THESIS FOR THE DEGREE OF MASTER OF SCIENCE.

THE PHOTO-OXIDATION OF
POLY α METHYL STYRENE, POLY PARA METHYL STYRENE POLY 2,5 DIMETHYL STYRENE, POLY 2,4,6 TRIMETHYL STYRENE AND POLYSTYRENE.

by

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PREFACE.

The work described in this Thesis was carried out in the period May 1963 to January 1966, at the University of Glasgow in the department of Physical Chemisty, which is under the supervision of Professor J.M. Robertson, F.R.S.

I am grateful for the assistance given to me by the technical staff of this department , in particular Mr. R. Smith.

My thanks are also due to my colleagues in/polymer department, in particular Dr. I.G. Meldrum, J. Lawrance, S.I. Haider and T.M. Makhdumi for valuable discussion and suggestions.

I wish to thank Dr. N. Grassie for his general supervision and for granting a Research Scholarship during my second year of research. Also I am grateful to Dr. I.C. McNeil for using his apparatus in thermal degradation.

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CHAPTER I

Introduction

The use of synthetic polymer as substitute for natural materials is growing in importance. Their use, however, creates new problems associated with the prevention of their detoriation. If these problems can be solved, the useful life of these materials will be prolonged.

In general the ageing process is due to the simultaneous effects of oxygen, sunlight and heat. However, to study these combined chemicals processes is quite complicated. It is much more profitable to study these effects one by one. As far as the effect of heat is concerned, a great deal of work has been done on the thermal degradation of poly(methacrylate), polystyrene, poly(vinyl chloride) and many other materials.(1)

On the other hand, the mechanism of the deterioriation due to oxidation and radiation is less well known although a considerable amount of work has been done. In recent years interest in space exploration has made new and unusual demands upon synthetic materials. This has lead to renew interest in photo-degradation.

To study the mechanism of oxidation it is necessary to identify the reaction products as well as to obtain intimate knowledge of the initiation step. Due to the small concentration of the reaction products in the initial stages it is difficult to identify them. At higher extents of reaction the reaction products become more numerous and more complicated and this makes it difficult to use them as a basis for studying the initiation reaction. To avoid secondary processes dominating the rate of the overall reaction it is advantageous to study model compounds of polymers, ie. small molecules having the same functional groups as the polymers. This has been done, for example in the cases of Nylon(2), Rayon(3,4,5), and rubber(6-11).

However, care must be observed in the use of model compounds since the polymer chain environment and factors like crystallinity can have a large effect on the course of reaction in polymer.

A lot of progress has been made in the study of olefins which are model compounds for rubber. It is useful, therefore, before considering the oxidation of polystyrene to discuss olefin oxidation.

Oxidation of Olefin

A vast amount of research has been done on this subject. Recently great progress has been made in this field notably by Criegee(12-13) and Farmer(14) who showed independently that the initial product ~~product~~ of oxidation of cyclohexane was a hydroperoxide. Farmer suggested that the oxidation of olefins is a chain reaction involving the addition of a molecule of oxygen to the carbon atom adjacent to a double bond, to form a hydroperoxide.

$$-CH_2-CH=CH- + O_2 \rightarrow -CH(OOH)-CH=CH-$$

This was supported by a large amount of experimental evidence by Farmer and his coworkers(15-19). The mechanism and kinetics of reaction was established by Bolland, Bateman, Gee and their coworkers(20-21). They determined rates of oxidation of ethyl linoleate by measuring the oxygen absorbtion. They found that the rate increased linearly with the amount of oxygen absorbed. They showed that the reaction was initiated by the thermal decomposition of the ethyl linoleate hydroperoxide, the sole product of the early stage of the reaction, and that the autocatalytic nature of the reaction derived from this.

The following mechanism(22) accounted for their experimental observation of olefins oxidation. RH represents the olefin with an α methylenic hydrogen atom H, r_i is the rate of chain initiation, and the k's are the velocity coefficients of reaction indicated.

Initiation :	**Production of R' or ROO' radicals**			r_i
Propagation:	$R' + O_2 \longrightarrow$		ROO'	k_2
	$ROO' + RH \longrightarrow$		ROOH + R'	k_3
Termination :	$R' + R'$	$\left.\right\}$	**Non initiating**	k_4
	$R' + ROO'$		**or propagating**	k_5
	$ROO' + ROO'$		**products.**	k_6

In respect to these reactions the rate of oxidation is related to the rates of elementary reactions by the equation.

Error

$$X \quad -\frac{d(O_2)}{d(t)} = \frac{r_1 k_3 k_6^{\frac{1}{2}}(RH) k_2 k_6^{\frac{1}{2}}(O_2)}{k_3 k_4^{\frac{1}{2}}(RH) + k_2 k_6^{\frac{1}{2}}(O_2) + (k_4 k_6 r_1)^{\frac{1}{2}}} \quad X$$

This was found to apply to a large numbe. to olefins and diolefins(23-26).

The oxidation of cumene, a model coumpound for polystyrene **also obeys the above equation**(27,28,29).

The oxidation of polystyrene.

(1).Introduction.

Studies of the oxidation of several polymers has been done by Mesrobian and Tobolsky(30) by measuring the volume of oxygen absorbed.Using the rate of oxygen uptake as a critarion of oxidisibility they showed that polymers with double bonds in their backbones were particularly susceptible to oxidative degration and those with electrophilic side groups,like chlorine,carbonyl and phenyl (polystyrene) were much less reactive.A qualitative relationship between ease of oxidation or oxidisibility and ease of polymerisation was pointed out by the same authors.

(2).Jellinek's Hydroperoxide Theory

Studies of the oxidation of polystyrene in air in the temperature range 180°C to 230°C have been carried out by Jellinek(31,32).He followed the progress of oxidation by determining the viscosity M.Wt. of the residual material at certain intervals.A rapid initial decrease in viscosity was observed,followed by a tail off.He attempted to explain his results in terms of the theory of random scission,which predicts a linear relation between the average number of chain breaks per original chain and the time of degradation for the initial stages of the degradation.Straight lines were,however,not obtained, instead a rapid tailing off was observed.This led him to the conclusion that inhibitor in the form of anteoxidants were formed concurrently with the chain breaks.The antioxidant was proved to be benzaldehyde.The following reaction scheme was therefore proposed.

Polystyrene + O_2

↓

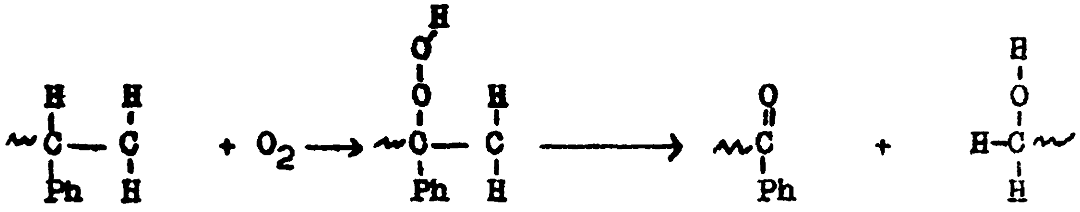
Polystyrene hydroperoxide

↓

Chain scission

↓

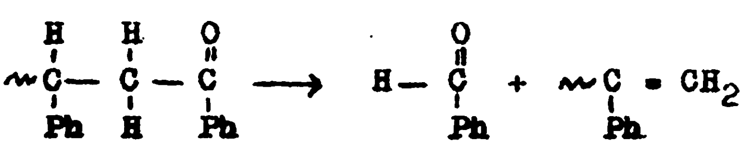
<u>Inhibitors</u>



$$\sim\!\mathrm{C(H)(Ph)}-\mathrm{CH_2} + O_2 \longrightarrow \sim\!\mathrm{C(OOH)(Ph)}-\mathrm{CH_2} \longrightarrow \sim\!\mathrm{C(=O)Ph} + \mathrm{H_2C(OH)}\!\sim$$

<u>Hydroperoxide</u> <u>Chain scission</u>

Benzaldehyde is then formed by the breaking off of the oxidised chain ends,



$$\sim\!\mathrm{C(H)(Ph)}-\mathrm{CH_2}-\mathrm{C(=O)Ph} \longrightarrow \mathrm{H}-\mathrm{C(=O)Ph} + \sim\!\mathrm{C(Ph)}=\mathrm{CH_2}$$

The inhibition was assumed due to the reaction of benzaldehyde with the polystyrene hydroperoxide producing a benzalhydroperoxide thus preventing the styrene chain from breaking.

Evidence for Jellinek's Theory.

(1).Achhammer(33)studied the infra red spectra of polystyrene irradiated and heated in air and came to the conclusion that the presence of carbonyl and hydroxyl groups were due to decomposition of hydroperoxide.

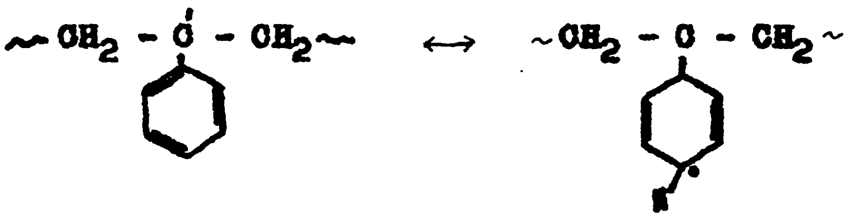
Zaitoun(34)resolved the spectra of carbonyl band into aldehyde,ketone and acid absorption.

(2).Achhammer and Wall(35-36)studied the gaseous products of thermal and photo-oxidation of polystyrene by mass-spectrometry.They found that the products could come from the decomposition of a hydroperoxide formed at the α position to the phenyl group.Thus the products of oxidation were in agreement with these expected from the reaction mechanism postulated by Jellinek.

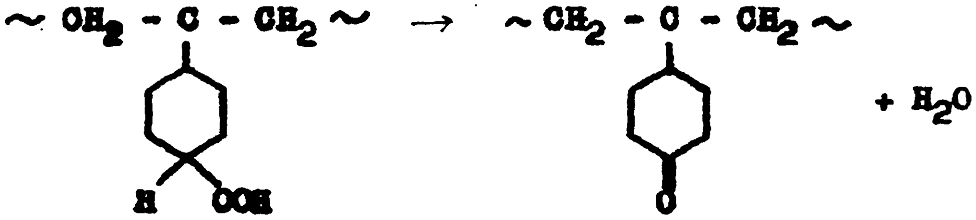
(3).Beachell and Nemphos(37)demonstrated that replacement of hydrogen atom at the α position to the phenyl group by deuterium changes the rate of oxidation,while replacement at the β position results in no appreciable change of rate.

The coluration of polystyrene.

The coluration which occurs in use is one of the most undesireble properties of polystyrene. This was originally associated with oxidation. Achhammer(38) suggested that the color of oxidised polystyrene may be due to the formation of quinoid structures, resulting from peroxidation of the phenyl group in the para position.

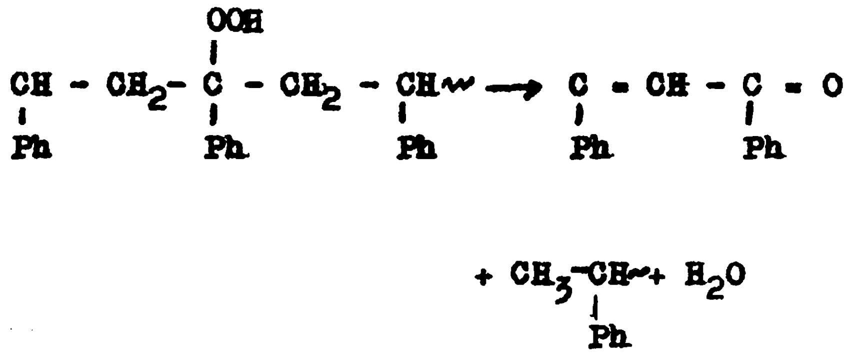


which could lead to



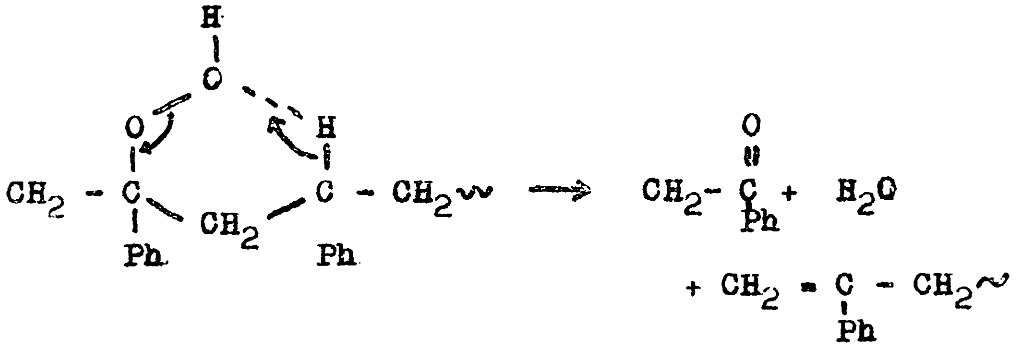
Such quinoid structures could lead to high absorption in the ultra-violet region and yellowing in the visible region of the spectrum.

Wall and his coworker(39,40,41) suggested an alternative theory to account for the changes which occurred in the visible and ultra- violet spectra of photo-oxidised polystyrene and also for certain post-irradiation effects. They suggested that the chromophores are closely related to benzalacetophenone of which hydroperoxide is the precursor.



$$\underset{Ph}{CH} - CH_2 - \underset{Ph}{\overset{OOH}{C}} - CH_2 - \underset{Ph}{CH}\sim \longrightarrow \underset{Ph}{C} = CH - \underset{Ph}{C} = O + CH_3 - \underset{Ph}{CH}\sim + H_2O$$

Grassie(42) suggested that since the rate of coloration in presence and absence of oxygen are comparable and the principle characteristics are similar, it seems more probable that the hydroperoxide would decompose by way of a six-membered ring transition state rather than the direct formation of a substituted benzalacetophenone as formulated above.



It was also suggested that the color in polystyrene is due to conjugated carbon - carbon double bond in the polystyrene backbone.

Feng and Kennedy (43) found that the coloration produced in polystyrene by β irradiation in air is approximately proportional to the radiation dosage but very little color change is observed in the case of irradiation in vacuum. The maximum of absorption occurs at approximately 340 mμ.

It is clear that a great deal of work still remains to be done to clarify the above reactions.

Recent studies on photolysis and photo-oxidation.

Recently Grassie made a study of the photolysis and photo-oxidation of polystyrene using 2537 Å radiation. He found during photolysis that hydrogen is the only volatile product.

This is in agreement with the finding of Wall and Brown(44), who found the product of radiolysis of a number of deuterated and ordinary polystyrenes exposed to gamma-rays from a Cobalt-60 sourse to be exclusively hydrogen with small amount of benzene arising from the solvent left in the polymer films.

In photo-oxidation at 25°C Grassie(45) found that the only volatile products of oxidation were carbon dioxide and water.

The effect of ultra-violet absorbers which are commonly used as stabilisers were also studied .

Aims of the present work.

This work was initially carried out as a continuation of the work on the photo-oxidation of polystyrene carried out by N.A. Weir. (Glasgow University Ph.D thesis 1963) He developed a piece of apparatus in which oxidation, photo-oxidation and photolysis could be carried out. This apparatus was based on a simple differential manometer with some modifications. He also studied the effect of such variables as oxygen pressure, light intensity and temperature.

In the present work certain improvements and corrections which are described in Chapter 2, were made to the apparatus and a correct oxygen uptake relationship was deduced.

In this work the effect of methyl substitution in various positions in the polystyrene molecule on oxidation, photolysis and colouration was studied. The effect of such variables as oxygen pressure, light intensity etc were also studied.

CHAPTER 2

1. Preparation of Polymers.

(a). Introduction.

In order that the polymers might be as pure as possible, monomers were carefully purified and polymerized in vacuum, except for poly (α-methyl styrene) and poly (2,4,6 - trimethyl styrene) which were polymerised cationically under pure nitrogen.

Poly (α- methyl styrene).

α- methyl styrene made by L. Light & Co was used. The inhibitor was removed from the monomer by successive washings with sodium hydroxide solution (10 %) until no pink colour appeared. Finally the monomer was washed with distilled water until washing were not longer alkaline to litmus. After standing for twenty hours over calcium chloride (anhydrous) the monomer was distilled at 54 °C , 20 mm. Hg pressure , the middle fraction being collected and stored at - 20 °C.

First it was attempted to polymerise this monomer at -130 °C using the method of Herzberger A.B. and coworkers(46). However difficulties in controlling temperature at -130° and obtaining pure anhydrous aluminium chloride resulted in insoluble polymer. This might be crosslinked polymer or very high molecular weight polymer which was partially crystalline.

Due to this a higher polymerisation temperature was used.

30 ml of α-methyl styrene monomer was added to 300 ml of distilled methylene chloride in a five necked detachable flask . This flask was cooled to - 80°C in a dry ice (solid carbon dioxide) and acetone mixture. About 2 ml of stannic chloride was introduced into the solution with a syringe. The temperature of the reaction mixture rose rapidly to - 66°C. The reaction was continued until the temperature dropped back to - 78°C. A roughly equal volume of Analar methanol was added which precipitated the polymer as a white jelly. This polymer dissolved slowly and the solution in chloroform was filtered through a sintered glass crucible (G.1.). The filtrate was reprecipitated by Analar methanol.

This procedure was repeated , the resulting polymer was filtered off and dried under vacuum.

The yield was 63 % . Molecular weight : 67.000

Since stannic chloride was never used before as a catalyst to polymerise~~d~~ α-methyl styrene monomer, two more batches of α-methyl styrene monomer were polymerised in the same method in order to be sure. Almost the same results were obtained.

Poly (2,4,6 Trimethyl Styrene).

This monomer (Koch Laboratories) did not contain inhibitor. Attempts to purify it by reduced pressure distillation (water tap) resulted in polymerisation of the monomer. Distillation under high vacuum was succesful .

However attempts to polymerise this monomer thermally at 80°C and also using azoisobutyronitrile as catalyst resulted only in low yields (1 %) and of low molecular weight (12.000) material, after 30 hours polymerisation period.

Cationically, polymerisation using the same technique as in the polymerisation of α- methyl styrene monomer was successful giving satisfactory yields (60 - 70%) and high molecular weight (74.000 and 56.000).

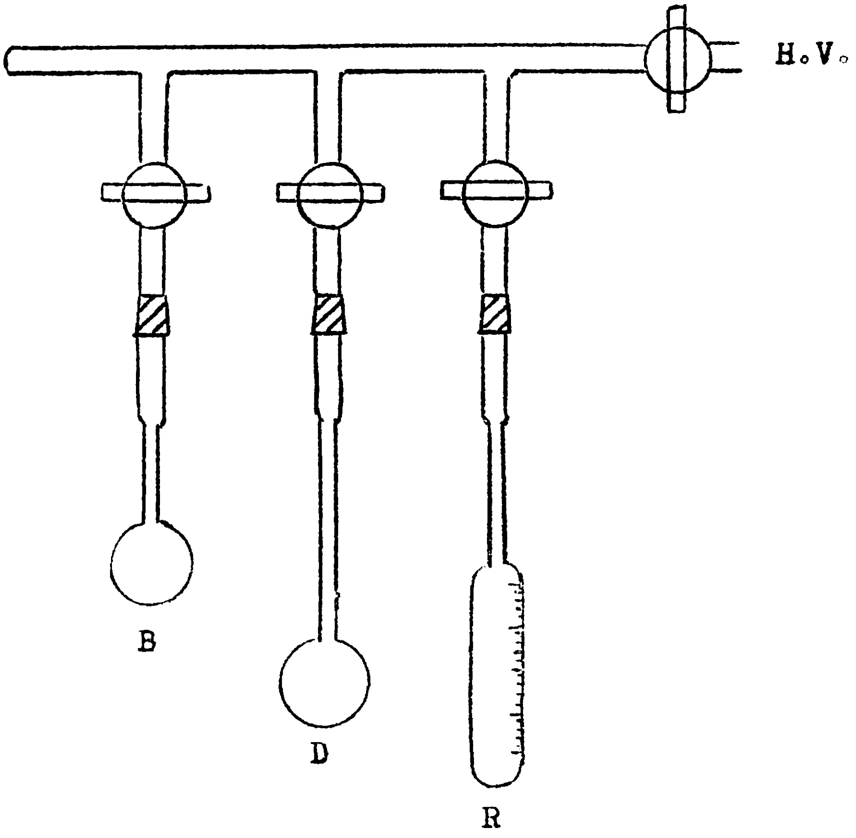
Polystyrene, Poly (para methyl styrene) and Poly (2,5 dimethyl styrene)

Styrene (Light & Co), para methyl styrene (Koch) and 2,5 dimethyl styrene were polymerised at 60°C using azoisobutyronitrile as catalyst. These monomers were purified by distillation under reduced pressure after inhibitor had been removed by caustic soda solution as in the case of α-methyl styrene.

