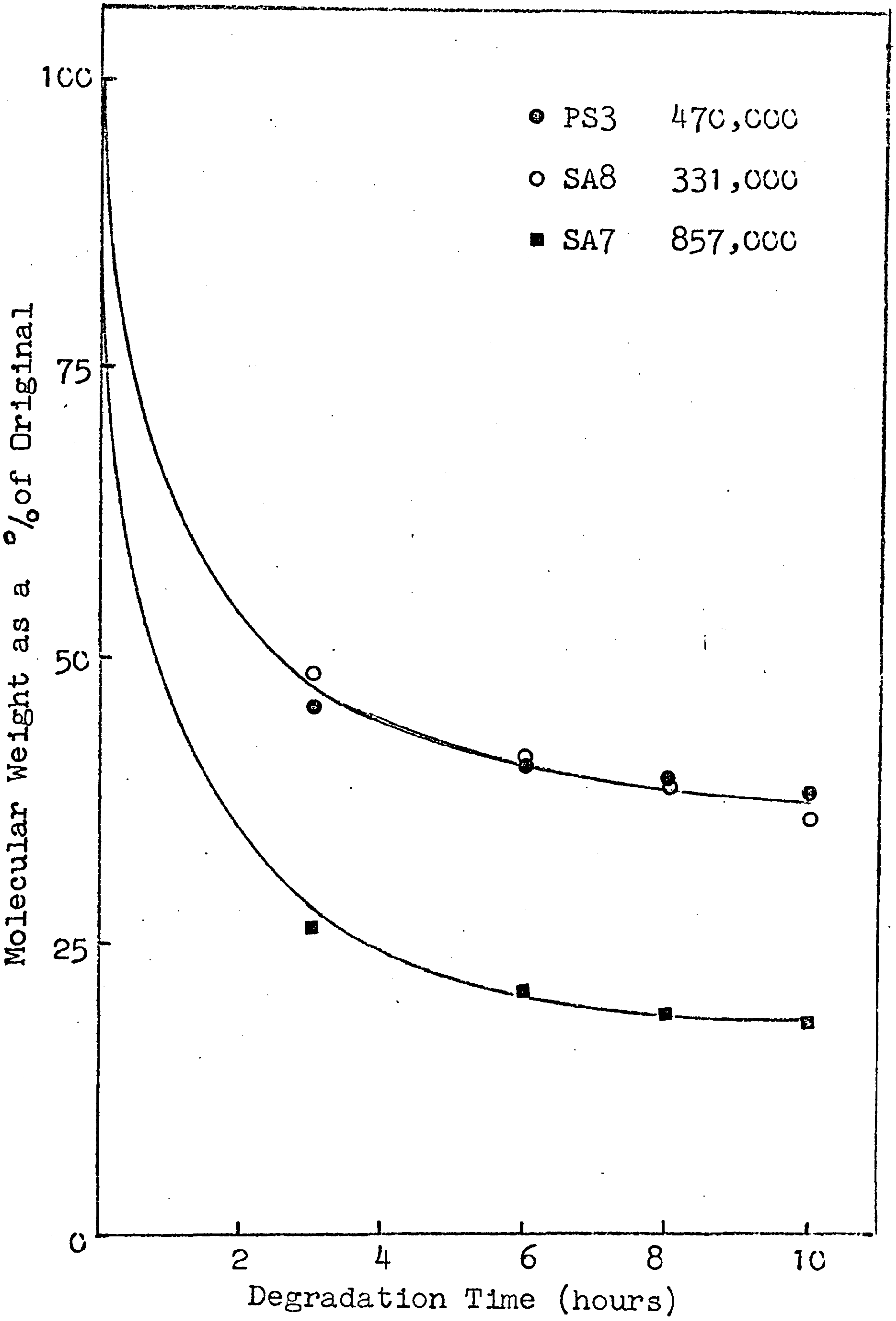


Fig. 5.5 Changes in Molecular Weight with Time of Degradation in Copolymers SA7, SA8 and Polystyrene PS3

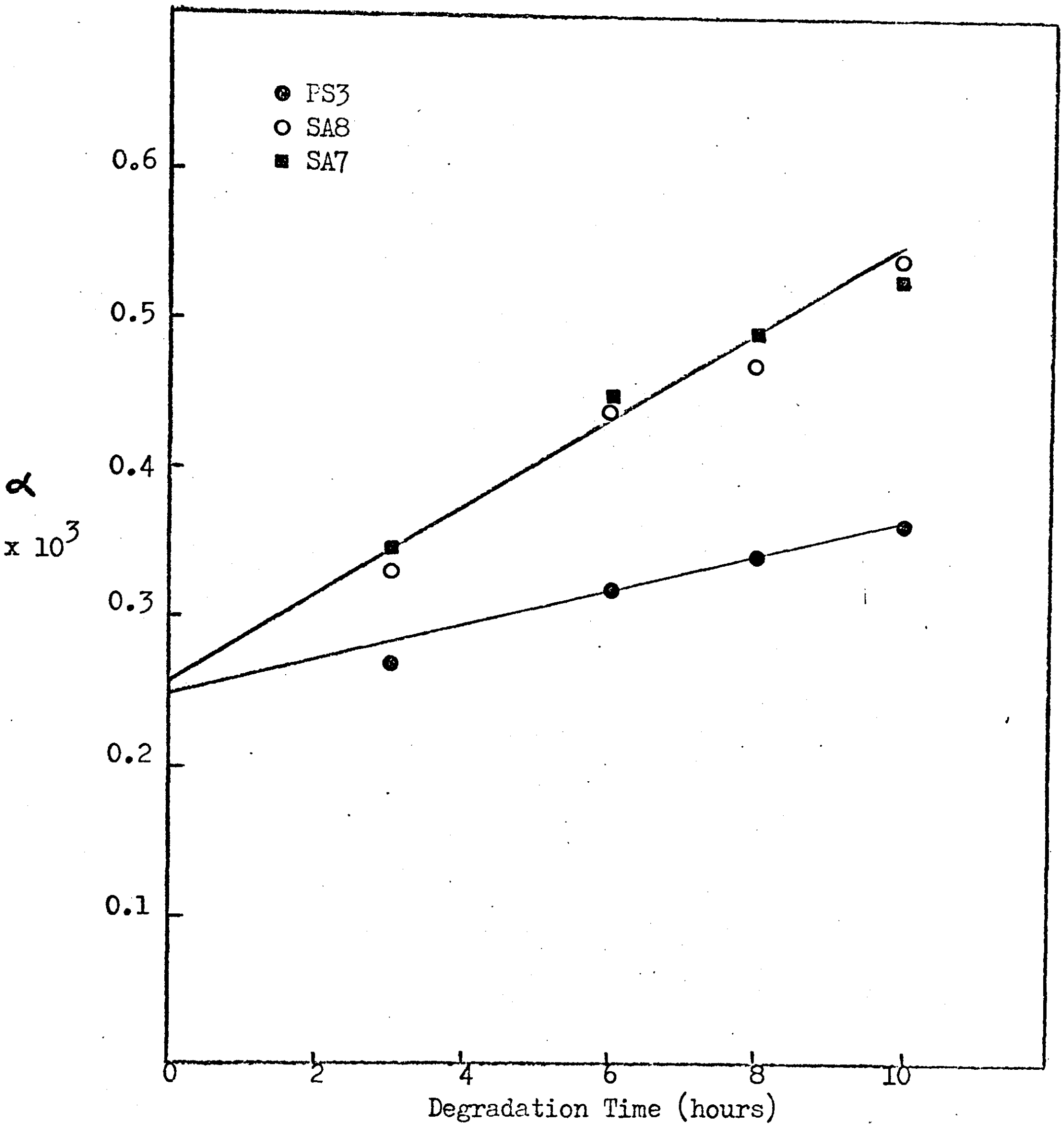


Fig. 5.6 Fraction of Original Bonds Broken against Time of Degradation for Copolymers SA7, SA8 and Polystyrene PS3

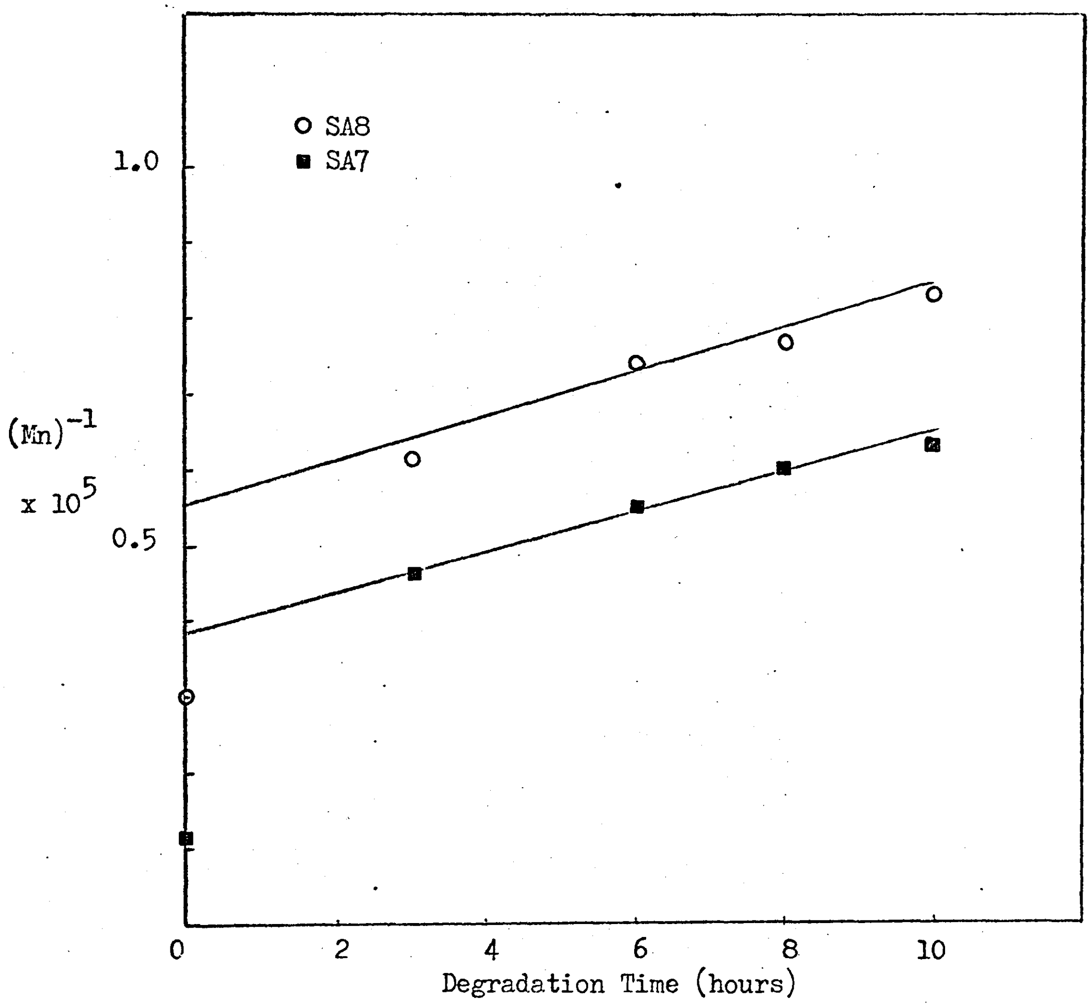


Fig. 5.7 $(Mn)^{-1}$ against Time of Degradation for Copolymers SA7 and SA8 at 262°C

The degradation of the polystyrene "standard" is included for comparison. Both copolymers show identical α-intercepts which, within the limits of experimental error, are the same as those of the polystyrene "standard". The rates of chain scission, measured from the α and (molecular weight)$^{-1}$ graphs are identical, and faster than the corresponding reaction in polystyrene at this temperature. The common value of the α-intercepts reinforces the belief that "weak links" are a property of the styrene units. The observation that no change in the rate of normal scission occurs with increasing molecular weight, is in contrast to the findings of Kerr who showed a non-linear, increasing dependence between the rate of chain scission and the molecular weight in anionic polystyrenes.[34]

(c) Volatilisation at 262°C

To comply with the restrictions on the theoretical treatment of chain scission, only reactions showing less than 2 per cent volatilisation were considered useful in the measurement of rate of chain scission in the previous section. It was apparent however, that, even at temperatures as low as 262°C, volatilisation was becoming a problem, particularly in the copolymers with a high acrylonitrile concentration. Degradations could not be continued for more than 6-8 hours and this severely restricted the range over which the rate of chain scission could be measured. A plot of the change in molecular weight against percentage volatilisation for copolymer SA10 is shown in Fig. 5.8. Comparing the results of volatilisation at 262°C and 292°C, for copolymers SA8 and SA6 (Fig. 5.9 and 5.10 respectively), within the limits of experimental error, the points lie on the same curve. Once the molecular weight has fallen to 20-30 per cent of its original value this represents a considerable number of unstable chain ends which are capable of re-initiation and depropagation to produce volatile products.[33] As in polystyrene, the evidence at 262°C and also the results of isothermal TGA discussed in Chapter 6, favour scission to produce molecules by "cage" disproportion. The increase in volatilisation at 262°C in the copolymers of high acrylonitrile concentration is in keeping with the increased chain scission at acrylonitrile units.

