THESIS FOR THE DEGREE OF MASTER OF SCIENCE.

RADIOCHEMICAL INVESTIGATION OF UNSATURATION IN POLYSTYRENE PREPARED BY A FREE RADICAL MECHANISM.

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RADIOCHEMICAL INVESTIGATION OF UNSATURATION IN POLYSTYRENE PREPARED BY A FREE RADICAL MECHANISM.

TARIQ. M. MAKHDUMI.

TO

MY DEAREST UNCLE

AYYUB AHMED MAKHDUMI.

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PREFACE

This research project was carried out during the period October, 1962 to September, 1964 at the University of Glasgow in the department of Physical Chemistry, which is under the supervision of Prof. J. M. Robertson, F.R.S.

I am grateful for the assistance rendered by the technical staff, during my stay in this department.

I would also like to thank my colleagues, Miss E. Morrison, Miss Rizkalah and Messrs. J. K. Pang, S. I. Haider, J. C. Lawrence, for useful discussions.

Lastly I would like to express my thanks to Dr. Ian C. McNeill for his kind, invaluable help, and guidance throughout the period of research, especially at the time of writing this manuscript.

(Tariq. M. Makhdumi).

SUMMARY

Quantitative information regarding very small amounts of unsaturation in polystyrene is of importance in the understanding of two problems associated with this polymer: the presence or absence of weak links, which could be associated with main chain unsaturation, and the mechanism of thermal initiation, which might result in terminal unsaturation.

Terminal unsaturation is unlikely for catalysed polymers, since catalysed fragments would be expected at both chain ends. This can be tested by determining unsaturation of a series of polymers of different molecular weights prepared using different initiator concentrations at the same temperature.

With this in view, six polymers of different molecular weight were prepared at 60° using benzoyl peroxide as initiator. The unsaturations were examined to determine if there is any effect of molecular weight on the unsaturation. If terminal double bonds are present, then the unsaturation should increase for a given weight of polymer, as the molecular weight decreases. On the other hand, if there is no terminal unsaturation, all these samples should show the same unsaturation.

A polymer was prepared at 80° in order that the effect of polymerisation temperature on unsaturation could be seen by comparison of polymers prepared at 60° and 80°.

Two polymers were prepared by thermal initiation, at 120^{o} and 140^{o}, to see whether unsaturation measurements could provide any evidence on the mechanism of thermal initiation.

Polymer samples were purified by precipitation from carbontetrachloride using methanol as non-solvent and the number average molecular weights were determined.

Lastly, the unsaturation of partially degraded polystyrene was measured to provide additional information on the mechanism of chain scission in the degradation of polystyrene.

Polymer unsaturations were determined by reaction with radiochlorine. A known quantity of chlorine-36 of known specific activity was distilled into a reaction tube containing polymer solution in carbon tetrachloride. Chlorine was allowed to react with the polymer for one hour in sealed tubes at 25^{o} in the absence of light and air.

Purified reacted polymer samples were counted in carbontetrachloride solution in a liquid type Geiger counter. From the activities the chlorine content and hence the unsaturation of each sample could be calculated.

It was found that the unsaturations of all the polystyrene samples are small, and in fact of the same order as the "weak links" concentrations as calculated by Grassie and Kerr. No increase in unsaturation was found in the polymer prepared at 80^{o}, however, contrary to what would be expected from these workers conclusions.

The unsaturations of polymers of different molecular weight prepared at the same temperature were found to be identical. This indicates the absence of an end group effect, all the double bonds being present in the main chain. This result is in accordance with the previous evidence that termination in free radical polymerisation of styrene is by combination of radicals.

By comparing the results of present work with the ozonolysis data of Grassie and Cameron, it can be seen that the two methods are in fair agreement as to the main chain unsaturation in polystyrene. Grassie and Cameron estimated a double concentration of the order of 1 double bond per 1,000 monomer units, while the results obtained from present work show 1.5 double bond per 1,000 monomer units.

It seems clear from the present work, however, that although there is main chain unsaturation, this is not associated with weak links. This conclusion is reinforced by the fact that no difference in thermal stability was found between polymer samples before and after reaction with chlorine. If the double bonds were weak links some difference in behaviour might be expected. Possible ways in which unsaturation could arise in polystyrene are discussed.

The observed unsaturations for the thermally initiated polymers are higher than 1 double bond per chain, and appear to indicate the presence of terminal as well as main chain unsaturation. This result lends support to theories of monoradical rather than diradical initiation.

Results obtained for the unsaturation of partially degraded polystyrene indicate an appreciable increase in unsaturation. This is difficult to interpret, however, in the absence of evidence as to the location of the double bonds in the chain.

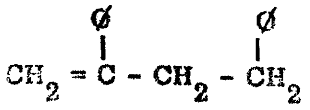
PART I.

INTRODUCTION.

1. Early Work and the Random Theory of Degradation.

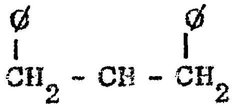
Since the time plastics first came onto the market studies have been made with the object of detecting the causes of the undesirable deterioration which they undergo when exposed to weathering and other adverse influences, bringing about drastic changes in their physical and chemical properties.

Early experiments on the degradation of polymers were made to reveal the molecular structure of natural polymers like rubbers, starch and cellulose. As far back as 1845, however, it was known that styrene can be recovered by the pyrolysis of a glassy solid formed by heating styrene or allowing it to stand in air. As the nature of the glassy solid was not known, detailed study of the pyrolysis was postponed and it was not until 1935 that the destructive distillation of the glassy mass was critically examined by Staudinger and Steinhofer[1]. The glassy mass, known as polystyrene, gave the following compounds besides monomeric styrene as the pyrolysis products.



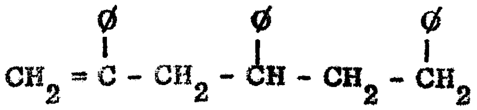
$CH_2 = \overset{\phi}{\overset{|}{C}} - CH_2 - \overset{\phi}{\overset{|}{C}}H_2$

2, 4 - diphenyl-1-butene.



$\overset{\phi}{\overset{|}{C}}H_2 - CH - \overset{\phi}{\overset{|}{C}}H_2$

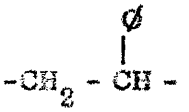
1, 3 - diphenyl propane.



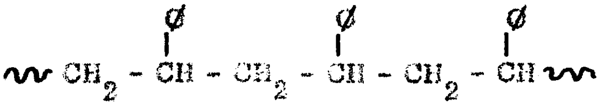
$CH_2 = \overset{\phi}{\overset{|}{C}} - CH_2 - \overset{\phi}{\overset{|}{C}}H - CH_2 - \overset{\phi}{\overset{|}{C}}H_2$

2, 4, 6 - triphenyl-1-hexane.

As none of these compounds obtained contained the benzene rings on the adjacent carbon atoms, they concluded that polystyrene possesses a 'head to tail' structure of



$-CH_2-\overset{\phi}{CH}-$ units



$\sim CH_2-\overset{\phi}{CH}-CH_2-\overset{\phi}{CH}-CH_2-\overset{\phi}{CH}\sim$

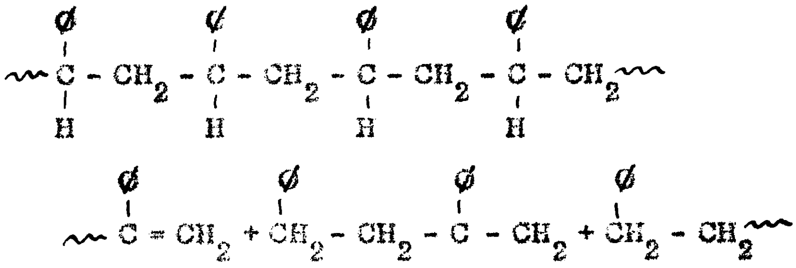
This structure was heavily criticised, but it has withstood all criticism[2,3] and is now generally accepted.

The concept of random degradation had been introduced some years before Staudinger published his work on pyrolysis of polystyrene. The Random Theory was based on the work of Freudenberg[4], Meyer, Hoff and Mark[5], and Kuhn[6], who studied the hydrolytic degradation of starch and cellulose.

By then it was established that starch, glucose and polysaccharides consisted of glucose units linked in chains of various lengths. During hydrolysis, the viscosity of these materials decreased continuously, and appreciable amounts of the unit molecules, namely glucose, did not appear early in the reaction. As each act of hydrolysis must proceed individually of all the others, these results point to a reaction occurring at random along the polymer chain. Kuhn used a statistical approach to random degradation, and his mathematical treatment after a slight modification to account for the increased reactivity of terminal bonds was found to satisfy the experimental results[7].

In 1942 Votinov, Kobeko and Marei[8] examined the degradation of polymethyl methacrylate and polystyrene, explaining their results in terms of Kuhn's random theory.

In order to account for the various pyrolysis products in the degradation of polystyrene, Staudinger[9] assumed a random scission of carbon-carbon bonds along the polymer backbone, followed by the migration of tertiary hydrogen atoms.



$$\sim\underset{\displaystyle H}{\overset{\displaystyle \phi}{C}} - CH_2 - \underset{\displaystyle H}{\overset{\displaystyle \phi}{C}} - CH_2 - \underset{\displaystyle H}{\overset{\displaystyle \phi}{C}} - CH_2 - \underset{\displaystyle H}{\overset{\displaystyle \phi}{C}} - CH_2\sim$$

$$\sim\overset{\displaystyle \phi}{C} = CH_2 + \overset{\displaystyle \phi}{C}H_2 - CH_2 - \overset{\displaystyle \phi}{C} - CH_2 + \overset{\displaystyle \phi}{C}H_2 - CH_2\sim$$

It was pointed out that the carbon-carbon bond next but one to an unsaturated centre, is slightly weaker than the normal carbon-carbon linkage, a concept which at that time appeared to be supported by the greater thermal stability of polyvinyl cyclohexane.

Grassie and Melville[10] re-examined the degradation of polymethyl methacrylate, determining the changes in molecular weight of polymer and the initial rate of production of monomer. From these results they concluded that the reaction is solely initiated at chain ends, producing radicals which liberate monomer in a reverse polymerisation process. This accounted for the large amounts of monomer obtained even in the early stages of the reaction.

Grassie and Melville found evidence that two distinct reactions were occurring in the degradation of this polymer, both resulting in monomer as the sole product, and having energies of activation of 31 and 42 K calories, respectively. They suggested that these two values corresponded to depolymerization reactions initiated at the two types of chain end produced in the disproportionation process responsible for termination during polymerisation. The lower value was attributed to reaction at the unsaturated chain end structures. Grassie and Vance[11] were subsequently able to show that if the proportion of unsaturated ends was reduced by polymerisation in presence of a suitable transfer agent, the rate of initiation of degradation was also reduced. It has been shown more recently, however, by Brockhaus and Jenckel[12] that the depolymerisation process with the higher energy of activation is initiated not at the chain ends, as Grassie and Melville had supposed, but by random scission.

Around the time Grassie and Melville were carrying out their studies of polymethyl methacrylate Jellinek[13] was examining the degradation of polystyrene at various temperatures. He found that the molecular weight of the polymer falls to a limiting value, depending upon the temperature of degradation. An interesting feature of the reaction was that the drop in molecular weight was accompanied by the production of monomer in quantities which were about 10^3 or 10^4 times larger than were expected on the basis of a

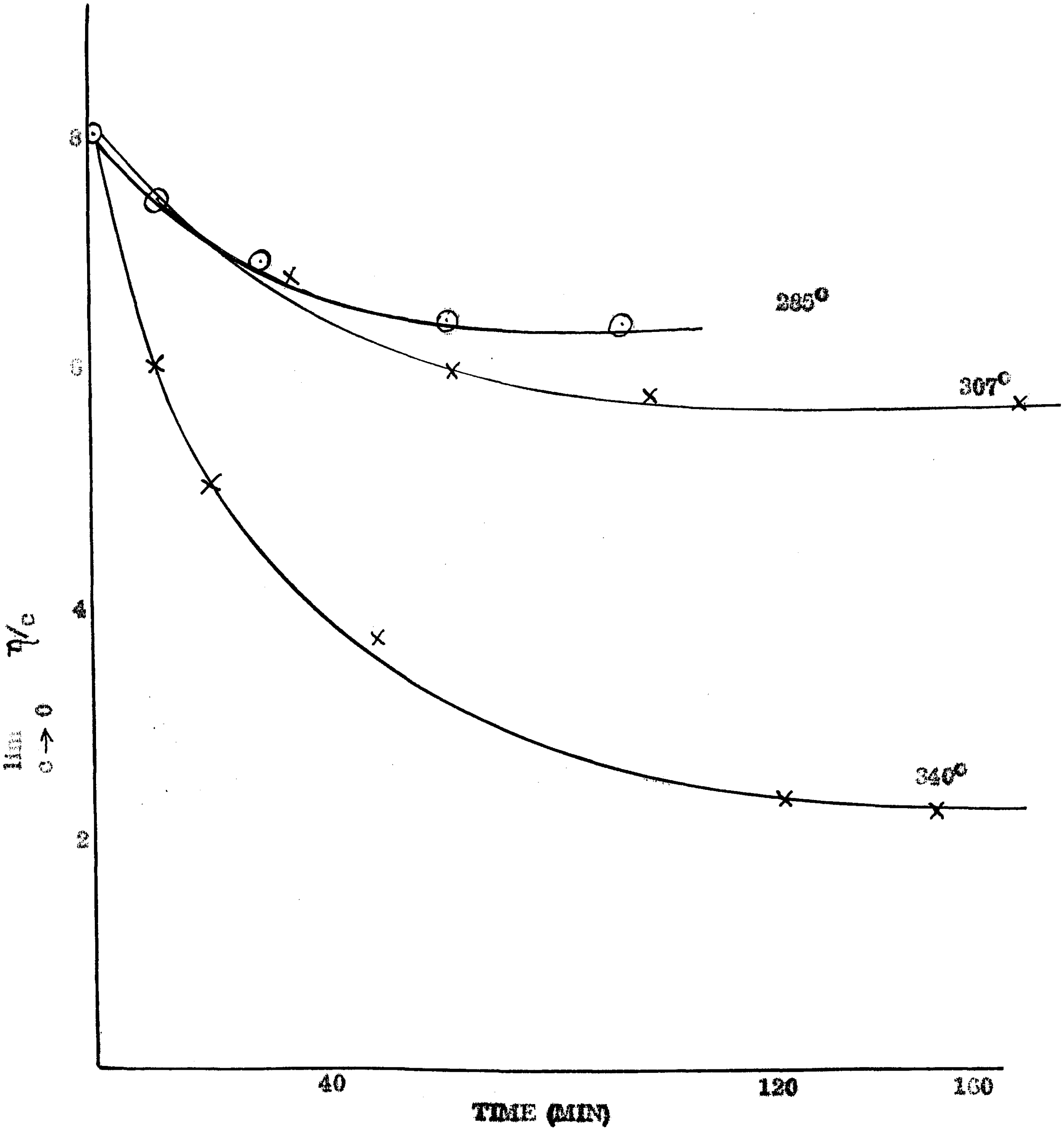


Figure 1: Changes in molecular weight (from solution viscosity measurements) during the degradation of polystyrene, found by Jellinek[13].

random mechanism. Furthermore, the molecular weight data obtained during these experiments were incompatible with a random theory of degradation. Consequently it was suggested that the random process of degradation was not generally applicable to the polymer degradation.

2. Weak Link Theory.

Jellinek[13] while thermally degrading polystyrene, found a sharp drop in its molecular weight early in the reaction, (Figure 1), which he suggested was due to the presence of a limited number of weak links distributed at random along the polymer chain. These weak links are unstable at higher temperatures.

Weak links have also been suggested to account for the degradation behaviour of other polymers, for example polyvinyl chloride[14, 15] and polymethacrylonitrile.[28]

3. Estimation of Concentration of Weak Links in Polystyrene.

During the degradation of polystyrene, two seperate reactions, namely chain scission and reverse polymerisation from the chain ends, are proceeding simultaneously. S, the number of weak links per molecule originally present in the polymer chain is given by the equation

$$S = \frac{MA}{ML} - 1$$

where MA is the average molecular weight of the undergraded polymer and ML is the limiting value to which molecular weight of

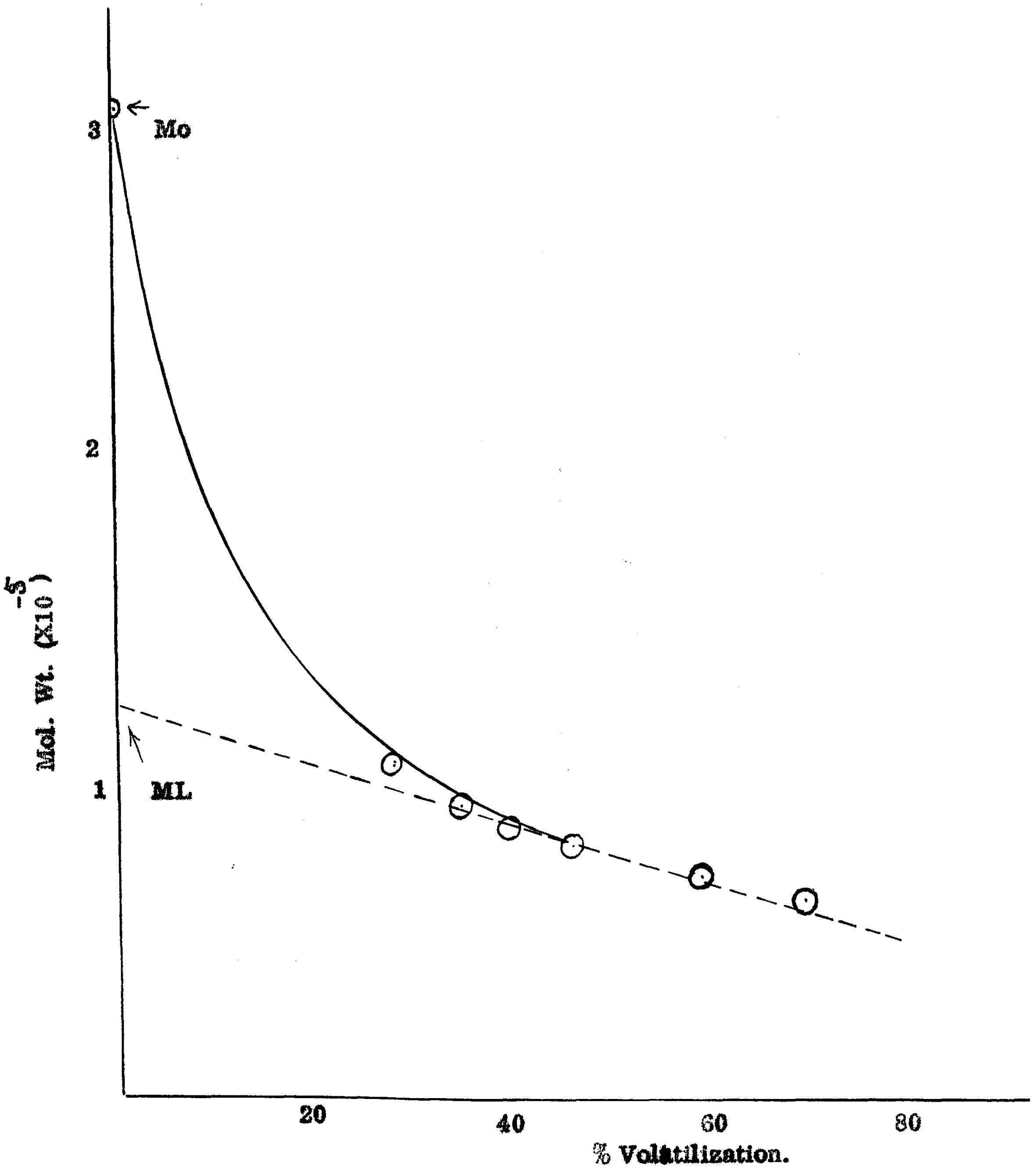


Figure 2: Extrapolation method used by Grassie and Kerr[21] for determination of M_L and hence the concentration of weak links.

the polymer would fall as a result of chain scission in the complete absence of depropagation. The fall in molecular weight up to 30 % volatilization is mainly due to chain scission, but the molecular weight at this time does not accurately represent ML, because of a small component decrease in molecular weight due to the reverse polymerisation process. An approximate estimate of the contribution of this reaction to the fall in molecular weight up to 30 % conversion, can therefore be obtained[21] by extrapolating the linear portion of the molecular weight conversion curve back to zero extent of volatilization (Figure 2).