Procedure:

The high vacuum apparatus used for filling the dil~~i~~atometer is shown in Figure 1 . Initiator was first introduced into the dil~~i~~atometer which was attached to the system. This was evacuated to 10^{-5} torr by a mercury diffusion pump backed by a rotary oil pump. The monomer was introduced into the reservoir tube and degassed three times under high vacuum by the alternate freezing and thawing technique. The first 10 % of the monomer was eliminated by distilling into the bulb, B. Then the monomer was distilled into the dil~~i~~atometer by

Figure 1



Apparatus for filling dilatometer.

B - Bulb, D - Dilatometer, R - Reservoir, H.V. - to High Vacuum immersing the dillatometer in liquid nitrogen until the required amount of monomer was obtained. Finally the dillatometer was sealed off under high vacuum.

Polymerisation.

The polymerisation was carried out at 60°C in a water thermostat controlled to ± 0.05°C by a Sunvic H.V.S. type relay actuated by a mercury toluene regulator. The contraction during polymerisation at 60°C was correlated with the degree or percentage of polymerisation using Melville & Valentine(47) data for polystyrene and Grassie & Riskalla data (private communication) for para methyl styrene.

The polymerisation was stopped at 10 % conversion by immersing the dilatometer in a freezing mixture. The polymer - monomer mixture was dissolved in analar chloroform and the polymer precipitated by adding this solution slowly to stirred methanol.

The polymer was then collected and roughly dried. It was then reprecipitated, collected and dried throughly under vacuum.

2) Molecular Weight Measurements.

All the molecular weights quated in this thesis were measured using a Mechrolab Model 501 High Speed Membrane Osmometer.

Describtion of the instrument.

A membrane is clamped horizontally between two stainless steel plates having special groove patterns for distribution of the solvent and solution. Fastened to the top plate are two tubes for introduction and withdrawal of solution (or solvent for reference). The bottom grooved plate has a 0.006" I.D. glass capillary connected to it.

When this system is filled with solvent, the hydrostatic pressure of the bottom of the membrane is adjusted by vertical motion of the solvent reservoir. The reservoir is mounted on vertical screw, which is driven by a srew motor to adjust the position of the reservoir. Digital and recorder read this position .

Solvent flow through the membrane is detected by focussing an optical system on the section of the lower capillary where a small air bubble has been introduced.

The light source has been focussed in such a way that the photocell placed at right angles to the source receives much more light with air inthe capillary than with solvent. By placing the top of the air bubble at the centre of the optical axis , the light intensity on the photocell will change sharply with movement of the bubble. This change of light intensity is used to drive the servomotor through the amplifier and thus to adjust the pressure on the bottom of the membrane.

In operation, the solvent is first placed on both sides of the membrane and a stable reading observed after about five minutes. The solvent on top of the membrane ~~is then replaced~~ is then replaced with solution and a new reading obtained. Provided no solute~~s~~ permeates the membrane, this reading should be obtained in about five minutes. The differences between the two readings is the osmotic pressure of the solution.

The basis equation for molecular weight calculation is

$\pi/C = RT / Mn$

π is osmotic pressure, C is concentration of the solution, R is gas constant, T is the absolute temperature and Mn is number average molecular weight.

$Mn = RT / \pi/C$

3. Preparation of Film.

a). Choice of Film Thickness.

The standard film thickness used in experiments was a compromise arrived at after consideration of a number of factors. A very definite lower limit results from the fact that very thin films are extremely brittle and difficult to handle. The limit at which this occurs varies very much from polymer to polymer. Except for poly (2,4,6 trimethyl styrene) all the other can be easily made at thickness of 0.007 inch.

b) Absorbance of 2537 A line.

All polymer studied have a high extinction coefficient for the 2537 A line, the intensity is reduced to less than 1 % by passage through a film of 0.01 mm. Thus films of 0.007 inch will absorb virtually all the incident light.

c) Diffusion of oxygen

The diffusion of oxygen will occur in the initial stage when oxygen comes into contact with the film. It will reach a stage that the number of moles of oxygen leaving the film will be the same as the number of moles of oxygen enter~~s~~ING into the film.

When the film is irradiated by U.V. this equilibrium has already been achieved. Oxidation occurs only near the surface of the film and the amount of reaction gradually decreases to zero in those layer of film which receive no U.V. radiation, that is at a depth of 0.01 mm.

The oxygen used during oxidation reaction is replaced by diffusion of oxygen from the cell.
The rate of diffusion of oxygen into polystyrene at 28°C and 600 mm is 7×10^{-7} cc/ cm^2/ mm/ minute or 19×10^{-8} moles/ cm^2/ .01 mm/ hour. (Barrer(48) and Stannett (49)). In oxidation experiments it was found that the rate of oxidation of polystyrene is 9×10^{-8} moles/ cm^2/ .01 mm/ hour., hence the rate of diffusion is at least two times greater than the rate of oxidation. This indicates that the oxygen used up is immediately replaced so that photo-oxidation reaction of polystyrene is not diffusion controlled, regardless

of the thickness of film used.

d) Preparation of film

Since this is a surface reaction it is important to have films of known area and thickness. Similar experiments carried out on the powder polymer would have yielded conflicting and erratic results due to such variables as surface area, layer thickness and so on.

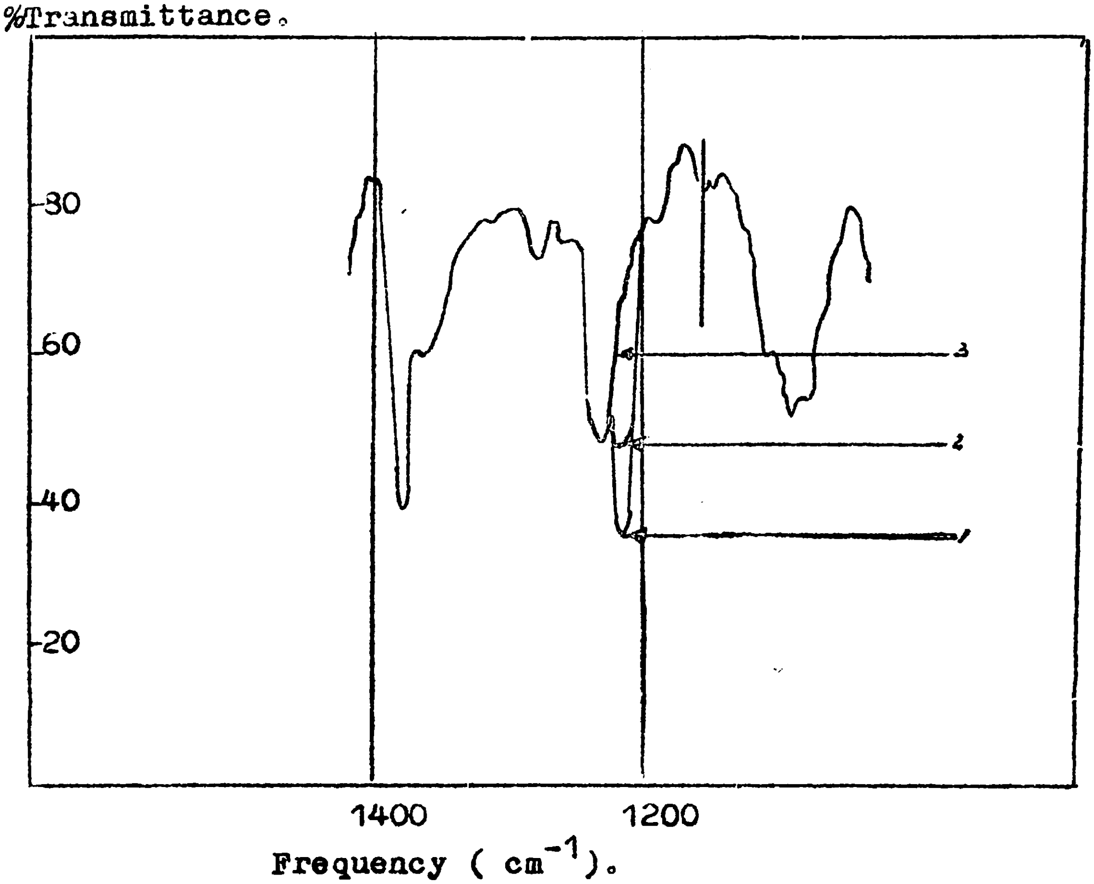
The polymer (1 gm) was dissolved in A.R.chloroform (20 ml) and the solution filtered. It was then poured into a petri disc containing carefully purified mercury. After 24 hours the solvent had evapourated and the film was freed from the side of the disc by cutting the edges with a razor or sometimes simply by agitating the mercury a little.

Traces of solvent might participate in the photo-oxidation reaction and for this reason it is necessary to remove it completely from the film. It was found that chloroform can not be removed by continous pumping under high vacuum at room temperature even if this was continued for several days. This can be seen from the deformation vibration peak of the C - Cl at 1218 cm^{-1} in the I.R. spectra. However if the film is heated at 130°C under high vacuum for a period of 3 hours the C - Cl peak disappeared. Figure 2.

The apparatus used is shown in Figure 3 . The film was placed in the socket S, which was attached to high vacuum system and the apparatus pumped at 10^{-5} for 3 hours, then placed in a furnace while pumping was continued. The temperature was held within the range 125 - 135°C.

Figure.2

Removal of chloroform from a p.α.m.s. film



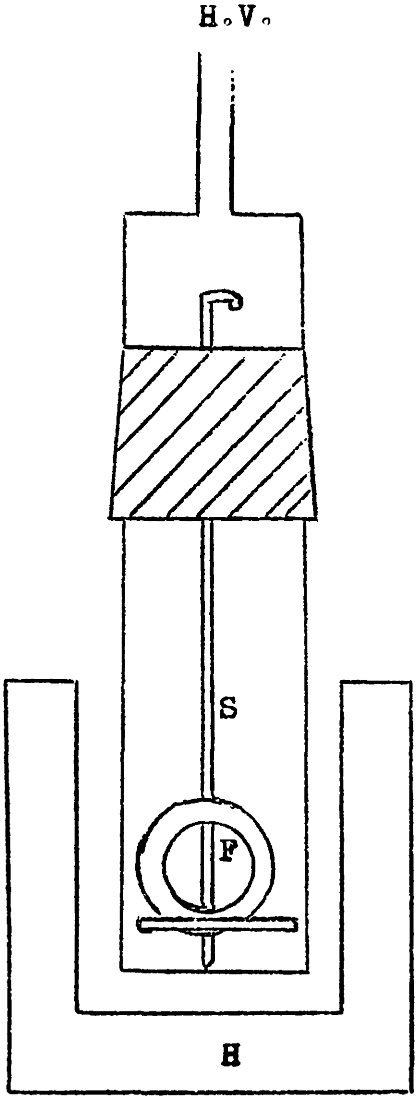
(1). Undried film's peak for C-H of Chloroform rocking vib.

(2). Dried at 130 C(10^{-5}torr) for 1 hour.

(3). Dried at 130 C (10^{-5} torr) for 3 hours.

It is clear from this I.R. spectra that the C-H rocking vibration peak of chloroform disappears completely after three hours of heating.

Figure 3



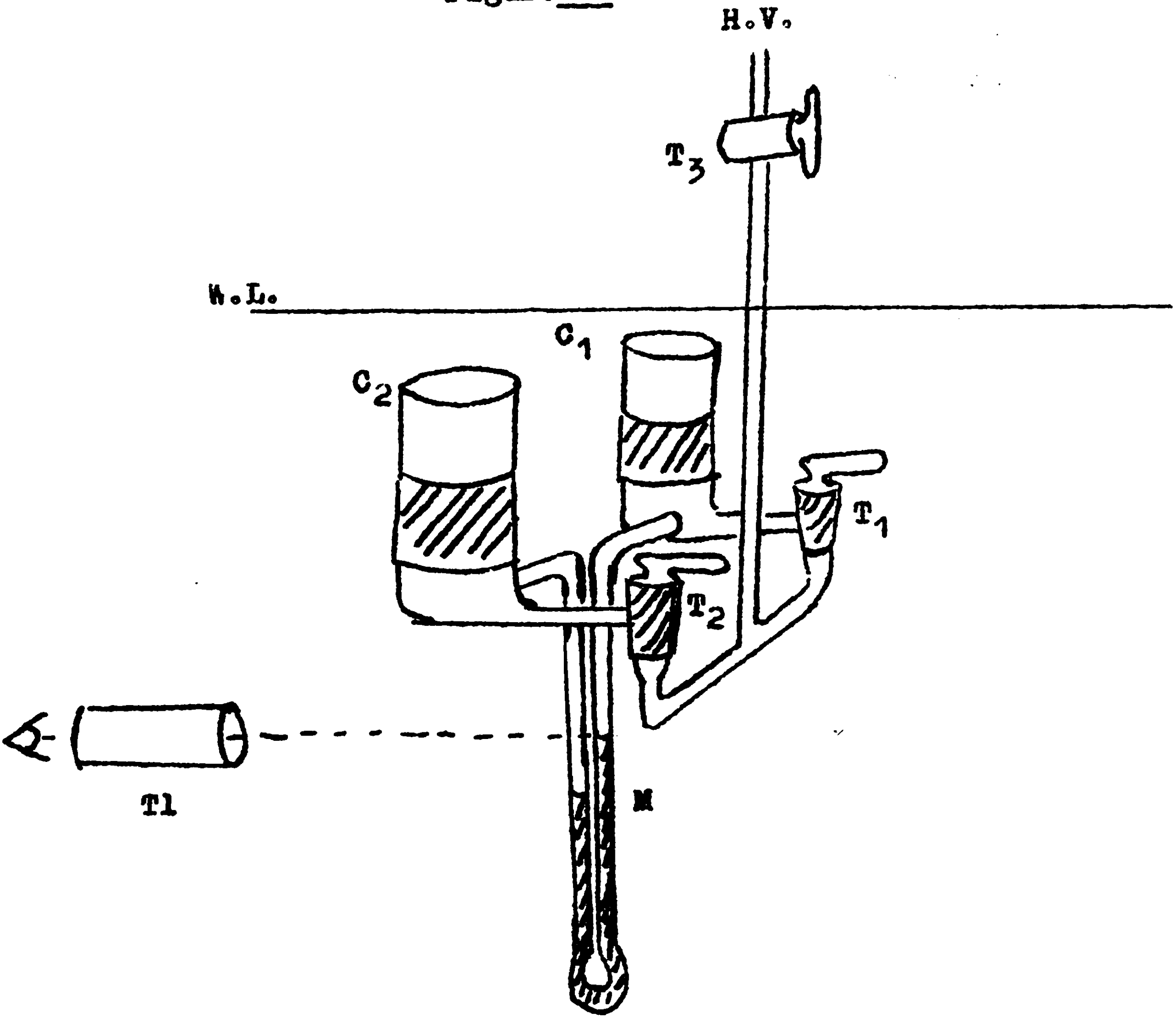
Apparatus for drying films.

F - Film, H - Heater, S - Socket, H.V. - High Vacuum.

Oxidation Apparatus

The apparatus was a modified version of that used by Grassie and Weir(50). It consisted of two cells of almost equal volume joined by a differential manometer. Figure 4. The lower part of the cells are constructed from B.40 pyrex cones and the upper parts consist of B.40 fused silica sockets (Thermal Syndicate Ltd) with flattened ends through which the ultra-violet radiation is transmitted. The cells are independently joined to the oxygen supply and high vacuum system. They can be isolated from these and from each other by closing stop-cock T_1 and T_2. The films are oxidised in one of the cells say C_1 while C_2 which is under the same condition of temperature, pressure and irradiation, acts as a compensating volume. In this way variation in pressure arising from small fluctuation in ambient temperature are balanced out. However later it will become clear that without C_2 the rate can not be calculated. The manometer is constructed from heavy wall precision bore tubing of diameter 3 mm.

Figure_4_



OXIDATION APPARATUS

C_1,C_2 : Cell 1 and cell 2 , M : manometer , W.L. : water level T_1,T_2,T_3 : stopcocks , H.V.: high vacuum system and oxygen supply system.

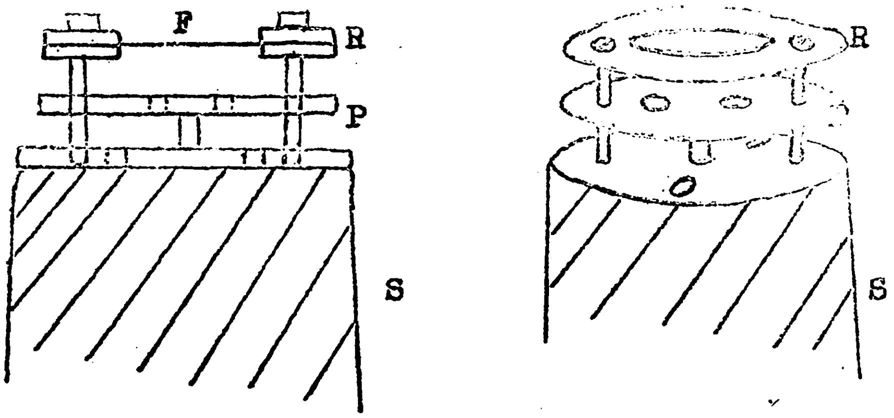
The volume of C_1 and C_2 including tubing T_1 and T_2 are 93.55 and 95.20 cc respectively.

The arrangement of the film in C_1 is shown in Figure 5A. It is placed between two stainless steel rings of inner radius 1 cm and out radius 1.7 cm (R). The rings was screwed to a platform (P) which consists of two perforated discs to avoid ultra-violet radiate~~s~~ on the grease or the absorbants. The absorbants are placed on little beakers in the cell, to remove the carbon dioxide and water produced during oxidation.

Identical compensating equipment~~s~~ (with the exception of the film) is placed in C_2.

The mercury lamp, with its arc in a horizontal position is placed vertically and symmetrically above the silica sockets.

Figure 5A



F - film, R - two stainless steel rings,
P - stainless steel platform, S - B.40 pyrex cone.

b) Calculation of Extend of Reaction.

Initially the rate of oxidation was calculated by the decrease in volume of oxygen in the cell containing the polymer film (C_1) using the equation of differential manometer. (N.A.Weir, Ph.D. thesis Glasgow University 1963, presubmitted). In which the amount of oxygen absorbed is correlated by this equation.

$$v = \frac{A.\ D.\ d.}{2 \times 13.6}$$

v is the volume of oxygen used by oxidation.

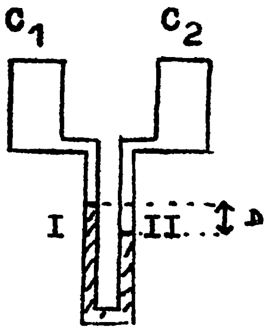
A is the area of cross-section of the manometer tube

D is the difference in manometer liquid height.

d is manometer liquid density.

However this equation was found unsuitable for this oxidation apparatus. This is because the pressure of oxygen in C_1 and C_2 changes simultaneously during oxidation hence the equation for differential manometer which demands that one pressure (C_2) remains constant during reaction is violated. However it was found possible to calculate the extend of reaction by using gas law. It is assumed that oxygen obeys the perfect gas laws at 27°C and within the pressure used.

V'_1 is the volume of C_1 and V''_1 is the volume of C_2. The pressure in C_1 and C_2 before reaction is P'_1 & P''_2, d is the density of manometric liquid, d_m (13.6) is the density of mercury in gms/cc, A is the surface area of cross-section of the manometer tube (in cm^2), D is the observed difference in levels (cm) and T is the reaction temperature (absolute)



During oxidation the meniscus of the manometer liquid in limb I rises and in limb II drops.

