

University of St Andrews



Full metadata for this thesis is available in
St Andrews Research Repository
at:

<http://research-repository.st-andrews.ac.uk/>

This thesis is protected by original copyright

(i)

A Study of the Oxidation of Polymers
using Excited Oxygen Species

A thesis
presented for the degree of
DOCTOR OF PHILOSOPHY
in the Faculty of Science of the
University of St. Andrews
by
CLIVE TAUNTON RANKIN, B.Sc.

May 1972

United College of St. Salvator
and St. Leonard, St. Andrews.



Tm 5958

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself and that it has not been submitted in any previous application for a Higher Degree.

This thesis describes the results of research carried out at the Chemistry Department, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Dr. J.R. MacCallum since 1st October 1969, the date of my admission as a research student.

(iii)

I hereby certify that Clive Taunton Rankin has spent eleven terms of research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

J.R. MacCallum.
Director of Research

ACKNOWLEDGEMENTS

I should like to record my appreciation of the help and encouragement given to me by Dr. James R. MacCallum, during all stages of the work in this thesis.

I am indebted to Courtaulds Educational Trust for the award of a research grant during the period 1969-72, and to Professor Lord Tedder for research facilities in the chemistry department during this time.

Finally I wish to express my gratitude to all the teaching and technical staff of the University of St. Andrews Chemistry Department, especially Mr. J. Rennie, Mr. J.G. Ward, Mr. N.G. West and Miss M. Pocwiardowska for their technical assistance, and Miss L. Peebles who typed this thesis.

CONTENTS

	<u>Page</u>
Declaration	(ii)
Certificate	(iii)
Acknowledgements	(iv)
Contents	(v)
List of Figures	(vi)
List of Tables	(viii)
Summary	(x)

<u>Chapter</u>		<u>Page</u>
1	Introduction	1
2	Experimental	32
3	Results	51
4	Discussion	81
	Bibliography	

List of Figures

<u>Figure</u>	<u>Title</u>	<u>Following Page</u>
1	Apparatus for Exposure of Polymer Films.	32
2	Apparatus for Exposure of Polymer Solutions.	34
3	Apparatus for Titration of Oxygen Atoms with Nitrogen Dioxide.	37
4	Optical Bench Camera System.	43
5	Determination of Rate of Weight Loss for various Polymers Exposed to Active Oxygen.	53
6	Determination of Rate of Weight Loss of Exposed Polystyrene, with Changing Power.	56
7	Determination of Change in Rate of Weight Loss with Changing Power (Polystyrene).	56
8	Determination of the dependence of Atomic Oxygen Flow Rate on Molecular Oxygen Flow Rate.	58
9	Determination of the dependence of Molecular Oxygen Flow Rate on Power, in order to produce a Constant Atomic Oxygen Flow Rate.	58
10	Determination of Change in Rate of Weight Loss with Changing Power. (Poly (vinyl chloride)).	59
11	Determination of Change in Rate of Weight Loss of Poly (vinyl chloride) with Changing Atomic Oxygen Flow Rate.	59
12	Determination of Change in Rate of Weight Loss of Polystyrene with Changing Molecular Oxygen Flow Rate.	61
13	Dependence of Pressure of Carbon Dioxide on Weight Loss of Polystyrene.	62
14	Dependence of Molecular Weight of Polystyrene on Time of Exposure to Active Oxygen.	63
15	Determination of Change in Molecular Weight of Polystyrene Film on Drying.	64

<u>Figure</u>	<u>Title</u>	<u>Following Page</u>
16	Determination of Change in Rate of Weight Loss of Polystyrene, before and after exposure to active oxygen, with Changing Temperature.	68
17	Determination of the Change in the Ratio w/wo for polystyrene, before and after exposure, with Changing Temperature.	68
18	Enlarged Photograph of Droplet of Water on Polymer Surface.	68
19	Determination of Change in Contact Angle, of various Polymers with water, with Exposure to Active Oxygen.	69
20	Determination of Change in Molecular Weight on Exposing Solutions of Polystyrene in Toluene to active Oxygen	73
21	Determination of the Change in the Ratio w/wo with Changing Temperature for Polystyrene precipitated from an exposed solution.	80
22	Determination of Change in the Number of Cross-Links per mole of Polymer with Time, on Exposing a Polystyrene/Toluene solution to Active Oxygen.	94

List of Tables

<u>Table</u>	<u>Title</u>	<u>Page</u>
1→5	Relationship between Weight Loss and Time of Exposure of Various Polymers to Active Oxygen Species.	51-53
6	Relationship between Rate of Weight Loss and Polymer	53
7→12	Relationship between Rate of Weight Loss and Power.	53-56
13→15	Determination of Change in Concentration of Oxygen Atoms with Changing Power and Flow of Molecular Oxygen	57-58
16	Rate of Change of Weight Loss with Power for Poly (vinyl chloride).	59
17	Rate of Change of Weight Loss with Changing Atomic Oxygen Flow Rate for Poly (vinyl chloride).	59
18	Rate of Weight Loss of Poly (vinyl chloride) at constant Atomic Oxygen Flow Rate, but Changing Power and Molecular Oxygen Flow Rate.	60
19	Rate of Change of Weight Loss, for Polystyrene, with Changing Molecular Oxygen Flow Rate.	61
20	Relationship between Pressure of Gaseous Products and Time of Exposure of Polystyrene.	62
21,22	Molecular Weight Changes of Polystyrene with Exposure	63
23	Molecular Weight Changes of a Polystyrene Film on Drying	64
24	Molecular Weight Changes of a Film of Poly (ethyl methacrylate) on Drying	65
25-32	Thermal Stability of Polystyrene After Exposure.	66-67
33	Changes in Contact Angles on Exposure.	68
34	Changes in Contact Angles After Exposure for One Hour.	69

<u>Table</u>	<u>Title</u>	<u>Page</u>
35-37	Modification of Inert Surfaces By treatment with Active Oxygen.	71-72
38-40	Change in Molecular Weight of Polystyrene on Exposing a Polystyrene/Toluene Solution to Active Oxygen.	72-73
41-42	Change in Molecular Weight of Poly(methyl methacrylate) on exposure of solution.	74
43-45	Change in Molecular Weight of Polystyrene on Exposing a Polystyrene/Carbon Tetrachloride Solution.	75-76
46-49	Exposure of Solvent	76-78
50	Exposure of Monomer	78
51-52	Thermal Stability of Polystyrene Precipitated from a Polystyrene/Toluene Solution After Exposure	79-80
53	Contact Angle Changes	87
54-56	Number of Cross Links per Mole of Polymer with exposure of solution	94

Summary

In this thesis, the work is concerned with the effects of exposing various polymers, both in the solid state and in solution, to 'active' oxygen species. In this case the active species are mainly $^1\Delta_g$ molecular oxygen and atomic oxygen, produced by microwave discharge of molecular oxygen. The experimental work is in two parts, the first is concerned with solid phase reactions and the second with reactions in solution.

The information derived may perhaps be used to elucidate the mechanisms by which polymers are oxidised, leading to a better understanding of polymer oxidations as a whole.

To
MY WIFE AND
MY PARENTS

CHAPTER I

INTRODUCTION

The ageing of high polymers was recognised early on to be due, in large part, to oxidation processes. The fact that, on following exposure to light and air, rubber, cellulose or other polymers underwent rapid deterioration, even in the absence of light or oxygen suggested the existence of long-lived intermediates that catalyze further oxidation. In certain cases the observation of a lowering of molecular weight, brought about by oxidative degradation, suggested chain cleavage. In other cases of degradation, cross-linking was observed giving rise to gelation and oxidative vulcanization. It was concluded from a study of these reactions that the catalytic effect of light and oxygen is due to radical reactions.¹

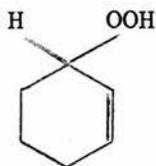
The importance of the effect of oxidative degradation on the lifetime of rubbers and other high polymers resulted in the introduction of antioxidants in the rubber industry in the 1930's. The result of this action was to increase the lifetime of rubber tyres by a factor of two to three.

At elevated temperatures it has been observed, from comparative studies of the rate of oxygen absorption of a variety of polymers, that the presence of double bonds and methyl groups along the chain appear to enhance the rate of oxidation, whereas certain other groups such as phenyl appear to retard it.²

The importance of hydroperoxide formation in olefinic systems, as emphasised by Farmer, was a major advance in the understanding of the mechanism of oxidative degradation of hydrocarbon polymers.

The postulation of Criegee³ et al. that the exposure of cyclohexene to oxygen and light gave rise to a hydroperoxide of the

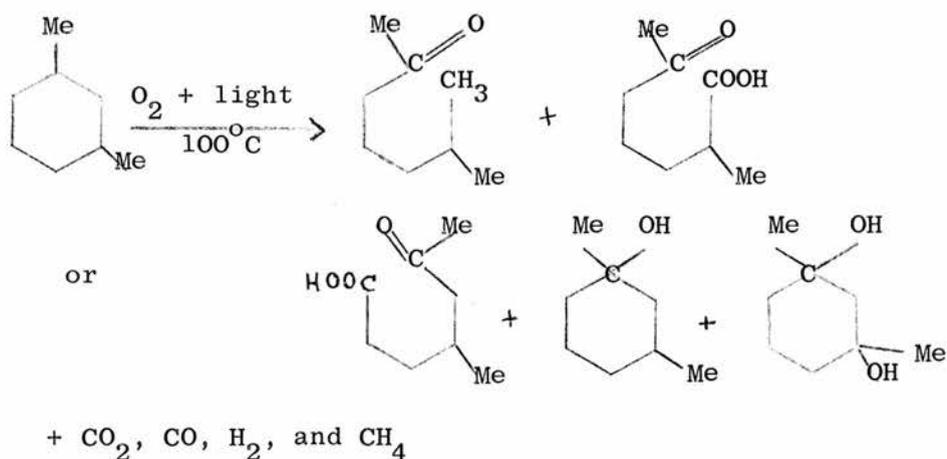
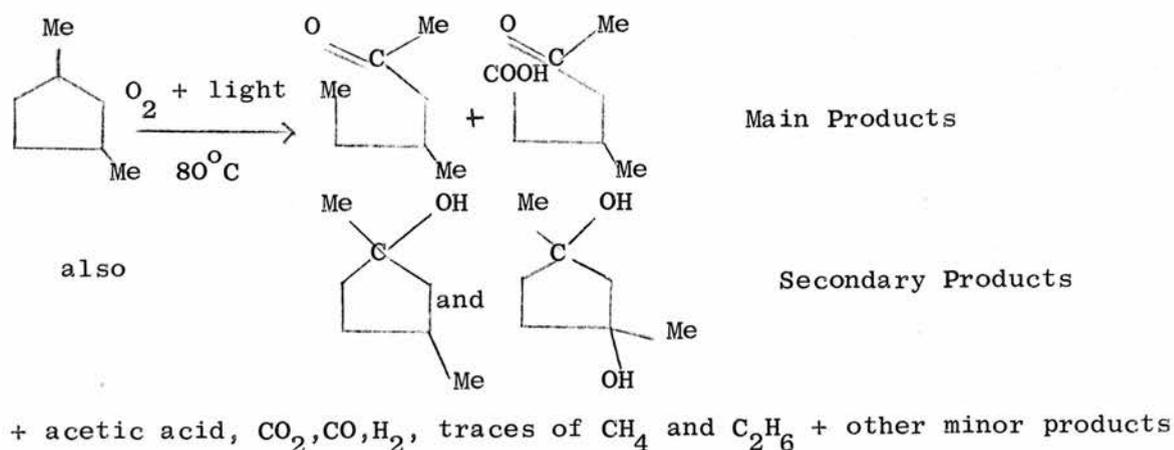
following structure:-



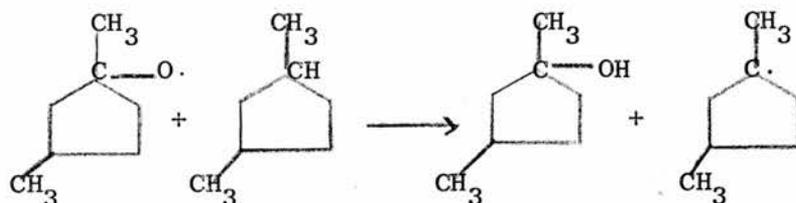
was first verified by Farmer and Sundralingham.⁴ It was observed that this hydroperoxide decomposed to give secondary oxidation products.

Farmer and his co-workers observed that during the oxidation of natural rubber and low molecular polyisoprenes, all of the oxygen absorbed in the initial stages entered the structure in peroxidic form without loss of unsaturation. They concluded that the primary products of oxidation are peroxides.

Experiments conducted by Chevanne⁵ on the uncatalysed oxidation of cyclopentane and cyclohexane derivatives at 80°C and 100°C produced the following results:-



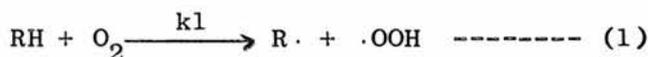
from a neighbouring hydrocarbon, to give a tertiary alcohol.



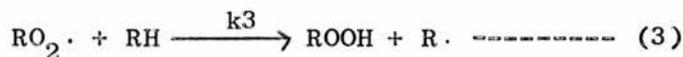
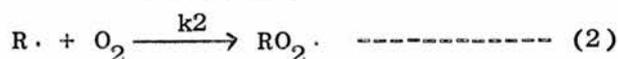
It can thus be postulated, from the above results, that the chemistry of hydrocarbon free radical oxidations is in large part the chemistry of the peroxy radical $RO_2\cdot$; the formation of the radical its propagation, and its termination.

I. Initiation

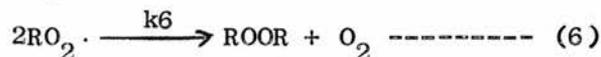
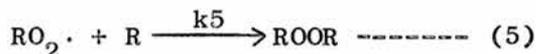
Production of $R\cdot$ or $RO_2\cdot$.



II. Propagation



III. Termination



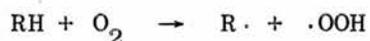
+ other nonradical products.

The above was postulated by Bolland and Gee⁸ as the mechanism in the oxidation of ethyl linoleate where RH represents the ethyl linoleate molecule:- $CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOEt$ and $R\cdot$ represents the radical $CH_3(CH_2)_4CH=CH\dot{C}HCH=CH(CH_2)_7COOEt$.

Many suggestions have been put forward as to how exactly hydroperoxides originate. This step, however, remains the most puzzling to all concerned in the field of oxidation.

A. The Initiation Step

(i) Hydrogen Abstraction of Oxygen

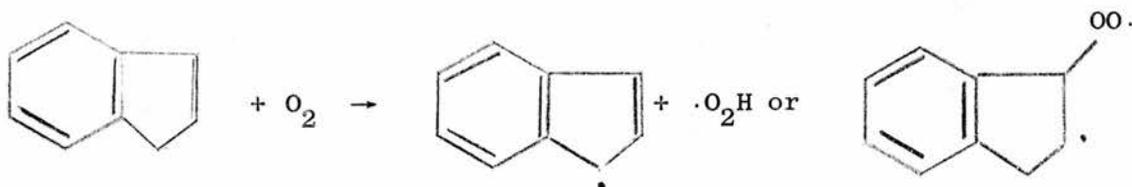


It has, however been calculated⁹ that this reaction should be endothermic by some 30 - 45 kcal mole⁻¹, and therefore should not be significant.

An alternative termolecular reaction which might be more energetically favourable has been suggested by Denisov.¹⁰



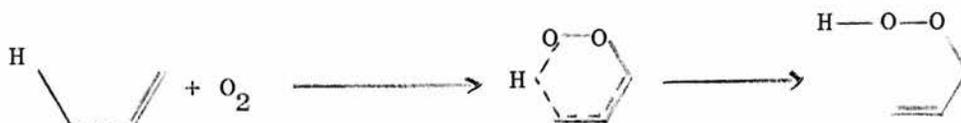
Nevertheless, it was the bimolecular reaction which Russell¹¹ postulated for the initiation mechanism in the oxidation of indene.



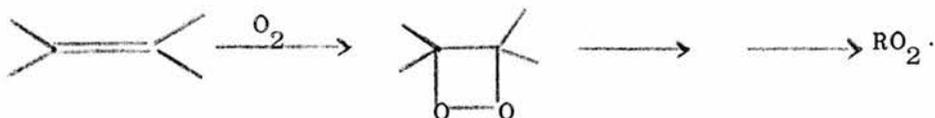
Russell's postulation has been verified by Howard and Ingold¹² who have shown that the hydroperoxy radical ($\cdot OOH$) is the main propagating and terminating radical in the autoxidation of 1,4-cyclohexadiene and 1,4-dihydronaphthalene.

(ii) Direct Formation of Hydroperoxides

Photosensitized oxidations can give rise to direct hydroperoxide formation:-



(iii) Direct oxygen Addition to a Double Bond



Although this reaction appears unlikely, it has been suggested in the oxidation of natural rubber¹³ and styrene butadiene rubber. There is no evidence as yet, however, for direct oxygen addition to the double bond of a hydrocarbon in the liquid phase.

(iv) Hydroperoxide Decomposition

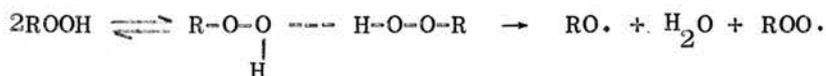
The previous three processes for initiation are negligible when one considers observable rates of oxidation. The formation of peroxy radicals arises from the decomposition reactions of hydroperoxides.

It has been shown¹⁴ that, in the early stages of olefinic oxidation, hydroperoxides decompose by a first-order process.



Bateman,¹⁵ however, has pointed out that the majority of cases in which first order decompositions were reported, were reactions carried out at temperatures above $130^\circ C$ where the unimolecular process is favoured.

As the hydroperoxide concentration increases, during the oxidation, the bimolecular reaction, which is less endothermic, will be of greater importance.