The molecular weight at this point will represent approximately the limit to which the molecular weight of the polymer would fall as a result of chain scission at weak links in the comple absence of depolymerisation from the chain ends, and is taken to represent ML in the above equation.

As the number of weak links present in polymers of different molecular weights will have to be compared, it is more convenient to discuss the results in terms of the number of weak links present per monomer unit

$$= \frac{S \times 104}{MA}$$

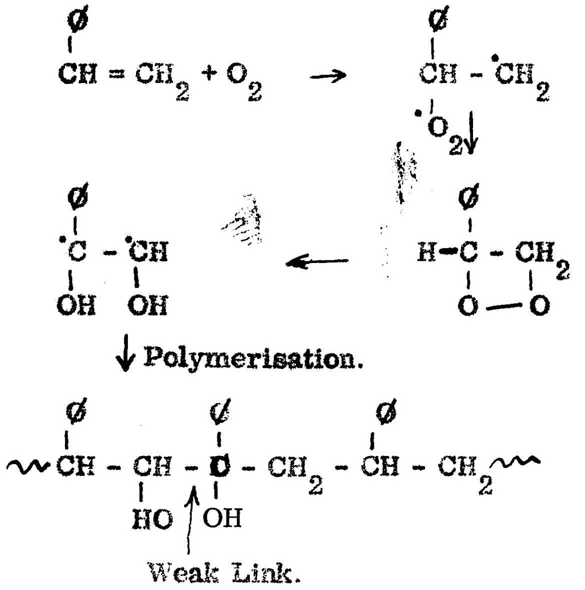
$$\text{or} \qquad = 104 \; \frac{1}{ML} - \frac{1}{MA}$$

104 being the molecular weight of the styrene monomer.

4. Possible Sources of Weak Links in Polystyrene.

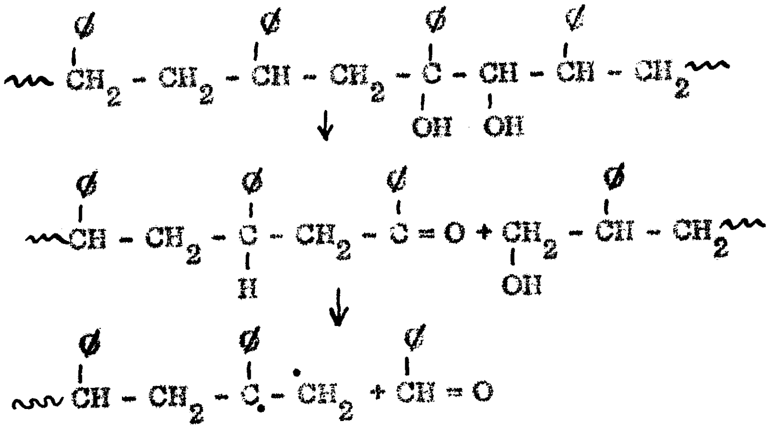
(i) Oxygenated Structures.

Jellinek[13] postulated that weak links might be formed by the incorporation of oxygen into the polymer during the polymerisation process.



According to Jellinek,[13] 0.3% by weight of oxygen is sufficient to produce such an effect. Concentrations of this order have been detected by Madorsky in polystyrene samples. As far back as 1929 Staundiger and co-workers[1] observed that polystyrene prepared with careful exclusion of oxygen is thermally more stable than that prepared in presence of oxygen.

According to Jellinek degradation takes place at the weak links in the following way.



$$\sim\overset{\phi}{CH_2}-CH_2-\overset{\phi}{CH}-CH_2-\underset{OH}{\overset{\phi}{C}}-\underset{OH}{CH}-\overset{\phi}{CH}-CH_2\sim$$

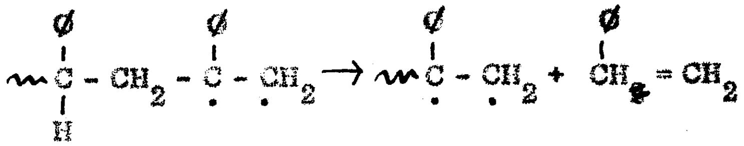
$$\downarrow$$

$$\sim\overset{\phi}{CH}-CH_2-\underset{H}{\overset{\phi}{C}}-CH_2-\overset{\phi}{C}=O+\underset{OH}{CH_2}-\overset{\phi}{CH}-CH_2\sim$$

$$\downarrow$$

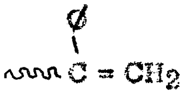
$$\sim\overset{\phi}{CH}-CH_2-\overset{\phi}{C}\cdot-\dot{C}H_2+\overset{\phi}{CH}=O$$

monomer being produced from the radical chain end



$$\sim\underset{H}{\overset{\phi}{C}}-CH_2-\underset{\cdot}{\overset{\phi}{C}}-\underset{\cdot}{CH_2}\rightarrow\sim\underset{\cdot}{\overset{\phi}{C}}-\underset{\cdot}{CH_2}+\overset{\phi}{CH}=CH_2$$

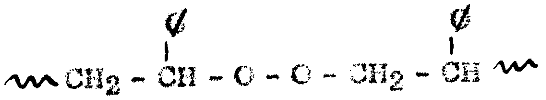
and termination occurring by the formation of a double bond.



$$\sim\overset{\phi}{C}=CH_2$$

As the production of monomer occurs simultaneously with the drop in molecular weight, Jellinek[16] deduced that during the weak link scission reaction about 5 - 10% of the polymer degrades, and 6 - 10 monomer units were produced per chain end formed. The monomer production reaction is similar to the one suggested by Grassie and Melville for polymethyl methyacrylate[10].

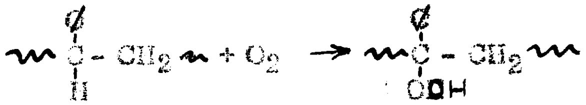
Jellinek's explanation regarding the weak links, can be criticised on the basis that styrene copolymerises with oxygen to form a poly peroxide:



$$\sim CH_2-\overset{\phi}{CH}-O-O-CH_2-\overset{\phi}{CH}\sim$$

According to Kolthoff and Bovey[17], a gem-diol seems highly unlikely. Such a peroxidic unit is thermolabile, but it is not clear whether it would disappear without chain scission.

Another theory is that weak links might be produced as a result of oxidation of polystyrene during storage.

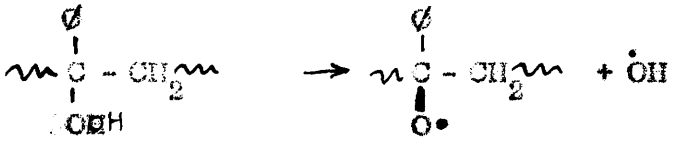


$$\sim\underset{H}{\overset{\phi}{C}}-CH_2\sim + O_2 \rightarrow \sim\underset{OOH}{\overset{\phi}{C}}-CH_2\sim$$

It is known that prolonged exposure of polystyrene film to light and air results in the appearance of bands at 3450 cm^{-1} and 1730 cm^{-1} in the infra red spectrum of polymer.

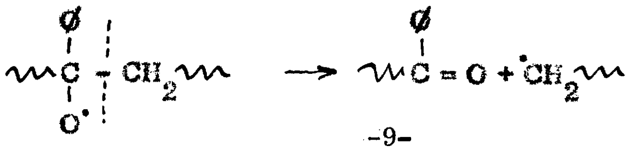
Achhammer[18] and co-workers attributed these to hydroxyl and carbonyl groups produced during the decomposition of hydroperoxide groups formed during the oxidation of polymer.

Decomposition of hydroperoxide groups at elevated temperatures would almost certainly result in chain scission:



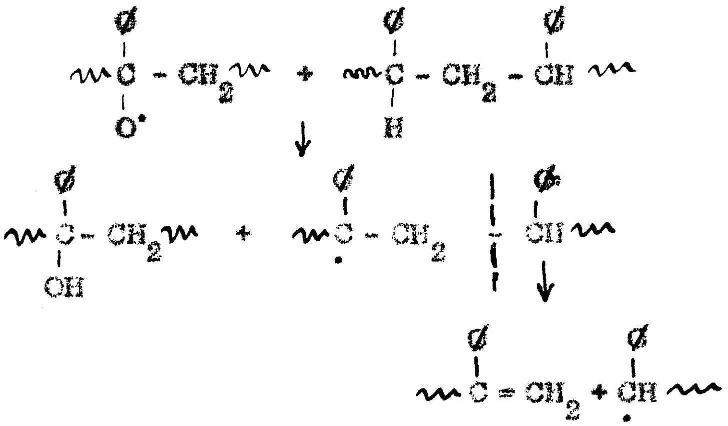
$$\sim\underset{OOH}{\overset{\phi}{C}}-CH_2\sim \rightarrow \sim\underset{O\cdot}{\overset{\phi}{C}}-CH_2\sim + \dot{O}H$$

followed by



$$\sim\underset{O^{\cdot}}{\overset{\phi}{C}}-CH_2\sim \rightarrow \sim\overset{\phi}{C}=O+\dot{C}H_2\sim$$

or



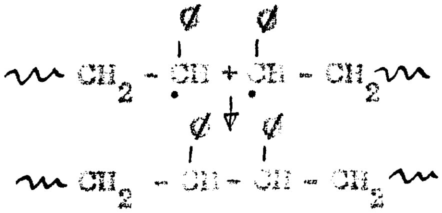
Such structures must accordingly be considered as another possible source of weak links. It is therefore obvious that the mode of preparation and storage of the polymer could have a strong effect on its degradation behaviour. It was with these points in mind that Grassie and Kerr undertook their thermal degradation studies of polystyrene.

Grassie and Kerr[19,20,21] showed that inclusion of oxygen is not the sole cause of weak links, since weak links are still found in the polymers polymerised from carefully purified monomer under high vacuum.

They also established that normal storage of the polymer does not introduce any fresh weak links.

(ii) Head to head addition of monomer.

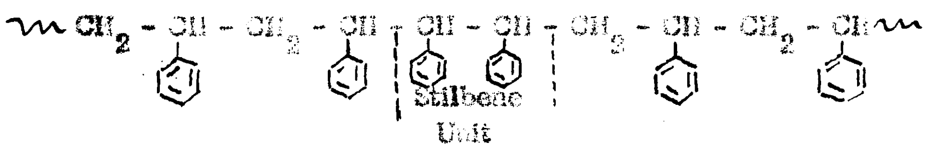
One possible source of weak links in polystyrene is the head to head addition of monomer units. Considerable evidence exists to suggest that termination during the polymerisation of styrene is by combination[22,23,24]. This means that every polymer molecule should contain at least one head to head link.



$$\sim CH_2-\overset{\phi}{\dot{C}H}+\overset{\phi}{\dot{C}H}-CH_2\sim \;\downarrow\; \sim CH_2-\overset{\phi}{CH}-\overset{\phi}{CH}-CH_2\sim$$

Certain low molecular weight polymers of Grassie and Kerr, however, contained less than one weak link per molecule, suggesting that head to head links can not be weak links.

Grassie and Cameron[25] concluded from their experiments with copolymers of styrene and radio-active stilbene, that head to head additions are not thermolabile points in polystyrene. These workers prepared copolymers containing 1 part stilbene in 157 and 1 part stilbene in 71 parts styrene. Such copolymers should contain the structure



which includes two head to head links of the type which could occur in polystyrene.

The molecular weight of the residue from pure polystyrene degradation at 300°C was found to decrease to approximately 80,000 to 140,000 in the weak link scission phase; the exact value depending upon the initial molecular weight as well as the proportion of weak links. If the stilbene units in the copolymers of styrene/stilbene behave on heating as weak links the molecular weight of the residual polymers should clearly tend to have abnormally low values of the order of 16,000 and 7,000 respectively. But from the curves obtained by Grassie and Cameron this does not appear to be the case. The two copolymers behave identically, their molecular weights decreasing only to a very slightly greater extent than that of a pure polystyrene prepared under identical conditions.

Grassie and Cameron therefore concluded that the weak links in polystyrene cannot be due to head to head structure.

(iii) Branching.

Though branching has been reported to be negligible[26] in polystyrene it is nevertheless considered important to investigate this aspect of the polymerisation process, as the number of branches required (if these were weak links) to account for the observed decrease in molecular weight during degradation would be extremely small. Branching during polymerisation proceeds through transfer to polymer and has a slightly higher energy of activation (7K calories/mole) than the competing propagation reaction (6.3K calories/mole). Consequently branching would be favoured at higher polymerisation temperatures. The degree of branching will increase with the extent of conversion of the monomer to polymer, as the probability of transfer must depend on the amount of polymer present in the system.

If chain branching is responsible for weak links, then as the temperature of polymerisation is increased, the concentration of the weak links in the system, for the same extent of conversion should increase in proportion.

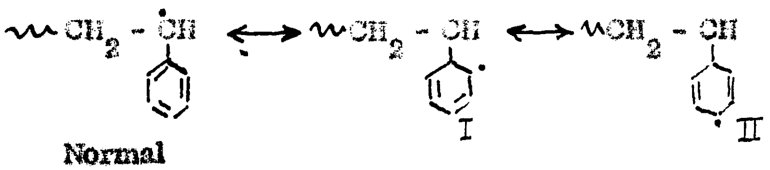
Grassie and Kerr[19] used the equation

$$\frac{\gamma}{\alpha N} = -\frac{k_{tr}}{k_p}\left[1 + \frac{1}{\alpha}\log(1-\alpha)\right]$$

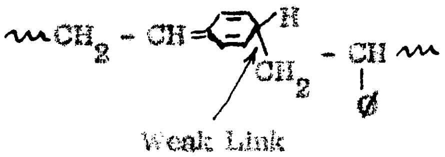
where α is the fraction of monomer molecules which have been polymerised out of a total of N in the system, and γ is the total number of branches. k_{tr} and k_p are the rate constants for chain branching and propagation respectively. From the application of this equation to their results it was concluded that weak links cannot be due to chain branching.

(iv) Abnormal Propagation Steps.

Grassie and Kerr[21] considered the possibility of polymerisation through a canonical form of the resonating polymer radical.



The structure resulting in the polymer chain from addition of polystyrene at the para position in this abnormal propagation step would thus be



and a corresponding structure can be written for addition at the ortho position. The carbon-carbon bond indicated is expected to be a weak link as it is next but one to the two double bonds[9]. The formation of these structures somewhat resembles that of the Ketene-imine linkages which have been found by Talat-Erben and Bywater[27] in polymethacrylonitrile and later confirmed by Grassie and McNeill[26], although these structures were found by the latter authors to be formed in an abnormal termination step. Similar observations have been made recently in polyacrylonitrile. 53

Polymerisation through the normal free radical leaves the benzene ring intact, while polymerisation through forms I and II destroys the aromatic character of benzene ring, with the result that a higher energy barrier for their formation would be expected.

An increase in abnormalities of this type in the structure of the polymer with the increase of temperature of polymerisation would be expected.

Grassie and Kerr[21] found an apparent increase in the number of weak links in polystyrene as the polymerisation temperature was increased, in keeping with the theory.