P'_1 = pressure in cell C_1

P''_1 = pressure in cell C_2

$P'_1 = P''_1$ (before oxidation)

P'_2 = pressure in C_1 during oxidation.

P''_2 = pressure in C_2 during oxidation.

$$P'_2 = P''_2 - \frac{d.D.}{d_m}$$

$$= \frac{P''_1 V''_1}{V''_1 + \tfrac{1}{2}A.D.} - \frac{d.D}{13.6.}$$

V'_2 = volume of oxygen in C_1, hence $V'_2 = V'_1 - \frac{1}{2}$ A.D.

The number of moles of oxygen used in oxidation

$(n - n') = (P'_1V'_1 - P''_2V'_2)/ RT$

By substituting the value of P'_2 and V'_2

$$n - n' = \frac{13.6\ A.D.P'_1\ (V'_1 + V''_1)}{27.2\ (V''_1 + \frac{1}{2}\ A.D\ )\ RT} + \frac{2d.V'_1.V''_1.D}{27.2(V''_1 + \frac{1}{2}A.D)RT}$$

$$- \frac{A.D^2.d(V''_1 - V'_1)}{27.2(V''_1 + \frac{1}{2}A.D)\ RT} - \frac{A^2.d.D^3}{5.44(V''_1 + \frac{1}{2}A.D)RT}$$

Since D, if measured every hour, is always in the range of 0.1 - 0.01 cm, ~~hence~~ D^2 and D^3 are small and can be regarded as negligible especially if $|V''_1 - V'_1| < 5$ cc. For this reason attempts had been made to make V'_1 as large as V''_2. Since in this case V'_1 & V''_1 are within 1-2 cc and $V''_1 + \frac{1}{2}A.D$ can be regarded as V''_1 or V'_1 and $V'_1 + V''_1$ is roughly equal to $2V'_1$ or $2V''_1$.

Hence the above equation can be simplified to

$$n - n' = \frac{A.D.P'_1}{RT} + \frac{d.D.V'_1}{13.6\ RT} = 2(A.P'_1/RT + d.V'_1/13.6RT\ )\ D/2.$$

$$= f.D/2.$$

f is the sensitivity of the apparatus if $D/2 = 0.001$ cm and it is clear that this sensitivity can be improved by making V_1' as small as possible. In this experiment a minimum volume of V_1' was about 95 cc. The sensitivity can also be increased by reducing the oxygen pressure P_1' or by increasing the temperature T, However the chemical reaction might be effected by the change of pressure or temperature.

Sensitivity of apparatus at 27°C and 600 mm Hg

A is 99/1400 cm^2, P_1' is 60 cm Hg , T is 300 K ,
R is 62400 cc. cm Hg / mole. degree.
V_1' is 51.40 + 42.15 cc = 93.55 cc.
and d is 94/100 gm/cc.
Hence the sensitivity (f) is 1.13 X 10^{-5} mole / cm.

The smallest amount of oxygen used during oxidation is f X 10^{-3} which is equal to 1.13 X 10^{-8} moles of oxygen. It will be shown later that it is quiet impossible to measure 1.13 X 10^{-3} moles of oxygen in practice.

It is of interest to calculate the change in sensitivity with pressure. It has been shown in page 28 that

$f = 2 (A.P_1' / RT + d.V_1' / 13.6 RT)$.
$f = k.P + C$. k and C are constants.
$k = 2A/RT = 7.55 X 10^{-8}$, $C = 2d.V_1' / 13.6 RT = .69 X 10^{-5}$.
Hence $f = 7.55 X 10^{-8} P + .69 X 10^{-5}$.

Calculation for photolysis.

For photolysis the same apparatus was used. The film was irradiated under vacuum.

$P_1 = 0. \quad P_2 = d.D/13.6$

$V_1 = V. \quad V_2 = V + A.D/2.$

$T_1 = T. \quad T_2 = T.$

$$n' - n = (P_2V_2 - P_1V_1)/RT = (\ d.D/13.6.\ X\ (V_1 + \tfrac{1}{2}AD) - 0)/RT$$

$$= (d.V_1/\ 13.6RT).D + (Ad/2X13.6\ RT\ )\ D^2.$$

If $D < 10^{-2}$ cm this is roughly equal to

$$n8 - n = (d.V_1/13.6\ RT)D = 6.9\ X\ 10^{-6}\ D/2.$$

Hence the smallest ~~mole~~ quantity of photolysis product which can be detected is $6.9\ X\ 10^{-9}$ mole.

c. Factors influencing the sensitivity of the oxidation apparatus

1. Area of cross-section of manometer-tube. From the equation it can be shown that the smaller A (area of cross-section) the smaller f becomes, that is, the more sensitive the aparatus becomes. However, this should not be too small to cause capillary effect on the manometer liquid.

2. A small volume would also mean a more sensitive apparatus. It is essential to construct the smallest effective volume V_1 and V_2 to obtain the maximum sensitivity of this apparatus.

3. The sensitivity of this apparatus is <u>not</u> inversely proportional to the density of its manometer fluid as was originally assumed. However, the sensitivity does decrease if the density increases. Eg. by using mercury as manometer fluid the sensitivity of this apparatus decreases by 9 times, but not by 16 times if mercury is used instead of dioctyl-sebacate.

Choice of manometer fluid is based on the following factors.

a. low density.
b. low vapour pressure.
c. low absorption of 2537 Å radiation.
d. low reactivity with oxygen.
e. low surface tension.
f. low viscosity.

3. On this basis, dioctyl-sebacate was chosen. However, silicone fluid might be more suitable due to its lower vapour pressure and lower surface tension although it has a slightly higher specific gravity.

4. The pressure and temperature will also influence the sensitivity of this apparatus, but they will also influence the reaction rate. 27 C and 600 mm. were found to be satisfactory standard conditions for the investigation.

D. <u>Factors which will influence the correct functioning of the apparatus</u>

1. Oxidation of grease. This is due to the 2537 Å ultraviolet light passing through the lower part of the B.40 fused silica sockets. It was found this effect caused a lot of irreproducable results until the silica sockets were covered by copper tube leaving only the top parts open to radiation.

2. Desorption of absorbed gases by the manometer fluid. This effect is especially apparent in the vacuum photolysis. It could be eliminated by degassing the fluid by freezing and thawing before carrying out the reaction.

3. Mercury vapour at room temperatue can interfere with the reaction in two ways.

a. It can be calculated (60) that 1 cm. column of air containing mercury vapour at 25°C is sufficient to reduce the intensity of 2537 A radiation to 20% of its incident value.

b. The absorption of 2537 A radiation by mercury vapour in an atmosphere of oxygen results in the production of ozone.

Absorption of radiation gives excited atoms of mercury.

$$Hg(6\ {}^1S_0) + h\nu\ (2537\ \text{Å}) \text{ —— } Hg^*\ (6\ {}^3P_1)$$

In absense of collisions these become deactivated by fluorescing, but oxygen quenches this fluorescence atomic oxygen and ozone being formed. (64)

$$Hg^*\ (6\,{}^3P_1) + O_2 \longrightarrow O + HgO$$
$$O + O_2 + M \longrightarrow O_3 + M$$

The overall reactions will be complicated if the oxygen contains ozone and this should be avoided.

4. To obtain a constant intensity of 2537 A radiation the silica sockets were cleaned thoroughly and the water level was kept constant at 1 cm. from the silica window. Dirt in the water can reduce the intensity of 2537 A so the water was changed after every experiment.

e. Estimation of Error.

The maximum error of this apparatus is given by the formula. (Derived from uptake equation on page 28)

$$\frac{dn}{n} = \frac{dA}{A} + \frac{dP}{P} + \frac{dV}{V} + \frac{d\ (\text{density})}{\text{density}} + \frac{dD}{D} + \frac{dT}{T}$$

$\frac{dA}{A}$ = since the manometer tubing is made of precision bore tubing this error would be very small.

$\frac{dP}{P}$ = dP can be in the range from 0 to 0.1 cm. Hg. and P taken as 60 cm.

$$\frac{dP}{P} = \frac{0.1}{60} = \frac{1}{600}$$

$\frac{dV}{V}$ = measurement of the volume of the cell in the oxidation apparatus is done by filling it from a burette. It can be reproduced to ± 1 cc.

Thus $\frac{dV}{V} = \frac{1}{93.55}$ or roughly $\frac{1}{100}$

$\frac{d\ (\text{density})}{\text{density}}$ = this can be assumed to be very small.

$\frac{dD}{D}$ = dD is difficult to judge since this depends on personal judgement of the manometer fluid level as seen through the microscope, but it would be reasonable to assume it to be ± 0.002 cm. In order to make $\frac{dD}{D}$ smaller, D is measured at a reasonable interval say every 30 to 60 minutes. D has a value between 0.30 - 0.80mm.

$$\text{Thus} \quad \frac{dD}{D} = \frac{0.002}{0.050} = \frac{2}{50} = \frac{4}{100}$$

The accuracy can be increased by increasing the interval time of reading. From this view it can be seen that however attractive is the idea to measure the initial rate of oxydation that is to say measuring every ten minutes it will cause great error. Since the difference in every ten minutes reading is about .008 cm. and the error due to.

a. reading the vernier can cause an error of ± 0.001 cm.

b. reading the meniscus of manometer liquid can at least cause an error of ± 0.001 cm. Adding this together the error in reading the movement of the manometer fluid is at least 0.002 cm.

Thus error of reading every ten minutes will be

$$\frac{0.002}{0.008} \times 100\% = 25\%.$$

d.T / T.   d.T is 0.01 K

T is 300 K

d.T / T = 0.01/300 which is small and can be neglected.

Thus $\frac{dm}{m} = \frac{dA}{A} + \frac{dP}{P} + \frac{dV}{V} + \frac{d(\text{density})}{\text{density}} + \frac{dD}{D} + \frac{dT}{T}$

$0 + 1/600 + 1/100 + 0 + 4/100 + 0$

$5/100.$

Thus by taking the reading every hour the accuracy or the limit of possible known error is 5%.

f. The oxygen supply system.

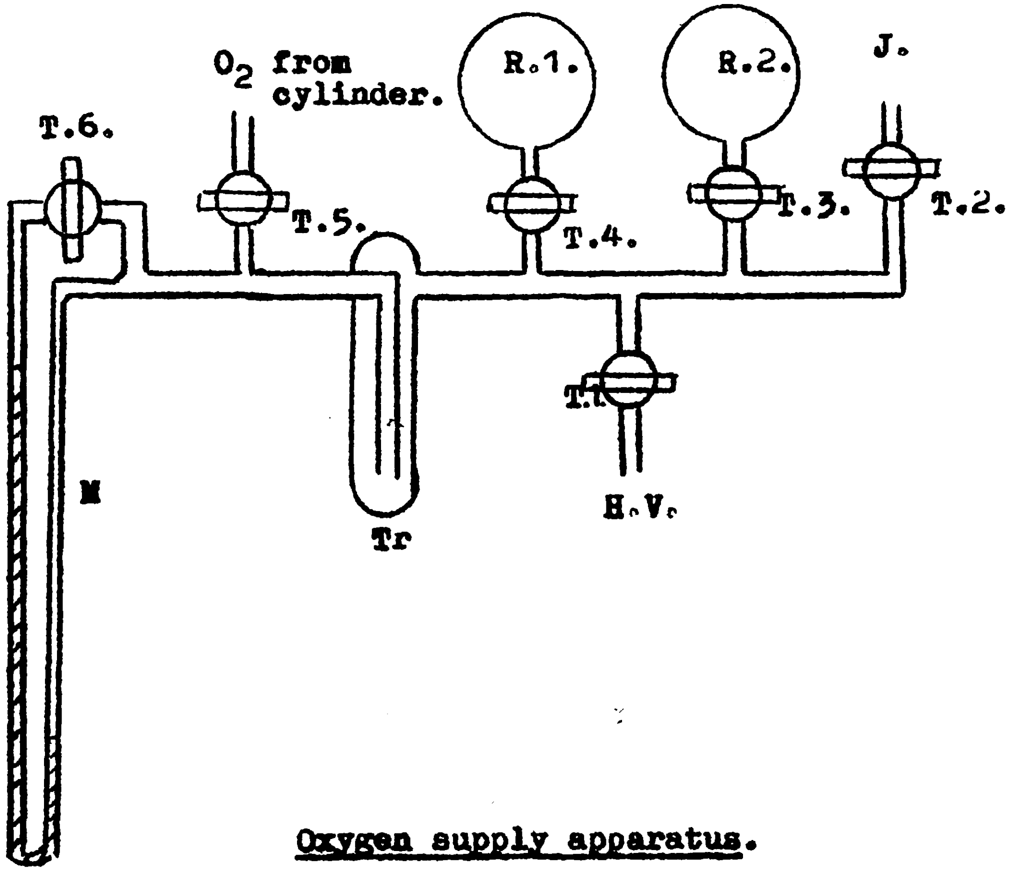
The system shown in Figure 5 is used to supply the oxidation apparatus with the required pressure of oxygen. This system is connected to the oxidation apparatus and evacuation is achieved by a mercury diffusion pump backed by a rotary oil pump.

The reservoir R.1. is filled with oxygen of about 700 mm Hg and R.2. with oxygen at a pressure of about 300 mm Hg or lower if the required pressured in the oxidation apparatus is lower than 300 mm Hg.

This system is supplied with oxygen direct from the cylinder by slowly opening the tap. If the pressure in the system is slightly less than the required pressure, the oxygen in R.2. is allowed to fill the gap. If the pressure in the system is slightly higher than the required pressure than some oxygen is allowed to enter R.1.

Water and other condensable gases (at - 78°C) from the oxygen cylinder are condensed in the cold trap.

Figure 5



Oxygen supply apparatus.

R.1, R.2, = Reservoirs, T1 to T6 → Stopcocks.

M - Manometer, Tr - cold trap, H.V. - to High Vacuum system.

J - Glass joint to oxidation apparatus.

Section 3

Analytical Techniques.

(1) Infra-red Spectra

A Perkin-Elmer Model 237 Spectrometer was used to measure infra-red absorption spectra of polystyrene films. The films were clipped in stainless steel rings. The film thickness used was 0.007 inches ± 0.001 inch.

(2). Ultra-violet Spectra.

A Unicam SP. ultra-violet and visible recording spectrometer was used. The films were clipped in stainless steel rings. The film thickness used was 0.007 inches ± 0.001 inch.

(3). Colourimeter Analysis.

The extent of colouration of polystyrene and methyl substituted polystyrenes were determined using an E.E.L. " Spectra " colourimeter, Films were fixed to the windows of sample compartment and oxidised in air.

(4)Mass Spectrometric Analysis of Products.

The gaseous products of photo-degradation were introduced into the sample inlet of an A.E.I.-M.S. 9 double focussing mass spectrometer . The sensitivity of this instrument is such that $10^{-6} - 10^{-5}$ mm Hg of volatile materials is adequate for analysis.

Instrument " blanks " were run and all peaks on the sample spectrum were compared with the corresponding peaks on the " blank " spectrum . The difference of the two spectrums was taken as the sample spectrum.

The photo-degradations were carried out in a specially made apparatus shown in Figure 7.

The Ultra-Violet lamp

The lamp used for producing short-wave ultra-violet radiation (2537 A) was a Hanovia " Chromatolite " lamp, which is a low pressure mercury arc.
The intensity of the two resonance lines at 1849 Å and 2537 Å are much greater than those of all the other wavelenghts present.
The output of this lamp was measured by Grassie and Weir.(51)

CHAPTER 3

CHAPTER 3

The high vacuum photolysis of p.α.m.s., polystyrene and various substituted polystyrene.

(1) Introduction.

To study how the photo-oxidation is initiated it has been found worthwhile to study the photolysis in order to define the action of ultra-violet radiation in promoting oxidation.

In order to avoid reaction with traces of oxygen, it was therefore necessary to eliminate the oxygen from the polymer by pumping it under high vacuum for a long period. The photolysis was also carried out under high vacuum condition.(10^{-5} mm Hg).

(2) Experimental.

a) Rate of Photolysis.

The photolysis was carried out in the oxidation apparatus at 27°C, as described in Chapter 2.

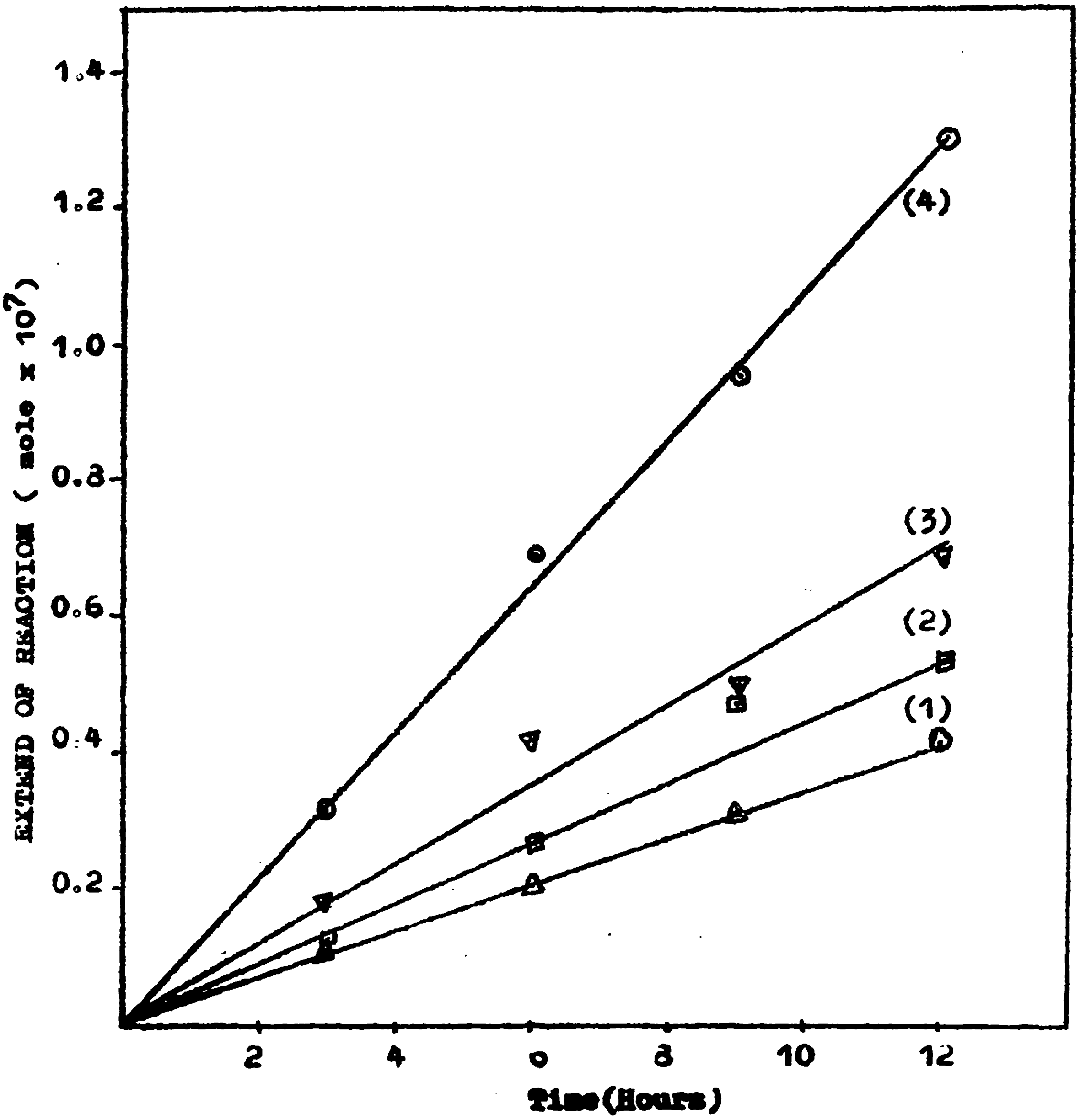
Films used were 0.007" ± 0.001" thick and the ultra-violet arc to film distance was 8 cm.