5.4 Degradations at 240°C and 252°C

Having established a kinetic scheme whereby the rate constant for scission at acrylonitrile units could be calculated, and shown that molecular weight does not affect the rate of chain scission, a series of degradations was carried out in an attempt to measure the activation energy of chain scission at acrylonitrile units. As volatilisation was already becoming a problem at 262°C in the copolymers of high acrylonitrile concentration, lower temperatures were used. Degradations were carried out at 252°C and 240°C. The results are presented in Tables 5.6 and 5.7. Fig. 5.11 illustrates the changes in molecular weight at 252°C and again

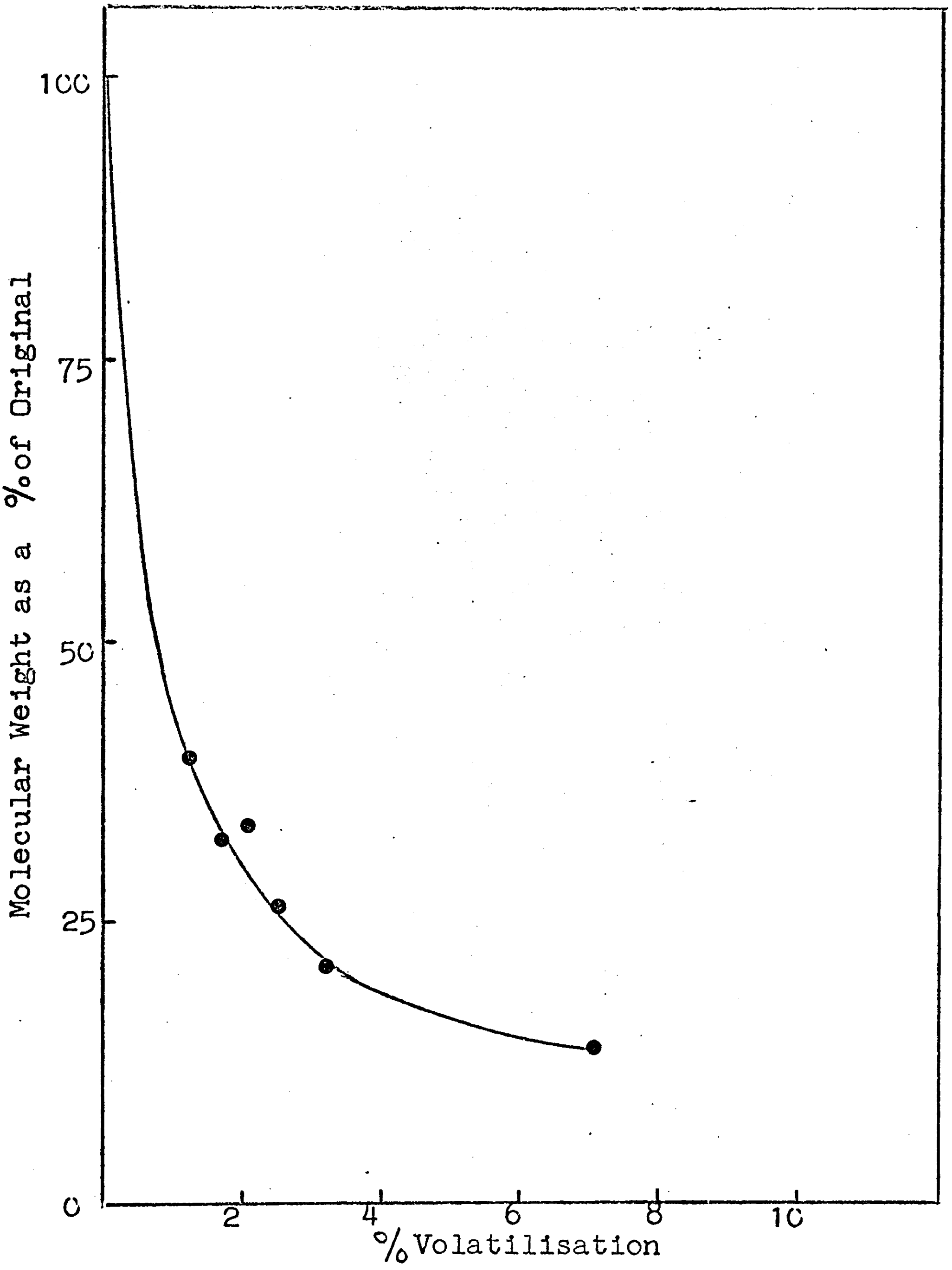


Fig. 5.8 Molecular Weight as a Function of Volatilisation for SA10 at 262°C

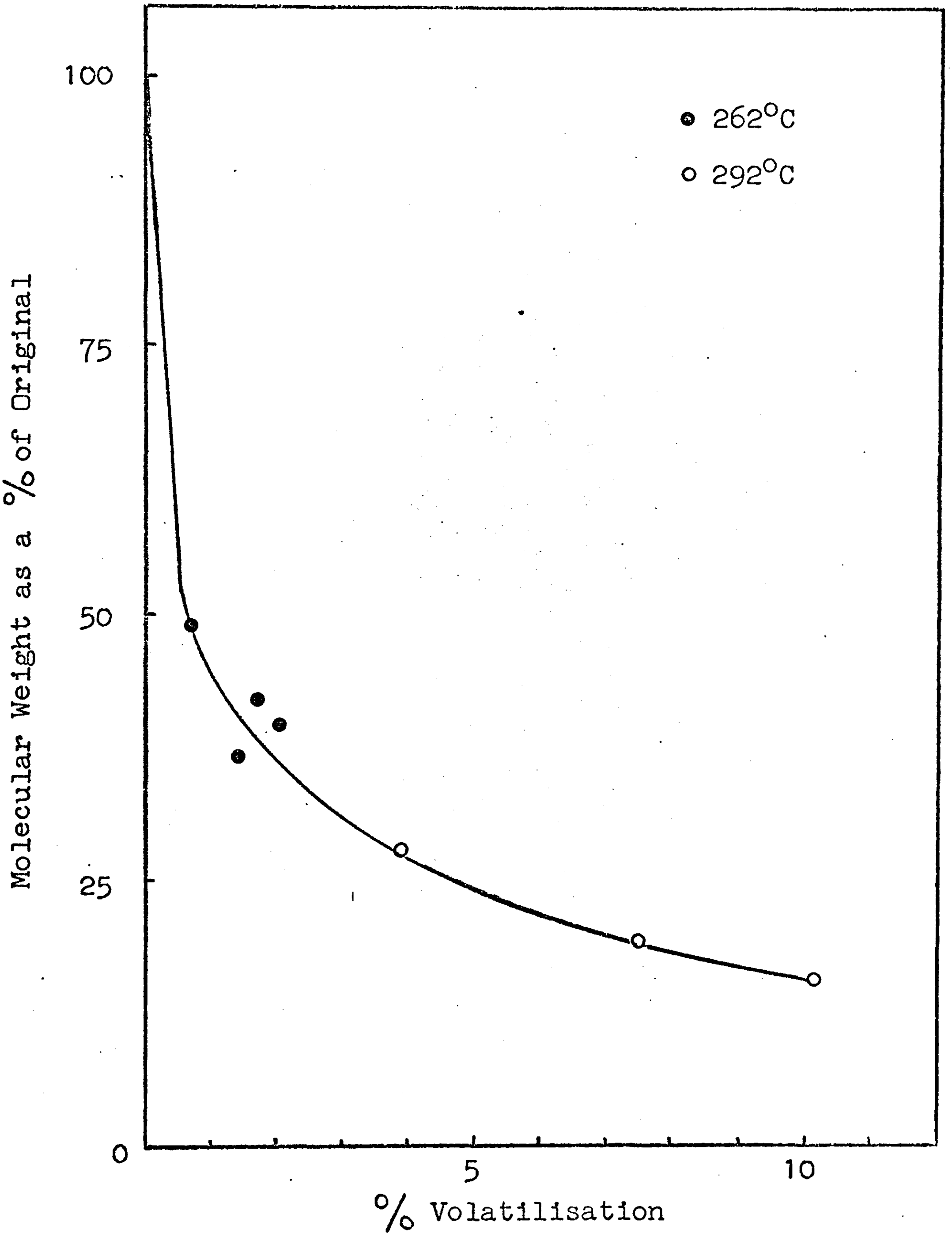


Fig. 5.9 Comparison of the Changes in Molecular Weight with the amount of Volatilisation at 262°C and 292°C in Copolymer SA8

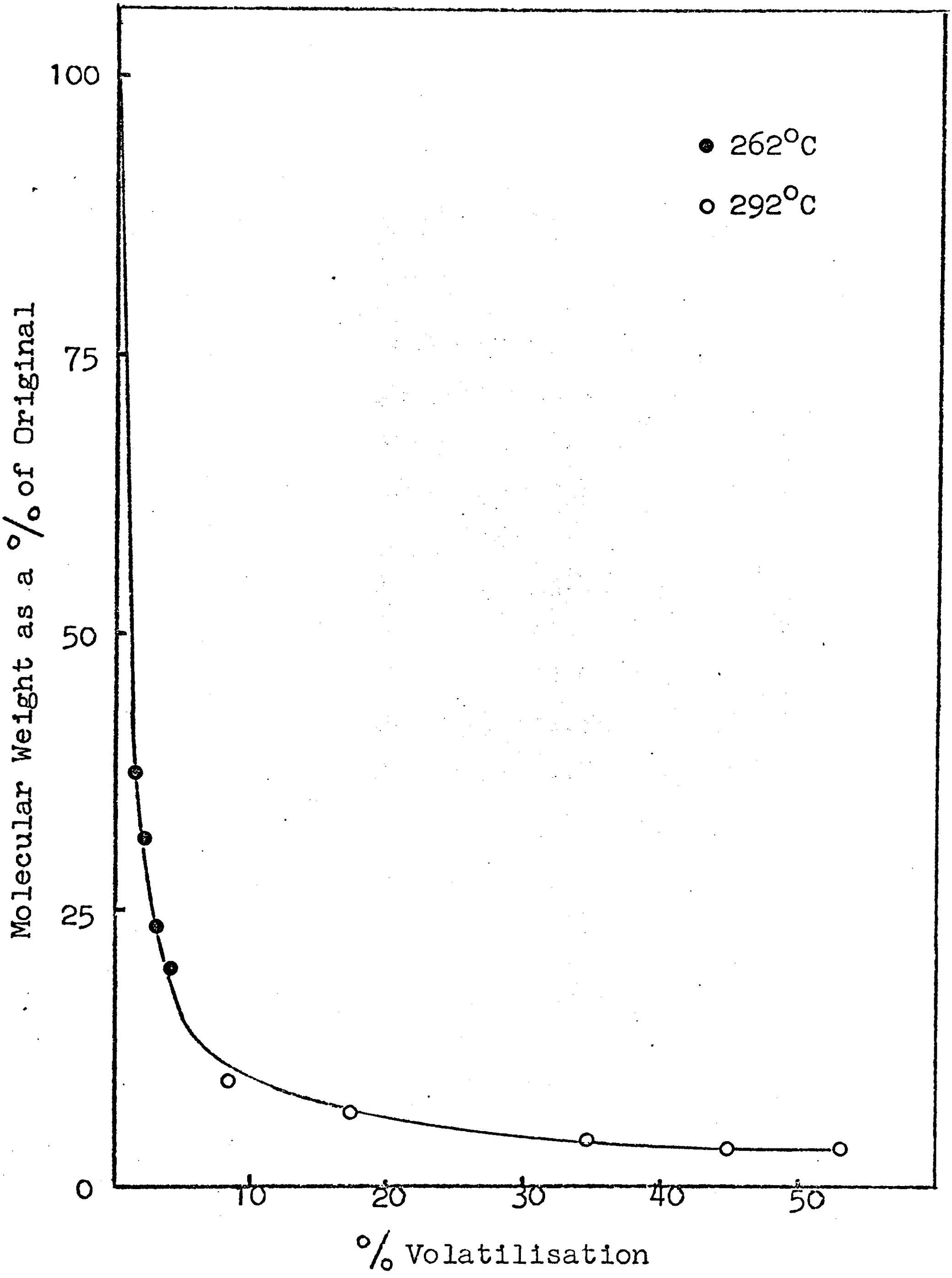


Fig. 5.10 Comparison of the Changes in Molecular Weight with the amount of Volatilisation at 262°C and 292°C in Copolymer SA6

