

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

THE "WEAK LINKS" IN POLYSTYRENE.

by

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## PREFACE.

This thesis is submitted for the Degree of Doctor of Philosophy and is an account of original researches carried out in the Chemistry Department of the University of Glasgow from September 1958 to March 1961.

Part of the work herein described has been published in the Journal of the Chemical Society and a preprint from this journal is included at the end of the type-script.

I wish to thank Dr. N. Grassie for his introduction to the work and for his assistance, encouragement and supervision during its execution. I am also indebted to Dr. S.J. Thomson for practical guidance in the radiochemical problems involved. My thanks are also due to Professor J.M. Robertson for the interest he has shown in this work and for the provision of laboratory facilities.

I gratefully acknowledge the general technical assistance, especially in the measurement of molecular weights, rendered by Messrs. Laurie and Orr.

Finally I wish to thank the Salters' Company for the award of a Fellowship (1958-60), and the Department of Scientific and Industrial Research for the award of a Fellowship (1960-61).

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CHAPTER I

INTRODUCTION

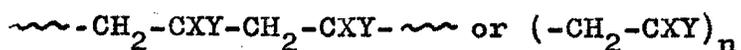
1. Degradation of High Polymers - The Role of Abnormal Linkages.

Until about 1930 interest in polymer degradation was focussed chiefly on the problem of unravelling the molecular structure of natural polymers such as starch, cellulose and rubber. In later years, however, the industrial exploitation of synthetic polymers forced chemists to examine the undesirable deterioration which takes place in many of these materials when they are subjected to weathering and other adverse influences. A fundamental approach to these reactions had to wait until more information was available on the detailed structure of polymers and as this emerged more and more kinetic and other studies were carried out on these degradation reactions.

As polymer degradation studies developed it became clear that though certain of these reactions in macromolecules were quite classical in nature, others were unknown in molecules of normal dimensions and were a direct consequence of their peculiar long

chain environment.

From both polymerisation and degradation studies it is known that macromolecules formed by addition polymerisation consist mainly of chains of monomer units linked together in a head to tail fashion. Accordingly these molecules are usually represented by such formulae as



If such formulae give a complete picture of the polymer molecule then it is reasonable to assume that its properties, and in particular its degradation properties, can be predicted by reference to those of simpler model compounds. Polyethylene, for example, should be comparable in heat stability with a shorter paraffin such as hexadecane or octadecane, since hydrocarbons containing linear chains of more than fifteen carbon atoms have virtually identical thermal stabilities as the series is ascended. At 400°C. hexadecane is quite stable but polyethylene begins to decompose about 290°C..

Oakes and Richards<sup>1</sup> studied the kinetics of the thermal degradation of polyethylene and discovered that degradation appears to be associated with weak points in the polymer molecules. They suggested that

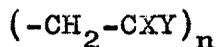
the weak points are caused by oxygenated structures in the polymer chains although chain branches also appear to play some part in the overall reaction. Both types of abnormalities, ie. branches and oxygenated groups, have been detected spectroscopically in polyethylene.<sup>2,3,4</sup>

In the degradation of polymethyl methacrylate Grassie and Melville<sup>5</sup> found that below 220°C. almost exactly 50 per cent by weight of the polymer is degradable to monomer. Above 220°C. conversion goes smoothly to 100 per cent. Clearly half of the chains are different in some way from the remainder. This was best explained by assuming two types of molecule- one with an unsaturated end group and the other wholly saturated. These different ends probably arise through the disproportionation reaction which terminates polymerisation. It was later shown that the unsaturated end group has the lower stability of the two, and the proportion of these can be reduced by carrying out the polymerisation in benzene which is a transfer agent.<sup>6</sup> By thus reducing the proportion of molecules with unsaturated ends the proportion stable up to 220°C. can be increased.

The presence of an occasional acrylonitrile unit in the methyl methacrylate chain completely changes the course of degradation.<sup>5</sup> Instead of the usual chain

end initiation and relatively slow drop in molecular weight during depolymerisation the outstanding feature of the reaction is an initial sharp fall in molecular weight during which very little volatile material is evolved. This is a similar type of reaction to that found in polyethylene but in this case the weak point in the polymer chain is associated with the methyl methacrylate/ acrylonitrile link.

The feature common to all three examples is that the degradation of the polymer is greatly influenced by small concentrations of abnormalities. These are not taken into account when the polymer structure is written in one of the usual forms, eg.



Similar observations have been made in a variety of other polymers.

It is clear, therefore, that any prediction of the degradation behaviour of a given polymer may be wide of the mark, as small traces of abnormalities can have an effect seemingly out of all proportion to their concentration. These abnormalities usually arise from some infrequent polymerisation step or as a result of trace impurities in the monomer.

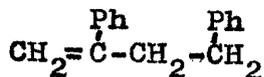
The degradation of polystyrene has received

considerable attention. It has also been the subject of some dispute for though its behaviour on pyrolysis is reminiscent of that of polyethylene, and therefore suggests the presence of weak points, the nature of the polymer lends itself readily to alternative and equally convincing explanations. Conflicting evidence has done much to confuse the issue. The object of the following sections of this chapter is to trace the development of degradation studies on this polymer and in doing so to present a picture of our knowledge of the reaction at the present time.

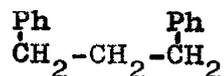
## 2. Early Experiments - The Random Theory of Degradation

As far back as 1845 the conversion of styrene to a glassy solid was recognised. This solid was known to form readily when styrene was heated or allowed to stand in air. Later investigators discovered that styrene monomer could be recovered by pyrolysing this glassy solid but no detailed chemical study of this pyrolysis was carried out for the very good reason that the nature of the glassy solid was not clearly understood. By the early nineteen thirties, however, ideas on polymer structure were beginning to crystallise and in 1935 Staudinger and Steinhoffer<sup>7</sup> published an account of the destructive distillation of polystyrene.

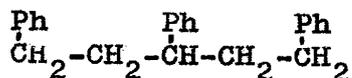
These authors found that, in addition to monomeric styrene, the reaction products contained, among others, the following compounds



2,4-diphenyl-1-butene

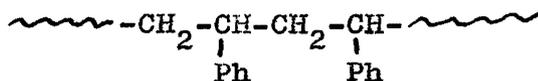


1,3-diphenyl propane



1,3,5-triphenyl pentane

None of the compounds isolated contained benzene rings on adjacent carbon atoms, and from this they concluded that polystyrene consists of chains of styrene units arranged in a head to tail sequence

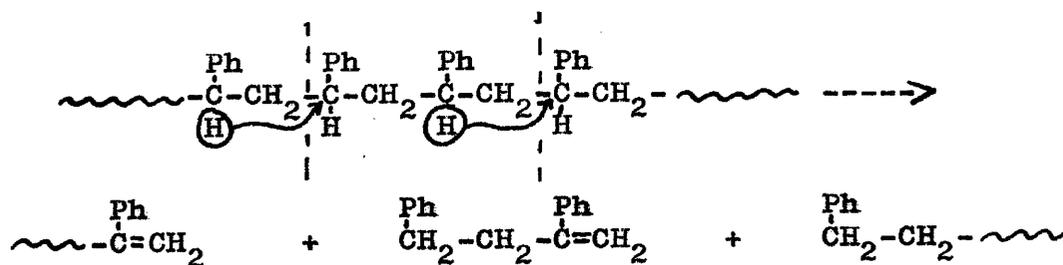


This head to tail structure was hotly disputed<sup>8,9</sup> but it has stood the test of time and is now generally accepted.

Some years before Staudinger published his work on the pyrolysis of polystyrene a random theory of degradation of polymers had emerged from the work of Meyer, Hopff and Mark,<sup>10</sup> Kuhn<sup>11</sup> and Freudenberg<sup>12</sup> who had studied the hydrolytic degradation of starch and cellulose. It was well known by then that the polysaccharides, starch and cellulose, consisted of glucose

units linked together in chains of varying lengths. During the hydrolysis of these materials the viscosity decreases continuously and appreciable amounts of the unit molecule - glucose - do not appear until late in the reaction. Each act of hydrolysis takes place independently of all the others and these results suggested a reaction occurring at random along the macromolecule. The random theory was applied mathematically by Kuhn<sup>11</sup> whose statistical treatment gave satisfactory agreement with experimental results when a small correction was applied taking into account the increased reactivity of terminal bonds.<sup>13</sup>

Staudinger, in his report on the pyrolysis of polystyrene,<sup>7</sup> suggested that a similar random process was operative. He accounted for the different products of degradation by assuming a random scission of carbon-carbon bonds along the polymer back-bone followed by migration of the tertiary hydrogen atoms



The carbon-carbon bonds along the chain, it was pointed out, are slightly weaker than normal carbon-carbon bonds,

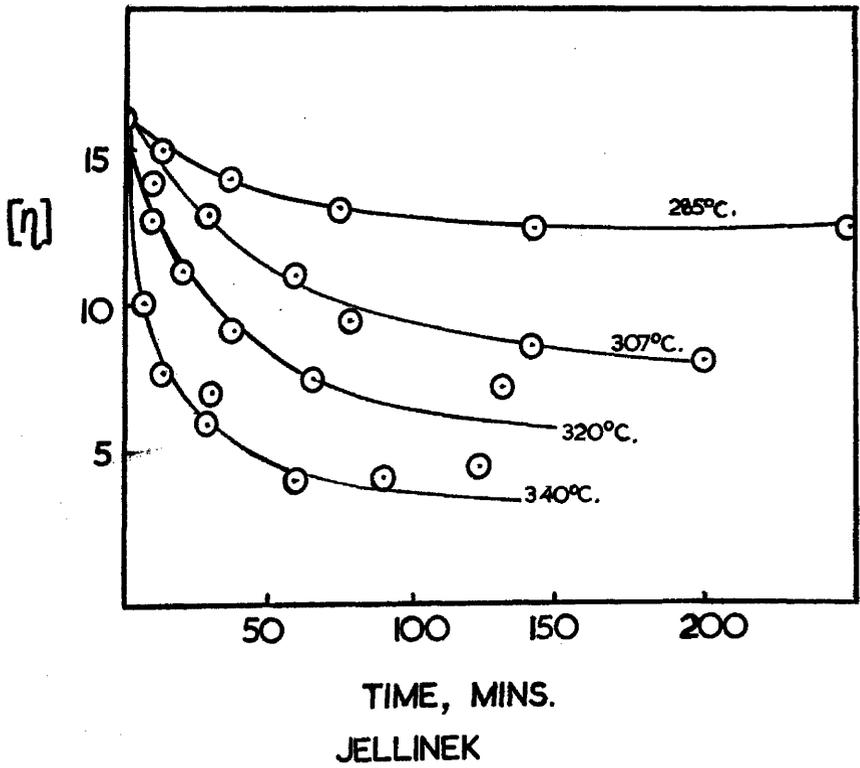
being next but one to the double bonds of the benzene rings. This was prompted by Schmidt's<sup>14</sup> pyrolysis studies of simpler molecules. The enhanced thermal stability of hydrogenated polystyrenes<sup>15</sup> appeared to support this suggestion.

Later workers who studied the thermal degradation of both polystyrene and polymethyl methacrylate supported the random theory and claimed good agreement between experimental results and Kuhn's theory despite the very obvious anomaly of large amounts of monomer produced early in the reaction.<sup>16</sup>

In more recent years others, among them Jellinek,<sup>17</sup> have studied the thermal degradation of polystyrene in more detail. Jellinek measured the molecular weight of the polymer during degradation between 240°C. and 340°C., finding that the molecular weight appeared to fall to a lower value the higher the temperature. (See Fig.1). Furthermore, these molecular weight data are incompatible with a random mechanism, as are the large amounts of monomer produced early in the reaction. Obviously the random process suggested by earlier workers for the degradation of polystyrene had to be rejected.

About the same time as Jellinek was studying polystyrene, Grassie and Melville<sup>5</sup> were reexamining the thermal degradation of polymethyl methacrylate. They

FIG. I

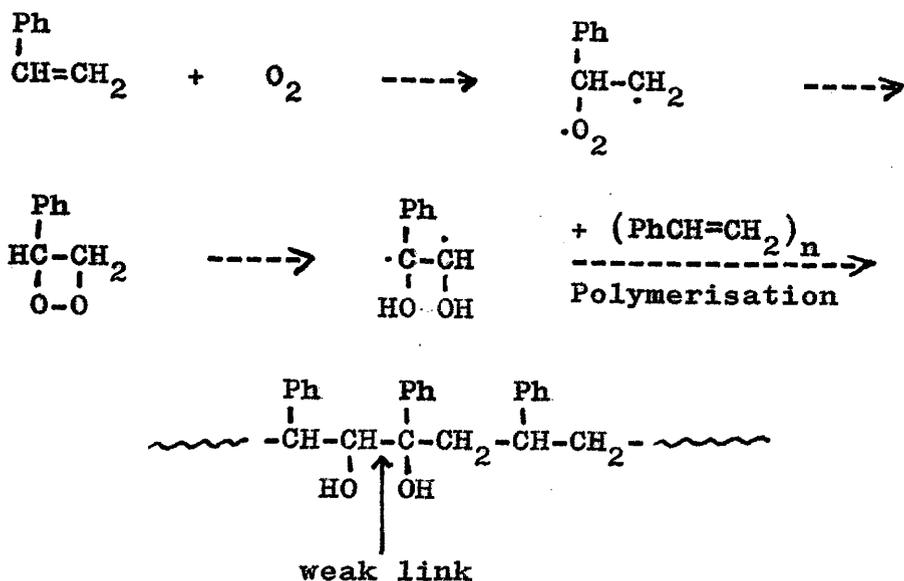


discovered that this reaction is not a random process and showed that the degradation is initiated solely at chain ends, radicals being produced which liberate monomer in a reverse polymerisation process. These authors based their conclusions on the study of the initial rates of monomer production and, like Jellinek, on changes in molecular weight during degradation.

### 3. Polystyrene Degradation - The Weak Link Theory.

The thermal degradations of polystyrene and polymethyl methacrylate have certain features in common, notably the large amounts of monomer produced. Unlike polymethyl methacrylate, however, polystyrene exhibits a sharp fall in molecular weight early in the reaction. Jellinek tried to account for this by postulating the existence of a limited number of weak bonds distributed at random in the macromolecules. The weak links, he suggested, become unstable within the temperature range employed and disappear in two competing processes, one involving chain scission and the other leaving the main chain unbroken. At higher temperatures the former reaction predominates thus accounting for the variation of molecular weight behaviour with temperature. Jellinek postulated that the weak links might be formed by incorporation of oxygen into the polymer during polymer-

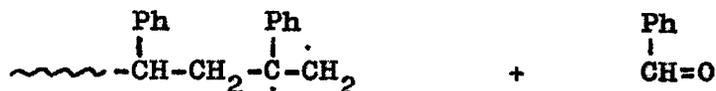
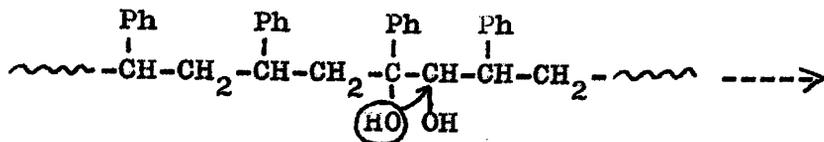
-isation.



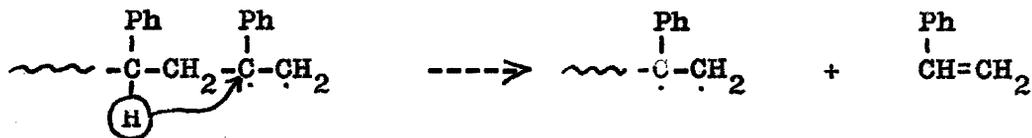
On examining the infra-red spectra of several undegraded polystyrenes Achhammer<sup>18</sup> could find no evidence of hydroxyl groups. It must be remembered, however, that the concentration of such abnormalities required to explain Jellinek's results is very small. Indeed Jellinek himself has pointed out that 0.3 per cent by weight of oxygen is sufficient to produce the observed effect. It is noteworthy that amounts of oxygen of this order have been detected in polystyrene samples,<sup>19</sup> and as far back as 1929 Staudinger and his co-workers<sup>15</sup> observed that polystyrene prepared with careful exclusion of oxygen is more stable thermally than the polymer prepared in the presence of oxygen.

Jellinek proposed that degradation takes place

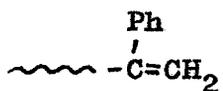
at the weak links in the following way



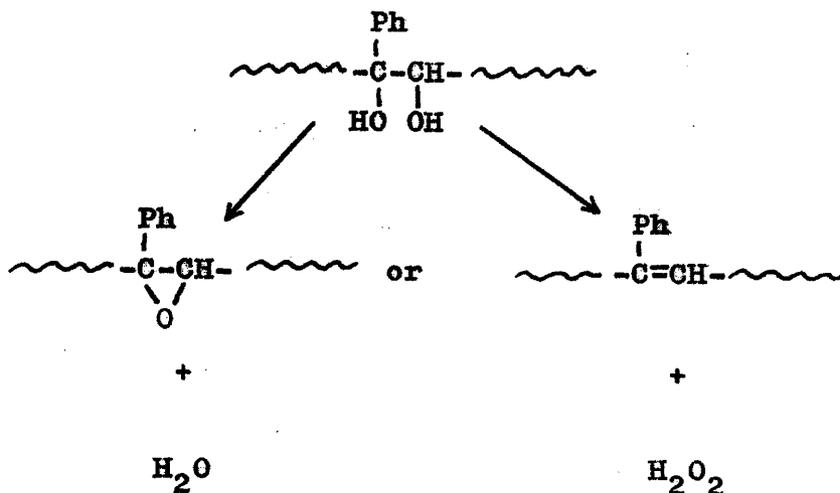
monomer being produced from the radical chain end



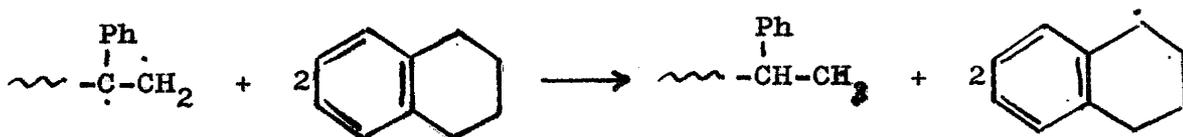
and termination occurring by the formation of a double bond



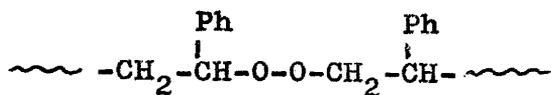
Monomer production was found to run parallel with the fall in molecular weight and Jellinek deduced that in the course of weak link scission, during which 5- 10 per cent of the polymer volatilised, six to ten monomer units are produced per chain scission. The disappearance of weak links without chain scission he explained in the following way



The monomer producing reaction is similar to that suggested by Grassie and Melville<sup>5</sup> for the analogous part of the polymethyl methacrylate degradation. Evidence in favour of such a reaction was later uncovered by Jellinek and Spencer<sup>46</sup> who compared the degradation of polystyrene in tetralin and naphthalene solutions. In tetralin the depolymerisation process was found to be suppressed and no loss in weight of polymer was detected, while in naphthalene the reaction appeared to proceed normally. Jellinek and Spencer attributed this effect to deactivation of the polymer radical by transfer of a reactive  $\alpha$ -hydrogen atom from the tetralin molecule leaving a relatively unreactive tetralyl radical.



The explanation Jellinek gives for the formation of weak links is immediately open to criticism because it is known that styrene copolymerises with oxygen to form a polyperoxide,



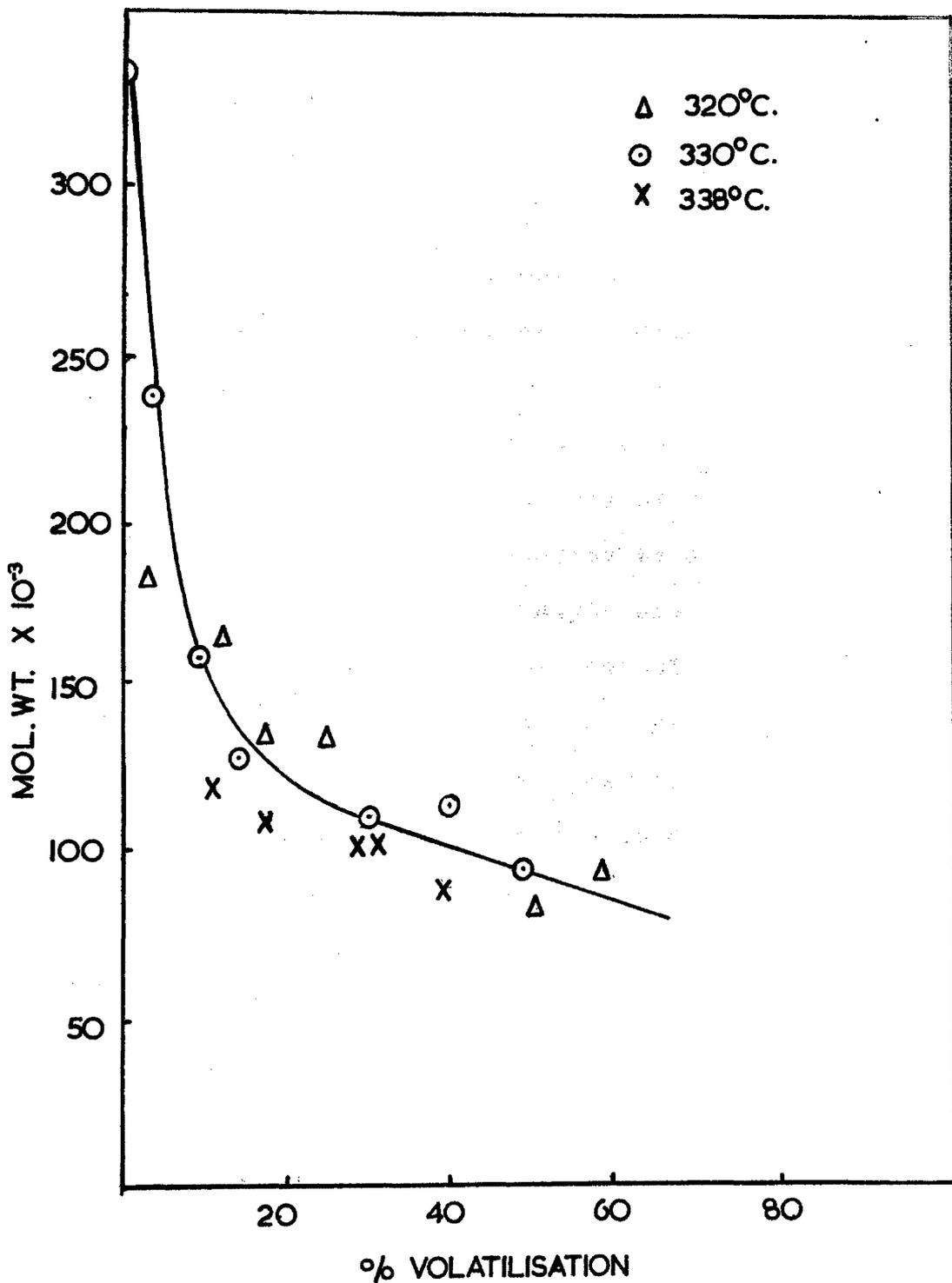
and the gem diol seems highly unlikely.<sup>20</sup> Such a peroxidic unit is almost certainly thermo-labile but whether it could disappear without apparent chain scission is open to doubt.

It is now obvious that the mode of preparation of a polymer may have a very marked effect upon its degradation behaviour. It was from this point of view that Grassie and Kerr undertook to study the thermal degradation of polystyrene.<sup>21,22,23</sup>

#### 4. The Work of Grassie and Kerr.

Grassie and Kerr showed that the presence of oxygen during the polymerisation of styrene monomer is not the sole cause of weak links in the polymer because these are still found in samples prepared from carefully purified monomer polymerised in vacuum. Their results also showed that the extent of molecular weight decrease due to weak link scission is independent of degradation temperature. (See Fig.2). This was obvious when

FIG. 2



GRASSIE & KERR

molecular weight data were plotted against percentage volatilisation during the reaction. Jellinek had plotted molecular weight against time (See Fig.1) and had been misled, by the rapidly changing reaction rate with temperature, into postulating a second reaction in which weak links could disappear without chain scission.

Since weak links cannot be fully accounted for in terms of the effects of oxygen, Grassie and Kerr reasoned that they must be produced as an integral part of the polymerisation process in pure styrene, and that their concentration might be expected to depend upon some polymerisation variable. They therefore investigated the effects of such factors as molecular weight, degree of conversion, initiation (catalytic, thermal and photo), and temperature of polymerisation on the concentration of weak links. It was found that of these only the temperature of polymerisation has any effect and that in general the concentration of weak links increases with temperature of polymerisation.

Though all this evidence appears to be strong support for a weak link theory the idea has not been universally accepted.

5. The Role of Transfer in the Degradation of Polystyrene.

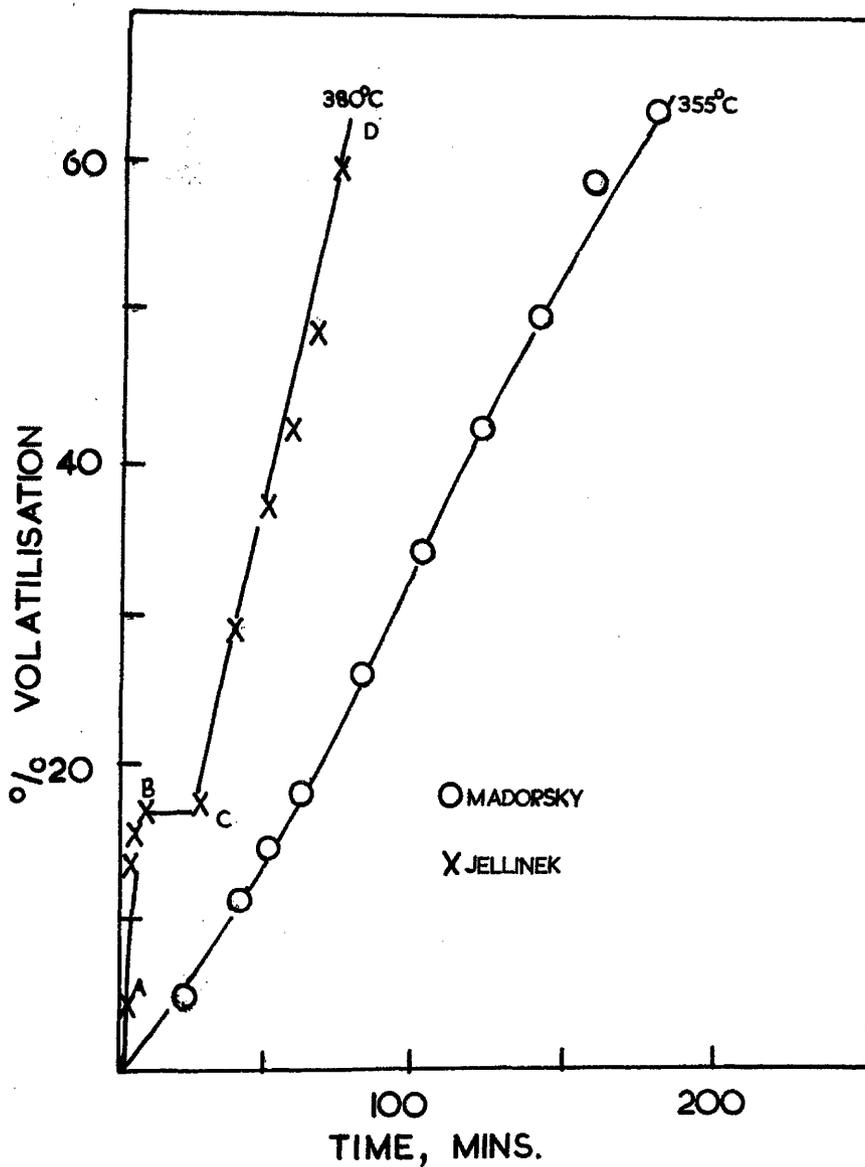
Analysis of the products of thermal degradation of polystyrene shows that considerable amounts of higher fragments such as dimer, trimer, tetramer and pentamer, as well as monomer, are produced during the reaction.<sup>19,24,25</sup> This suggests that chain transfer may play a significant part in the reaction.

Madorsky<sup>26</sup> has studied the rate of production of volatile material at temperatures above 340°C. where the initial steep fall in molecular weight is complete very early in the reaction. A typical result of Madorsky's work is shown in Fig.3. The curve is smooth from zero to high conversions and shows a rate maximum at 30 to 40 per cent conversion.

Similar studies were made by Jellinek<sup>17</sup> (also included in Fig.3) but his curves show an inhibition period which he claims was due to the formation of inhibitors during the weak link scission phase of the reaction. This work, however, has been disputed and doubts have been cast on both its validity and interpretation.<sup>27,28,29</sup>

Simha and Wall<sup>30</sup> interpreted the reaction in terms of a random scission process followed by inter- and intramolecular transfer, and derived a theoretical expression for the rate of conversion of polymer to

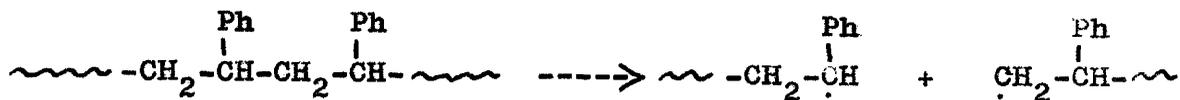
FIG. 3



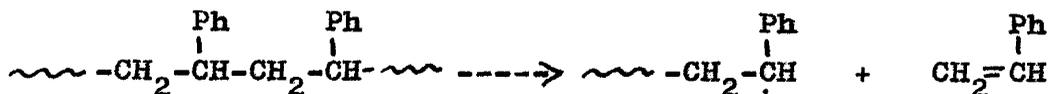
(A B - WEAK LINK SCISSION, B C - INHIBITION AND C D -  
DEPOLYMERISATION)

volatile material. The expression gives a rate maximum at 25 per cent conversion. The proposed sequence of reaction steps is

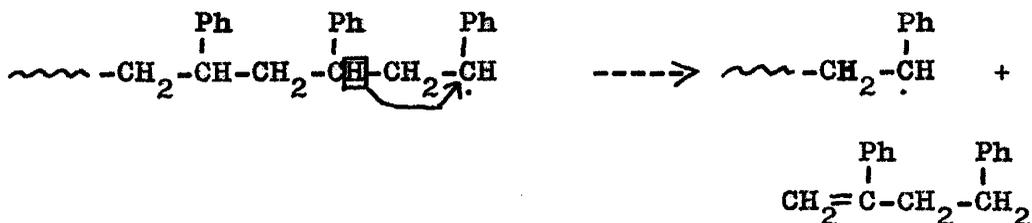
Initiation.