Typical photolysis results are given in Figure. 6 and Table 1 .

Table 1.

Polymer.	**Time.** (Hours)	**Extend of reaction.** (mole of products x 10^7)
(1). p.s.	0.0	0.0.
	3.0	0.11.
	6.0	0.20.
	9.0	0.31.
	12.0	0.42.
(2). p.p.m.s.	0.0	0.0.
	3.0	0.12
	6.0	0.26.
	9.0	0.47.
	12.0	0.53.
(3). p.2,5 di.m.s.	0.0	0.0.
	3.0	0.17.
	6.0	0.41
	9.0	0.49.
	12.0	0.69.
(4). P.α.m.s.	0.0	0.0.
	3.0	0.31.
	6.0	0.68.
	9.0	0.94.
	12.0	1.30.

Figure 6.



(1) - polystyrene, (2) - poly(para methyl styrene)

(3) - poly(2,5 dimethyl styrene),

(4) - p.α.m.s.

The rates of reaction are exceedingly small and not easily reproduced to a high degree of accuracy. In order to obtain more reliable relative values for the various polymers each experiment was repeated a number of times. The results obtained and the final average values are represented in Table 2.

Table 2.

Experiments	Number of moles of volatiles product per cm^2 of polymers with thickness of 0.007" per hour.			
	Polystyrene	p.para m.s.	p.2,5,m.s.	p.α.ms.
1	.390x 10^{-8}	.34x 10^{-8}	.62x 10^{-8}	1.05x 10^{-8}
2	.35 x 10^{-8}	.47 x10^{-8}	.71 x10^{-8}	.84 x 10^{-8}
3	.24 x 10^{-8}	.59 x10^{-8}	.59 x10^{-8}	1.20 x10^{-8}
4	.41 x 10^{-8}	.41 x10^{-8}	.51 x10^{-8}	1.14x 10^{-8}
5	.31 x 10^{-8}	.53 x10^{-8}	.65 x10^{-8}	.91 x10^{-8}
6		.37 x10^{-8}	.76 x10^{-8}	
Average	.34 x 10^{-8}	.45 x10^{-8}	.64 x10^{-8}	1.03x 10^{-8}

The above average results were taken as an hourly average of 12 hours photolysis products.

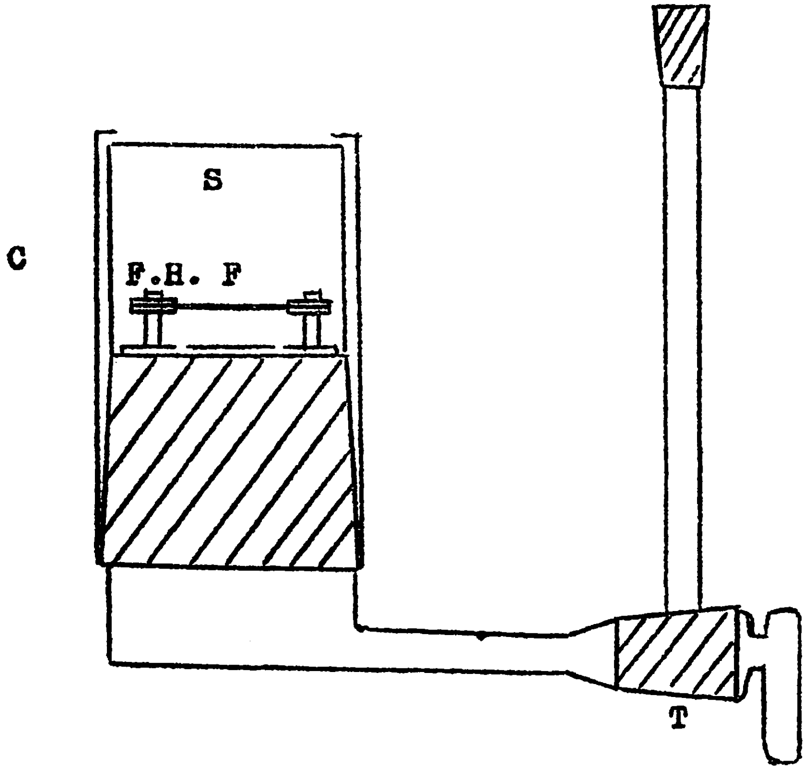
From these results it is obvious that polystyrene is the most stable polymer and polyα-methyl styrene is the least stable polymer among this group.The methyl substitution causes an increase in the rate of photolysis. A question which arises from this is whether methyl substitution makes the breaking of the C - H bond α to the phenyl group easier or whether it is due to the breaking of C - CH_3 itself. Information about this should be obtainable through an analysis of the products of degradation since some of the hydrogen which is the only volatile product of photolysis of polystyrene would be replaced by methane,mass spectrometric or radio-active tracer techniques might be applicable to the extremely small quantity of products available.

It seems possible that the increase in rate of photolysis is due to the combined effect of increase in C - H bond scission together with an additional contribution from C - CH_3 scission.

b) <u>Products of Photolysis.</u>

For the purpose of obtaining a sample of volatile products for analysis, photolysis was carried out in the modified apparatus illustrated in Figure 7.

Figure 7



Product of photolysis cell

F - Film, F.H. - Film-holder, S - Silica cell,

C - Cover to avoid irradiation of grease.

T - stopcock.

The analysis was carried out using an M.S.9 A.E.I. mass spectrometer. However, since the background peaks were large in comparison with the peaks from the volatile products the analysis of these products could not be made quantitative. It was established however, that products like H_2, CH_4, C_2H_6, are produced in the photolysis of poly -α- methyl styrene and the various substituted polystyrenes etc. Thus C-C as well as C-H bonds are broken during photolysis.

c. **Determination of Quantum Yield.**

Some information about the nature of a reaction mechanism can often be deduced from the value of the quantum yield. For example chain reactions often have overall quantum yields greater than unity. The quantum output of the source at 2537 A is 3.1×10^{-9} einsteins/cm^2/sec. at a distance of 3 inches. (57)

The quantum yield (ϕ) can be defined as

$$\phi = \frac{\text{Number of moles of gaseous product/cm}^2\text{/sec.}}{\text{Number of enisteins of 2537 A quanta absorbed/cm}^2\text{/sec.}}$$

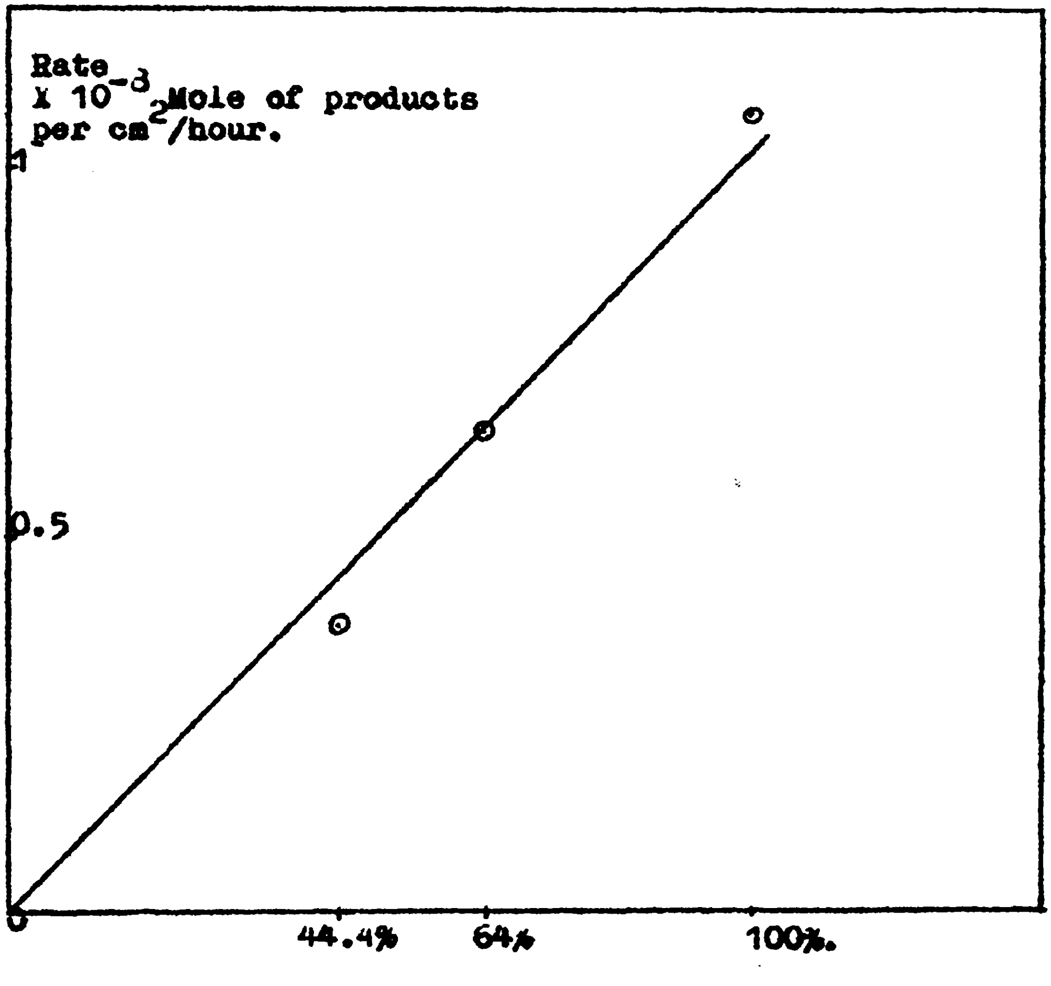
Polymer	Rate of gaseous products Produced/cm^2/hour	Quantum Yield
p.α.m.s.	1.03×10^{-8} mole	9.9×10^{-3}
polystyrene	0.37×10^{-8} "	3.2×10^{-3}
p.para. m.s.	0.45×10^{-8} "	4.0×10^{-3}
p.25 m.s.	0.64×10^{-8} "	5.7×10^{-3}

The quantum yield of all these polymers is less than unity, thus there is no positive evidence of a chain reaction.

d. Effect of Intensity on the Rate of Photolysis.

Due to difficulty in obtaining reproducible results in photolysis this experiment is limited to p.α.m.s. because this polymer gives the highest rate of production of volatiles. The result is shown in Fig. 8 which illustrates that the rate is proportional to the intensity of u.v. radiation. This is not conclusive evidence against a chain reaction which might be expected to give a square root relationship, but taken in conjunction with the relatively low overall quantum yield it does seem likely that a chain reaction is not involved.

Figure 3



Relative intensity.

3. Discussion of the Photolysis Processes.

a. Primary Processes.

In view of the fact that hydrogen is the only volatile product of photolysis of polystyrene the primary chemical effect of the 2537 A radiation must be to break C-H bonds. From methyl substituted styrenes methane also appears so that the scission of C-CH_3 bonds must also be considered as a possible primary chemical reaction in these polymers. It is, therefore, of interest to consider the most likely part at which bond scission will take place under the influence of radiation in the light of the experiments which have been described above as well as any independant evidence which is available.

Of course 2537 A quanta are not absorbed directly by C-C or C-H bonds, shorter wavelength of the value of 1600 A are required. Instead the 2537 A quanta must be absorbed by the orbitals of the benzene rings, the energy being subsequently transferred to the appropriate scissionable bond.

In polystyrene there are three types of C-H bonds, namely those joining the hydrogen atoms directly to the benzene ring, which are of type (sp^2) and the methylene and tertiary C-H bonds associated with the main chain carbon atom and both of which are of type (sp^3).

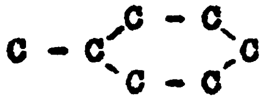
These bonds are not all equivalent and their order of breaking will be determined principally by two factors namely, bond dissociation energy and hyperconjugation.

Bond Dissociation Energy.

The concept of bond energies has been employed in the estimation of heats of atomization, stabilization and strain energy. Bond energies may be obtained from molecules free from conjugation strain etc. so that the difference between the observed and calculated values of heat of atomization would give a measure of the conjugation or resonance energy if this difference ~~is~~ were positive and strain if ~~this~~ it ~~is~~ were negative.

Recent results on bond energies in hydrocarbons was done by Bernstein(52), he found values, Table 3. for the various types of bonds of C-H and C-C bonds.

Table 3

	Bond type	Bond energy of C-H bond k.cal./mole.
sp^3	CH_4	99.49
	$-CH_3$	98.46
	$>CH_2$	97.57
	$\geqslant CH$	97.26
sp^2	$=CH_2$	103.0
	$\diagup\overset{H}{\overset{\vert}{C}}=$	102.3
		Bond energy of C-C
sp^3	$\geqslant C - C \leqslant$	85.45
sp^2	$=C - C=$	109.0
sp^3-sp^2		91.40

From the values of bond energy above it is clear that the easiest bond to break in photolysis is the C-C main chain bond followed by the C-C bond connecting the α carbon atom and the benzene ring, and then the C-H bond of the α hydrogen atom.

However, there is strong chemical evidence in favour of the breaking of C-H bond of the α carbon atom in the initiation reaction. This is supported by e.s.r. spectra of Gamma irradiation of polystyrene by Florin et el.(53) They found no strong hf interaction between the radical and main chain hydrogens. If this were so, the width of the bands in the e.s.r. spectrum of poly ($\alpha.\beta.\beta$ trideuterostyrene) would be reduced to about one third of its value in undeuterated polystyrene, also in place of three peaks, the deuterated compound would contain five.

The principle hf interaction is with the two ring hydrogens in the ortho position. Positions other than ortho are excluded by the fact that poly (p - deutrostyrene) and poly (m - methylstyrene) also have the common e.s.r. spectrum of irradiated polystyrene. The spectrum of irradiated poly (2,5 dichlorostyrene) is different, thus the whole distribution of the free electron wave function is altered.

From thermal degradation data which will be discussed later it is also noted that ortho substitution by methyl groups affected the rate of degradation to the greatest extent.

Overlapping of the p orbital of the α carbon, with the wave function of the ortho methyl group in the benzene ring may cause a reduction in the energy needed to form the radical and the α position.

The energy associated with 2537 A radiation (112 k. cal./mole) is sufficient to break all of these bonds.

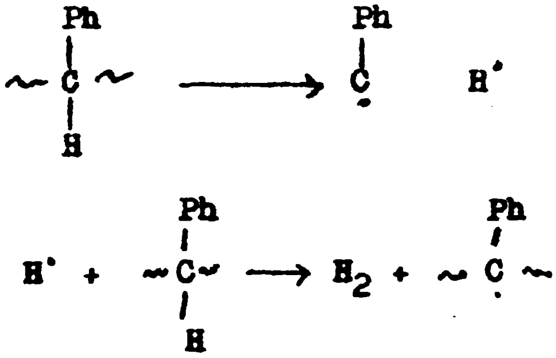
b. Secondary Processes

Kargin and his coworker (54) ~~who~~ found that on irradiating polystyrene with dosages of high energy radiation greater than 2500 M. rads, the contours of two bands in the infra-red spectrum altered markedly, shoulders appearing at 675 cm^{-1} on the very intense 700 cm^{-1} band and at 825 cm^{-1} on the weak band at 840 cm^{-1}. Absorption in the 825 and 675 cm^{-1} regions occur in the spectra of compounds containing double bonds of the type $RCH = CR_2$ (808 - 833 cm^{-1}) and cis $RCH = CHR$, (675 - 729 cm^{-1}) (55). Brockes (56) suggested the formation of conjugation in the polystyrene backbone. The hypothesis is supported by the fact that double bonds of the type $RCH = CR_2$, formed in this way, correspond to the bands at 825 cm^{-1} which is present in the spectrum or irradiated polystyrene.

The formation of such a system involves a decrease in the number of C - H bonds in the polymer backbone, which in fact occurs, because the intensity of the C - H bond at 1376 cm^{-1} decreases.

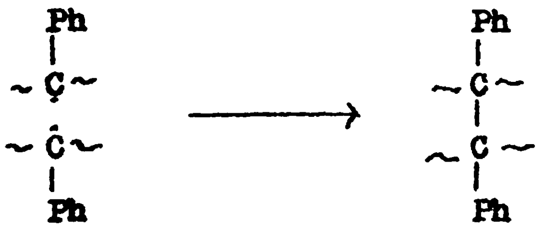
A number of well defined ~~factors~~ features of the overall effect of irradiation on polystyrene must be accounted for ~~the understanding~~ in terms of the secondary reactions of the primarily formed radicals. Insolubility develops due to crosslimking, hydrogen is produced and the polystyrene discolours.

The most obvious explaination of deyelopment of insolubility is that the hydrogen atom liberated in the primary step removes from an adjacent molecule another hydrogen atom, to form molecular hydrogen. The two polymer molecule then combining to form a cross-linked polymer.



$$\sim\overset{Ph}{\underset{H}{C}}\sim \longrightarrow \overset{Ph}{\dot{C}} \quad H^{\bullet}$$

$$H^{\bullet} + \sim\overset{Ph}{\underset{H}{C}}\sim \longrightarrow H_2 + \sim\overset{Ph}{\dot{C}}\sim$$



This implies that one hydrogen molecules is formed per cross-link, but Wall and Brown[44] found that the number of crosslinks formed in polystyrene on irradiation exceeds the number of H_2 molecules liberated. They suggested that crosslinks can be formed without H_2 production, by addition of the hydrogen atom produced by rupture of the C - H bond in the polystyrene backbone, and the residual polymer chain across a double bond in the benzene ring of a neighbouring molecule and forming a crosslink.

CHAPTER 4

Oxidation

Measurement of Rate

Polymer films of 0.007 inches in thickness were oxidised in the apparatus described in Chapter 2. Poly (2, 4, 6 trimethyl styrene) films were too brittle to handle, so they were cast on a glass surface and oxidised in this form.

The progress of the reactions were followed by measuring the rise in manometer liquid in the limb connected to the compartment containing the film. The rise in manometer liquid can be correlated to oxygen absorption (Chapter 2).

It was found that the rate during the first few hours tended to be slightly variable and since in any case the rates were relatively low it was found to be most convenient to take an average rate over the first 24 hours of reactions. Typical results are given in Table 4 and illustrated in Fig. 9

2. Factors causing variation in the initial rates.

It is not clear why the rate of oxygen absorption is so variable initially, but it may be due to one or more of the following factors.

Table 4

Photo-oxidation of p.α.m.s. at 27 C, 600 mm O_2.