Table 5.6

Degradations of Styrene/Acrylonitrile Copolymers at 252°C

Copolymer Code	Degradation Time	% Volatilisation	(Mn) x 10^{-5}	(Mn)$^{-1}$x 10^{5}	Mn as % Original
SA3	0	0	4.11	0.243	100
	3	1.3	2.46	0.406	60
	6	1.65	2.08	0.480	50.6
	8	2.0	1.93	0.520	47
	10	1.85	1.78	0.562	43.3
SA6	0	0	4.7	0.214	100
	3	2.4	2.32	0.433	49.5
	6	2.5	1.85	0.540	39.2
	8	1.9	1.53	0.653	32.6
	10	2.7	1.37	0.730	29.0
SA5	0	0	6.5	0.154	100
	3	2.7	2.26	0.463	34.8
	6	2.4	1.45	0.690	22.3
	8	3.0	1.27	0.780	19.5
	10	3.4	1.00	1.00	15.4
SA10	0	0	3.66	0.281	100
	3	1.3	1.58	0.635	43.2
	6	1.3	1.19	0.840	32.6
	8	2.4	1.04	0.962	28.5
	10	2.2	0.92	1.08	25.3

Table 5.7

Degradations of Styrene/Acrylonitrile Copolymers at 240°C

Copolymer Code	Degradation Time	% Volatilisation	$(\bar{M}n) \times 10^{-5}$	$(\bar{M}n)^{-1} \times 10^{5}$	Mn as % of Original
SA3	0	0	4.11	0.243	100
	3	1.3	2.18	0.46	53.0
	6	1.5	2.22	0.55	54.0
	8	1.4	2.10	0.47	51.5
	10	1.2	1.86	0.54	45.0
SA6	0	0	4.7	0.214	100
	3	1.6	3.05	0.328	65
	6	1.9	2.58	0.388	55
	8	2.0	1.99	0.50	42.5
	10	1.6	1.87	0.531	40
SA5	0	0	6.5	0.154	100
	3	1.5	2.36	0.424	36.3
	6	1.4	1.92	0.52	29.6
	8	1.7	1.93	0.52	29.7
	10	2.0	1.54	0.650	23.7
SA10	0	0	3.66	0.281	100
	3	1.5	1.89	0.530	51.5
	6	1.6	1.63	0.615	44.5
	8	1.2	1.51	0.662	41.2
	10	1.6	1.44	0.695	39.4
PS3	0	0	4.70	0.214	100
	3	0.4	3.28	0.305	70
	6	0.4	2.07	0.484	63

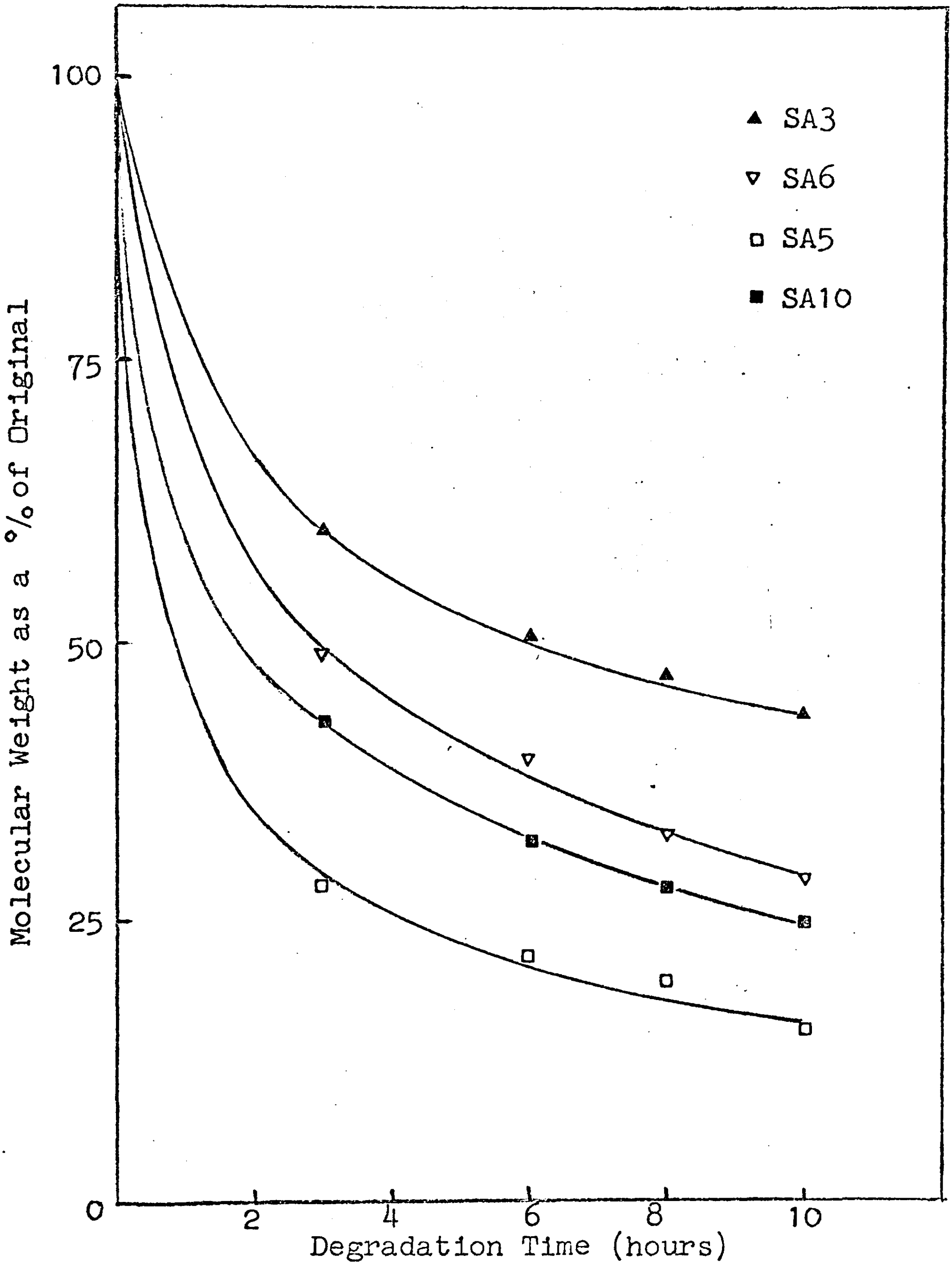


Fig. 5.11 Changes in Molecular Weight with Time of Degradation at 252°C

a rapid initial drop in molecular weight is observed. Fig. 5.12 shows a plot of (molecular weight)$^{-1}$ against time, and the gradients of the lines (the rates of chain scission) plotted against the concentration of acrylonitrile in the copolymers is shown in Fig. 5.13. While an increase in chain scission with increasing acrylonitrile concentration is observed, the relationship between rate and acrylonitrile concentration is not as well defined as at 262°C.

The results of degradation at 240°C are presented in Table 5.7 and illustrated as a molecular weight against time plot in Fig. 5.14 and (molecular weight)$^{-1}$ against time in Fig. 5.15. The rates of chain scission from Fig. 5.15 are illustrated as a function of the acrylonitrile concentration in Fig. 5.16, and it is seen that the relationship so clearly defined at 262°C is no longer obeyed at 240°C.

There are two main reasons for the decreasing relationship between the rate of chain scission and the concentration of acrylonitrile in the copolymers as the temperature of degradation is reduced from 262°C to 240°C.

(1) "Weak link" scission has not been investigated at temperatures as low as this and consequently neither the temperature at which the reaction begins, nor the limits of "weak link" scission have been determined. At 240°C considerable overlap may be occurring between scission at "weak links"

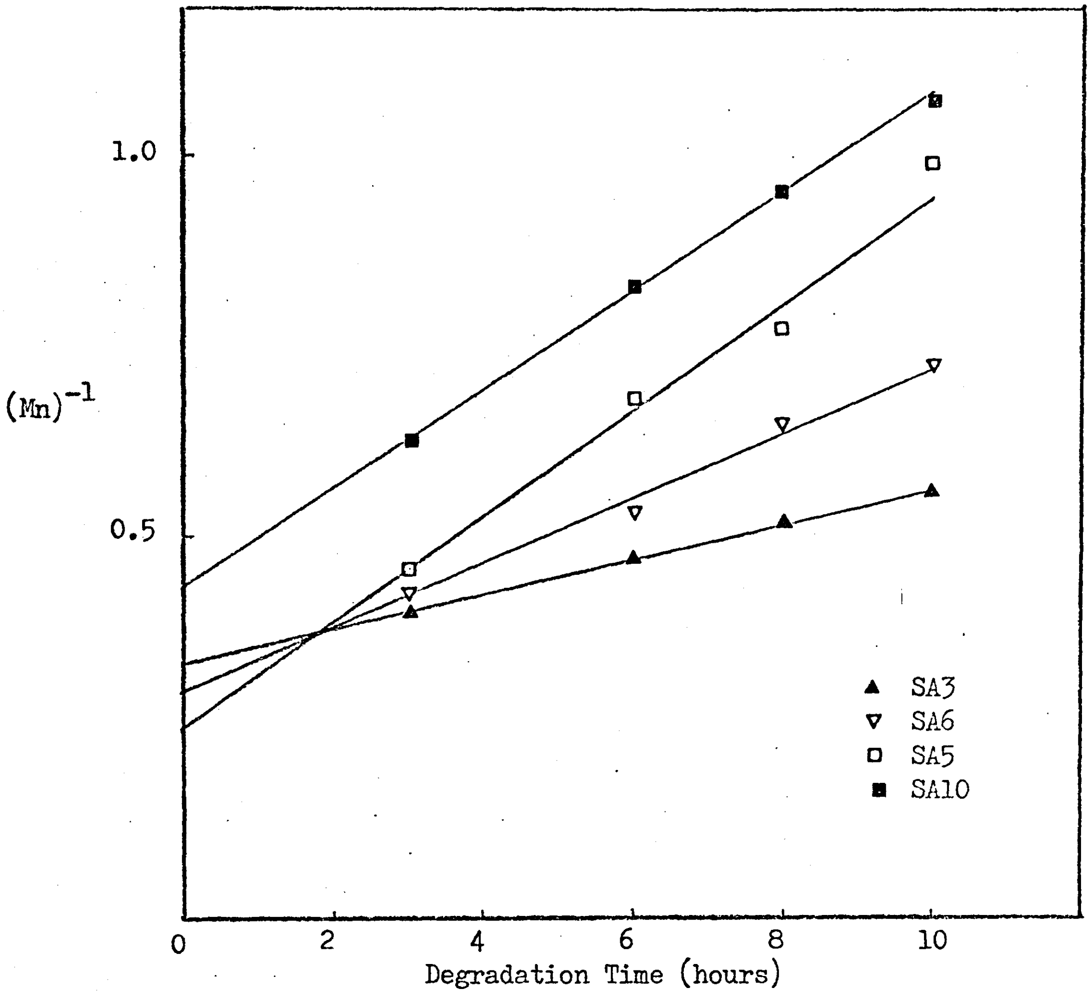


Fig. 5.12 $(Mn)^{-1}$ against Time of Degradation at 252°C

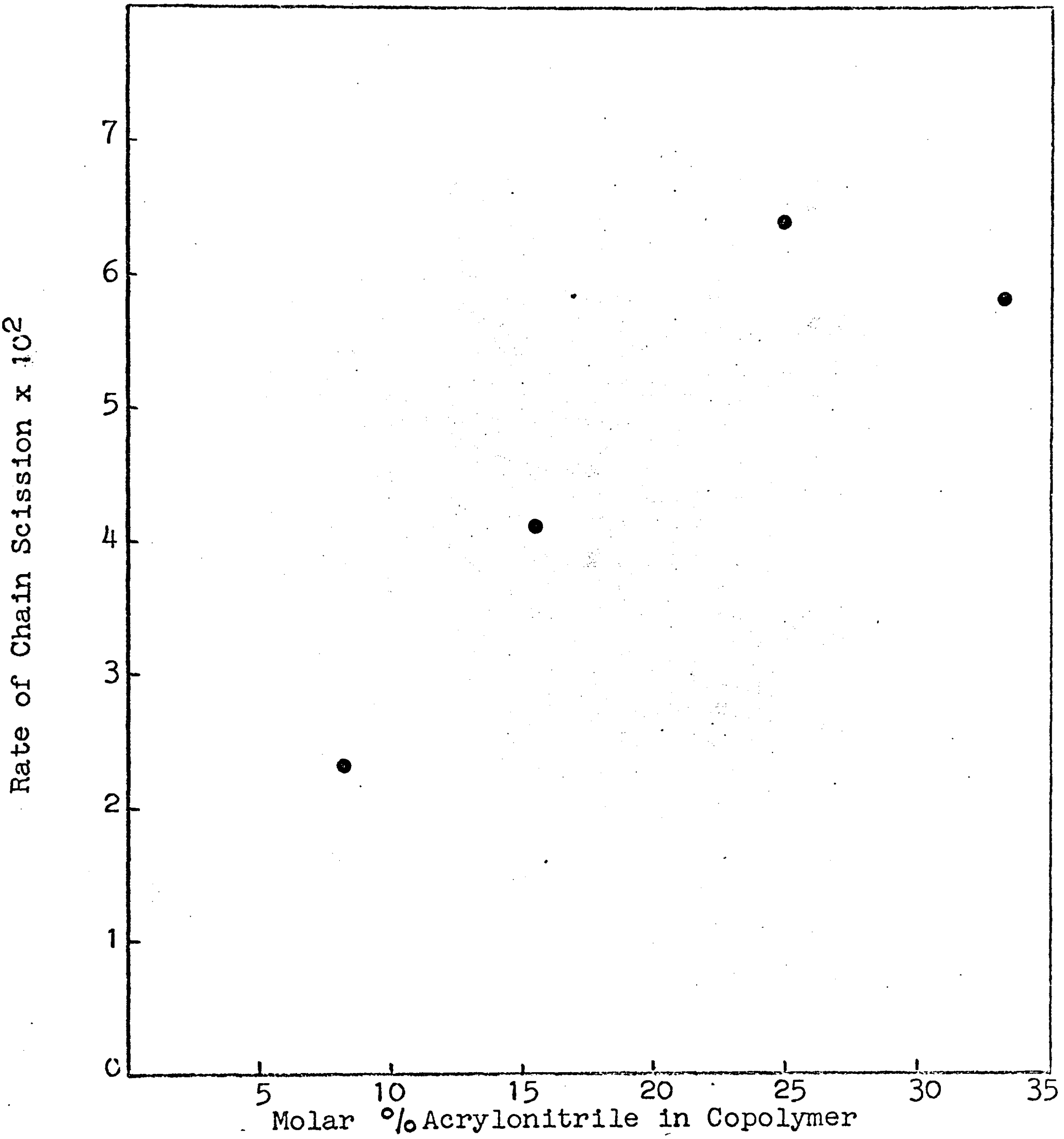


Fig. 5.13 Rate of Chain Scission at 252°C as a function of the Acrylonitrile Concentration of the Copolymers