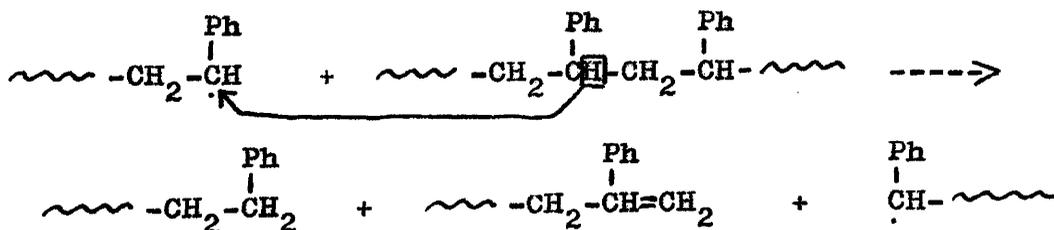
Depropagation.



Intramolecular Transfer.



Intermolecular Transfer.



Termination.



These authors explained the difference between the theoretical figure of 25 per cent and the experimental one of 30 to 40 per cent by postulating that the intra-

molecular transfer and monomer producing reactions are more important than the randomising intermolecular transfer.

In a later paper Madorsky and Strauss<sup>31</sup> demonstrated the importance of transfer reactions in the degradation of a variety of vinyl polymers. The results obtained by pyrolysing certain substituted polystyrenes are summarised in Table 1.

TABLE 1  
Degradation as a Function of Molecular Structure.  
Madorsky and Strauss.<sup>31</sup>

| Polymer                        | Structure   | Wt. %<br>monomer on<br>degradation |
|--------------------------------|---|------------------------------------|
| Polystyrene                    | $\begin{array}{c} \text{Ph} \\   \\ \sim\text{-CH}_2\text{-CH-}\sim \end{array}$                    | 42                                 |
| Poly- $\beta$ -deuterostyrene  | $\begin{array}{c} \text{D} \quad \text{Ph} \\   \quad   \\ \sim\text{-CH-CH-}\sim \end{array}$      | 42                                 |
| Poly- $\alpha$ -deuterostyrene | $\begin{array}{c} \text{Ph} \\   \\ \sim\text{-CH}_2\text{-C-}\sim \\   \\ \text{D} \end{array}$    | 70                                 |
| Poly- $\alpha$ -methylstyrene  | $\begin{array}{c} \text{Ph} \\   \\ \sim\text{-CH}_2\text{-C-}\sim \\   \\ \text{CH}_3 \end{array}$ | 100                                |

Higher chain fragments such as dimer, trimer, etc. are produced, according to Simha and Wall's scheme, by inter- and intramolecular transfer involving the  $\alpha$ -hydrogen atom, whereas monomer is produced by the depropagation reaction. The yield of monomer produced by a reaction should therefore be an indication of the relative importance of the depropagation and transfer steps. In poly- $\alpha$ -methyl styrene, for example, the yield of monomer is 100 per cent, so that there is no transfer involved here. With polystyrene, however, the monomer yield drops to 42 per cent because transfer of the tertiary hydrogen atom is extensive. Poly- $\alpha$ -deuterostyrene is intermediate between the two for transfer of the heavier deuterium atom, though slower than hydrogen, is still possible. When the deuterium atom is on the carbon atom the yield of monomer falls as transfer of the  $\alpha$ -hydrogen atom takes place as before.

All these observations support the theory that transfer of some kind is important in the thermal degradation of polystyrene but up to this point there is no real indication of the relative importance of each type of transfer. It is quite conceivable that one type of transfer occurs exclusively or almost exclusively.

A comparison of the rates of degradation of

poly- $\beta$ - and poly- $\alpha$ -deuterostyrenes with that of normal polystyrene was carried out by Brown, Hart and Wall.<sup>32</sup> They reasoned that if the initial fall in molecular weight is due to weak links alone then the rate of this part of the reaction should be the same for the poly- $\alpha$ -deuterostyrene and the normal polymer. The rate of degradation of poly- $\alpha$ -deuterostyrene, however, turned out to be about half that of normal polystyrene and they concluded that this was due to an isotope effect during intermolecular transfer which must then be the cause of the initial rapid fall in molecular weight. Viewed from this angle it seems that weak links are not the cause of this initial molecular weight drop.

More recently Gordon<sup>33</sup> has re-examined the results of previous authors<sup>22,26</sup> and has claimed, from a theoretical standpoint, that there is no need to invoke a weak link theory to explain the degradation of polystyrene. The scheme which Gordon supports is similar to that proposed by Simha and Wall.<sup>30</sup>

Simha and Wall's mechanism for the initial production of free radicals does not preclude a weak link break down but any change in molecular weight produced by this initial step would be obscured by the resulting randomising effect of intermolecular transfer.

## 6. Weak Links versus Intermolecular Transfer.

In favour of a weak link theory we have the results of Jellinek, and Grassie and Kerr. The latter authors point out that intermolecular transfer should result in a continuous decrease in molecular weight to values lower than those observed, but on the other hand Gordon claims, from theoretical considerations, that the molecular weights reached are quite consistent with a transfer mechanism.

Grassie and Kerr also showed, as was previously mentioned, that polymers prepared at different temperatures contain different numbers of "weak links". This is very strong support for a weak link theory and has never been satisfactorily explained by the proponents of the transfer mechanism.

On the other side, however, the results of the comparative pyrolysis of poly- $\alpha$ -deuterostyrene and normal polystyrene require explanation. That these results are compatible with a weak link theory is shown in the following way. Grassie and Kerr concluded from their work<sup>22</sup> that weak link scission does not give free radicals but stable molecules. If this is so, then a hydrogen transfer is necessary to remove the free radicals initially formed by homolytic fission. Assuming that the hydrogen atom involved is the one attached to the

tertiary carbon atom, obviously the most labile, then the difference in rate of molecular weight fall between normal polystyrene and poly- $\alpha$ -deuterostyrene can be accounted for satisfactorily. Such a mechanism is quite probable and the  $\alpha$ -hydrogen/deuterium transfer would be the rate determining step. This possibility has been indicated by Kerr.<sup>21</sup>

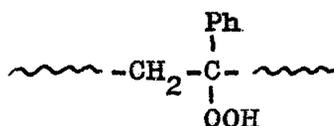
Grassie and Kerr have also pointed out that the ratio of monomer to non-monomer produced by the reaction remains sensibly constant throughout. This shows that intramolecular transfer is predominant in producing non-monomeric fragments. Even this evidence, however, may not exclude some intermolecular transfer, because the amount required by Simha and Wall's scheme to explain the initial rapid fall in molecular weight may be too small to make any significant difference to the monomer:non-monomer ratio during the course of the reaction.

To decide which of the two theories is correct from the above discussion is rather difficult but the balance of the evidence would seem to fall in favour of weak links. Certainly there is no conclusive evidence to prove that these do not exist in polystyrene.

## 7. The Possible Structure of Weak Links.

The oxygenated weak link theory of Jellinek has already been discussed (p.11). Grassie and Kerr have shown that such structures do not account completely for the weak links, but it must be remembered that their work does not exclude oxygenated structures as additional sources of weak links.

Another theory of oxygen-type weak links is that these might be produced by oxidation of the polymer, for example during storage. Peroxides of the type



could conceivably arise in this way and would be expected to produce thermo-labile points in the polymer chain. Achhammer, Reiney and Reinhart<sup>34</sup> have examined the oxidation of polystyrene, accelerating the process with ultra-violet irradiation. The infra-red spectrum of the oxidised polymer showed increased absorption at  $3450 \text{ cm.}^{-1}$  and  $1730 \text{ cm.}^{-1}$ . These bands were attributed to hydroxyl and carbonyl absorption respectively, arising, according to them, by decomposition of peroxides. Other workers have shown that similar effects can be achieved by simply heating polymers in air,<sup>35</sup> and indeed this has been used as a method of preparing graft copolymers by

by introducing radical producing side groups on the chain.

More recently Weir<sup>36</sup> has shown that traces of peroxide on polystyrene, undetectable by infra-red spectroscopy, are sufficient to give detectable chain scission when the polymer is subsequently heated.

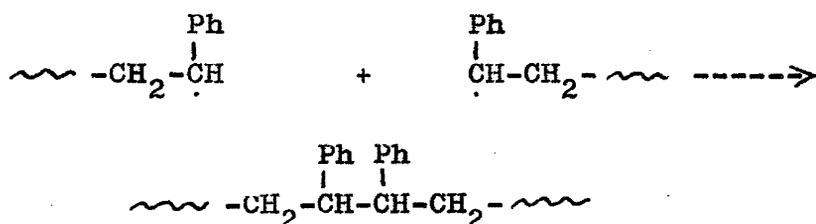
Normal storage conditions are, however, unlikely to affect the polymer. Grassie and Kerr<sup>21</sup> were unable to detect any difference in the degradation behaviour of a polymer which was stored under normal laboratory conditions for eight months.

The fact that post-polymerisation treatment of a polymer is important cannot be stressed too strongly, for such treatment can obviously affect degradation behaviour. This, together with polymerising conditions, may account for certain conflicting features in the results of other workers<sup>37</sup> many of whom used commercial polymers.

It has already been mentioned that Grassie and Kerr found that the weak link concentration is dependent only upon temperature of polymerisation, increasing with increasing temperature. Their interpretation of this was that weak links are formed in some process which competes directly with the normal propagation step but which has a slightly higher energy of

activation. They also showed that this is not a branching process and considered occasional head to head linkages to be a likely explanation.

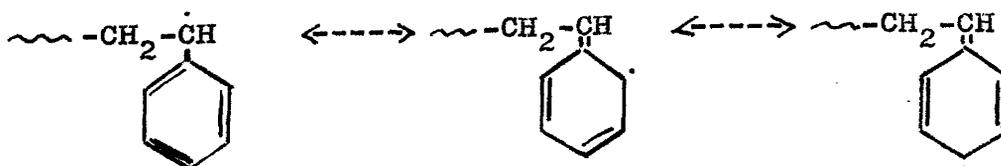
Considerable evidence exists to suggest that termination during polymerisation of styrene is by combination,<sup>39,40,41</sup> and this means that every polymer molecule should contain at least one head to head link.



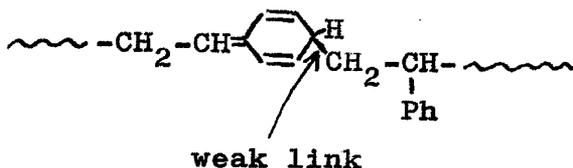
Grassie and Kerr, however, found that certain low molecular weight polymers contained, on the average, less than one weak link per molecule.

Nevertheless, head to head links cannot be excluded on this evidence alone and it is noteworthy that such structures have been detected in polyvinyl acetate by Flory and Leutner,<sup>38</sup> and more recently in polyvinylidene fluoride by Naylor and Lasoski.<sup>42</sup>

Finally, Grassie and Kerr considered the possibility of polymerisation through a canonical form of the resonating polymer radical.



This might give rise to structures of the type



The carbon-carbon bond indicated would be expected to be a weak one since it is next but one to two double bonds.<sup>14</sup> This type of structure is analogous to the ketene-imine linkages which Talat-Erben and Bywater<sup>43</sup> detected in polymethacrylonitrile and which were later confirmed by Grassie and McNeill<sup>44</sup> who showed that the occurrence of these abnormalities is dependent upon polymerising conditions. Similar observations have been made more recently in polyacrylonitrile.<sup>45</sup>

There are therefore no reasons for discounting the possibility of such structures in polystyrene and since the concentrations required to explain experimental results are so small ( $<0.1\%$ ) it is not surprising that spectroscopic methods have failed so far to detect their existence.

The object of the work described in this thesis was to seek a conclusive answer on the role of intermolecular transfer in polystyrene degradation, and to examine the two types of abnormalities described above and attempt to confirm or refute their existence.

To avoid, as far as possible, any confusing evidence the polymers used in this work were prepared under strictly controlled laboratory conditions. Care was also taken to store these polymers away from direct sunlight or other adverse influences.

## CHAPTER II

### EXPERIMENTAL TECHNIQUES

#### 1. Preparation of Polymers.

It has been pointed out in the previous chapter that conditions of polymerisation can affect the degradation behaviour of polystyrene samples. In order to avoid any confusing or conflicting results from this source, polymers were prepared from very pure materials under carefully controlled conditions with oxygen rigorously excluded. The following techniques were adopted with this aim in mind.

##### i) Purification of Initiator.

The only initiator used in this work was 2:2'-azoisobutyronitrile (AIBN) and this only in the preparation of one polymer - S/GC/5. The initiator was recrystallised from methanol before use.

##### ii) Purification of Monomer.

Styrene monomer (Forth Chemicals Ltd.) contained p-tert.-butyl catechol inhibitor. This was removed by repeated washing with sodium hydroxide solution.

After a further two washings with water the inhibitor-free monomer was dried over calcium chloride for forty eight hours. The styrene was then distilled under vacuum, the first 20 per cent of the distillate being discarded. During distillation the monomer in the distillation flask became quite viscous, a further indication that inhibitors had been removed effectively. In all cases, the distillate was a colourless, water-white liquid and its purity was checked by infra-red spectroscopy and gas-liquid chromatography.

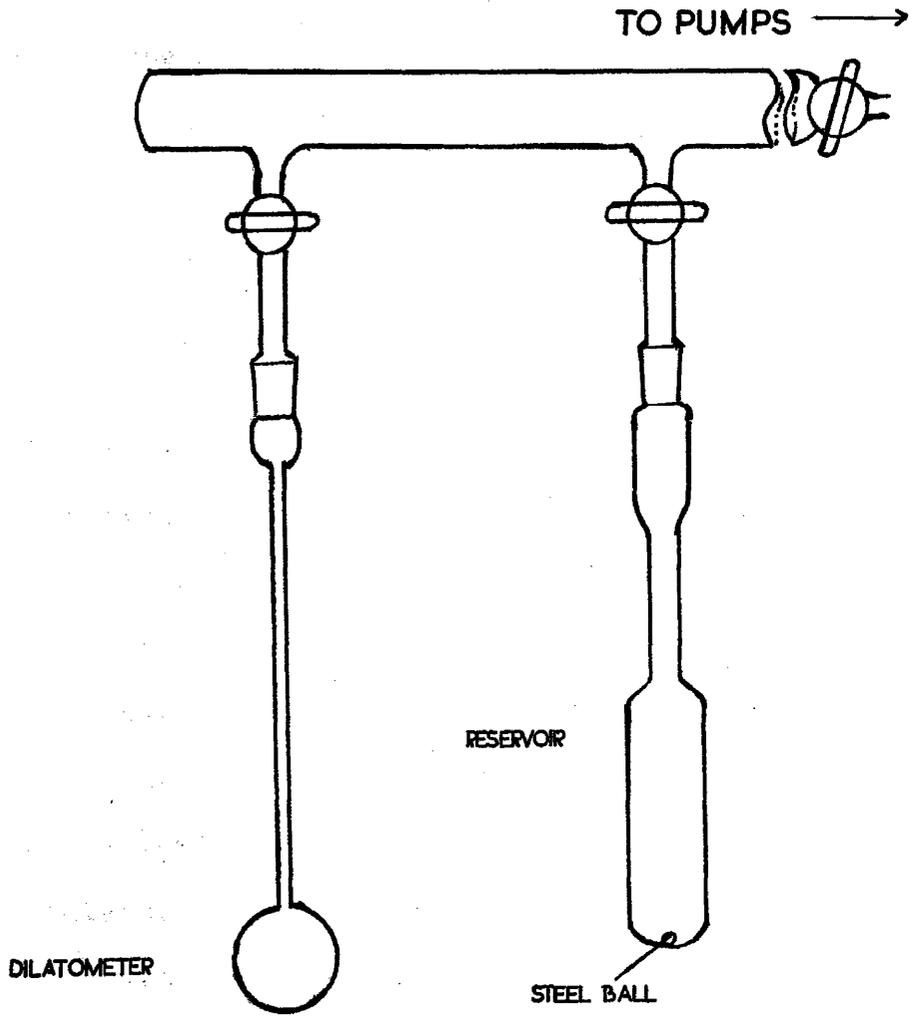
iii) Purification of trans-Stilbene.

trans-Stilbene (Eastman Kodak Ltd.) was found to be very pure as supplied. Before use, however, it was recrystallised three times from ethanol. (M.P. 125°C.)

iv) Filling of Dilatometers.

The vacuum system used for filling dilatometers is shown in Fig.4. The monomer was placed in the reservoir tube and degassed four times in the usual manner by alternate freezing and thawing etc.. Evacuation was achieved with a mercury diffusion pump backed by a rotary oil pump which gave a vacuum of the order  $10^{-5}$  mm. Hg. After the final thawing the first 20 ml. were distilled off before filling the dilatometer.

FIG. 4



During distillation some of the monomer in the reservoir tube polymerised and tended to form a surface film. This was most conveniently broken up by means of a small steel ball which was raised and lowered with a magnet. When the required amount of monomer had been distilled into the dilatometer it was sealed off under high vacuum.

When stilbene was being used as a comonomer it was first added to the dilatometer and washed down with a little pure acetone. Before distilling styrene into the dilatometer the acetone was pumped out and pumping was continued for some time with the stilbene cooled in liquid air, preventing any loss by sublimation, to ensure that all traces of air had been removed. As a further safeguard against traces of occluded air in the stilbene the monomer mixture was degassed once more before sealing off the tubes.

Catalyst, when required, was added to the dilatometer in the same way.

#### v) Polymerisation.

Polymerisations were carried out in a water bath controlled to  $\pm 0.05^{\circ}\text{C}$ . by a Sunvic H.V.S. Relay and a spiral-type mercury-toluene regulator. The contraction of monomer during polymerisation was calculated

from the data of Melville and Valentine,<sup>47</sup> a linear relationship being assumed between percentage contraction and temperature of polymerisation.

In the case of styrene-stilbene copolymers the system was treated as if the stilbene played a negligible part in the change of volume during polymerisation, as it was considered that only a trace, if any, would copolymerise.

vi) Precipitation and Purification of Polymers.

On completion of polymerisation the contents of the dilatometers were poured into an equal volume of benzene, and the polymer was precipitated by pouring this solution into methanol. This process was repeated to remove any monomer, or stilbene, and after filtering the polymer was allowed to dry overnight at room temperature.

For degradation experiments the polymer was required in the form of a fine powder. To achieve this the polymer was dissolved in a large excess of dioxan and the resulting solution poured, via a fine jet, into methanol which was vigorously agitated with a vibratory stirrer. This treatment gave a milk-white emulsion in which the individual particles of polymer were indistinguishable. On standing the polymer particles settled and were filtered off after decantation of the super-

natant liquid. The polymer was allowed to dry in air, ground to a fine powder and finally, thoroughly dried by high vacuum pumping at room temperature.

## 2. Preparation of Copolymer with Labelled Stilbene.

### i) Preparation of trans-Stilbene Labelled with Tritium.

A sample of pure trans-stilbene was labelled with tritium by the gas exposure method which has been applied successfully to other organic compounds.<sup>48,49</sup> This method was chosen for its simplicity, since other methods such as recoil labelling require fairly complicated experimental procedures.<sup>50</sup>

The apparatus used for exposing the stilbene sample is shown in Fig.5. Powdered stilbene (2g.) was sealed into a tube with a glass sinter at the neck. This sinter prevented the fine powder from blowing about when it was exposed to sudden changes in pressure.

With the 2curie tube of tritium (U.K.A.E.A., Harwell) sealed in place the whole apparatus was evacuated under high vacuum for 2 days to remove all oxygen from the stilbene. At the end of this time the apparatus was sealed off at the constriction, still under high vacuum. The break-seal A was then broken with the steel ball, allowing the tritium to reach the stilbene.

FIG. 5

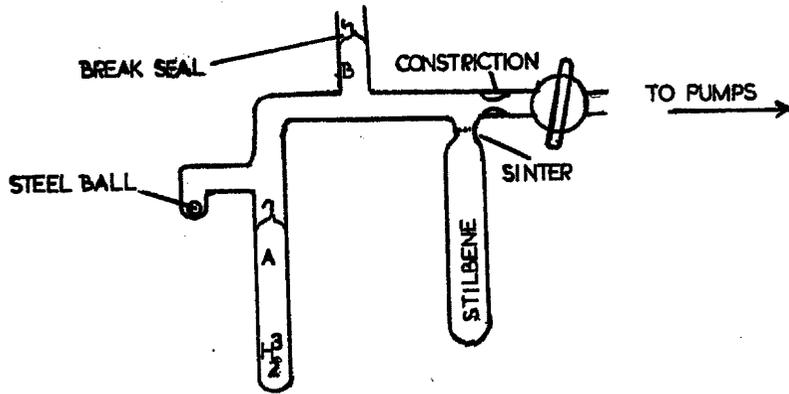
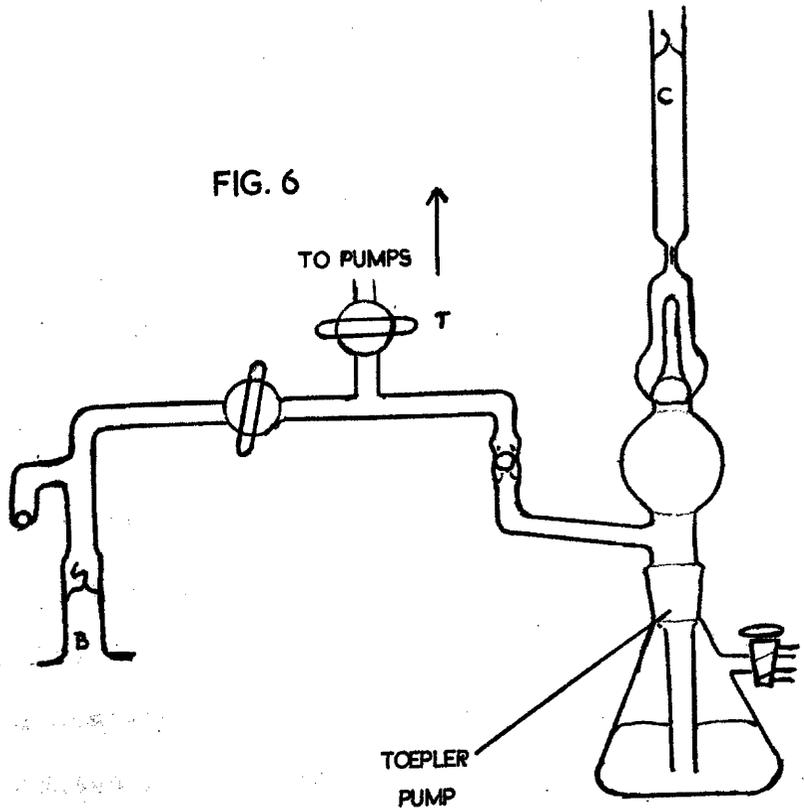


FIG. 6



Contact between tritium and stilbene was maintained for 16 days, after which the tritium was returned to another break-seal storage tube for future use. The apparatus used in this operation is shown in Fig.6. By means of the break-seal B the exposure tube was connected to a Toepler pump to which a fresh break-seal tube C had been attached. After vigorous evacuation of the apparatus the tap T was closed, break-seal B was opened and the tritium pumped into the receiver C which was then sealed off.

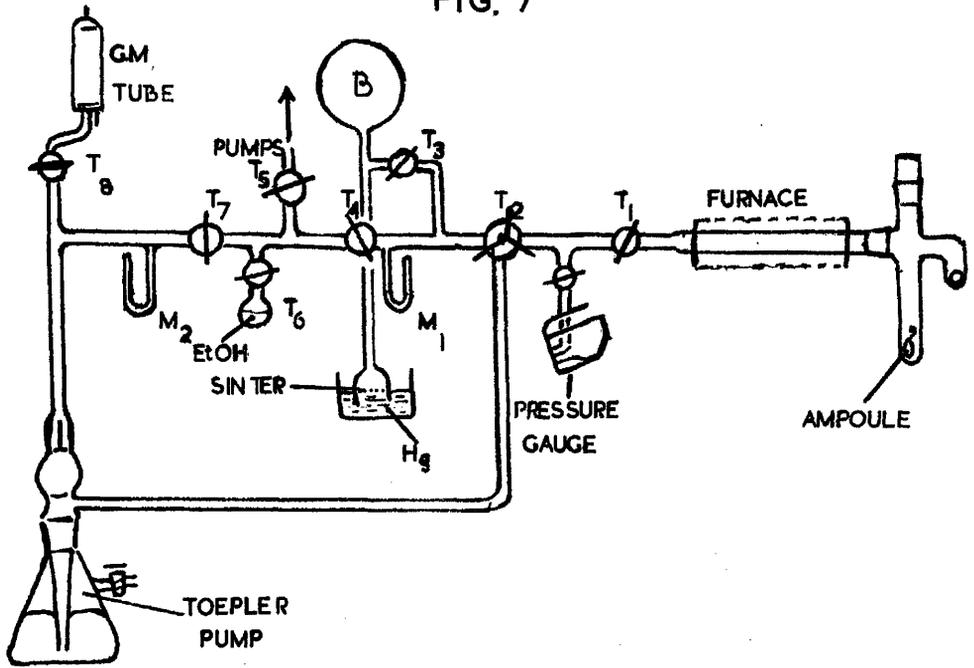
The stilbene tube was then opened and its contents recrystallised twice from ethanol giving a product of M.P.  $125^{\circ}\text{C}.$ . The radio-purity of this product was subsequently investigated.

ii) The Counting Technique and Apparatus.

The tritium content of the stilbene was measured in the following way.<sup>51</sup> The sample was diluted with inactive stilbene and burned to carbon dioxide and water in a conventional combustion apparatus. The water was condensed and transferred to thin walled ampoules to be used in the counting apparatus shown diagrammatically in Fig.7.

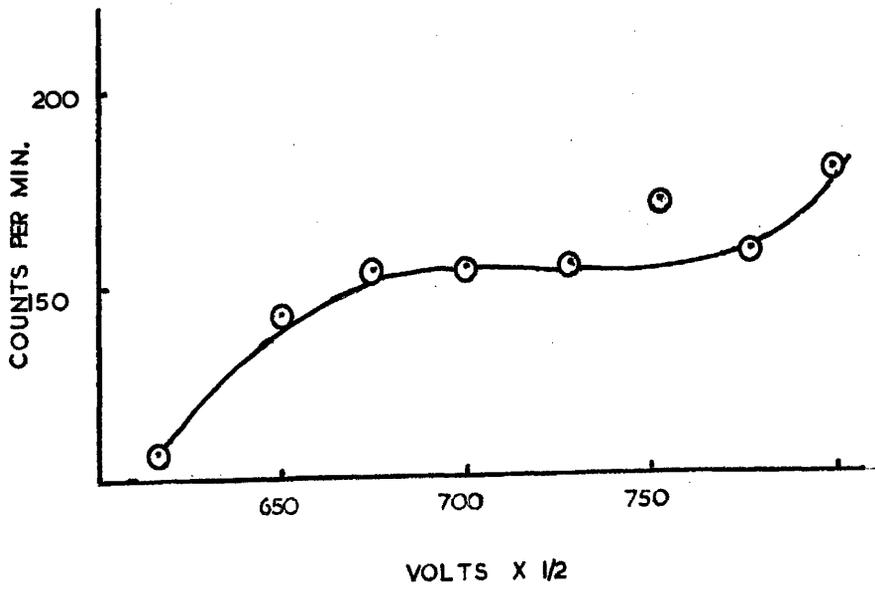
Grignard grade magnesium turnings were heated in the furnace to  $500^{\circ}\text{C}.$  under high vacuum until no more

FIG. 7



GAS COUNTING APPARATUS

FIG. 8



G.M. TUBE PLATEAU

volatile material was evolved. This usually took 6 to 8 hours, after which the whole apparatus was thoroughly degassed, then  $T_5$  was closed. With  $T_3$  open,  $T_2$  open to the furnace and storage bulb B,  $T_1$  open and  $T_4$  closed, the ampoule of water was broken with the steel ball. The water vapourised slowly and was converted to hydrogen which streamed into B. When volatilisation of the water began to slow down  $T_2$  was opened to the Toepler pump,  $T_7$  and  $T_4$  were opened,  $T_8$  closed and the remainder of the water was drawn slowly over the magnesium, by means of the Toepler pump, and the hydrogen transferred to B. When the water sample had been completely vapourised,  $T_1$  was closed and the furnace switched off.

The hydrogen was then transferred from B into the Geiger-Muller Tube (G.M.T.), with  $T_7$  closed, until 8cm. (Hg) pressure of hydrogen existed in this section of the apparatus.  $T_3$  was then closed,  $T_4$  and  $T_5$  opened and the residue of gas pumped off to waste. Ethanol (quenching agent) was released into the apparatus by opening  $T_6$  (still with  $T_7$  closed). When the pressure in manometer  $M_1$  had reached the desired level  $T_4$  was closed and the vapour between taps  $T_4$ ,  $T_3$  and  $T_2$  pumped into the G.M.T. section. The whole apparatus had been previously calibrated so that it was known what partial pressure of ethanol would exist in the G.M.T. section

for a given pressure between taps  $T_4$ ,  $T_3$  and  $T_2$ . The pressure in  $M_1$  was allowed to reach a level which would give 2 cm. pressure of ethanol vapour in the G.M.T. section (checked with manometer  $M_2$ ) when all the gas had been transferred there from the section bounded by  $T_4$ ,  $T_3$  and  $T_2$ .