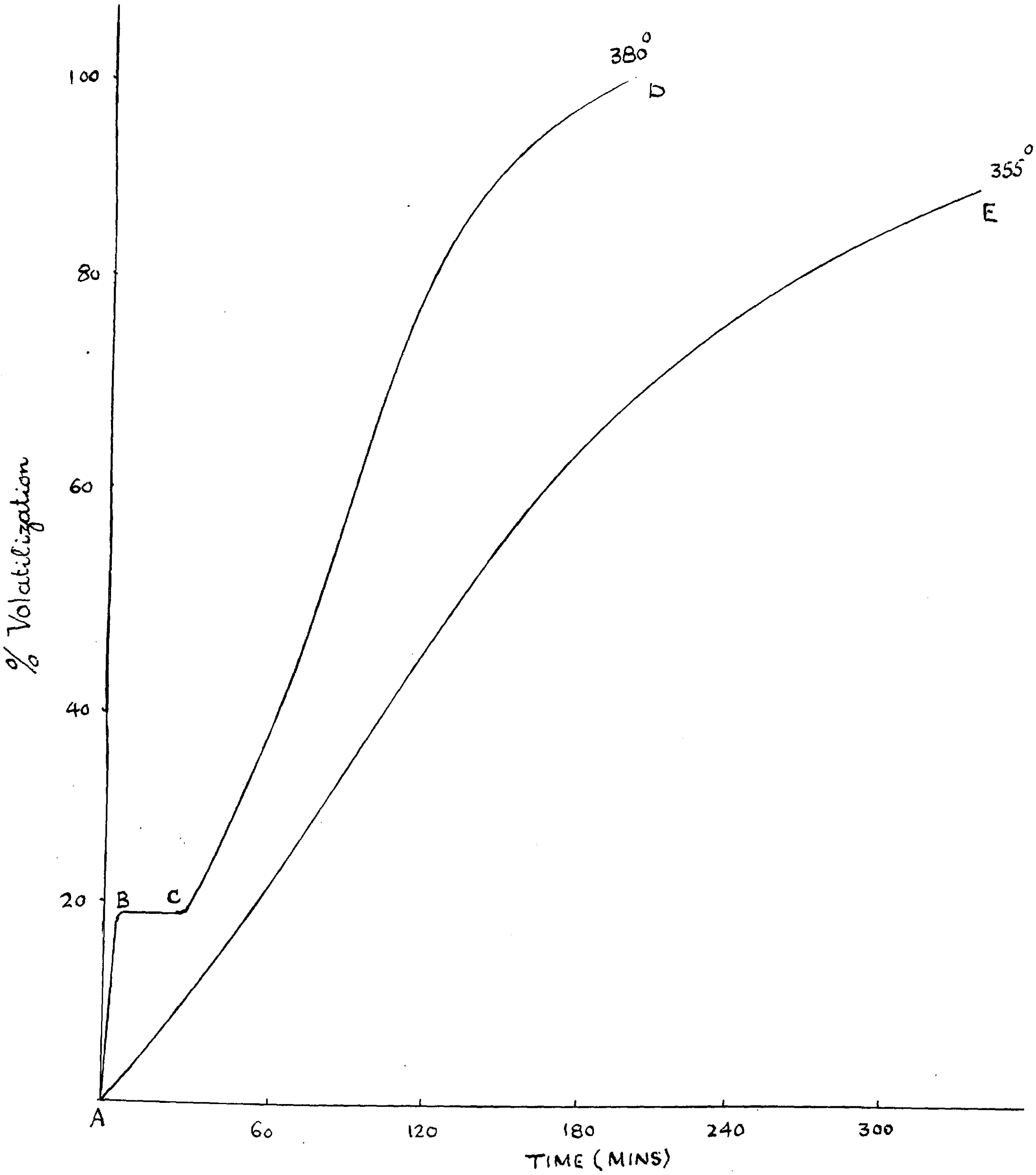
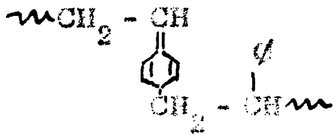


Figure 3: % Volatilization versus time data of Madorsky[31] (curve AE) and Jellinek[30] (curve ABCD)

Grassie and Cameron[29] subsequently obtained evidence (discussed later in this thesis) suggesting that double bond structures are closely associated with the thermolabile points in the polymer chains. This does not, however, prove quinonoid type structures to be weak links,



though it lends support to this possibility.

5. Role ~~and~~ of Transfer in the Degradation of Polystyrene.

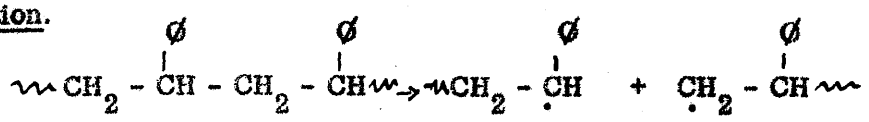
An alternative explanation of the observed degradation behaviour of polystyrene has been put forward in terms of transfer reactions.

Polystyrene when degraded gives higher fragments such as dimer, trimer, tetramer and pentamer as well as monomer. This suggests that chain transfer may play a significant part in the reaction.

Jellinek[30] and Madorsky[31] both studied the rate of production of volatile material in this temperature range. (Figure 8). Jellinck's curve shows an inhibition period (BC), which he attributed to the formation of inhibitors during the earlier weak link scission phase (AB). The discrepancies in these results have been the subject of dispute[30,31]. For both curves, however, the rate shows a maximum at 30 - 40% conversion. Simha and Wall[32] explained the reaction in terms of a random scission process followed by inter and intra molecular transfer. They derived an expression for the degradation of polymer to volatile materials, which gives rise to a maximum rate at 25% conversion.

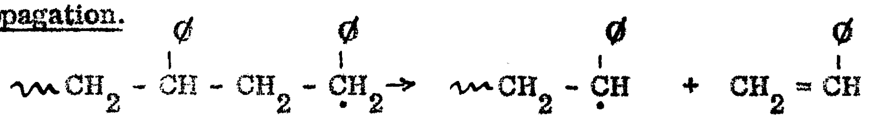
Reaction Steps:

Initiation.



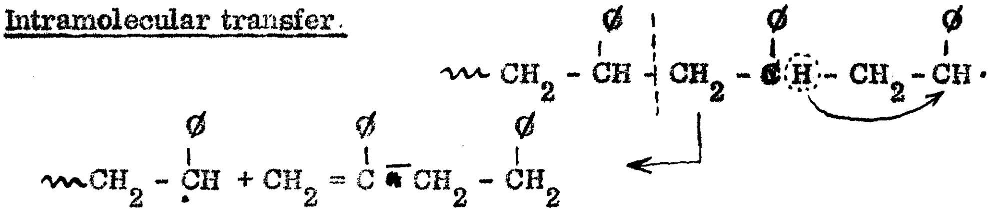
$$\sim CH_2-\overset{\phi}{CH}-CH_2-\overset{\phi}{CH}\sim \rightarrow \sim CH_2-\underset{\bullet}{\overset{\phi}{CH}} + \underset{\bullet}{CH_2}-\overset{\phi}{CH}\sim$$

Depropagation.



$$\sim CH_2-\overset{\phi}{CH}-CH_2-\underset{\bullet}{\overset{\phi}{CH_2}} \rightarrow \sim CH_2-\underset{\bullet}{\overset{\phi}{CH}} + CH_2=\overset{\phi}{CH}$$

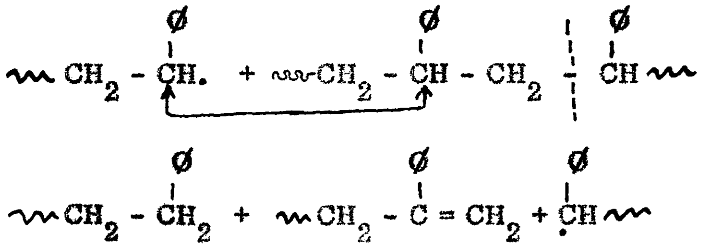
Intramolecular transfer.



$$\sim CH_2-\overset{\phi}{CH}-CH_2-\overset{\phi}{C}H-CH_2-\overset{\phi}{CH}\cdot$$

$$\sim CH_2-\underset{\bullet}{\overset{\phi}{CH}} + CH_2=\overset{\phi}{C}-CH_2-\overset{\phi}{CH_2}$$

Intermolecular transfer.



$$\sim CH_2-\overset{\phi}{CH}. + \sim CH_2-\overset{\phi}{CH}-CH_2-\overset{\phi}{CH}\sim$$

$$\sim CH_2-\overset{\phi}{CH_2} + \sim CH_2-\overset{\phi}{C}=CH_2 + \underset{\bullet}{\overset{\phi}{CH}}\sim$$

Termination.

2 Radicals → 2 polymer chains.

Simha and Wall explained the difference in theoretical (25%) and experimental (30 - 40%) values for the percentage conversion at the rate maximum on the basis of random breaking of bonds followed by intermolecular transfer.

6. Discussion of Weak Links Versus Intermolecular Transfer.

Jellinek,[13] Grassie and Kerr[21] favour the weak link theory. If intermolecular transfer were occurring, Grassie and Kerr argued, the molecular weight of the polymer should drop to values lower than those obtained. As mentioned earlier, Grassie and Kerr from their degradation experiments of polystyrene concluded on the basis of molecular weight measurements that polymers prepared at different temperatures have different proportions of weak links. This result, which strongly favours the weak link theory has not been explained satisfactorily by the proponents of transfer mechanism.

The molecular weight changes obtained on pyrolysis of normal polystyrene and poly -α deuterostyrene are different.[54] These results are compatible with the weak link theory.

According to Grassie and Kerr weak link scission does not give rise to free radicals, but stable molecules. A hydrogen transfer is necessary to convert the free radicals formed initially by homolytic fission into stable molecules.

The discrepancy in rate of molecular weight drop between normal polystyrene and poly - α - deutrostyrene can satisfactorily be explained on the assumption that the hydrogen atom involved is the one attached to the tertiary carbon atom.

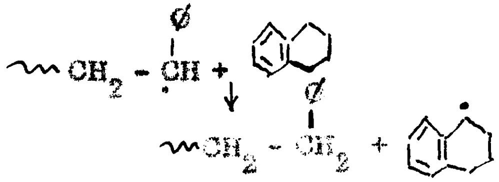
The ratio of monomer to non-monomeric products remains constant throughout the reaction, favouring intramolecular transfer as the source of non-monomeric fragments. But this evidence is not sufficient to exclude the possibility of intermolecular transfer. It is therefore not easy to decide as to which one of the two theories is correct, though the balance of evidence seems to favour weak links.

7. Further Evidence for Weak Links in Polystyrene.

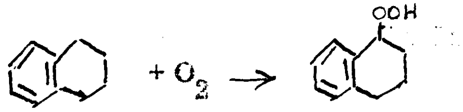
The original evidence on which the weak link theory for polystyrene degradation was based consisted solely of the shapes of the molecular weight versus percentage degradation curves. More recently, however, evidence for weak links has been found from two other directions.

(a) Solution Degradation.

Grassie and Cameron[33] examined the degradation of polystyrene in naphthalene and in tetralin solution. Tetralin was found to inhibit the production of volatile products, and the molecular weight of the polymer fell rapidly to a limiting value which agreed, within experimental error, with that obtained by extrapolating the linear portion of the molecular weight versus % conversion curve for bulk degradation of the same sample. The inhibitor action may proceed in the following way:



Tetryl radicals disappear by mutual interaction in pairs. The α hydrogen of tetralin molecule would be transferred in the reaction, since peroxidation of tetralin takes place at this active centre.



Depropagation in naphthalene proceeds in the usual way, as there is no reactive point for transfer reactions in the naphthalene molecule.

In the light of the intermolecular transfer theory, the radicals causing depropagation to volatile material should also be responsible for the initial drop in molecular weight. However, although the depropagation step in case of tetralin is suppressed the initial rapid fall of molecular weight is totally unaffected, and proceeds at almost the same rate as for bulk and naphthalene degradations.

According to the weak link theory the overall reaction consists of two distinctly independent reactions.

(a) Weak link scission.

(b) Depropagation.

The depropagation reaction is inhibited by the free radical acceptor. According to the weak link theory, the inhibition of the depropagation reaction as well as the decrease in concentration of polymer could not be held responsible for the initial fall in molecular weight which must therefore be due to weak link scission in the polymer chain. Non-monomeric fragments are produced by the intramolecular transfer reaction.

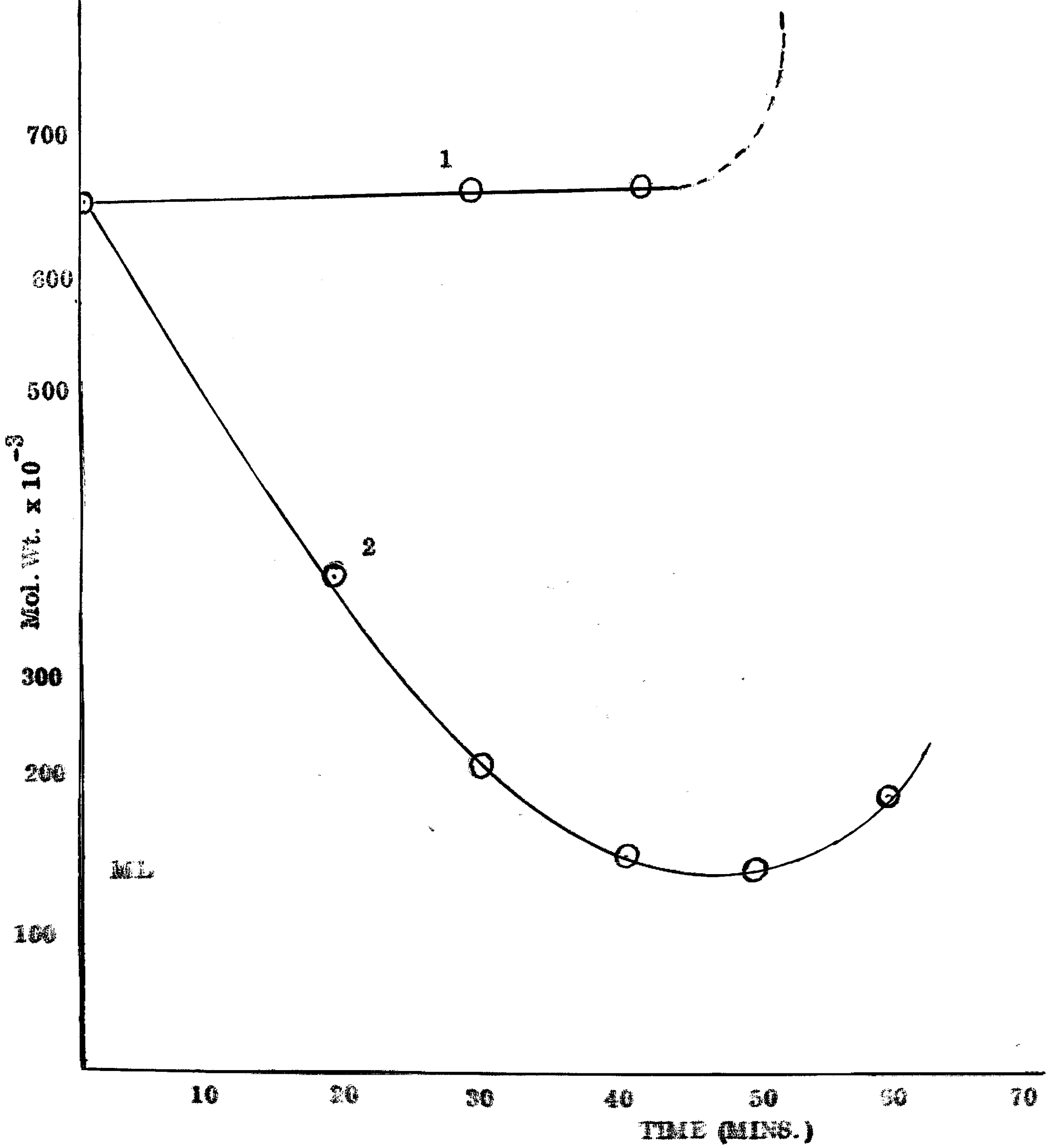


Figure 4: Grassie and Cameron's[29] data for ozonolysis of polystyrene. Curve 1: Molecular weight of ozonide. Curve 2: Molecular weight of ozonide after cleaveage with zinc and acetic acid. M_L is the limiting molecular weight of the same polymer on thermal degradation.

(b) Ozonolysis experiments:

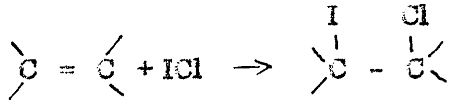
Only about 0.1% of styrene units in polystyrene are associated with weak links. It is not surprising, therefore, that close scrutiny of infra red spectra of undegraded and thermally degraded polystyrenes has failed to reveal any evidence of them. For the same reason estimation by normal analytical methods is not possible. However, if weak links are associated with unsaturation in the polymer backbone then molecular weight measurements represent a very sensitive method for their estimation if they can be selectively broken chemically. This method has also the advantage that chain terminal unsaturation will not interfere since the molecular weight changes associated with its destruction will be negligible. So with these considerations in mind Grassie and Cameron[29] ozonised polystyrene in "Analar" grade chloroform solution, and measured the molecular weight of the ozonide after various times of reaction. The molecular weight of the ozonide after cleavage by reduction with zinc and acetic acid was also measured. Grassie and Cameron's data are shown in Figure 4. Ozonolysis resulted in an increase in molecular weight. For the first 40 minutes of reaction, however, the molecular weight of the ozonide remained constant. If the ozonide is cleaved by reduction, the molecular weight falls during this initial period, then begins to rise. The minimum in the molecular weight of the cleaved ozonide corresponds closely with the limiting molecular weight obtained by the extrapolation procedure in thermal degradation of the polymer.

From these experiments, they concluded that weak links in polystyrene are associated with structural abnormalities incorporating unsaturation. No further evidence could be obtained, however, of their chemical nature. It became clear that any method by which unsaturation in polystyrene could be measured accurately could contribute greatly to further understanding of the nature of the weak links. It was from this stand point that the work of this thesis was approached.

8. Methods for the Determination of Unsaturation in Polymers.

Various chemical methods are available for polymer unsaturation determination down to about 0.5 mole per cent.

Most of the published work on unsaturation of polymers has been on butyl rubbers having unsaturation in the range of 1 - 5 mole per cent. A variety of procedures[34, 35] have been adopted to determine the unsaturation. Out of these the iodine/mercuric acetate method of Gallo, Weise, and Nelson[36], and the iodine chloride method of Lee, Kolthoff and Johnson[37] appear to be the most satisfactory. The former method is a standard procedure used industrially for butyl rubbers. Rubber samples in carbon tetrachloride are allowed to react with iodine in the presence of mercuric acetate. This method yields reproducible results provided time of reaction and concentration of reagent are strictly standardised. It suffers however from the disadvantage that the nature of reaction is not well understood and in order to calculate unsaturation values an empirical assumption must be be made that 3 iodine atoms are consumed per double bond. In case of the iodine chloride method the procedure usually consists in adding to a solution of unsaturated compound an excess of iodine chloride, and after a suitable reaction time determining by titration the amount of iodine chloride consumed.



The reaction of isoprene butyl rubber and butadiene butyl - rubber with iodine chloride in carbon tetrachloride solution has been the subject of a very careful study in which it was shown that the reaction with double bonds of butadiene type is straight forward addition of a molecule of ICl. Where there are substituents are in the vicinity of double bond, however, the reaction is complicated with side effects since the initially formed products possess steric strain and decompose by splitting out HI. The reaction is believed to involve following stages:

(i) ICl addition.