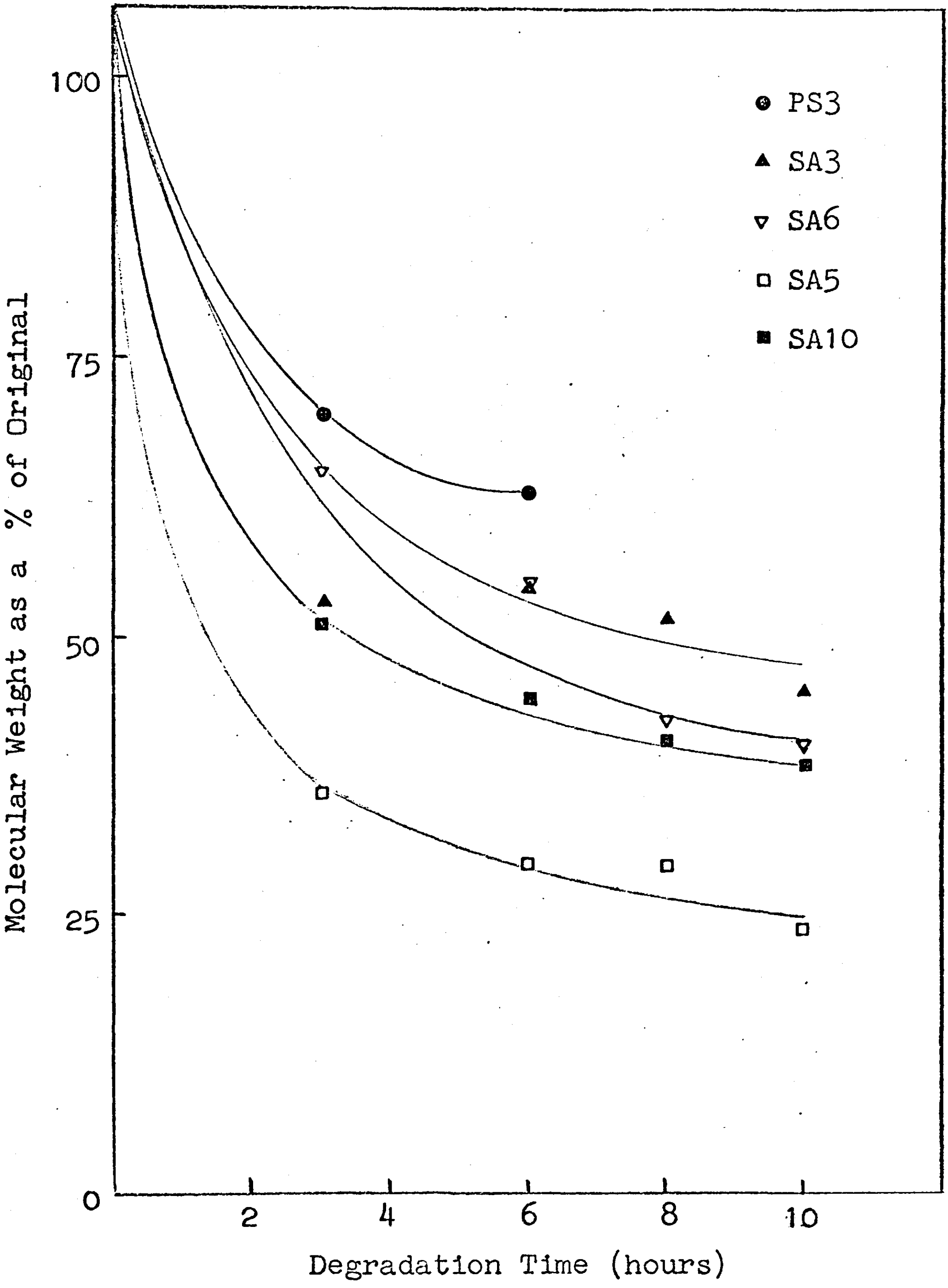


Fig. 5.14 Changes in Molecular Weight with Time of Degradation at 240°C

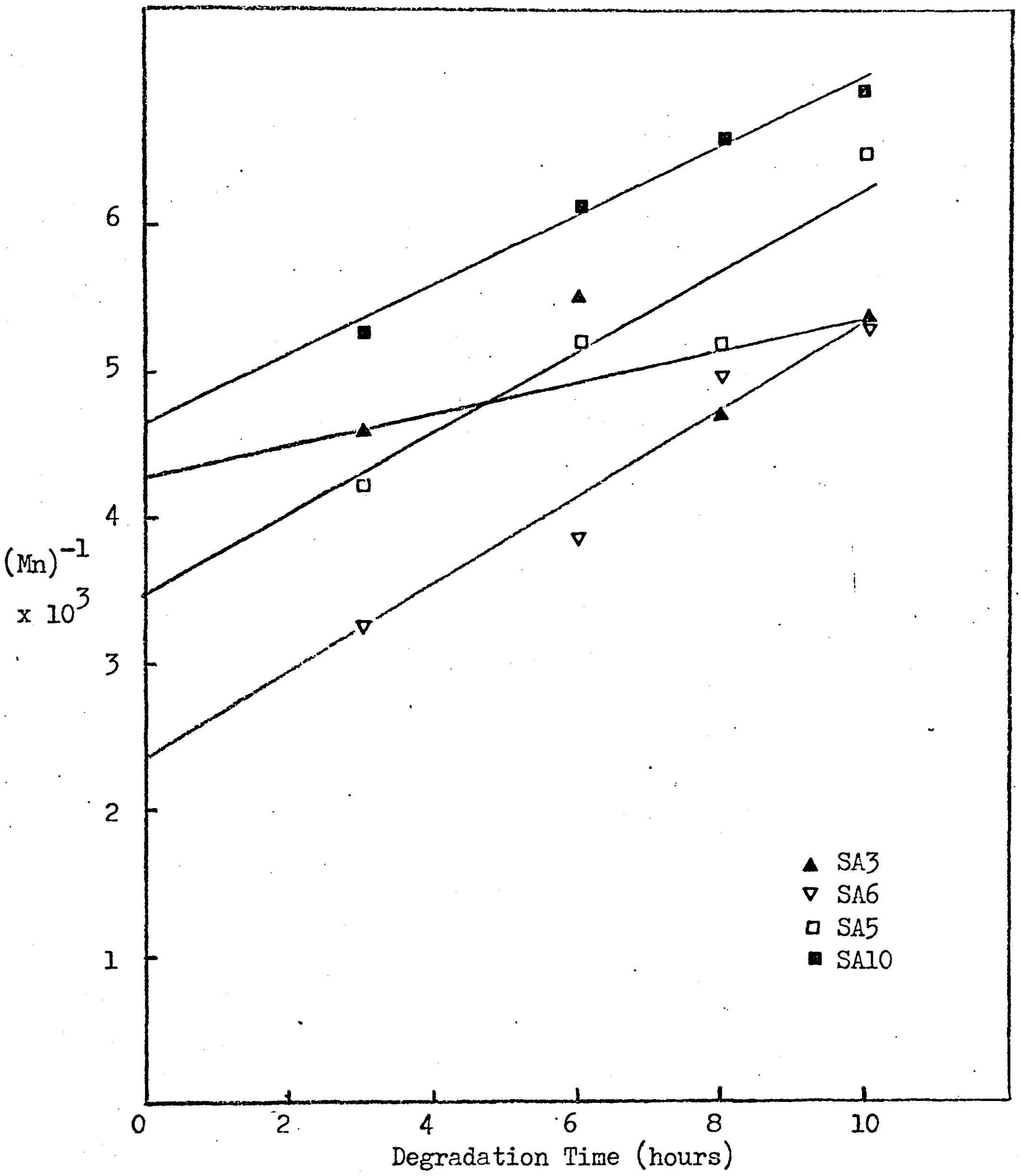


Fig. 5.15 $(\overline{M}n)^{-1}$ against Time of Degradation at 240°C

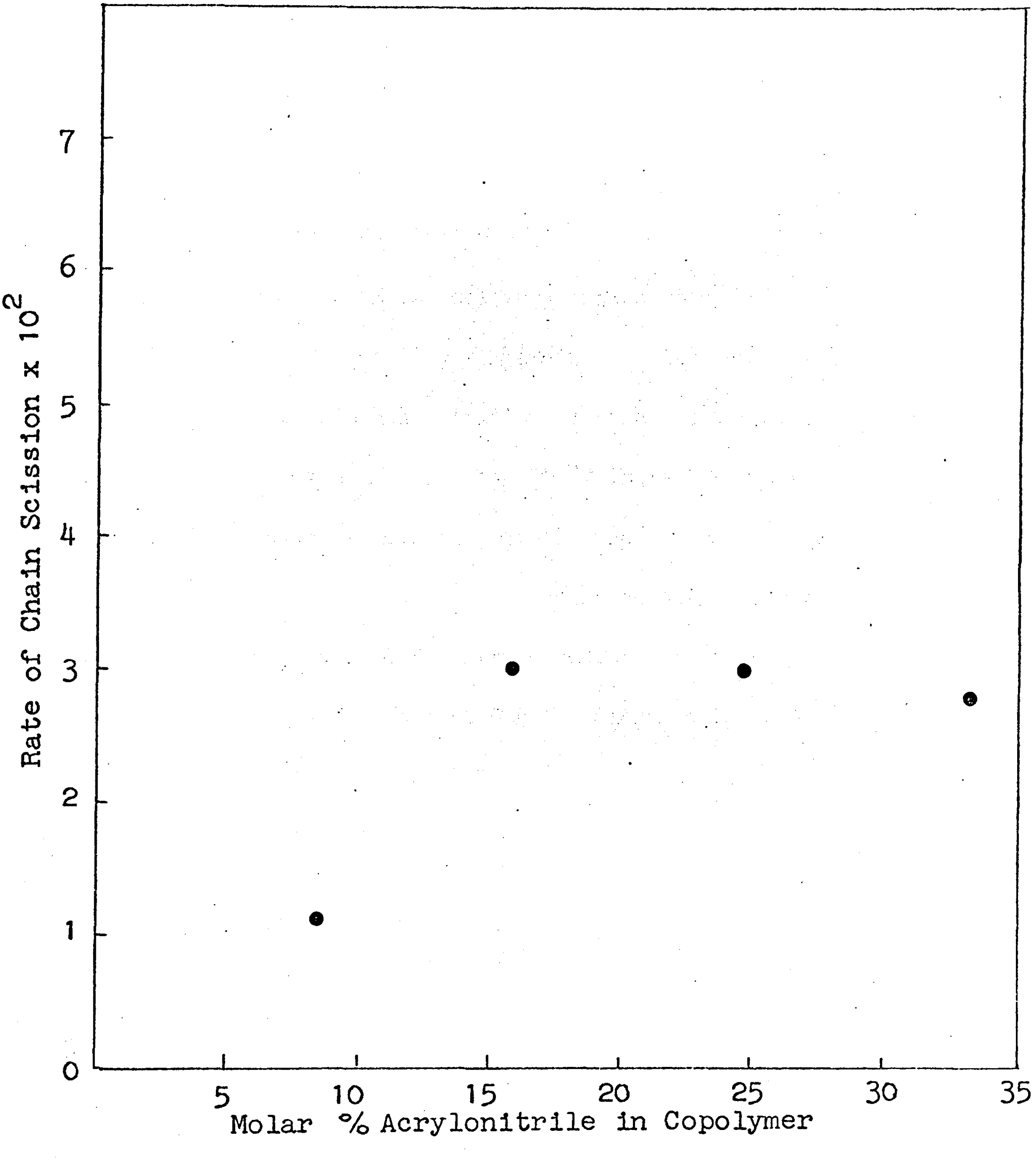


Fig. 5.16 Rate of Chain Scission at 240°C as a Function of the Acrylonitrile Concentration of the Copolymer

and at acrylonitrile units. Polystyrene was shown to undergo chain scission at 240°C, but this aspect of polystyrene degradation requires a more detailed investigation.