B. Propagation

With such uncertainty concerning the exact initiation mechanisms, researchers studying the propagation and termination reactions have found it necessary to use external initiators in order to obtain known rates of initiation.

The propagation rate may be due to several peroxy radical reactions, e.g.:-

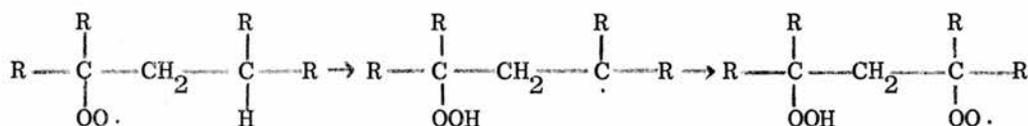
(i) Hydrogen Abstraction



Both polar and steric effects in the hydrocarbon RH, and steric effects in the attacking radical influence the hydrogen abstraction reaction.¹⁶

Peroxy radicals are found to be fairly selective electrophilic species. They will abstract tertiary hydrogens in preference to secondary and primary ones. If there is more than one removable hydrogen available then either inter- or -intramolecular reactions may occur:-

e.g.

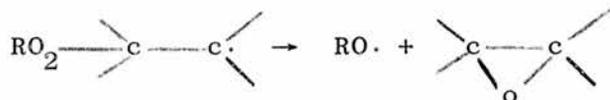


Blocks of hydroperoxides¹⁷ may be formed with several of these intramolecular steps. Bimolecular hydroperoxide decomposition is facilitated in this manner.

(ii) Double Bond Epoxidation by Peroxy Radicals

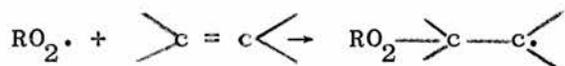


It has been demonstrated¹⁸ that prior peroxy radical addition to an olefin is involved in this reaction.



Epoxide yields are dependent on the competition between the reaction of the β -alkylperoxyalkyl radical with oxygen, and its rearrangement. For any given olefin epoxide formation is favoured at low oxygen pressures. This fact has been demonstrated by Miller and Mayo¹⁹ who found yields of styrene oxide in the oxidation of styrene at low pressures, even although the ratio of addition to rearrangement is very high for styrene (c. $10^5:1$).

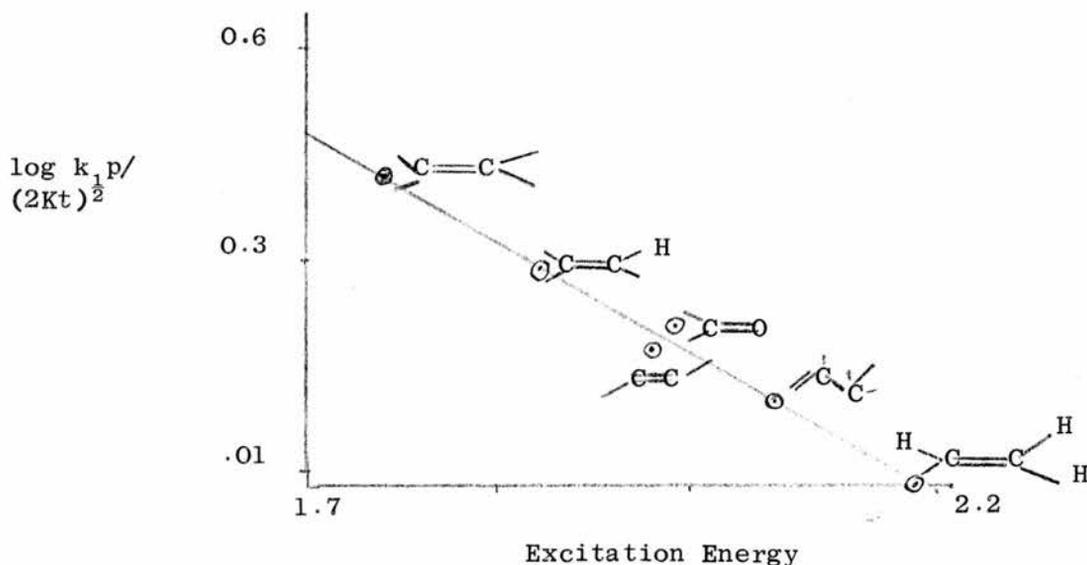
(iii) Addition of the Peroxy Radical to an Unsaturated Hydrocarbon



Van Sickle et al.²⁰ in their studies of the competition between the addition and abstraction reactions for various olefins were able to correlate the rate of addition with the electronic excitation energies of the alkenes.

The electronic excitation energy is the calculated difference between the ground-state singlet and the average energy of the first excited-state singlet and triplet.

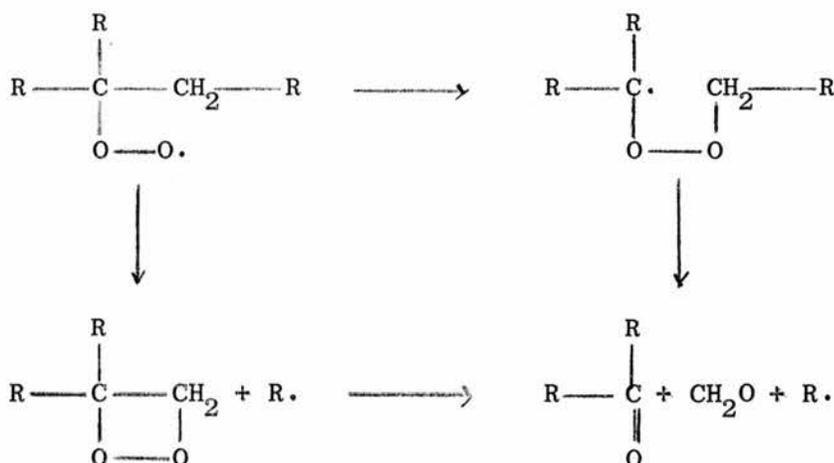
A plot of the rates of addition of alkylperoxy radicals to alkenes as a function of energy gave the following graph:-



They found that the lower the electronic excitation energy, the higher the rate of addition. Their results also show that there is a definite steric effect; the least substituted carbon being the one to which the radical adds.

(iv) Isomerization Reactions

It has been postulated²¹ that unimolecular decomposition reactions such as the following:-



occur in the gas phase. In the liquid phase there is little evidence for such a reaction.

C TERMINATION

(i) Peroxy Radical Interactions

The chemistry of the termination reaction has proved to be difficult to determine due to the fact that kinetic chain lengths in the liquid oxidations, which have been studied, are usually large, with the result that any products formed in termination are minor ones.

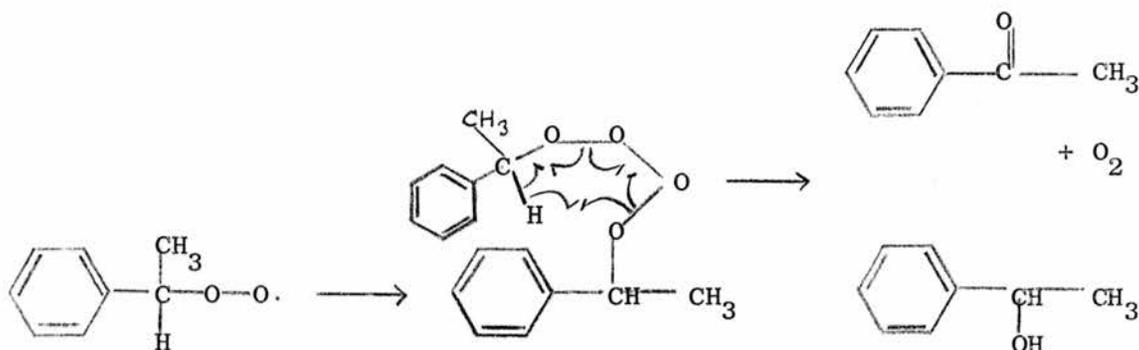
The interaction of two peroxy radicals is the only chain termination step for most reactions, at a pressure of 1 atmosphere of oxygen. At lower pressures the relative contributions of

three chain-stopping processes have been evaluated.²²

At 1 atmosphere pressure of oxygen reaction (2) (see back P.4.) is so much faster than (3) the $[R.] \ll [RO_2.]$. Termination can be assumed to occur entirely by reaction (6).

At lower pressures the importance of reaction (3) increases until eventually $[R.]$ is not negligible compared with $[RO_2.]$.

A simple termination reaction is possible for oxidations involving primary or secondary peroxy radicals. For example, the following termination reaction has been proposed by Russell²³ for the oxidation of ethylbenzene:-



He proposed the breaking of a CH bond, in the termination reaction, on finding that the *o*-phenethylperoxy radicals interact 1.9 times as readily as their *o*-deutero derivatives in forming nonradical products.

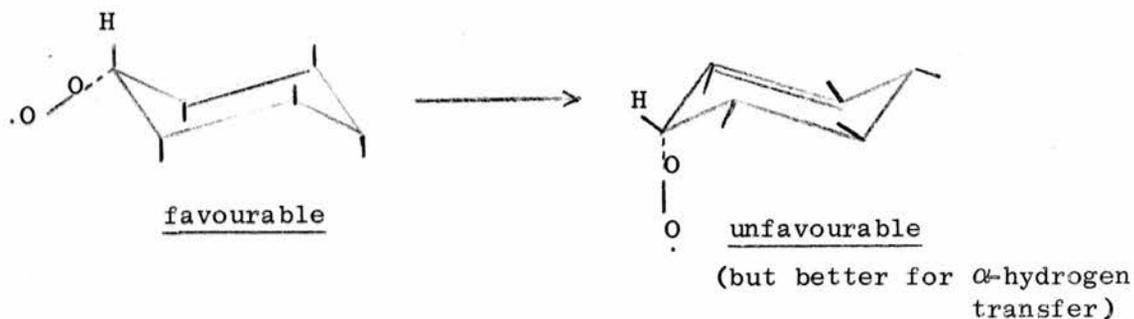
This type of termination reaction can be used with all primary and secondary peroxy radicals, but not so with tertiary radicals. Russell has also shown²⁴ that the termination with primary and secondary peroxy radicals is much more rapid than with tertiary radicals, indicating that without the available hydrogen for transfer, a different termination mechanism must occur.

Extensive studies of termination rate constants have been carried out by Howard and Ingold²⁵ who have discovered that the rates

are very sensitive to structure. The rate constant is greatly affected by the ease with which hydrogen is transferred in terminations involving primary and secondary peroxy radicals. The rate of the reaction is reduced by steric hindrance at the reaction site.

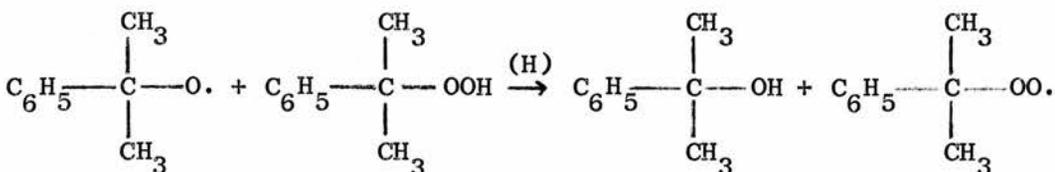
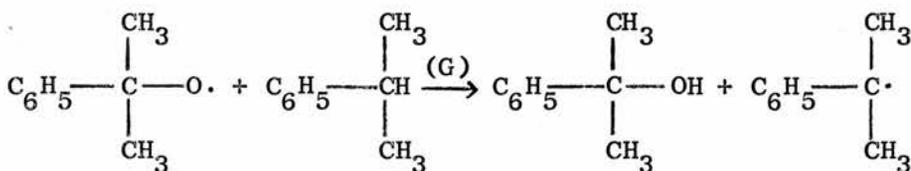
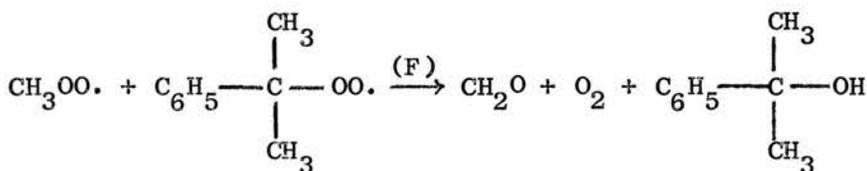
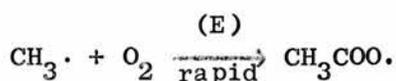
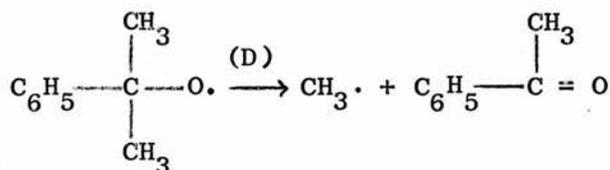
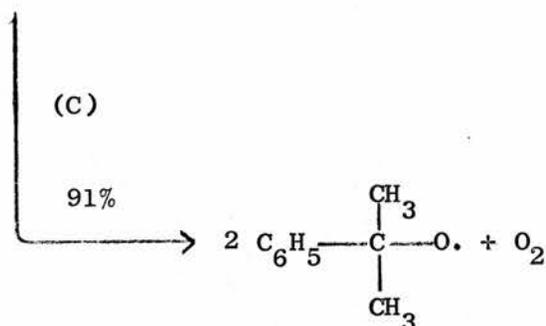
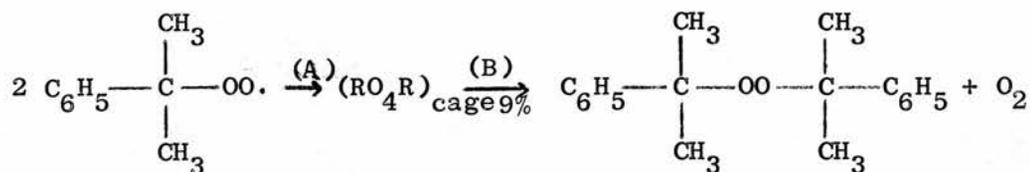
The lower termination rate constant values for peroxy radicals of cyclic olefins, especially cyclohexene and tetralin, can be partially explained by steric hindrance.

These compounds have non-planar, six-membered rings. This leads to steric hindrance in termination because one radical must have its peroxy group in the unfavourable axial position in order for its α -hydrogen to be in the most favoured position for transfer.



With five-membered ring compounds the lower termination rate values are thought to be due to an increase in ring strain in going to the transition state from the ground state.

In the case of tertiary peroxy radicals, the termination step is a much more complicated process. It has been shown²⁶ that the process of termination for the tertiary cumylperoxy radical can be written as follows:-



It was found that although hydroperoxide is a better hydrogen atom source than cumene its low concentration meant that although reaction (H) occurred, it did not prevent reaction (D) from occurring also.

Boozer et al.²⁷ found that deuterocumenes, labelled in the methyl groups, oxidised faster than cumene itself. The explanation for this²⁸ is that the cumyloxy radical is stabilised to cleavage and hence termination by such substitution. The deuterated radical abstracts hydrogen [reaction (G)] to continue the kinetic chain, rather than forming acetophenone and the methyl radical [reaction (D)].

Howard and Ingold²⁹ and Hendry and Russell³⁰ found that the polarity of solvents affected the termination reaction. They demonstrated that as the polarity of a solvent is increased k_6 is decreased with k_3 (see back) relatively unaffected. From the data it appears that the peroxy radical with some polar character in its ground state reacts less readily to form nonpolar termination products in the more polar solvents.

It appears, however, that solvent polarity has two opposing effects on termination. On examining the work of Walling and Wagner,³¹ one finds that increasing solvent polarity increases the rate of the cleavage reaction relative to the propagation reaction for t-butoxy radicals.

(ii) Reactions of Alkoxy Radicals

The subsequent reactions of the alkoxy radical (RO.) that is formed will determine whether the interaction of the two peroxy radicals leads to chain termination or propagation.

There are six available reaction paths for this radical:-^{32,33}

(1) Coupling



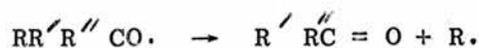
(2) Hydrogen Transfer (Disproportionation)



(3) Inter- or Intramolecular Hydrogen Abstraction



(4) Cleavage



(5) Rearrangement (Unlikely for alkylalkoxy radicals)



(6) addition to Double Bond



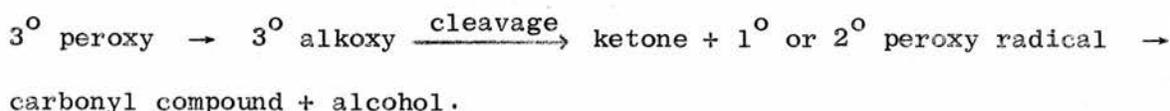
Reaction (2) is available only to primary and secondary alkoxy radicals, whereas only reactions (1) and (4) lead directly to termination. It is, however, possible for the other reactions to lead ultimately to termination if primary or secondary radicals are formed. The easiest and most common way for this to occur is via cleavage of a tertiary alkoxy radical.

The decomposition of a series of alkoxy radicals produced from their corresponding peroxides was studied by Kochi.³⁴ A selectivity in cleavage is noted with such tertiary alkoxy radicals with three alkyl groups. Kochi found the relative rates of radical formation to be:- methyl, 0.003; ethyl, 1.0; n-propyl, 0.65; n-butyl, 0.43; benzyl, very high.

The fact that that cleavage of the cumyloxy radical gives products resulting only from the methyl radical means that the phenyl radical must form less readily than the latter.

In that they will display an unusual stability to cleavage and will be excellent propagating radicals, t-butoxy and cumyloxy radicals are unique. Alkoxy radicals with substituents other than phenyl or methyl will cleave rapidly to give, in the presence of oxygen, peroxy radicals. One cannot, however, liken the behaviour of these alkoxy radicals completely to t-butoxy and cumyloxy radicals.