(ii) Splitting out of HI, which reacts with ICl to give HCl and I_2.

(iii) Gradual addition of ICl to the double bond resulted from stage (ii).

Lee, Kolthoff and Johnson[37] devised a method of calculating ~~of~~ unsaturation values from iodine chloride experiments giving values which were considered reliable for materials such as butyl rubbers. Results so obtained were in good agreement with those obtained by the drastic iodine-mercuric acetate methods.

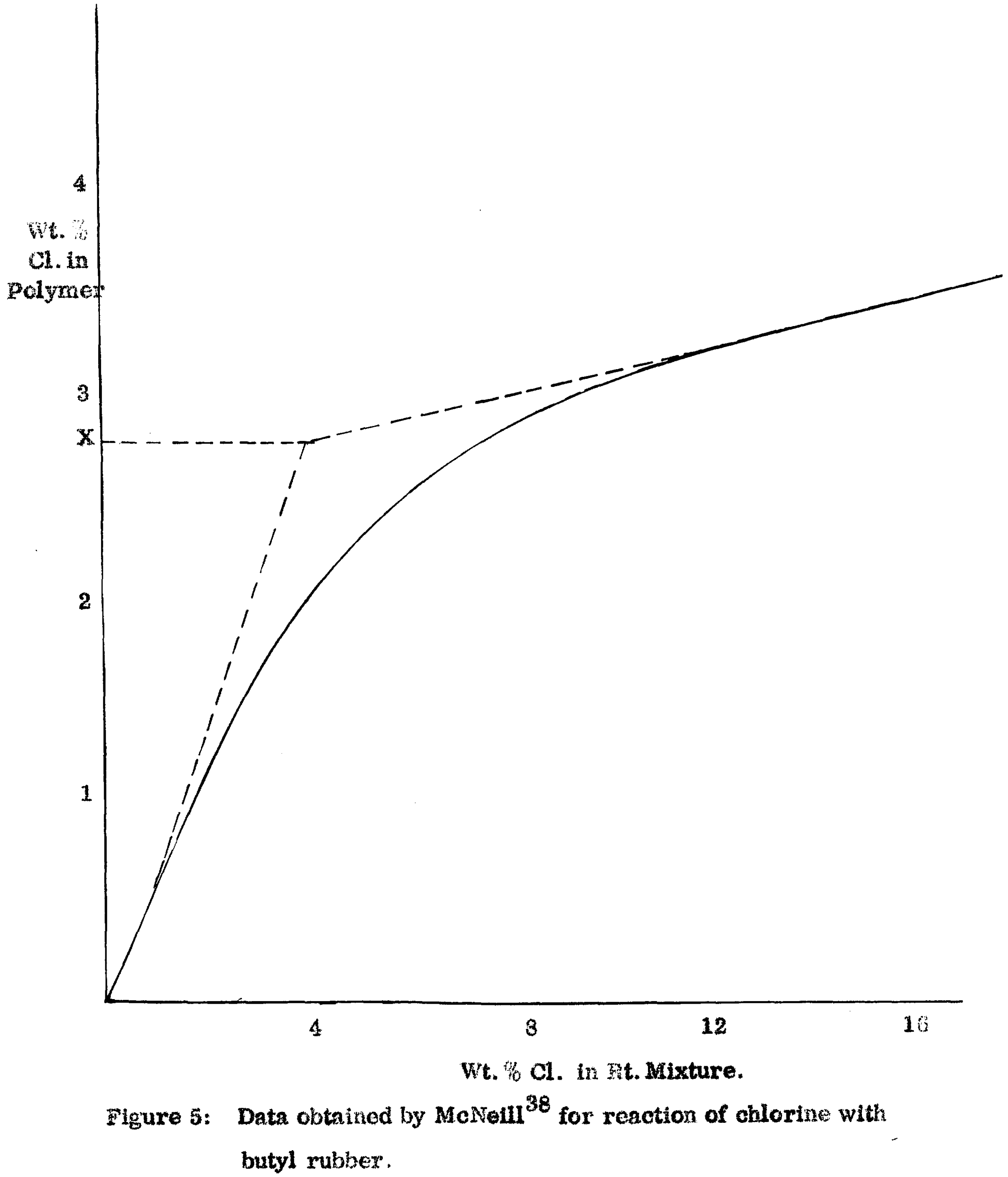


Figure 5: Data obtained by McNeill[38] for reaction of chlorine with butyl rubber.

As mentioned earlier, these methods are available for unsaturations which are above 0.5 mole %, but they are inadequate for unsaturations which lie below this limit. Thus while there is great interest in unsaturations far below 0.5 mole %, there are no satisfactory quantitative chemical methods for investigating these. Radio-chemical techniques enable us to overcome this difficulty. Very low double bond contents can be accurately determined using a re-agent labelled with a suitable radioactive isotope.

A radio chemical method using chlorine labelled with Cl^{36} as re-agent has been used successfully by McNeill[36] for butyl rubbers with unsaturation around one mole per cent. This technique is capable of measuring unsaturation of a very low order.

For reaction with butyl rubber the effect of varying the concentration of chlorine with reaction mixture was observed. The graph of chlorine content of polymer against chlorine content of reaction mixture has an initial steeply sloping linear part then a gradual transistion to a linear part of small slope (Figure 5). Extrapolation of the two linear portions as shown gave a point of intersection which corresponded to 2 atoms of chlorine per original double bond.

Chlorine does not react with butyl rubber by addition, since, even with prolonged reaction and excess polymer, McNeill found that only 50%, or less, of the Cl_2 initially present appeared in the reacted polymer. Similarly, isobutene monomer reacts with chlorine (1 mole) by the substitution reaction.

Chlorine reacts with styrene, however, by addition. Thus the mode of reaction in a particular case will depend on the environment of the reacting double bond. In the case of polymer the behaviour of the corresponding monomer or a suitable model compound will normally provide a guide to the type of reaction to be expected at double bonds in the polymer.

9. Possible Sources of Unsaturation in Polystyrene.

It is important to recognise that unsaturation in polystyrene could conceivably arise in other ways to that suggested in the "quinonoid" weak link structure theory. Terminal unsaturation might be present which has no bearing on weak link scission. Terminal unsaturation is unlikely for polymers prepared in the presence of initiator since initiator fragments would be expected at both chain ends. This follows from the fact that termination in the polymerisation of styrene is exclusively by combination of radicals[22, 23, 24].

The possibility can be tested, however, by examining the unsaturations of a series of polymers of different molecular weights prepared using different initiator concentrations at the same temperature. If there is no terminal unsaturation all should show the same apparent unsaturation.

Terminal unsaturation could arise, however, in the case of polymers prepared by thermal initiation. The mechanism of this process is not understood, although a number of theories have been put forward[39, 40, 41].

10. Scope and Aim of the Present Work.

The intention of the work described in this thesis was to use the radiochlorine method for studying low unsaturations to provide information on the concentration of double bonds in various polystyrene samples.

(a) Polymers of different molecular weight were prepared at 60° using benzoyl peroxide as initiator. The unsaturations were examined to determine if there is any effect of molecular weight on the unsaturation. If terminal double bonds are present, then the unsaturation should increase, for a given weight of polymer, as the molecular weight decreases. On the other hand, if there is no terminal unsaturation all these samples should show the same unsaturation.

(b) A polymer was prepared at 80° in order that the effect of polymerisation temperature on unsaturation could be seen by comparison of polymers prepared at 60° and 80°.

(c) The results of (a) and (b) should shed further light on the nature of the supposed weak links in polystyrene.

(d) Two polymers were prepared by thermal initiation, at 120° and 140°, to see whether unsaturation measurements could provide any evidence on the mechanism of thermal initiation.

(e) The unsaturation of partially degraded polystyrene was measured to provide additional information on the mechanism of chain scission in the degradation of polystyrene.

PART II

EXPERIMENTAL TECHNIQUES
AND
RESULTS.

1. Preparation of Polymers.

As pointed out earlier, polymerisation conditions are very important and can effect the structure of the polymer. In addition, as it is not yet fully known at what stage weak links may be formed, it is advisable that as many variables as possible should be eliminated from the polymerisation process. Keeping this aim in mind, the following techniques were adopted.

(i) Purification of initiator:-

Benzoyl peroxide, which was used as initiator, contained 20 % water. It was dissolved in chloroform and a saturated solution was filtered and precipitated with A.R. methanol at room temperature. It was stored in the dark over calcium chloride.

(ii) Purification of monomer:-

Inhibitor was removed from the monomer by repeated washing with 20 % sodium hydroxide solution, and when further washing did not produce any reddish-brown colouration in the aqueous layer, the monomer was then washed freely with water to get rid of any alkali left, and tested with litmus. Inhibitor free monomer was then dried over calcium chloride for about 48 hours. Monomer was then distilled under vacuum, the first 30 cc. of distillate being discarded. The monomer obtained was a colourless, water white liquid.

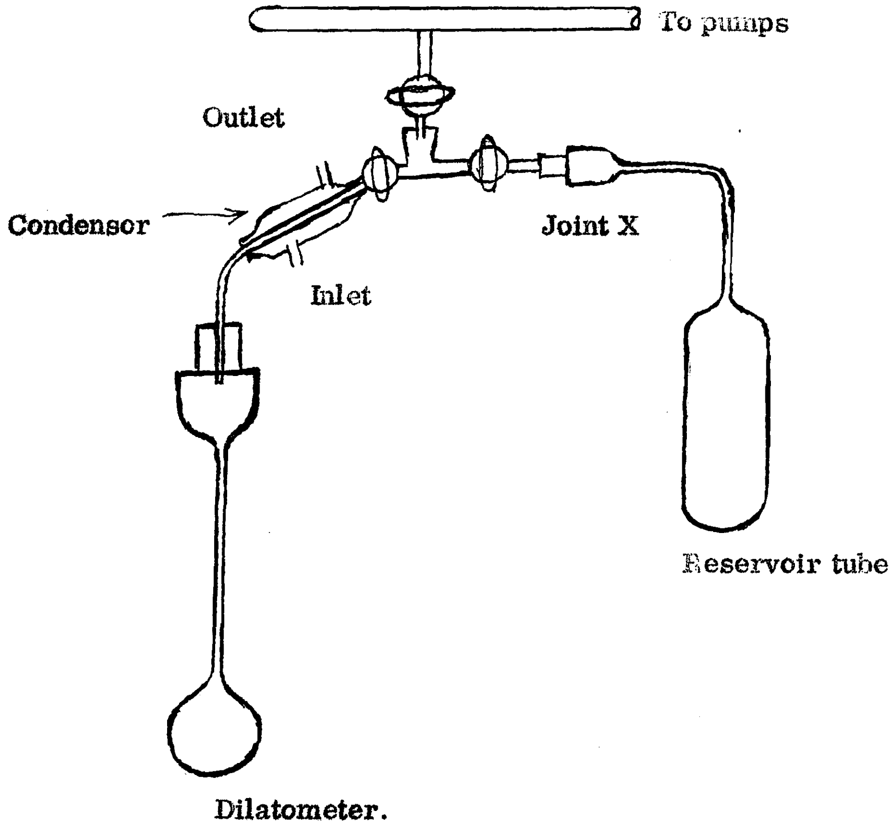


Figure 6: Vacuum system used in filling dilatometers.

(iii) Filling of dilatometers:-

The vacuum system used in filling of dilatometers is shown in Figure 6. A vacuum of the order of 10^{-5} mm Hg was obtained using a mercury diffusion pump backed by a rotary oil pump. Monomer was degassed four times by freezing and thawing, and 25 cc of the first distillate discarded before filling the dilatometer. A water condenser was used as shown in Figure 6 to accelerate the distillation, and was found very efficient, it reduced the distillation time by three quarters.

A polymer film which was found to form in reservoir tube was broken periodically by shaking the reservoir tube round the joint X. Thus distillation was continuous. When the required amount of monomer had distilled over, the dilatometer was sealed under vacuum and the monomer was thawed and placed in a refrigerator at -16°C till needed.

Whenever polymerisation in presence of initiator was intended, the required amount of initiator was first introduced into the dilatometer along with a small quantity of chloroform to dissolve it. The chloroform was removed under vacuum and the dilatometer was then attached to the system as before and monomer distilled over.

(iv) Polymerisation in presence of initiator:-

The polymerisation was carried out in a water tank controlled to $\pm 0.05^{\circ}$C by a Sunvic H.V.S. Relay and a spiral-type mercury - toluene regulator. The initial expansion of the monomer and its subsequent contraction on polymerisation were calculated from the data of Melville and Valentine[42].

(v) Thermal polymerisation:

Thermal polymerisations at 120°C and 140°C were carried out using vapour jackets of boiling per-chloroethylene and m- xylene respectively. These polymerisation temperatures are the boiling points of the liquids.

2 Precipitation of Polymers.

When the polymerisation was complete to the extent needed, the contents of the dilatometer were precipitated in 'Analar' methanol. After this process had been repeated several times, the polymer, obtained in white fluffy form, was dried under vacuum for over two days. It was then stored in dark bottles. Polymers were further dried by heating to 105° under vacuum for 1 hour before use in chlorination experiments. It was verified that no change in molecular weight occurred during this drying process.

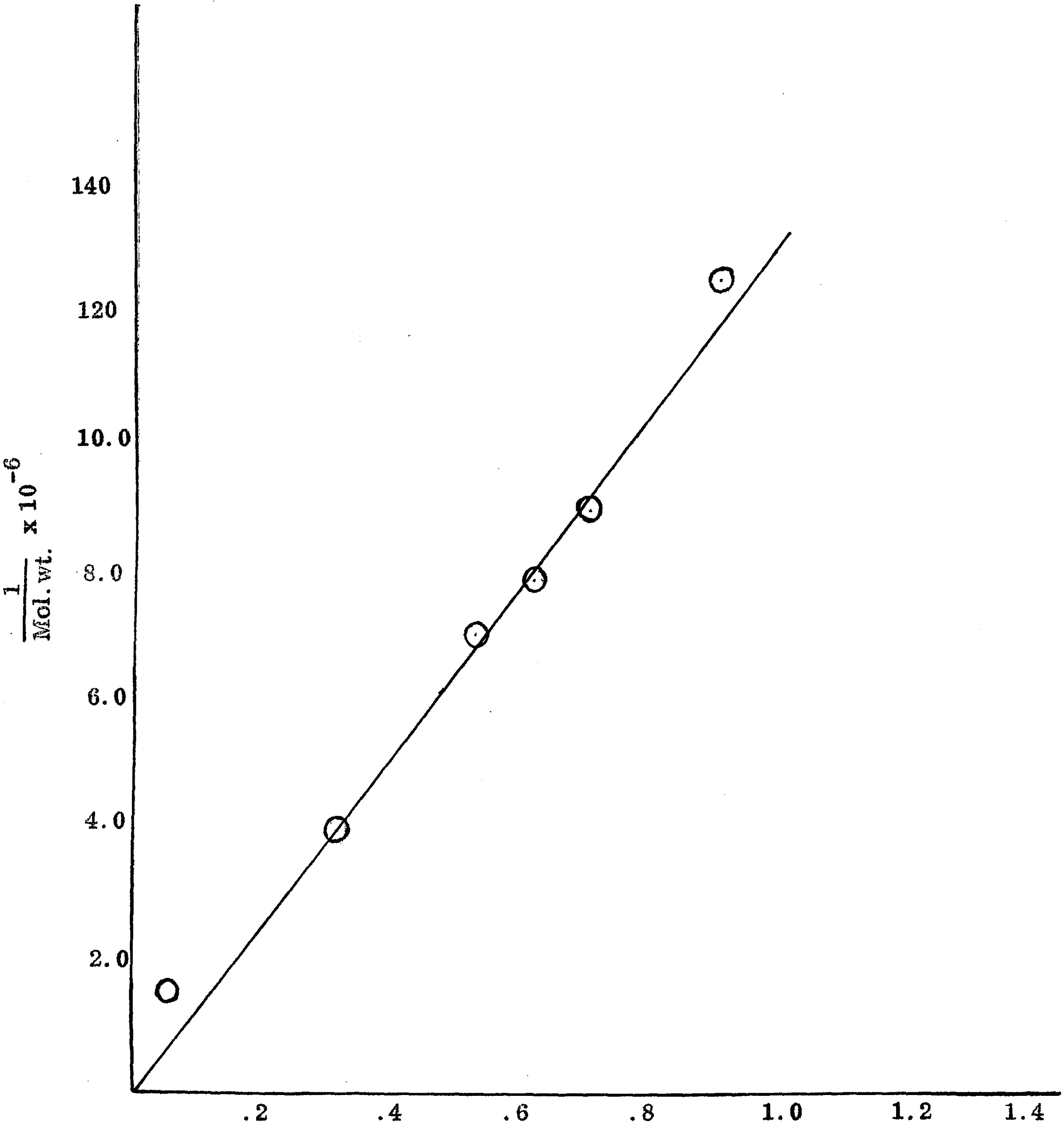


Figure 7: Reciprocal molecular wt. versus square root of initiator concentration for polymers initiated using benzoyl peroxide at 60°C.

3. Measurement of Molecular Weights.

The initial molecular weight measurements were carried out using the osmometer described by McNeill[43]. This permitted one determination per day to be carried out. In the later stages of the work the Mechrolab High Speed Membrane Osmometer[44] became available. With this instrument several molecular weights could be determined in a day. Sylvania 300 grade celephane membranes, conditioned as described by McNeill, were used in both instruments.

Since two different types of osmometers were used, it was important to establish that results were directly comparable. Equally good π/C versus C plots were obtained with both instruments and in all cases where samples were examined in the two osmometers the results obtained were in excellent agreement.

The polymerisation conditions and molecular weights of the polymers are given in Table I. The reciprocal of the molecular weight is plotted against square root of the initiator concentration in Figure 7. Since the line obtained passes through the origin, transfer cannot occur to any significant extent in these polymerisations. Osmotic pressure data with McNeill's osmometer appear in Figure 8 and for the Mechrolab osmometer in Figures 9 and 10.