Time. (hour)	Manometer reading increment X 10^3cm for film (1)	(2)	(3).	(per hour)
1	39	74	68	
2	37	68	61	
3	36	46	57	
4	36	48	44	
5	35	36	40	
6	37	40	36	
7	36	44	35	
8	36	36	36	
9	35	36	34	
10	33	37	33	
11	34	35	34	
20	33	35	35	(average hourly reading when left overnight)
21	33	34	34	
22	36	30	35	
23	33	30	38	
24	32	24	35	
25	27	29	32	

Figure 9

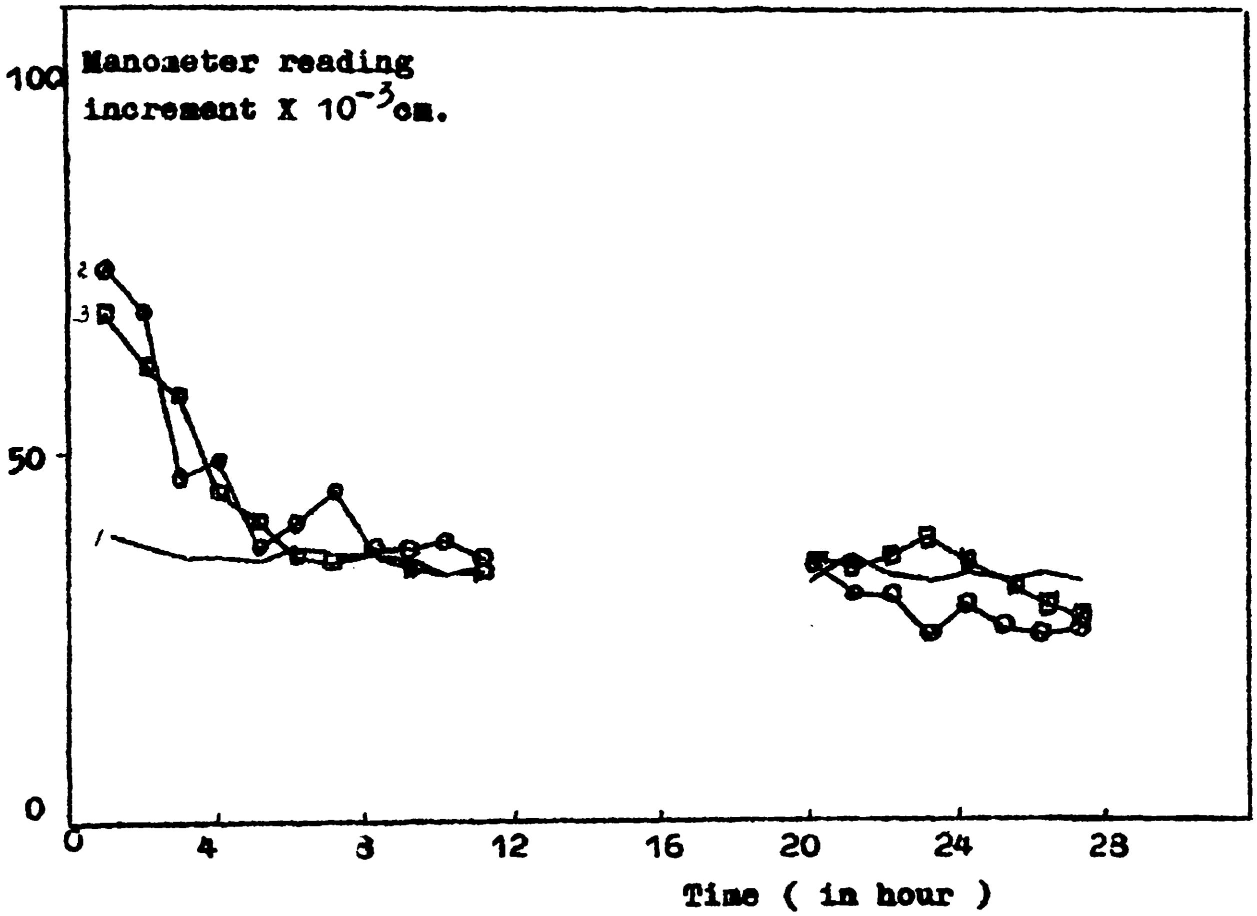


Photo-oxidation of p.α.m.s. at 27 C.

Three typically good results of photo-oxidation. Curve 2 and 3 show good agreement, but curve 1 shows Some deviation. However by taking the average reading for 24 hours (or more) the results are in reasonable agreement.

a. Formation of volatile products

Gaseous products are formed in the cell during oxidation and their volume would compensate or partially compensate for the volume of oxygen lost by polymer absorption and this will result in an apparent deceleration in the rate of oxygen uptake.

It is to be expected that a high proportion of the products would be carbon dioxide and water, and these may be removed by the introduction of appropriate absorbants into the oxidation cell.

0.5 gm. of anhydrous magnesium perchlorate (M. A. R. grade) to remove water and roughly 0.5 gm. carbsorb (M. A. R. grade) to remove carbon dioxide were introduced into the cell in a small beaker. Similar amounts were put in the other to compensate for change in volume and to remove any water vapour and carbon dioxide if they were present. Obviously carbon dioxide and water vapour are formed since the rate is greater in presence of the absorbants. However, they do not in any way change the general shape of the reaction curve nor do they improve the degree of reproducibility. These absorbants were used in all subsequent experiments.

b. Diffusion

During reaction the polymer contains a certain concentration of oxygen. This concentration must be determined by the equilibrium between the consumption of oxygen by the reaction and the replacement of oxygen by diffusion from the oxygen atmosphere in the reaction cell. In Chapter 2, (Section - choice of film thickness) it has been shown that the rate of diffusion is greater than the rate of reaction thus this is not a diffusion controlled reaction.

c. Reduction of Light Intensity.

It has been shown by Achhammer (57) et el. that carbonyl and other unsaturated chromophores are formed on the chain during the oxidation of polystyrene. Since these compounds have high extinction coefficients for 2537 Å radiation, a build up of these on the surface would result in a considerable decrease in intensity of radiation reaching the bulk of the polymer. Thus the surface layer containing these highly absorbing groups would act as an internal filter protecting the bulk of the polymer from the activating radiation, and this would be reflected in a diminished rate of oxidation.

d. Formation of Inhibitors

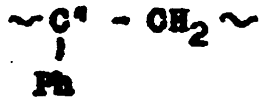
Radical reaction inhibitors like benzaldehyde are formed during oxidation of polystyrene (58) This can suppress the chain scission which occurs during oxidation, and it is probable that such compounds can also retard the oxidation process itself.

e. The Reaction Mechanism

It has been shown (59) that in the oxidation of cumene the reaction of two peroxy radicals to yield an oxygen molecule occurs.

$$2\ ROO^{\cdot} \longrightarrow O_2 + ROOR.$$

It is possible that this effect may also occur in polystyrene oxidation. It is reasonable to assume that the first layers of polymers are most subjected to oxidation because they received most of the photons and they are in close contact with oxygen.

Assuming this radical 

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

is an active centre. The rate of production of active centre can be given as

$$V = k_a I. C\alpha.$$

k_a = a constant.

I = Intensity of radiation in Einstein/cm^2

C_α = number of unreacted α hydrogens per cm^2 within the thickness of 0.001 mm.

Suppose N is the total number of molecules of oxygen in gas phase, which is of volume V. Then the concentration of oxygen is

$$N/V \text{ molecules/cc.} = C$$

The rate of oxidation can be expressed as

$$V \propto (k_a\ I\ C_\alpha\ )\ C.$$
$$= k.\ k_a\ I\ C_\alpha\ C.$$
$$= K\ I.\ C_\alpha\ C.$$

C_α is steadily decreasing because once an active centre get oxidised it becomes a non-active centre or a non initiating and propagating centre.

Eg. $2\ ROO' \rightarrow ROOR + O_2$

C can be assumed to be constant because the amount of oxygen used in the reaction is small compared to the available oxygen. Hence it can be concluded that the rate of oxidation decreases with the decrease of C_α

3. Effect of variables on rate of oxidation

The effects of several variables on the rate of oxidation were investigated. The standard conditions of the reaction are, oxygen pressure 600 mm. Hg, film thickness 0.007", temperature 27 C, and distance between u.v. arc and film 8 cm. (which is regarded as 100% intensity).

a. Effect of oxygen pressure.

It has already been shown that for each rate of oxidation at a particular pressure, several oxidation experiments have to be carried out in order to get a good statistical average. However, this consumes a lot of laboratory time, hence it was decided to do one oxidation rate for each particular pressure, except for p. α. m. s. and polystyrene where several rates were averaged Table 5 and Fig. 12-16 show the results of rate of oxidation against pressure of oxygen.

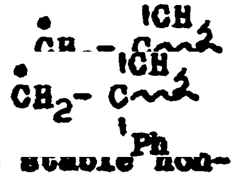
Table 5.

Oxygen Pressure	Rate of oxidation		10^8 mole/cm^2/hour	
(mm. Hg).	p.α.m.s.	p.s.	p.p.m.s.	p.2,5 di.m.s.
600	17.30	8.95	12.60	13.92
500				16.56
400	13.35	10.21	11.84	14.45
300		7.89	11.05	11.72
200	8.86	8.54	13.15	15.76
100	5.48	7.15	9.77	14.80
50	4.69		11.82	
40				
30		8.20		
20	2.2		6.30	8.69
10	1.53	4.16		

From these results it is clear that except for p.α.m.s. the rate of oxidation of all the other materials are independent of oxygen pressure abuve approximately 50–100 mm. Hg.

This is in agreement with the results of Bolland (21) and Bateman (20) who concluded that in general the more difficult substances to oxidise showed little if any pressure dependance above a few mm. Hg. of oxygen.

In the case of p.α.m.s. it is probable the

In the case of p.α.m.s. it is probable the  $\dot{C}H_2-\overset{CH_3}{\underset{Ph}{C}}\sim$ is very unstable and decomposes very quickly to stable non-radical compounds if it does not immediately react with an oxygen molecule. Thus in this case one would expect the rate of oxidation to be dependant upon the concentration of oxygen to much higher oxygen pressures.

b. Effect of Radiation Intensities.

The intensities of 2537 Å radiation incident on the polymer film was varied by varying the arc-film distance and the corresponding rates of absorption of oxygen were obtained. Table 6 Fig. 10, 11.

The graph shows that the rate of oxidation of p.α.m.s. and polystyrene is proportional to the intensity of radiation.

Table 6

Intensity of radiation	Rate in mole/cm^2/hour	
	p.α.m.s.	p.s.
100%	1.73×10^{-7}	0.90×10^{-7}
64%	0.97×10^{-7}	0.78×10^{-7}
44.4%	0.76×10^{-7}	0.31×10^{-7}

Figure 10

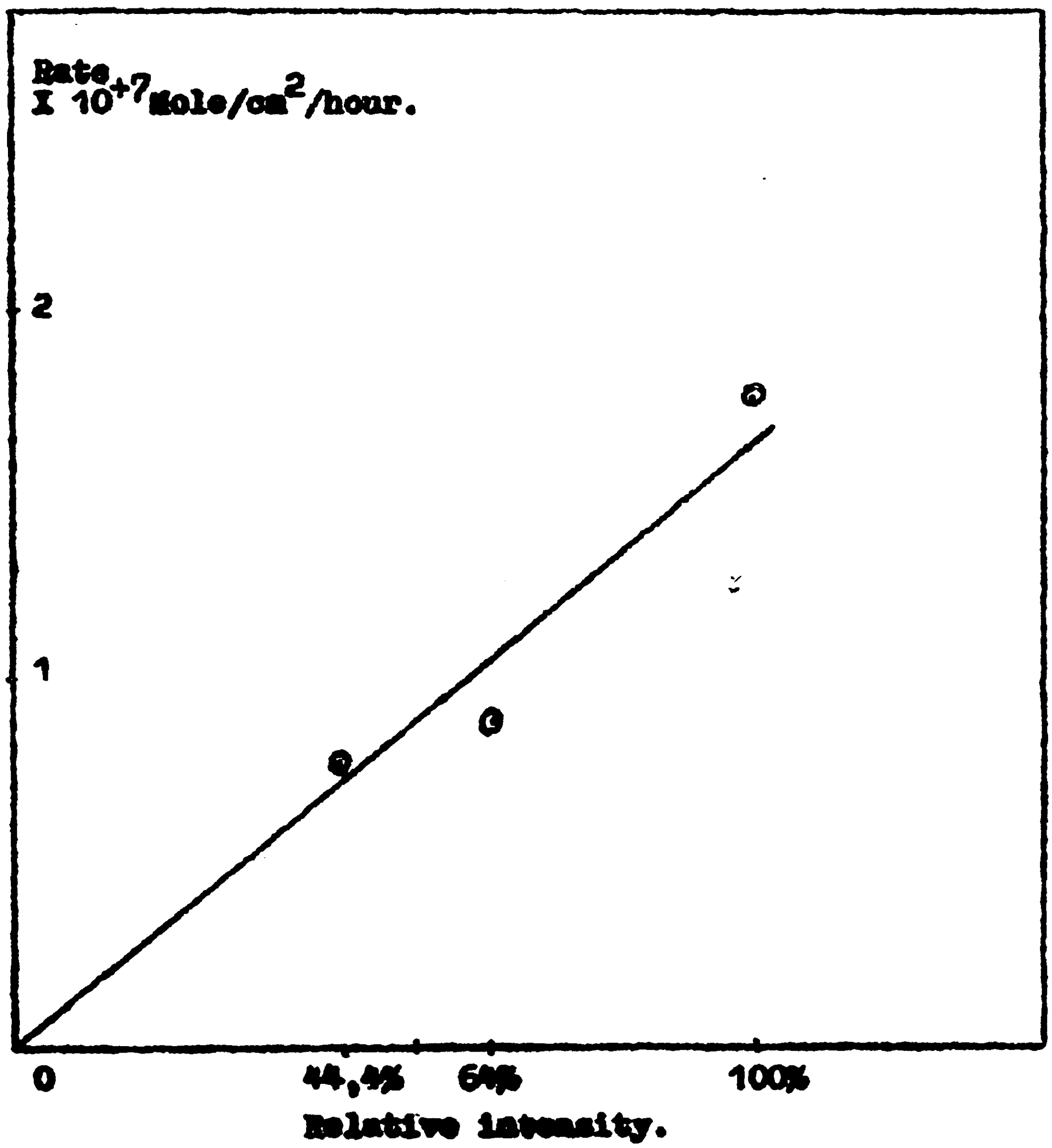
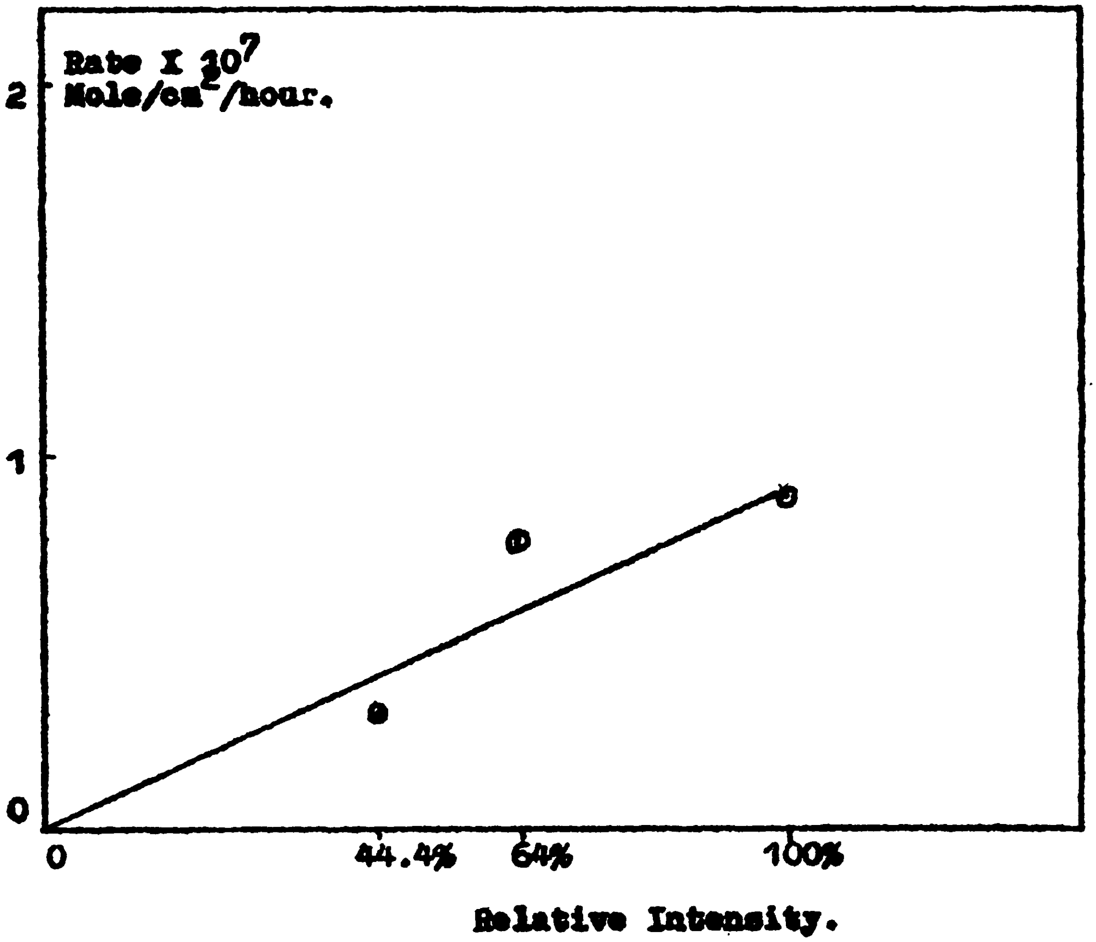


Figure 11



The rate is thus a first order function of intensity. This indicates that there are no excess active radicals unattacked by oxygen because if this were so then the rate would be independent of the radiation intensity.

c. The Quantum Yield

The quantum yield, ϕ , for this reaction can be defined by

$$\phi = \frac{\text{Number of moles of } O_2 \text{ absorbed/cm}^2\text{/sec.}}{\text{Number of einsteins of 2537 A quanta absorbed/cm}^2\text{/sec.}}$$

Using rates of oxidation obtained as in Fig. 12,13,14,15,16 and the quanta output of the lamps quoted [illegible] 51., the following values of quantum yield shown in Table 7 were obtained.

Table 7

Polymer	Rate of oxidation mole/cm^2/hour	Quantum Yield
p.α.m.s.	1.73×10^{-7}	1.54×10^{-2}
polystyrene	0.90×10^{-7}	0.83×10^{-2}
p.p.m.s.	1.20×10^{-7}	1.07×10^{-2}
p.2,5 m.s.	1.48×10^{-7}	1.32×10^{-2}
p.2,7,6 m.s.	2.10×10^{-7}	1.87×10^{-2}

Figure 12

p.α.m.s.

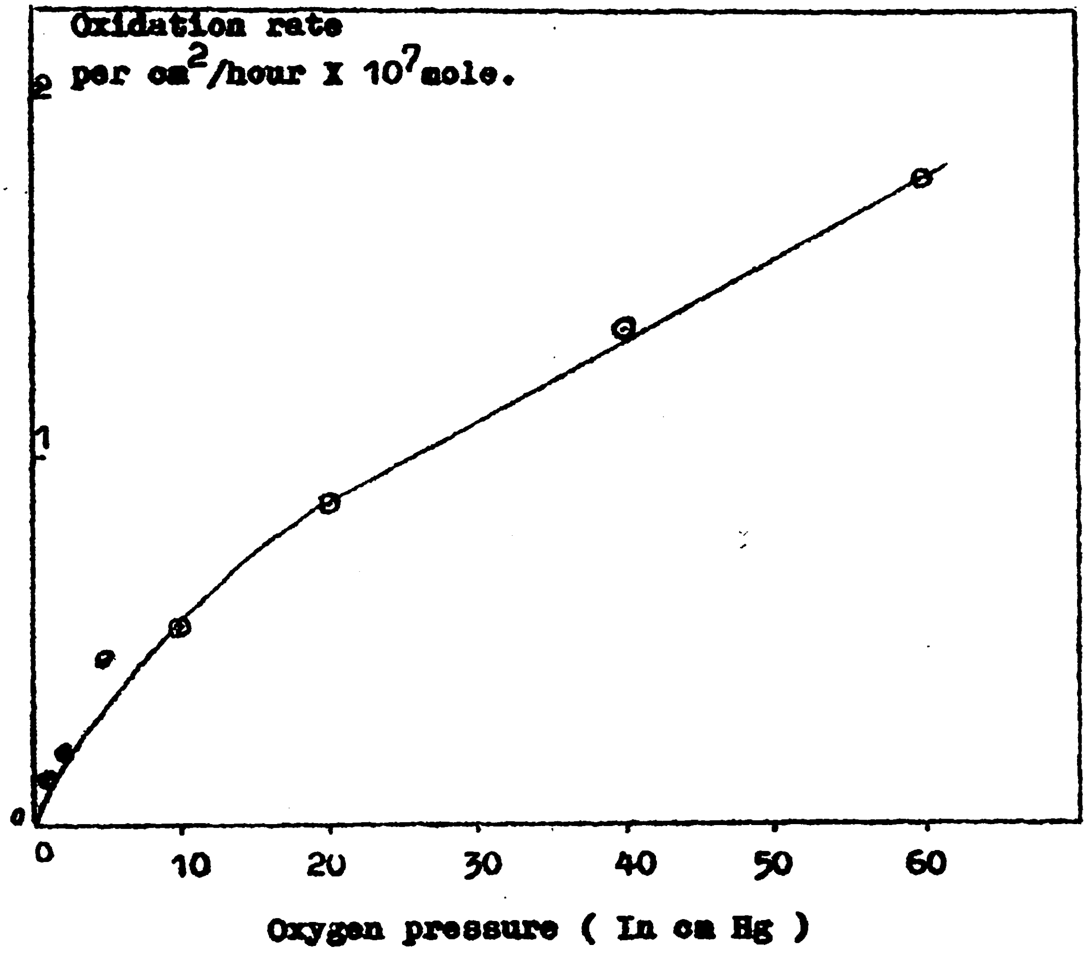


Figure 13

Polystyrene.