The termination route for tertiary peroxy radicals, thus apparently involves the following transformations:-



When alkoxy radicals are produced in reactions such as epoxidation reactions or the formation of sulfones, where only one peroxy radical is involved, it is possible that the rate-determining step for termination will become first order in peroxy radicals rather than second order.

(iii) Unimolecular Termination Reactions of Peroxy Radicals

Howard and Ingold³⁵ have noticed such a first-order termination process in the oxidation of styrene and related aromatics. It is not seen in aliphatics. Deuterium substitution in the alpha position eliminates this reaction which competes with the normal bimolecular termination reaction. The unimolecular formation of an alkoxy radical does not appear to be involved in the mechanism, but rather it proceeds by intramolecular hydrogen abstraction and generation, of hydroxyl radicals. These form phenols which terminate a kinetic chain.

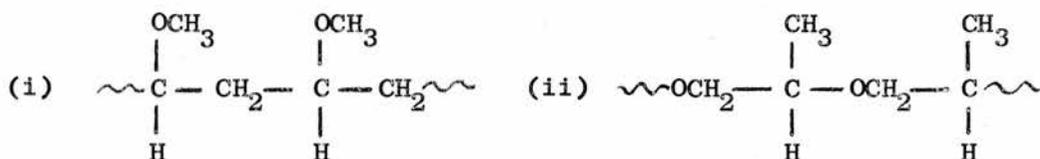
OXIDATION OF POLYMERS

There are many factors which affect these reactions, of which a

few are mentioned below.

(a) Steric Effects

Middleton and Ingold,³⁶ in their work on liquid phase oxidations, observed the effect of steric control on reactions of peroxy radicals. A most important factor in polymer oxidations in which all reactants are bulky can be steric hindrance in the substrate, RH. The oxidation of isomeric ethers, (i) poly (vinyl methyl ether) and (ii) polypropylene oxide, in which the tertiary hydrogens enjoy similar electronic environments, can best demonstrate this.



Easier access to the tertiary hydrogen in the 1,4 arrangement is shown by the fact that the rate is greater in the polypropylene oxide than in the poly (vinyl methyl ether). Russell and Bridger,³⁷ using model compounds, have shown that tertiary hydrogens, separated by two or more methylene groups, are more reactive to hydrogen abstraction, than tertiary hydrogens, separated by only one methylene group.

One of the most dramatic examples of steric hindrance is the stability of polystyrene to oxidation.³⁸ At times this stability has been attributed to inhibitor formation³⁹ or to the difficulty of the radical, on the stiff polymer chain, to attain sp^2 hybridization, presumably required during hydrogen abstraction.⁴⁰ Since, however, Bartlett et al.⁴¹ have shown that non planar radicals form readily, and since cumene, which has a hydrogen electronically similar to polystyrene, can be readily oxidised, the argument for

steric hindrance seems the most plausible.

The autoxidation of a series of polymers in which the phenyl group was progressively removed from the tertiary hydrogen has been studied by Hansen et al.⁴²: - polystyrene, poly-3-phenylpropene-1, poly-4-phenylbutene-1, poly-5-phenylpentene-1, and poly-6-phenylhexene-1. In this series the induction periods at 110°C in the order stated were 10,000; 1,900; 30; 23, and 13 hours.

(b) High-Viscosity Effects

The competing reactions of peroxy radicals have produced most speculation on the effects of high viscosity. The probability of bimolecular radical interactions should decrease as free radical mobility is decreased. Since, however, the propagation reaction involves a unimolecular peroxy radical mechanism it should not be retarded to the same extent. The rate of oxidation should, therefore, increase as the viscosity is increased. This effect, in the gamma ray - initiated oxidation of similar alkenes; hexadecene and docosene-1, has in fact been observed by Betts and Uri.⁴³ Under similar conditions, the rates of oxygen uptake were greater for the solid material than for the liquid.

Hiatt and Traylor⁴⁴ have shown that reactions of radicals in a solvent cage will depend on the viscosity of the solvent. This work has two important implications for polymer oxidations. First of all, the fact that a cage reaction is involved in the termination means that whether the radicals escape the cage after reaction or react within the cage may be a function of the viscosity. Secondly, if in studying the oxidation of a polymer, an initiator is added, then the efficiency with which radicals escape the cage in order to initiate the reaction may be a function of viscosity.

The bimolecular reaction may be replaced by, or forced to compete with a unimolecular termination process at high viscosities. The kinetics of the solid phase oxidations of isotactic polyolefins have been analysed by Notely⁴⁵ and Reich and Stivala⁴⁶ who have proposed a scheme for the peroxy radical, involving a unimolecular termination reaction. In the rubbery phase, however, the predominant reaction is still the bimolecular termination. The chemistry of the process is unknown.

(c) Tacticity

It is very likely that, apart from the effect on the crystallinity of a polymer, stereoregularity will facilitate intramolecular reactions of peroxy radicals. The differences in the kinetics of oxidation, in solution, between isotactic fractions of polypropylene and polybutene-1 and their atactic fractions⁴⁷ may be attributed to the formation and decomposition of blocks of hydroperoxide in the tactic polymers.

(d) Morphology

It has been shown by workers at the Bell Telephone Laboratories^{48,49} that the apparent degree of crystallinity of a polymer changes with the extent of oxidation, and that crystalline regions within semi-crystalline polymers are less vulnerable to oxidation than the amorphous regions.

(e) Diffusion Control

Increasing the rate of oxygen flowing through a liquid, and thereby increasing the rate of agitation of the sample, is usually sufficient to readily overcome any diffusion control of reactions in the liquid phase. This problem is not, however, as easily surmounted when dealing with polymer oxidations. The rate of absorption of oxygen by the polymer will determine the rate of oxidation unless polymer films are exceedingly thin. The reaction taking

place when thick samples are used will depend on the distance of the reaction site from the polymer surface. Two particular effects of oxygen pressure were noted in the previous discussion of the reactions of peroxy radicals. At low pressures not all termination will take place by the mutual reaction of peroxy radicals. Cross-links will be formed by alkyl radicals coupling with themselves and with peroxy radicals. Epoxides will appear as more significant products in the oxidation of unsaturated polymers. As the oxidation proceeds secondary effects of cross-linking and chain scission will be felt.

The physical properties of a polymer may be greatly affected even although only a small proportion of the oxidation products may be those formed by a cross-linking reaction or by the cleavage of a backbone carbon-carbon bond. A brittle network impervious to oxygen may be created by cross-linking; or a solid polymer may be turned into a flowing liquid by scission. Both of these reactions may take place in the same polymer sample; one at the surface and the other internally.

From the previous discussion, it is seen that of all the steps involved in oxidation, the initiation step is the one about which there is the greatest uncertainty.

It is very likely that, with polymers, steric effects, such as those observed by Middleton and Ingold³⁶ will play an important part in the initiation mechanism and rate.

It is perhaps possible that a contribution to the initiation step is brought about by the reaction, on the polymer surface, with singlet or atomic oxygen; both of which are believed to exist in

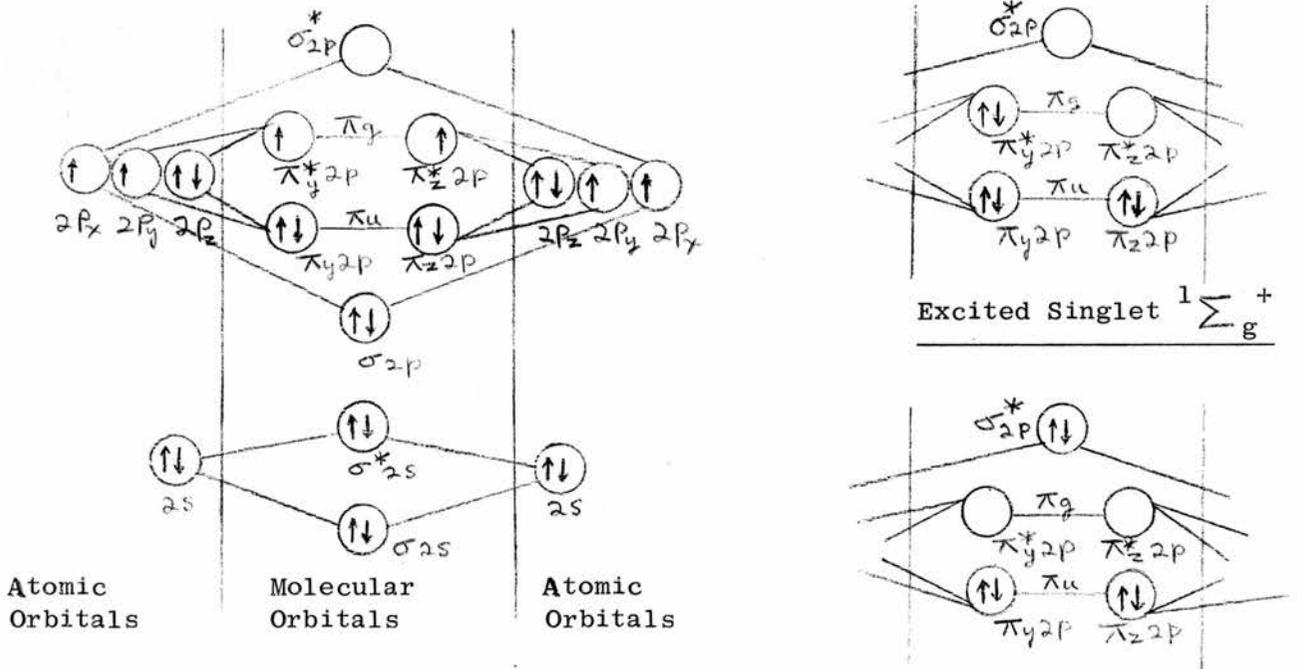
the atmosphere under normal conditions.

It is relevant to consider briefly the electronic energy levels of molecular oxygen.

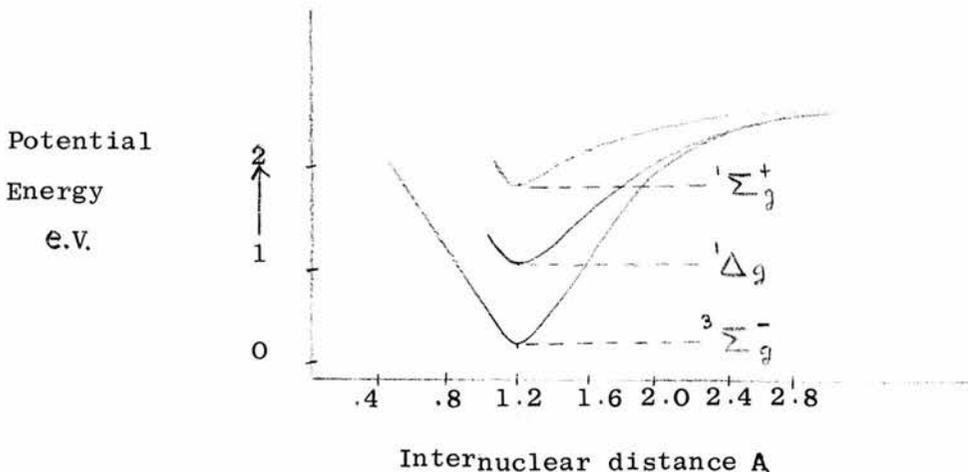
The ground-state configuration of molecular oxygen is $k\bar{k} (\sigma_g 2s)^2 (\sigma_u 2s)^2 (\pi_u 2p)^4 (\pi_g 2p)^2$, and can give rise to the three states $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$. The ground state is $^3\Sigma_g^-$, and the states $^1\Delta_g$ and $^1\Sigma_g^+$ lie above it at 0.98 eV and 1.63 eV respectively.

Ground State $^3\Sigma_g^-$

Excited Singlet $^1\Delta_g$



The two parallel spins in the degenerate π_g level lead to a triplet ground state.



Methods of generating Singlet and Atomic oxygen:-

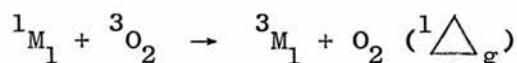
I. Singlet Oxygen

There are three main methods:-

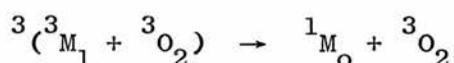
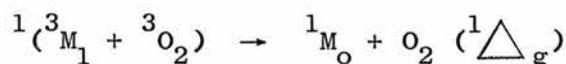
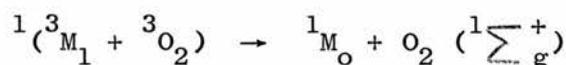
(i) Photolytically

Singlet oxygen molecules may be generated with high efficiency in dye-sensitized photo-oxygenation reactions. This is believed to occur by energy transfer from excited triplet state sensitizer molecules, and possibly from excited singlet state sensitizers. ⁵⁰⁻⁵³

e.g. (a) Oxygen quenching of excited singlet molecules.



(b) Oxygen quenching of excited triplet molecules



(ii) Chemically.

Singlet oxygen may be prepared by the decomposition of hydrogen peroxide. This method, which was used to provide the first definite evidence for the participation of singlet oxygen in photo-oxygenation reactions, ⁵⁴⁻⁵⁷ has played an important part in the chemistry of singlet oxygen.

(iii) Gaseous Discharge

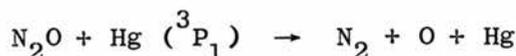
Microwave and radiofrequency discharges have proved to be two of the most convenient sources of singlet oxygen, since it is possible to excite about 10% of the oxygen to the ${}^1\Delta_g$ state, in a flow

discharge.

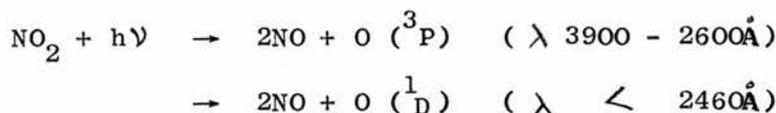
II Atomic Oxygen

(i) Photosensitized Decomposition of Nitrous Oxide

It has been shown⁵⁸ that the primary process in the quenching of Hg (3P_1) atoms by nitrous oxide is production of a molecule of nitrogen and an atom of oxygen.

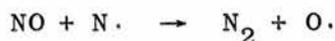


(ii) Photolysis of Nitrogen Dioxide



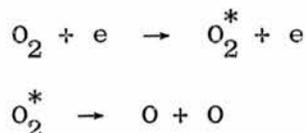
(iii) Titration of Nitrogen Atoms with Nitric Oxide

Nitrogen atoms, produced by passing molecular nitrogen through a microwave discharge cavity, are titrated with nitric oxide to produce oxygen atoms.



(iv) Production by Radio Frequency or Microwave Discharge

Atomic oxygen is produced by passing a stream of molecular oxygen through either a radio-frequency coil or a microwave discharge cavity.



The Chemistry of Atomic and Singlet Oxygen

I Atomic Oxygen

In the atmosphere, oxygen atoms, produced by the photodecomposition of NO_2 and O_3 are present in greater concentration than any other reactive atomic or free radical species.⁵⁹

The reactions of atomic oxygen with various organic materials

have been studied in the laboratory using several methods of production.

The reaction of oxygen atoms, produced by mercury photosensitized decomposition of nitrous oxide, with ethylene, has been studied⁶⁰ at room temperature and 123°C. An intermediate, formed by direct addition of the atom to the double bond, which undergoes further reactions, appears to be the primary step of the process.

A pronounced change in the amounts and the nature of the products was observed in the presence of molecular oxygen. There was a large increase in the rate of CO formation while ethane and hydrogen were completely suppressed and methane and aldehydes drastically reduced. Important quantities of products, normally encountered in the reactions of free alkyl radicals with molecular oxygen, such as HCHO, HCOOH, alcohols, and water, were found.

From the results it was suggested that the primary reaction of oxygen atoms with ethylene is not affected by the presence of molecular oxygen and that the pronounced change in the over-all course of the reaction is due to the interaction of molecular oxygen with free radicals formed in the primary process.

C.A. Arrington et al.⁶¹ have studied the reaction of acetylene with atomic oxygen at room temperature. The major products of the reaction were found to be carbon monoxide and hydrogen. In this case the atomic oxygen was produced by titrating nitrogen atoms with nitric oxide.⁶² The reaction mechanism which they suggested included a primary step the same as the primary step suggested by Cvetanovic in the reaction of ethylene with oxygen atoms. They found that there was a first-order dependence of the rate of reaction on

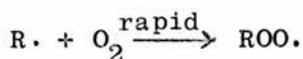
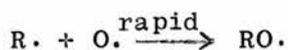
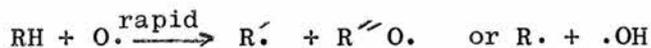
both acetylene and atomic oxygen, showing that the initial reaction, $C_2H_2 + O \rightarrow$ products, is rate controlling.

	Ethylene + O atoms	Ethylene + O atoms + Molecular oxygen	Acetylene + O atoms
P	CO	increased CO	CO
R			
O	CH_4, C_2H_6	Alcohols	H_2
D	C_3H_8, C_4H_{10}	water	+ minor
U	H_2	HCOOH	products
C			
T	CH_3CHO	Decrease in	
S	C_2H_5CHO	amount of	
	C_3H_7CHO	aldehydes	

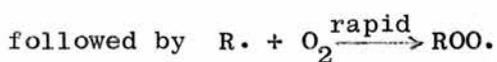
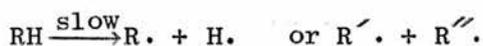
The effect of atomic oxygen on polymers was studied by R.H. Hansen et al. in 1965.⁶³ In their experiments a stream of atomic oxygen produced by passing oxygen, at low pressure, through a radio-frequency coil, was allowed to impinge on films prepared from several dozen different polymers. They found that the rapid reactions which occurred at the polymer film - oxygen radical interface were greatly affected by the structure of the polymer.

They suggested that the mechanism by which a hydrocarbon polymer is attacked by the mixture of oxygen atoms and singlet oxygen molecules, is different from the mechanism proposed for simple thermal oxidation of hydrocarbons. The initiation stage is thought to be a direct and rapid attack on the polymer, accounting for a much greater proportion of overall oxidation than the corresponding initiation for simple oxidation does.