When all the ethanol vapour had been pumped to the G.M.T. section, the mercury in the Toepler pump was raised and lowered twelve times, with the valve held off its seat by a magnet, to ensure thorough mixing of the hydrogen and ethanol. The gas in the Geiger-Muller tube was then ready for counting to measure its tritium content.  $T_3$  was closed and the Geiger-Muller tube terminals connected to an Ekco Scaler.

Sufficient stilbene was burned in each case to provide enough hydrogen for three separate counts. Before and after each sample had been measured the apparatus was flushed out several times with pure hydrogen and a background count taken. The background was usually in the region of 100-150 counts per minute (c.p.m.) per 8 cm. pressure of pure hydrogen.

All measurements were corrected for a dead time of 500  $\mu$ secs. but no statistical corrections were applied as the results were too well defined to require them.

iii) The Geiger-Muller Tube.

The Geiger-Muller Tube comprised a polished copper cylinder about 4 ins. long and 1 ins. in diameter (the cathode) with a fine tungsten wire placed coaxially inside (the anode). A characteristic background plateau of this tube is shown in Fig.8.

iv) Purification of the Labelled trans-Stilbene.

The specific activity of the stilbene directly after exposure was too high for accurate measurement ( $5.16 \times 10^6 \mu\text{c/mole}$ ). In checking its radiochemical purity it was necessary to dilute it  $10^6$  times with pure inactive trans-stilbene, homogeneous mixing of the two being ensured by recrystallising the mixture from ethanol.

Radiochemical purity was investigated by chromatography of the diluted material on Brockmann Grade III alumina, benzene:light petroleum (B.P. 40-60°C.) (4:1 v/v) being used as solvent. Table 2 shows the activities of various fractions.

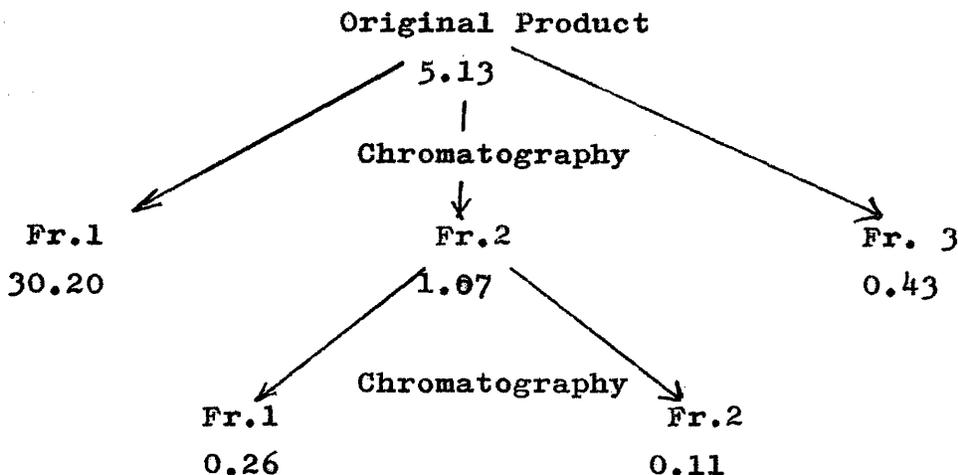
It is clear from the table that the product thus far was not radiochemically pure; and column chromatography was clearly not suitable for achieving purity, though it could be used as a test for it.

Zone melting was also investigated as a method for obtaining a radiochemically pure product but again

fractions were not uniform in activity.

TABLE 2

Specific Activity ( $\mu\text{c}/\text{mole}$ ) of Labeled trans-Stilbene  
Fractions.



Radiochemical purity was eventually achieved by passing the undiluted product through a sequence of chemical reactions likely to isolate only trans-stilbene. This was done by preparing the dibromide from pyridinium bromide perbromide in acetic acid solution. The dibromide quickly precipitated and was filtered off, then recrystallised twice from hot xylene. It was debrominated with zinc dust in ethanol<sup>52</sup> and the recovered trans-stilbene recrystallised. (M.P. 125°C.)

Radiochemical purity was checked by chromatography as before. The first fraction had an activity of  $3.85 \times 10^4 \mu\text{c}/\text{mole}$ , and the second of  $3.94 \times 10^4 \mu\text{c}/\text{mole}$ .

The second fraction was rechromatographed and gave two more fractions each of activity  $3.94 \times 10^4 \mu\text{c}/\text{mole}$ .

Such a multi-stage confirmatory test is generally considered to be adequate proof of radiochemical purity.<sup>53</sup>

The activity of the purified stilbene ( $3.94 \times 10^4 \mu\text{c/mole}$ ), compared with that of the original ( $5.16 \times 10^6 \mu\text{c/mole}$ ), showed that the latter contained considerable active impurity. This may have arisen by addition of tritium at the double bond. Such addition is known to take place with a number of unsaturated compounds.<sup>54</sup>

By the procedure outlined above 0.81g. (40% yield) of pure tritium-labelled trans-stilbene was obtained, though this yield could be improved now that the way to purity has been established.

v) Preparation and Purification of the Copolymer of Styrene and Labelled trans-Stilbene.

This copolymer was prepared in exactly the same way as the others, except that the quantities involved were very much smaller.

The radioactive copolymer was reprecipitated six times in the usual way and its activity measured. The activity was found to be rather high for very accurate counting so the polymer was diluted with inactive polystyrene and reprecipitated a further three times. In this way the polymer was shown to have reached constant activity after six precipitations.

The tritium content of the polymer was measured using the same apparatus as for the labelled stilbene.

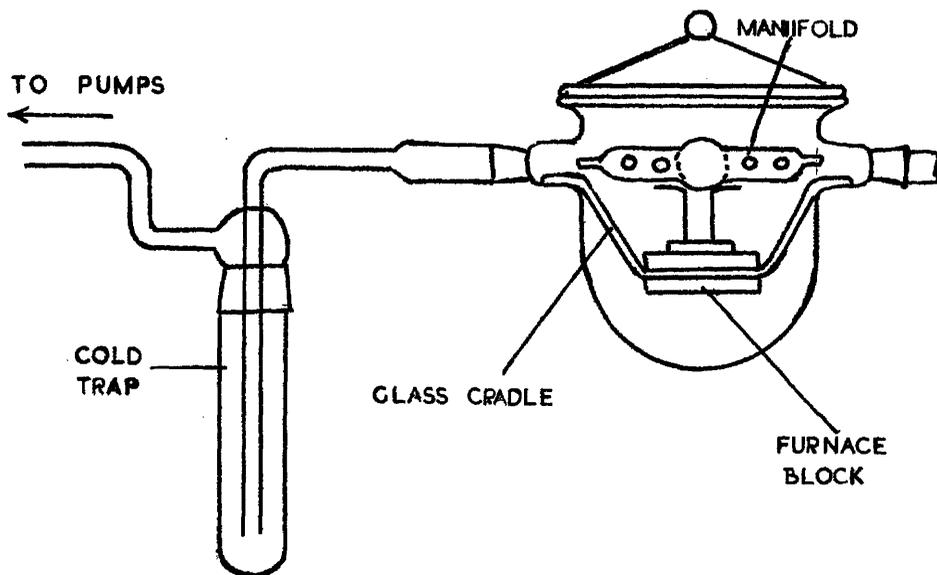
### 3. The Bulk Degradation of Polymers.

#### i) The Glass Apparatus.

Bulk degradations were conducted in a molecular still of the type described by Grassie and Melville.<sup>5</sup> This apparatus allows degradation to be carried out in vacuum, thus avoiding any complicating oxidative side reactions, and at the same time allowing rapid removal of volatile products from the reaction zone.

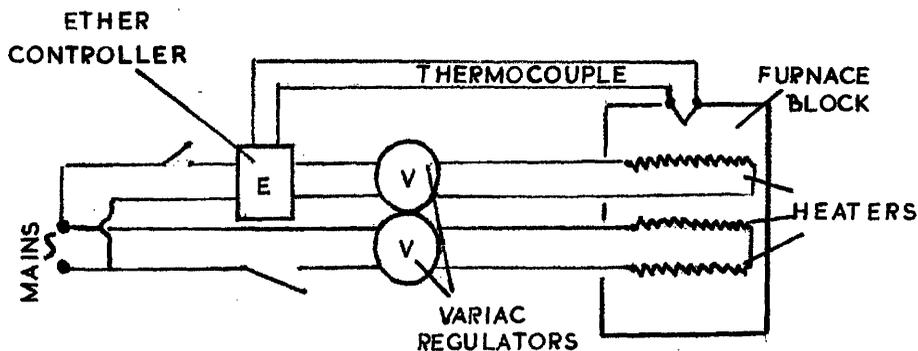
The glasswork and its contents are shown diagrammatically in Fig.9. The still was supplied by Quickfit Ltd. and consisted of a heavy glass cylinder (internal diameter 12cm.), rounded at the bottom and closed with a desiccator lid on a ground glass flange. Inside, the furnace was supported on a glass cradle slung between two of the four B24 sockets on the sides of the still. Electrical leads to and from the furnace and tray were led into the still through a manifold in one of the B24 sockets. Vacuum-tight seals in this manifold were effected with Picien wax.

FIG. 9



BULK DEGRADATION APPARATUS

FIG. 10



FURNACE CIRCUITS

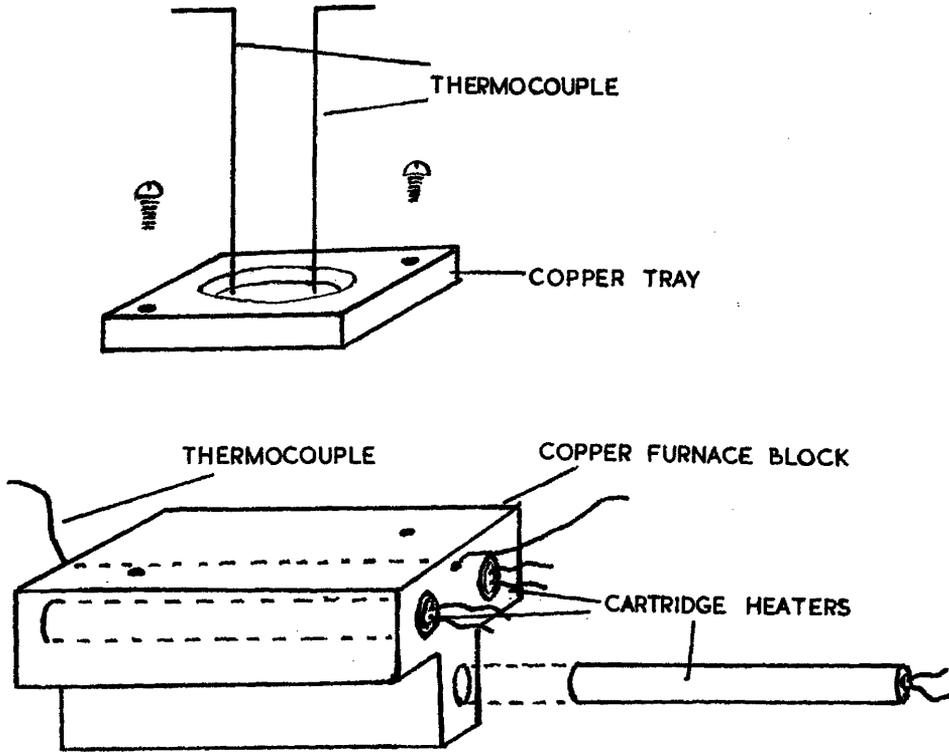
ii) Furnace Construction and Control.

A diagram of the furnace and degradation tray is shown in Fig.11. The furnace block was heated by three 50W/24V cartridge heaters (Hedin Ltd., Type22092). During an experiment the heat output of the two upper heaters was constant while the lower one provided control by its intermittent action. The voltage across the heaters was controlled by two Variac Voltage Regulators fed from the mains.

Above the two constant heaters a small hole was drilled to house a copper/constantan thermocouple which controlled the action of the intermittent heater. The signal from the thermocouple was passed to an Ether Transitrol Temperature Controller (Type 991) which switched on and off the intermittent heater as the thermocouple signal dictated. The electrical circuits to the furnace block are shown in Fig.10.

With the heating and controlling system described above, temperature fluctuations could be limited to  $\pm 0.5^{\circ}\text{C}$ . at  $335^{\circ}\text{C}$ . provided optimum voltages to the heaters were carefully chosen (18V intermittent, 12V constant at  $335^{\circ}\text{C}$ .). The heating up period was cut to a minimum by putting the heaters on full load.

FIG. II



COPPER TRAY AND FURNACE BLOCK

iii) The Degradation Tray.

The dimensions of the copper degradation tray were 37mm. x 37mm. x 7mm., with a circular cavity 32mm. in diameter and 4mm. deep. For recording temperature a copper/constantan thermocouple was silver-soldered to the surface of the cavity. Its output was calibrated against a standard mercury thermometer. The tray temperature could thus be read to within 1°C..

Good thermal contact between the tray and the block was ensured by grinding the two surfaces together with carborundum, and by screwing the two firmly together before each experiment.

iv) The Copper Powder.

During bulk degradations the polymer was covered with a layer of copper powder (0.25-0.30g. polymer and ca. 12g. copper powder) to reduce temperature gradients within the melt and to eliminate sputtering.

The copper powder used in previous work<sup>22,23</sup> was found to have certain limitations. For example, coal gas reduction of the oxide always resulted in a layer of a dark-coloured compound on the copper surface, and frequently abnormally large amounts of volatiles were given off when it was heated. Reduction of surface oxides with formic acid vapour was more efficient but

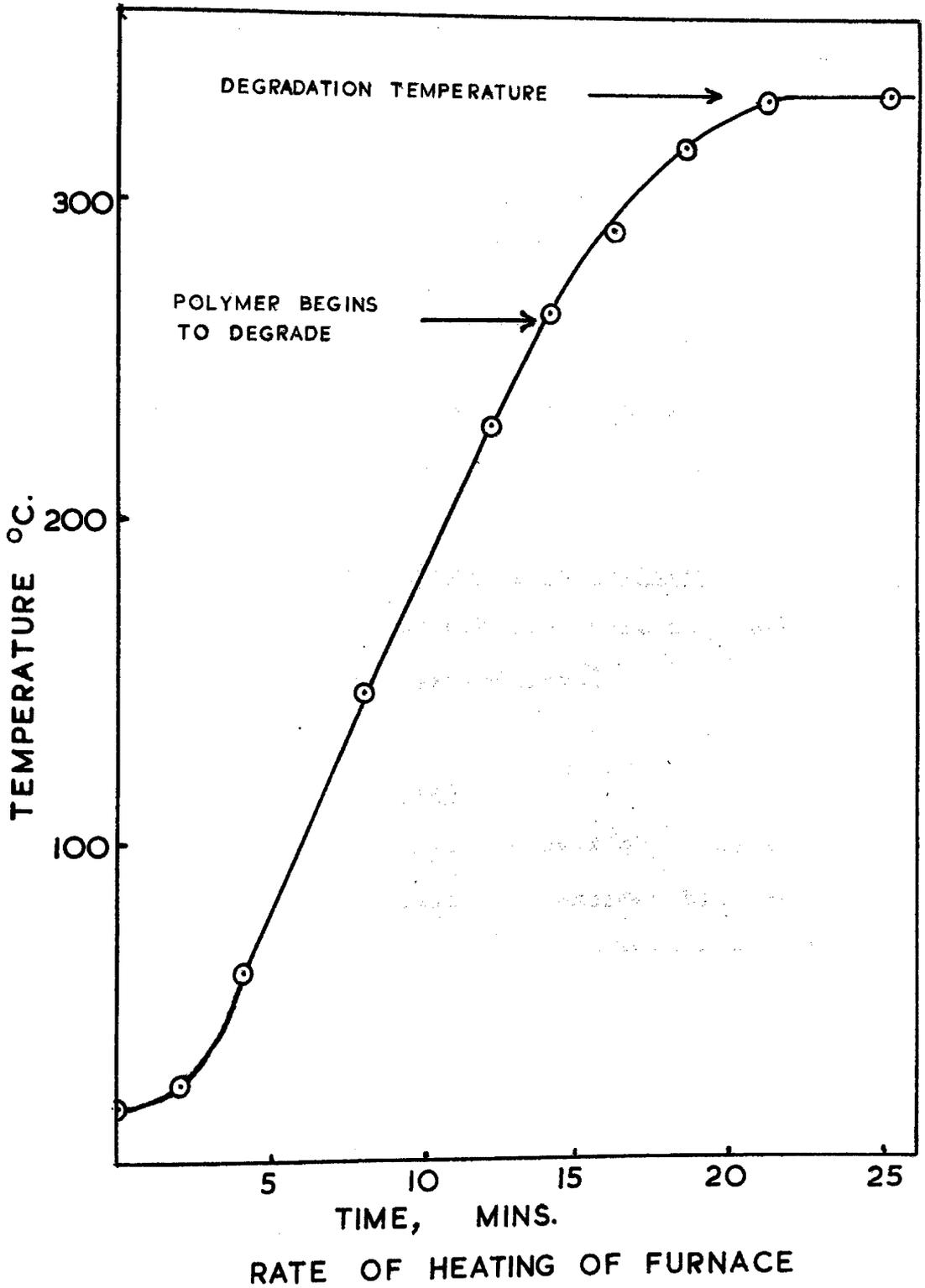
the method was somewhat tedious.

Supplies of copper powder of regular particle size (60-80 mesh) and virtually oxide-free were obtained from Hopkin and Williams Ltd.. This material proved excellent for degradation work, as it was easily handled and showed no tendency to oxidise if stored in a tightly closed tin.

v) The Efficiency of the Heaters.

Where rate measurements are made in a system such as the one described, it is essential that the temperature of degradation should not only be kept constant but should be reached rapidly. This is especially important in cases where the reaction takes place at a significant rate at a temperature below those at which the measurements are to be made. With the system described above a temperature of  $335^{\circ}\text{C}$ . could normally be attained in about 22 minutes. Polystyrene begins to degrade appreciably at  $280^{\circ}\text{C}$ . and it can be seen from Fig.12 that the polymer has been degrading at a reduced rate for about 8 or 9 minutes before the reaction temperature is reached. As degradations were normally carried on for several hours any error introduced during this period, or the corresponding cool-down period, were considered negligible.

FIG. 12



vi) Estimation of Extent of Volatilisation During Degradation.

The conversion of polymer to volatile material during degradation was found by weighing the tray and contents before and after heating. The polymer as prepared usually contained traces of volatile material in the form of solvents, but as this was generally about 1 per cent by weight, and therefore within the experimental error of the degradation experiments, it was not normally taken into account.

4. The Solution Degradation of Polystyrene.

Tetralin and naphthalene were used as solvents in solution degradation experiments.

i) Purification of Tetralin.

The tetralin which is available commercially (L. Light and Co. Ltd.) contains considerable amounts of peroxides. It was purified by the method described by Vogel.<sup>55</sup> The tetralin was shaken up repeatedly with half its volume of concentrated sulphuric acid until the acid layer showed no further colouration. It was then washed once with water, twice with strong caustic soda solution and once more with water. Thereafter it was dried over calcium chloride in a well stoppered flask and refluxed

for forty eight hours over sodium to remove all traces of water and peroxides. The tetralin was stored over sodium and immediately before use it was refluxed again for four or five hours, and finally it was vacuum distilled over sodium. In each case the first 20-30 ml. were rejected.

ii) Purification of the Naphthalene.

Jellinek has already studied the degradation of polystyrene in naphthalene solution,<sup>46,56</sup> and he reported that special purification of the naphthalene is necessary for this purpose.<sup>56</sup> In this work Jellinek's observations were corroborated. It was found that naphthalene scales (May and Baker Ltd.) gave black specks and smelt of sulphur compounds when heated in a sealed tube to temperatures above 300°C..

Purification of the naphthalene was effected as follows. It was first vacuum sublimed, transferred to a heavy walled glass tube, connected to the high vacuum system and degassed by alternate melting and freezing in the normal way. The tube was then sealed off under high vacuum and placed in an electrically heated furnace at 350°C. for eight hours. At the end of this time the tube was cooled and the contents dissolved in ethanol. This solution was filtered and

the naphthalene allowed to crystallise. Three crops of crystals were collected and after drying in vacuo the naphthalene was twice vacuum sublimed. This purified naphthalene gave neither black specks nor smell on heating.

iii) Filling of Reaction Tubes.

In all solution degradations heavy walled Pyrex tubing was used. These tubes had to be carefully annealed during fabrication and sealing, as considerable pressures are developed above 300°C.. As the two solvents - naphthalene and tetralin - are solid and liquid respectively two different techniques for filling the reaction tubes were adopted.

a) With Tetralin as Solvent.

To ensure that all oxygen was removed from the system the following procedure was employed. 0.25g. polystyrene was weighed into a 50ml. Quickfit flask and 15ml. freshly distilled tetralin added. The mixture was immediately evacuated until all the air bubbles were removed, and then allowed to stand until solution was complete - usually four to five hours. The vacuum was then released and the solution filtered into a degradation tube and degassed under vacuum. A dozen cycles of freezing and thawing were usually necessary to achieve this,

after which the contents of the tube were frozen and it was sealed off under high vacuum. The sealed end was shaped into a small hook to facilitate removal from the furnace block. (See Fig.13)

b) With Naphthalene as Solvent.

The procedure adopted with this solvent was similar to that described by Jellinek,<sup>56</sup> and Fig.13 shows the apparatus used. 0.24-0.25g. polymer was weighed accurately into tube A which was then sealed on to B. 10g. naphthalene were placed in C and the apparatus slowly evacuated with C immersed in liquid air to prevent loss of naphthalene. Evacuation was continued for one hour after which the Wood's metal bath, at 80-90°C., was placed round the lower third of A. The temperature of the bath was slowly raised to 200°C. and held there for three hours, the tube remaining open to vacuum. With this treatment the polymer first sintered then fused to a viscous melt entirely free of bubbles. After degassing, the polymer was cooled to 80°C. and the naphthalene degassed. This was done by subliming it into D then back into C which had been recooled to receive it, and the apparatus reopened to high vacuum. This operation was repeated four times. A was then cooled in liquid air and the naphthalene sublimed into it quantitatively. When this was complete A was sealed

FIG. 13

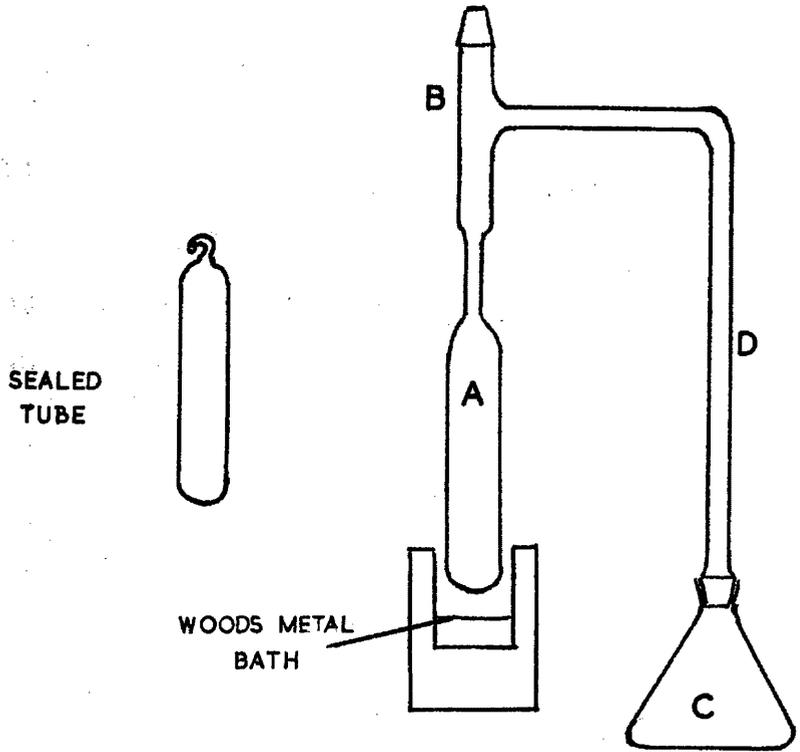
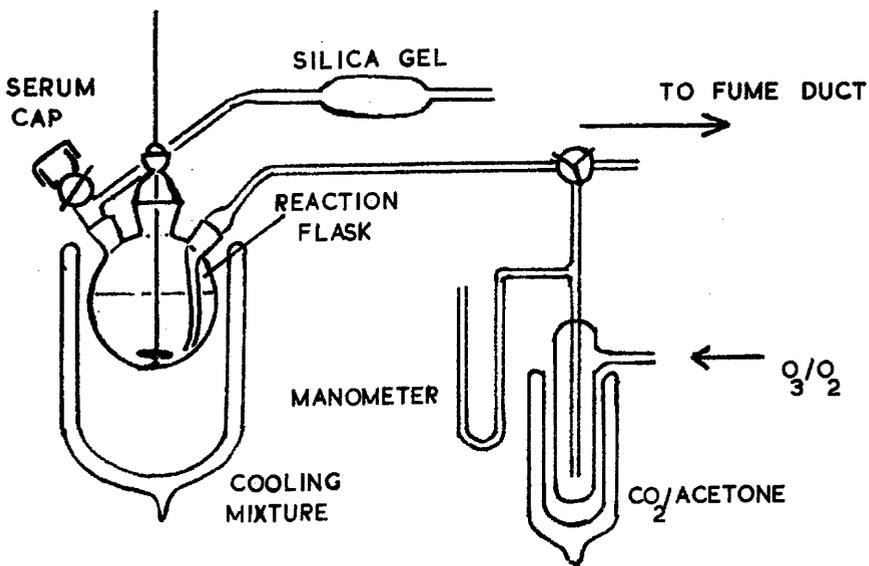


FIG. 14



OZONOLYSIS APPARATUS

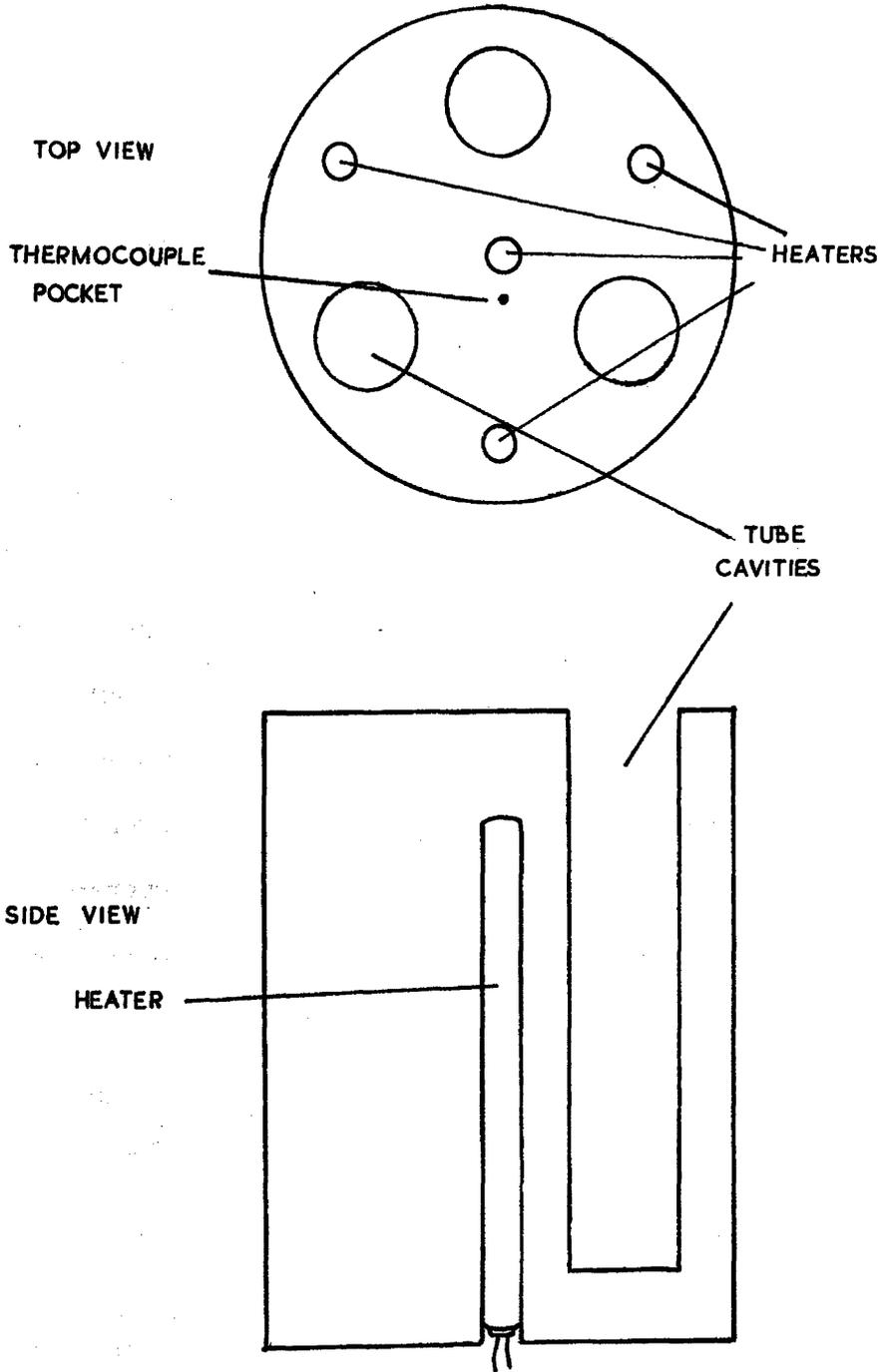
off under high vacuum in the usual manner.

iv) Construction of Copper Block and its Temperature Control.

Fig.15 shows a diagram of the copper heating block which was drilled from a piece of solid copper 13.5cm. deep and 10cm. in diameter. Three cavities for reaction tubes were drilled from the top, each 12cm. deep and 2.4cm. in diameter. From the bottom, four sockets were drilled to house the 100W/240V cartridge heaters (Hedin Ltd., Type 26625). The three outer heaters, in parallel, between the tube cavities were constant in output while the central heater controlled the temperature with its intermittent action.