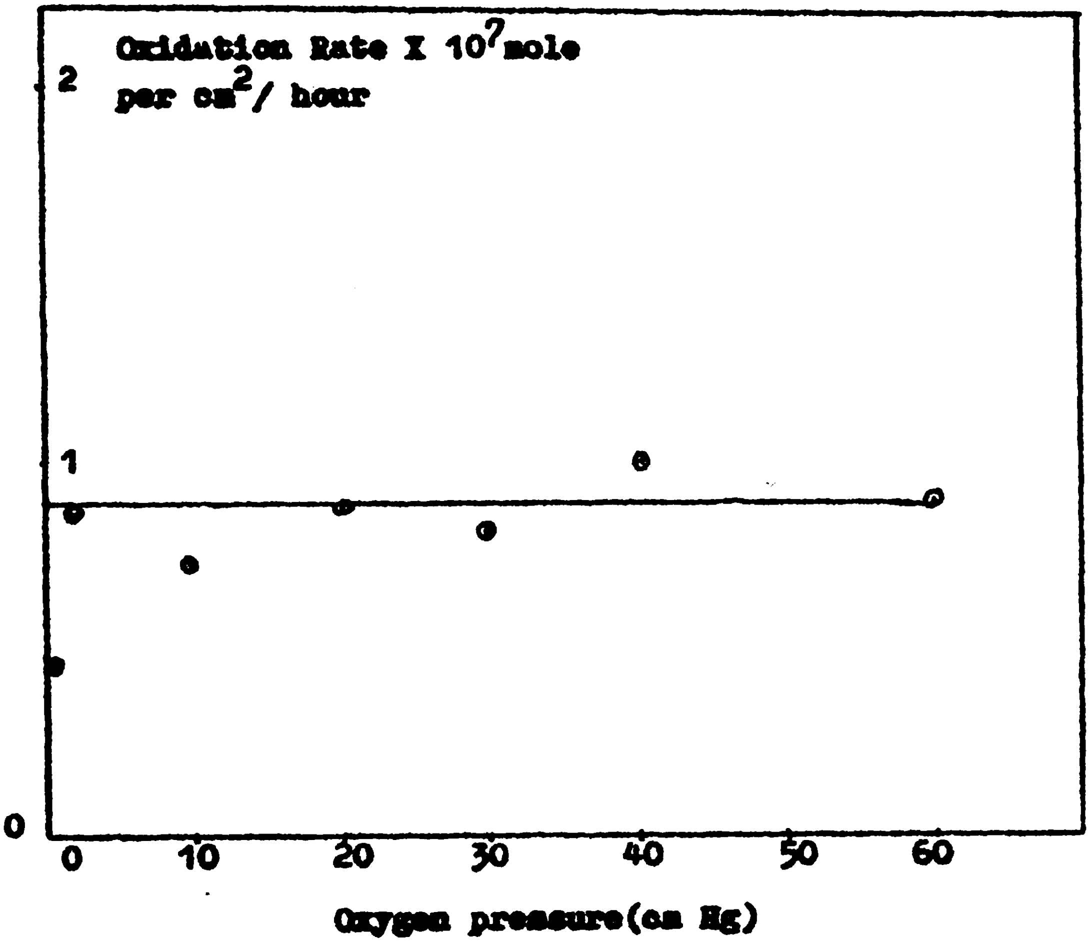


Figure 14

Poly(2,4,6 trimethyl styrene).

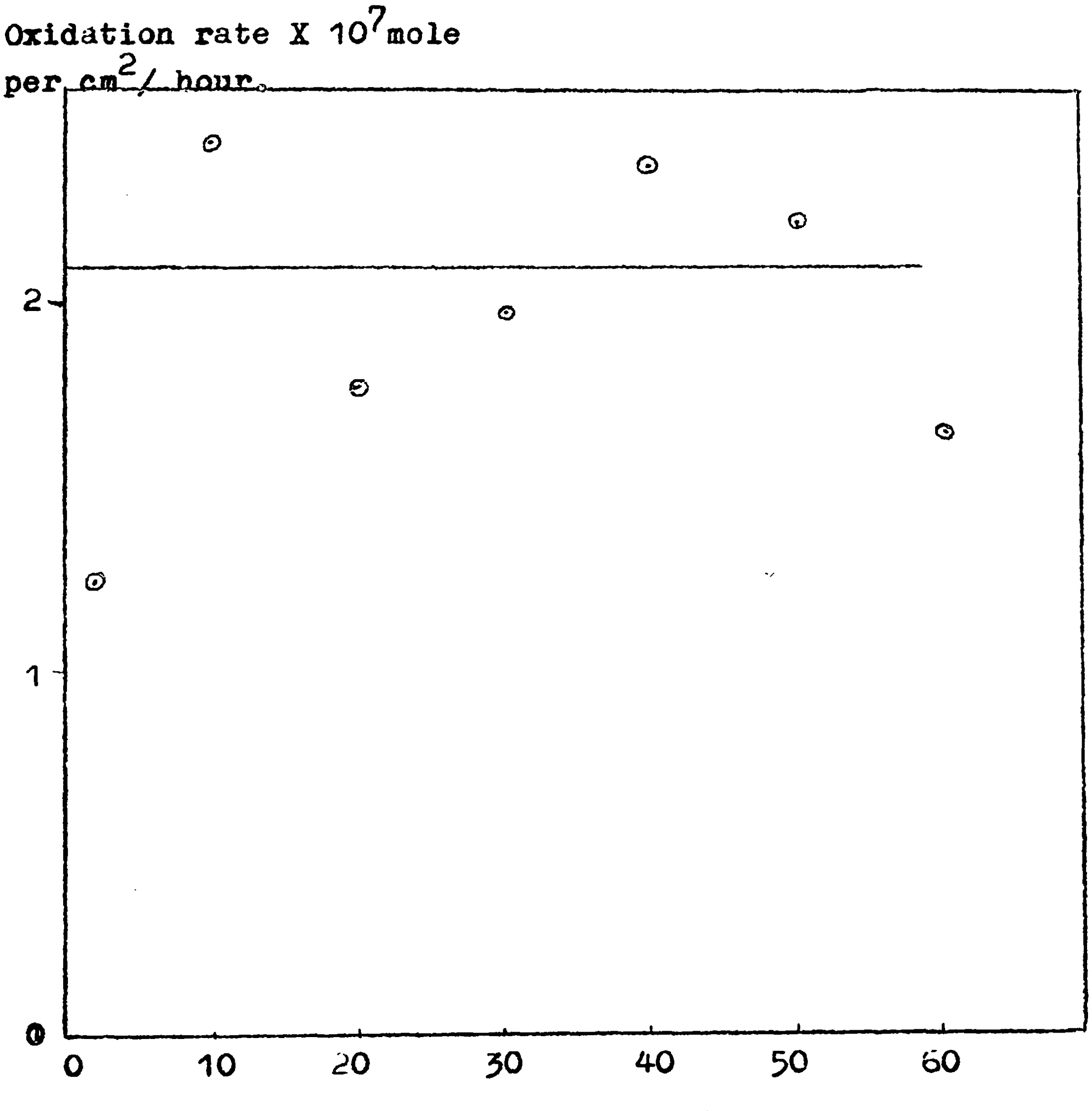


Figure 15.

Poly(2,5 dimethyl styrene).

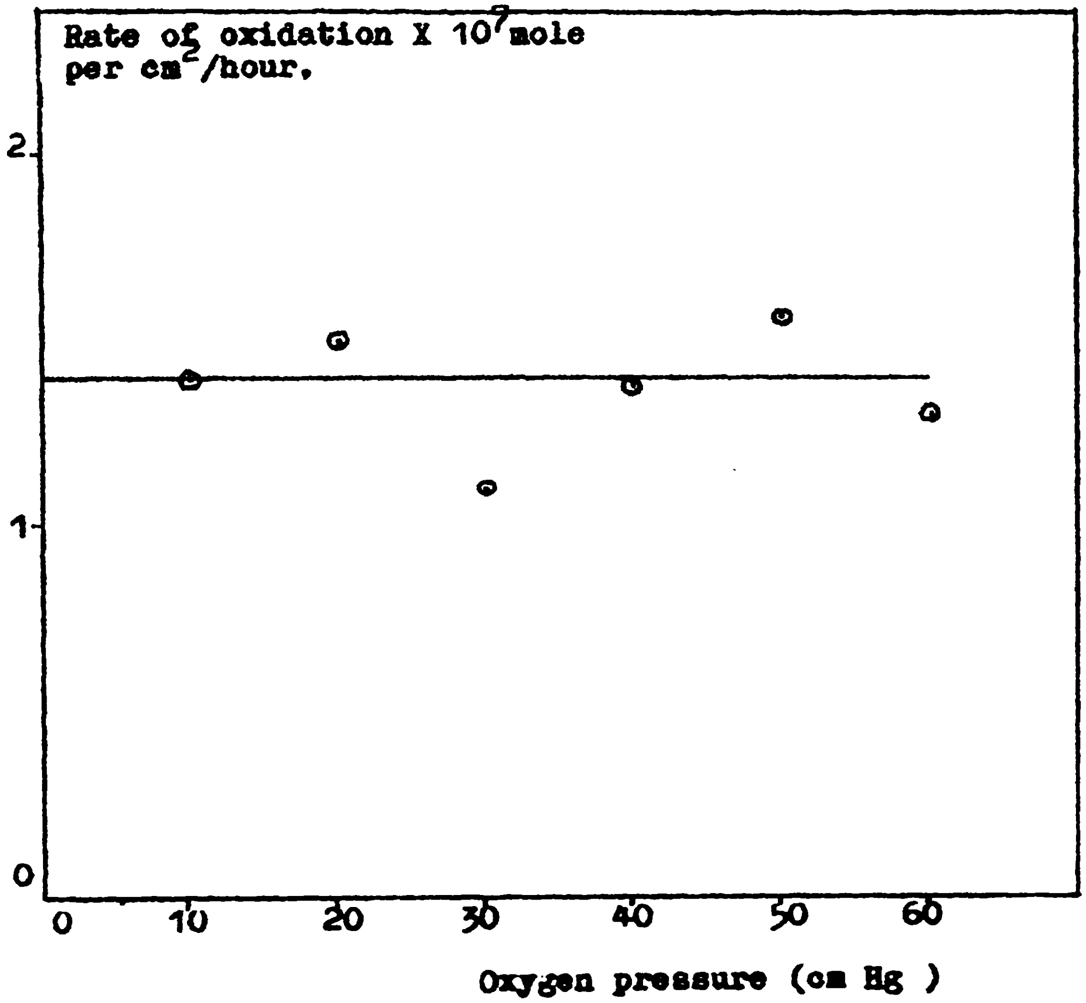
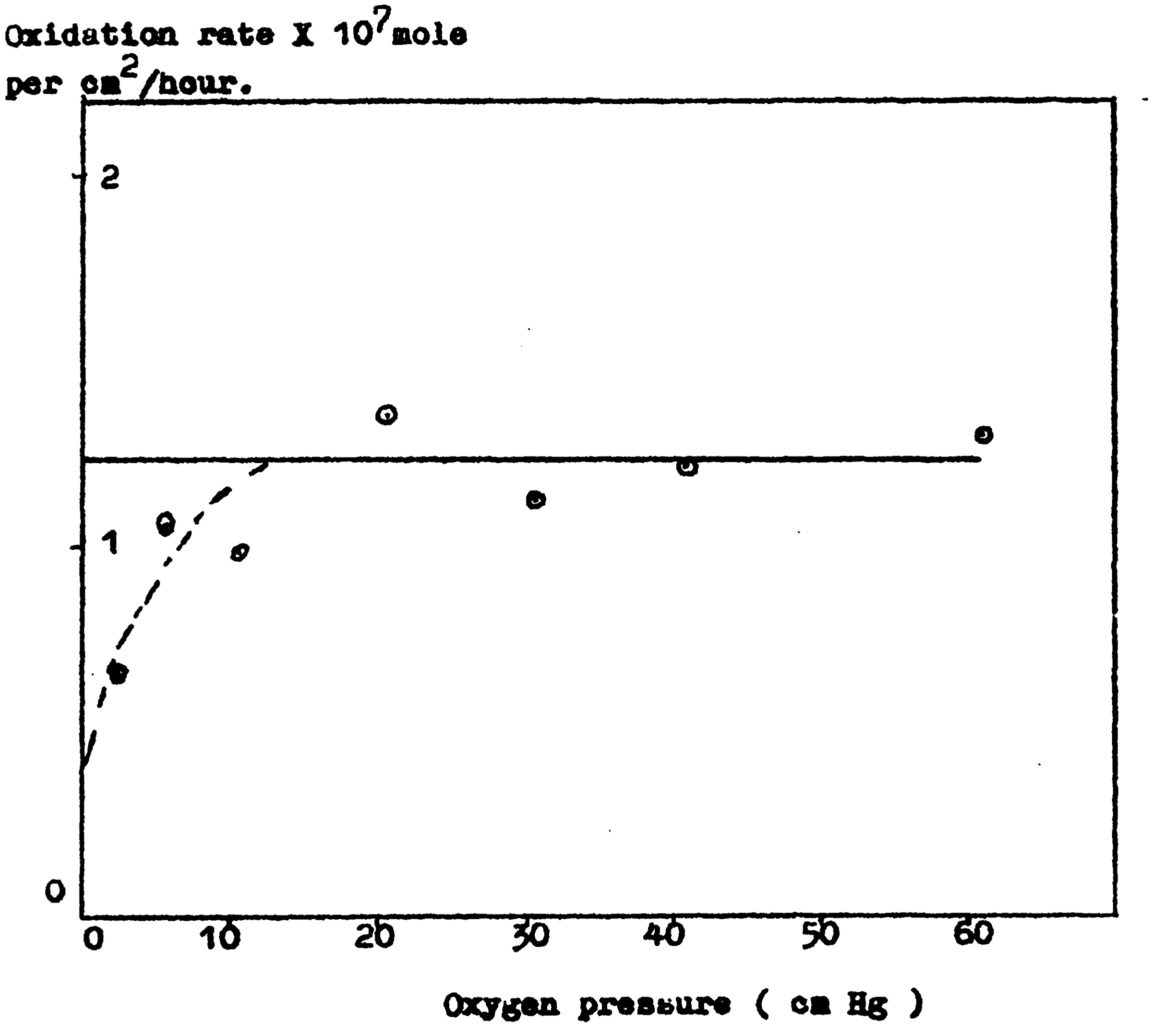


Figure 16

Poly-para methyl styrene.



The low value of less than unity obtained in each case indicates that the oxidation of polystyrene p.α.m.s. and other substituted styrenes do not proceed by a chain reaction.

d. Effect of Film Thickness

It is known that because of the high extinction coefficient at 2537 Å absorption of the incident radiation is almost complete across a film 0.01 mm. thick. Hence the greater part of the photo-oxidation will take place in a 0.01 mm. layer of polymer adjacent to the illuminated surface, the bulk of the polymer being relatively unaffected. Films used in all the experiments are of 0.007" thick which is equal to 0.025 cm. thick or 0.25 mm. thick.

However, in order to avoid any doubt that the film thickness might effect the rate of oxidation an experiment with p.α.m.s. with different thickness was made. The results are shown in Table 8.

Table 8

Polymer Film Thickness	p.α.m.s. Rate of oxidation 10^8 mole/hour
0.007 inches	17.30
0.014 "	17.90
0.020 "	17.70

CHAPTER 5

Chapter 5

1. The mechanism of the oxidation reaction.

a. Primary Processes

It was shown in Chapter 3 that the high vacuum irradiation of polystyrene with 2537 A quanta leads to the fission of tertiary C-H bonds, that is

$$RH \longleftrightarrow \dot{R} + \mathring{H}$$

The vacuum irradiation of p.α.m.s. results in chain scissions with the production of monomers and a range of volatile products mainly benzene and hydrogen.

$$R_n \xrightarrow[-]{h\nu} \dot{R}_{n-i} + \mathring{R}_i$$

In the presence of oxygen molecules it is expected that the life time of these radicals is much shorter due to combination with oxygen.

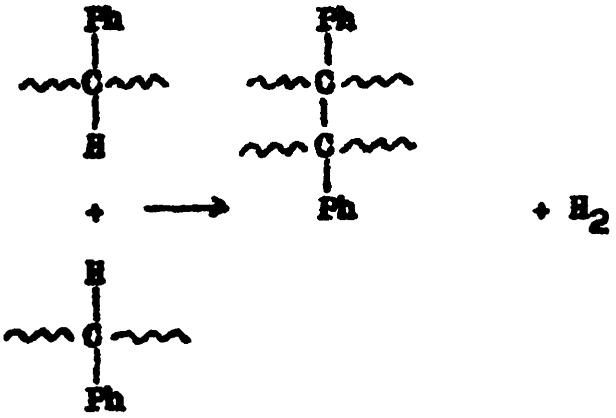
b. Secondary Processes

The radicals produced in the primary initiation process will combine with oxygen to form the corresponding radicals.

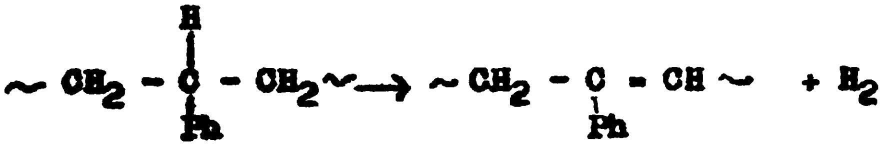
$$\dot{H} + O_2 \longrightarrow \dot{H}O_2$$

$$\dot{R} + O_2 \longrightarrow \dot{R}O_2$$

Before discussing further it is advantageous to compare the results of photolysis and photo-oxidation. In photolysis the number of moles of volatile products was measured. For every molecule of hydrogen produced it was shown that overall effect is that a cross-link may be produced,

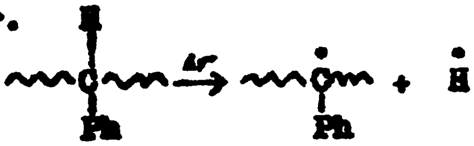


or a double bond formed.



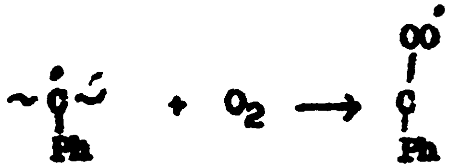
$$\sim CH_2 - \underset{Ph}{\overset{H}{C}} - CH_2 \sim \longrightarrow \sim CH_2 - \underset{Ph}{C} = CH \sim \quad + H_2$$

In the presence of oxygen these reactions are likely to occur.

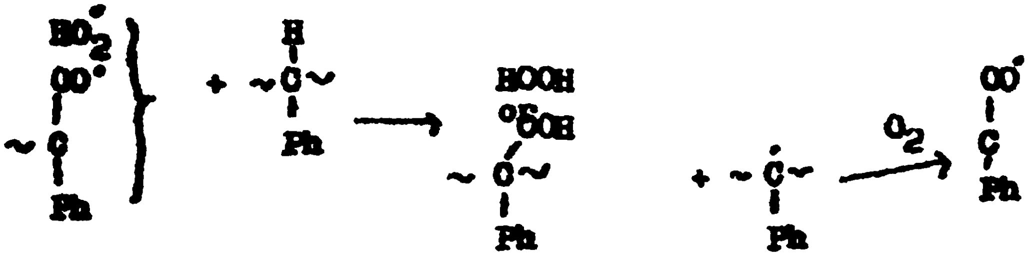


$$\sim\sim \underset{Ph}{\overset{H}{C}} \sim\sim \xrightarrow{h\nu} \sim\sim \underset{Ph}{\dot{C}} \sim\sim + \dot{H}$$

$$\dot{H} + O_2 \rightarrow H\dot{O}_2$$



The resulting radicals may either destroy each other or abstract further hydrogen atoms from the polymer and thus establish what amounts to a chain process.