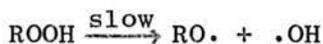
They suggested:-



Whereas in simple thermal oxidation the initiation is the relatively slow formation of hydrocarbon radicals:-



The following steps are common to both:-



This latter slow step is suggested as the reason why polymer beneath the surface is unaffected.

That the latter two mechanisms are unimportant in the oxidation of polymers by active oxygen species was also demonstrated by the fact that antioxidants were ineffective as protectants.

They also noted that the oxidised polymer surfaces exhibited remarkably low contact angles with water. This suggests that the surfaces of the polymers have become somewhat polar. Possibly due to the formation of hydroxyl groups.

II Singlet Oxygen

The chemistry of an electronically excited species may remotely resemble that of the ground-state species, but it may effectively be regarded as concerning a new chemical substance. In the case of oxygen, the properties of the low-lying singlet excited states of molecular oxygen are quite significantly different from those of the ground state.

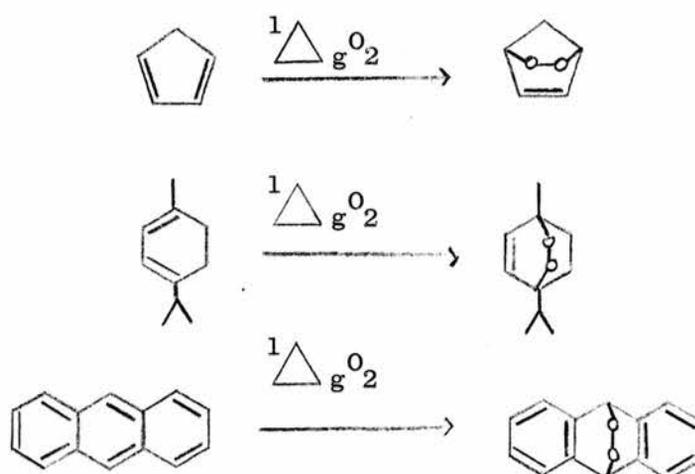
(a) Photodegradation Reactions

Recently strong evidence has been produced for identifying singlet oxygen molecules as the reactive intermediates in dye-sensitized photo-oxygenation reactions.^{50-53, 64} The case rests largely on demonstrating that results from reactions such as dye-sensitized photo-oxygenation can be reproduced using reagents which are known producers of singlet oxygen (Microwave discharge, decomposition of hydrogen peroxide).^{50,65}

These comparisons show that the products of the oxygenation reactions are the same for a given acceptor. This provides convincing evidence that free singlet oxygen molecules are indeed the reactive intermediates in many dye-sensitized photo-oxygenation reactions.

(b) Reactions with Dienes and Aromatic Hydrocarbons

Singlet oxygen appears to behave as a good dienophile in the presence of cis dienes or aromatic hydrocarbons:-



In general it is found that the molecules which are most reactive towards singlet oxygen are those which are also most reactive in Diels-Alder reactions. For example, naphthalene appears

to be unreactive toward singlet oxygen and all but the very strongest dienophiles,⁶⁶ whereas anthracene reacts well, both with singlet oxygen and other good dienophiles.

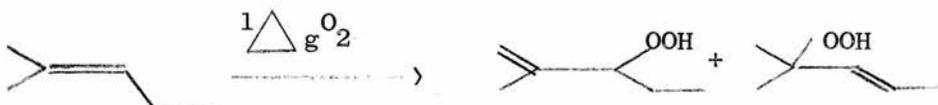
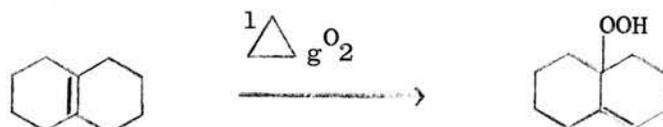
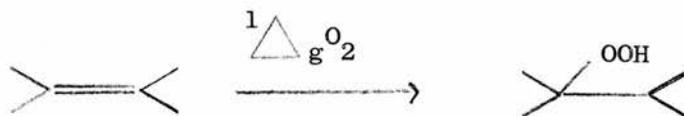
Corey and Taylor⁶⁷ proved that the cyclic peroxide products are in fact the result of addition of singlet molecular oxygen, by showing that $^1\Delta_g$ molecular oxygen, produced by a radio frequency discharge, reacts with anthracene to produce the same peroxides that are observed from sensitized photo-oxygenation experiments. Foote and Wexler⁵⁶ reacted singlet oxygen produced by hydrogen peroxide decomposition, with 2,5-dimethylfuran and 1,3-cyclohexadiene to obtain the same products previously reported for the photo-oxygenation reactions. It, therefore, seems quite conclusive that singlet oxygen is the reactive intermediate in these reactions.

(c) Reactions with Olefins

(i) Formation of Allylic Hydroperoxides

Perhaps the most thoroughly studied type of reaction with singlet oxygen is the 'ene' reaction in which oxygen adds to olefins to form allylic hydroperoxides.^{50,51,52,68,69}

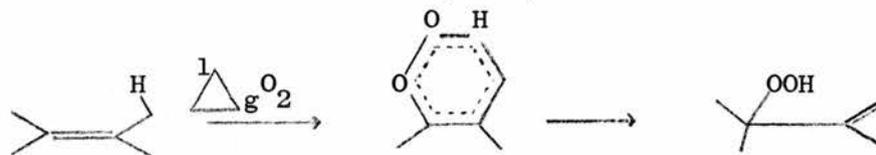
e.g.



Several mechanisms have been suggested:-

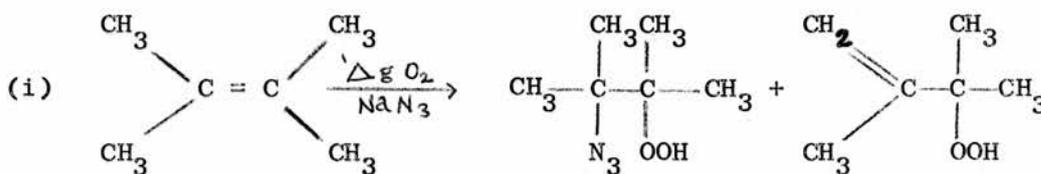
(a) The 'Ene' Mechanism

This mechanism is favoured by many authors.^{50,51,52,70,71}

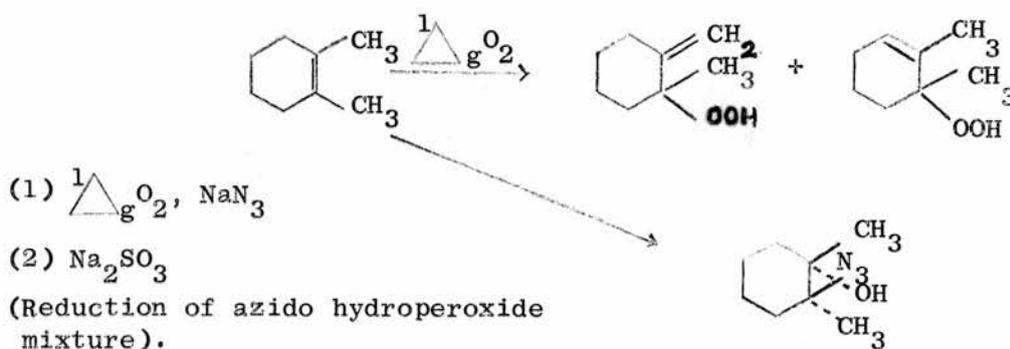


There is, however, strong evidence that this is not the correct mechanism. The addition of NaN_3 to oxygenation systems causes a reduction in the normal oxygenation products and the appearance of trans-azido hydroperoxides in their place. The azide quenching studies are definitely not consistent with the 'ene' mechanisms.^{72,73}

e.g. The following experiments were carried out by Kearns et al.:-⁷³

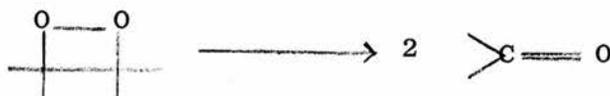


(ii)



These results completely rule out the concerted 'ene' mechanism

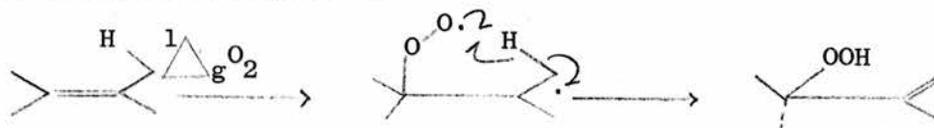
as the route to allylic hydroperoxides. They are consistent only with a reaction path involving an intermediate susceptible to attack by a suitable nucleophile. The stereospecificity of the nucleophilic displacement indicates that the intermediate is either a dioxetane:-



or a perepoxide



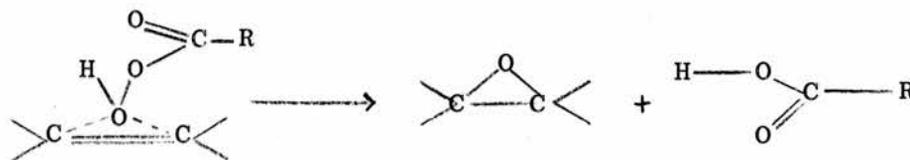
(b) Radical Intermediates



This mechanism is not favoured since it has been discovered that radical traps do not quench singlet oxygen reactions.

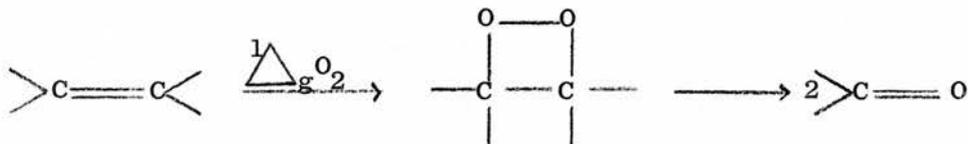
(c) Peroxirane Intermediates

This mechanism appears to be consistent with all experimental observations. The excellent correlation between rates of all peracid oxidation of olefins and their rates of reaction with singlet oxygen is thought to be due to the similarity of the two mechanisms. ⁷⁴

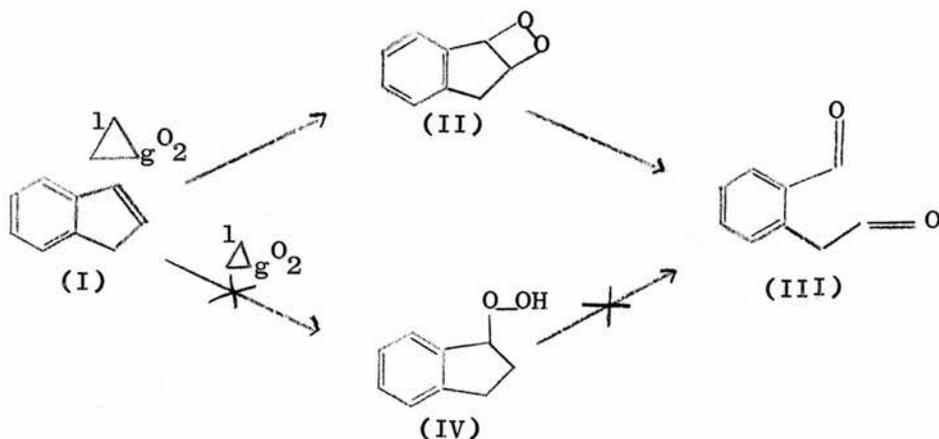


(ii) Formation of Dioxetane

Another possibility suggested several years ago⁵¹ for the reaction of singlet oxygen with olefins is 1,2 cycloaddition to form relatively unstable dioxetanes which may cleave to yield carbonyl fragments.



The general significance of dioxetane as an intermediate in singlet oxygen reactions with electron-rich olefins became clear when it was shown that a dialdehyde (III), the sole product from the sensitized photo-oxygenation of indene (I) does not arise from rearrangement of an unstable allylic hydroperoxide (IV).⁷⁵



Indisputable evidence for the intermediacy of dioxetanes in the reaction of singlet oxygen with certain olefins was finally obtained when a dioxetane was isolated from the photo-oxygenation of *cis*-diethoxyethylene.⁷⁶

Purpose of This Investigation

It can be clearly seen from the previous discussion that, of all the steps involved in an oxidation reaction, the one about which there is least certainty is the first step, the process of initiation.

There have been several postulated mechanisms for this step,¹⁰⁻¹⁵ but as yet there are no definite conclusions and in particular there is very little published work on the subject in connection with the oxidation of polymers.

It is, therefore, the purpose of this investigation to examine the effects of exposing various polymers, both in the solid state and in solution, to 'active' oxygen species. In this case the 'active' species are mainly $^1\Delta_g$ molecular oxygen and atomic oxygen, produced by microwave discharge of molecular oxygen.

It is the hope of the investigators that by studying the products and residues of the various reactions of polymers with the active species, they might gain an insight into the mechanism of initiation and a better understanding of polymer oxidations as a whole, leading perhaps to better polymer stability or if required, easier polymer photodegradation.

Chapter 2

Experimental

Oxidation of polymers under natural conditions is a very slow process and therefore, as a subject for investigation, has practical limitations. Since natural oxidation conditions probably involve excited energy rich oxygen molecules, and even oxygen atoms, as reactive intermediates, it was decided to undertake a study of a series of polymer substrates using these species, generated at relatively high concentrations, with a view to investigating the factors affecting stability to oxidation.

Polymer Samples

Solid state work was carried out using various polymer films, and solution work using different polymers in a variety of solvents.

Some of the polymer films used were commercially prepared samples, but polystyrene, on which the bulk of the work was done, was prepared by casting concentrated solutions of the polymer on to the surface of mercury. After evaporation of the majority of the solvent, the film was peeled off the mercury surface, cleaned, and put into a vacuum oven at 40°C, for several days, in order to dry it thoroughly.

Experimental work was then carried out using polymer films of constant area, cut from the larger film which was stored in the vacuum oven.

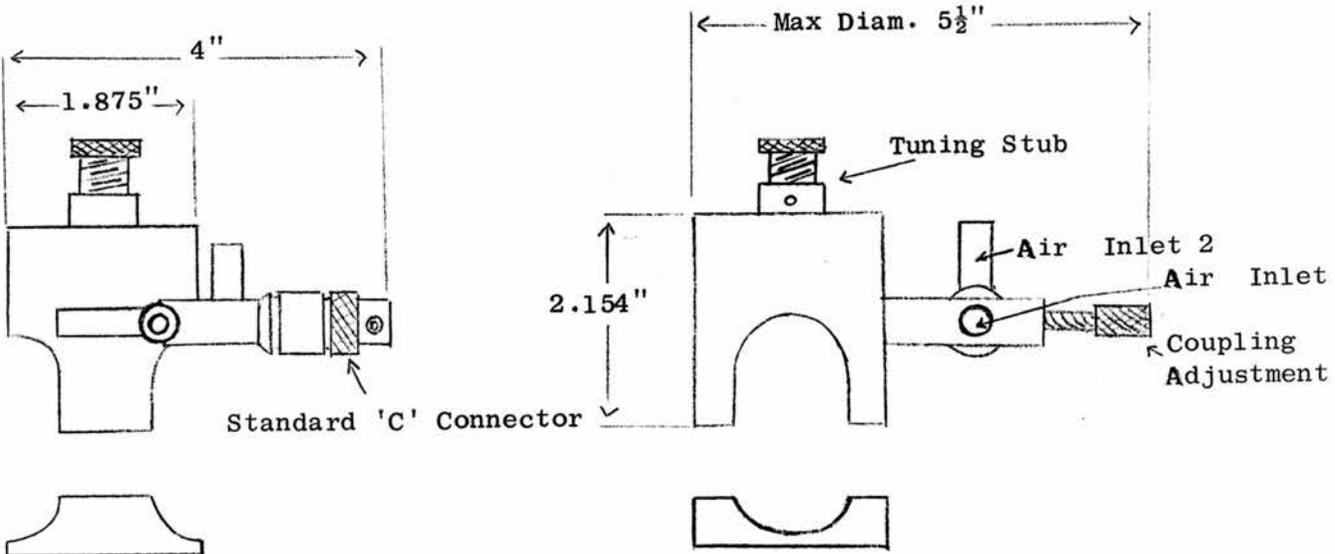
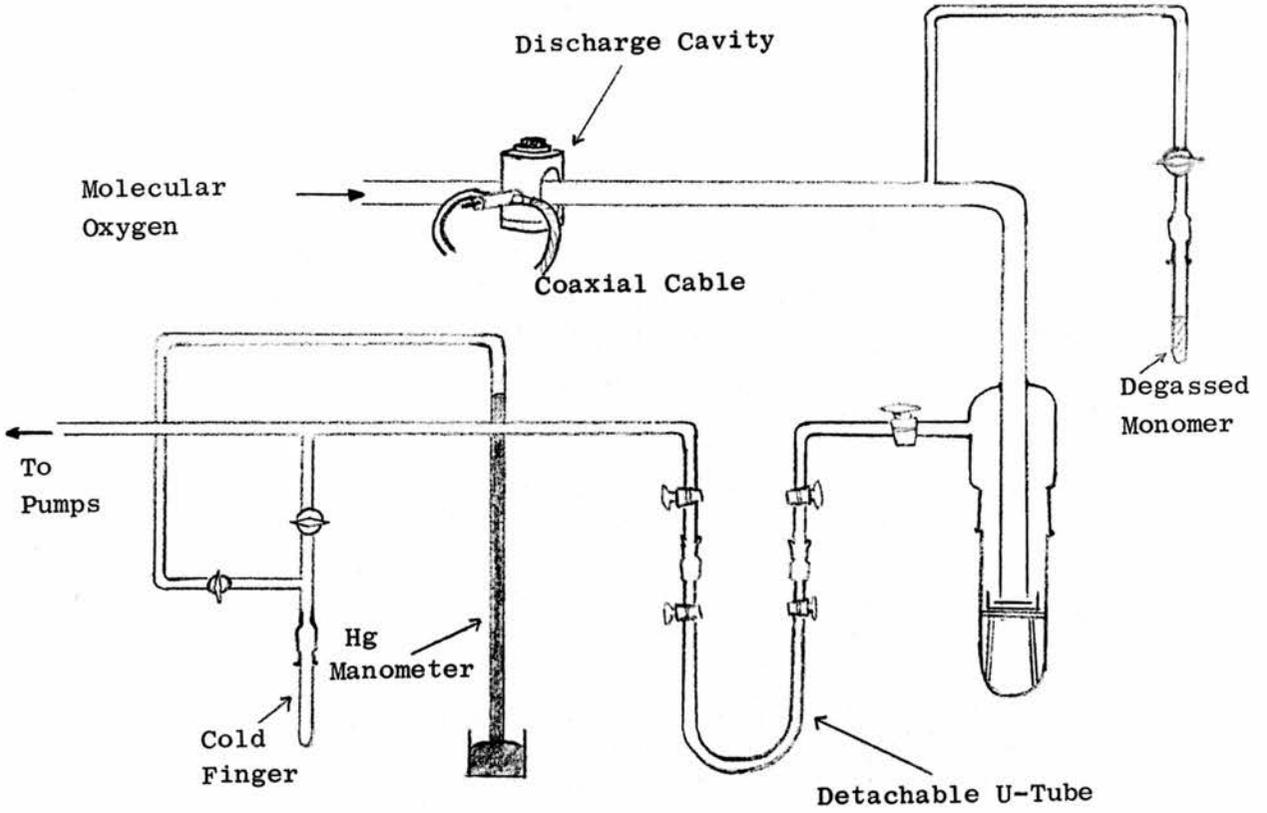
Apparatus

(a) Polymer Films

Polymer films were exposed to active oxygen species produced by passing molecular oxygen through a microwave discharge cavity.