(2) The melting point of polystyrene is quoted as 235-250°C; polyacrylonitrile has an estimated melting point of 319°C.[82] Assuming only a small increase in the melting temperature of the copolymers with increasing acrylonitrile concentration compared with that of polystyrene, chain scission at temperatures below 262°C is taking place in the high viscosity medium near the melting point. The increase in viscosity favours radical recombination even if chain scission does occur initially. Therefore a slight increase in melting temperature with increasing acrylonitrile concentration can account for the decrease in chain scission observed in the copolymers of highest acrylonitrile concentration as the degradation temperature is lowered.

5.5 Conclusions

At 262°C, the increase in the rate of chain scission over that of polystyrene is proportional to the concentration of acrylonitrile in the copolymers, and independent of molecular weight. As in styrene/stilbene copolymers[34] this increase in rate is observed as an increase in the rate of "normal" scission. The "weak link" concentration is greatest in copolymers of highest styrene concentration and is therefore a property of the styrene units.

Degradations below 262°C show a decrease in the effect of acrylonitrile units on the rate of chain scission. This effect is attributed to an overlap of "weak link" and acrylonitrile scission and also to an increase in radical recombination in the high viscosity medium near the melting points of the copolymers. Both factors require further investigation.

The production of volatiles from copolymers of high acrylonitrile concentration, at temperatures as low as 262°C, is indicative of the increase in the number of unstable end structures produced by chain scission. As in polystyrene, it appears that scission initially results in molecules by "cage" disproportionation. Thereafter volatilisation is initiated at the unsaturated end structures.

CHAPTER 6

THERMAL ANALYSIS OF STYRENE/ACRYLONITRILE COPOLYMERS

6.1 Thermal Volatilisation Analysis (TVA)

The use of TVA to provide preliminary information about the degradation pattern of the copolymers has already been described in Chapter 3. This technique can in itself provide valuable information about the stability and mechanism of degradation of copolymers.[57] The technique has been further extended to incorporate differential condensation, as described in Chapter 2.[69]

Using this latest development, all copolymers were examined in an attempt to establish some convenient parameter whereby they might be characterised according to acrylonitrile concentration. 50 mg. samples were heated to 500°C at a programmed heating rate of 10°C per minute. The chain fragments, collected as the cold ring fraction above the reaction vessel, were colourless and no residue remained at 500°C. Thermograms of two copolymers of different compositions are shown in Fig. 6.1 and the data from the complete series of copolymers is presented in Table 6.1.

An examination of the temperature at which the rate of volatilisation reaches a maximum (T_{max} in Table 6.1) shows that apart from copolymer SA9 little change occurs over a wide range of copolymer composition.

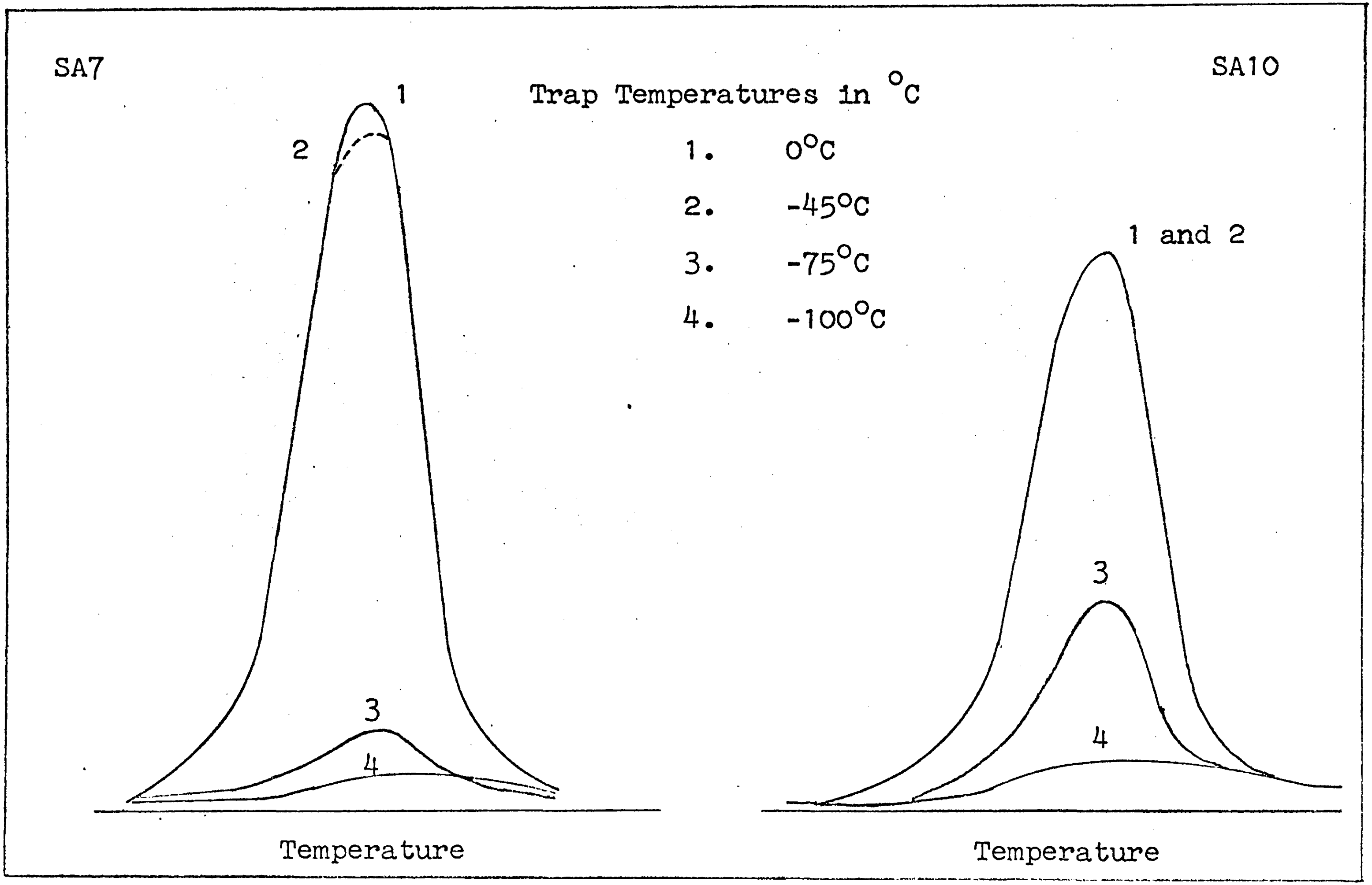


Fig. 6.1 Differential Condensation TVA Thermograms of Copolymers of Different Acrylonitrile Content

Table 6.1

Data Obtained from Differential Condensation TVA

Copolymer	% Acrylonitrile	T_{max} (°C)	Height of Pressure Peaks (units) -100°C	-75°C	-45°C	0°C
PS3	0	429	0.2	0.18	4.07	4.35
SA4	0.25	425	0.5	0.29	3.90	4.28
SA2	1.0	425	0.8	0.20	3.68	4.15
SA7	4.7	423	0.17	0.43	4.10	4.28
SA8	4.7	427	0.15	0.45	4.0	4.15
SA3	8.3	425	0.38	0.58	3.75	3.95
SA6	15.5	427	0.20	0.90	3.80	4.0
SA5	24.9	427	0.40	1.20	3.60	3.81
SA10	33.4	427	0.28	1.20	3.38	3.40
SA9	50.0	405	0.45	0.90	1.88	1.90

Results of isothermal degradation show an increase in the rate of chain scission and rate of volatilisation as the acrylonitrile concentration increases. It is hardly surprising that SA9, with 90 per cent of the bonds styrene to acrylonitrile, shows a decrease in stability. The high rate of bond scission must result in the disappearance of whole molecules very early in the reaction. A decrease in the height of the main pressure peak, measured in the region of the cold trap at 0°C, occurs in copolymers of high acrylonitrile concentration. This is due to the increase in chain fragments and subsequent decrease in the monomer produced as the acrylonitrile concentration increases.

The fact that the pressure in the cold trap at -100°C increased with increasing acrylonitrile concentration suggested the presence of some degradation product associated with acrylonitrile which was not condensing at this temperature. Examination of the vapour pressures of the degradation products suggested hydrogen cyanide or acrylonitrile. Both were confirmed by mass spectrometry.

The TVA thermograms suggest no change in the overall mechanism of degradation over the composition range studied. This is in agreement with the results of isothermal degradation studies. The basic difference between the copolymers lies in the rate of chain scission, a feature not revealed by this technique.

6.2 Thermogravimetric Analysis (TGA)

(a) Introduction

In the early studies of polystyrene degradation, Jellinek[10] and Madorsky[14] investigated the rate of degradation of the polymer by thermogravimetry. Jellinek found that the degradation followed a zero order rate equation with an activation energy of 45 kcal./mole. Madorsky found a reaction order of between zero and one, and an activation energy of 58 kcal./mole. Anderson and Freeman in a later investigation found that the activation energy was a function of temperature.[83] This was suggested as the cause of the discrepancy between the results obtained by Jellinek and Madorsky. A study by Falb and Berry,[84] showed an activation energy of 44.5-46 kcal./mole in a zero order reaction. Recent reviews[65,67] on the application of TGA to the measurement of kinetic parameters suggest that results must be interpreted with caution, particularly when the polymer breaks down in more than one stage. The effects of sample size and geometry, heating rate, molecular weight and the conditions under which the data are obtained, that is in vacuum or in an inert atmosphere, can have a profound effect on the results obtained.

A detailed kinetic investigation of the copolymers was considered outside the scope of this thesis, in view of the number of parameters which must be investigated to make such a study worthwhile. However, isothermal thermogravimetry provides a convenient method of following the rate of degradation as a function of conversion. Polystyrene exhibits a rate maximum at 30-40 per cent conversion;[14] observations with the Pirani gauge, discussed in Chapter 3, suggest that the rate maximum occurs much earlier in the copolymer degradation. This effect was further investigated by a series of isothermal degradations.

(b) Isothermal TGA Investigations

5 mg. samples of the copolymers and the polystyrene "standard" PS3 were degraded in an atmosphere of nitrogen at approximately 330°C. The integral thermograms obtained for polystyrene and the copolymer SA10 (33.4 per cent acrylonitrile) are shown in Fig. 6.2. Manual differentiation resulted in the rate of weight loss against conversion graphs shown in Fig. 6.3. The results confirm the observation that the rate maximum occurs earlier in the degradation. Because of the way in which the derivative curves are obtained, it is difficult to locate the rate maximum exactly as a function of acrylonitrile concentration. In all cases the maximum is attained below 30 per cent conversion, and the greater the acrylonitrile concentration the earlier the rate maximum occurs.

Kinetic rate plots for polystyrene and copolymer SA10 (33.4 per cent acrylonitrile) are shown in Fig. 6.4 and 6.5. After the initial 10-15 per cent conversion, polystyrene follows zero order kinetics to approximately 50 per cent conversion, thereafter a first order rate equation is obeyed. A similar situation exists in the copolymer SA10, except that the zero order rate equation is obeyed after approximately 5 per cent conversion. This initial period, which is small compared with that observed for polystyrene, is probably due to the chain scission reaction, which is much faster in the copolymer than in polystyrene. The changeover to first