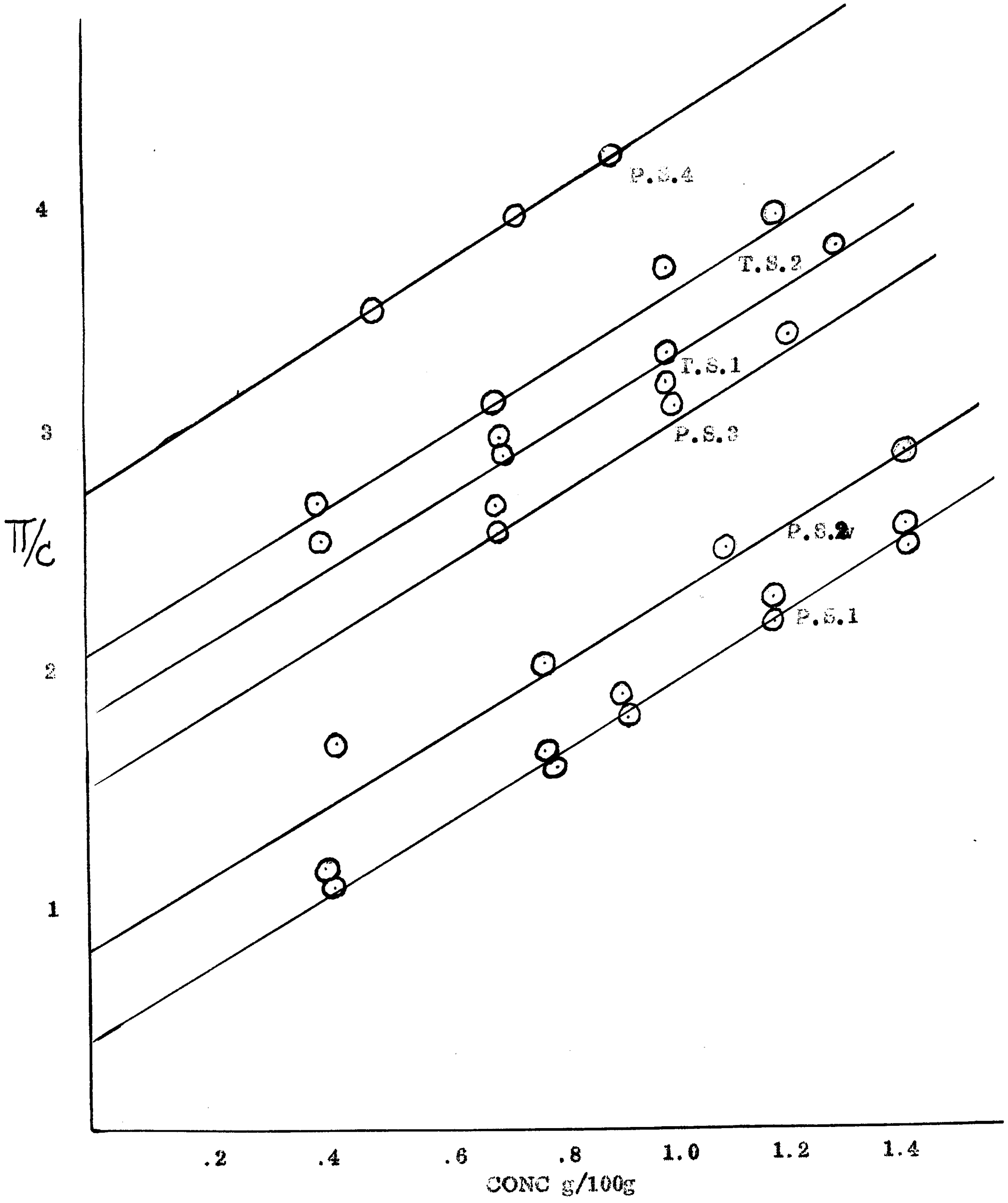
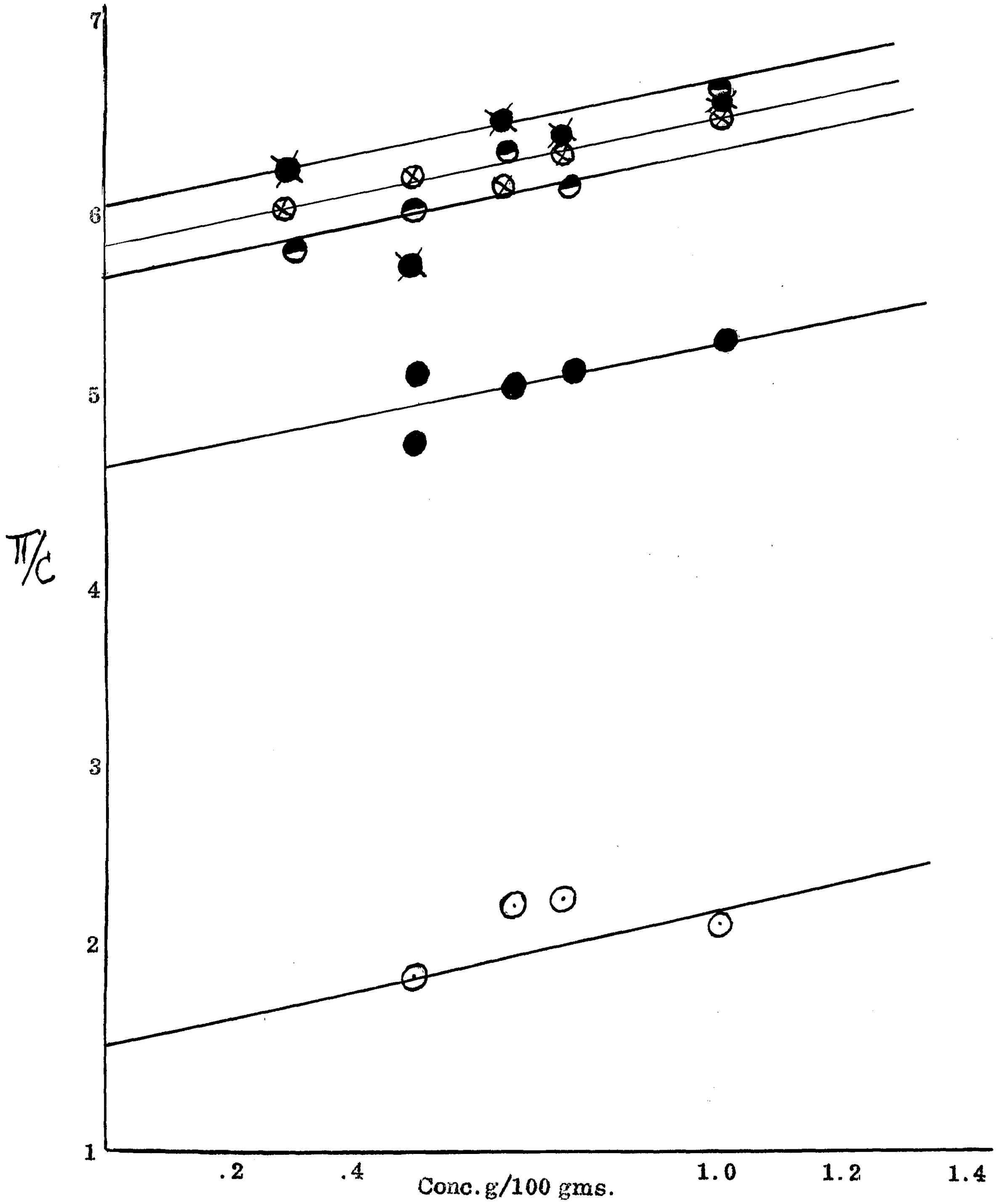


Figure 8: Π/c versus C plots for polymers obtained using the osmometer of McNeill[45].



Key Undergraded ⊙ 12.5% ● 32.5% ⊖ 41.5% ⊗ 55% ✖

Figure 10: π/c versus c plots for undergraded P.S.$_8$ and for samples degraded to different extents. (Mechrolab osmometer).

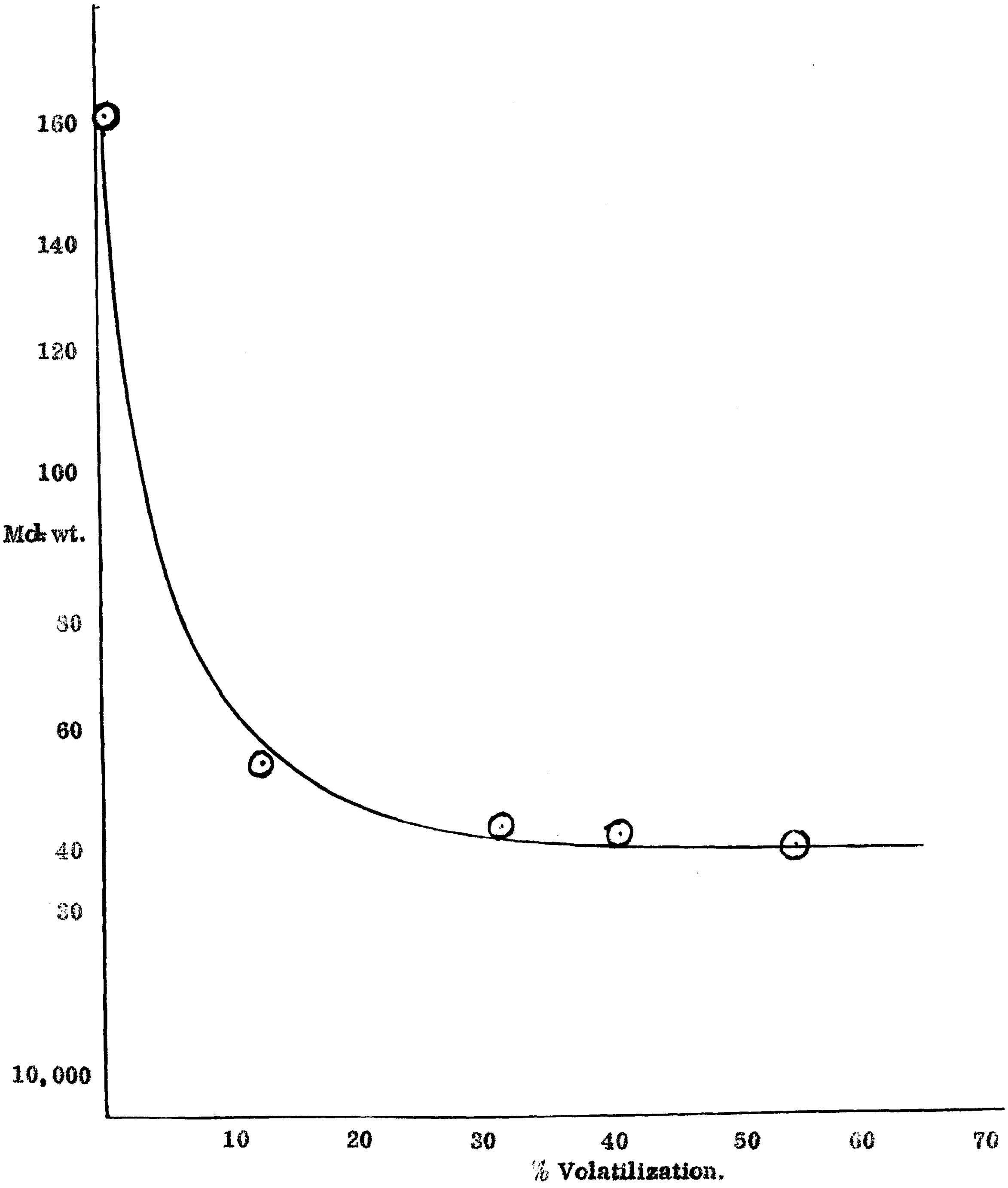


Figure 11: Molecular weight versus % volatilization for polymer P.S.$_8$ degraded at 330°.

4. Design and Operation of the Radio-Chlorine Gas Apparatus.

(i) Preparation of radiochlorine:-

Radiochlorine was prepared[45] by the decomposition of radioactive palladous chloride, which was obtained by the exchange of radio active HCl solution with palladous chloride.

$$\mathrm{HCl^*} + \mathrm{PdCl_2} \rightleftharpoons \mathrm{PdCl_2^*} + \underset{\substack{\downarrow\\ \text{less radio active}}}{\mathrm{HCl}}$$

$$\mathrm{PdCl_2^*} \xrightarrow{\text{heat}} \mathrm{Pd} + \mathrm{Cl_2^*}$$

About 100 mgs of palladous chloride were placed in a flask, with an extended neck. 5 ml of radioactive HCl were then pipetted into the flask. The sides and neck of the flask were washed down with distilled water, the neck was then bent over at about 90°, and the mixture shaken gently, heating all the time slowly on a micro burner until the palladous chloride dissolved. The aqueous HCl, now less radioactive because of the exchange with $\mathrm{PdCl_2}$, was distilled into another flask. It was important not to distil the solution completely to dryness because of the risk of overheating the palladous chloride.

Radioactive palladous chloride was further dried by placing the flask in a container heated to about 110°C. The drops of distillate which appeared on the side arm of the flask were removed by means of paper tissue. A plug of glass wool was inserted into the arm of the flask, which was then connected to bulb F in the vacuum system shown in Figure 12. Stopcocks 1 - 6 were greaseless

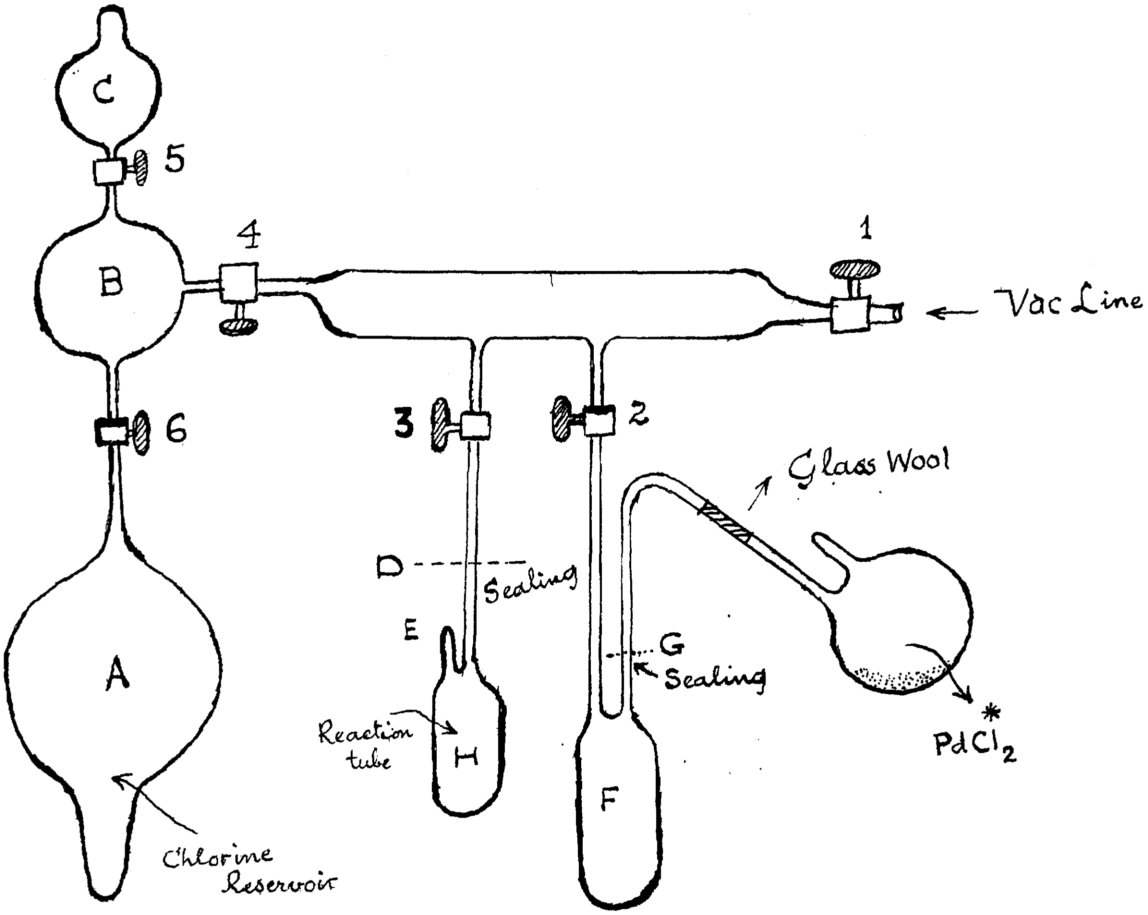


Figure 12:- Apparatus for handling radioactive chlorine.

stopcocks with Viton A fluorocarbon diaphragms (G. Springham & Co. Ltd.).

The system was evacuated, and left under vacuum for a few hours; to ensure that the palladous chloride was completely free from moisture. The greaseless stopcock 2 was then closed and the flask containing dry palladous chloride was heated gently with a large luminous flame, keeping the flame moving all the time. If a portion of flask is overheated, being under high vacuum, it may implode. Chlorine was condensed in bulb F, which was dipping in liquid nitrogen. Heating was continued till a 'palladium mirror' was formed and all traces of red palladous chloride had disappeared. The bulb was then drawn off.

Stopcocks 1, 3 and 5 were closed and chlorine was then finally transferred into the reservoir bulb A by thawing F, opening stopcock 2 and freezing the tail of A in liquid nitrogen.

(ii) <u>Delivery fraction</u>:-

A definite fraction of the total weight of chlorine present in bulb A can be removed by evacuating bulbs B and C, opening stopcock 6, (keeping stopcocks 4 and 5 closed), allowing the chlorine to expand into bulb B, and giving it 5 minutes to reach the same pressure in both bulbs. Stopcock 6 is now closed. B contains a weight of chlorine given by the original weight in A multiplied by the 'delivery fraction' $= \dfrac{\text{Vol of B}}{\text{Vol of A} + \text{Vol of B}}$, which can be distilled into a calibrated reaction tube H.

Further portions of chlorine from A may be removed by repeating these operations, the amount removed being a constant fraction of that present in bulb A before expansion into B. Similarly the delivery fraction between the reservoir and bulbs B + C can be calculated.

(iii) Filling the reaction tube:

Reaction tubes were of about 20 ml capacity and had two arms (H, Figure 12). One arm of H is fused on to the apparatus at D, and the polymer solution for reaction is added through the other arm using a hypodermic syringe. The latter arm is then sealed at E. The solution in H is degassed four times, by freezing and thawing. Radiochlorine from the bulb system is then distilled into the frozen mixture. Finally the reaction tube is removed by drawing off at D, and thawed to the reaction temperature, 25°C.

(iv) Calibration of radiochlorine gas apparatus:-

The apparatus is calibrated for use by determining the delivery fraction. Two methods may be used.