A diagram of the apparatus used is shown in Figure 1. The right-angled bend in the discharge tube between the cavity and the polymer

Fig. 1



sample is necessary in order to prevent breakdown of the polymer by radiation emitted from the discharge.

The discharge cavity (Fig. 1) was cooled by compressed air and powered by a Microtron 200 Microwave Power Generator Unit Mark II. The heart of the Microwave Generator is the 'Magnetron', which is basically a vacuum tube operated in a magnetic field, which produces microwave energy direct to a special coaxial cable. The power to the Microtron 200 is produced by a specially designed transformer, the output from which is full-wave rectified and smoothed so as to produce a low ripple D.C. supply to the Magnetron. The microwave generator has a variable power output of 20-200 watts, and operates at a frequency of 2450 ± 25 megacycles.

In order to protect the generator it is essential that the microwave energy is dissipated in the gas discharge and not reflected back down the cable to the magnetron valve, so causing excessive overheating and possible damage to the magnetron cathode. The Microtron 200 Mk. II is, therefore, fitted with a reflected power meter which gives automatic protection to the magnetron valve in the generator, should the gas discharge fail, or for any reason which causes an excess amount of power to be reflected. The meter reads directly, in watts, the power not being absorbed at the discharge cavity.

The discharge cavity is an Electro-Medical Supplies' cavity Type No. 214L, 2" diameter by $2 \frac{1}{4}$ " long with variable coupling at right angles to the cavity length. It has a coaxial input connector, integral with cooling air inlets and a tuning stub in line with the length of the cavity. There is a removable

end cap for fitting the resonator on an existing vacuum system. The cavity is fitted with a 'c' type connector which will accept the coaxial output cable from the Microtron 200 generator.

The gas discharge is fired by use of a 'Tesla Coil'. The microwave generator is then adjusted to the required output, and the discharge cavity is tuned so as to give a minimum reading on the reflected power meter. The tuning procedure is to screw the top tuning stub its range for each movement of the side coupling adjustment. Movement of the coupling adjustment one turn anticlockwise at a time, with a run through the range of the tuning stub, ensures that the optimum setting of the cavity will be found. Final slight adjustment of each control for the minimum reflected power, in turn, produces the best results.

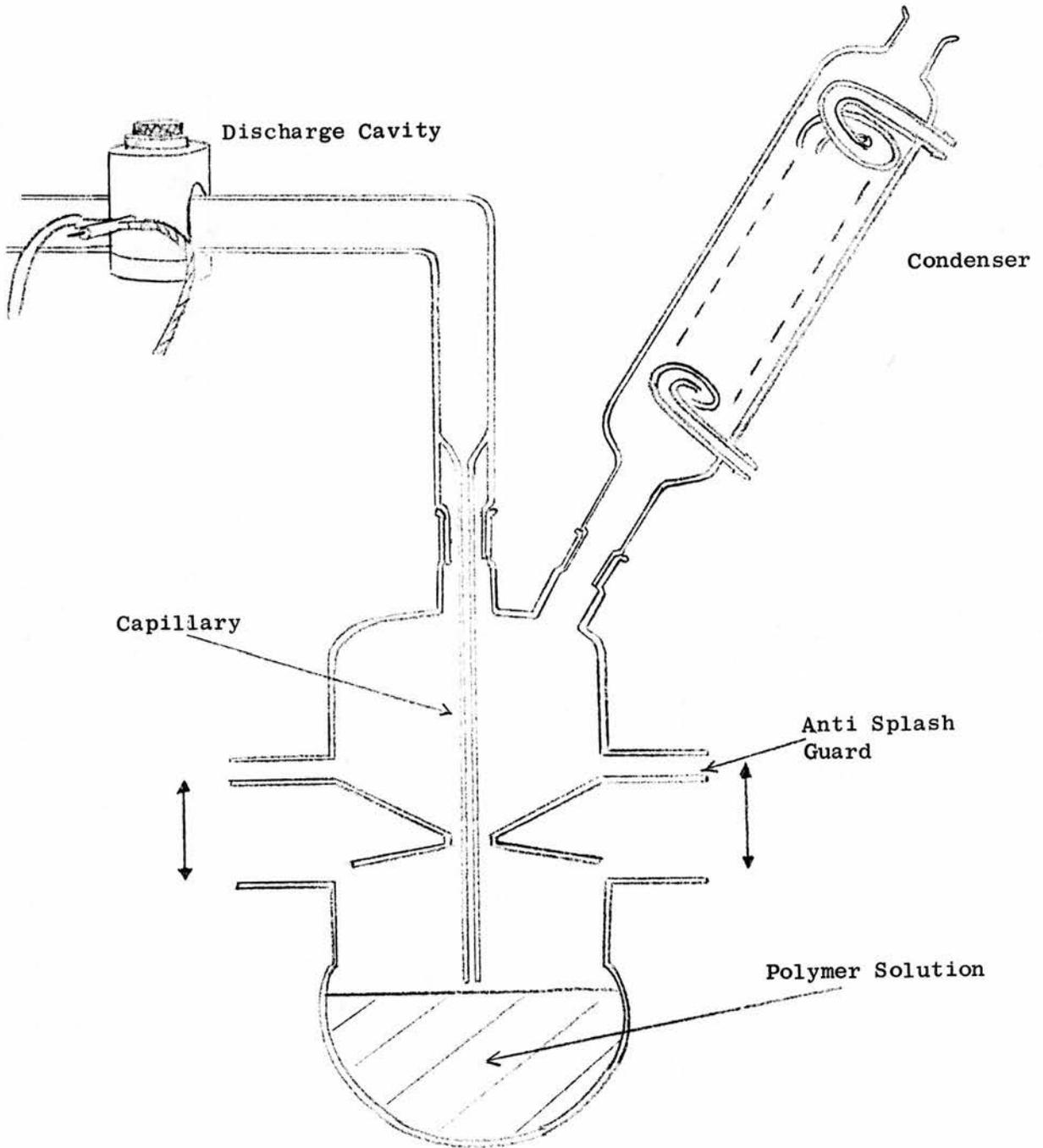
(b) Polymer Solutions

A diagram of the apparatus used is shown in Figure 2. As with the polymer films, the power unit is a Microtron 200, but due to the different bore of the tubing, the cavity used has slightly different dimensions.

Nature of the discharge

In the case of discharged oxygen, there is an appreciable concentration (10 - 20%) of oxygen atoms generated in the plasma region, and depending on the conditions, an equivalent amount of electronically excited molecular oxygen in the ${}^1\Delta_g$ state. The rest of the plasma consists of a mixture of normal ground state oxygen molecules, free electrons, and ionized species. Both of the latter entities have disappeared within a few millimetres of the glow region leaving only 'active' oxygen, ie. atomic and ${}^1\Delta_g$

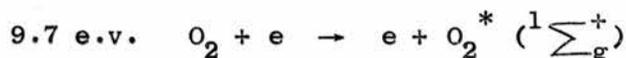
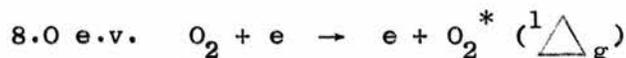
Fig. 2



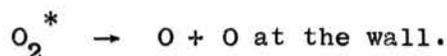
Solution Apparatus

molecular oxygen, which are carried downstream where they deactivate reactively or by collision.

The production of oxygen atoms in the discharge glow region is due to several reactions, namely; electron-molecule reactions, molecule ion-electron reactions, and electronically excited molecular oxygen ($^1\Delta_g$) dissociation. It has in fact been calculated⁷⁷ that, in the case of oxygen, the cross-sections for vibrational excitation are so small that they can be neglected. Thus the production of oxygen atoms is due mainly, in the absence of foreign gases, to electronic excitation. This can be of three forms the most important two being at 8.0 and 9.7 e.v.



Followed by

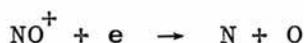
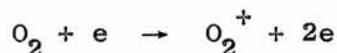
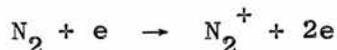


Above the ionization potential for oxygen (12.5 e.v.), at which $\text{O}_2 + e \rightarrow \text{O}_2^+ + 2e$ occurs, the following two processes take place:-



The rates of these reactions, however, are so slow that they cannot account for the large concentration of oxygen atoms actually generated. The production of this high concentration is due in large part to the catalytic effects by the presence of other 'foreign' gases, such as hydrogen, nitrogen or water vapour. These impurities provide many of the kinetic pathways leading to atomic oxygen production. With nitrogen as the main impurity in the discharged

oxygen, the following reactions may participate:-



The following reactions may also occur:-



Thus if very pure oxygen is discharged, one will find the usual glow breakdown characteristics, but the plasma will consist of a very low level per cent of oxygen atoms.

The usual impurities in bottled oxygen, however, prove to be sufficient to give the catalytic activity desired for the production of atomic oxygen in appreciable quantity.

It was later found that the concentration of nitrogen in the molecular oxygen is not constant. This proved to be insignificant however, since reproducible results were obtained. It therefore appears that nitrogen acts mainly as a catalyst and therefore its concentration is unimportant, provided that it is low.

Experimental Procedure

A. Polymer Films

(i) Relationship between weight loss and time of exposure to active oxygen.

Films of constant area, $2.5 \times 10^{-4} \text{ m}^2$, were cut using a cork borer, and placed in the reaction vessel (Fig. 1). The vacuum line was then pumped flat using a rotary oil pump and a mercury diffusion pump. Oxygen was then admitted to the system, via a

needle valve, until the pressure rose to 6.67 Nm^{-2} .

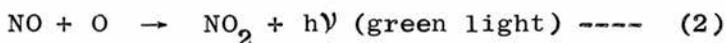
When the pressure was steady the discharge was fired by means of a 'Tesla Coil', and the power output of the Microtron 200 was adjusted to 40 watts. The discharge cavity was then tuned to give a minimum of reflected power (< 5 watts). The polymer sample was removed from the system and weighed at regular intervals. This process was repeated for several different polymer samples. In each case a graph of weight loss versus time was plotted and the results compared.

(ii) Determination as to which of the active oxygen species is the reactive agent

The only active species that one need be concerned with, ie. the only species which will live long enough to reach the polymer sample, are excited singlet molecular oxygen in the $^1\Delta_g$ state, and atomic oxygen.

In order to determine which of these two species is the reactive one, it was necessary to redesign the reaction vessel. This was done such that NO_2 could be introduced into the vessel at a point just above the surface of the polymer film. (Fig, 3).

By this method all of the oxygen atoms could be removed, leaving excited singlet molecular oxygen as the only active species. On introduction of NO_2 into the stream of oxygen atoms the following reactions occurred:-



As long as there was excess oxygen then reaction (2) could occur, emitting a pale green light. When the flow rate of NO_2

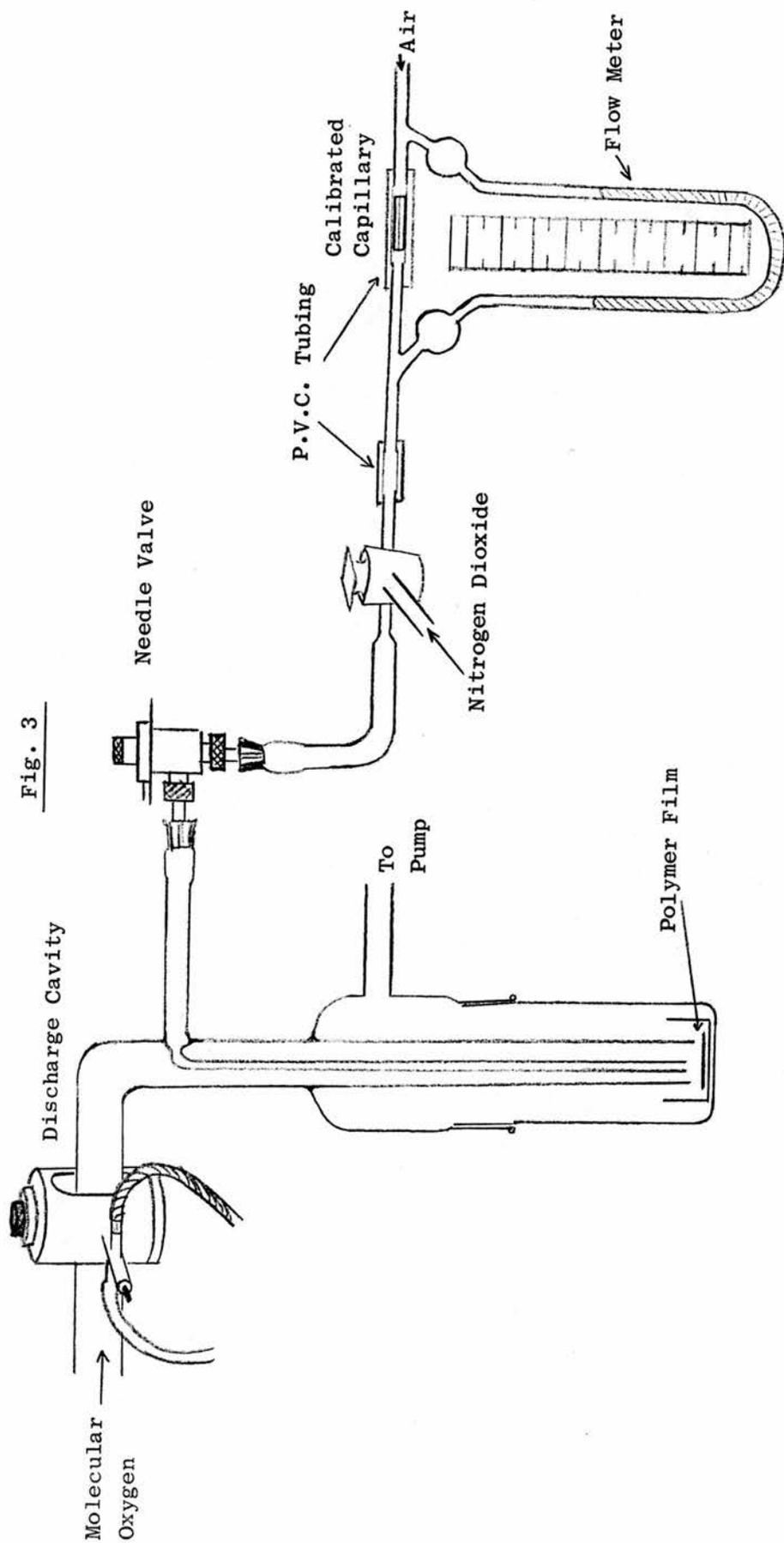


Fig. 3

equals the flow rate of oxygen atoms, however, then there is no excess atomic oxygen to react with the nitric oxide, with the result that, at this point, ie. the end point of a gas-phase titration, the green glow is sharply extinguished.

The experimental procedure carried out in (i) was then repeated with samples of polystyrene and poly (vinyl chloride). In this case however, all of the oxygen atoms were titrated out using NO_2 so that the polymer samples were exposed only to $\frac{1}{2}$ molecular oxygen.

(iii) Determination of Change in Concentration of Oxygen Atoms with changing Power and Flow of Molecular Oxygen

The flow rate of oxygen atoms, in mls/min, was determined by titrating the oxygen atoms, as previously described, with NO_2 . A flow meter with a calibrated capillary (Gallenkamp FL-556, size No. 1, Serial No. 3751) was connected to the system in order to measure the flow rate of NO_2 (Fig. 3).

The capillary was calibrated for air. It, therefore, had to be connected to the system in such a way as to draw air through it at the same rate as NO_2 . This was achieved by means of a three-way tap which could be adjusted to let either air or NO_2 flow into the system through the needle valve. With NO_2 flowing into the system the needle valve was opened until the green glow, produced by atomic oxygen reacting with nitric oxide, was just extinguished. At this point the flow rate of the NO_2 was equal to the flow rate of oxygen atoms. The three-way tap was then adjusted so as to cut off the flow of NO_2 into the system and allow air to be drawn in through the capillary of the flow meter. Since the needle valve setting was the same, then the flow rate of air was equal to the

flow rate of NO_2 and therefore that of oxygen atoms, and could be read off directly from the flow meter calibration graph.