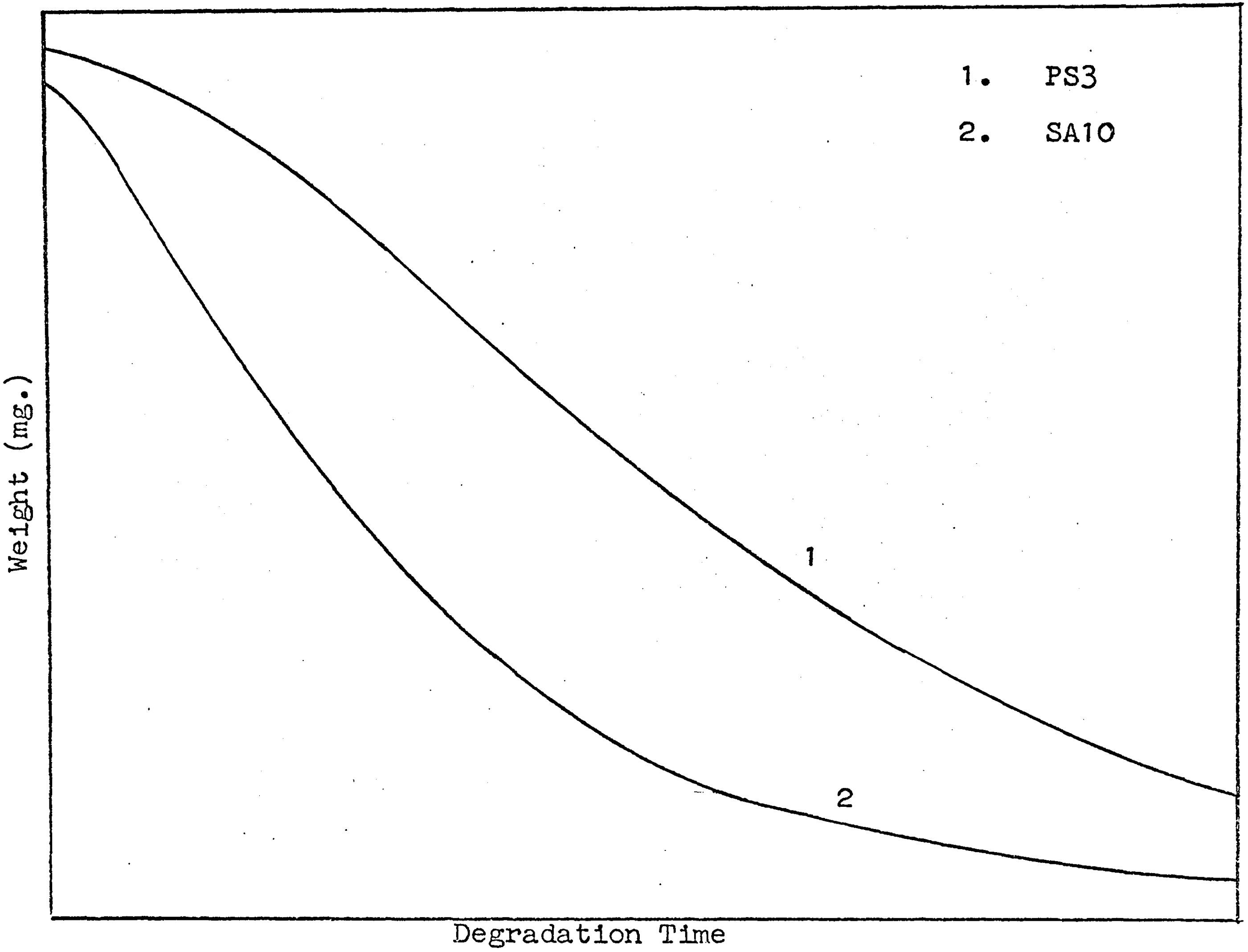


Fig. 6.2 Integral Isothermal Thermograms at 330°C

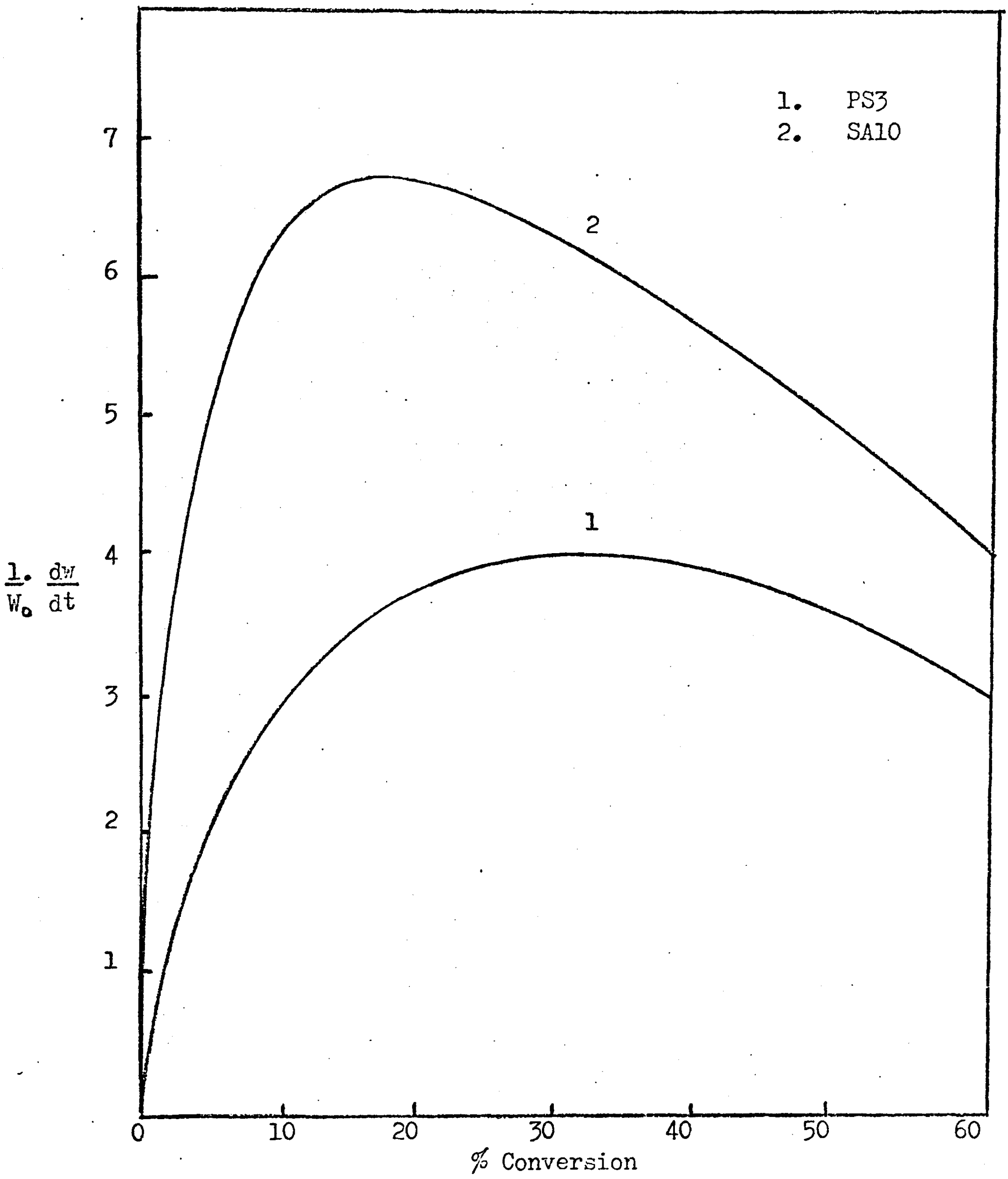


Fig. 6.3 Thermograms Obtained by Differentiating the Graphs in Fig. 6.2

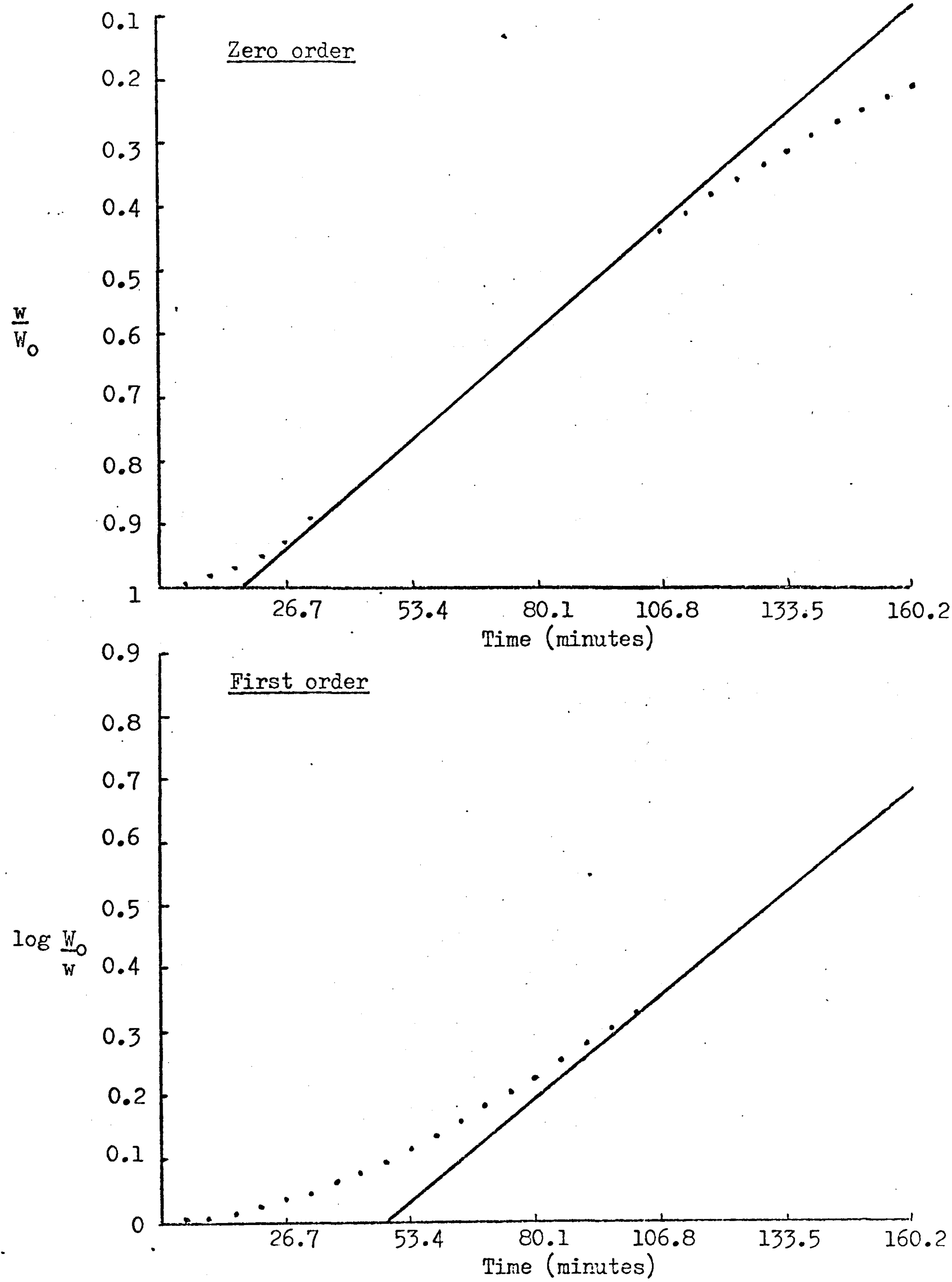
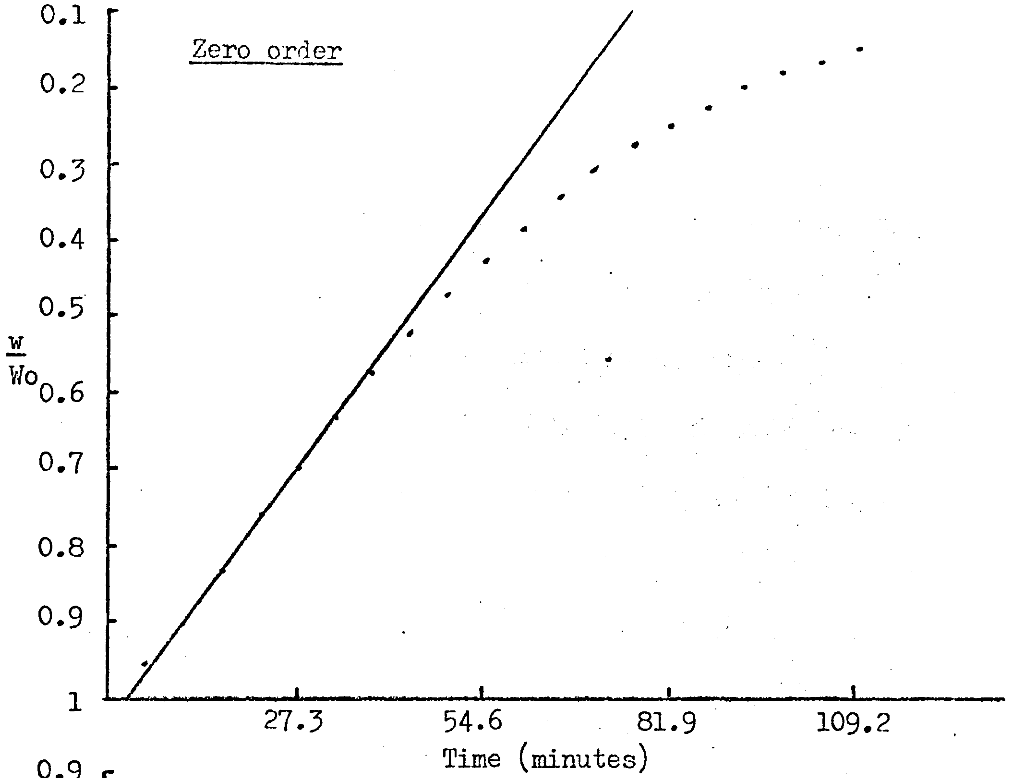


Fig. 6.4 Zero and First Order Plots of the Isothermal Degradation of Polystyrene at 334°C