(a) Successive portions of inactive chlorine are collected in reaction tubes, containing 10 ml of $\frac{N}{10}$ potassium iodide solution, which has been degassed four times by freezing and thawing. The tubes are sealed under vacuum, and thawed at room temperature. The amount of iodine liberated estimated by titration against $\frac{N}{10}$ sodium thiosulphate.

The ratio of litres from successive samples is

$$1 - \frac{\text{Vol of A}}{\text{Vol of A + Vol of B}}$$

Similarly, the ratio of litres from successive samples from A, expanded into B and C =

$$1 - \frac{\text{Vol of A}}{\text{Vol of A + Vol of B + Vol of C}}$$

Hence the delivery fraction can be calculated in each case.

Results for a series of successive operations are given in Table 2.

(b) The delivery fraction can be determined radiochemically with radiochlorine initially in bulb A. Successive portions are collected using the same technique as above in reaction tubes containing 5 ml of a 5% V/v solution of styrene in AR. carbon tetrachloride, the sealed tubes are thawed at room temperature and left in the dark for more than two hours. The contents of each tube are then made up to 25 ml with CCl_4, and 10 ml portions of these solutions are counted in a liquid counter. The ratio of counts from successive samples, corrected for background, allows the delivery fraction to be calculated. As can be seen from results in Table 2, the values of the delivery fraction obtained by both methods are in good agreement.

TABLE 2.

CALIBERATION OF RADIOCHLORINE GAS APPARATUS.

For expansion into B only.

Operation No.	Thiosulphate Used	Counts/Minute	Ratio
1	2.68 ml	-	
2	2.12 ml	-	0.791
3	1.675 ml	-	0.790
4	1.325 ml	-	0.791
A		6309)	0.792
B		5008)	

Mean ratio:- 0.791

Delivery fraction:- 0.209

For expansion into B + C.

1	1.78	-	
2	1.31	-	0.736
3	0.960	-	0.732
4	0.710	-	0.739
5	0.520	-	0.732
A	-	1182	
B	-	869	0.735
C	-	636	0.732
D	-	470	0.739

Mean ratio:- 0.734

Delivery fraction:- 0.266

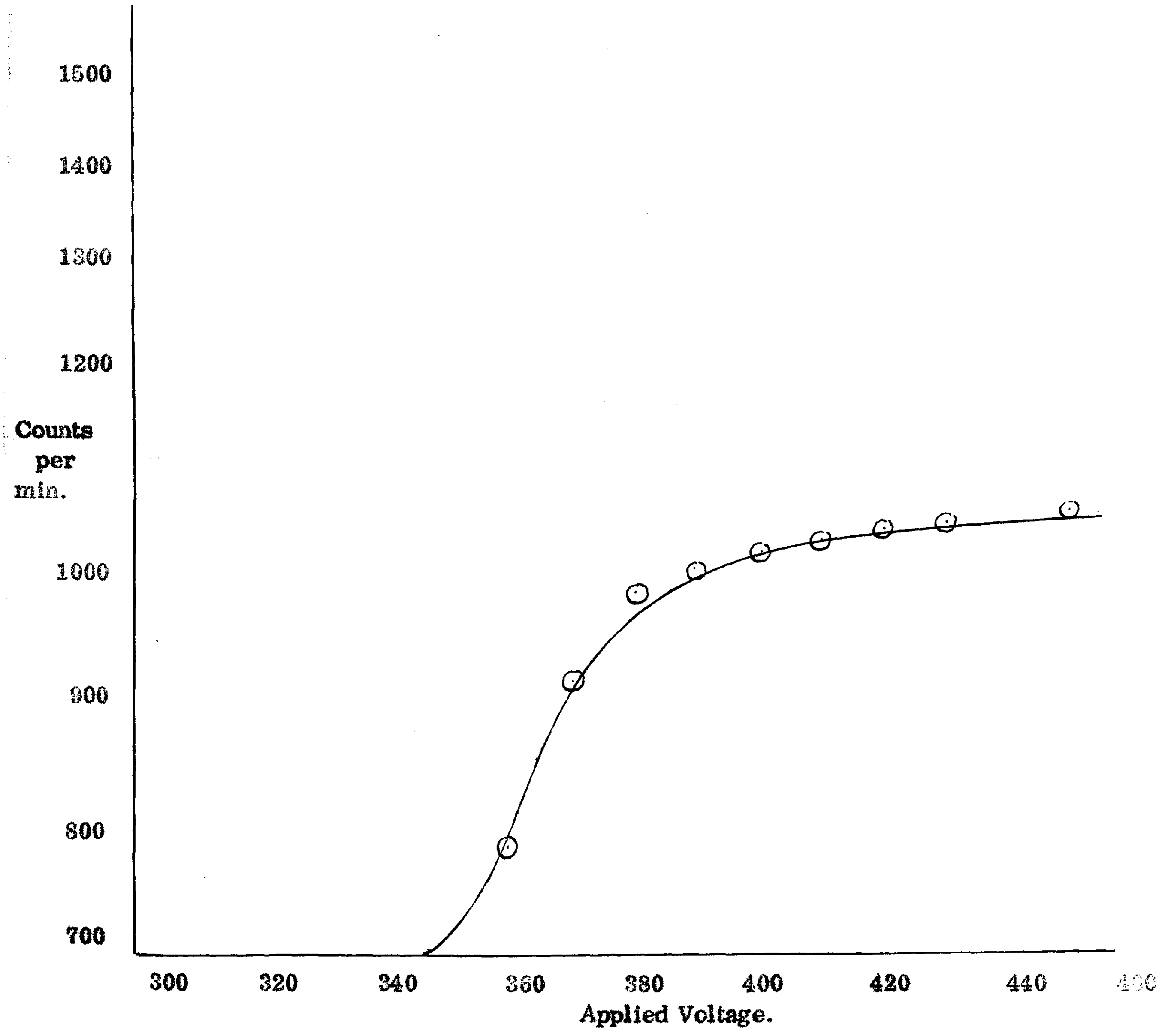


Figure 13: Determination of plateau for liquid Geiger counter tube, using uranyl nitrate solution.

5. Counting Technique.

10 ml portions of solutions were counted in a liquid Geiger counter tube (Mullard type Mx 124), using a Bendix Ericsson scaler type 121A and a type 110A probe unit. Paralysis time on the probe unit was set at 400 microseconds. The liquid counter was supported in a Panax lead castle.

The plateau of the liquid counter was obtained (Figure 13) by plotting applied voltage against counting rate while using as a standard source a solution of uranyl nitrate. It had a plateau which extended over 100 volts, and counts were taken using an applied potential of 400 volts. The counter efficiency was checked periodically with the same standard source and was found to remain constant.

In each determination of polymer activity, 10 ml of polymer solution in carbon tetrachloride were counted, due allowance was made for counter dead time and background, and the activity per gram of polymer was calculated. When the counter was emptied of polymer solution, it was rinsed twice with CCl_4, then with chromic acid, washed with water and finally rinsed with acetone. The counter was dried by blowing a jet of compressed air into it. At the end of each day, the counter was filled with chromic acid, and left over night.

6. Determination of Specific Activity of Radiochlorine.

Two methods were used.

(1) The specific activity of radiochlorine was determined from two successive operations of the apparatus. The first sample of radiochlorine was collected in aqueous KI, as described earlier and chlorine estimated by titration of the liberated iodine with $\frac{N}{10}$ sodium thiosulphate. The second sample of chlorine was distilled into a reaction tube containing 5% V/V styrene in carbon tetrachloride and made up to a standard volume for counting.

The weight of chlorine in the latter sample was calculated from the former result multiplied by (1 - delivery fraction). The specific activity of radiochlorine can thus be expressed as counts/min./ mg chlorine when counted in carbon tetrachloride solution.

(2) Radio chlorine is very expensive, and in the above method, two samples of radio chlorine had to be used in order to get the specific activity. Therefore the following method was tried, and found to give excellent results.

A portion (x grams) of radio chlorine was distilled into a reaction tube containing 10 ml of aqueous $\frac{N}{10}$ potassium iodide solution (degassed): the tube was sealed under vacuum, and then thawed to room temperature. The contents of the tube were made up to 20 ml, 10 ml portions of this were counted and the counts corrected for dead time and background. This 20 ml of radioactive potassium iodide solution was then titrated against sodium thiosulphate as before, giving the amount of Cl_2 distilled over.

If χ mgs of Cl_2 give N counts/min.

then, 1 " " " " $= \frac{N}{\chi}$ c.p.m.

but this is counted in aqueous solution.

Dividing by the density of carbon tetrachloride (1.59), we get the specific activity of radiochlorine in the CCl_4 solution.

$$\frac{N}{\chi} \times \frac{1}{1.59} = \frac{N}{1.59\chi} \text{ counts/Min./mg}Cl_2$$

Results thus obtained were compared with those obtained by the first method, and were found to be in quite good agreement (Table 3).

7. Reaction of Polystyrene with Radiochlorine.

Accurately weighed polymer samples of approximately 250 mgs dried as above were dissolved in 10 ml of carbon tetrachloride (over night). Solutions were then transferred to the reaction tube attached to vacuum line using a hypodermic syringe. By adding washings from the flask and syringe, the liquid in the reaction tube was made up to a calibration mark corresponding to a volume of 15 ml. The side arm E as shown in Figure 12, through which the polymer solution was added to the reaction tube, was then sealed. Solutions were then thoroughly degassed as already described and radio chlorine passed as before. After the reaction vessels had been sealed off, and thawed, they were immersed in a bath at 25°C, and left to react for 1 hour, with exclusion of light.

8. Purification of reacted polymer.

Solutions after reacting with radiochlorine contain reacted polymer and unreacted chlorine. Before counts may be made on the polymer it is necessary that the excess radiochlorine must be removed.

Immediately after each reaction tube was opened, it was poured into 500 ml of AR methanol, which was being vigorously stirred using a magnetic stirrer. The polymer thus obtained was redissolved in carbon tetrachloride, and reprecipitated three times. It was then dried in a vacuum desiccator for about 48 hours. The dried reacted polymer was weighed into a 12 ml standard flask, thoroughly dissolved in carbon tetrachloride and made up to the mark. A 10 ml portion of this solution was pipotted into a liquid counter, and counted over one hour. The polymer was reprecipitated in AR methanol, dried, weighed, dissolved and counted again. The activity obtained was compared with that obtained after the third reprecipitation. No difference was found, showing that after three precipitations there is no free chlorine left trapped in the polymer. From the activity, knowing the specific activity of chlorine and the weight of reacted polymer, the weight per cent chlorine in the polymer can be calculated.

It was verified that, as expected, the concentration of the polymer solution had no significant effect on the observed activity per gram of polymer.

9. Degradation Experiments.

The apparatus used was similar to that of Grassie and Kerr[19]

TABLE 3.

Comparison of two methods for determination of the specific activity of radiochlorine in CCl_4 solution.

(Delivery fraction of apparatus = 0.209)

Operation No.	Wt. of Cl_2 present in 10 ml.		C.p.m. for 10 ml.		Specific Activity c.p.m./mgCl.		
	by titrn.	calc. from D.F.	aq.KI	CCl_4.	aq.KI	CCl_4.	$\frac{\text{aq.KI}}{1.59}$
1	1.96	-	9191	-	4690	-	2947
2	-	1.55	-	4629	-	2986	-
3	-	1.23	-	3640	-	2969	-
4	0.997	(0.980)	4732	-	4745	-	2980

The extent of volatilisation was calculated from the loss in weight of the polymer. Four samples of polymer P.S.8 (M.W.=160,000) were degraded at 330° to different extents, the polymer residue was dissolved and the molecular weight of the degraded polymer was measured using the Mechrolab osmometer. The plot of molecular weight versus % volatilisation obtained from these results is shown in Figure 11.

The stability of polymer samples which had been reacted with radio chlorine was investigated. If chlorine is reacting with weak links in the polymer, then the change in structure on chlorination might cause some difference in behaviour. No such difference was observed.

Determination of Unsaturation of Polystyrene Samples.

The method of obtaining the unsaturation of butyl rubbers by reaction with radiochlorine, used by McNeill[45] has already been discussed (see page 23 and Figure 5). Essentially this consisted of reacting samples of polymer with different concentrations of chlorine and determining the amount of chlorine present in the polymer. A graph was drawn of wt. % Cl in polymer versus wt. % Cl in reaction mixture.

The approach used in the present work was similar, but because of the very small amounts of chlorine involved it was not feasible to work with very low values of wt. % Cl in the reaction mixture. The initial linear portion of the graph could not therefore be obtained. The results shown in the figures which follow, however, indicate that, as with butyl rubber, a second linear portion is obtained once chlorination is complete. The very small slope with polystyrene indicates the almost complete absence of side reactions such as main chain chlorination, under the conditions used. By extrapolating the linear portion to the axis, a value (W) of wt. % Cl in the polymer corresponding to complete reaction of any double bond present is obtained.

In order to determine the unsaturation, it is necessary to assume that two atoms of chlorine are incorporated in the polymer per double bond. This assumption is reasonable by analogy with the behaviour of styrene monomer, which is found to add 2 atoms of chlorine.

It follows that the unsaturation expressed as moles per cent (U) is given by

$$U = W \times \frac{\text{molecular weight of monomer}}{\text{molecular weight of chlorine}}$$

It is more convenient to express the unsaturation as a number of double bonds per 1000 monomer units (D) or as a number of double bonds per chain (C).

$$\text{Thus} \quad D = 10\,U = \frac{1040W}{70.9} = 14.7\,W$$

$$\text{and} \quad C = D \times \frac{\text{chain length}}{1000}$$

$$= D \times \frac{\text{mol. wt.}}{1000 \times 104}$$

$$= \frac{10 \times W \times \text{mol. wt.} \times 104}{1000 \times 104 \times 70.9}$$

$$= \frac{W \times M}{100 \times 70.9}$$

$$= \underline{1.41\, W\, M \times 10^{-4}}$$

The results obtained for eight polymers are presented in Tables 4 to 11 and shown graphically in Figures 14 to 18.

All the results are summarised in Table 12, page 53.

Molecular Weight of Chlorinated Polymer.

The shape of the plots of wt. % Cl in polymer versus wt. % Cl in reaction mixture suggests that side reactions are negligible. If the reaction of chlorine with double bonds is a straight forward addition, no chain scission would be expected. On both these grounds, therefore, no change in the molecular weight of the polymer should occur as a result of chlorination. This was tested by measuring the molecular weights of a number of chlorinated samples of polymer. No change in molecular weight was observed.

TABLE 4

Reaction of Polymer P.S.1 (peroxide initiated, 60°C) with Radiochlorine in carbon tetrachloride solution at 25°.

Time of reaction: 1 hour.

Radiochlorine specific activity: 3460 C.p.m./mgcl.

Operation No.	Wt. % Cl in reaction mixture.	Activity of polymer c.p.m./g.	Wt. % Cl in polymer (W)
1	3.03	3596	0.104
2	2.47	3299	0.095 ~~0.100~~
3	1.85	1852	0.051
4	1.60	1742	0.050
5	1.23	1546	0.045
6	0.99	1396	0.040

Extrapolated Value of W = 0.10~~2~~ ± 0.1

TABLE 5

Reaction of Polymer P.S.2 (peroxide initiated, 60°C) with Radiochlorine, in carbon tetrachloride solution at 25°.

Time of reaction: 1 hour.

Radiochlorine specific activity: 3951 c.p.m./mgcl.

Operation No.	Wt. % Cl in reaction mixture.	Activity of polymer c.p.m./g.	Wt. % Cl in polymer (W)
1	4.5	3991	0.100
2	3.34	4242	0.107
3	1.77	3396	0.086
4	1.24	2642	0.067
5	0.82	1806	0.046

Extrapolated Value of W = 0.10~~2~~ ± 0.01

TABLE 6

Reaction of Polymer P.S.3 (peroxide initiated, 60°C) with Radiochlorine, in carbon tetrachloride solution at 25°.

Time of reaction: 1 hour.

Radiochlorine specific activity: 1518 c.p.m./mgcl.

Operation No.	Wt. % Cl in reaction mixture.	Activity of polymer c.p.m./g.	Wt. % Cl in polymer (W)
1	4.33	1554	0.102
2	3.80	1521	0.100
3	2.51	1122	0.073
4	1.50	975	0.064
		Specific activity:	2770 c.p.m./mgcl.
5	1.00	859	0.030

Extrapolated Value of W = 0.10%. ± 0.01

TABLE 7

Reaction of Polymer P.S.4 (peroxide initiated, 60°C) with Radiochlorine, in carbon tetrachloride solution at 25°.

Time of reaction: 1 hour.

Radiochlorine specific activity: 3899 c.p.m./mgcl.

Operation No.	Wt. % Cl in reaction mixture.	Activity of polymer c.p.m./g.	Wt. % Cl in polymer (W)'
1	4.0	4130	0.106
2	1.81	3550	0.087
3	1.42	2857	0.073
4	1.08	1711	0.043

Extrapolated Value of W = 0.10%. ± 0.01

TABLE 8

Reaction of Polymer P.S.5 (peroxide initiated, 60°C) with Radiochlorine, in carbon tetrachloride solution at 25°.

Time of reaction: 1 hour.

Radiochlorine specific activity: 2550 cp.m./mgcl.

Operation No.	Wt. % Cl in reaction mixture	Activity of polymer c.p.m./g.	Wt. % Cl in polymer (W)
1	6.1	2696	0.105
2	5.2	2726	0.106
3	4.4	2290	0.089
4	4.0	2577	0.100

Extrapolated Value of W = 0.10%. ± 0.01

TABLE [illegible]

Reaction of Polymer P.S.3 (thermal initiation, 120°) with Radiochlorine, in carbon tetrachloride solution at 25°.

Time of reaction: 1 hour.

Radiochlorine specific activity: 3936 c.p.m./mgCl.

Operation No.	Wt. % Cl in reaction mixture	Activity of polymer c.p.m./g.	Wt. % Cl in polymer (W)
1	14.11	5876	0.148
2	9.95	5071	0.129
3	7.6	5692	0.144
4	4.1	5363	0.136
5	2.1	2443	0.062

Extrapolated Value of W = 0.14%. ± 0.01

TABLE 10

Reaction of Polymer P.S.9 (thermal, 140°C) with Radiochlorine, in carbon tetrachloride solution at 25°.

Time of reaction: 1 hour.

Radiochlorine specific activity: 757 c.p.m./mgcl.