Comparison of rates of photolysis and oxidation give the ratios shown in Table 9. between the number of molecules of oxygen absorbed during photo-oxidation and the number of molecules of volatile material evolved during photolysis.

Table 9

Polymer	$R = \frac{\text{No. of molecules of } O_2 \text{ absorbed/sec.}}{\text{No. of molecules volatiles evolved/sec.}}$
p.α.m.s.	18
polystyrene	26
poly 2,5 m.styrene	23
poly p.m. styrene	26

To explain how the oxygen molecules are being used in such quantity there are these possibilities.

i. A high rate of recombination of the $R^{\cdot}$ and $H^{\cdot}$ radicals during photolysis which is not so great during oxidation because of the competition of the recombination reactions with the reaction of these radicals with oxygen.

This also explains the apparent low quantum yield of photolysis which is of the order of 10^{-3} compared with the quantum yield of photo-oxidation which is of the order of 10^{-2}.

ii. Since it has been shown that the only significant products of oxidation are CO_2 and H_2O it may be that other possible primary products of oxidation such as formaldehyde or benzaldehyde are being further oxidised so that relatively large amounts of oxygen would be required.

iii. Finally large values of R in Table 9 would naturally follow if a chain process, as illustrated in the mechanism above, were occurring during oxidation.

It has been observed that cross-linking also occurs during oxidation. This can readily be explained in terms of bimolecular combination of chain radicals for example.

$$2R^{\bullet} \longrightarrow R - R$$

$$R^{\bullet} + RO_2^{\bullet} \longrightarrow ROOR$$

$$RO_2^{\bullet} + RO_2^{\bullet} \longrightarrow ROOR + O_2$$

In p.α.m.s. the ratio of number of molecules of oxygen absorbed to the number of molecules of volatiles produced is much smaller than in the styrene family, but these two cases are not strictly comparable because it is known that irradiation of p.α.m.s. by 2537 Å radiation results in main chain scission rather than C-H bond scission, while the two long chain radicals thus formed will still be capable of reacting with oxygen the characteristic of this and the recombination must be quite different ~~than~~ from the polystyryl radicals.

2. The Kinetics of Oxidation

Due to the many possible reaction paths the overall photo-oxidation reaction must be very complicated. However, in the early stages of the reaction, in which these studies have been made, the rate of reaction will, be given approximately ~~by.~~ by,

$$V = k I C_{\alpha} C.$$

in which k is a constant.

I is the intensity of radiation and

C_{α} is the concentration of hydrogen atoms /cm^2 of 0.01 mm. thick polymers of the styrene family.

In case, p.α.m.s., this will be the concentration of $C_{\alpha} - C_{\beta}$ bonds per cm^2 of 0.01 mm. thick p.α.m.s.

C is the concentration of oxygen. It must be admitted that this equation represents an over-simplification. It does not take into account the oxidation products which cannot be absorbed by the absorbants, and it does not give allowance for volatiles like hydrogen being given off. Certainly these kinds of products will upset the measured oxygen uptake rate if they are appreciable. It is fair to assume that these products are small in comparison with the volume of oxygen absorbed.

It has been observed that the rate is first order with respect to radiation intensity and also the rate is independant of oxygen pressure for pressures above 50 or 100 mm. Hg.

Poly (α methyl styrene) is an exception. In this case the rate of reaction is a function of oxygen pressure as shown in Figure 12. However assuming that the rate is given generally by the relationship

$$\text{Rate} = K.P_0^{\alpha}$$

$$\text{then} \quad \text{Log.Rate} = \text{Log.}K + \text{Log.}P_0^{\alpha}$$

The results in Figure 12 are replotted in Figure 12A according to the above equation for which it may be deduced that $\alpha = 0.6$.

The independence of rate on pressure shows that above a certain concentration of oxygen the reactions

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$$

$$\text{and} \quad H^{\cdot} + O_2 \longrightarrow HOO^{\cdot} \quad \text{are 100\% efficient.}$$

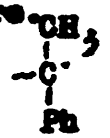
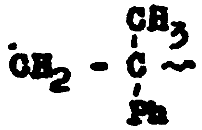
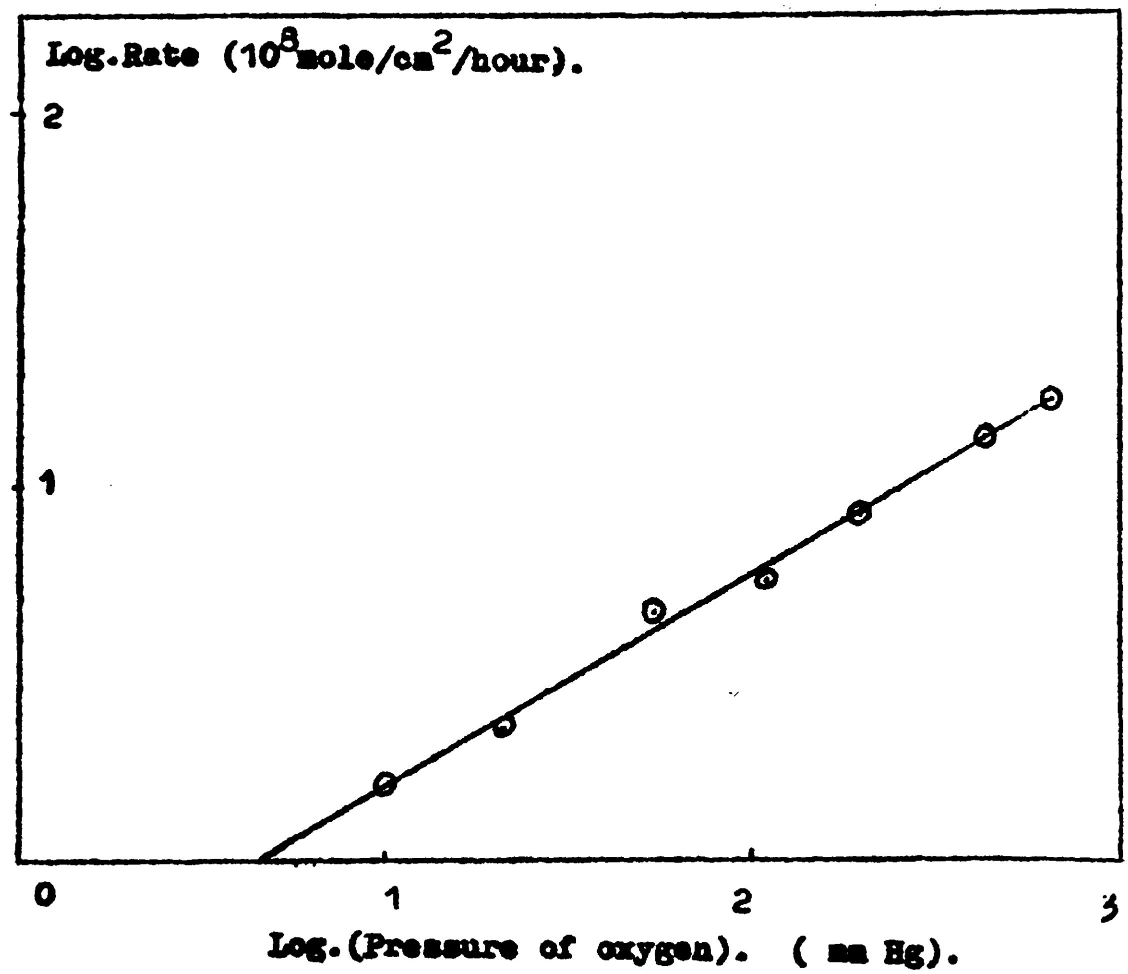
In the case of p.α.m.s. the rate of oxidation is very much increased by the increase of oxygen pressure. This is probable due to the short life time of  $\sim\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C^{\cdot}}}$ Or  $\overset{\cdot}{C}H_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}\sim$ radicals, so that their other possible reactions can compete effectively with the reaction with oxygen at much higher oxygen pressure.

Figure 12A

P.α.M.S.



Effect of methyl substitution on ease of oxidation

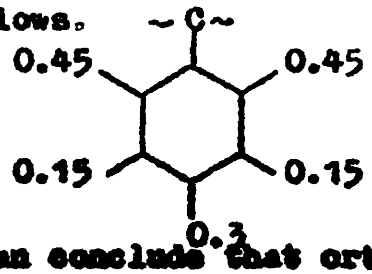
It is interesting to consider the influence of ring substitution on the rate of oxidation of polystyrene. The rates are given in the first row in Table 10

Table 10

Rates (x 10^7) of oxidation of ring substituted polystyrene.

Polystyrene.	p.para.methyl.s	p.2,5 d.m.s.	p.2,4,6 m.s.
0.9	1.2	1.5	2.1
	0.9 + 0.3	0.9 + 0.6	0.9 + 1.2

Assuming 0.9×10^{-7} to be the basic rate of oxidation of unsubstituted polystyrene, the increase of rates due to substitution are illustrated in the second row of the table. Hence the contribution of the various possible substitution position in the polystyrene molecule may be easily calculated as follows.



From this we can conclude that ortho substitution has the greatest effect on oxidation. This however is most probably a reflection of the rate of initiation of oxidation, that is, the effect of radiation in forming the primary radical

THERMAL DEGRADATION.

Introduction.

Interest in the thermal degradation of polymers has existed since these materials began to be exploited commercially. This led to an interest in the chemistry of these degradation processes and to the publication of a number of monographs on the subjects (63,64,65).

Degradation of a polymer molecule may occur as a result of various agencies, both chemical (eg. oxygen or ozone) and physical (light, ultrasonic, heat). In this chapter degradation by heat will be discussed. The synthetic organic polymers have a limited temperature resistance (a few hundred degree centigrade) due to the properties of C - C and C - H bonds which they contain. Thermal degradation processes of polymers can be divided into two main classes, namely, depolymerisation or chain scission and substituent or non-chain-scission reactions. The depolymerisation reaction is characterised by the breaking of the main polymer chain back-bone so that at any intermediate stage the reaction products are similar chemically to the parent material.

This kind of reaction can be described in terms of some or all of the following primary steps,

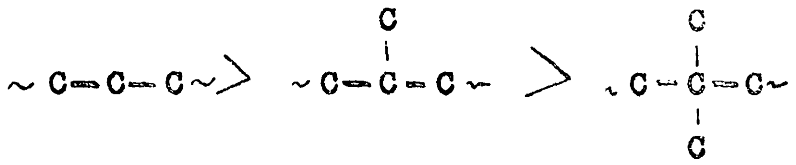
1) Random Initiation. $Mn \longrightarrow Pj + Pn-j$.
2) Terminal Initiation. $Mn \longrightarrow Pn-1 + P1$.
3) Depropagation $Pi \longrightarrow Pi-1 + Mi$.
4) Transfer $Pi + Mn \longrightarrow Mi + Pj + Mn-1$.
5) Termination $Pi + Pj \longrightarrow Mi + Mj$ or $Mi+j$.

in which P and M represent respectively a long chain radical and a dead polymer molecule. The subscripts represent the number of monomer units in P or M.

In thermal degradation, when the temperature of the molecule is raised, the vibration of the atoms within it increases. A temperature will ultimately be reached at which the weakest bonds in the molecule will break. The weak bond can be due to oxygenated structures [65] arising during polymerisation process or in subsequent weathering of the polymer.

The weak bond can also due to the fact that different C - C bonds have different strengths and the weakest carbon-carbon bonds can be expected to break preferentially.

Madorsky.S.L. and Straus.S.[66] have established an order of relative bond strengths, to be used as a guide in deciding which bonds in the polymer chain are likely to break first.



$$\sim C-C-C\sim \;>\; \sim C-\overset{C}{\overset{|}{C}}-C\sim \;>\; \sim C-\overset{C}{\overset{|}{\underset{C}{\underset{|}{C}}}}-C\sim$$

where C—C represents the bond under discussion.

If a radical stabilised by delocalisation can be achieved by scission of a bond then that bond will also constitutes a point of weakness in the chain eg. a bond beta to a double bond in the chain.

$$\sim C-C-C{=}C\sim \;\rightarrow\; \sim C^{\bullet} + {}^{\circ}C-C{=}C\sim \;\leftrightarrow\; C{=}C-\overset{\circ}{C}\sim$$

In a perfectly regular chain structures such as that of polymethylene, these scissions will take place in a purely random fashion, since each carbon-carbon in the chain is equivalent.

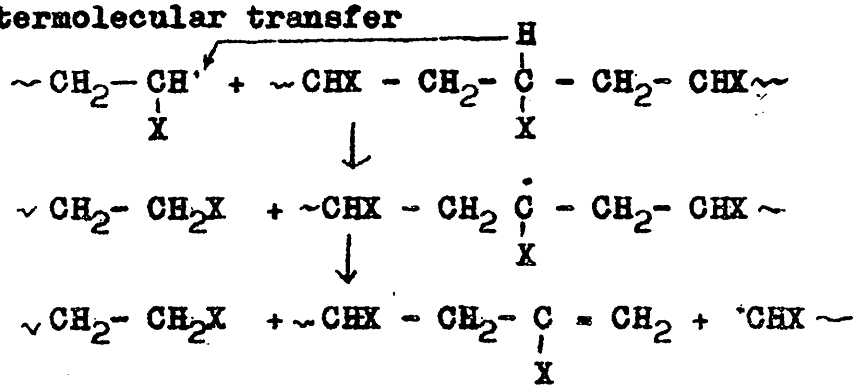
Terminal initiation occurs in the particular situation in which the terminal structures incorporate bonds which which are weaker than those in the body of the chain. Random initiation occurs with polyα methyl styrene,

(Brown and Wall [67]) and in case of poly-methyl-methacrylate chain ends initiation predominates.(Grassie and Melville[68])

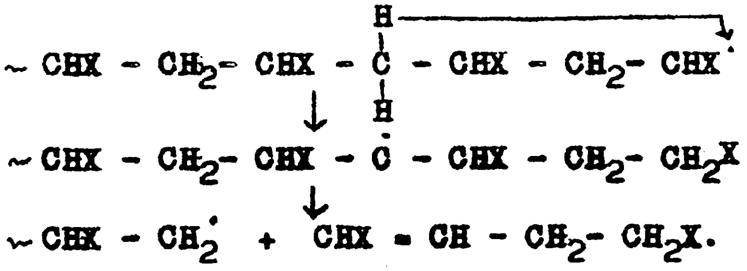
Transfer involves a transfer of radical activity from one site to another, usually involving the movement of a hydrogen atom or some others atoms.

This process can occur within a polymer molecule (intra-molecular transfer) or between two molecules(intermolecular transfer) for example:

Intermolecular transfer



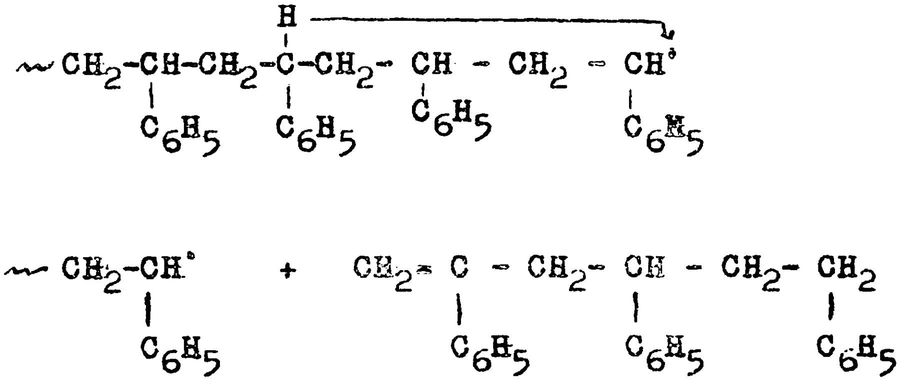
Intramolecular transfer:



The result in both cases is the formation of one saturated end, one unsaturated end, and a new free radical.

Wall and Strauss[69] suggested that branching of polymer chains will result in an increase in intramolecular hydrogen transfer over intermolecular transfer since the close approach of the radical and hydrogen atom which is required for transfer is blocked in the intermolecular case by steric repulsion from side groups.

In the case of the styrene family of polystyrene the transfer is mainly intermolecular transfer of the α hydrogen atoms and this transfer is responsible for the production of dimer, trimer and tetramer.



$$\sim CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{\overset{H}{C}}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH^{\bullet}}$$

$$\sim CH_2-\underset{C_6H_5}{CH^{\bullet}} \quad + \quad CH_2=\underset{C_6H_5}{C}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH_2}$$

Substitution of the hydrogen by methyl groups suppresses the transfer completely as in poly metyl styrene which produces 100% monomer on pyrolysis. Substitution of the hydrogen atoms by deuterium atoms results in an increase in yield of monomer from 42% to 70% at the expense of the larger fragments because of the partial suppression of the transfer. However methyl substitution in the ring has only a small effect.

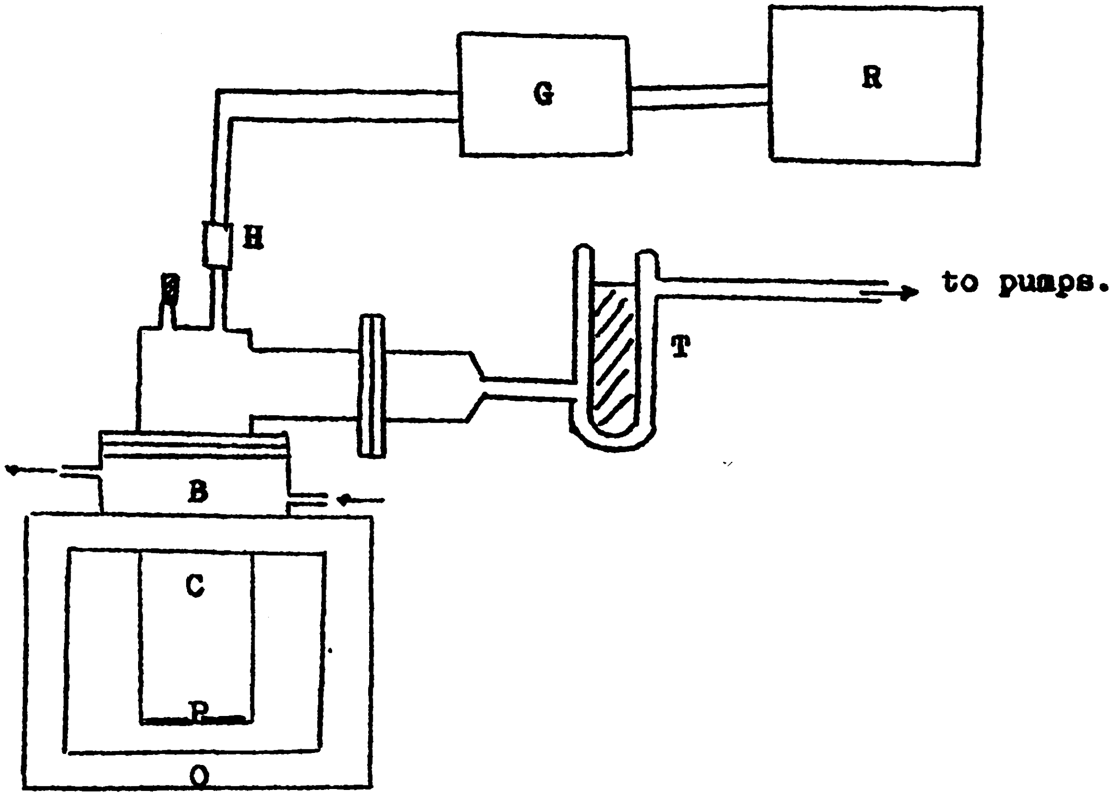
Experimental

The apparatus in Figure 22 was developed by Dr.I.C.McNeil in this department. It enables the pressure of the volatile products from thermally degrading polymer to be continuously measured as the temperature rises at a constant rate.

The samples used were in the form of a film. This was placed in a cylindrical pyrex tube with a flat base which in turn was placed in a linear programmed temperature oven as shown in the diagram. The rate of temperature rise for these experiments was adjusted to 10°C per minute . The pressure of volatile products of degradation was measured by pirani gauge connected to a recorder.