The central heater was cut on and off by the Ether Controller which was actuated by a copper/constantan thermocouple set into the block near the central heater. The response of this thermocouple was very rapid and for this reason temperature fluctuations were virtually non-existent. Steady temperature control was enhanced by the large heat capacity of the block. To reduce heat losses the copper block was surrounded by an asbestos-lined tin and, for safety reasons, the whole apparatus was covered with an aluminium hood. The degradation temperature was recorded with a calibrated copper/

FIG. 15



SOLUTION DEGRADATION APPARATUS

constantan thermocouple placed in a glass tube inside one of the cavities.

With an apparatus of this kind the heating and cooling periods are unimportant since the reaction tubes can be put in place when the block has reached the required temperature ( $325^{\circ}\text{C}.$ ), and can be removed at any time while the block is still hot. During degradation experiments the mouths of the tube cavities were closed with asbestos wool to reduce any temperature gradients.

The voltage input to the heaters was regulated as before with two Variac Voltage Regulators. For best working conditions the input to the constant heaters was reduced to 180V and to the intermittent heater to 200V. This gave excellent control at  $320\text{-}330^{\circ}\text{C}.$  As before maximum voltage was applied during the heating up stage which took about 50 minutes.

vi) Precipitation of Degraded Polymers.

After the required reaction time the tubes were removed from the furnace block, and were cooled quickly. With tetralin as solvent precipitation was achieved with 250ml. dry ethanol. Methanol is immiscible with tetralin and cannot be used for this purpose, and even ethanol has to be fairly dry.

With naphthalene as solvent the contents of

the tubes were dissolved in the minimum amount of benzene and the polymer precipitated by pouring this solution into 250ml. methanol.

Recoveries were estimated by filtering the precipitated polymers through weighed sintered glass crucibles and drying to constant weight under vacuum. The polymers were then dissolved in pure benzene for molecular weight measurement and after washing with benzene the crucibles were reweighed.

#### 5. The Degradation of Polystyrene with Ozonised Oxygen.

One of the problems in degrading polymers with ozone is to find a good solvent for both the unozonised and ozonised polymer, and which itself possesses reasonable ozone resistance. In the case of polystyrene chloroform was found to be suitable. "Analar" grade chloroform was used, being first passed through a silica gel column to remove traces of moisture.

##### i) Apparatus and Technique.

Ozonolysis was carried out in chloroform solution at  $-21^{\circ}\text{C}$ . with a polymer concentration of 0.5g. per 100ml.. The ozone was produced by an E.C.D. Ozoniser which was capable of producing a fairly constant oxygen:ozone ratio over periods of several hours.

The apparatus is shown in Fig.14. Oxygen was metered to the ozoniser by means of a needle valve and a calibrated capillary flow-meter. After leaving the ozoniser the gas stream was dried by an acetone/solid carbon dioxide cooled trap, thence it was passed to the three-necked reaction flask the contents of which were stirred with a cup and ball sealed stirrer. The outgoing gases were passed through a silica gel tube to a fume duct. Samples were withdrawn through a serum cap by means of a hypodermic syringe. The serum cap was protected from the ozone by means of a stop-cock which was opened only while samples were being withdrawn.

As polystyrene is eventually cross-linked and rendered insoluble by ozone it was necessary to retard this process by ensuring that only a relatively dilute ozone/oxygen mixture reached the polymer. The most convenient concentration was found to be 10 l. per hour of oxygen with an ozone rate of  $2.7 \times 10^{-3}$  moles per hour. Under these conditions it was found that the polymer remained soluble for about one hour.

The reaction flask was cooled to  $-21^{\circ}\text{C}$ . by frozen brine (330g. sodium chloride in 1000ml. water) in equilibrium with its own liquid phase. The brine was most conveniently frozen in a copper basin surrounded by solid carbon dioxide. Temperature reproducibility

with this system was excellent and it was much more easily manipulated than the conventional salt/snow mixture.

ii) Cleavage of the Ozonide.

After ozonolysis the polymer solution was transferred to a 150ml. three-necked flask fitted with a reflux condenser and a stirrer. To this mixture 20ml. glacial acetic acid and 2-3g. activated zinc dust were added. The mixture was warmed slowly on a steam bath with gentle stirring until hydrogen evolution had begun. This was allowed to continue until the reaction had visibly slowed down when heating was restarted and the mixture refluxed gently for six hours. During this time a copious incrustation of zinc acetate formed on the walls of the reaction vessel.

Granulated zinc was originally used but was found to give incomplete cleavage of the ozonide and the more vigorous treatment outlined above was substituted. The zinc dust ("Analar" grade) was activated with boiling acetic acid to remove the oxide layer. Before use it was washed twice with water and then reheated with fresh acetic acid. Zinc dust treated in this way becomes quite warm when dried in air, presumably from surface oxidation.

After reduction the polymer was precipitated

by pouring the solution into 500ml. methanol and the reaction flask was rinsed out with chloroform. Any zinc acetate passing into the methanol appeared to dissolve. The precipitated polymer was allowed to settle overnight before filtration through a glass sinter, and after drying under high vacuum it was dissolved in benzene for osmotic pressure measurements.

## 6. Measurement of Molecular Weights.

The number average molecular weights of the polymers were measured on a modified Fuoss-Mead osmometer using a bacterial cellulose membrane.<sup>57</sup> The osmometer was thermostated by means of water jackets through which water was pumped at constant speed from a water bath controlled at  $30^{\circ}\text{C.} \pm 0.05^{\circ}\text{C.}$  by a spiral-type mercury-toluene regulator and a Sunvic H.V.S. Relay. Benzene was used as solvent and cell constants were taken before and after each measurement.

Before each measurement the osmometer was washed out six times with solvent followed by six rinses with the solution under examination. Osmotic pressures were measured statically. Solution concentrations were determined by running about 10ml. of the solution from the cell face into a weighing bottle, and evaporating the solvent in an air oven overnight at  $110^{\circ}\text{C.}$ .

Though it has been pointed out by Grassie<sup>58</sup> that small amounts of volatiles occluded in some polymers may cause errors as high as 10 per cent in concentration determinations, Kerr<sup>21</sup> found that the above method was completely satisfactory with polystyrene solutions provided heating was continued for at least seventeen hours.

For molecular weight data on undegraded polymers 0.5g. polymer in 50ml. benzene was used. Lower concentrations were obtained by dilution. With degraded polymers the residue was extracted from the copper tray or sintered glass crucible by allowing it to dissolve in benzene at room temperature. The copper powder, when used, was then filtered off and osmotic pressure measurements taken after making the solution up to 50ml..

The benzene used in these measurements was "Analar" grade. It was dried over calcium chloride and distilled through a fractionating column. In all cases the first 25 per cent of the distillate was discarded.

#### 7. Interpretation of Molecular Weight Data.

Benzene was used as solvent for molecular weight determinations because it gives a linear plot of the  $\pi/c$  versus  $c$  relationship with polystyrene, where  $\pi$  is the osmotic pressure and  $c$  the solution concentration.<sup>59,60</sup>

The molecular weights of the polymers were obtained by applying the Van't Hoff Equation at infinite dilution. The density of the solution was considered to be the same as that of the solvent, within the experimental error of the osmotic pressure determinations. Where the osmotic pressure  $\pi$  is measured in cm. benzene and the solution concentration  $c$  in g. per 100g. solution, the molecular weight  $M$  is given by

$$M = \frac{10330xRT}{\frac{\pi}{c}}$$

$c \rightarrow 0$

where  $R$  is the Gas Constant and  $T$  the Absolute Temperature.

Kerr<sup>21</sup> noted that after about 5 per cent volatilisation the slopes of the  $\pi/c$  versus  $c$  plots were constant for degraded polystyrenes. In this work the same observations were made but a discussion of these and other osmotic pressure data is postponed until Chapter VI.

Details of all the polymers used are given in Table 3.

TABLE 3Details of the Preparation of Polymers.

| Polymer            | Temp. of<br>Polymer-<br>isation<br>°C. | Initiator        | %<br>Stilbene<br>in mono-<br>mer mixt. | %<br>Polymer-<br>isation | Mol. Wt.<br>x 10 <sup>-3</sup> |
|--------------------|--|------------------|--|--------------------------|--------------------------------|
| S/GC/1             | 60                                     | None             | 0                                      | 12.5                     | Very<br>High                   |
| SS/GC/1            | 60                                     | "                | 11                                     | 12.5                     | "                              |
| SS/GC/2            | 60                                     | "                | 21.5                                   | 12.5                     | "                              |
| S/GC/5             | 60                                     | AIBN<br>(0.03%)  | 0                                      | 13.5                     | 530                            |
| S.7 *              | 120                                    | None             | 0                                      | 15.0                     | 640                            |
| S1159 <sup>†</sup> | -                                      | Butyl<br>Lithium | 0                                      | -                        | 570                            |

\* - Prepared by Grassie and Kerr

† - Supplied by Dow Chemical Co. Ltd.

CHAPTER III

THE DEGRADATION OF POLYSTYRENE IN SOLUTION

1. Introduction.

It is clear from the material discussed in Chapter I that no completely conclusive evidence so far exists to establish either of the two main theories ( weak links or intermolecular transfer) which have been proposed to account for the initial rapid fall in molecular weight during the thermal degradation of polystyrene. The evidence produced by Grassie and Kerr, however, would seem to favour scission at a limited number of weak links in the polymer chain, rather than intermolecular transfer of a depolymerising radical with another polystyrene chain and subsequent scission of that chain at the point of transfer.

The intermolecular transfer theory implies that the chain scission process and the production of volatile material are parts of the same overall radical reaction. Radicals are formed by some initiation process, and the monomer producing and transfer reactions may be regarded as two competing propagation steps. On the other hand, the weak link theory, as proposed by

Grassie and Kerr, implies that the reactions governing the initial steep fall in molecular weight and the production of volatiles are absolutely separate and independent. On the transfer reaction theory, therefore, inhibition of the production of volatiles should effectively inhibit molecular weight changes and vice versa, while on the weak link theory inhibition of the production of volatiles should have no effect on the initial rapid decrease in molecular weight.

Thus to distinguish between the two mechanisms it is only necessary to carry out the thermal degradation in the presence of an inhibitor, and study changes in molecular weight and volatilisation. Most of the usual inhibitors, such as quinones, are very volatile under bulk degradation conditions (high vacuum and temperatures greater than 300°C.) and quickly evaporate from the reaction zone. Even the anthraquinone dyestuffs which have been employed successfully in the bulk degradation of polymethyl methacrylate<sup>5</sup> at rather lower temperatures, quickly vapourise under these conditions. Degradation in the liquid phase in a closed system, however, is free from such problems and appears more promising provided a suitable solvent can be found.

Jellinek and his co-workers have already degraded polystyrene in two different solvents - tetralin

and naphthalene.<sup>46, 56</sup> They reported that degradation in naphthalene is comparable with degradation in bulk, but that degradation in tetralin completely inhibits the production of volatiles. Tetralin, therefore, seems to be both a good solvent and an inhibitor.

It was decided in the present work to compare the degradation of a polystyrene - S/GC/5 - in bulk, in naphthalene and in tetralin at 325°C., contrasting the reactions by following both changes in number average molecular weight and degree of volatilisation. The techniques employed in these experiments have been described in Chapter II.

Jellinek's work on the degradation of polystyrene in tetralin was exploratory in nature and consequently rather incomplete. His degradation studies in naphthalene, on the other hand, were fairly detailed but he made no direct comparison of the degradation in bulk and in naphthalene of a given polystyrene sample. As the detailed degradation behaviour of different polystyrene samples can vary quite markedly, as has already been indicated, it is vital in quantitative work of this nature that the same polymer sample should be used throughout, otherwise close comparisons are of doubtful validity.

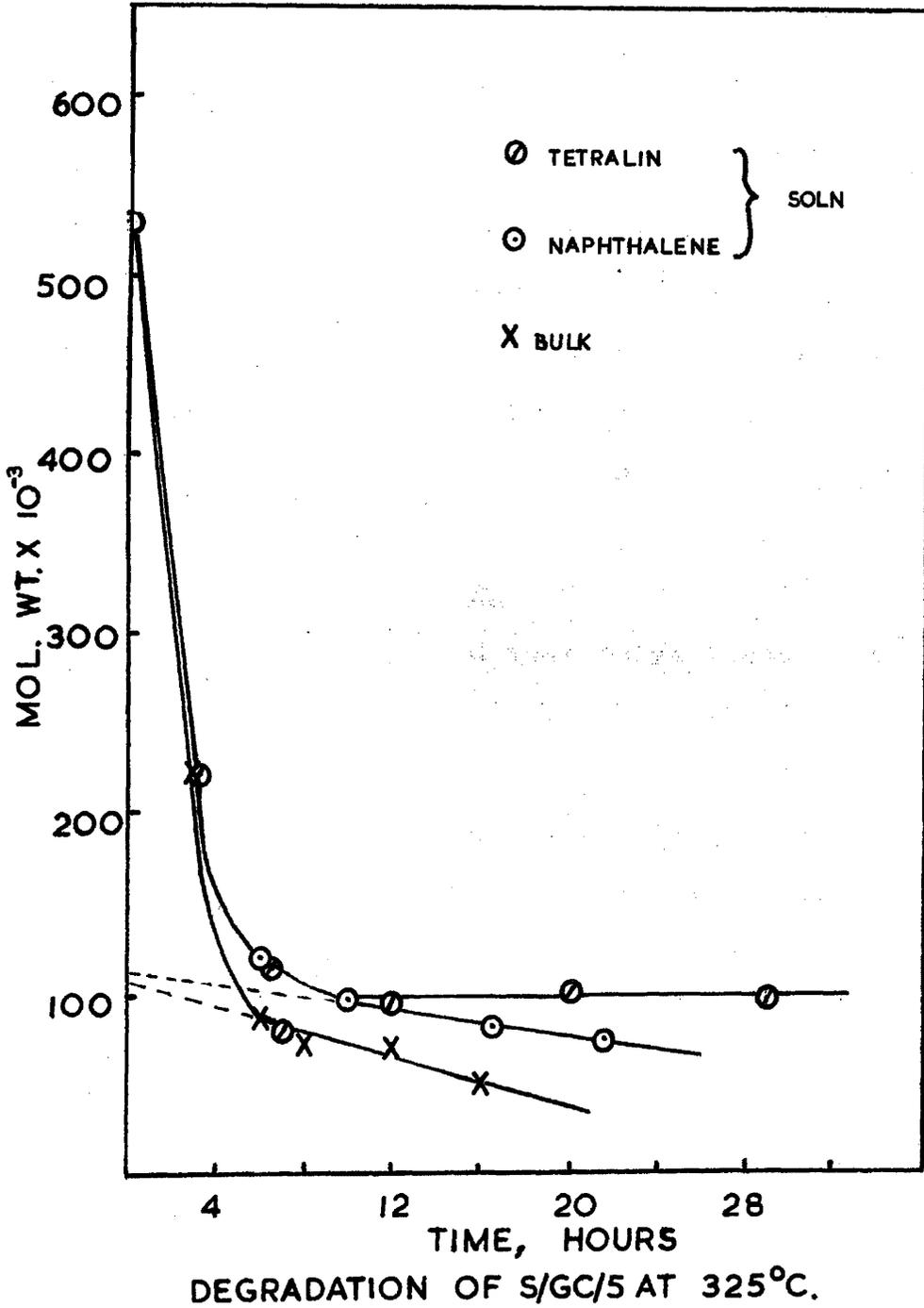
The purpose of the comparison of the degradation of polystyrene in bulk and in naphthalene was to

ensure that degradation in the liquid phase is quite "normal" and comparable with that in bulk. As naphthalene is a good solvent for the polymer and similar to tetralin in structure, without being an inhibitor, a comparison of the degradations in naphthalene and in tetralin should show the effect of the inhibition of any radical process taking place in the latter.

## 2. Degradation in Naphthalene and in Bulk.

The changes in molecular weight with time of heating at  $325^{\circ}\text{C}$ . of polymer S/GC/5 in naphthalene and in bulk are shown in Fig.16. It is obvious that the general behaviour in both media is the same. In naphthalene, both effects - initial rapid fall in molecular weight and volatilisation - still occur, and strikingly the former proceeds at approximately the same rate as in bulk. It was found from polymer recoveries that in naphthalene a progressive conversion of polymer to volatile products still occurs. In a closed system, such as that used in solution degradations, it is essential to establish this fact which indicates that there is no polymer-monomer equilibrium, that is to say that experiments are being carried out above the ceiling temperature of the monomer. The ceiling temperature for styrene has been estimated as ca.  $300^{\circ}\text{C}$ .<sup>61</sup> but this would be considerably lowered at the concentrations used

FIG. 16



in these experiments (ca. 2 per cent). Nevertheless, the possible errors in ceiling temperature estimations make this safeguard necessary.

Fig.16 shows that the limiting molecular weights, by extrapolation to zero time, in the two media are in good agreement. The conclusion drawn from these experiments is that thermal degradations of polystyrene in the liquid phase and in bulk are comparable.

It was found that the rate of production of volatiles in naphthalene was slower than in bulk. This observation accords with those of Jellinek and Turner and will be discussed later in this chapter.

### 3. Degradation in Tetralin.

Having verified that polystyrene degradations in bulk and in solution are essentially similar, polymer S/GC/5 was then degraded in tetralin solution at 325°C.. For convenient comparison the results of these experiments are also included in Fig.16. As before, the initial rapid fall in molecular weight to about 100,000 still takes place and at approximately the same rate as for bulk and naphthalene solution degradations. After this first phase of the reaction, however, the molecular weight in tetralin solution remains constant. This is in marked contrast to the degradation behaviour in bulk and in

naphthalene, in which the molecular weight continues to fall slowly after the initial sharp decrease.

No loss in weight of the polymer was detected at any stage of the reaction in tetralin solution, an observation in agreement with Jellinek and Spencer's.<sup>46</sup> Together with the constant molecular weight after the initial decrease, this strongly supports the view that the depolymerisation reaction is effectively eliminated in tetralin. The apparent stability of the polymer in tetralin cannot be due to a polymer-monomer equilibrium greatly favouring polymer, because degradation in naphthalene, a comparable solvent, is quite normal. That the depropagation reaction is inhibited in tetralin is further supported by the results of osmometric examination of the degraded polymers. Polystyrene degraded in bulk and in naphthalene solution normally showed diffusion of short chain molecules through the osmometer membrane after extensive depropagation. Samples degraded in tetralin, however, never showed such diffusion at any stage of the reaction, suggesting that the proportion of diffusible molecules remained very low due to lack of depropagation.

The molecular weights of polymer S/GC/5 at various stages of the reactions in all three media are summarised in Table 4.

TABLE 4

The Degradation of Polymer S/GC/5 at 325°C..

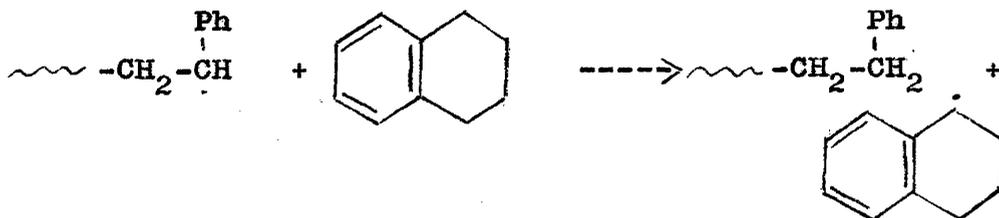
Initial Molecular Wt. 530,000

| Medium      | Time of heating (Hrs.) | Molecular Wt. | % Volatilisation |
|-------------|------------------------|---------------|------------------|
| Bulk        | 3.0                    | 224,000       | 9.1              |
| "           | 6.0                    | 88,000        | 24.9             |
| "           | 8.0                    | 74,000        | 39.9             |
| "           | 12.0                   | 72,000        | 60.5             |
| "           | 16.0                   | 53,000        | 93.0             |
| -----       |                        |               |                  |
| Naphthalene | 6.0                    | 120,000       | 7.1              |
| "           | 10.0                   | 98,000        | 17.2             |
| "           | 16.5                   | 83,000        | 22.6             |
| "           | 21.5                   | 75,000        | 28.5             |
| -----       |                        |               |                  |
| Tetralin    | 3.25                   | 222,000       | 0                |
| "           | 6.5                    | 115,000       | 0                |
| "           | 7.0                    | 79,000        | 0                |
| "           | 12.0                   | 96,000        | 0                |
| "           | 20.0                   | 101,000       | 0                |
| "           | 29.0                   | 98,000        | 0                |

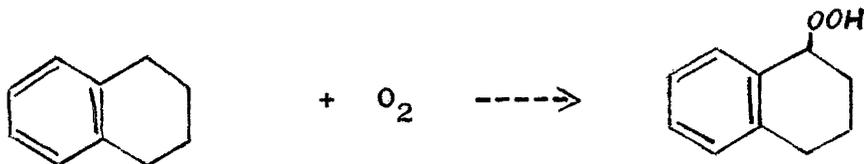
4. Discussion.

1) Evidence for Weak Links in Polystyrene.

It has now been established that degradation of polystyrene in an inert solvent like naphthalene at 325°C. is comparable with degradation in bulk at the same temperature, showing no complicating back reactions. By comparison tetralin appears to be an effective inhibitor for the depropagation reaction. The inhibition reaction by the tetralin molecules is probably of the type



the tetralyl radicals disappearing by mutual interaction in pairs. The  $\alpha$ -hydrogen atom on the tetralin molecule is the most likely to be involved because it is at this active position that peroxidation takes place.



In an inert solvent like naphthalene, on the other hand, depropagation proceeds in the normal manner, as there is no reactive point for transfer reactions to the naph-

thalene molecule.

According to the intermolecular transfer theory the radicals causing depropagation to volatile material also cause the initial rapid drop in molecular weight, and inhibition of one process should also inhibit the other. It has been shown, however, that in tetralin the depropagation reaction is wholly suppressed while the initial rapid decrease in molecular weight is completely unaffected and proceeds at the same rate as for bulk and naphthalene degradations. The experimental facts are thus incompatible with a transfer theory which cannot concede inhibition of depropagation without inhibition of the molecular weight decrease. Nor is the absence of a dilution effect in the liquid phase compatible with intermolecular transfer. Satisfactory explanation of these results can be offered only in terms of a weak link theory, according to which the overall reaction consists of two distinct and independent reactions - weak link scission and depropagation. Of these two reactions only the latter will be inhibited by a free radical acceptor. A weak link theory then, predicts that neither inhibition of the depropagation reaction, which produces volatiles, nor a decrease in polymer concentration can affect the initial steep fall in molecular weight. This is exactly the picture that has

emerged from these experiments and the conclusion drawn from them is that intermolecular transfer plays a negligible part in the degradation, the initial steep fall in molecular weight being caused by weak links in the polymer chain. It follows that non-monomeric fragments like dimer, trimer etc. are produced by an intramolecular transfer mechanism.

It might be argued that the initially formed tetralyl radicals could transfer back to the polymer during degradation in this solvent and thus cause the observed decrease in molecular weight, but if this were so the molecular weight would never reach a steady value. Instead it would continue to fall, because radicals are constantly being formed and transferred to solvent molecules during the reaction in such a system.

The limiting molecular weights (obtained by extrapolating the post-weak link scission part of the curves to zero time) for the degradations in all three media are in good agreement. (See Fig.16). This too is strong support for a weak link theory, because the predicted variation in intermolecular transfer behaviour in different media would almost certainly give widely divergent limiting molecular weights. On the basis of the weak link theory the limiting molecular weights may be regarded as the molecular weights to which polymers

fall by the process of weak link scission alone. Some further comments on limiting molecular weights are made later in this discussion.

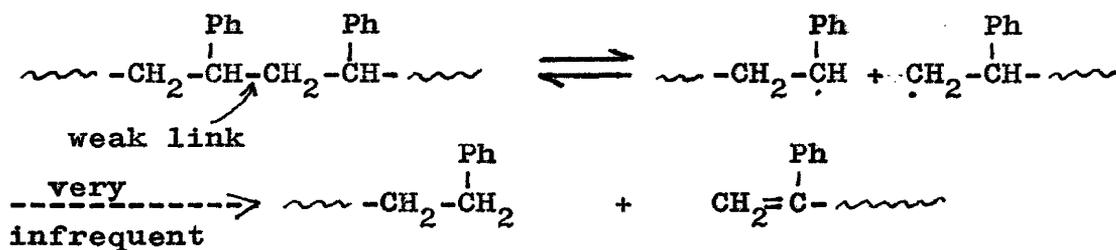
ii) The Reaction Mechanism.

The work discussed above proves that the thermal degradation of polystyrene comprises two separate and unrelated reactions - weak link scission and depropagation. Further light, however, is also thrown upon these individual processes.

Grassie and Kerr<sup>22</sup> proposed that, after weak link scission, the depropagation reaction causes the more gradual decrease in molecular weight. Comparative studies of the degradation in bulk and in tetralin solution substantiate this theory, because, where depropagation is absent, as in tetralin solution, the molecular weight, after weak link scission, remains constant, and where depropagation occurs, as in bulk or naphthalene solution, the molecular weight continues to fall.

In the same paper these authors suggested that a "cage effect" might be operative during the weak link scission phase of the degradation reaction in bulk, and that this might be one of the reasons why so many polymer degradations are initiated at chain ends. They showed that the weak link scission step results in stable

chain ends and not radicals, as Jellinek supposed. Grassie and Kerr suggested that initial homolytic fission at weak bonds produces radical chain ends which are very rapidly deactivated by two competing processes, - recombination and disproportionation - the former greatly predominating. The measurable permanent chain scission in polystyrene, they proposed, is probably the result of the small proportion of these short-lived radical pairs which disproportionate. The following is the sort of reaction which they envisaged



though this scheme does not purport to illustrate the actual structure of a weak link.

In other reactions of this sort proceeding in a solid or highly viscous phase there is evidence to suggest that such a cage effect does exist. Pike and Watson,<sup>62</sup> for example, showed that the molecular weight decrease observed during cold mastication of rubber in air is due to stabilisation of the initially formed free radicals by oxygen. In the absence of oxygen these normally recombine and no appreciable change in molecular

weight takes place.

The effect of an inhibitor, like tetralin, on the thermal scission of weak links in polystyrene should be similar to the effect of oxygen on the mastication of rubber. It has been shown, however, that the rate of weak link scission is constant at a given temperature whether tetralin is present or not. If a cage effect existed during weak link scission in bulk, then in tetralin the effective rate of this process should increase, because of immediate stabilisation of the initially formed radicals and a consequent marked reduction in the frequency of the recombination process. The absence of this phenomenon would seem to preclude a cage effect.

To further clarify this point two portions of polymer S/GC/5 were heated at 270°C. for forty hours - one in bulk and one in tetralin. At this temperature both depropagation and weak link scission are very slow, and the bulk phase is much more viscous than at 325°C., thus favouring a cage effect. After this treatment, however, the molecular weights of both samples had decreased to the same value. Again the absence of a cage effect is inferred. Further evidence for this is discussed in Chapter V.

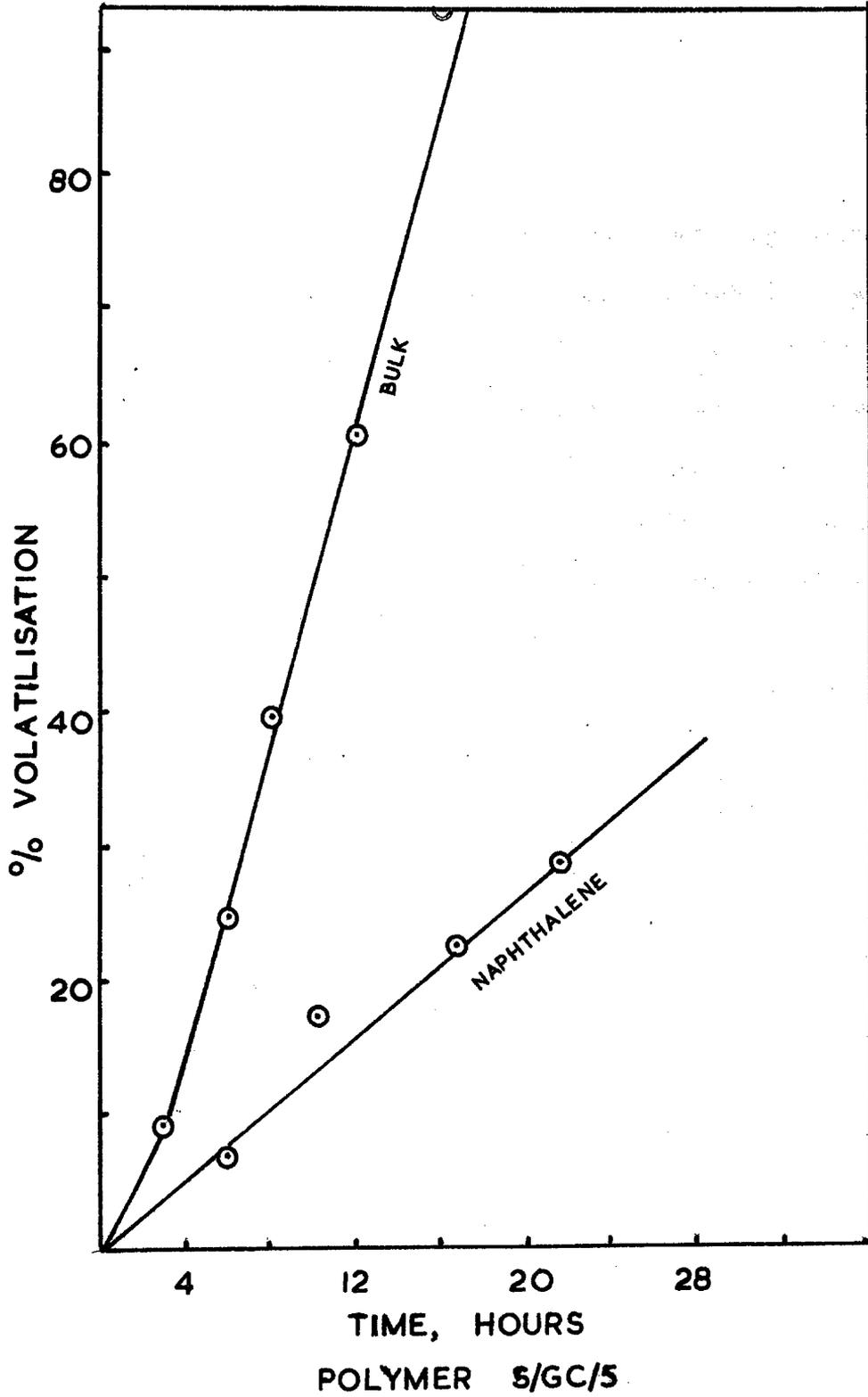
These results show that weak link scission is an irreversible process, and that if free radicals are

involved they must immediately disproportionate by a mechanism of the type shown above. Further consideration is given to the mechanism of weak link scission in Chapter V.

iii) Degradation in Naphthalene and in Bulk.