Operation No.	Wt. % Cl in reaction mixture	Activity of polymer c.p.m./g.	Wt. % Cl in polymer (W)
1	10.75	1221	0.161
2	8.9	1198	0.158
3	7.97	1188	0.15~~7~~
4	4.41	1209	0.159
5	2.5	908	0.121

Extrapolated Value of W = 0.16~~0~~. ± 0.01

TABLE 11

Reaction of partly degraded polystyrene (polymer P.S.8, thermal initiation, 120° degraded at 330°C to 12.5% volatilisation) with radiochlorine, in carbon tetrachloride solution at 25°.

Time of reaction: 1 hour.

Radiochlorine specific activity: 2915 c.p.m./mgcl.

Operation No.	Wt. % Cl in reaction mixture	Activity of polymer c.p.m./g.	Wt. % Cl in polymer (W)
1	11.0	9312	0.319
2	8.89	9200	0.315
3	7.4	9147	0.313
4	5.7	8632	0.291

Extrapolated Value of W = .31~~0~~. ± 0.03

TABLE 12.

Summary of Unsaturation Determinations on Polystyrene Samples.

Polymer	Polymerisation Temperature	Number Average Molecular Weight	W	D	C
P S 1*	60°	632,000	0.102	1.50	9.1
P S 2*	60°	280,000	0.102	1.50	4.0
P S 3*	60°	160,000	0.102	1.50	2.3
P S 4*	60°	92,000	0.102	1.50	1.3
P S 5*	80°	184,000	0.102	1.50	2.7
P S 7**	120°	134,000	0.143	2.10	3.4
P S 8**	140°	160,000	0.160	2.35	3.5
P S 8 Degraded to 12.5%		52,000	0.31	4.56	2.3

* Benzoyl peroxide initiated.　　　　** Thermally initiated.

W = Wt. % Cl in polymer after chlorination.

D = No. of double bonds per 1000 monomer units.

C = No. of double bonds per chain.

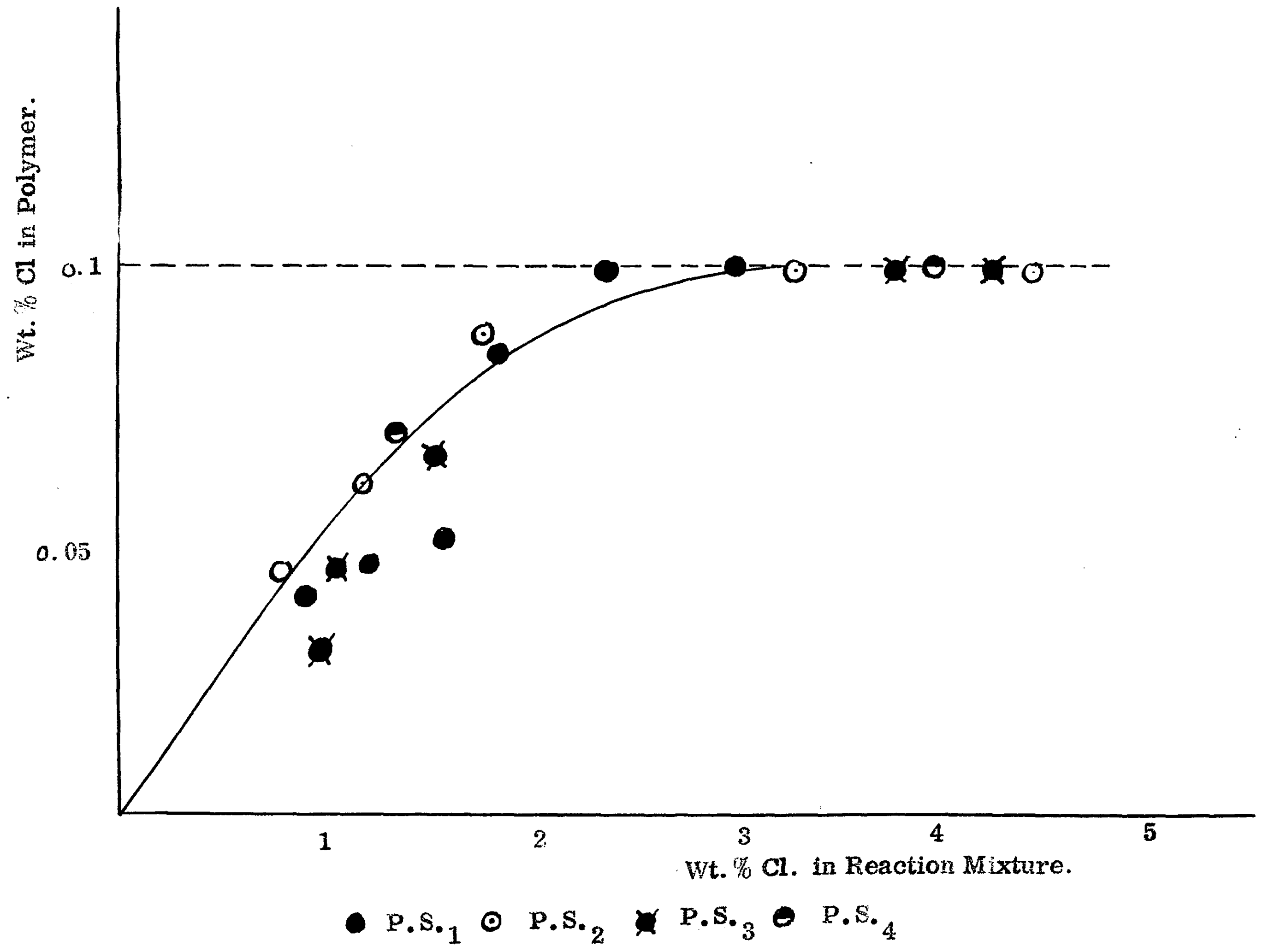


Figure 14: Chlorination of Polymers P.S.1, P.S.2, P.S.3, and P.S.4.

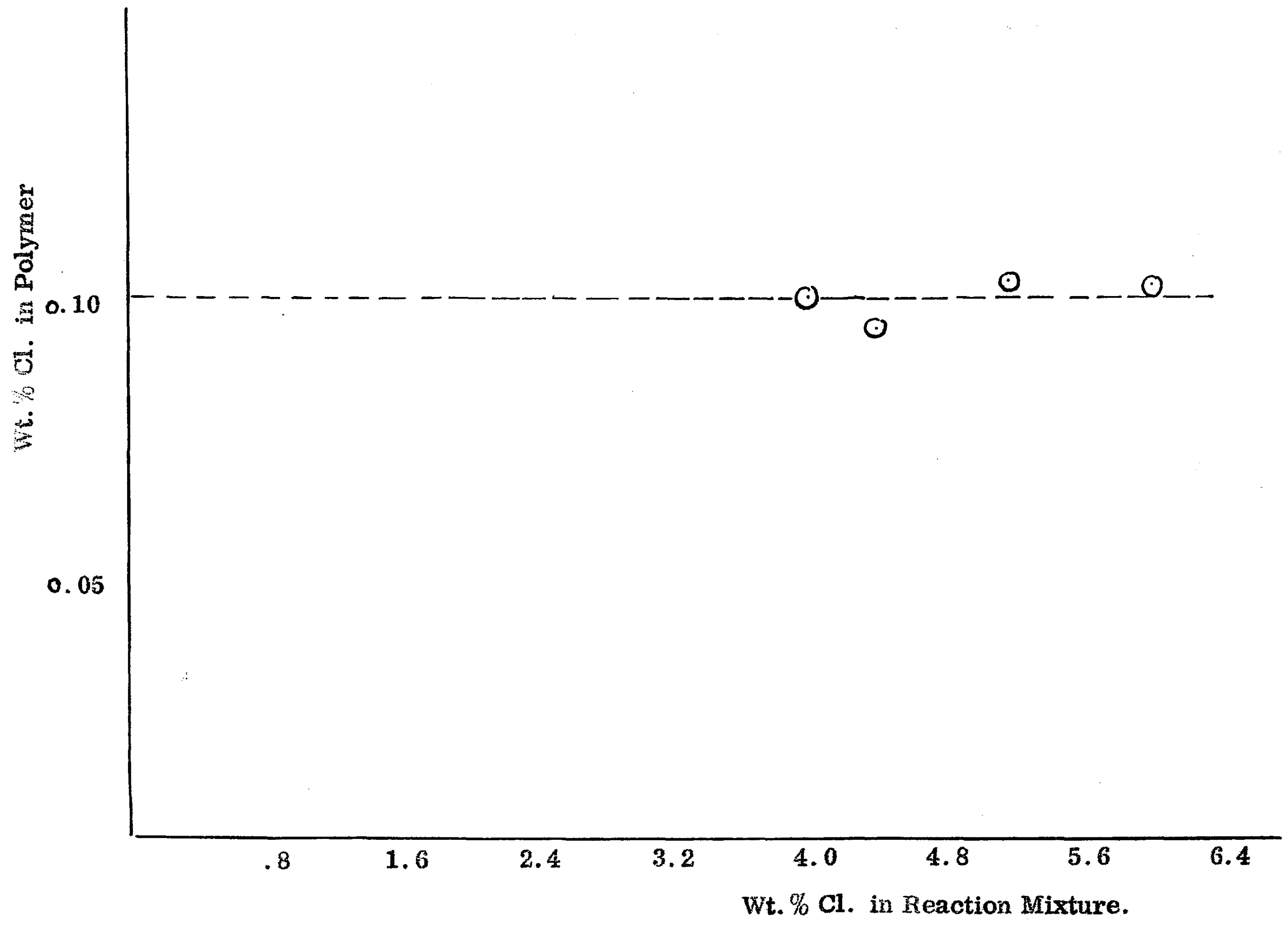


Figure 15: Chlorination of Polymer P.S.5.

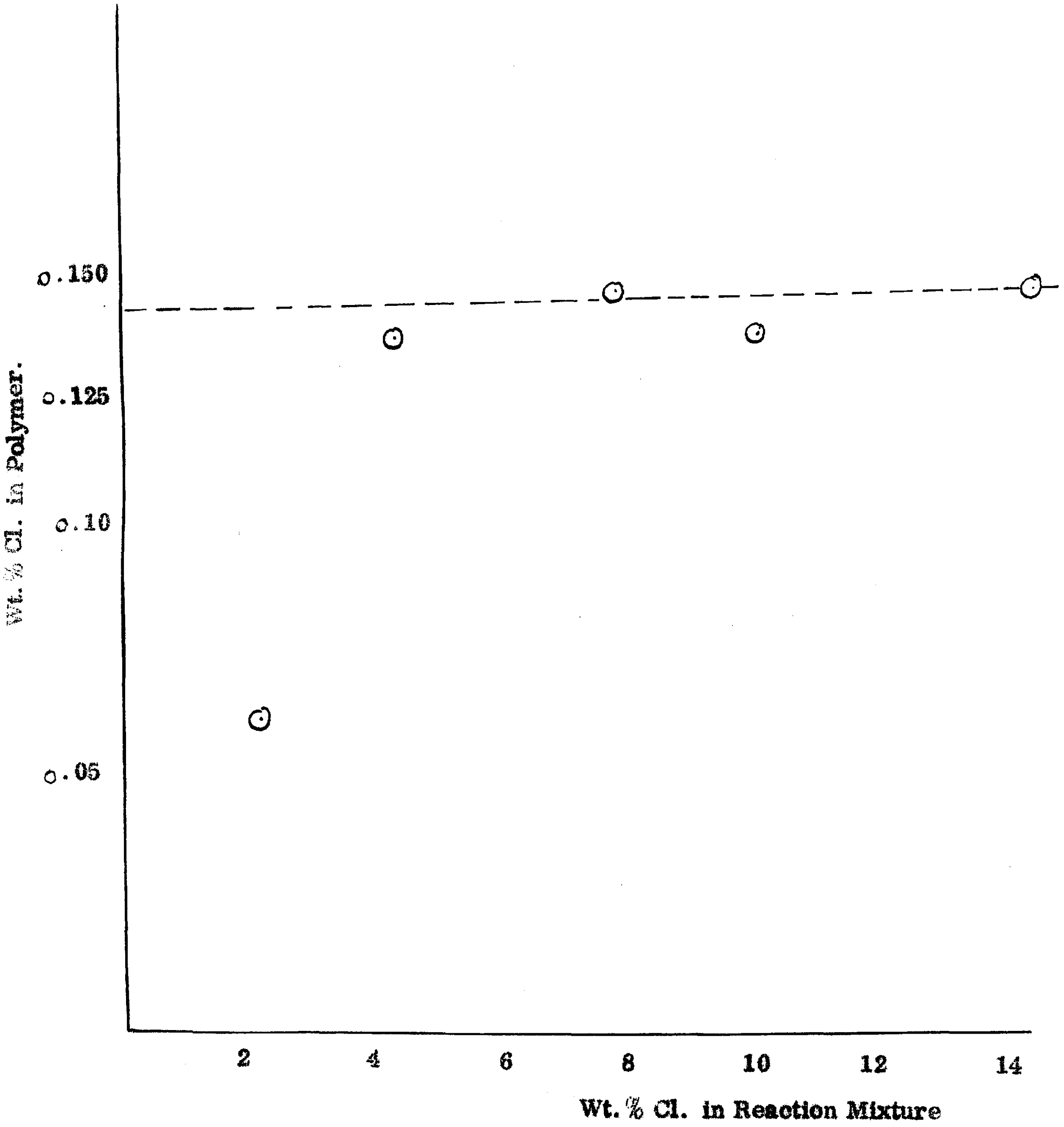


Figure 16: Chlorination of Polymer P.S.7.

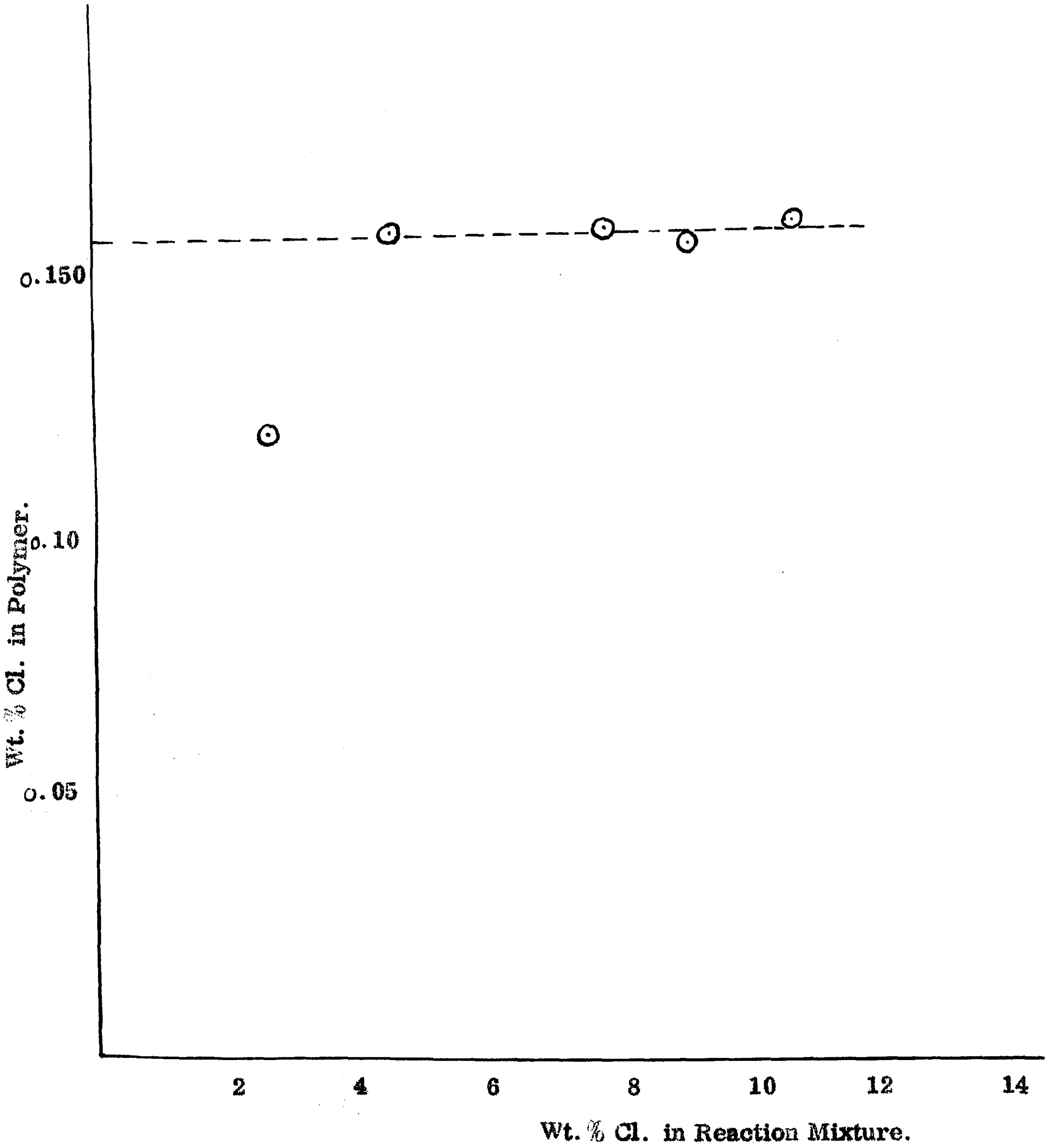


Figure 17: Chlorination of Polymer P. S. 8.