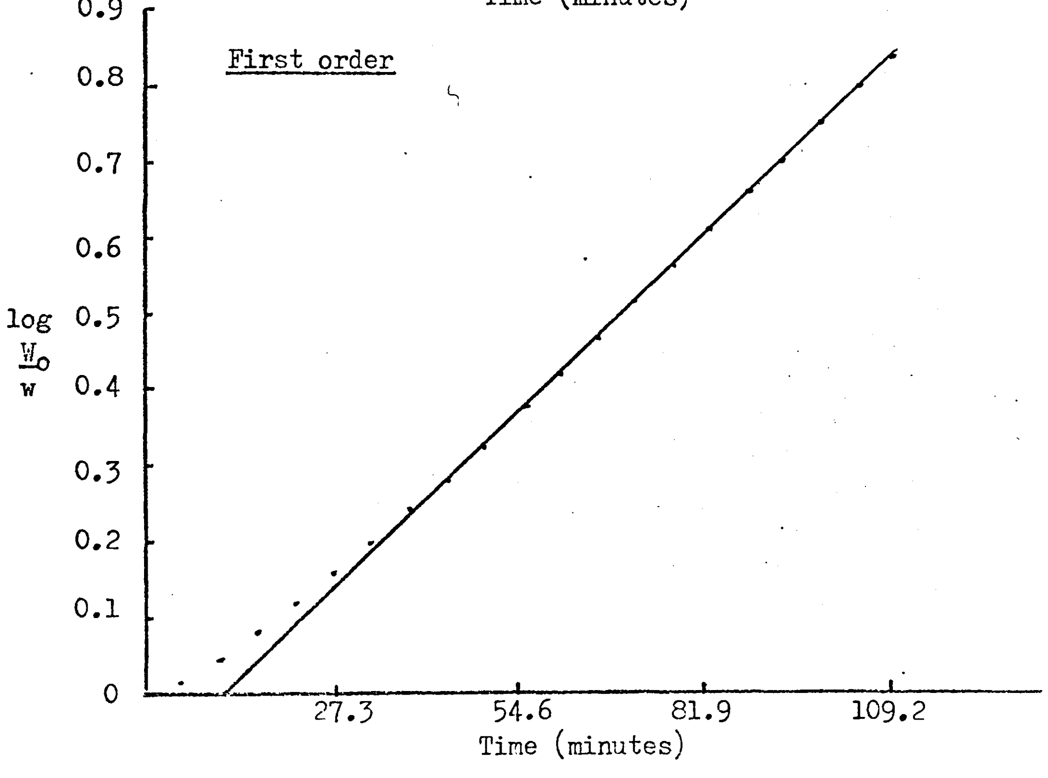


Fig. 6.5 Zero and First Order Plots of the Isothermal Degradation of SA10 at 331°C

order kinetics after approximately 50 per cent conversion requires further investigation. Falb and Berry found that the degradation of polystyrene obeyed zero order kinetics up to 80 per cent conversion but no details of the sample size was given.[84] It may be that the zero order reaction is due to diffusion control in the initial stages of degradation. When the sample size has decreased sufficiently to permit unhindered departure of volatiles the reaction order could change to first order.

(c) Temperature Programmed TGA

The effects of molecular weight and copolymer composition on the thermal stability of styrene/acrylonitrile copolymers were investigated by Igarashi and Kambe.[85] It was found that molecular weight had little effect on the TGA curves obtained. The rate maximum in the differential TGA curves occurred at lower temperatures as the acrylonitrile concentration increased, but this decrease in T_{max} was only significant in copolymers of greater than 50 moles per cent acrylonitrile. Similar effects were obtained from the copolymers studied in this investigation. Like TVA, temperature programmed TGA showed little difference between the stability of copolymers containing less than 50 per cent acrylonitrile.

CHAPTER 7

THE DEGRADATION REACTION REVIEWED

7.1 Introduction

From the various aspects of the degradation detailed in Chapters 3-6, it is possible to build up a composite mechanism for the degradation of styrene/acrylonitrile copolymers containing up to 50 per cent acrylonitrile. Because of the very different degradation reactions of the homopolymers, it is necessary to define the composition limits rather carefully. Sequence distribution calculations (Chapter 3) show that, for concentrations of up to 50 per cent acrylonitrile, the bulk of the acrylonitrile exists as single units in the copolymer chain. The overall environment is therefore very similar to that of polystyrene and the conjugation of the nitrile groups is inhibited by the styrene units. Grassie and Hay observed that small quantities of styrene and methyl methacrylate reduce the rate of coloration of polyacrylonitrile by breaking up the nitrile sequence.[42,43] These copolymers were however studied at 175°C, and the rates of volatilisation and chain scission at higher temperatures were not measured. The weak coloration found in the copolymers discussed in this work is due to low unsaturation in the main chain, caused by elimination of hydrogen cyanide from the acrylonitrile units.

7.2 The Chain Scission Reaction

The most striking feature of the degradation of the copolymers is the decrease in molecular weight at temperatures as low as 240°C, with negligible production of volatiles. "Weak link" scission, responsible for the initial drop in molecular weight, is a property of the styrene unit. The increase in the rate of "normal" chain scission over that found in polystyrene is proportional to the amount of acrylonitrile in the copolymer at temperatures above 262°C. As the temperature of degradation increases "normal" scission also occurs in the polystyrene regions. Because of the problems of volatilisation at temperatures above 262°C, attempts were made to measure the activation energy of acrylonitrile scission by degradation at lower temperatures. This proved unsuccessful because of the deteriorating relationship between the rate of chain scission and the acrylonitrile concentration as the temperature was reduced to 240°C. This is thought to be due to overlap of "weak link" scission and scission at acrylonitrile units, and also to an increase in the radical recombination in the high viscosity medium, near the melting point of the copolymers. Both factors require further investigation.

It is interesting to compare the effect of acrylonitrile on the chain scission of styrene/acrylonitrile copolymers with effects observed in other copolymer systems. In the degradation of methyl methacrylate at

280°C the acrylonitrile units inhibit the chain scission reaction.[8] In the photochemical degradation of methyl methacrylate/acrylonitrile copolymers however, scission increases with increasing acrylonitrile concentration, though it is not directly proportional to it. Radiation is absorbed by the acrylonitrile units followed by scission of the main chain. It has been suggested that the observed amount of scission is reduced because of radical recombination in the high viscosity melt.[86] A similar reduction in chain scission occurs in the styrene/acrylonitrile copolymers at temperatures below 262°C. In styrene/methyl methacrylate copolymers, chain scission is shown to increase with styrene concentration.

In comparing the degradation of styrene/acrylonitrile and styrene/α-chloroacrylonitrile[55] copolymers, two different reactions are being considered. Whereas the decrease in molecular weight in styrene/acrylonitrile copolymers is by scission of the main chain, predominantly at acrylonitrile units, α-chloroacrylonitrile acts as a source of "weak links" by a side group reaction. Poly(α-chloroacrylonitrile) degrades at 150°C by scission of the C-Cl bond to produce a chlorine radical. The chlorine radical then abstracts the adjacent hydrogen atom or another tertiary hydrogen atom from elsewhere. This results in the production of hydrogen chloride and chain scission.[53] An identical reaction occurs in the styrene/α-chloroacrylonitrile copolymers. Since the reaction occurs at

150°C the degradation is not complicated by scission at the "weak links" normally found in polystyrene. This is shown by a plot of (molecular weight)$^{-1}$ against time, which has the ordinate intercept at $(M_o)^{-1}$ as predicted by the random scission equation. This system illustrates the effect of a monomer with a labile side group on the stability of the copolymer, particularly when the side group reaction involves the formation of free radicals.

Another source of chain scission is observed in copolymers of methyl acrylate/methyl methacrylate. As well as random scission, chain scission occurs by intermolecular transfer. This is indicated by the low energy of activation of chain scission, suggesting that a free radical process is involved.

It is clear that a variety of chain scission reactions can occur depending on the individual characteristics of the monomer units. As well as chemical differences in the monomers, physical factors such as melt viscosity can influence the amount of chain scission observed. Comonomers can introduce "weak links" into the chain, either by increasing the rate of random scission, or as the result of secondary reaction of a reactive side group. Considerable similarity is found between the thermal scission of styrene/acrylonitrile copolymers and the photo reaction in methyl methacrylate/acrylonitrile copolymers.

7.3 Rate of Production of Volatile Material

The increase in the rate of production of volatiles in styrene/acrylonitrile copolymers over that of polystyrene, is proportional to the concentration of acrylonitrile in the copolymers, as is the rate of chain scission. The close relationship between the production of volatiles and chain scission is not wholly unexpected from the previously reported work on polystyrene. The rate maximum in polystyrene is attributed to a maximum number of chain ends formed by chain scission, followed by initiation at unstable terminal structures to produce volatiles. Initially scission results in molecules by "cage" disproportionation, the unsaturated structures then acting as initiation sites. A similar situation undoubtedly exists in the copolymers, which also show a maximum rate of volatilisation but much earlier in the reaction than in polystyrene.

The importance of unsaturated terminal structures as sites of initiation of monomer production from poly(methyl methacrylate) has already been established by Grassie and Vance.[87] MacNeill has shown that partially degraded polystyrene is less stable than the undegraded polymer.[88] In the copolymerisation of styrene and acrylonitrile, as in the homopolymers, termination appears to occur by radical combination. This means that initially the chain ends are saturated initiator fragments. However Cameron has shown that the number of unsaturated end structures can build up in polystyrene.[33] This is discussed in Chapter 1, and results indicate a similar reaction for the copolymers. Grassie and Farish have shown that styrene increases the stability of poly(methyl methacrylate), not only by blocking the depolymerisation reaction, but by decreasing the amount of disproportionation termination in the copolymerisation. This reduces the number of unsaturated terminal structures initially present.[7]

The close interdependence of the rate of volatilisation on the rate of chain scission is illustrated in a comparison of the three systems - polystyrene, styrene/acrylonitrile and styrene/α-chloroacrylonitrile. The rate of volatilisation increases in that order, as does the rate of chain scission. So rapid is the chain scission reaction in styrene/α-chloroacrylonitrile that a high rate of volatilisation is immediately observed, a situation similar to that in poly(methyl methacrylate). In the volatilisation of styrene/acrylonitrile copolymers, the rate maximum still occurs but at very much lower conversion than the 30-40 per cent conversion observed for polystyrene.

Another important way in which a comonomer can influence the rate of production of volatiles is in blocking the depropagation reaction. For this reason, small quantities of acrylates are added to poly(methyl methacrylate). Acrylonitrile has also been shown to inhibit the depolymerisation reaction in poly(methyl methacrylate).[8,52] A measure of the blocking effect is obtained from the amount of monomer found in the volatile products. In the thermal degradation of methyl methacrylate/ methyl acrylate copolymers, one in four of the methyl acrylate units appears as monomer;[56] in styrene/acrylonitrile, one in two acrylonitrile units is recovered as monomer. The fact that no overall decrease in the rate of volatilisation is observed is attributed to the fast scission reaction at acrylonitrile units and also to the ready production of chain fragments, both monomers having tertiary α-hydrogen atoms.

The reaction occurring when a blocking unit is encountered depends on the temperature as well as the structure of the monomer. In methyl methacrylate/acrylonitrile copolymers at 220°C, depolymerisation is stopped by the first acrylonitrile unit. If the temperature is raised to 280°C, random scission occurs in the methyl methacrylate units and monomer is produced. Acrylonitrile is also detected in the products of degradation at 280°C indicating that the unzipping reaction is not totally inhibited by the acrylonitrile units at this temperature. When the depropagation reaches a blocking unit, several reactions are possible.

(1) Depolymerisation through the unit producing monomer.

(2) Intermolecular scission causing chain scission and large radicals or molecules.

(3) Intramolecular transfer producing chain fragments.

(4) Termination.

The amount of each reaction depends on the characteristics of the system. The interplay between these reactions and the effects on the products is discussed by Grassie and Torrance for methyl methacrylate/methyl acrylate copolymers.[56] In the styrene/acrylonitrile copolymers, only reactions (1),(3) and to a lesser extent (4) are important. The small amount of termination which occurs at pairs of acrylonitrile units results in a small decrease in the amount of volatiles produced per chain scission. This does not affect the overall rate of reaction however, because of the increased scission at acrylonitrile units.

7.4 Products of Degradation

The products of degradation of the styrene/acrylonitrile studied were hydrogen cyanide, acrylonitrile, benzene, toluene, styrene and a variety of chain fragments, some containing acrylonitrile. Hummel also obtained mixed chain fragments from the degradation of butadiene/acrylonitrile copolymers.[72] The distribution of the acrylonitrile as single units in the chain allows their participation in the reactions normally found in polystyrene, that is depolymerisation to monomer and intramolecular transfer. The increase in the amount of chain fragments produced with increasing acrylonitrile concentration, is favoured by the fact that both monomer units have a tertiary α-hydrogen atom. The substitution of the monomer is important in the formation of degradation products. Polymers from α-disubstituted monomers, like methyl methacrylate, α-methyl styrene and even α-deutero-styrene, all give high monomer yields on degradation. Chain fragments form an important part of the degradation of polystyrene, poly(methyl acrylate) and polyethylene.

Side group reactions are relatively unimportant in the degradation of styrene/acrylonitrile copolymers. This is not always the case. The appearance of hydrogen chloride among the products of degradation of copolymers of α-chloroacrylonitrile with styrene and methyl methacrylate,[55] and the production of carbon dioxide from methyl methacrylate/methyl acrylate copolymers is of considerable mechanistic significance. As substituent groups become more bulky and reactive (for example the higher acrylates), they play a more important part in the degradation.