By keeping the power constant and varying the flow rate of molecular oxygen it was possible to obtain a plot of molecular oxygen flow rate versus oxygen atom flow rate. Similarly, by keeping the flow rate of molecular oxygen constant and varying the power it was possible to obtain a plot of power versus oxygen atom flow rate.

(iv) Relationship between Rate of Weight Loss (-dw/dt) and Power

The pressure in the vacuum system was kept constant at 6.67 Nm^{-2} , thus ensuring a constant flow of molecular oxygen. Weight loss versus time runs were then carried out, as previously explained, with polystyrene, at a specific power. The power was then altered and the runs were repeated at the same pressure as before. This was repeated several times enabling a graph of (-dw/dt) versus Power to be obtained. The process was later repeated with poly (vinyl chloride).

(v) Identification of Products

Two methods were used for analysing the gaseous products. The products were trapped out in the U-tube (Fig. 1) and either distilled over into the cold finger which could be removed and attached directly to a mass spectrometer, or else distilled over into an infrared gas cell. In this way mass spectra and infrared spectra of the gaseous products were obtained.

The residual films were examined for chemical changes by infrared spectroscopy, both transmission and attenuated total reflection, using an ATR, TR-9 Perkin-Elmer unit with a KRS trapezoid crystal.

(vi) Relationship between the Pressure of Gaseous Product and Time of Exposure

Using the cold finger attached to the Hg manometer (Fig. 1), gaseous product was trapped out and its pressure measured at regular intervals.

The gaseous product was initially trapped out in the U-tube and, when a pressure reading was required, distilled over into the cold finger. The cold finger was then isolated from the rest of the system and opened to the Hg manometer. It was then warmed to room temperature and the pressure of the gaseous product read off directly from the manometer. This was repeated several times in order to obtain enough data for a plot.

(vii) Molecular Weight Changes in Polystyrene with Exposure

Using the apparatus shown in Fig. 1., polystyrene films were exposed to active oxygen species for varying lengths of time. At the end of each reaction the exposed film was removed from the vacuum system and the molecular weight was determined by viscometry using the following equations:-

$$[\eta] \text{ intrinsic viscosity} = \lim_{C \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 C} = KM^\alpha$$

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

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

where t = efflux time of solution in seconds
and t₀ = efflux time of solvent in seconds.

Therefore, by plotting η_{sp}/c versus C one obtains $[\eta]$ as intercept and the average viscometry Molecular Weight, M, from the

Mark-Houwink equation⁷⁸ $[\eta] = KM^\alpha$

Where, for polystyrene

$$K = 1.1 \times 10^{-4} \text{ dl/g} \quad \text{at } 30^\circ\text{C in Toluene.}$$
$$\alpha = 0.725$$

After exposure various concentrations of solutions of polystyrene in toluene were made up and put in the viscometer which was kept in a thermostatic bath at 30°C . The viscometer used was a PSL ref. BS/1P/SL size No. 2, suspended-level viscometer.

The experiment was then repeated using films of polystyrene prepared by a different method, in order to eliminate solvent effects.

In this case the polystyrene films were prepared without the use of solvent. Pellets of the polymer were placed in a KBr die, which was then heated to above the T.G. of polystyrene ($\sim 100^\circ\text{C}$). Pressure was then applied ($3.4 \times 10^6 \text{ Nm}^{-2}$) to the die with a hydrolic press, thus moulding the pellets into a film. Films prepared in this way were checked by viscometry. The results indicated no change in molecular weight. Therefore, no degradation had occurred.

The results obtained using films prepared by casting and films prepared by pressure and heat were then compared.

(viii) Molecular Weight Changes in a Cast Film

A film of polystyrene was prepared by dissolving pellets of the polymer in carbon tetrachloride and casting the solution on to the surface of mercury. The film was then peeled off the mercury surface, after evaporation of solvent and as before left in a vacuum oven at 40°C to dry. The molecular weight of the polymer was then checked every few days by viscometry.

The experiment was repeated using poly (methyl methacrylate). In this case films were cast directly on to the surface of small brass vessels. This was done by placing samples of reprecipitated polymer in the vessels and then dripping acetone on to the polymer until it just dissolved. Within a few hours the solvent had evaporated off sufficiently to allow the vessels to be placed in the vacuum oven. Once again samples were taken from the oven every few days and the flow time of a 0.2% solution recorded. In this case the molecular weight was not calculated. The changes in the efflux time gave a good indication of any molecular weight changes. A reprecipitated sample of poly (methyl methacrylate) powder was placed in the vacuum oven along with films, and its efflux time (0.2% solution) was also recorded every few days.

(ix) Thermal Stability After Exposure

Films of polystyrene were exposed to active oxygen for varying lengths of time and then degraded on a modified Stanton Massflow Thermobalance.⁷⁹ A plot of film weight versus temperature was obtained directly from the recorder of the balance. The plots obtained were then compared with the plot for the thermal degradation of an untreated sample of polystyrene film, in order to determine whether exposure to active oxygen species caused any changes thermal stability.

(x) Constant Angle Measurements

Surface changes in exposed polymer films may be examined by studying the contact angle of a liquid on the surface of the film.

In this case the liquid used was purified water and the polymers, polystyrene, polyethylene terephthalate, poly (vinyl chloride), polyacrylonitrile and nylon 66. Measurements were made before and

after exposure of the films to active oxygen species.

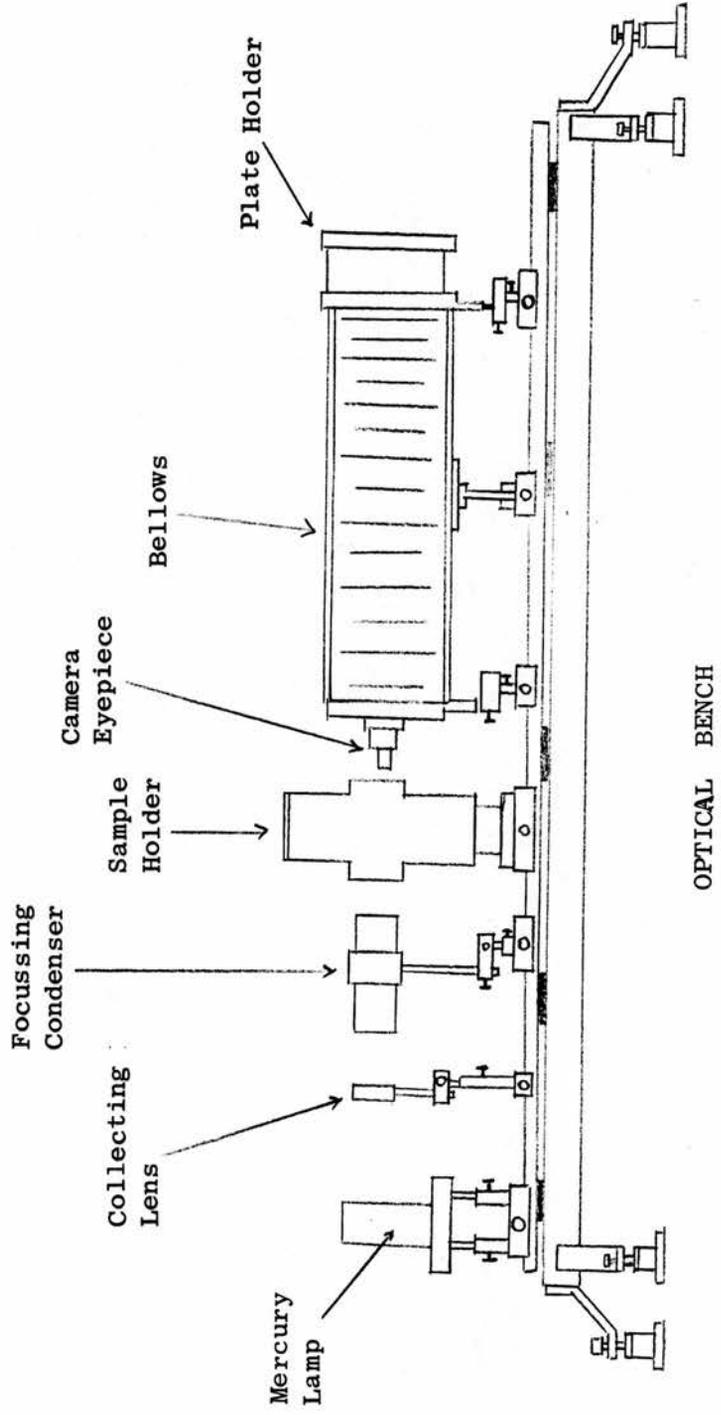
The contact angle of purified water with the surface of the exposed film was measured from a photograph of the drop of water on the surface taken using an optical bench camera system. (Fig. 4). The light source for the camera was a high pressure mercury lamp mounted on a saddle base positioned at one end of an optical bench. The lamp could be adjusted vertically. The camera and the rest of the lens systems were also mounted on similar saddle stands which provided for adjustments being made in both vertical and transverse directions with respect to the bench.

Light from the mercury lamp was collected by a condenser lens of focal length 2 inches. It was used to focus the light source on to the collimator pin hole. The collimator was comprised of a Dallmeyer achromatic lens of focal length 2 inches, fitted into the end of a brass tube adjusted so that the pin hole was at its focal length. From the collimator the light beam passed through the sample holder into the 2 inch projector lens of the camera eyepiece. The camera had a bellows extension of about 100 cm connecting the eyepiece with the quarter plate holder. This provided a maximum magnification of about 18 times the size of the drop.

A Rowi-pneu standard shutter operator was fitted to the camera, which was capable of giving exposure times down to 1/500th sec. The stop could be varied from f.8 to f.64.

For display and focussing purposes a ground glass screen was mounted into a quarter plate holder which could be fitted to the camera in place of the photographic plate. This made possible initial examination of the image of the drop of water on the surface of the polymer film before photographs were taken.

Fig. 4



After obtaining a series of measurements of contact angle for various times of exposure of polystyrene to active oxygen, the experiment was repeated using the other polymers.

Photographs of the drops of water on the film surfaces were enlarged and measurements taken directly from the enlargements. Graphs were then plotted of contact angle versus time of exposure to active oxygen species.

(xi) Introduction of Monomer to Exposed Poly (vinyl chloride)

Using the apparatus shown in Fig. 1., monomer vapour was bled into the evacuated vessel containing the exposed polymer film. The monomer used was methyl methacrylate whose major peaks on an infrared spectrum are at 1640 and 1725 cms.^{-1} . Due to the fact that these peaks would be masked on an infrared spectrum of polystyrene it was decided that poly (vinyl chloride) should be used as substrate.

Before exposing the polymer, the monomer in the side arm was degassed. After exposing the film to active oxygen species for 4 hours the discharge was stopped, the reaction vessel evacuated, and then sealed off from the rest of the system. Monomer vapour was then bled into the reaction vessel by opening the tap in the side arm leading to the degassed sample. After half an hour the reaction vessel was opened to the rest of the vacuum system and evacuated, in order to remove any unreacted monomer. After pumping for several hours, the polymer film was removed from the system and its infrared spectrum obtained. This spectrum was then compared with the spectrum of untreated polymer. The treated film was then soaked in methanol in order to remove any absorbed monomer

and a further infra red spectrum obtained. The film was then placed in a vacuum oven for $2\frac{1}{2}$ hours at 110°C and yet another infra red spectrum recorded. All the spectra were then compared and interpreted.

A sample of poly (vinyl chloride) was then saturated with monomer vapour for half an hour, without previously exposing it to active oxygen. An infrared spectrum of this film was then recorded and compared with the previous ones.

(xii) Modification of Inert Surfaces by Treatment with Active Oxygen Species

Thin discs ($3.4 \times 10^{-4} \text{ m}^2$ in area) of stainless steel and glass were exposed for two or three hours to a mixture of oxygen atoms and singlet oxygen molecules, using the apparatus shown in Fig. 1, at a pressure of 6.67 Nm^{-2} .

The flow of oxygen and the discharge were stopped and monomer vapour pumped over the disc for half an hour. After discontinuing the flow of monomer, the sample was pumped out for a further hour. It was then removed and the contact angle was measured, as previously described, both before and after washing with solvent. Identical discs were dipped into solutions of the corresponding polymers and the solvent evaporated leaving a thin film of the polymer on the surface. The contact angles of pure water with those surfaces were then measured for comparison with the treated samples.

B. Solutions

The apparatus shown in Fig. 2 was used for all the experiments involving solutions.

Molecular oxygen was passed through the discharge cavity using argon as carrier gas. The active oxygen was then carried down a

capillary tube and bubbled into the polymer solution. Due to the heat generated in the discharge at atmospheric pressure it was found that it was necessary to replace the pyrex tubing with quartz tubing, which could withstand the high temperature without melting.

It was found that stirring of the polymer solution was unnecessary since the bubbling of the gases caused sufficient agitation.

With the original apparatus it was found that polymer solution lost weight by splashing and evaporation. The apparatus was then redesigned (Fig. 2) such that splashing would be eliminated and evaporation cut down. This was done by incorporating a splash guard in the reaction vessel and by passing the 'exhaust' gases through a condenser.

Any weight loss was, therefore, due to evaporation of pure solvent, and could be rectified by weighing the polymer solution both before and after reacting with active oxygen, and adding solvent to make up the weight difference.

Molecular Weight Measurements

The molecular weights of the polymer solutions were determined by viscometry, using the Mark-Houwink equation $[\eta] = KM^\alpha$; where $[\eta]$ = intrinsic viscosity, K and α are constants dependent on the temperature and the solvent and M is the viscometry average molecular weight.

In order to save time and effort it was convenient to determine the intrinsic viscosity from one-point measurements.⁸⁰

Intrinsic viscosities are generally determined by plotting η_{sp}/C or $\ln \eta_r/C$, where η_r (relative viscosity) = $\eta_{sp} + 1$, against C, and extrapolating to C = 0. In the region of linearity,

the plots obtained can be represented by the following equations:-

$$(1) \quad \eta_{sp}/C = [\eta] + \alpha C$$

$$(2) \quad \ln \eta_r/C = [\zeta] - \beta C$$

where α and β are constants. Letting $\gamma = \alpha/\beta$ and multiplying equation (2) by γ , the result obtained is:-

$$(3) \quad (\gamma \ln \eta_r)/C = \gamma [\zeta] - \alpha C$$

Adding (1) and (3)

$$(\eta_{sp}/C) + (\gamma \ln \eta_r)/C = (1 + \gamma) [\eta]$$

and therefore

$$(4) \quad [\eta] = \frac{(\eta_{sp}/C) + (\gamma \ln \eta_r)/C}{(1 + \gamma)}$$
$$= \frac{\eta_{sp} + \gamma \ln \eta_r}{(1 + \gamma)C}$$

For each polymer/solvent system at a given temperature γ is constant and independent of the molecular weight. Therefore, if γ were determined on one sample of a polymer in a given solvent, the same value of γ should apply to all other samples, and equation (4) would be sufficient to yield $[\eta]$ from a single viscosity measurement.

The parameter γ is readily obtained from plots of η_{sp}/C and $\ln \eta_r/C$ against C . γ is equal to the ratio of the two slopes.

Using the above equation enabled changes in the molecular weight of a polymer in solution to be calculated at regular intervals.

The initial viscometry measurements were carried out using a suspended-level viscometer (BS/IP/SL, size No. 2) in a Townson and Mercer thermostatic bath, using a mercury temperature regulator.

Flow times were measured using a stop watch, and the solution was influxed by means of a hand pump.

The results obtained were found to be inaccurate and could not be reproduced. There were several reasons for this which had to be rectified:- (1) Although the solutions were filtered it was found that they very quickly picked up dust to which the viscometer was very sensitive. This was rectified by filtering the solution through a sintered glass tube adapted to fit directly into the viscometer. Even this method was not completely unsuccessful, and it was necessary to periodically clean the viscometer with permanganic acid. In this way any errors in timing due to particles of dust were eliminated. (2) Temperature fluctuations, although small ($< \pm 0.1$) were in fact large enough to cause variations in the efflux time, which were often larger than the change in flow time caused by the reaction with active oxygen. This error was eliminated by changing to a Townson and Mercer bridge controlled thermostat bath accurate to $\pm .01^{\circ}\text{C}$ (3) The error in timing with a stop watch is far too great. This was rectified by using a Hewlett Packard auto-viscometer system, model 5901B. With this system the solution in the viscometer was automatically influxed to the same level, thus erradicating variations in efflux time due to drainage error. The flow time was measured with a photo-detector attached to the viscometer. The detector consisted of an upper and lower photo-diode, each complete with a lamp unit, and was sensitive to the change in light transmission caused by a passing meniscus. The response time was 10 microseconds and the measurement of efflux time was accurate to $\pm .01$ seconds. The timing accuracy was based on a quartz crystal

oscillator with a stability of better than 2 parts per million per week and was not affected by variations in the frequency of mains power.

Thus very small changes in molecular weight, giving rise to very small changes in efflux time could be detected.

Solutions of polystyrene in toluene and carbon tetrachloride, and poly (methyl methacrylate) in toluene were treated with the active gases as previously described. At regular intervals the reaction was stopped, the polymer solution made up to its initial weight by addition of solvent, and a sample taken for viscometry. The polymer solution was reweighed before starting the reaction again.

Pure solvent was also exposed to the active oxygen and its efflux time measured at regular intervals. This was done both with and without correction for evaporation.

Changes in Thermal Stability

After several hours exposure to active oxygen, polystyrene was reprecipitated from a solution of toluene, and dried in a vacuum oven for several days. The sample was then degraded on a modified Stanton Massflow Thermobalance, and a plot of weight of sample versus temperature obtained. This plot was then compared with one obtained by degrading a sample of untreated polystyrene reprecipitated in the same manner.