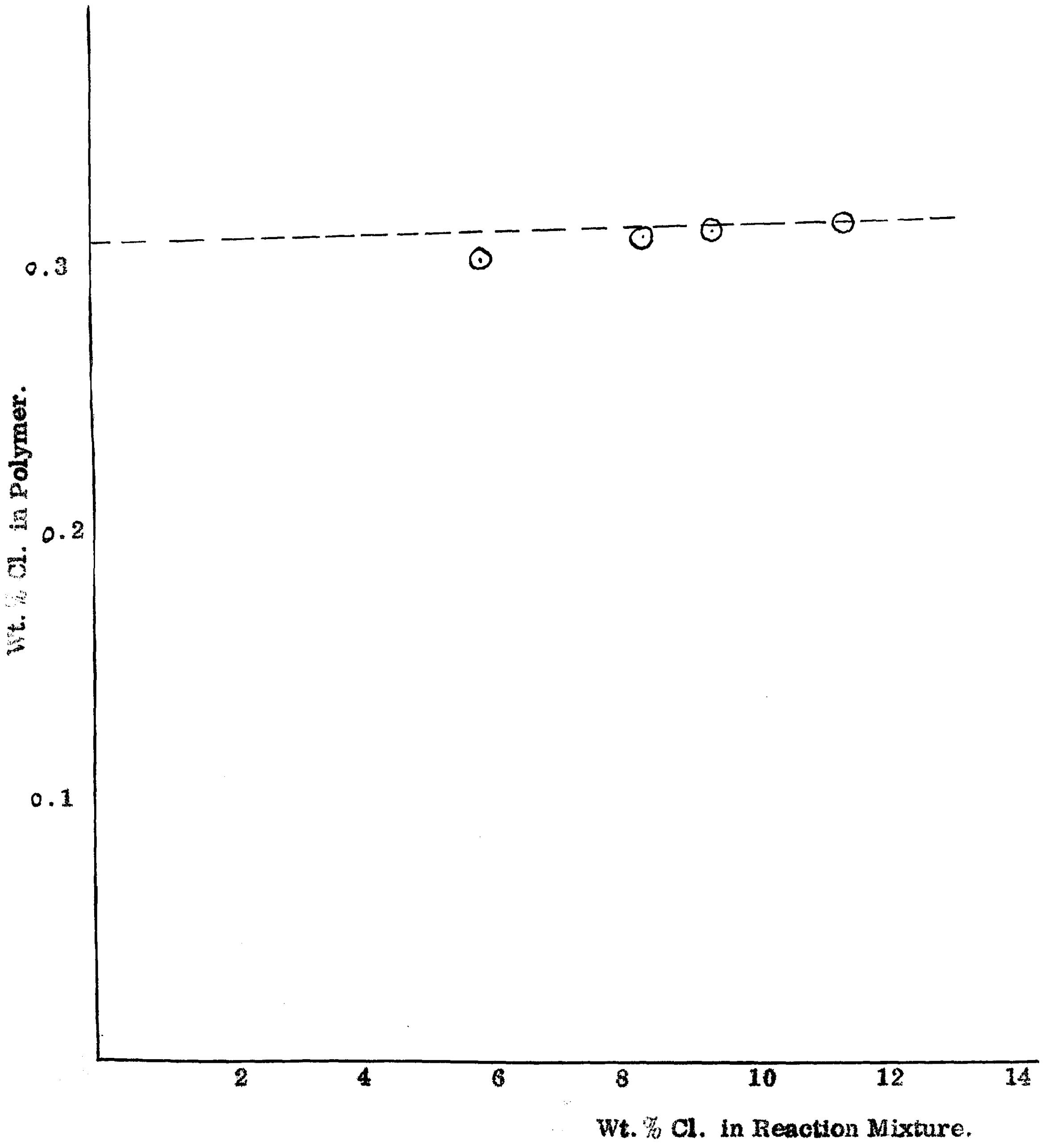


Figure 18: Chlorination of Partially Degraded Polymer P.S.8.

PART III

DISCUSSION.

1. Summary of Conclusions.

Before considering the bearing which the results obtained in this work have on theories of the mechanism of free radical and of thermal initiation in polystyrene it is desirable to summarise the conclusions which may be drawn.

(1) The unsaturations of all the polystyrene samples are small, but not negligible. They are in fact of the same order as the "weak link" concentrations calculated by Grassie and Kerr[19].

(2) The unsaturations of the polymers PS_1 to PS_4, which were prepared at the same temperature but have different molecular weights, are all the same.

This indicates unambiguously the absence of any end group effect - all the double bonds present are in the main chain.

This result is consistent with previous evidence that termination in the free radical polymerisation of styrene is by combination of radicals,[22, 23, 24] and with the evidence of Figure 7 which proves transfer to be absent in the polymerisation.

(3) There is no appreciable increase in unsaturation between polymers PS_1 to PS_4 prepared at 60° and polymer PS_5, prepared at 80°.

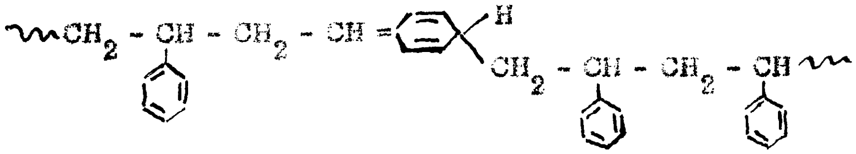
(4) Polymers prepared by thermal initiation show somewhat higher unsaturation than those prepared in present of benzoyl peroxide at lower temperatures.

(5) The unsaturation of partially degraded polystyrene is higher than that of the same polymer before degradation.

2. The Mechanism of Degradation of Polystyrene.

As discussed at length in the introduction, the two main theories which have been put forward to account for the observed features in the molecular weight and rate versus conversion curves are (a) the weak link theory (b) the theory of inter-molecular transfer.

During the course of the present work, the weak link theory, as developed by Grassie and Kerr and Grassie and Cameron appeared to offer the better explanation of the available facts. It was supposed that double bonds arose in the main chain of the polymer by an occasional abnormal propogation step through the benzene ring.



The main evidence in support of this consisted of the following:-

(i) Ozonolysis experiments indicated the presence of unsaturation.

(ii) The concentration of weak links, measured by the method outlined on page 5, appeared to increase with increase in polymerisation temperature, as would be expected for an abnormal propagation step with slightly higher energy of activation than normal propagation.

(iii) Grassie and Cameron found that polystyrene showed a molecular weight drop to a steady value similar to the limiting value in bulk degradation at the same temperature on heating in tetralin solution, despite the fact that the production of monomer was inhibited.

The results summarised in Table 12 support the "quinonoid" weak link theory to the extent that the unsaturations are of the same order as the supposed weak link concentrations, and are higher at higher temperatures. The same unsaturation was found, however, for polymers prepared at 60^C and 80^C, and the results can be explained in another way, as discussed subsequently. Two important new pieces of evidence have appeared very recently, however, McNeill[43] has pointed out the errors which can arise in osmometry when large membranes are used. It has been shown, moreover, that a polystyrene sample which gave a molecular weight of 99,000 using the Fuoss Mead osmometer used by Grassie and Kerr, and Grassie and Cameron, has a true molecular weight substantially lower than this, viz 68,000. No matter how meticulous the measurements, therefore, the determination of molecular weight of degraded polystyrene carried out by these workers in the low molecular weight region cannot be regarded as completely reliable. All the estimates of weak link concentrations were based on extrapolation of results quoted as values below 100,000. It seems reasonable to suggest, therefore, that the difference in weak link concentrations which these authors find, might not be significant and could represent simply uncertainty in molecular weights due to osmometry errors. Since these errors could easily approach 100% for more extensively degraded samples, and the full range of weak link concentrations reported involves only about a two fold change over a large number of polymers it would not be unreasonable to suggest that in fact there are no weak links and all the polymers apart from differences due to their initial molecular weights, degraded in the same way.

This conclusion is reinforced by the second piece of evidence mentioned above. Haider and McNeill[47], using similar techniques to those of the present work, have shown conclusively that polystyrene prepared by a cationic (or strictly "Pseudo Cationic" in Plesch's [48,49,] view) mechanism shows no main chain unsaturation whatever, yet the molecular weight falls during degradation in a manner closely similar to that of free radical polystyrene. In the light of this evidence the theory that polystyrene possesses weak links due to main chain unsaturation can not be upheld. It would be difficult, moreover, to reconcile the similar behaviour of polystyrenes prepared under such drastically different conditions with any weak link theory. It is not possible to discount the possibility of weak links altogether, however, without giving further consideration to the results of Grassie and Cameron for solution degradation of polystyrene in naphthalene and tetralin. The apparent levelling off of the molecular weight versus conversion curve in tetralin is one of the strongest pieces of evidence on which the weak link theory is based. Two criticisms can be made of this evidence, however. Firstly, only one polymer was studied. Other samples might conceivably have behaved differently. Secondly, Grassie and Cameron results are not quite compatible with the similar results of Jellinek and Spenser[16]. The latter determined molecular weights viscometrically and found the molecular weight continued to fall slowly, after the initial steep drop. The discrepancy between the results of these workers may be explained in terms of osmometry error, as discussed previously, in the case of the Fuoss Mead osmometer.

A further piece of evidence against the weak link theory emerges from a closer examination of the results of Grassie and Cameron"s solution experiments. The rate of degradation in naphthalene solution is slower than for bulk polymer. For a first order reaction, as required by weak link theory, this can only be explained in terms of transfer to solvents. It may be explained much more readily in terms of the intermolecular transfer theory as being simply a dilution effect.

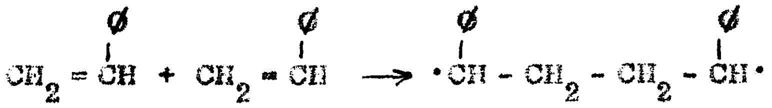
It can be seen by comparing the results of Table 12 with the ozonolysis data of Grassie and Cameron[29], that the two methods are in fair agreement as to the main chain unsaturation in polystyrene. Grassie and Cameron estimate a double bond concentration of the order of 1 Double Bond per 1000 monomer units. The corresponding result of Table 12 is 1.5 double bond per 1000 monomer unit. It seems clear from the present work, and that of Haider and McNeill[47], however, that although there is main chain unsaturation, this is not associated with weak links.

This conclusion is reinforced by the fact that no difference in thermal stability was found (page 42) between polymer samples before and after reaction with chlorine. If the double bonds were weak links, some difference in behaviour might be repeated.

The significant of the result for the unsaturation of degraded polystyrene is discussed after consideration of the question of thermal initiation.

3. The Mechanism of Thermal Initiation, in the Polymerisation of Styrene.

The mechanism of this process is not well understood. Flory[39] has suggested that the following diradical initiation



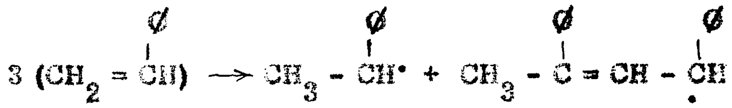
$$\mathrm{CH_2=\overset{\overset{\phi}{|}}{C}H + CH_2=\overset{\overset{\phi}{|}}{C}H \longrightarrow \cdot\overset{\overset{\phi}{|}}{C}H - CH_2 - CH_2 - \overset{\overset{\phi}{|}}{C}H\cdot}$$

is more likely than the possible hydrogen transfer reaction[40]

$$\mathrm{CH_2=\overset{\overset{\phi}{|}}{C}H + CH_2=\overset{\overset{\phi}{|}}{C}H \longrightarrow CH_3 - \overset{\overset{\phi}{|}}{C}H\cdot + CH_2=\overset{\overset{\phi}{|}}{C}\cdot}$$

Rossell and Tobolsky[41] found in inhibition experiments that the rate of thermal initiation of styrene polymerisation calculated from the rate of polymerisation was considerably less than that obtained from the rate of consumption of inhibitor. When an initiator was present the two sets of measurements were in agreement. They concluded that in thermal reaction diradicals were initially formed but nearly all cyclised readily and polymerisation resulted only from those diradicals which had been converted into monoradicals by transfer before cyclisation could occur.

Mayo[50] proposed that thermal initiation of styrene proceeds by a termolecular reaction producing monoradicals:



$$3\,(CH_2=\overset{\phi}{\overset{|}{C}}H) \longrightarrow CH_3-\overset{\phi}{\overset{|}{C}}H^{\bullet} + CH_3-\overset{\phi}{\overset{|}{C}}=CH-\underset{\bullet}{\overset{\phi}{\overset{|}{C}}H}$$

Termolecular reactions are however extremely rare, and it would perhaps be more likely that an initially formed diradical would react by the transfer with a monomer molecule to give two monoradicals.

In the case of both the Rossell and Tobolsky[41], and Mayo[50] mechanisms, one half of the initiating radicals would produce chains with terminal unsaturation. Since the chain termination process is known to be combination[22,23,24] in the case of styrene, it follows that, on average, every molecule would possess oneterminal double bond.

On the other hand, diradical initiation would result in chains with no unsaturation.

The results of Table 12 may be considered in the light of these theories. The issue is complicated, however, by the presence of main chain unsaturation. It is instructive to calculate the unsaturation to be expected for $P.S_7$ and $P.S_8$ on the basis of one terminal double bond per chain and compare these values with the results obtained. This is shown in Table 13.

The observed unsaturations are considerably higher than 1 double bond per chain. If allowance is made for main chain unsaturation on the basis that it is similar to that estimated for peroxide initiated polymers at 60°, it is found that the difference between C_{obs} and $C_{main\ chain}$ agrees quite well with C_{calc}.

These results lend support to the theories of monoradical initiation. Because of the assumption which has to be made regarding main chain unsaturation, however, they do not provide conclusive proof.

It would be a comparitively simple matter to obtain the necessary proof. All that is required is to fractionate a thermally initiated polymer and to measure the unsaturations and molecular weights of the fractions. A plot of ^{1}/chain length versus unsaturation then allows both main chain and terminal unsaturation to be estimated. Experimentally this is time consuming and time did not permit it to be done.

4. Unsaturation of Degraded Polystyrene.

In assessing the change in unsaturation in polymer $P.S._7$ (Table 12), on degradation, account must be taken of the fact that initially both main chain and terminal double bonds are present.

TABLE 13

Observed and Calculated Unsaturations for Thermally Initiated Polystyrenes.

Polymer	$P.S_7$	$P.S_8$
$\bar{M}n$	184,000	160,000
C_{calc}	1.0	1.0
C_{obs}	3.4	3.3
$C_{main\ chain}$	2.6	2.3

If the original main chain unsaturation is assumed to play no part in the chain scission process then this may be allowed for by subtracting the appropriate quantity from the original and degraded polymer results. (Table 14).

The results suggest that the degraded sample contains more than one double bond per chain. In the absence of direct evidence as to whether these are in the main chain or at the ends, further discussion does not appear fruitful.

5. Origin of Main Chain Unsaturation in Undegraded Polystyrene.

"Quinonoid" structures have already been discounted as possible weak links in the polymer. It is unlikely that such structures could exist in the chain and not behave as weak links.

Some alternative explanation for unsaturation in the main chain must therefore be found.

The main steps in radical polymerisation can give rise directly only to terminal unsaturation. Main chain unsaturation can arise only by some abnormal propagation process, or by a reaction occurring in a polymer after its formation. Three possible reactions may be suggested.

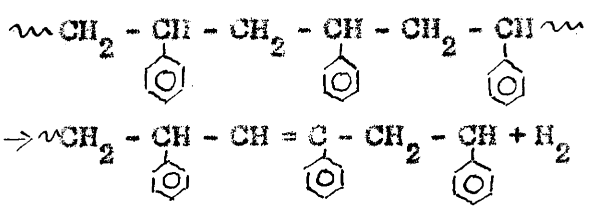
(i) Direct loss of hydrogen.

It is conceivable that polystyrene might lose a hydrogen molecule at occasional points in the chain, leaving a double bond in conjugation with a benzene ring:

TABLE 14

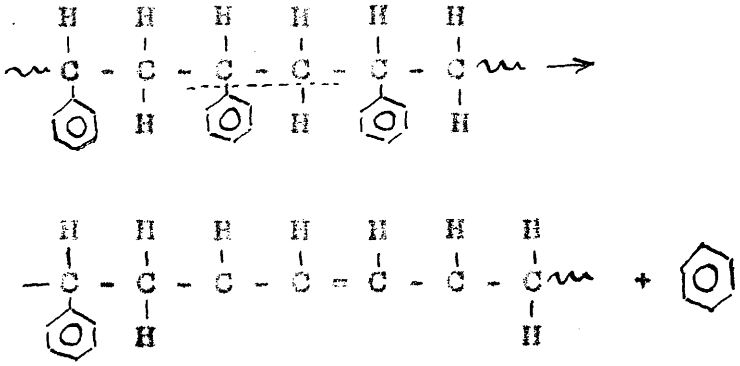
Change in Unsaturation of Polystyrene $P.S_7$ on Degradation.

Polymer	P.S 7 Undegraded	P.S 7 12.5% Degraded
$\bar{M}n$	184,000	52,000
C_{obs}	3.4	2.3
$C_{main\ chain}$	2.6	0.8
$C_{obs} - C_{main\ chain}$	0.8	1.5



(ii) Direct loss of benzene.

Benzene is present in appreciable quantities in the products of degradation of polystyrene at temperatures of 500° and over[51]. It could arise by a straight forward splitting out:



It would seem possible that this reaction might also occur to a very small extent in the course of the polymerisation process.

Reactions such as (i) and (ii) might be initiated by benzoyl peroxide, and it would therefore be of interest to test the possibility by heating a solution of polystyrene in the presence of benzoyl peroxide for some time and determining whether any change in unsaturation had occurred.

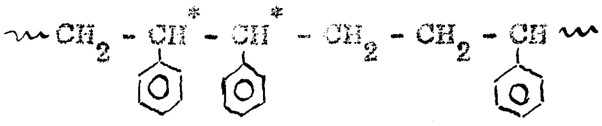
In the present work, polymers $P.S_1$ to $P.S_5$ all had the same unsaturation, despite considerable difference in benzoyl peroxide concentration, but it must be remembered that all were polymerised to the same conversion.

The reaction would need to occur only very rarely to account for the extremely low unsaturations observed.

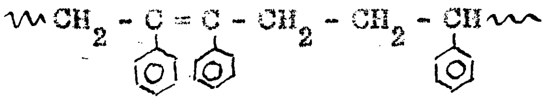
Weir[52] has observed that polystyrene upon UV-irradiation in vacuo develops a yellow colour, which must be attributed to conjugation, probably as a result of loss of hydrogen or benzene.

(iii) Loss of hydrogen from head to head structures.

If a head to head structure arose in polystyrene, as has already been discussed,



the loss of the hydrogen atoms indicated by asterisks should be a relatively easy process since the double bond resulting could be in conjugation with two benzene rings:



The loss of hydrogen might be expected to occur immediately following the abnormal addition of the monomer unit, since in this way the radical centre is also stabilised by being α to a double bond.

Grassie and Cameron rejected the possibility of head to head structures as weak links in polystyrene, but they did not produce any evidence that this type of structure cannot be present. Head to head links are known to occur in a number of vinyl polymers and there seems no reason why polystyrene should behave differently.

Whatever the mechanism, the absence of main chain unsaturation in cationic polystyrene is explicable by the fact that the reactions described would be expected to take place much less readily in the course of a polymerisation at - 78°C, in the absence of free radicals.

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