The importance of sequence distribution on the products of degradation is illustrated by the use of degradation to determine the distribution of monomer units in the copolymers.[73,76] The effects of sequence distribution on the production of methanol from copolymers of methyl methacrylate/methyl acrylate,[56] and ethylene/methyl acrylate,[77] have already been discussed. In the styrene/acrylonitrile copolymers studied, the separation of the acrylonitrile units by styrene allows complete conversion to volatile products by inhibiting the nitrile conjugation.

Copolymers of greater than 50 moles per cent acrylonitrile produce a carbonaceous residue by cyclisation at adjacent nitrile units.[85]

7.5 Conclusion

The overall mechanism of the degradation of styrene/acrylonitrile copolymers, containing up to 50 moles per cent acrylonitrile, in the temperature range 240°C to 330°C can be rationalised in terms of a reaction involving initial chain scission at "weak links" associated with styrene units, followed by "normal" scission predominantly at acrylonitrile units. Volatile products are formed by depropagation and intermolecular transfer, producing monomer and chain fragments respectively, the principal products of the degradation. The increase in both the rate of chain scission and the rate of volatilisation over that found in polystyrene is proportional to the concentration of acrylonitrile in the copolymers.

The increase in the chain fragment to monomer ratio with increasing acrylonitrile concentration in the copolymer, results from the blocking of the depolymerisation by acrylonitrile units. The appearance of one in two acrylonitrile units as monomer, indicates that the depolymerisation can pass through acrylonitrile units, and gives some measure of their blocking effect. A small decrease in the amount of volatiles produced per chain scission is due to termination at pairs of acrylonitrile units in copolymers of high acrylonitrile concentration.

The appearance of a rate maximum in the production of volatiles, at lower conversion than that observed in polystyrene, is explained by the increased rate of scission at acrylonitrile units. As in polystyrene, chain scission appears to be followed by "cage" disproportionation. Monomer and chain fragments are then produced by initiation at unsaturated terminal structures.

Elimination of hydrogen cyanide results in a small amount of unsaturation in the polymer backbone, and hence coloration. Nitrile conjugation is completely inhibited by styrene units and the copolymers can be completely converted to volatile products below 500°C.

CHAPTER 8

SUGGESTIONS FOR FURTHER WORK

In the study of the degradation of copolymers of styrene and acrylonitrile, chain scission was found to constitute an important part of the reaction. Investigation of the scission reaction associated with acrylonitrile units was considerably complicated by "weak link" scission at styrene units in copolymers prepared using free radical initiators. However since "weak links" are not found in polystyrenes prepared by "living polymer techniques", this method offers a possible route to styrene/acrylonitrile copolymers free from the troublesome "weak links". This would allow scission associated with acrylonitrile to be much more thoroughly investigated and the activation energy of this type of scission measured.

Further investigations on polystyrenes synthesised using AIBN as initiator are necessary to clarify the results of degradations of the copolymers below 262°C. Neither the lowest temperature at which "weak link" scission occurs, nor the limits of this type of scission have been determined. An accurate determination of the melting points of the copolymers and the melt viscosity at around 250°C would also assist in explaining the results of the low temperature degradation.

Although intermolecular transfer is not thought to be the cause of increased chain scission at acrylonitrile units in the copolymers studied, it is impossible to eliminate this reaction completely from the results so far obtained. However comparison of the rates of degradation of styrene/acrylonitrile and α-deuterostyrene/α-deuteroacrylonitrile copolymers of identical compositions and molecular weights would effectively differentiate between random scission and scission by intermolecular transfer. If intermolecular transfer is important as a source of chain scission, then the slower abstraction of the α-deuterium atoms, at sub-volatilisation temperatures, would considerably decrease the rate of scission of the α-deuterated copolymer compared with that of the normal styrene/acrylonitrile copolymer. To prevent any complications of "weak link" scission, the copolymers used in this investigation should also be synthesised by anionic techniques.

α-Deuteration could also influence the products of degradation. It is known that α-deuteration in polystyrene results in a decrease in the amount of chain fragments formed by intramolecular transfer. Comparison of the non-monomer to monomer ratio obtained from degradation of styrene/α-deuteroacrylonitrile and α-deuterostyrene/acrylonitrile copolymers would give some measure of the reactivity of the α-hydrogen in each monomer unit in intramolecular transfer reactions. α-Deuterated chain fragments would also be useful in structural investigations by mass spectrometry, to study hydrogen migration and elimination.

REFERENCES

1. C. G. Williams, Phil. Trans. 150 (1860) 241.
2. H. Staudinger and A. Steinhofer, Ann. Chem. 517 (1935) 35.
3. N. Grassie, Chemistry of High Polymer Degradation Processes (Butterworths 1965).
4. H. H. G. Jellinek, Degradation of Vinyl Polymers. (Academic Press,1955).
5. S. L. Madorsky, Thermal Degradation of Organic Polymers (Interscience 1964).
6. Polymer Degradation Processes, NBS Circular 525 (1951).
7. N. Grassie and E. Farish, Europ. Polym. J. 3 (1967) 305.
8. N. Grassie and E. Farish, Europ. Polym. J. 3 (1967) 619.
9. F. O. Rice and K. F. Herzfield, J. Amer. Chem. Soc. 56 (1934) 284.
10. H. H. G. Jellinck, J. Pol. Sci. 3 (1948) 850.
    J. Pol. Sci. 4 (1949) 1.
    J. Pol. Sci. 4 (1949) 111.
11. H. H. G. Jellinek and L. B. Spencer, J. Pol. Sci. 8 (1952) 573.
12. S. L. Madorsky, J. Res. Natl. Bur. Stand. 40 (1948) 417.
13. L. A. Wall, J. Res. Natl. Bur. Stand. 41 (1948) 315.
14. S. L. Madorsky, J. Pol. Sci. 9 (1952) 133.
15. S. L. Madorsky, J. Pol. Sci. 11 (1953) 491.
16. R. Simha, L. A. Wall, and P. J. Blatz, J. Pol. Sci. 5 (1950) 615..

17. R. Simha and L. A. Wall, J. Pol. Sci. 6 (1951) 39.

18. R. Simha and L. A. Wall, J. Phys. Chem. 56 (1952) 707.

19. L. A. Wall, D. W. Brown and V. E. Hart, J. Pol. Sci. 15 (1955) 157.

20. N. Grassie and W. W. Kerr, Trans. Far. Soc. 53 (1957) 234.

21. W. W. Kerr, Ph.D. Thesis (Glasgow 1957).

22. N. Grassie and W. W. Kerr, Trans. Far. Soc. 55 (1959) 1050.

23. N. Grassie and G. G. Cameron, Makromol. Chem. 51 (1962) 130.

24. N. Grassie and G. G. Cameron, Polymer 2 (1961) 367.

25. N. Grassie and G. G. Cameron, Makromol. Chem. 53 (1962) 72.

26. M. Gordon, Trans. Far. Soc. 53 (1957) 1662.

27. J. R. MacCallum, Makromol. Chem. 83 (1965) 129.

28. W. E. Oakes and R. B. Richards, J. Chem. Soc. (1949) 2929.

29. T. E. Davies, R. L. Tobias and E. B. Petereli, J. Pol. Sci. 56 (1962) 485.

30. J. Boon and G. Challa, Makromol. Chem. 84 (1965) 25.

31. A. Nakajima, F. Hamada and T. Shimizu, Makromol. Chem. 90 (1966) 229.

32. L. A. Wall et al., J. Phys. Chem. 70 (1966) 53.

33. G. G. Cameron, Makromol. Chem. 100 (1967) 255.

34. G. P. Kerr, Ph.D. Thesis (St. Andrews 1967).

35. L. A. Wall and J. H. Flynn, Rubber Chem. Tech. 35 (1962) 1157.

36. I. C. McNeill and T. H. Makdumi, Europ. Polym. J. 3 (1967) 637.

37. I. C. McNeill and S. A. Haider, Europ. Polym. J. 3 (1967) 551.

38. T. L. Cottrell, The Strength of Chemical Bonds (Butterworth 1954).

39. N. Grassie and I. C. McNeill, J. Chem. Soc. (1958) 3929.

40. N. Grassie and I. C. McNeill, J. Pol. Sci. 27 (1958) 209.

41. W. Skoda and J. Shurz, Makromol. Chem. 21 (1959) 156.

42. N. Grassie and J. N. Hay, J. Pol. Sci. 56 (1962) 189.

43. N. Grassie and J. N. Hay, S.C.I. Monograph No. 13 (1961) 184.

44. L. W. Kerr and A. Fernow, Rubber Chem. Tech. 17 (1964) 350.

45. W. J. Burlant and J. L. Parsons, J. Pol. Sci. 22 (1956) 249.

46. H. Nagas et al., Kogyo Kagaku Zasshi, 59 (1958) 698.

47. Y. Takayama, Kogyo Kagaku Zasshi 61 (1958) 1021.

48. S. Strauss and S. L. Madorsky, J. Res. Natl. Bur. Stand. 61 (1958) 77.

49. S. L. Madorsky and S. Strauss, J. Res. Natl. Bur. Stand. 63A (1959) 261.

50. A. R. Monahan, J. Pol. Sci. A1,4 (1966) 2391.

51. N. Grassie, S.C.I. Monograph No. 26 (1967).

52. N. Grassie and H. W. Melville, Proc. Roy. Soc. A199 (1949) 1.

53. N. Grassie and E. M. Grant, Prague Symposium (1965).

54. N. Grassie in Chemical Reactions of Polymers. Ed. E. M. Fettes (Interscience 1964).

55. N. Grassie and E. M. Grant, Europ. Polym. J. 2 (1966) 255.

56. N. Grassie and B. J. D. Torrance, J. Pol. Sci. In Press.

57. I. C. McNeill, Europ. Polym. J. 4 (1968) 21.

58. C. H. Bamford and A. D. Jenkins, Proc. Roy. Soc. A210 (1953) 315.

59. H. W. Melville and L. Valentine, Trans. Far. Soc. 46 (1950) 210.

60. R. Simha and H. Bransen, J. Chem. Phys. 12 (1944) 253.

61. T. Alfrey Jr. and G. Goldfinger, J. Chem. Phys. 12 (1944) 205.

62. F. Mayo and F. M. Lewis, J. Amer. Chem. Soc. 66 (1944) 1594.

63. F. T. Wall, J. Amer. Chem. Soc. 66 (1944) 2050.

64. F. M. Lewis, F. R. Mayo, W. F. Hulse, J. Amer. Chem. Soc. 67 (1945) 1701.

65. P. E. Slade and L. T. Jenkins, Techniques and Methods of Polymer Analysis Vol.1 Thermal Analysis (Arnold 1966).

66. Bacon Ke, Polymer Reviews Vol.6. Newer Methods of Polymer Characterisation (Interscience).

67. H. L. Friedman, J. Macromol. Sci. (Chem.) A1(1) (1967) 57.

68. I. C. McNeill, J. Pol. Sci. A1,4 (1966) 2479.
    Europ. Polym. J. 3 (1967) 409.

69. I. C. McNeill, 2nd Int. Conf. on Thermal Analysis, Worscester, Mass. 1968.

70. H. T. Hookway in Techniques of Polymer Characterisation. Ed. P. W. Allen (Butterworth 1959).

71. R. E. Steele, W. E. Walker, D. E. Burge and H. C. Ehrmantrant, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1963.

72. D. O. Hummel and H. D. R. Schüddemage, International Mass Spectrometry Conference Berlin, 1967.

73. H. J. Harwood, Angew. Chem. Int. Ed. 4 (1965) 483.

74. C. E. J. Jones and G. E. J. Reynolds, S.C.I. Monograph No. 26 (1967).

75. Yosho Shibasaki, J. Pol. Sci. A1, 5 (1967) 21.

76. G. Nencini, G. Guiliana and T. Salvatori, J. Pol. Sci. B3 (1965) 483.

77. K. J. Bombaugh, C. E. Cook, and B. H. Clampitt, Anal. Chem. 35 (1963) 1834.

78. H. C. Hill, Introduction to Mass Spectrometry (Heyden 1966).

79. L. J. Bellamy, The Infra-Red Spectrum of Complex Molecules (Methuen 1954).

80. J. R. MacCallum, B.Sc. Thesis (Glasgow 1958).

81. W. Kuhn, Z. Physik. Chem. A159 (1932) 484.

82. Polymer Handbook, Ed. J. Brandrup and E. H. Immergut (Interscience 1966).

83. D. A. Anderson and E. S. Freeman, J. Pol. Sci. 54 (1961) 253.

84. R. D. Falb and D. A. Berry, ACS Polymer Preprints 7 No.2 (1966) 495.

85. S. Igarashi and H. Kambe, Makromol. Chem. 79 (1964) 180.

86. N. Grassie and E. Farish, Europ. Polym. J. 3 (1967) 627.

87. N. Grassie and E. Vance, Trans. Far. Soc. 49 (1953) 84.

88. I. C. McNeill, Unpublished Communication.