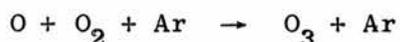
Exposure of Monomer

Redistilled ethyl methacrylate was exposed to active oxygen in the same manner as the polymer solutions. At regular intervals the reaction was stopped and a sample of monomer removed. Using a suspended level viscometer, as before, the efflux time of the exposed monomer was recorded. Any changes in time gave an indication of changes in molecular weight.

After several hours exposure the monomer was allowed to evaporate to see if there was any residue.

Detection of Ozone (O₃)

Since the discharge is taking place at atmospheric pressure it is possible that ozone may be formed as follows:-



It was, therefore, decided that ozone must be looked for. The presence of ozone in a gas may be detected by reaction with indigo (I) or a (I) derivative, on SiO₂ which acts as a catalyst for the solid phase reaction.⁸¹ No solvent is required, and thus the reagent is stable indefinitely. The colour formed cannot be removed from the carrier by solvents. The reaction is specific for O₃. Halogens, nitrous gases, and SO₂ do not interfere. The reaction is based on an ozonide intermediate and formation of isatine (II) or a (II) derivative, which are only faintly coloured compared with (I)

100gms. of purified SiO₂ was uniformly impregnated with a 0.01% solution of (I) in 1:1 EtOH: H₂O. The solvent was volatilized at 100°C to constant weight. Only 1 part per million of O₃ is sufficient to discolour a 50mm length of tubing of the detector, per litre of gas passed.

Even after several hours of exposure to active oxygen, no colour change was detectable. It was, therefore, concluded that there was no ozone present.

Results

Relationship between Weight Loss and Time of Exposure to Active
Oxygen Species

(i) Polystyrene

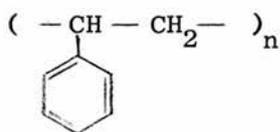


Table 1

Weight of Polymer Film mg.	Loss in Weight mg.	Total Weight Loss mg.	Time of Exposure	Total Exposure Time
53.5	0.0	0.0	0 hr.	0 hr.
53.2	0.3	0.3	1.0	1.0
52.1	1.1	1.4	2.5	3.5
51.0	1.1	2.5	2.5	6.0
49.8	1.2	3.7	2.5	8.5
48.6	1.2	4.9	2.5	11.0
47.6	1.0	5.9	2.5	13.5
46.3	1.3	7.2	2.5	16.0
45.0	1.3	8.5	2.5	18.5
43.8	1.2	9.7	2.5	21.0
42.6	1.2	10.9	2.5	23.5

(ii) Poly(vinyl chloride)

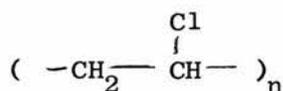
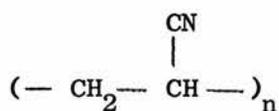
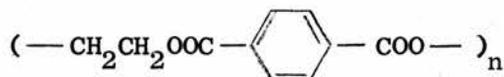


Table 2

Weight of Polymer Film mg.	Loss in Weight mg.	Total Weight Loss mg.	Time of Exposure	Total Exposure Time
18.7	1.3	1.3	2.0 hr.	2.0hr.
14.1	4.6	5.9	2.0	4.0
10.9	3.2	9.1	2.0	6.0
6.2	4.7	13.8	2.0	8.0

(iii) PolyacrylonitrileTable 3

Weight of Polymer Film mg.	Loss in Weight mg.	Total Weight Loss mg.	Time of Exposure	Total Time
35.9	0	0	0 hr.	0 hr.
34.3	1.6	1.6	2	2
33.0	1.3	2.9	2	4
32.0	1.0	3.9	2	6
30.8	1.2	5.1	2	8
29.8	1.0	6.1	2	10
28.5	1.3	7.4	2	12

(iv) Polyethylene TerephthalateTable 4

Weight of Polymer Film mg.	Loss in Weight mg.	Total Weight Loss mg.	Time of Exposure	Total Time
17.8	0	0	0 hr.	0 hr.
17.5	0.3	0.3	2	2
17.3	0.2	0.5	2	4
16.9	0.4	0.9	2	6
16.6	0.3	1.2	2	8
16.4	0.2	1.4	2	10
16.1	0.3	1.7	2	12
15.8	0.3	2.0	2	14

(v) Nylon 66



Table 5

Weight of Polymer Film mg	Loss in Weight mg	Total Weight Loss mg	Time of Exposure	Total Time
15.7	0	0	0 hr.	0 hr.
14.7	1.0	1.0	3	3
14.2	0.5	1.5	3	6
13.4	0.8	2.3	3	9
12.7	0.7	3.0	3	12
12.2	0.5	3.5	3	15

The above results were plotted (see Fig. 5: Polymer Weight Loss/mgs. vs. Time of Exposure/Hrs.) and, from the slopes the rates of weight loss (-dw/dt) for the various polymers were obtained.

Table 6

Polymer	-dw/dt
Polystyrene	0.46 mg./hr
Poly (vinyl chloride)	2.50 mg./hr
Polyacrylonitrile	0.57 mg./hr
Polyethylene Terephthalate	0.15 mg./hr
Nylon 66	0.22 mg./hr

Relationship between Rate of Weight Loss (-dw/dt) and Power

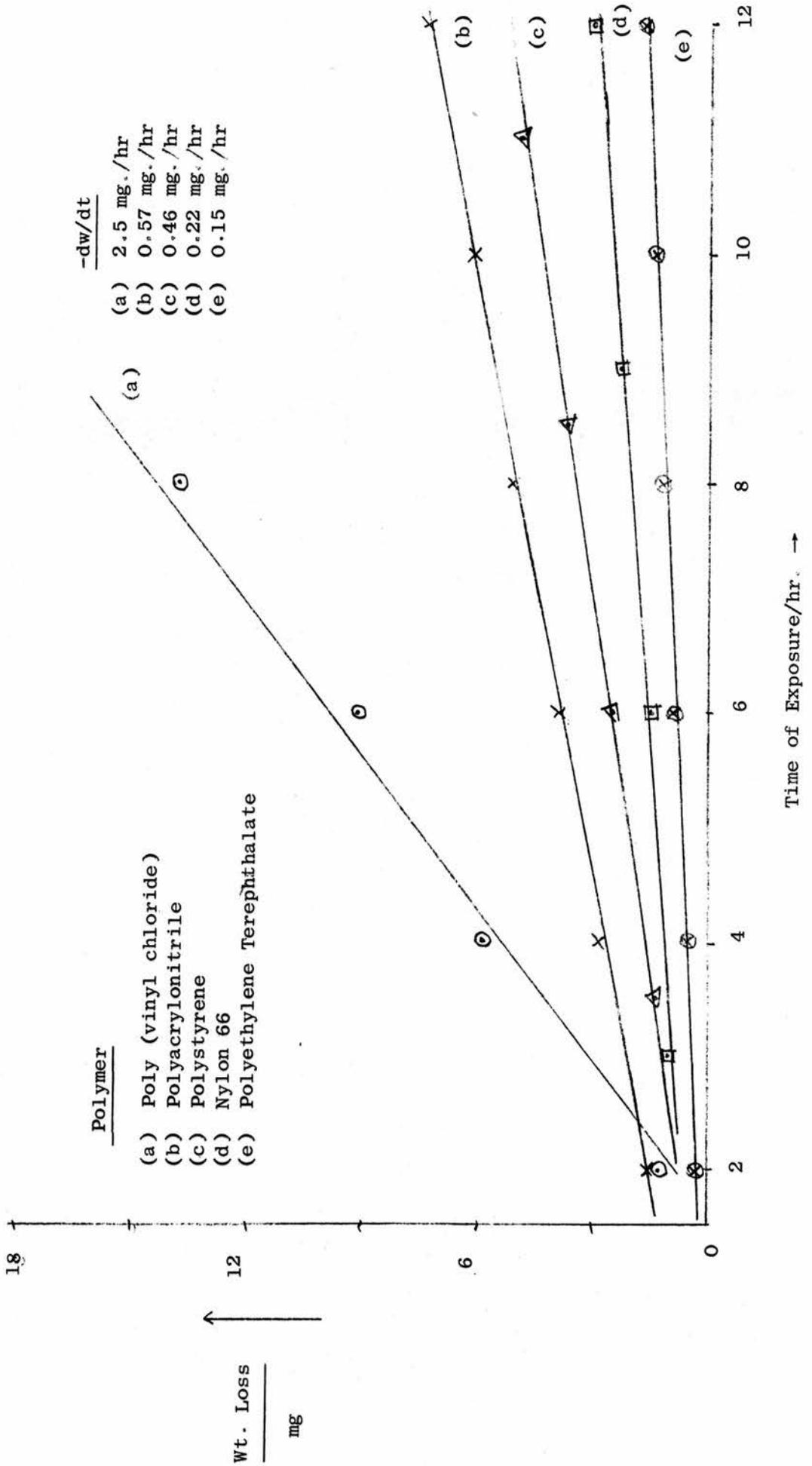
The pressure is kept constant at 6.67 Nm^{-2} , thus maintaining a constant flow rate of molecular oxygen.

The polymer used was polystyrene.

40 Watts See back (Table 1)

Fig. 5

Weight Loss vs. Time of Exposure



60 Watts

Table 7

Weight of Polymer Film mg.	Loss in Weight mg.	Total Weight Loss mg.	Time of Exposure	Total Time
51.0	0	0	0 hr.	0hr.
49.6	1.4	1.4	2	2
48.2	1.4	2.8	2	4
46.9	1.3	4.1	2	6
45.5	1.4	5.5	2	8
44.1	1.4	6.9	2	10
42.6	1.5	8.4	2	12

80 Watts

Table 8

Weight of Polymer Film mg.	Loss in Weight mg.	Total Weight Loss mg.	Time of Exposure	Total Time
43.2	0	0	0 hr.	0 hr.
41.6	1.6	1.6	2	2
39.8	1.8	3.4	2	4
38.1	1.7	5.1	2	6
36.1	2.0	7.1	2	8
34.4	1.7	8.8	2	10
32.4	2.0	10.8	2	12

100 Watts

Table 9

Weight of Polymer Film mg.	Loss in Weight mg.	Total Weight Loss mg.	Time of Exposure	Total Time
103.3	0	0	0 hr.	0 hr.
100.9	2.4	2.4	2	2
98.8	2.1	4.5	2	4
96.7	2.1	6.6	2	6
94.5	2.2	8.8	2	8
92.4	2.1	10.9	2	10
90.3	2.1	13.0	2	12

120 Watts

Table 10

Weight of Polymer Film mg.	Loss in Weight mg.	Total Weight Loss mg.	Time of Exposure	Total Time
90.3	0	0	0 hr.	0 hr.
87.6	2.7	2.7	2	2
84.8	2.8	5.5	2	4
82.0	2.8	8.3	2	6
79.4	2.6	10.9	2	8
76.8	2.6	13.5	2	10
74.4	2.4	15.9	2	12

140 Watts

Table 11

Weight of Polymer Film mg	Loss in Weight mg	Total Weight Loss mg	Time of Exposure	Total Time
72.5	0	0	0 hr	0 hr
69.5	3.0	3.0	2	2
66.4	3.1	6.1	2	4
63.2	3.2	9.3	2	6
60.0	3.2	12.5	2	8
57.1	2.9	15.4	2	10
54.0	3.1	18.5	2	12

The above results were plotted, (see Fig. 6, Weight Loss versus Time of Exposure), and $-dw/dt$ obtained:-

Table 12

Power	$-dw/dt$
40 watts	0.46 mg./hr
60 watts	0.70 mg./hr
80 watts	0.90 mg./hr
100 watts	1.10 mg./hr
120 watts	1.30 mg./hr
140 watts	1.50 mg./hr

A plot of Power versus $-dw/dt$ may now be plotted (Fig. 7)

Fig 6

Weight Loss vs. Time of Exposure

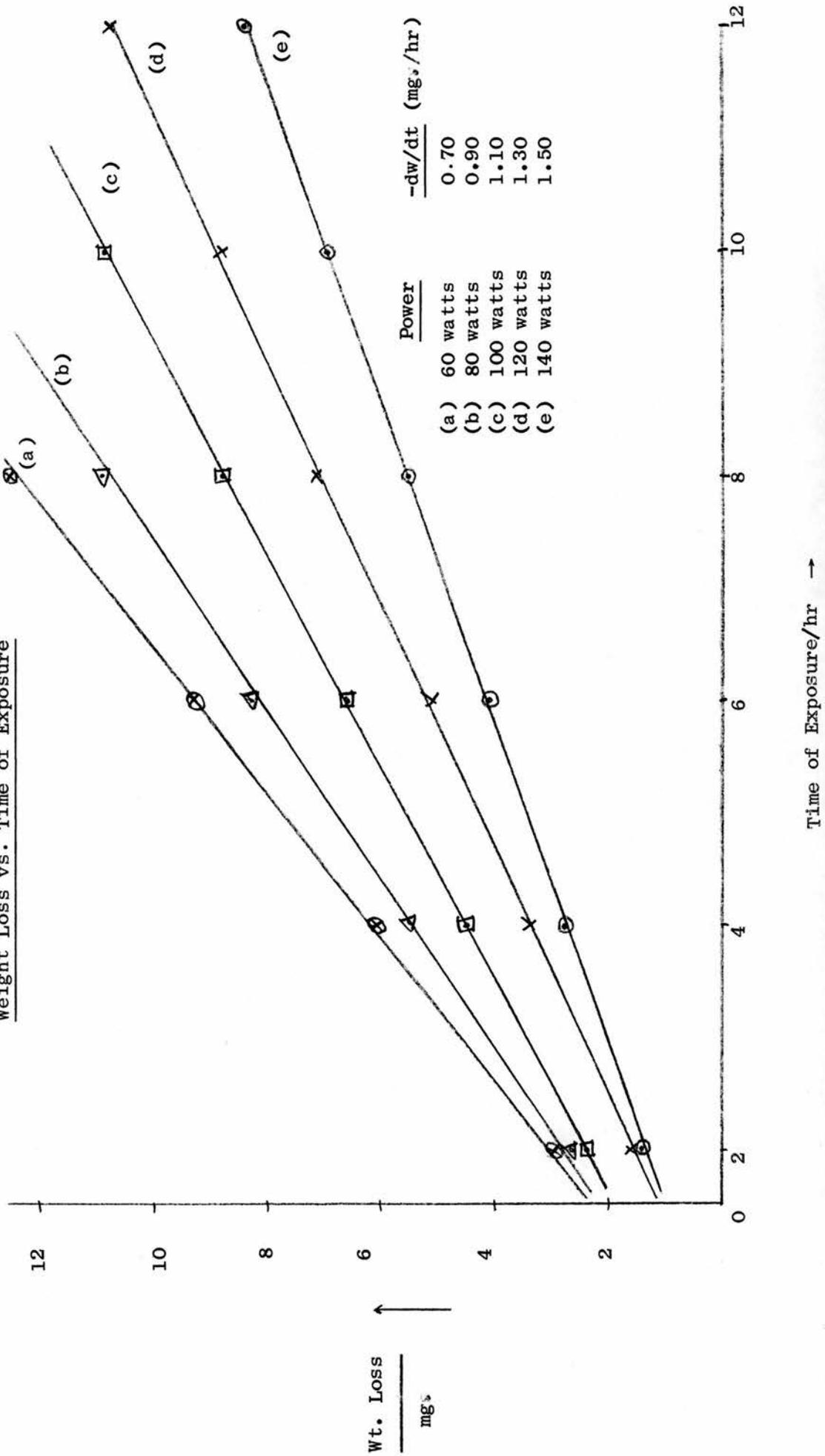
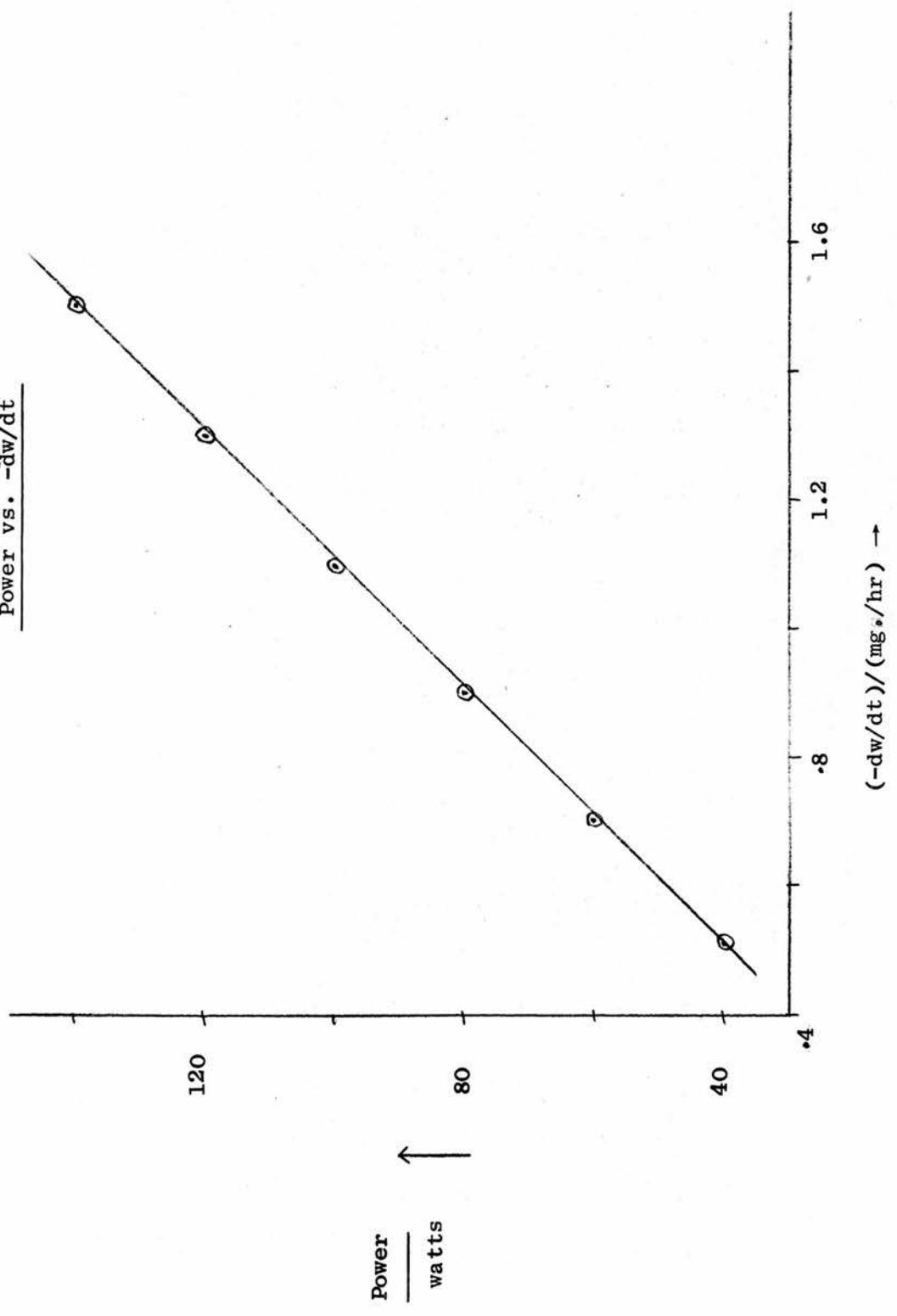
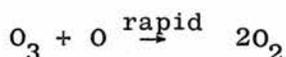
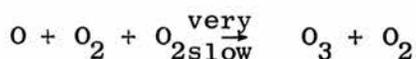
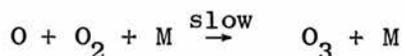


Fig. 7
Power vs. $-dw/dt$



Determination as to which of the Active Oxygen Species is the Reactive Agent

As was stated in Chapter 2 the only active species to be concerned with are excited singlet molecular oxygen in the $^1\Delta_g$ state, and atomic oxygen. Ozone is not regarded as taking any significant part in the reaction. There are two main reasons for this, firstly ozone can be formed only relatively slowly, but removed rapidly:-



Secondly as will be shown later, none of the products identified were consistent with reactions with ozone.