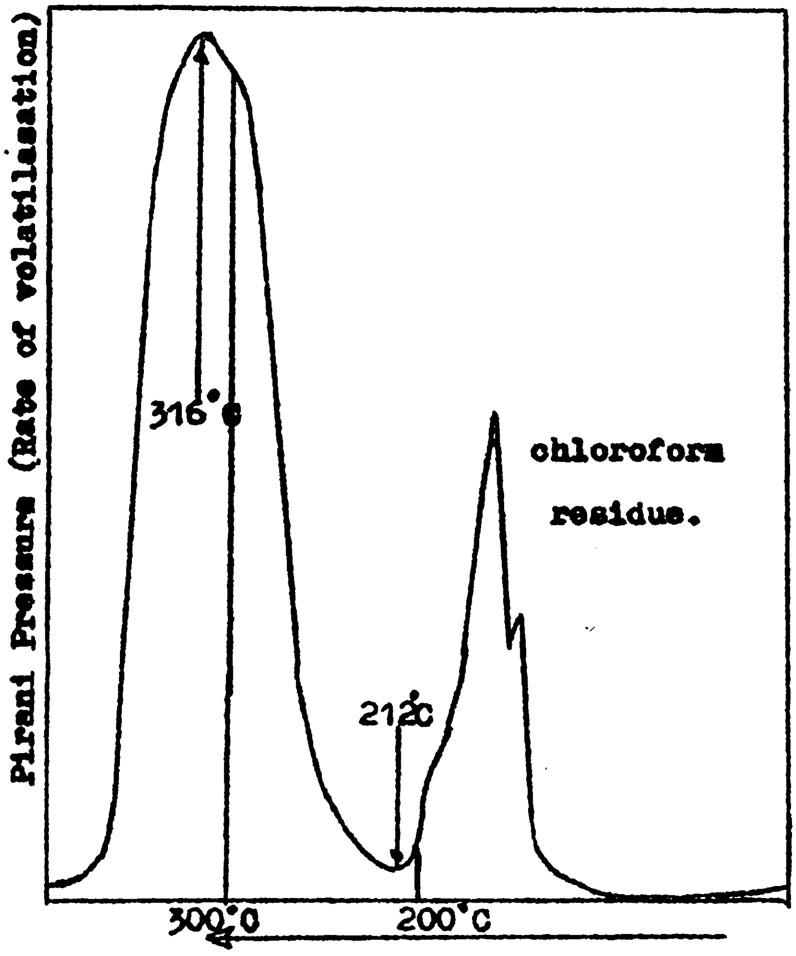
The temperature inside the cylindrical pyrex tube was calibrated against the temperature in the oven. Hence the temperature inside the cylindrical pyrex tube can be deduced from the oven temperature.

Figure 22



O - linear temperature programmed oven, P - polymer,
C - cylindrical pyrex tube with flat base,
B - cooling block, H - pirani head, G - pirani gauge,
R - recorder, T - liquid N_2 trap.

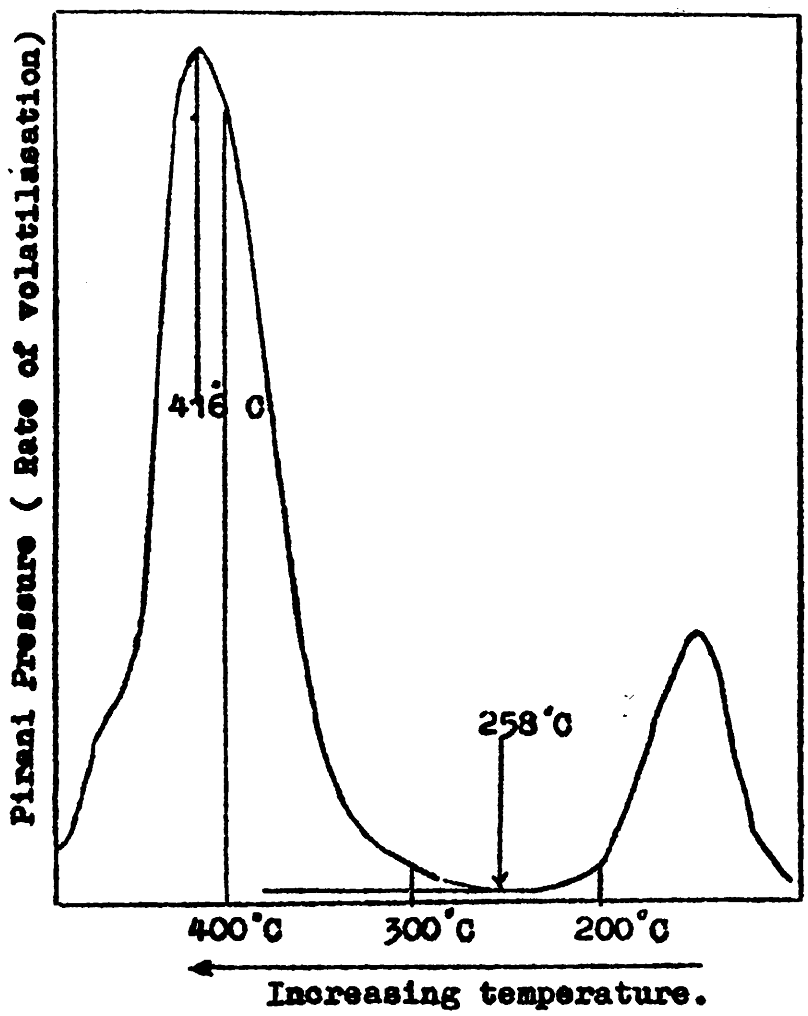
Figure 17



Increasing temperature.

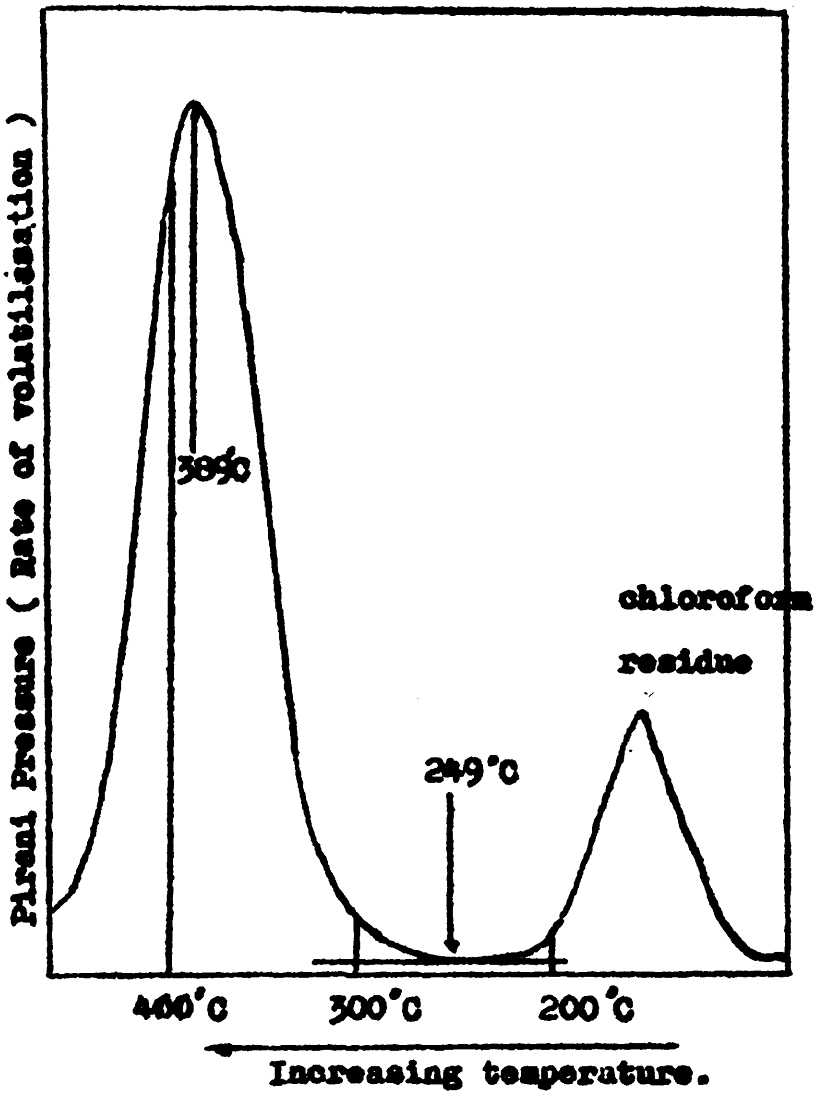
Temperature programmed degradation of p.α.m.s.

Figure 18



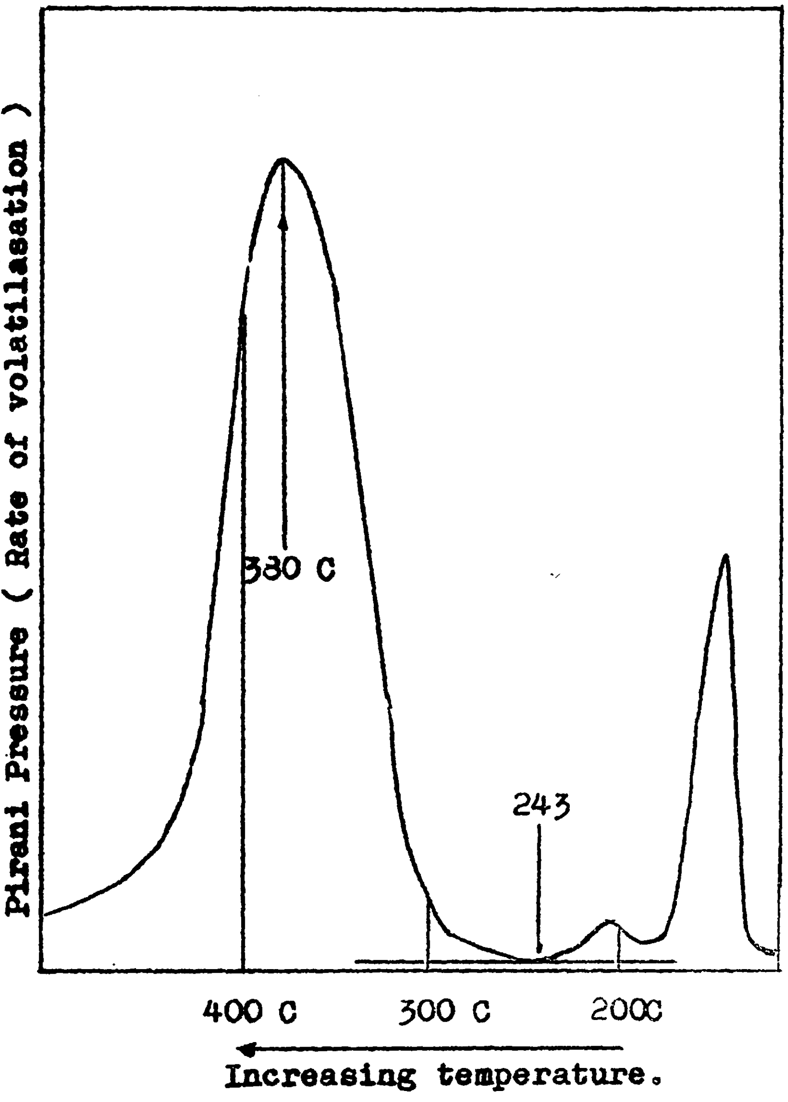
Temperature programmed degradation of polystyrene.

Figure 19



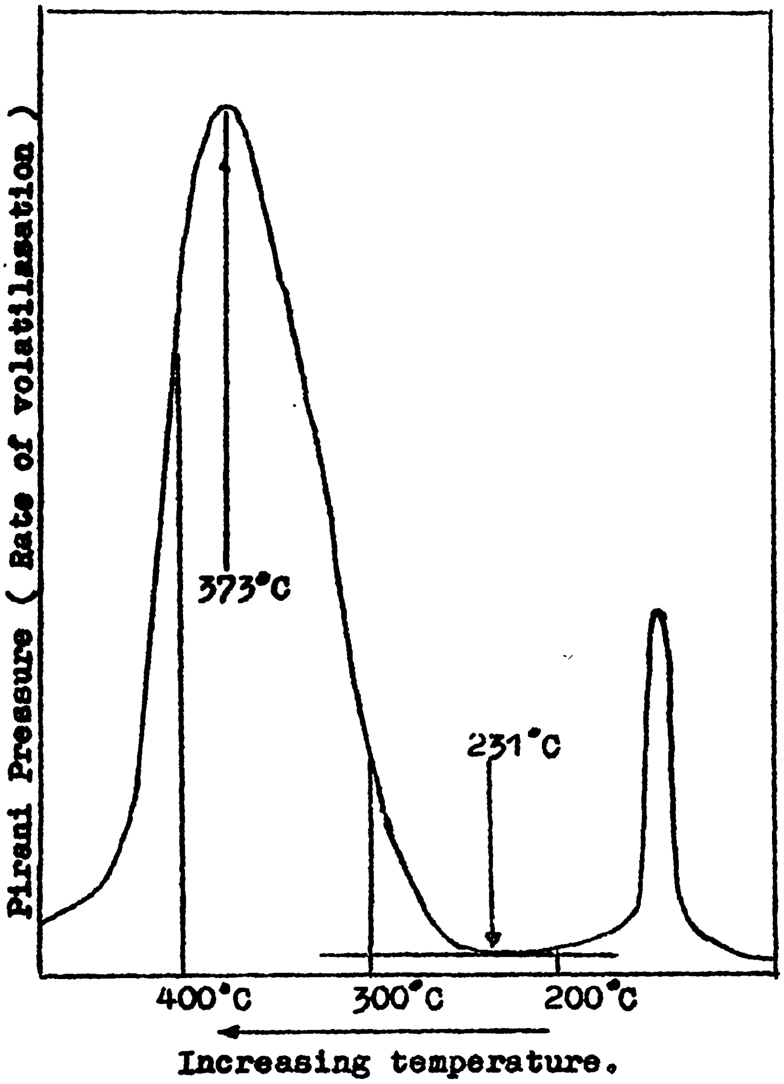
Temperature programmed degradation of poly-para-methylstyrene.

Figure 20



Temperature programmed degradation of poly (2,4,6 trimethyl styrene)

Figure 21



Temperature programmed degradation of poly (2,5 dimethyl styrene).

Summary

Both the threshhold temperature at which degradation of the polymer occurs and the temperature of the rate maximum indicate the following order of thermal stability of these substituted polystyrene.

p.α. m.s < p.2,5 m. s.< p.2,4,6 m.s.< p.p.m.s.<p.s.

From the general similarity of the shapes of these degradation curves the nature of the reaction is clearly similar.

It is of interest that this is a different order from that obtained from photo-oxidation stability althought in both cases polystyrene turns out to be the most stable.

COLOURATION

Introduction.

Colouration of polystyrene due to exposure to sun light can be a most undesireable property from the industrial and commercial point of view.
This has always been associated with oxidation until recently Grassie and Weir[42] found that colouration can also occur by irradiating polymers in vacuum with 2537 Å radiation. This was explained by the formation of conjugated carbon-carbon double bonds in the polymer backbone due to abstraction by the primarily formed hydrogen atom of a hydrogen atom on the adjacent carbon atom in the same chain.

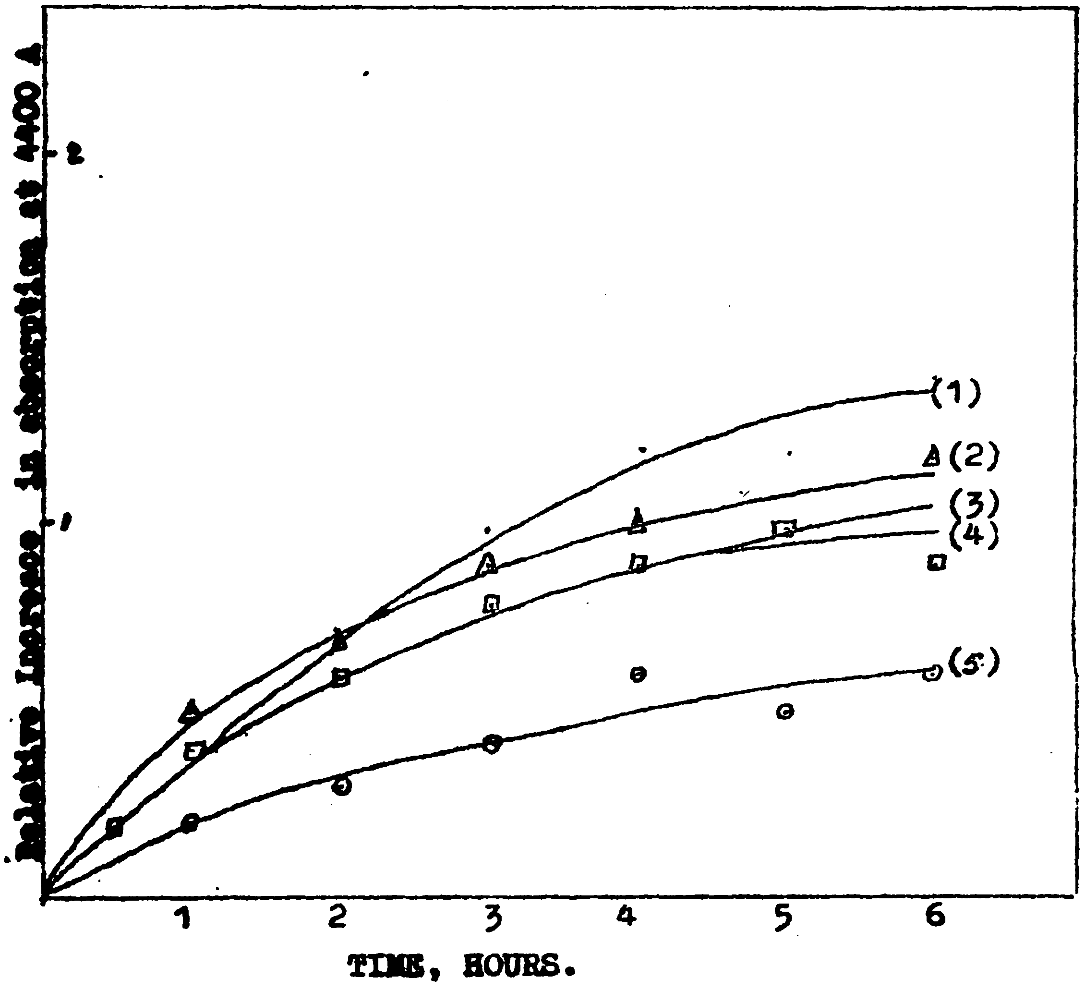
Achhammer[38] suggested that the colour of oxidised polystyrene was due to quinomethanes produced by reaction of the polystyryl radical in an alternative cononical form. Wall and his coworker[39,40,41] suggested that the chromophores are closely related to benzalacetophenone of which hydroperoxide is the precursor. Grassie[42] suggested that since the rate of colouration in presente and absence of oxygen are comparable and the principle characteristics are similar, it seems more probable that the hydroperoxide would decompose by way of a six-membered ring transition state. These have been explained in page 8,9 and10.

Experimental.

The extent of colouration of polymers films was measured by the increase in absorbtion at 4400 A by the use of a E.E.L. Spectra colourimeter. Because the sample cell of the apparatus does not transmit light of 2537 A, the films were attached to the windows of the cells holder by means of Sellotape.

The holder with films of different polymers was irradiated with 2537 A. The absorption at 4400 A was measured from time to time. All experiments were carried out at room temperature.

Figure 23



(1) - polystyrene, (2) - poly para methyl styrene,

(3) - poly(2,5 dimethyl styrene),

(4) - poly(2,4,6 trimethyl styrene),

(5) - p.α.m.s.

SUMMARY.

It is clear from the data in figure 23 that polyαmethyl-styrene colours at the slowest rate. This is expected since in the case, if the suggested mechanism of colouration is correct, methane rather than hydrogen would have been been liberated and thus, bearing the mechanism in mind, should be a more difficult process. As it has been shown in photo-oxidation that chain-scission occurs in case of polyαmethyl styrene. The tendencies of the ring substituted styrene to colour are rather similar to polystyrene although in contrast with the thermal and photo-oxidative stability , polystyrene is least colour stable.

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