Though the series of experiments with naphthalene as solvent was originally undertaken to ensure that thermal degradation in the liquid phase is free from complicating side reactions, the system is worthy of study for its own sake. Jellinek and Turner<sup>56</sup> reported that in naphthalene solution the energy of activation for the depropagation reaction, during thermal degradation of polystyrene, is somewhat higher than in bulk, resulting in a lower rate of conversion of polymer to volatile material at a given temperature. They suggested that this might be an effect of the different polymer samples used in the two series of experiments, since different polymer samples frequently show differences in degradation behaviour, or it might be an effect of the reaction medium. In the present work the same observations were made and Fig.17 shows that in bulk degradation the conversion of polystyrene to volatile material is about four times faster than in naphthalene solution. As the same polymer sample S/GC/5 was used

FIG. 17



for each set of experiments this rate difference (ie. apparent activation energy difference) must be due to the medium and not to some inherent differences in the polymer.

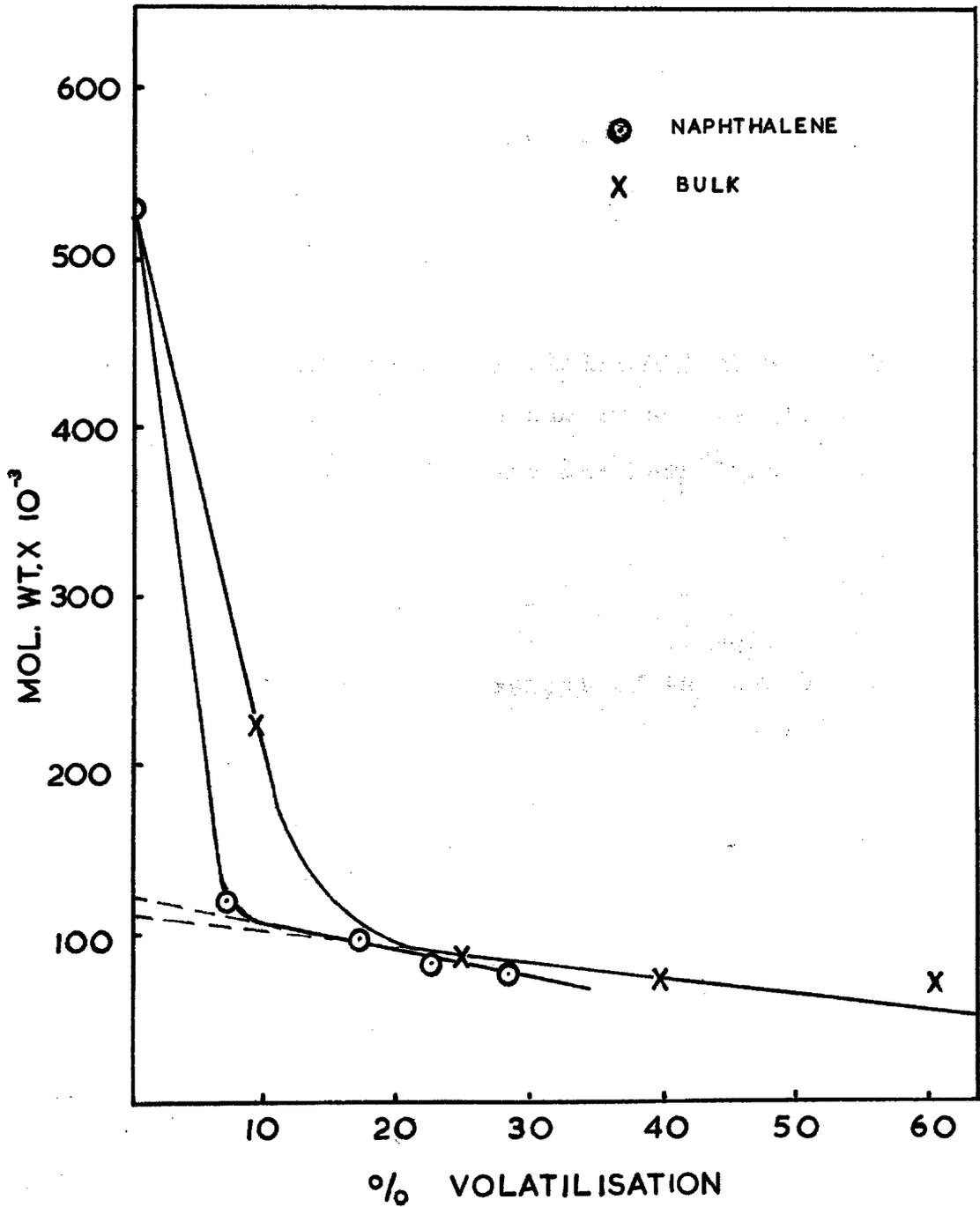
At first sight it is not clear why there should be a rate difference in the two media, but the reason may be connected with the fact that in bulk degradation the system is under high vacuum, while in solution it is under considerable pressure and this may retard the formation of potentially gaseous products such as monomer. Such an effect has been observed by Brockhaus and Jenckel<sup>67</sup> in the case of the degradation of polymethyl methacrylate. They found that the rate of evolution of monomer diminished as the pressure of an inert gas in the reaction vessel was increased. Furthermore, in the case in point, naphthalene itself may be a mild transfer agent or may contain traces of retarders which would give the same effect.

The difference in rate of evolution of volatile material in bulk and in naphthalene is therefore due to the different reaction media, but this does not necessarily imply a difference in activation energy. The observed rate difference could be due simply to a shorter kinetic chain length in naphthalene solution, the reduction being caused by either a pressure effect or mild

inhibition in this solvent.

Grassie and Kerr<sup>22</sup> have already pointed out that the flatter portion of the polystyrene degradation curve (molecular weight versus percentage volatilisation) lies between the horizontal and the diagonal running to zero molecular weight and 100 per cent volatilisation. The implication of such a result has already been fully discussed in the case polymethyl methacrylate degradation,<sup>5</sup> and it means that on the average less than one stable polymer residue remains for each activation. In Fig.18 are plotted the molecular weight changes with conversion to volatile material for degradations in bulk and in naphthalene. For the bulk degradation the flatter portion of the curve is, as usual, between the horizontal and the diagonal, but the corresponding part of the degradation curve in naphthalene lies approximately on the diagonal. This means that in naphthalene solution one stable polymer residue on the average is produced from each reacting molecule. Therefore, in bulk the "un-zipping" process which produces monomer etc. is kinetically longer than the same process in naphthalene; that is, in naphthalene the kinetic chain length is shorter. As has been pointed out in the previous paragraph this difference in kinetic chain length would account for the apparent difference in activation energies in the two

FIG. 18



POLYMER S/GC/5

media.

Fig.18 also shows that in naphthalene solution weak link scission is complete after about 8 per cent volatilisation compared with 25-30 per cent in bulk degradation. This effect is a reflection of the different rates of volatilisation coupled with the same rate of weak link scission.

iv) Estimation of Number of Weak Links in a Polymer.

In estimating the number of weak links  $S$  in a polystyrene sample, Grassie and Kerr<sup>22</sup> used the relationship

$$S = \frac{M_o}{M_d} - 1$$

where  $M_o$  is the molecular weight of the undegraded polymer and  $M_d$  the limiting molecular weight to which the polymer falls on degradation.  $M_d$  was estimated by extrapolating the linear part of the degradation curve (molecular weight versus percentage volatilisation) to zero volatilisation, at which stage it was assumed that the change in molecular weight due to weak link scission alone was being measured. Clearly the accuracy of this calculation depends on the accuracy and validity of the extrapolation.

Degradations in tetralin solution give a more

accurate estimate of molecular weight change due to weak link scission alone, since the complications of depropagation are avoided. Extrapolation of both curves in Fig.18 to zero volatilisation shows slight differences in limiting molecular weights compared with the value of ca. 100,000 obtained from degradation in tetralin. Nevertheless it is clear that Grassie and Kerr's method of estimating weak link concentration by extrapolation is essentially correct, though slight errors are produced where changes in degradation conditions affect the relative rates of the two component reactions - weak link scission and depropagation (vide reactions in naphthalene and in bulk). Grassie and Kerr<sup>22</sup> noticed a similar source of error in their bulk degradation experiments which showed a slight tendency to lower limiting molecular weights at higher degradation temperatures; this effect they attributed to an increase in relative rate of weak link scission over depropagation at higher temperatures.

## 5. Summary.

From the results discussed, it is proposed that the initial steep fall in molecular weight on thermal degradation of polystyrene is produced by chain scission at a limited number of weak links distributed at random

along the polymer chains, the intermolecular transfer theory being incompatible with the experimental facts.

The results also support Grassie and Kerr's theory that the continuing gradual decrease in molecular weight after weak link scission in bulk degradation is due to the free radical depropagation reaction which produces monomer, dimer and other volatile molecules, the non-monomeric fragments being produced by an intramolecular transfer process. Furthermore, this depropagation reaction is quite independent of the weak link scission process.

The "cage effect" suggested by these authors, however, is absent during weak link scission which is an irreversible process.

It has also been shown that the thermal degradation of polystyrene in naphthalene solution is comparable with that in bulk, but with a shorter kinetic chain length due to a pressure effect or mild inhibition, or a combination of both. This accounts for the slower volatilisation in naphthalene and there is no need to postulate a higher energy of activation in this solvent.

Finally, support has been given for the extrapolation method of Grassie and Kerr in determining the concentration of weak links in a polymer.

No suggestion has been made about the chemical

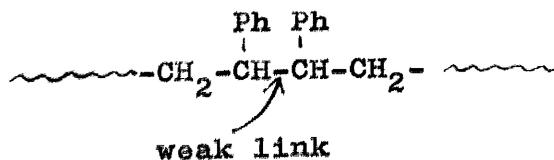
nature of these weak links in polystyrene. It is to this aspect that the following chapters are devoted.

CHAPTER IV

THE ROLE OF HEAD TO HEAD ADDITIONS IN THE THERMAL  
DEGRADATION OF POLYSTYRENE.

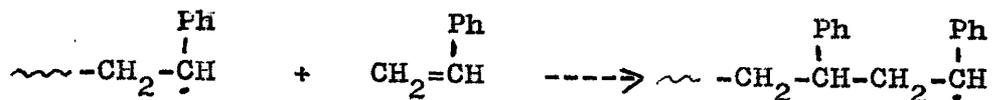
1. Introduction.

The work described in the previous chapter served to prove that weak links certainly occur in polystyrene molecules and that they are responsible for the initial rapid fall in molecular weight when the polymer is pyrolysed. Grassie and Kerr<sup>23</sup> have shown that these abnormalities appear to be a result of some very infrequent polymerisation step with an activation energy somewhat higher than that of the normal propagation process. These authors found that, in general, the concentration of these abnormalities increases with increasing temperature of polymerisation, and, having eliminated points of branching as potential weak links, they considered that head to head structures

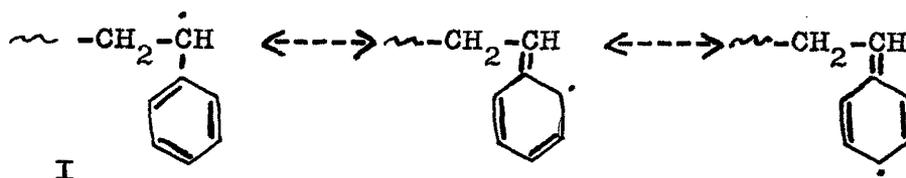


might be the thermolabile points. This chapter is concerned with the role of possible head to head linkages in the degradation of polystyrene.

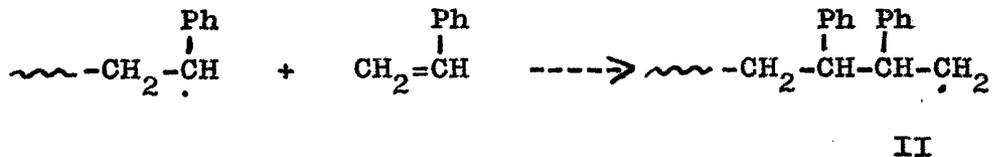
It is generally accepted that free radical polymerisation of styrene proceeds in the following manner



favouring a head to tail structure, since the resultant radical is resonance stabilised by the benzene ring, thus



A head to head addition is less likely



because the product radical has the free electron on the carbon atom  $\beta$  to the benzene ring and thus lacks the resonance stabilisation of radical I. From energetic considerations therefore, head to tail additions are likely to predominate. Furthermore, steric considerations would favour a head to tail process since the bulky phenyl groups would retard head to head additions. It follows then, that head to head addition would probably occur very infrequently during polymerisation, but an increase in temperature of polymerisation might well

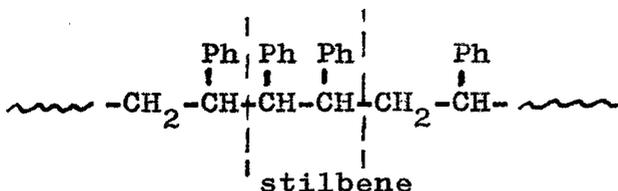
increase the proportion of such additions, since their formation probably requires a higher energy.

The small difference in atomic environments between normal and head to head links in polystyrene, and the relative rarity of the latter, make spectroscopic detection virtually impossible. A close examination of the infra-red spectra of degraded and undegraded polystyrene samples has so far revealed no differences.<sup>63</sup> A more indirect approach to the problem is therefore necessary and for this reason it was decided that it might be possible to introduce controlled amounts of head to head units by copolymerisation techniques.

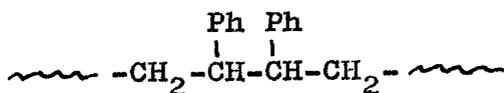
Various diphenyl butadienes were considered as possible comonomers for polymerisation with styrene, since these may already contain the desired head to head structure, but as these compounds are doubly unsaturated the idea was rejected because of the likelihood of complicating side chains or cross-links through polymerisation at the pendant double bond after 1,2-additions.

The only other compound of interest in this respect is stilbene, but it suffers the drawback common to all 1,2-disubstituted ethylenes that it does not polymerise or copolymerise readily with other monomers. Attempts to homopolymerise stilbene at 90°C. under 5000 atmospheres pressure in the presence of peroxides have

been reported as unsuccessful.<sup>64</sup> A copolymer of stilbene with methyl methacrylate containing about 18 per cent stilbene, however, has been reported by Wall,<sup>65</sup> and Marvel and Anderson have prepared a copolymer of 1,3-butadiene and stilbene containing about 1 per cent stilbene.<sup>66</sup> These two results, both achieved with free radical initiators, suggested that if styrene were polymerised in the presence of stilbene a few stilbene molecules might enter the growing polymer to give occasional structures of the type



Such structures, though not identical with a head to head structure



might reasonably be expected to behave in much the same way on pyrolysis, being in effect two adjacent head to head links.

It was anticipated that, if weak links are caused by head to head additions, polymers prepared in the presence of stilbene would degrade to lower limiting molecular weights, provided some stilbene units entered

the growing polymer. Furthermore, as the percentage stilbene in the monomer mixture is increased the limiting molecular weight of the resulting polymer should decrease.

## 2. Degradation of Styrene-Stilbene Polymers.

### i) Results

As a starting point in this investigation three polymers were prepared for comparison. The first of these - S/GC/1 - was pure polystyrene, prepared in bulk. The second, - SS/GC/1 - was polystyrene polymerised in the presence of 11 per cent (w/w) trans-stilbene, and the third - SS/GC/2 - in the presence of 21.5 per cent (w/w) trans-stilbene. All three polymers were prepared, by the method outlined in Chapter II, at 60°C. without initiator. The molecular weights of the three polymers were too high for accurate osmotic measurements, but viscometric comparisons showed that they were the same within experimental error. (See Fig.19).

Degradations were carried out in bulk at 335°C. as described in Chapter II, and the changes in molecular weight with percentage volatilisation for the three polymers are shown in Fig.20. In every case volatilisation was taken beyond the weak link scission phase of the reaction to the linear portion of the curve,

FIG. 19

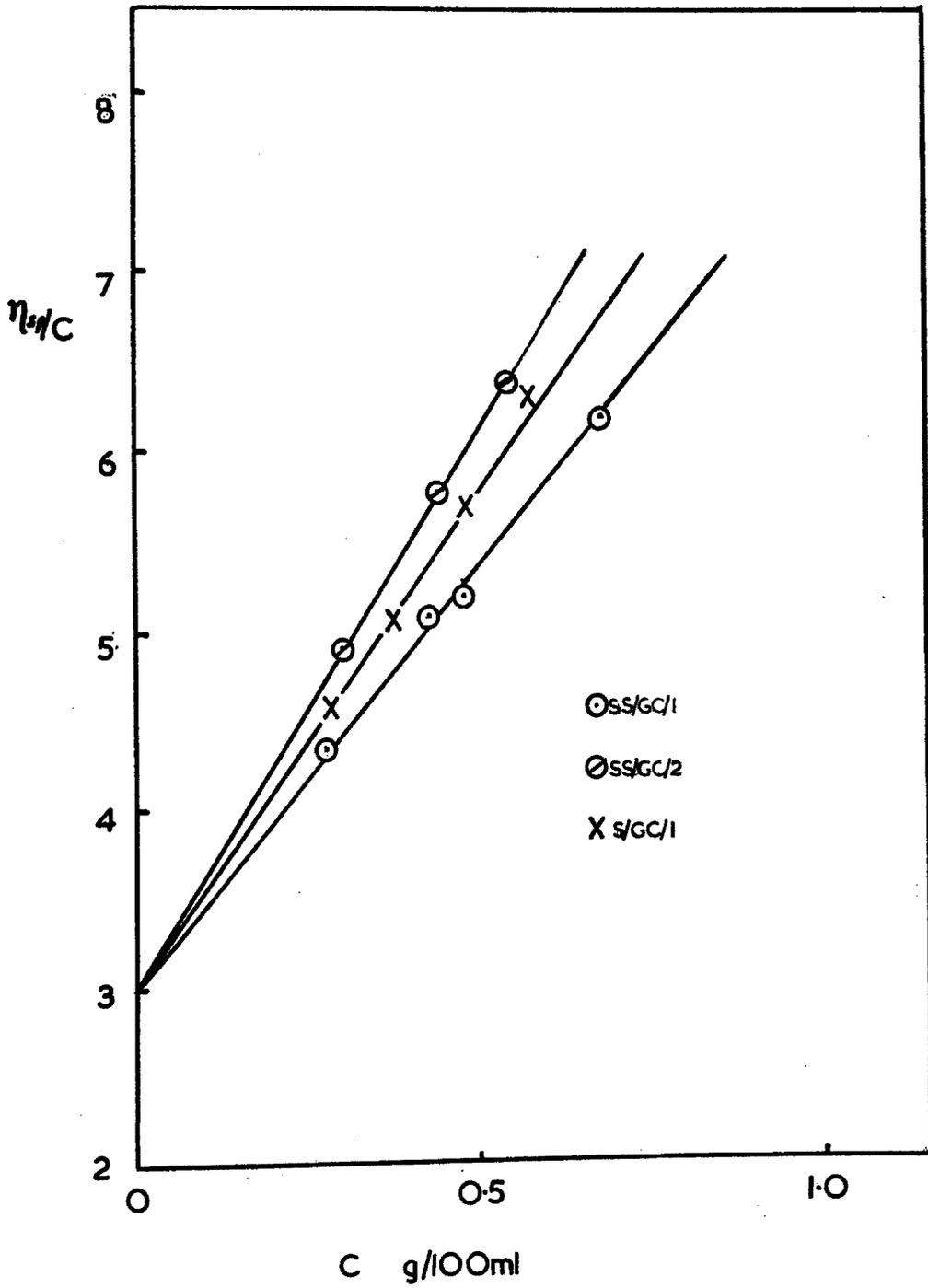


FIG. 20

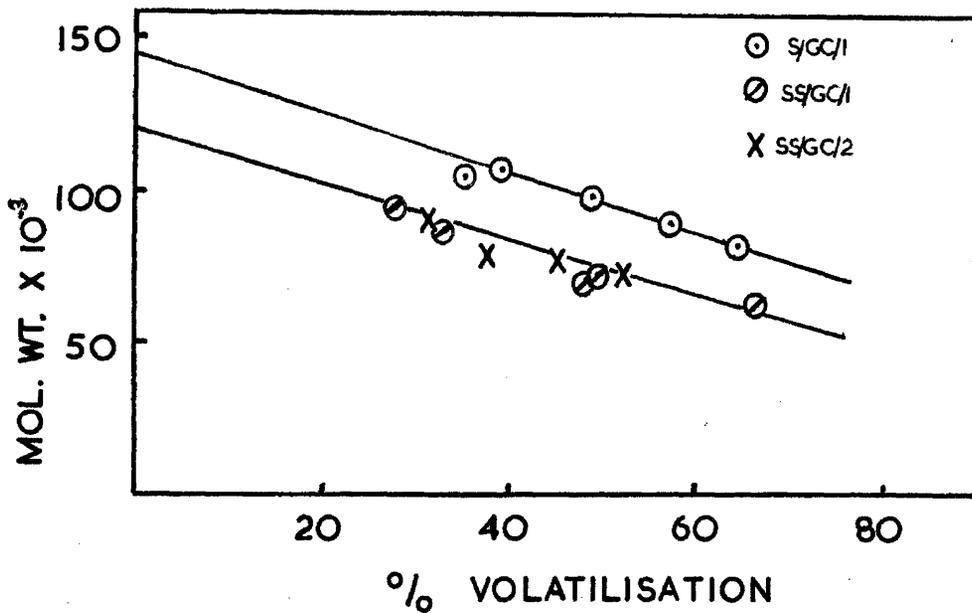
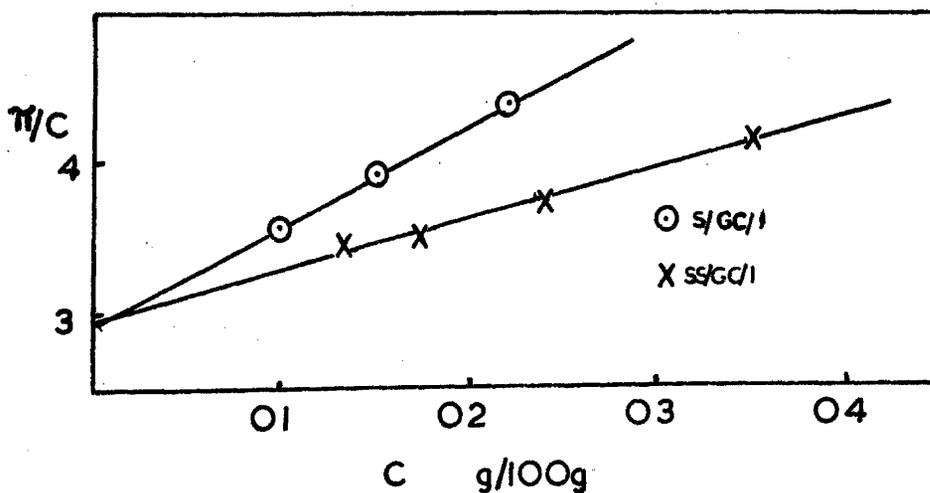


FIG. 21



OSMOTIC PRESSURE - DEGRADED POLYMERS

and the limiting molecular weights obtained by extrapolation in the usual manner.

Data for the degradations of these three polymers are summarised in Table 5.

TABLE 5

Degradation of Polymers S/GC/1, SS/GC/1 and SS/GC/2 at 335°C.

| Polymer | Time of Heating<br>(Hrs.) | Percentage Volatilisation | Mol. Wt. |
|---------|---------------------------|---------------------------|----------|
| S/GC/1  | 5.0                       | 35.2                      | 104,000  |
| "       | 5.0                       | 38.5                      | 109,000  |
| "       | 6.0                       | 48.2                      | 100,000  |
| "       | 6.5                       | 57.2                      | 89,000   |
| "       | 8.0                       | 65.3                      | 80,000   |
| -----   |                           |                           |          |
| SS/GC/1 | 1.0                       | 27.9                      | 97,000   |
| "       | 1.25                      | 33.2                      | 87,000   |
| "       | 1.5                       | 48.0                      | 69,000   |
| "       | 2.0                       | 48.6                      | 72,000   |
| "       | 5.0                       | 67.2                      | 62,000   |
| -----   |                           |                           |          |
| SS/GC/2 | 1.0                       | 31.7                      | 93,000   |
| "       | 1.25                      | 37.5                      | 78,000   |
| "       | 2.0                       | 44.4                      | 76,000   |
| "       | 2.5                       | 51.6                      | 73,000   |

ii) Discussion.

The results show that the two stilbene copolymers (they will be referred to as such for convenience) have the same limiting molecular weight which is about 26,000 lower than that of the pure polymer sample. At first sight this might seem to be caused by an increase in the number of weak links in the former, but if this were so, it is surprising that the limiting molecular weight of SS/GC/2 (21.5 per cent stilbene in monomer mixture) is not lower than that of SS/GC/1 (11 per cent stilbene in monomer mixture). The difference between the limiting molecular weights of the pure polymer S/GC/1 and the stilbene copolymers is not as wide as was hoped, because it leaves the issue in doubt, and it certainly cannot be regarded as conclusive evidence for additional weak links in the copolymers.

In fact, there would seem to be some doubt as to whether the so-called copolymers contain any stilbene at all. The two copolymers, however, show certain differences from the comparable pure polymer suggesting that they are genuine copolymers. For example, it was found that they evolve volatiles more rapidly than the pure polymer, though why they should is certainly not clear. Indeed, this difference in rate of volatilisation could explain the small difference in limiting molecular

weights. (See Chapter III, p.86.). In addition, they also show differences in osmotic behaviour after degradation. It has been mentioned in Chapter II that after degradation beyond about 5 per cent volatilisation the osmotic slopes of degraded polystyrenes reach a constant value. In the same way the osmotic slopes of the stilbene copolymers also reach a constant value after about 5 per cent volatilisation but this slope is lower than that of normal polystyrenes. (See Fig.21).

Since the presence or absence of stilbene is the only variable throughout the whole history of the polymers compared in this work, it must be the presence, in the polymer chain, of this substance which affects the osmotic slopes. It can only do so by remaining after degradation which, it will be recalled, was carried beyond weak link scission on every occasion. If stilbene units can remain in the polymer chain after weak link scission clearly they themselves cannot constitute weak links. This evidence leads to the conclusion that stilbene units, and hence possible head to head additions, are not the weak links in polystyrene.

At this stage it was felt, however, that the picture was rather incomplete for an outright rejection of the head to head weak link theory. The main weakness obviously lay in the fact that there was insufficient

direct proof of any stilbene entering the polymer chains, and the next stage of the problem was to ascertain this.

In this connection it was found that direct analytical procedures were impracticable in the analysis of small amounts of stilbene against a structurally similar background such as exists in polystyrene. Marvel and Anderson<sup>66</sup> were able to estimate stilbene in their copolymers by ultra-violet spectroscopy, but this method is not practicable with polymers of styrene which itself absorbs strongly at the useful wavelengths. Wall,<sup>65</sup> on the other hand, estimated the carbon:hydrogen ratio in his copolymers of stilbene, but this ratio is not sufficiently disturbed, in the copolymers used in the present work, to give an answer of reasonable accuracy.

### 3. The Use of Radio-tracer Stilbene.

It was finally decided that a practicable way round the analytical problem was to use stilbene labelled with a radio-active atom. As the stilbene content of the copolymers was likely to be very low, carbon-14 was not used as the labelling atom because it is a relatively inactive  $\beta$ -emitter (half-life 5,568 years) and might have given very low, and therefore inaccurate, count rates. Tritium was chosen as the labelling atom because it is a much more active  $\beta$ -emitter (half-life 12.46 years),

and can be estimated more accurately in high dilution.

### i) Results

The preparation and purification of both tritium-labelled stilbene and the resulting radio-active polymer have been described in Chapter II. The labelled polymer was prepared by polymerising styrene monomer thermally in the presence of 10 per cent (w/w) radio-stilbene at 60°C.. The polymer is therefore comparable in stilbene content to SS/GC/1 (prepared in the presence of 11 per cent (w/w) stilbene). After purification to constant activity, the hydrogen from the polymer had a count rate of 4090 counts per minute per cm. (Hg) pressure (c.p.m. per cm.).

### ii) Discussion

The significance of the polymer activity quoted above can be seen in the following way.

Let us assume, first of all, that the limiting molecular weight difference between S/GC/1 and SS/GC/1 is due to additional weak links created by stilbene units in the latter, and let us calculate from this information the concentration of stilbene in SS/GC/1.

In any polymer the number of weak links S per polymer molecule is given by

$$S = \frac{M_o}{M_d} - 1$$

where  $M_o$  is the original molecular weight of the polymer, and  $M_d$  the limiting molecular weight after degradation. This may also be expressed as the number of weak links  $N$  per monomer unit

$$N = \frac{104}{M_o} \left[ \begin{array}{cc} M_o & - 1 \\ M_d & \end{array} \right]$$

$$= 104 \left[ \begin{array}{cc} 1 & - 1 \\ M_d & M_o \end{array} \right]$$

104 being the molecular weight of styrene monomer.

For polymers S/GC/1 and SS/GC/1, the difference in number of weak links is given by

$$N_1 - N_2 = 104 \left\{ \left[ \begin{array}{cc} 1 & - 1 \\ M_{1d} & M_{1o} \end{array} \right] - \left[ \begin{array}{cc} 1 & - 1 \\ M_{2d} & M_{2o} \end{array} \right] \right\}$$

where suffixes 1 and 2 represent polymers SS/GC/1 and S/GC/1 respectively.

But, as the undegraded polymers have the same molecular weight,  $M_{1o} = M_{2o}$  and

$$N_1 - N_2 = 104 \left[ \begin{array}{cc} 1 & - 1 \\ M_{1d} & M_{2d} \end{array} \right]$$

From the thermal degradation of these polymers,  $M_{1d} = 120,000$  and  $M_{2d} = 146,000$ , and substituting these values in the above expression we have

$$\begin{aligned} N_1 - N_2 &= 104 \times 10^{-3} \left[ \frac{1}{120} - \frac{1}{146} \right] \\ &= 1.54 \times 10^{-4} \end{aligned}$$

This value is the additional number of weak links per monomer unit in SS/GC/1. Assuming that each of these additional weak links is a stilbene unit in the polymer chain, the mole ratio of stilbene:styrene in SS/GC/1 is given by

$$\frac{\text{(Stilbene)}}{\text{(Styrene)}} = 1.54 \times 10^{-4}$$

Let us now consider the radio-active copolymer and, knowing the activity of the stilbene prior to polymerisation, we can calculate what the activity of this polymer should be using the mole ratio of stilbene:styrene given above, because the radio-active copolymer and SS/GC/1 are comparable in stilbene content, as has been pointed out.

1 mole stilbene gives 6 moles hydrogen and 1 mole styrene gives 4 moles hydrogen, and the mole ratio of hydrogen from stilbene to that from styrene is

$$\frac{\text{(H}_2 \text{ from Stilbene)}}{\text{(H}_2 \text{ from Styrene)}} = 1.54 \times 10^{-4} \times 6/4$$

$$\begin{aligned} \text{Therefore, the mole fraction of } H_2 \text{ from the stilbene in polymer} &= \frac{3 \times 1.54 \times 10^{-4}}{2 + 1.54 \times 3 \times 10^{-4}} \\ &= 1.5 \times 1.54 \times 10^{-4} \end{aligned}$$

since  $1.54 \times 3 \times 10^{-4}$  is small enough to be neglected.

$$\begin{aligned} \text{Activity of hydrogen from} & \\ \text{labelled stilbene before} &= 4.8 \times 10^5 \text{ c.p.m./cm.} \\ \text{polymerisation} & \end{aligned}$$

$$\begin{aligned} \text{Therefore, activity of hydrogen} & \\ \text{after dilution in the polymer} &= 1.5 \times 1.54 \times 10^{-4} \\ &\quad \times 4.8 \times 10^5 \text{ c.p.m./cm.} \\ &= \underline{111 \text{ c.p.m./cm.}} \end{aligned}$$

Thus, assuming that stilbene units cause the 26,000 difference in limiting molecular weights between S/GC/1 and SS/GC/1, the activity of the hydrogen from the polymer prepared with labelled stilbene should be ca. 111 c.p.m./cm.. The observed activity for the hydrogen from this polymer, however, is 4,090 c.p.m./cm., which means conversely that there is about 37 times more stilbene in the polymer SS/GC/1 than there are additional weak links. Clearly stilbene units, and hence any head to head additions, do not form weak links in polystyrene.

This result can be expressed conveniently in terms of the limiting molecular weight to which SS/GC/1 would fall if all its stilbene units formed weak links.

$$\begin{aligned} \text{Activity of } H_2 \text{ from pure} & \\ \text{labelled stilbene} &= 4.8 \times 10^5 \text{ c.p.m./cm.} \end{aligned}$$

Activity of H<sub>2</sub> from pure  
labelled copolymer = 4.1 x 10<sup>3</sup> c.p.m./cm.

The hydrogen from the stilbene has been diluted 4.8 x 10<sup>5</sup>/  
4.1 x 10<sup>3</sup> times by incorporation of the stilbene into  
the polymer.

Therefore, in polymer SS/GC/1 -

$$\frac{(\text{H}_2 \text{ from styrene})}{(\text{H}_2 \text{ from stilbene})} = \frac{4.8 \times 10^5}{4.1 \times 10^3}$$
$$= 1.17 \times 10^2$$

But, as before, 1 mole stilbene gives 6 moles  
hydrogen and 1 mole styrene gives 4 moles hydrogen, and  
therefore the mole ratio of styrene:stilbene in SS/GC/1  
is given by

$$\frac{(\text{Styrene})}{(\text{Stilbene})} = 1.17 \times 10^2 \times \frac{6}{4}$$
$$= 1.75 \times 10^2$$

Thus, if each stilbene unit is regarded as a  
potential weak link 1.75 x 10<sup>2</sup> units of styrene, on the  
average, should separate each stilbene unit, and after  
complete weak link scission the molecular weight of the  
resulting polystyrene molecules should be approximately  
1.75 x 10<sup>2</sup> x 10<sup>4</sup> (ie. 18,300). That is, the limiting  
molecular weight should be 18,300. The observed lim-  
iting molecular weight of SS/GC/1 is, however, 120,000  
and again it is clear that stilbene units cannot be

capable of forming weak points in the polymer chain. The calculated figure of 18,300 does not take inherent weak links into account, and the actual limiting molecular weight would be somewhat lower than this.

There is no doubt that the stilbene copolymers contain more stilbene than was originally anticipated. The actual stilbene content of the labelled copolymer is 1 per cent.

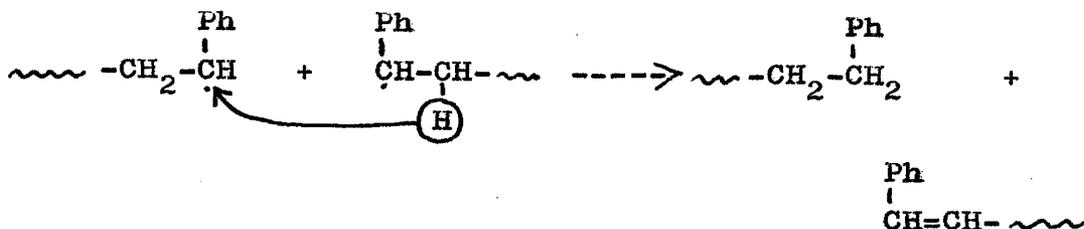
#### 4. Discussion.

The results outlined above show conclusively that head to head additions are not thermo-labile points in polystyrene, though there is no evidence to show that head to head links do or do not exist in this polymer.

This conclusion is in accord with other experimental facts. It has been mentioned previously that Grassie and Kerr<sup>23</sup> found certain polystyrenes in which there was less than one weak link per polymer molecule on the average. If head to head links were thermo-labile points in the polymer chain this result would be hard to explain as there is considerable evidence to suggest that termination during polymerisation is by combination, and by this means alone each polymer molecule should contain one head to head linkage.<sup>39,40,41</sup>

It is also noteworthy that the results of Brown,





so that Kerr's explanation would appear to be invalid. Thus it is difficult to explain Brown, Hart and Wall's results on the basis of a head to head weak link.

### 5. Summary.

Using a radiochemical technique it has been shown that stilbene is capable of copolymerising with styrene. The copolymers so formed, however, degrade thermally in essentially the same way as polystyrene, in particular showing no appreciable increase in weak link content. It is therefore concluded that head to head links, which may exist in polystyrene, are not the thermo-labile points in the polymer chain. It has also been shown that this conclusion fits in with other experimental data.

### Appendix.

The preparation and purification of pure tritium-labelled trans-stilbene have been described in Chapter II, though no comment has been made on the significance of the results. This short appendix endeavours to point

out certain short-comings in the exposure method which was used.

The attraction of the gas exposure method is that it is apparently very simple, requiring no complicated apparatus. Recoil labelling by tritons produced from neutron irradiation of a compound in admixture with a lithium salt, for example, requires a neutron source among other fairly complicated pieces of equipment. Direct chemical synthesis, on the other hand, is not always possible, or is laborious. With these facts in mind the exposure method was adopted for the present work.

The crude radio-stilbene had an activity of  $5.16 \times 10^6 \mu\text{c}/\text{mole}$  compared with  $3.94 \times 10^4 \mu\text{c}/\text{mole}$  for the purified product, a difference which suggested considerable contamination by radio-active impurities. These may have arisen by addition of tritium at the ethylenic double bond, since this behaviour has been noted in other unsaturated compounds.<sup>54</sup> This may also account for the relatively low final activity, since toluene and benzoic acid under similar treatment gave activities between 10 and 25 mc/g.<sup>49</sup>

For ethylenic compounds like stilbene, the chemical preparation of labelled material is therefore probably more satisfactory. This has been done by Bernstein and co-workers<sup>68</sup> who obtained pure tritiated

trans-stilbene of activity  $6.4 \times 10^7 \mu\text{c/mole}$ , with a mass yield of 67 per cent, by controlled reduction of 1,2-diphenyl acetylene with a tritium/hydrogen mixture. The purification procedure employed by these authors was much simpler than that used in the present work.

It is concluded that the ease of labelling by the gas exposure technique is deceptive, and should only be used where chemical synthesis is impossible. Furthermore, if this method is used strict precautions must be taken to isolate radiochemically pure products. In the case of stilbene, however, this method proved satisfactory because the purification technique was efficient.

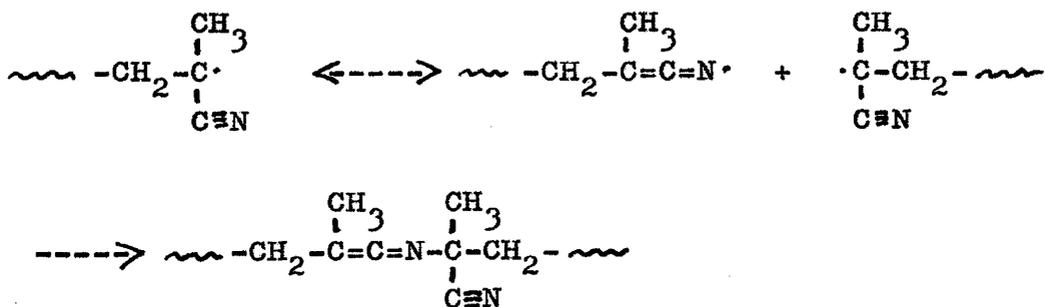
CHAPTER V

THE DEGRADATION OF POLYSTYRENE WITH OZONE.

1. Introduction.

It has been shown in the previous chapter that head to head links are not the weak points in polystyrene chains, and it is therefore necessary to consider other types of abnormal structures which might arise during polymerisation.

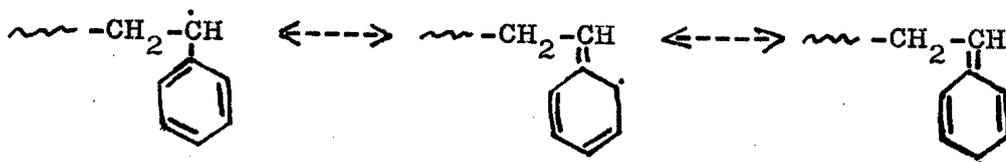
At the end of Chapter I a brief mention was made of ketene-imine structural abnormalities in polymethacrylonitrile.<sup>44</sup> Grassie and McNeill showed that these are formed through a resonance form of the growing polymer radical during the termination step of polymerisation.



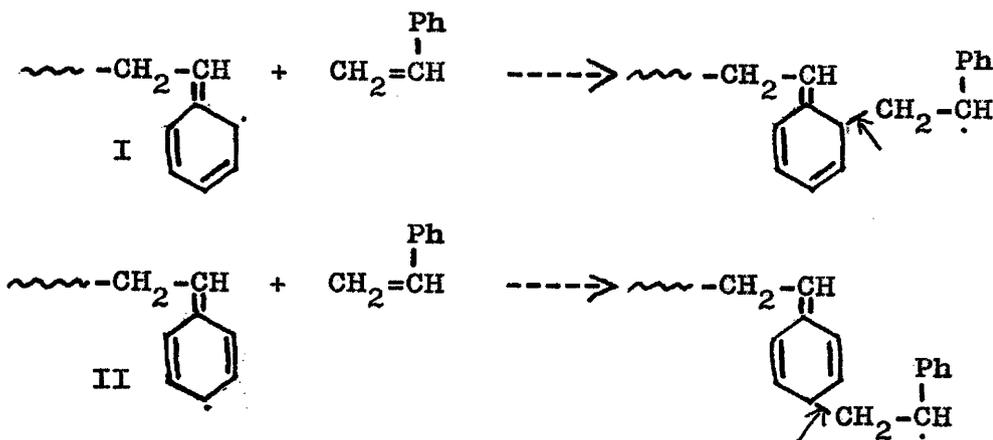
They found that these ketene-imine structures are formed only at relatively low temperatures of polymerisation and are readily broken down at temperatures above 60°C..

The growing polystyrene radical is also capable

of resonating into various canonical forms



which offer alternative positions of addition for the next reacting monomer molecule.

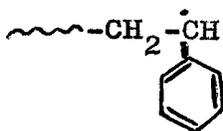


The present chapter is concerned with the possible occurrence of such quinonoid structures in polystyrene molecules and whether or not they might function as weak links.

The bonds indicated in structures I and II above would be expected to be more thermo-labile than the other carbon-carbon bonds in the polymer back-bone being next but one to two double bonds.<sup>14</sup>

The predominantly head to tail structure of polystyrene confirms that normal addition is greatly favoured during polymerisation, so that the resonance

form



of the polymerising free radical is obviously the most stable, that is, the form of lowest energy, and therefore as the temperature of polymerisation is increased the probability that the free radical will be in forms I and II must also be increased. Furthermore, polymerisation through the normal free radical above leaves the benzene ring intact, but polymerisation through forms I and II completely destroys the normal resonating powers of the aromatic ring so that the resulting structures probably possess higher energy barriers for their formation. This factor too should favour a relative increase in the proportion of these abnormalities as the temperature of polymerisation is raised which is in accordance with the experimental findings of Grassie and Kerr.

If the above theory is correct and if some method of estimating quinonoid structures can be found then the number of such structures should be found to be the same as the number of thermo-labile points in a given polymer chain.

## 2. Possible Methods of Estimating Quinonoid Structures.

It has been mentioned previously that the concentration of weak links is so low (<0.1 per cent) that certain analytical techniques, such as spectroscopy, are not practicable for their estimation. Since the proposed structural abnormalities contain double bonds several other methods of estimation come to mind.

Of these direct bromination is the most obvious. In the present problem, however, bromination was considered unsuitable for the following reasons:-

- a) Bromine can degrade polystyrene.<sup>69</sup>
- b) The reaction of bromine with polystyrene is extremely slow.<sup>70</sup> Bromination was originally employed in attempts to estimate terminal double bonds in polystyrene,<sup>69,70</sup> but Boyer and Simha<sup>71</sup> have pointed out that the reaction may take several days for completion in very low molecular weight material and is probably unreliable when high polymers are studied, when there is also a risk of side reactions.
- c) The presence of an unknown number of terminal double bonds might confuse the issue.

It was eventually decided that the most convenient method of estimation would be one in which the polymer molecules were broken at the double bonds, so

that subsequent molecular weight measurements could reveal the number of breaks, on the average, which had occurred. Using a method involving this principle terminal double bonds would not interfere, because the molecular weight change induced by their destruction would be negligible. Furthermore, a group of double bonds such as those found in the quinonoid structure would behave in effect like one double bond, since complete destruction of such a grouping would give only one break in the chain, and small two- or three-carbon fragments would be undetectable in molecular weight measurements. Thus, such a method would be unable to distinguish between one main chain double bond and two or three conjugated double bonds in the same position.

Two methods of cleaving double bonds in polymers have been described. The first of these involves addition of osmium tetroxide at the double bond followed by scission of the osmic ester with tert.-butyl hydroperoxide. This method has been used for the estimation of lengths of styrene unit sequences in GR-S<sup>72</sup> and for the analysis of carbon black filled elastomers.<sup>73</sup> The method, however, was found to be inapplicable to the present problem which depends for its resolution upon molecular weight changes during the reaction, because, at the temperature required to decompose the osmic ester,

tert.-butyl hydroperoxide alone is capable of degrading polystyrene.

The alternative method involves ozonolysis followed by cleavage of the ozonide. This procedure has been employed with some success to elucidate the structure of butyl rubber<sup>79</sup> and certain other polymers, the structures of the ozonised fragments, after suitable decomposition, showing the positions of the double bonds in the polymer molecules. It was considered that double bonds in the polystyrene back-bone might be estimated by comparing the molecular weight of the polymer before and after ozonolysis.

The action of ozone on pure polystyrene has been the subject of several conflicting reports. Staudinger and his co-workers<sup>69</sup> were probably the first to examine the reaction as one of a large series dealing with the effects of various substances on polystyrene. They found that when a stream of ozonised oxygen is passed through a solution of polystyrene in carbon tetrachloride the viscosity of the solution first decreases then increases again with the eventual formation of an insoluble gel. No satisfactory explanation was given for this effect. Later workers, on examining the effects of ozone on polystyrene, postulated that the points of ozone attack are the tertiary hydrogen atoms, a hydro-

peroxide being formed in the process.<sup>80</sup> On the other hand, Lebel<sup>81</sup> has pointed out that at low temperatures ozone does not attack the polystyrene back-bone which receives a measure of protection from the benzene rings, these being attacked preferentially. It is quite probable that ozonised oxygen has two modes of action on polystyrene depending on the reaction temperature; it is possible that at room temperature and above the originally formed ozonides decompose to produce peroxides of sufficient activity to bring about some chain scission, while at lower temperatures the ozonides remain unchanged. For the present problem it was decided to investigate the effects of ozonolysis of polystyrene at temperatures below 0°C..

### 3. Some Preliminary Experiments.

Before employing ozonolysis to check the theory that quinonoid structures could be the weak links in polystyrene it was necessary to ensure that any change in molecular weight was caused by cleavage at the double bonds in the polymer chain, and not by some side reactions during or after ozonolysis. The experiments described in this section were designed to ensure that the method and proposed interpretation of the results were valid.

i) Stability of the Ozonide.

During preliminary experiments to find the best conditions for ozonolysis it was found that at  $-21^{\circ}\text{C}$ . no change in molecular weight of polystyrene occurred in the initial stages of the reaction. As ozonolysis proceeded, however, the molecular weight was observed to rise abruptly eventually giving an insoluble gel, presumably due to some cross-linking reaction. The fact that initially no decrease in molecular weight was observed suggested that either no double bonds are present in the polymer back-bone or that the initially formed ozonide does not decompose spontaneously. The second suggestion seemed not improbable as there is wide variation in ozonide stabilities.

There are several methods of decomposing ozonides quantitatively. The simplest, which is to treat the compound with hot water, is impracticable, however, with polymer solutions which are immiscible with water. The procedure finally adopted was reductive cleavage with zinc and acetic acid. For this purpose granulated zinc is unsuitable, but activated zinc dust (see Chapter II) was found to react cleanly and efficiently, the polymer remaining in solution throughout the reaction. After such treatment the molecular weight of an ozonised polystyrene sample was found to have decreased, suggesting

that ozonide structures somewhere in the polymer backbone had been decomposed. To ensure that the zinc/acetic acid treatment alone was not causing degradation a blank was carried out using unozonised polystyrene. In this case the molecular weight was found to be unchanged.

ii) Ozonolysis of Thermally Degraded Polystyrene.

Though the experiments just described seemed to support the idea of double bond structures in the polymer backbone, two questions remained to be answered before this could be regarded as unequivocally established. Firstly, is it possible that the ozone-zinc/acetic acid treatment of polystyrene results in a decrease in molecular weight due to some unforeseen side reaction, and secondly, if double bond structures are the thermo-labile points, can a polystyrene molecule, or at least its backbone, be rendered insensitive to ozone by pyrolysis beyond the weak link scission phase?

To answer these questions it was decided to ozonise a sample of polystyrene which had been previously thermally degraded until weak links were completely removed. Accordingly a sample of polymer S/GC/1 was pyrolysed beyond 30 per cent volatilisation and treated with ozone for 35 mins. under the conditions described in Chapter II. It was subsequently treated in the usual

manner with zinc and acetic acid. Polystyrene samples given this ozone dosage and reductive cleavage invariably showed a distinct decrease in molecular weight, but the pyrolysed sample was found to have the same molecular weight (80,000) before and after ozonolysis. If ozone is capable of causing chain scission at normal parts of polystyrene molecules by a side reaction, the molecular weight of the pyrolysed sample should have decreased after ozone-zinc/acetic acid treatment. The fact that it did not is clear proof that there are no chain-breaking side reactions during the ozonolysis of polystyrene and subsequent reductive cleavage.

It is also quite clear that heating does remove the ozone-sensitive points in the polymer back-bone. All this is fairly strong evidence that the weak links in polystyrene are associated with double bonds in the main chain. It is very probable, of course, that pyrolytic weak link scission produces double bonds at chain ends, but scission of the molecules at these points will have no obvious effect on the molecular weight of the polymer. If the ozonolysis of the pyrolysed polymer had produced a decrease in molecular weight it would not have been possible to have said whether ozone had caused chain scission by a side reaction or by attack at double bonds.

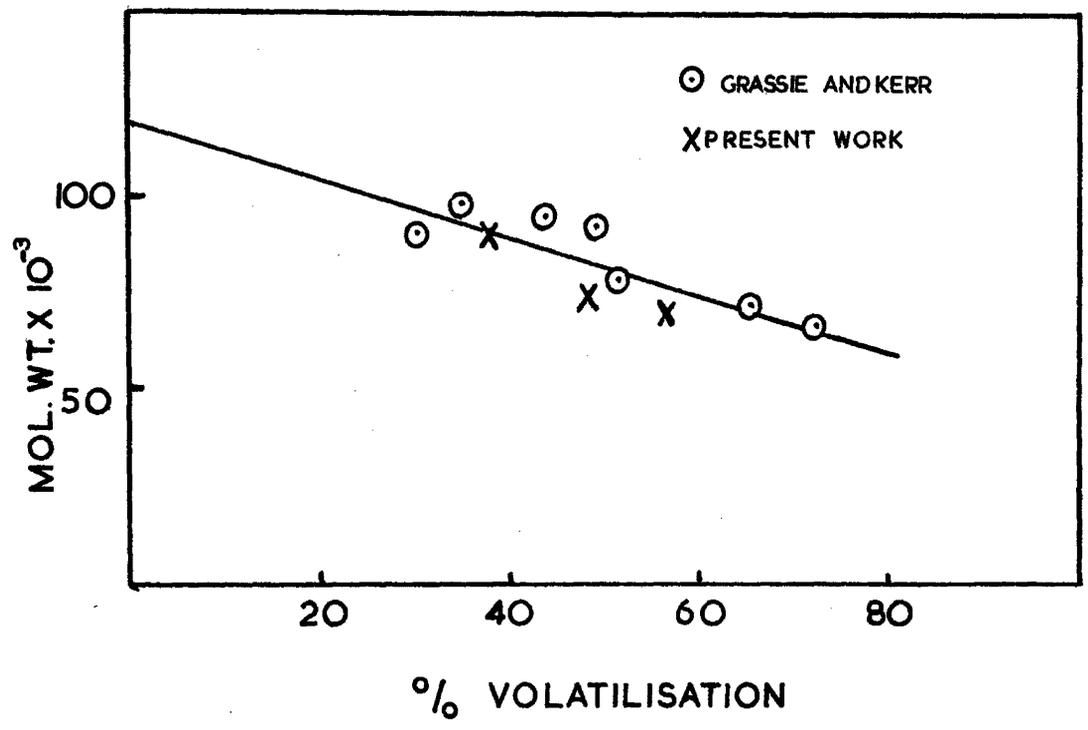
At this point it had been shown that the conditions of ozonolysis employed gave no complicating chain-breaking side reactions and that ozone-sensitive points are removed by thermal degradation. The only competing process in the overall reaction appeared to be cross-linking and this became obvious only after extensive ozone dosages. The way now lay clear for quantitative ozonolysis.

#### 4. Quantitative Ozonolysis.

The concentration of weak links and double bond structures in polymer S.7 was compared by examining the molecular weight changes during degradation by ozone and by heat. Kerr<sup>21</sup> has already degraded this polymer thermally and it was chosen for this work because its molecular weight changes during degradation lay in a convenient range for measurement. The thermal degradation curve is shown in Fig.22 and the limiting molecular weight thus obtained is approximately 118,000. If the theory of weak link structure previously outlined is correct, then the minimum molecular weight achieved during ozonolytic scission of double bonds in the polymer should also be about 118,000.

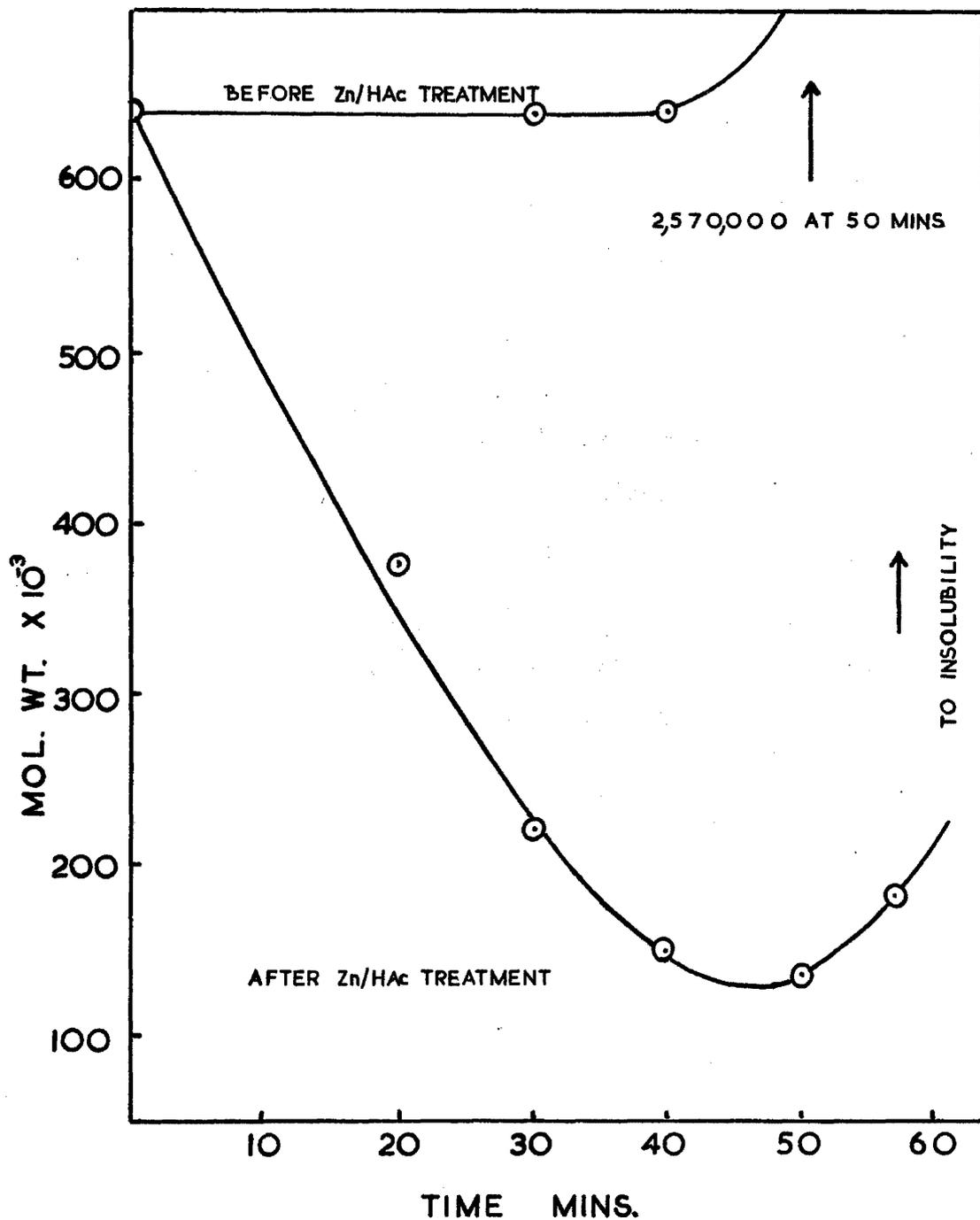
Fig.23 shows the molecular weight changes which occur in polymer S.7 during ozonolysis. This was

FIG, 22



THERMAL DEGRADATION POLYMER S7

FIG. 23



OZONE DEGRADATION OF POLYMER S7

carried out by the method described in Chapter II and samples of polymer were withdrawn at convenient time intervals. The upper and lower curves show respectively the molecular weights of these samples before and after reductive cleavage. The upper curve shows that, up until about 45 mins., no cross-linking takes place but once this process begins the molecular weight rises very rapidly and at about 60 mins. particles of insoluble gel appear. The lower curve shows a minimum between 45 and 50 mins. reaction time and points on this curve cannot be obtained beyond about 55 mins. because of the formation of insoluble material.

The lower curve appears to be parabolic around its minimum, and a reasonable estimation of the minimum point can be obtained from the mathematical expression for a parabola -  $y = ax^2 + bx + c$ . Substituting the values shown in Fig.23 the minimum emerges as 126,000 from this expression. This is in reasonable agreement with the limiting molecular weight of 118,000 obtained from thermal degradation.

The molecular weight changes with time of ozonolysis of polymer S.7 are summarised in Table 6.

TABLE 6

Ozonolysis of Polymer S.7 at -21°C.

$2.7 \times 10^{-3}$  moles  $O_3$  in 10 l.  $O_2$ /hr.

| <u>Time of Ozone</u><br><u>Addition</u><br><u>(mins.)</u> | <u>Mol. Wt.</u><br><u>(after reductive</u><br><u>cleavage)</u> |
|---|--|
| 0   | 640,000  |
| 20  | 375,000  |
| 30  | 220,000  |
| 40  | 150,000  |
| 50  | 135,000  |
| 57  | 185,000  |

5. Discussion.

i) The Concentration of Double Bond Structures and  
Thermo-labile Points.

The results just described show that two competing reactions occur during ozonolysis of polystyrene. One of these is addition of ozone at double bonds in the polymer back-bone and the other is probably attack at

the pendant benzene rings. The latter may lead to the observed cross-linking reaction, two ozonised benzene rings on different polymer molecules interacting in some way to form a bond between the two. Such a scheme would explain the induction period, before cross-linking becomes obvious, during which the concentration of ozonised benzene rings is building up.

The cross-linking process complicates interpretation of the results since there is no guarantee that ozone addition to the back-bone double bonds is complete before cross-linking sets in. Indeed it would be very surprising if one reaction began when the other was just complete. This means that it is very unlikely that the figure of 126,000 previously quoted is a true value of the molecular weight when chain scission at all the double bonds is complete. The true value should be somewhat lower than this. An approximate calculation of the minimum molecular weight can be made by examination of the molecular weights of the decomposed and intact ozonides.

In this calculation it is assumed that complete ozonolysis of the back-bone double bonds occurs at some point after the minimum at 46 mins. on the degradation curve.

The molecular weight of the untreated ozonised polymer after 50 mins. reaction time is ca. 2,570,000 compared with 135,000 for the same sample after reductive

cleavage. Knowing the molecular weight of the original polymer it is possible to calculate the number of cross-links formed (per monomer unit) after 50 mins.. This number is the same for both treated and untreated ozonised samples, so that the molecular weight of the treated sample minus the effects of cross-links can be calculated.

$$\text{No. cross-links } N \text{ at 50 mins.} = \frac{P_1}{P_0} - 1$$

where  $P_0$  is the chain length of the original polymer and  $P_1$  that of the cross-linked material before reductive cleavage.

$$\begin{aligned} \text{Thus, } N &= \frac{24,700}{6,150} - 1 \\ &= 3.02 \end{aligned}$$

Let the true chain length (ie. the chain length minus the effect of cross-links) of the treated ozonised polymer after 50 mins. reaction be  $x$  monomer units.

There are 24,700 monomer units involved with 3.02 cross-links. That is, there are 3.02 cross-links for every  $\frac{24,700}{x}$  chains in the treated sample.

If each cross-link joins two molecules of length  $x$ , then from  $\frac{24,700}{x}$  molecules there are on the average  $(24,700/x - 6.04)$  molecules of length  $x$ , and 3.02 molecules of length  $2x$  after complete cross-linking.

$$\text{But } \bar{M}_n = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$$

$$\text{ie. } 1,300 = \frac{(24,700/x - 6.04)x + 3.02 \times 2x}{24,700/x - 6.04 + 3.02}$$

where 1,300 is the observed chain length after reductive cleavage of the polymer ozonised for 50 mins..

By rearrangement of the above expression -

$$x = 1125$$

Therefore, the true molecular weight after 50 mins. if cross-links were absent =  $1125 \times 10^4$   
= 117,000

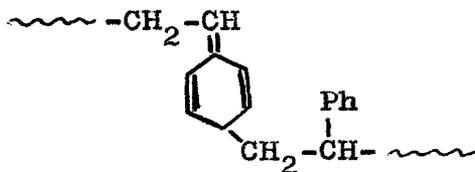
Thus the molecular weight after deduction of the effects of cross-linking is in very good agreement with the figure of 118,000 - the limiting molecular weight from thermal degradation. Ideally the ozonolysis graph should show a sudden drop in molecular weight as the double bonds are broken, after which the molecular weight should remain constant as it does during thermal degradation of polystyrene in tetralin. If the figure of 117,000 at 50 mins. is plotted in Fig.23 it is clear that the curve is flattening out about this level and that this is probably a fairly realistic estimate of the molecular weight of the polymer when all the double bonds have been split. The agreement between this figure and the value of 118,000 obtained from thermal degradation

must be considered very satisfactory. It is clear that the number of double bond structures per polymer chain is the same as the number of thermo-labile weak links.

The results obtained from the experiments described up to this point may be summarised as follows:-

- a) Polystyrene contains weak links which are not head to head additions.
- b) Polystyrene contains back-bone double bond structures in the same concentration as its weak links.
- c) Thermal removal of weak links removes the double bonds.

The conclusion drawn from these results is that the double bond structures are closely associated with the thermo-labile points in the polymer chains. They do not, of course, prove categorically that the quinonoid structures, for example,



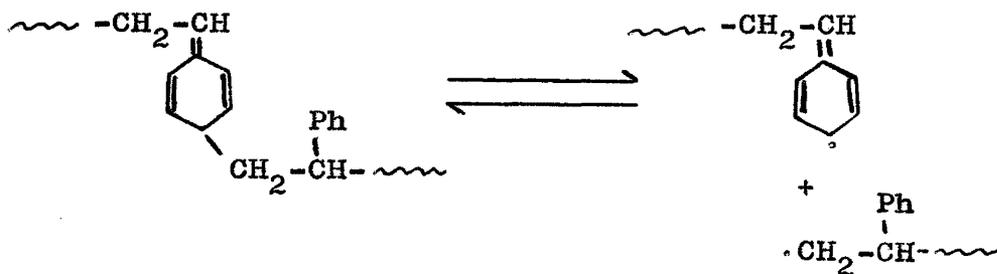
discussed earlier in the chapter are the weak links, though this remains a reasonable possibility.

ii) The Cage Effect During Weak Link Scission.

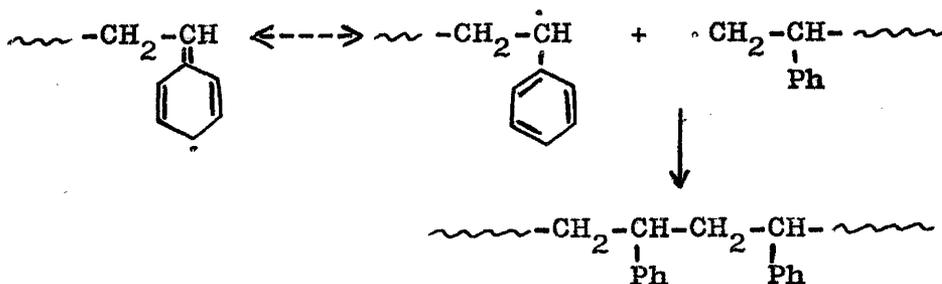
The possibility of a cage effect occurring during weak link scission has already been discussed in

Chapter III in which strong evidence for its absence was produced. It is interesting, nevertheless, to speculate on the outcome of a cage effect on scission of weak links of the type just described.

According to Grassie and Kerr's theory weak links in the polymer chain repeatedly break and recombine and only occasionally disproportionate. With a quinonoid type of weak link this implies the following reaction



Kerr assumed that recombination of the initially formed radicals leaves the weak link structure unchanged, but the quinonoid radical shown above would probably resonate fairly frequently back to the form of lowest energy before recombination.



In this event the weak link structure is completely destroyed and such a process would predict that, as

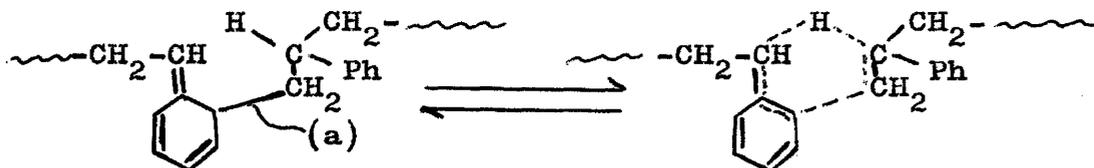
degradation temperatures are varied, the measured number of weak links would vary, since the recombination process would be favoured at lower temperatures. This prediction is scarcely upheld by the results of Grassie and Kerr which show only marginal differences in limiting molecular weights when degradation temperatures are changed. As a further check on this, however, a sample of polystyrene S.7 was preheated at 270°C. for 90 hours then degraded at 335°C. in the usual way beyond 30 per cent volatilisation. At 270°C. depropagation is virtually absent and weak link scission is very slow. In addition, the polymer melt is more viscous than at 335°C. and a cage effect is thus encouraged (that is, an increase in the proportion of recombinations compared with disproportionations would be expected on weak link scission). On measuring the molecular weight of this sample, however, it was found to lie within experimental error on the degradation curve shown in Fig.22. Clearly the preheating treatment does not reduce the number of weak links in the polymer chains and further supports the conclusion arrived at in Chapter III that there is no cage effect associated with weak link scission, though this support rests on the assumption that weak links are quinonoid in nature.

iii) The Mechanism of Weak Link Scission.

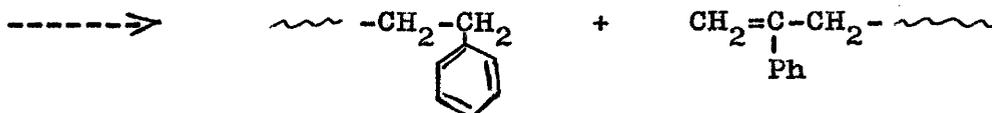
In his original theory of weak links Jellinek<sup>17</sup> postulated that these break down homolytically to give free radicals which then depropagate. This idea was later modified by Grassie and Kerr<sup>22</sup> who showed that weak link scission gives stable chain ends depropagation of which involves some other initiation process. Nevertheless, they also assumed that initial scission of weak links gives free radicals, but postulated that these immediately recombine or disproportionate to give stable chain ends. On this basis Kerr<sup>21</sup> was able to account for the lower rate of weak link scission of poly- $\alpha$ -deuterostyrene by pointing out that since the disproportionation process consists of transfer of an  $\alpha$ -hydrogen atom replacement of this by deuterium should affect the reaction rate. It is known from the present work, however, that weak link scission is irreversible (see Chapter III) and if this process gives radicals initially which do not recombine it is difficult to see how the  $\alpha$ -hydrogen atom can affect the reaction rate. From this point of view the work of Brown, Hart and Wall on poly- $\alpha$ -deuterostyrene cannot be explained satisfactorily.

There is no evidence to support the contention that weak link scission gives radicals at any stage of

the reaction. On the contrary, Grassie and Kerr's observation that stable chain ends are produced greatly weakens any theory involving free radicals, since this necessitates the additional assumption that these radicals are stabilised immediately, and there is no justification for assuming that pairs of free radicals invariably combine or disproportionate rather than begin to depropagate. Thus, a weak link scission mechanism producing free radicals is not entirely satisfactory. A possible alternative mechanism is shown below. This scheme assumes that weak links are quinonoid structures, but no free radicals appear at any stage of the breakdown.



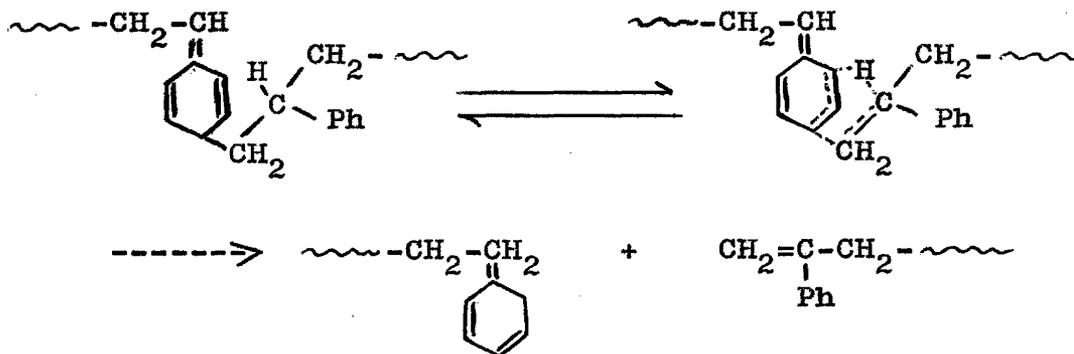
Transition State



This reaction scheme is similar to the Hurd and Blunk mechanism for decomposition of esters into olefins and acids,<sup>82</sup> or the mechanism proposed to account for the decomposition of vinyl iso-propyl ether into propylene and acetaldehyde.<sup>83</sup> It is noteworthy that this

scheme involves scission of the weakest carbon-carbon bond (a) in the system, and also an  $\alpha$ -hydrogen transfer which, once accomplished, would be irreversible and could well be the rate-determining step in the process. It is interesting too that the aromatic ring is restored. Such a reaction scheme, therefore, accounts for all the important features of weak link scission - it is irreversible, it does not involve free radicals and it explains the isotope effect in the degradation of poly- $\alpha$ -deuterostyrene.

The para-quinonoid structure may decompose in the same way though it is more difficult to illustrate graphically, being in three dimensions.



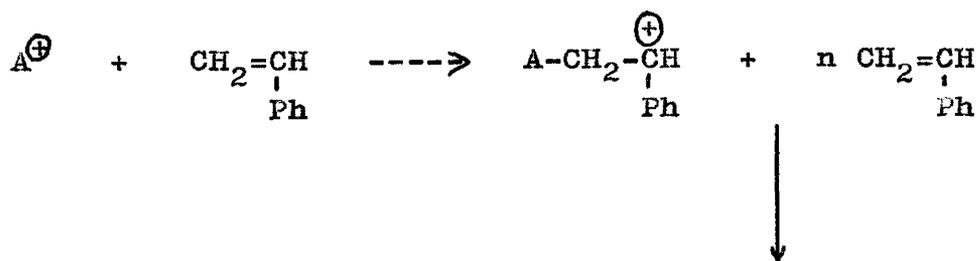
In this case the  $\alpha$ -hydrogen atom transfers to the ortho-position for which there are two possibilities. With such a mechanism, however, the aromatic ring is not restored.

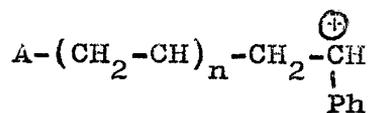
6. The Degradation of Ionically Prepared Polystyrenes.

i) Introduction.

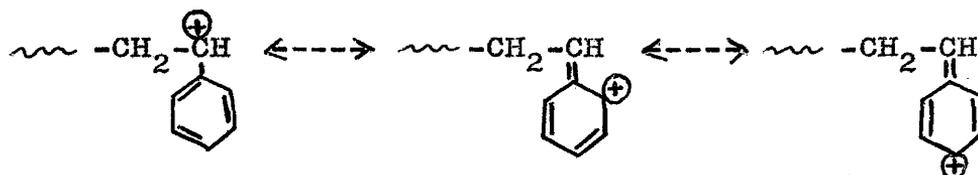
So far, only polymers prepared by free radical mechanisms have been discussed but any weak link theory must also account for the degradation behaviour of ionically prepared polystyrenes since these also appear to contain structural abnormalities. Kerr<sup>21</sup> pyrolysed a polystyrene sample prepared cationically and found that it degraded in exactly the same way as samples prepared by free radical methods, showing the characteristic steep fall in molecular weight at the beginning of the reaction followed by the more gradual decrease when weak link scission was complete. Surprisingly, he found that the weak link concentration was of the same order as that of a polystyrene prepared by free radical means and of a similar molecular weight. (Ionic -  $4.95 \times 10^{-4}$  and free radical -  $2.41 \times 10^{-4}$  weak links per monomer unit).

The initiation and propagation steps for cationic polymerisation of styrene probably follow this sequence

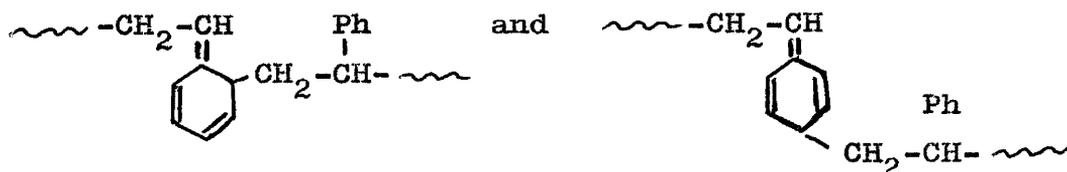




Under the influence of an electrophilic reagent such as a carbonium ion the benzene ring probably acts as an electron source<sup>74</sup> as shown above, thus favouring a head to tail addition of monomer units. Polarisation of the olefinic double bond in the opposite sense may also be possible, however, since the benzene ring can also act as an electron sink, and this would offer the opportunity for head to head additions. Head to tail addition would, nevertheless, be favoured from energy considerations because, as in free radical polymerisation, resonance stabilisation with the benzene ring is probable.



The existence of such structures will also render possible the propagation of the polymer chain through the ortho- or para-positions of the benzene ring giving structures of the type

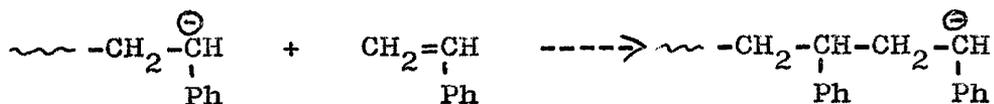


Such structures have already been discussed as possible weak links in polymers prepared by free radical means,

so that the degradation behaviour of cationically prepared polystyrene can be explained in terms of the same structures.

Isotactic polystyrene has also been pyrolysed<sup>21,75</sup> and surprisingly behaves in the same way as other polystyrenes. The polymerisation of isotactic polystyrene is also an ionic reaction and therefore may also result in abnormalities of the type just described. The first isotactic polymers were prepared with heterogeneous catalyst systems<sup>76</sup> but more recently it has been found that homogeneous systems are capable of producing stereospecific polymers provided the solvent is carefully chosen.<sup>77</sup> This second type of catalyst system is of further interest because it is anionic in nature and can produce "living" polymers, that is, polymers with active ends capable of further growth to which another substance, such as water, has to be added to bring about termination. Living polymers were first investigated by Szwarc and his co-workers.<sup>78</sup>

An example of an anionic catalyst capable of producing living polymers is butyl lithium. With this catalyst propagation proceeds as follows



A polystyrene prepared by this means might be

expected to have different degradation characteristics from the others studied so far, since it appears that weak links result from some abnormal polymerisation step. For this reason it was decided to degrade thermally a polystyrene prepared anionically.

ii) Degradation of Anionically Prepared Polystyrene.

For these experiments a sample of polystyrene S1159, supplied by Dow Chemical Company, was employed. This polymer was prepared with butyl lithium as catalyst and was purely atactic. (The insolubility of isotactic polymers in the usual solvents makes them difficult to work with).

Samples of S1159 were degraded thermally at 335°C. and their molecular weights measured in the usual way. The degradation curve is shown in Fig.24 in which points beyond weak link scission only are recorded. The main features of the degradation are exactly the same as before, the initial steep fall in molecular weight showing the presence of weak links.

Since this polymer responded to pyrolysis in exactly the same manner as all the others which have been examined so far it was decided to degrade it with ozone and compare its behaviour with that of polymer S.7.

Ozonolysis was carried out in the manner

previously described and each sample on withdrawal from the reaction flask was treated with zinc and acetic acid in the usual way. The changes in molecular weight with time of ozonolysis of S1159 are also included in Fig.24. Again the ozone treatment causes a decrease in molecular weight followed by a rise, with eventual gel formation. The minimum molecular weight of 114,000 obtained from the ozone degradation curve is in good agreement with the value of 113,000 - the limiting molecular weight from thermal degradation. Clearly this polymer responds to heat and ozone in exactly the same way as polystyrene S.7.

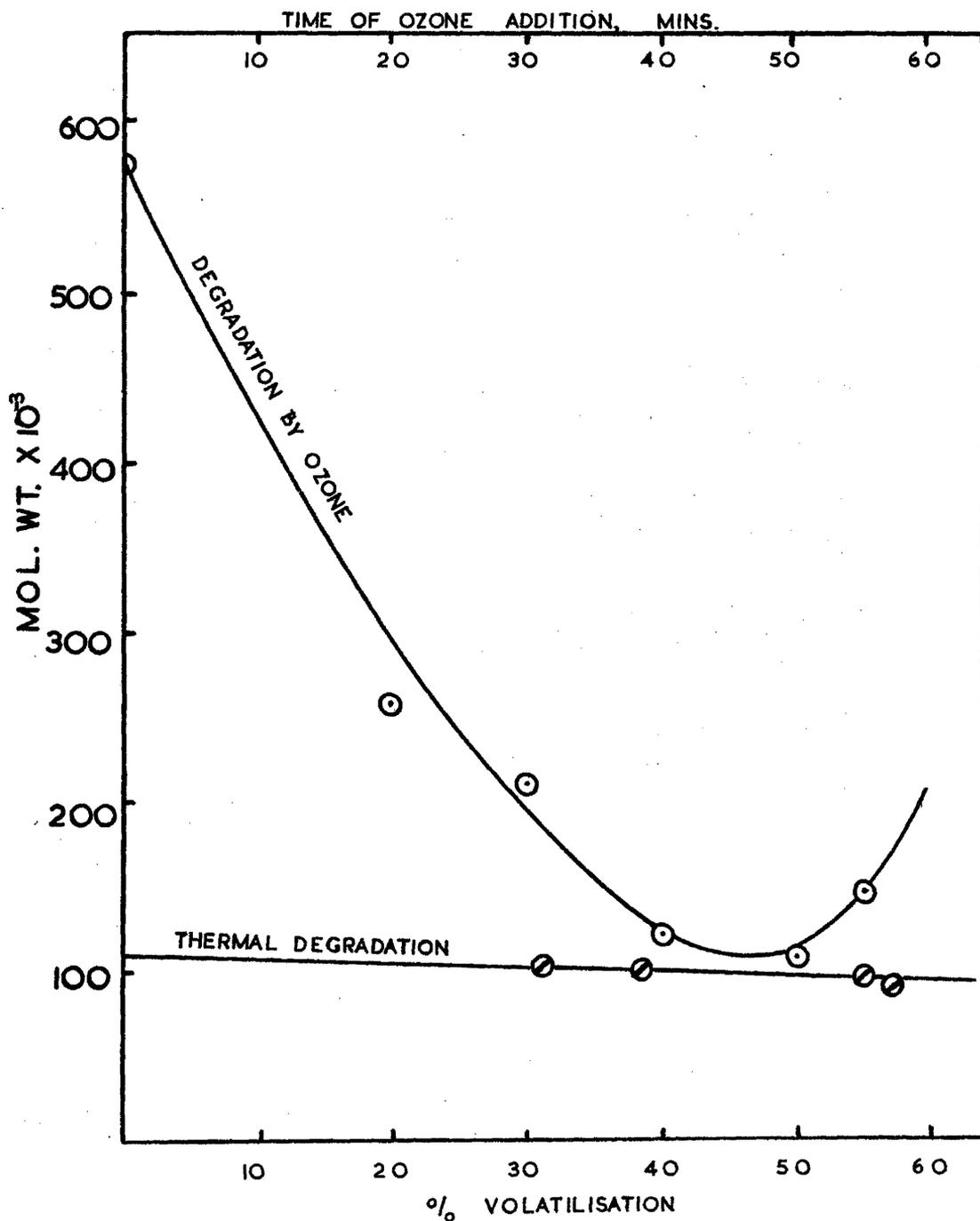
The results of the degradations of polymer S1159 by heat and by ozone are summarised in Tables 7 and 8 respectively.

TABLE 7

The Thermal Degradation of Polymer S1159 at 335°C..

| Time of Heating (hrs.) | Percentage Volatilisation | Mol. Wt. |
|------------------------|---------------------------|----------|
| 3.0                    | 31.3                      | 105,000  |
| 4.0                    | 38.4                      | 103,000  |
| 5.0                    | 55.8                      | 97,000   |
| 5.25                   | 58.0                      | 90,000   |

FIG. 24



POLYMER S1159

TABLE 8

Ozonolysis of Polymer S1159 at -21°C..

$2.7 \times 10^{-3}$  moles  $O_3$  in 10 l.  $O_2$ /hr.

| Time of Ozone<br>Addition<br>(mins.) | Mol. Wt.<br>(after reductive<br>cleavage) |
|--------------------------------------|---|
| 0                                    | 570,000                                   |
| 20                                   | 257,000                                   |
| 30                                   | 212,000                                   |
| 40                                   | 125,000                                   |
| 50                                   | 110,000                                   |
| 55                                   | 140,000                                   |

The concentration of weak links per monomer unit in any polystyrene can be found from the expression

$$N = 10^4 \left[ \frac{1}{M_d} - \frac{1}{M_o} \right] \quad (\text{See Chapter IV})$$

and by applying this to certain thermally degraded polymers Table 9 has been compiled.

TABLE 9

Summarised Data for Some Degraded Polymers.

| Polymer | $M_o \times 10^{-3}$ | $M_d \times 10^{-3}$ | $N \times 10^4$ | Mode of<br>Prep. | Ref. |
|---------|----------------------|----------------------|-----------------|------------------|------|
| S.7     | 640                  | 118                  | 7.2             | Free Rad.        | 21   |
| Ionic   | 129.6                | 80                   | 5.0             | Cationic         | 21   |

TABLE 9 (contd.)

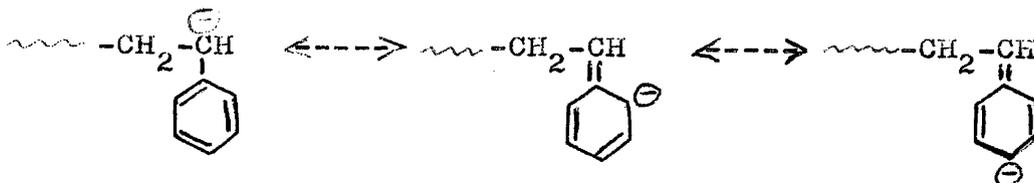
|        |     |     |     |           |         |
|--------|-----|-----|-----|-----------|---------|
| S/GC/5 | 530 | 100 | 8.4 | Free Rad. | present |
| S1159  | 570 | 113 | 7.1 | Anionic   | "       |

---

iii) Discussion.

The experiments described above show that a polymer prepared anionically contains weak links which break down on heating or on treatment with ozone in the same way as those in a polymer initiated by free radicals. The difference between the limiting molecular weights from ozone and thermal degradations is less than that observed in S.7, but in this case no attempt was made to correct for cross-linking. If this correction were made, assuming the same amount of cross-linking as for polymer S.7, The minimum from the ozone degradation curve would be slightly lower than the limiting value from thermal degradation but still in reasonable agreement.

The methods by which abnormalities can appear in polystyrene chains prepared cationically and by free radicals have already been indicated, and examination of the anionic polymerisation of styrene shows that analogous resonance behaviour can still take place so that the presence of weak links in the resulting polymer chains can be explained in terms of the same quinonoid structures as before.



Comparison of the weak link concentration in a variety of polystyrenes can be made from Table 9. The weak link concentration of S1159 lies within the range already observed for polymers prepared by free radical means. This is rather surprising, for, though the presence of weak links in S1159 can be accounted for, a somewhat different concentration seems likely. The similarity in weak link concentration of S1159 and other polymers might, of course, be coincidence and it is quite possible that a variation in conditions for ionic polymerisation will have the same effect on weak link concentration as has temperature in free radical polymerisation. On the other hand, since the proposed formation of weak links is so similar in both free radical and ionic polymerisations, the similarity in their concentrations is perhaps not so surprising.

It is concluded therefore, that the same abnormalities are responsible for weak links in polystyrenes prepared by all three methods - free radical, cationic and anionic. Alternative sources of weak links in ionically prepared polystyrenes are difficult to envisage because it has already been proved that head to head

additions do not constitute weak links. It must be admitted, however, that no direct proof for the proposed quinonoid structures has been discovered as yet, but from our present knowledge of the polymer it is difficult to conceive of an alternative.

## 7. Summary.

From the foregoing results and discussion it is proposed that the thermo-labile points in polystyrene are associated with double bonds in the polymer chain. The formation of double bonds is best explained by postulating an abnormal polymerisation step through a resonance form of the growing free radical. Analogous reactions have been shown to be possible in both anionic and cationic polymerisation of styrene, though the weak link concentrations, which are of the same order in all three types of polystyrenes, seem rather surprising.

If a quinonoid type of weak link, formed in the manner previously described, is assumed it is possible to explain all the important features of polystyrene degradation. Thus, the fact that certain polymers have on the average less than one weak link per molecule can be accounted for, since the frequency of formation of the quinonoid structure depends only on the temperature of polymerisation (for the free radical reaction) and

not, for example, on the termination step.

In addition, a reaction scheme for the breakdown of these weak links has been proposed. This mechanism accounts for three important features of weak link scission - the production of stable chain ends, the irreversibility of the process and the rate determining effect of the  $\alpha$ -hydrogen atom.

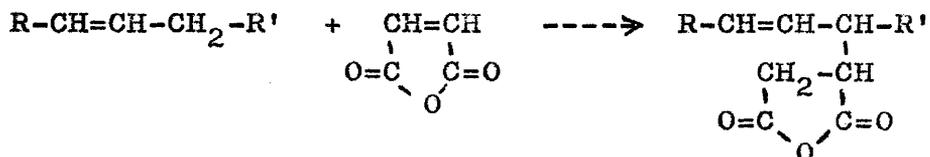
It must be admitted, however, that the existence of quinonoid structures in polystyrene has not been proved categorically, but in the present state of knowledge of the polymer these seem the only reasonable structures which can account for all the facts.

Note.

The proposed quinonoid structure for weak links contains conjugated double bonds and should therefore be capable of reaction with dienophiles such as maleic anhydride. In this connection a few exploratory experiments have been conducted. After refluxing a mixture of maleic anhydride and polystyrene in benzene the resulting polymer was found to have a small peak at  $1260 \text{ cm.}^{-1}$  in its infra-red spectrum. This peak could not be diminished or removed by repeated reprecipitation. Most anhydrides, including maleic anhydride, show strong absorption bands in this region and it is concluded that the observed

peak is caused by a small amount of maleic anhydride chemically bound to the polymer molecules. Physical admixture is precluded because of the lack of response to reprecipitation.

Maleic anhydride has two possible modes of addition to unsaturated molecules. The first of these - the Diels-Alder reaction - takes place only with conjugated dienes and proceeds readily at temperatures up to 100°C.. On the other hand, maleic anhydride can add to mono-olefins at an  $\alpha$ -methylene hydrogen atom by a different mechanism, but this is reported to proceed at temperatures above 200°C. or in the presence of peroxides.<sup>101</sup>



The  $\alpha$ -hydrogen atom in polystyrene might react in this way but in boiling benzene the usual conditions for the reaction do not prevail, unless, of course, traces of peroxide remain in the polymer. The normal Diels-Alder reaction appears more likely and a systematic approach to this possibility seems worth while because it could lead to strong evidence in favour of quinonoid-type weak links.

CHAPTER VI

OSMOTIC PRESSURE DATA OF DEGRADED POLYSTYRENE.

1. Introduction.

In the course of studying the thermal degradation of polystyrene a considerable amount of osmotic molecular weight data have been accumulated. The present chapter is intended to present an overall picture of these results.

Grassie and Kerr have already reported certain features of interest in the osmotic behaviour of thermally degraded polystyrene.<sup>84</sup> They found that after degradation the slope of the  $\pi/c$  versus  $c$  curves, for polystyrene in benzene solution, increases. In addition, this slope reaches a maximum before 20 per cent volatilisation is achieved and remains constant thereafter for all polystyrenes degraded beyond this level. Using a selection of polystyrenes with widely varying histories it was observed that the maximum osmotic slope was the same, within experimental error, for each sample after degradation.

It has already been mentioned in Chapter II that the  $\pi/c$  versus  $c$  curves for polystyrene in benzene are linear and may be represented by the expression

$$\bar{\pi}/c = A + Bc$$

in which B, according to the Flory-Huggins theory,<sup>85,86</sup> is given by

$$B = RT\left(\frac{1}{2} - \mu\right)/v\rho^2$$

where V is the partial molar volume of the solvent,  $\rho$  the partial specific density of the solute and  $\mu$  a constant which is a measure of the tendency to polymer-polymer rather than polymer-solvent interaction. B represents the slope of the  $\bar{\pi}/c$  versus c line so that an increase in B is caused by a decrease in  $\mu$ , that is, a decrease in polymer-polymer interaction. The observations of Grassie and Kerr are therefore explained as an increase in polymer-solvent interaction on degradation.

In the present work Grassie and Kerr's results were corroborated but, while these authors used an osmometer controlled at 25°C., the present measurements were made at 30°C. at which temperature some additional features revealed themselves.

## 2. Results and Discussion.

### i) Polymer-Solvent Interaction of Thermally Degraded Polystyrene.

$\bar{\pi}/c$  versus c curves for a series of polymers

degraded to different extents are shown in Fig.25. Most of these measurements were made at 30°C. but for comparison Fig.25 also includes one line, from a degraded polymer, obtained at 25°C.. To illustrate more clearly the considerable change in slope after degradation the osmotic slope of an undegraded polystyrene sample is also included in Fig.25.

In calculating  $\mu$  for these samples the value of  $\rho$  was taken as 1.105; this is the reciprocal of the partial specific volume of polystyrene in benzene at 25°C. and is probably the most accurate estimate of  $\rho$  available.<sup>96</sup> The results are summarised and compared with Grassie and Kerr's data in Table 10. These authors evaluated  $\mu$  using 1.054 (the bulk density of polystyrene) as the value of  $\rho$ , and to bring their data into line with the present results their original values have been recalculated using  $\rho$  1.105 as above.

ii) Polymer-Solvent Interaction of Thermally Degraded Polystyrene after Reprecipitation.

During the course of this work it was discovered that if a thermally degraded polystyrene sample is dissolved in benzene, precipitated and redissolved in benzene the osmotic slope of the second solution is less than that of the first (that is, the value of  $\mu$  is greater)

though not as great as the value for undegraded samples. In Fig.26 the osmotic curves of several degraded polystyrenes, measured after precipitation, are shown. All of these were measured at 30°C. as before, except one (indicated) at 25°C.. This figure also includes data from polystyrene samples degraded in solution since these were perforce precipitated before examination.

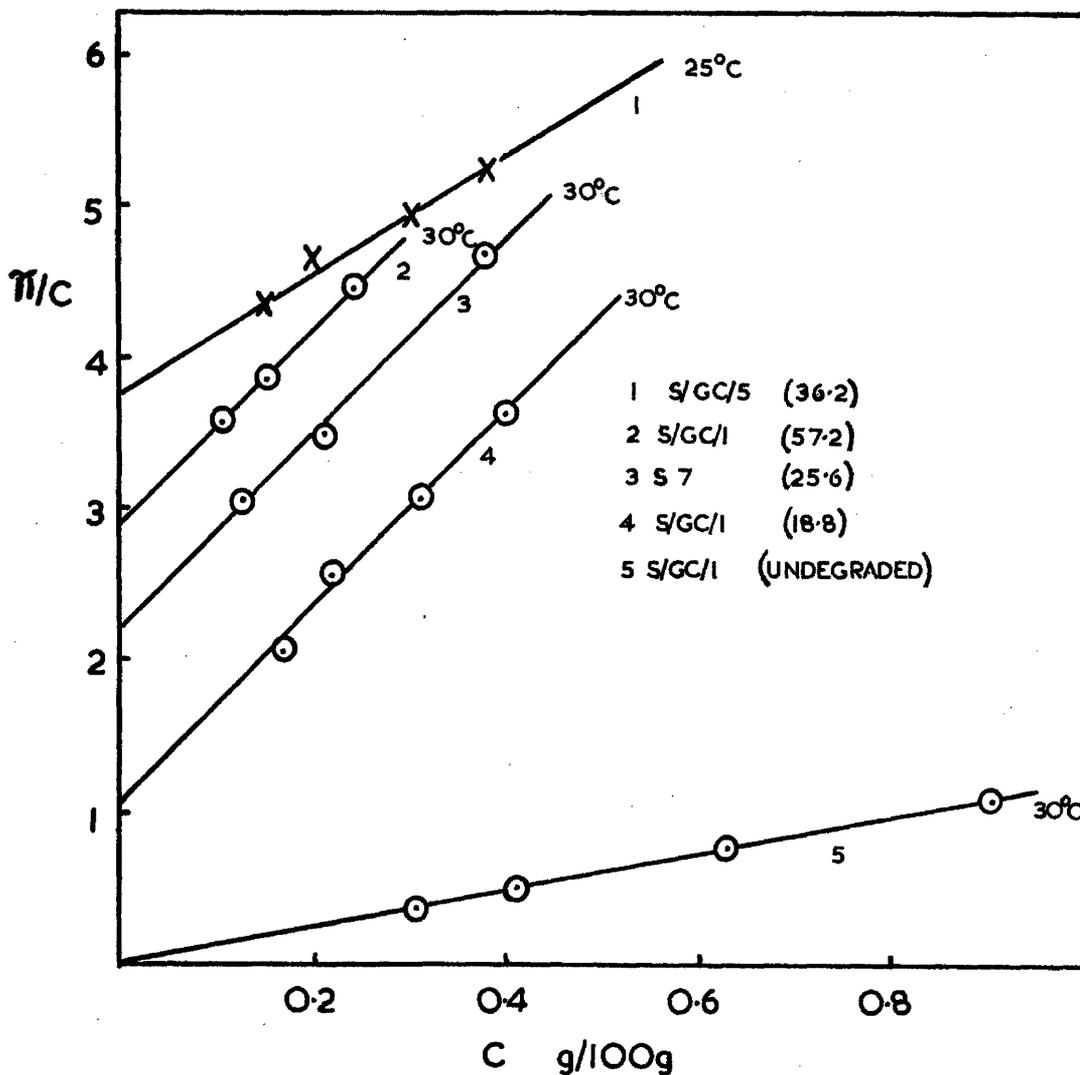
Values of  $\mu$  for these lines are also given in Table 10.

TABLE 10

Values of  $\mu$  for Polystyrene.

| Pretreatment                         | Temp. of<br>Osmometer<br>(°C.) | Reference | $\mu$ |
|--------------------------------------|--------------------------------|-----------|-------|
| Thermal Degradtn.                    | 30                             | Present   | 0.165 |
| " "                                  | 25                             | "         | 0.312 |
| " "                                  | 25                             | 84        | 0.328 |
| Thermal Degradtn.<br>& Precipitation | 30                             | Present   | 0.267 |
| Thermal Degradtn.<br>& Precipitation | 25                             | "         | 0.362 |
| Soln. Degradtn.<br>& Precipitation   | 30                             | "         | 0.262 |
| Undegraded (S/GC/1)                  | 30                             | Present   | 0.441 |
| " (S.7)                              | 30                             | "         | 0.410 |
| "                                    | 25                             | 84        | 0.428 |
| "                                    | 25-30                          | 93        | 0.423 |
| "                                    | -                              | 94        | 0.460 |
| " (In Toluene)                       | -                              | 94        | 0.409 |

FIG. 25

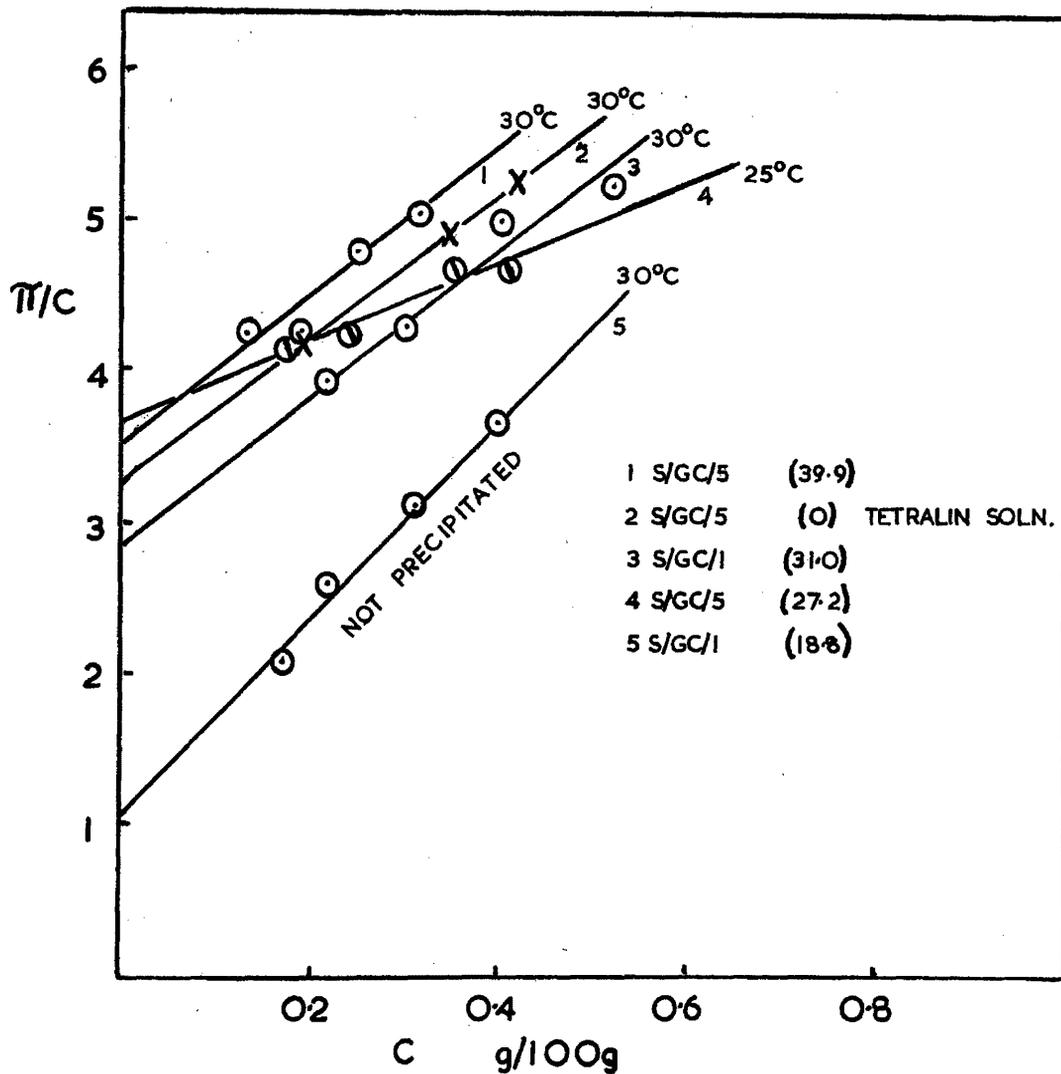


OSMOTIC PRESSURE DATA - DEGRADED  
POLYSTYRENES

FIGURES IN BRACKETS SHOW % VOLATILISATION

OSMOMETER TEMPERATURE IS SHOWN OPPOSITE EACH LINE

FIG. 26



OSMOTIC PRESSURE DATA - DEGRADED  
POLYSTYRENES AFTER PRECIPITATION

FIGURES IN BRACKETS SHOW % VOLATILISATION

OSMOMETER TEMPERATURE IS SHOWN OPPOSITE EACH LINE

iii) Discussion.

Fig.25 shows that, in accordance with Grassie and Kerr's observations, the osmotic slopes of thermally degraded polystyrenes reach a maximum value which is unaffected by further depolymerisation. The value of  $\mu$  is greatly affected by association and poor solvents, but in addition to these major factors a number of minor effects have also been studied in various polymer-solvent systems. Molecular weight, for example, is the subject of several conflicting reports. According to Huggins' original theory<sup>85</sup>  $\mu$  should be independent of molecular weight, and certain authors have recorded results to support this view.<sup>87-89</sup> On the other hand, others have reported that an increase in molecular weight results in an increase in  $\mu$ .<sup>90-92</sup> The values of  $\mu$  for undegraded polymers (also listed in Table 10) obtained from the present work might seem to suggest an increase in  $\mu$  with molecular weight (comparing S.7 with S/GC/1) but taken against the background of other results this seems less likely. Grassie and Kerr pointed out that if a molecular weight effect does exist it is small and probably lies within experimental error. Their own results undoubtedly support this view, because they found that the values of  $\mu$ , for a wide range of molecular weights of undegraded polystyrenes, are the same within experi-

mental error. The change in  $\mu$  (0.428 to 0.328) which these authors noted in degraded polystyrene cannot therefore be attributed to the molecular weight decrease on degradation, especially since certain of their undegraded samples have lower molecular weights than other degraded ones but still exhibit a higher value of  $\mu$ . It has to be concluded then, that thermal degradation of polystyrene radically alters one or more physical features of the polymer chains. The same conclusions hold in the present work; from values of  $\mu$  around 0.41-0.44 the samples change on thermal degradation to a  $\mu$  value of 0.165.

The value of  $\mu$  for degraded polymers noted by Grassie and Kerr - 0.328 - is considerably higher than the value obtained from the present work. The only difference between the two determinations was osmometer temperature - 25°C. compared with 30°C. for the present work. In both cases the same instrument and membrane were used, and confirmation of this abnormal temperature effect was obtained in this instance by carrying out one measurement at 25°C.. The value of  $\mu$  from this determination is 0.312 which compares favourably with Grassie and Kerr's value of 0.328. A temperature effect of this magnitude is surprising and is certainly not observed in undegraded polystyrene. Indeed, for most polymers  $\mu$  is said to be independent of temperature<sup>95</sup> and this has

been shown strikingly in the case of polyvinyl chloride, in a variety of solvents, by Boyer and Spencer.<sup>97</sup> Temperature dependence in  $\mu$  might be found in the case of a poor solvent the efficiency of which could vary considerably with temperature, but for a good solvent like benzene a negligible temperature effect would be expected. It must be concluded that not only does thermal degradation of polystyrene increase polymer-solvent interaction but it renders this interaction very susceptible to changes in temperature, at least with benzene as solvent.

The significance of the decrease in  $\mu$  on thermal degradation of polystyrene has already been discussed in some detail by Grassie and Kerr.<sup>84</sup> They concluded that the increase in polymer-solvent interaction on degradation is due to the disappearance of weak links (the main effect on thermal degradation), suggesting that these might be associated with polymer-polymer interactions in solution. Against this, however, they could find no correlation between polymer-polymer interaction and weak link concentration in their series of undegraded polymers within which weak link concentration varied by a factor of four. It is difficult to imagine how a low concentration of weak link structures, such as quinonoid groups, could have such a pronounced effect on polymer-polymer interaction, but, of course, it is equally strange how small

amounts of stilbene can affect the osmotic slopes of thermally degraded stilbene-styrene copolymers. (See Chapter IV).

The possibility of a variation in microtacticity in segments of polymer chains was also considered by Grassie and Kerr. Any randomising of such structures would be expected to affect the osmotic slope in the direction observed. The parent polymers, however, should also show differences in microtacticity, being prepared in the range  $30^{\circ}$ - $120^{\circ}$ C., but no corresponding differences in osmotic slopes were observed. Furthermore, it is not possible to alter the stereo-regularity of adjacent units in a stereospecific sequence without breaking bonds. Only conformational changes can be brought about by free rotation.

A further point of interest in this work is the effect of reprecipitation on  $\mu$ . Table 10 shows that when a thermally degraded polystyrene sample is dissolved in benzene, precipitated in methanol, dried and redissolved it shows a higher value of  $\mu$  than samples dissolved directly. This increase in  $\mu$  was observed at  $30^{\circ}$ C. and  $25^{\circ}$ C.. Similarly polystyrene samples degraded in solution, and perforce reprecipitated before osmotic measurement, were found to have a higher value of  $\mu$  than normal. The most likely explanation of this effect

seemed to be traces of methanol left in the polymer after drying, since this might be expected to increase polymer-polymer interactions or reduce the efficiency of the solvent. No difference in slope, however, could be induced in these cases by varying the efficiency of the drying process. Besides, the undegraded polymers used by Grassie and Kerr did not respond to prolonged heating in vacuum below degradation temperatures<sup>84</sup> - treatment which undoubtedly removes traces of volatiles such as methanol from which these polymers had been precipitated. This explanation therefore seems unlikely, and the conclusion follows that some fundamental physical difference exists, in solution, between degraded polystyrenes which have been precipitated and those which have not.

A complete explanation of these results is clearly not possible on such fragmentary evidence. It is tempting, nevertheless, to speculate on possibilities. One physical difference which exists between fused and freshly precipitated polymers is the relative extents of molecular ordering. In the case of polymethyl methacrylate it has been shown that a degree of molecular ordering obtained by annealing is completely destroyed by reprecipitation.<sup>100</sup> If such a theory is extended to the present problem it implies that, on heating to degradation temperatures, conformational or ordering

changes take place in the polymer melt and these changes permit more complete solvation on subsequent dissolution. If the polymer thus treated, however, is reprecipitated it is restored to its original state showing a reduced degree of polymer-solvent interaction in solution. Such a theory is open to several criticisms. In the first place a decrease in  $\mu$  is observed only when polystyrene is degraded, but the theory outlined above would predict a decrease in  $\mu$  when a sample is subjected to prolonged heating at temperatures just below degradation level, and such a prediction does not seem to be supported experimentally. Furthermore, precipitation, according to this theory, should fully restore  $\mu$  to its original value, but it does not. To account for this further discrepancy it is necessary to postulate a second effect during degradation, and knowing the mechanism of this process the obvious choice is the removal of weak links.

On this basis then, the decrease in  $\mu$  observed on degradation might be due to a two-fold effect - removal of weak links and changes in conformation. Reprecipitation is capable of restoring the latter but has no effect on the former. It must be emphasised that these ideas are in no way conclusive but are presented as a possible basis for further studies for which there is a definite need. As has already been mentioned,

these observations are a side issue of the main problem, and a systematic approach to the whole question is obviously called for. In this connection a closer study of the effects of conformational changes in polymers on their solution properties might prove fruitful. The effects of traces of other substances, both as comonomers and as trace impurities, might also be worth investigating.

### 3. Viscometric Behaviour of Degraded Polystyrene.

One of the most widely used empirical relationships for the concentration dependence of the viscosity of polymer solutions is that proposed by Huggins<sup>98</sup>

$$n_{sp}/c = (\eta) + k'(\eta)^2 c$$

where  $(\eta)$  is the limiting viscosity number and  $c$  the concentration in g. per 100ml. of solution.  $k'$  is a constant which is a measure of polymer-polymer interaction, in a like manner to  $\mu$  in the osmotic pressure relationship. (See p.146).

For any polymer-solvent system a decrease in  $\mu$  should also be reflected in a decrease in  $k'$ . To check whether such an effect exists in degraded polystyrene a number of experiments were carried out to estimate  $k'$  for thermally degraded polymers in benzene solution at 30°C.. A P.C.L. Suspended Level Viscometer was used for these determinations and the value of  $k'$

was calculated from the slope of the resulting  $n_{sp}/c$  versus  $c$  plot. With the system benzene-polystyrene  $n_{sp}/c$  versus  $c$  is a straight line and  $k'(n)^2$  represents its slope, and conversely  $k' = \text{slope}/(n)^2$ . Bawn<sup>99</sup> has shown that for undegraded polystyrene in benzene solution  $k'$  is 0.35 and is constant over a range of molecular weight from 72,000 to 1,600,000. Some viscometric data for degraded polystyrene samples are shown in Table 11.

TABLE 11

Values of  $k'$  for Degraded Polystyrene in Benzene Solution at 30°C.

| Polymer | Percentage Volatilisation. | $k'$ |
|---------|----------------------------|------|
| SG.1    | 0                          | 0.37 |
| "       | 3.0                        | 0.21 |
| "       | 9.3                        | 0.11 |
| "       | 24.0                       | 0.19 |
| SG.3    | 3.5                        | 0.18 |
| "       | 9.4                        | 0.21 |
| "       | 20.2                       | 0.15 |
| "       | 30.4                       | 0.17 |
| SG.4    | 1.7                        | 0.31 |
| "       | 17.2                       | 0.30 |
| "       | 26.2                       | 0.27 |
| "       | 43.3                       | 0.18 |
| S.7     | 0                          | 0.30 |
| "       | 6.9                        | 0.28 |
| "       | 28.7                       | 0.24 |

Samples SG.1, SG.3 and SG.4 were prepared for degradation studies by Grassie and Kerr. Their molecular weights are greater than  $2 \times 10^6$ .

It is possible that the viscometer used for this work was insufficiently sensitive, especially for samples of high molecular weight which show high rates of shear. For low values of  $(n)$ , which give almost horizontal lines, accurate assessment of  $k'$  is extremely difficult since slight errors in  $(n)$  and slope grossly affect the fraction  $\text{slope}/(n)^2$ .

Nevertheless, the results in Table 11 show that as degradation proceeds the value of  $k'$  decreases, but there is no indication that it reaches a constant value as does  $\mu$  from osmotic measurements. Probably owing to the high experimental error there is no obvious correlation of  $k'$  values within the series. For this reason no quantitative significance can be attached to these figures, but qualitatively they are in the predicted direction, and are in agreement with osmotic pressure measurements in indicating a decrease in polymer-polymer interaction in solution after degradation.

#### 4. Summary.

Osmotic molecular weight determinations have shown that in benzene solution thermally degraded poly-

styrene samples show an abnormally high degree of polymer-solvent interaction which is much more temperature sensitive than the corresponding values for undegraded material. An analogous observation has been made on the viscometric behaviour of thermally degraded polystyrene. It has also been found that if these samples are precipitated and redissolved in benzene before osmotic data are recorded the osmotic slopes decrease once more (that is, polymer-polymer interaction increases once more) though not to the original values for undegraded polystyrene.

It has been proposed that these changes in solution properties are caused by a twofold effect of degradation - the removal of weak links and changes in conformation or molecular ordering. This proposal, however, has to be treated with reservation as the evidence on which it is based is fragmentary, and a possible course of further work to clear up the problem has been suggested.

CHAPTER VII

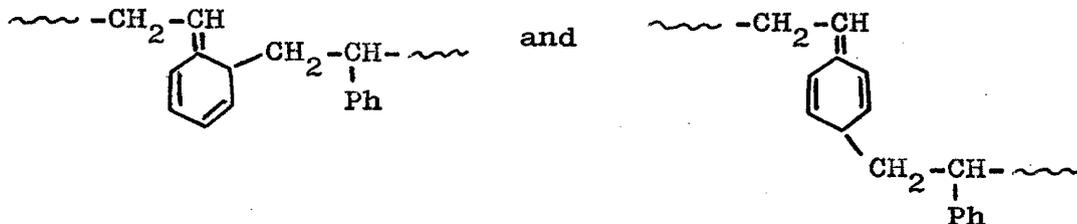
THE PROBLEM REVIEWED.

Detailed summaries of the work have already been given at the ends of each of the foregoing chapters, and in this chapter it is intended to draw a broader general picture of the overall results and to outline further possible courses of investigation.

The studies of thermal degradation of polystyrene in solution have clearly shown that the initial steep fall in molecular weight is due to scission of weak links and not to intermolecular transfer, and that weak link scission and depropagation are separate and independent processes.

Some progress has also been made towards establishing the exact nature of these weak links. Thus, the possibility of their being head to head structures has been eliminated by means of styrene-stilbene copolymer degradation studies. It is known from the work of Grassie and Kerr that weak links are formed in some process competing with the normal propagation reaction during polymerisation. Since this process is not head to head addition a second possibility, that of polymerisation through a resonance form of the growing free radical,

has been considered. Such an abnormal polymerisation step would give rise to structures of the type



Ozonolysis of polystyrene has shown that it contains back-bone double bonds in the same concentration as thermo-labile links, and the quinonoid structure shown above can reasonably account for these. Polystyrenes prepared anionically also contain weak links which respond to heat and ozone in the same way as those in samples prepared by free radical means. This supports the view that the weak links are the same in both types of polymer, and indeed quinonoid structures can easily be accounted for in ionically prepared polymers. Ionic polymerisation of styrene involves resonance of the growing ion and this would account for the presence of quinonoid groups as before. One apparent anomaly in this work, however, is the similarity of weak link concentration in ionic and free radical polymers. From the different modes of preparation of these polymers a wider variation in weak link concentration would have been expected.

Assuming a quinonoid type structure as above

a reaction scheme has been proposed for weak link scission. This mechanism is capable of explaining all the important features of weak link scission - irreversibility, the production of stable chain ends and the rate determining effect of the  $\alpha$ -hydrogen atom. The acceptance of such a weak link structure also allows ready explanation of the fact that certain polystyrenes contain less than one weak link per molecule on the average.

Finally, certain interesting features of the solution properties of thermally degraded polystyrene have been recorded. The abnormally high polymer-solvent interaction possessed by such samples has been shown to be reduced by reprecipitation and to be temperature sensitive. A tentative explanation for these effects has been offered on the basis of the disappearance of weak links and conformational changes brought about by degradation, though the need for further systematic study has been emphasised.

On the immediate problem of weak links it has to be admitted that final proof of their structure is still lacking. The evidence from the present work, though fairly strong, would benefit from further support. The note concerning the reaction of maleic anhydride and polystyrene (at the end of Chapter V) is an indication of a course worth investigating. Systematic study of

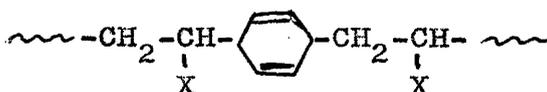
this reaction on a quantitative basis, perhaps using radio-active maleic anhydride, appears worth while.

Other possibilities can be classified under two general headings. Firstly, an endeavour to obtain a polystyrene, or a closely related compound, completely devoid of weak links would be worth making. And, secondly, it might be useful to try to make a polystyrene containing a known concentration of quinonoid structures by copolymerisation techniques. Degradation studies on compounds of either type could yield useful information.

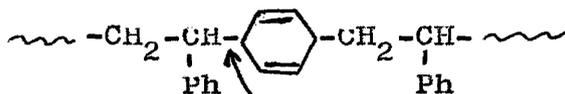
Of the first possibility it can be said that the chances of preparing a polystyrene devoid of weak links seem rather remote, since every sample so far examined, regardless of mode of preparation, has been found to contain weak links. Substituted styrenes, in the ortho- and para-positions, might, however, yield a completely "normal" polymer as bulky groups in these positions could effectively prevent abnormal additions. In this connection the methyl substituted styrenes would be worth examining, though it is by no means certain that methyl groups are sufficiently bulky to give complete steric hindrance. Nevertheless, a significant reduction in weak link concentration in polymers of these monomers would constitute some support. Larger groups, such as isopropyl or isobutyl, should be more efficient blocking

agents but there is a chance of transfer reactions, especially with the former, which might give undesirable branching.

There is no obvious way of introducing into the polystyrene chain quinonoid structures which are identical to those proposed as weak links. It is known, however, that benzene can act as a comonomer in certain systems, such as the polymerisation of vinyl acetate,<sup>102</sup> to give structures of the type



If known amounts of benzene could be introduced into polystyrene chains structures such as



would result. The bond indicated would be expected to be more thermo-labile than the other carbon-carbon bonds in the chain and should function as an additional weak link. In addition, this structure would be attacked by ozone so that thermo-labile structures and double bond concentrations should agree as before.

In the case of the osmotic behaviour of degraded polystyrenes suggestions for future work have already been indicated in Chapter VI. As changes in solution properties appear to be connected in some way with the disappearance of weak links, investigations in

this field may eventually throw some light on the nature of the weak links themselves.

Going further afield from the present problem of weak links, studies of thermal degradation of polymers in solution look quite promising. One of the main difficulties associated with depolymerisation work lies in observing the effects of inhibitors on the reaction. The problem of studying inhibition in bulk degradation of polymers has been mentioned in Chapter III. In attempting to inhibit bulk degradations there is always the risk that the inhibitor will distil out of the system or will be unable to function properly because of the high viscosity of the polymer melt. In solution both of these risks are eliminated and the success of the method has been demonstrated in the case of polystyrene in tetralin, which is not only a solvent but a free radical acceptor. It may not always be necessary or even desirable to use tetralin. An inert solvent such as naphthalene with controlled inhibitor concentration might be a more versatile combination which could yield useful kinetic information such as rates of initiation.

The findings of this work can be very briefly summarised as follows:-

a) The initial steep fall in molecular weight observed

during thermal degradation of polystyrene is due to weak links and not to intermolecular transfer.

b) Scission of these weak links is an irreversible process not involving free radicals at any stage.

c) The weak links are not caused by occasional head to head additions during polymerisation.

d) Weak links are associated with double bonds in the polymer back-bone.

e) The solution properties of polystyrene are affected by thermal degradation.

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