On exposure to singlet oxygen, ie. atomic oxygen having been removed by NO_2 , films of both polystyrene and poly (vinyl chloride) showed no loss in weight, even after 24 hrs.

It can thus be concluded that any reaction with singlet oxygen is negligible and that the reactive agent is atomic oxygen.

Determination of Change in Concentration of Oxygen Atoms with Changing Power and Flow of Molecular Oxygen

The following results were obtained for the concentration of oxygen atoms in mls/min with varying power and varying flow rate (mls/min) of molecular oxygen:-

Table 13

Gas	Flow Meter Reading	Flow Rate	Power
Oxygen	6.6 cm	3 ml./min	-
Nitrogen Dioxide	2.1 cm	1.0 ml./min	40 watts
NO_2	2.3 cm	1.1 ml./min	70 watts
NO_2	2.5 cm	1.2 ml./min	100 watts
NO_2	2.7 cm	1.27 ml./min	130 watts
NO_2	2.9 cm	1.35 ml./min	160 watts

Table 14

Gas	Flow Meter Reading	Flow Rate	Power
Oxygen	3.9 cm	1.8 ml./min	-
Nitrogen Dioxide	0.95 cm	0.5 ml./min	40 watts
NO ₂	1.2 cm	0.6 ml./min	70 watts
NO ₂	1.45 cm	0.73 ml./min	100 watts
NO ₂	1.70 cm	0.85 ml./min	130 watts
NO ₂	2.0 cm	0.97 ml./min	160 watts

Table 15

Gas	Flow Meter Reading	Flow Rate	Power
Oxygen	9.1 cm	4.1 ml./min	-
Nitrogen Dioxide	3.0 cm	1.4 ml./min	40 watts
NO ₂	3.2 cm	1.5 ml./min	70 watts
NO ₂	3.4 cm	1.58 ml./min	100 watts
NO ₂	3.6 cm	1.65 ml./min	130 watts
NO ₂	3.8 cm	1.75 ml./min	160 watts

In the above results the flow rate of the nitrogen dioxide is equivalent to the flow rate of atomic oxygen.

From these results two graphs were plotted:-

(1) Atomic Oxygen Flow Rate versus Molecular Oxygen Flow Rate (Constant Power)

(2) Power Input versus Molecular Oxygen Flow Rate. (Constant Atomic Oxygen Flow Rate). See Figs. 8,9.

Fig. 8

Atomic Oxygen Flow Rate vs. Molecular Oxygen Flow Rate

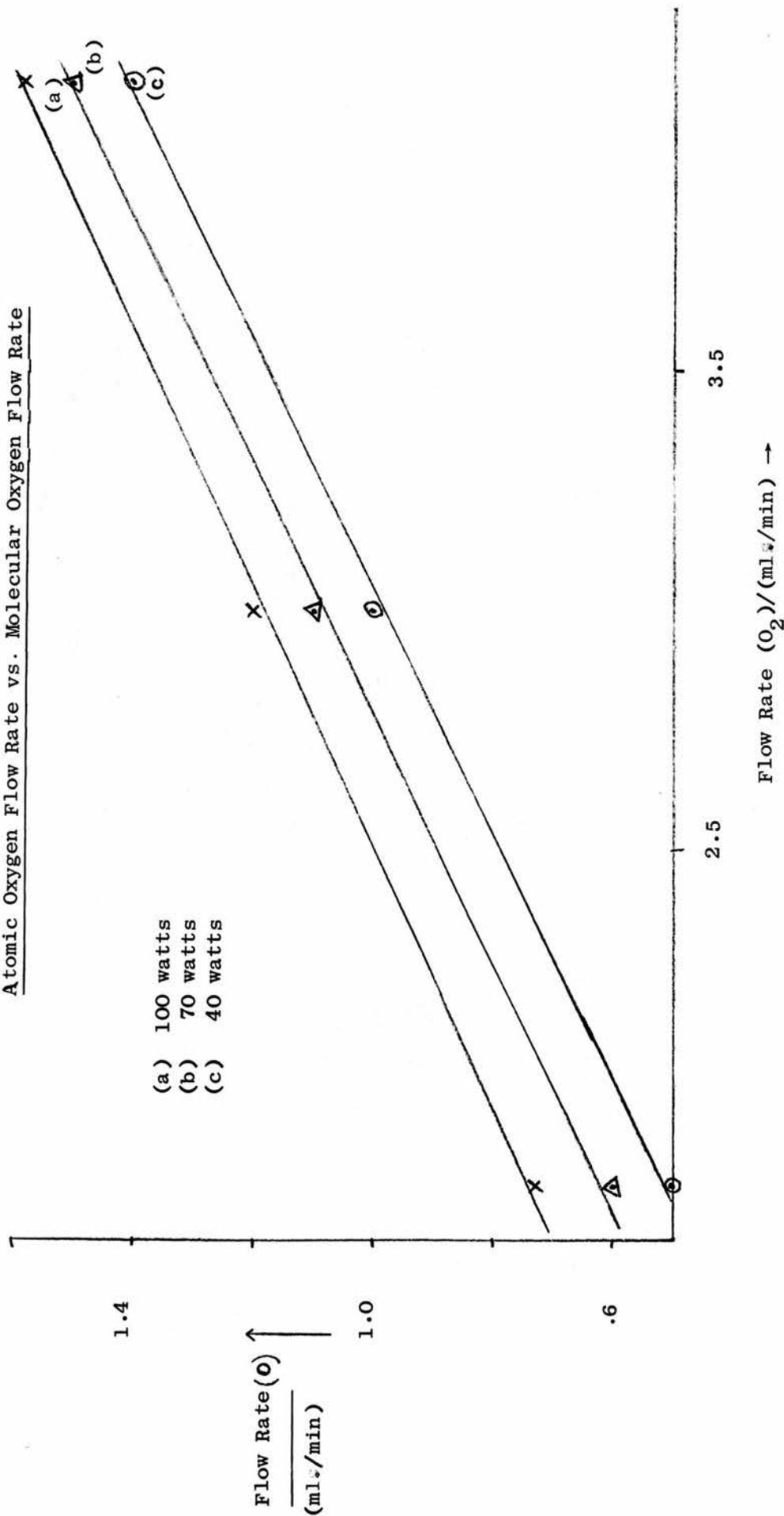
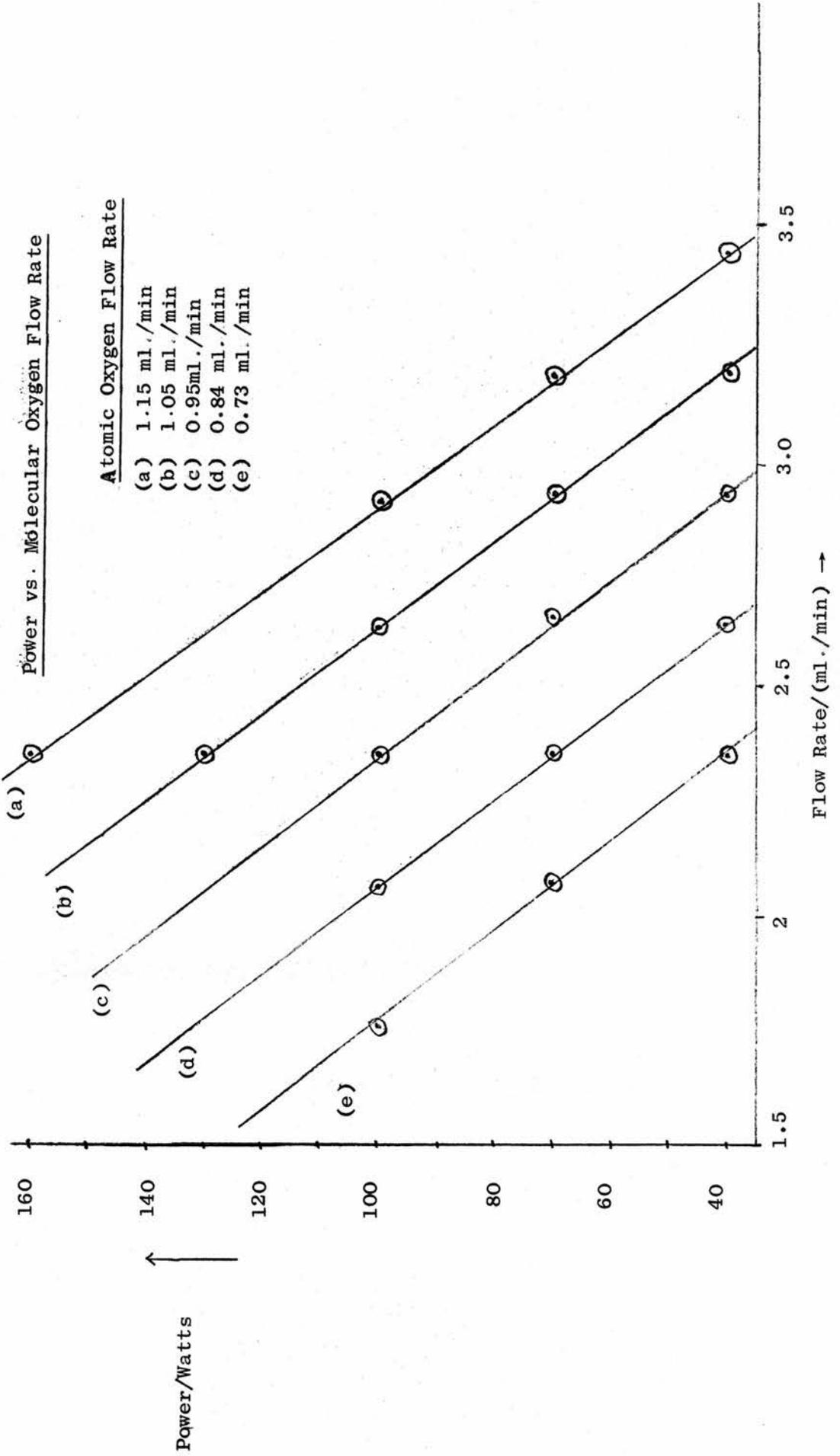


Fig. 9

Power vs. Molecular Oxygen Flow Rate

Atomic Oxygen Flow Rate

- (a) 1.15 ml./min
- (b) 1.05 ml./min
- (c) 0.95 ml./min
- (d) 0.84 ml./min
- (e) 0.73 ml./min



Using poly (vinyl chloride), weight loss runs were then carried out at different power inputs, as with polystyrene, for a constant molecular oxygen flow rate of 2.55 ml./min. From the results a plot of $-dw/dt$ versus Power was obtained (Fig 10). Using this graph in conjunction with the graph of Power versus molecular oxygen flow rate for a constant atomic oxygen flow, a plot of $-dw/dt$ versus Atomic Oxygen Flow Rate was obtained (Fig.11).

$-dw/dt$ vs. Power

Table 16

$-dw/dt$	Power
1.6 mg./hr	40 watts
1.8 mg./hr	60 watts
2.0 mg./hr	80 watts
2.2 mg./hr	100 watts
2.4 mg./hr	120 watts
2.6 mg./hr	140 watts
2.8 mg./hr	160 watts

$-dw/dt$ vs. Atomic Oxygen Flow Rate

Table 17

Atomic Oxygen Flow Rate	$-dw/dt$	Corrected Power
0.73 ml./min	1.44 mg./hr	26 watts
0.84 ml./min	1.70 mg./hr	54 watts
0.95 ml./min	2.04 mg./hr	85 watts
1.05 ml./min	2.32 mg./hr	113 watts
1.15 ml./min	2.62 mg./hr	143 watts

The plot of $-dw/dt$ versus Atomic Oxygen Flow Rate was a straight line graph. Thus the rate of weight loss is directly proportional to the flow rate of atomic oxygen.

If this is so then by adjusting the power and the flow rate of molecular oxygen to various values, each set of values giving the same atomic oxygen flow rate, the results obtained for $-dw/dt$ should be constant.

To check this a film of poly (vinyl chloride) was exposed to active oxygen at different power inputs. For each power input the

Fig. 10

$-dw/dt$ vs. Power

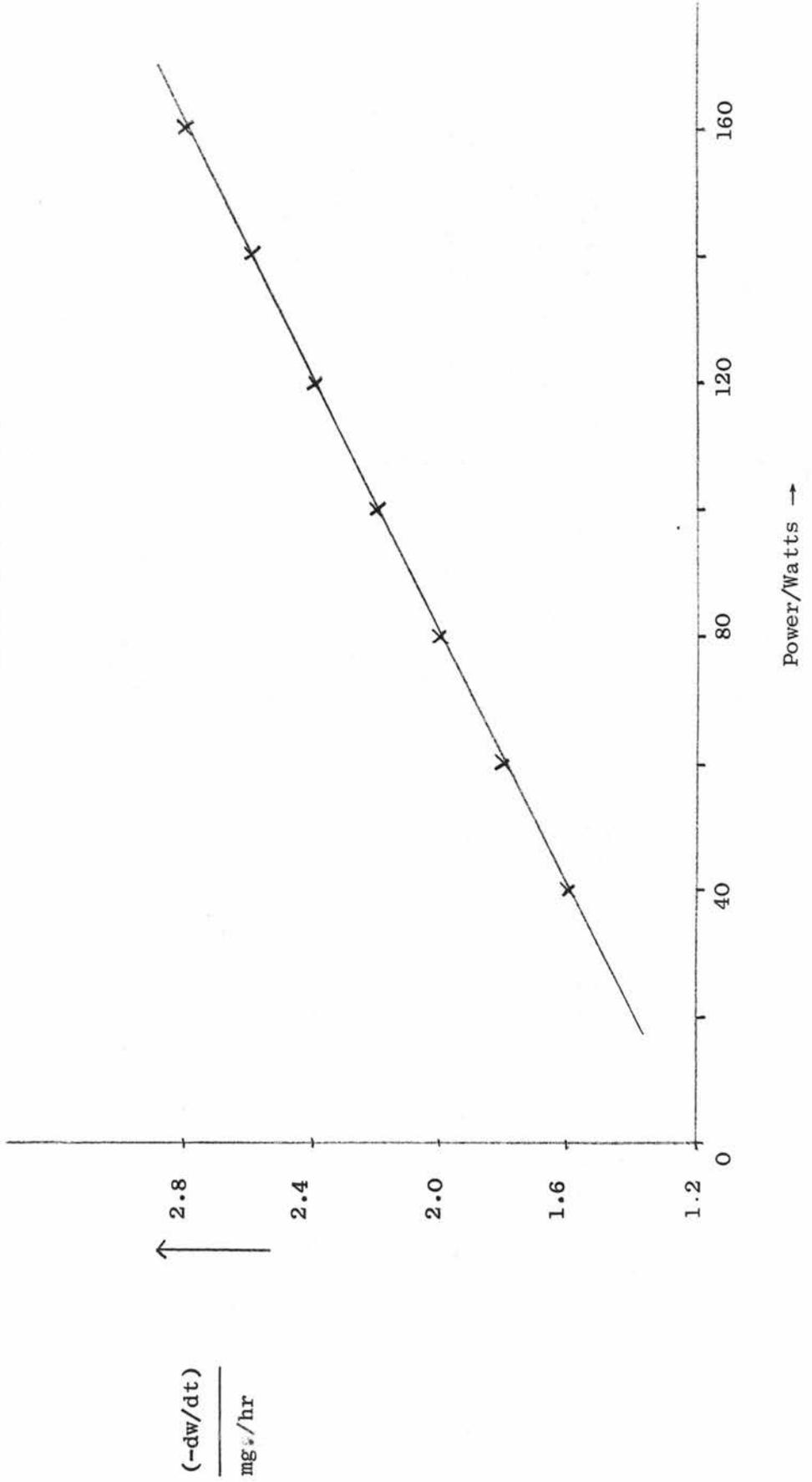
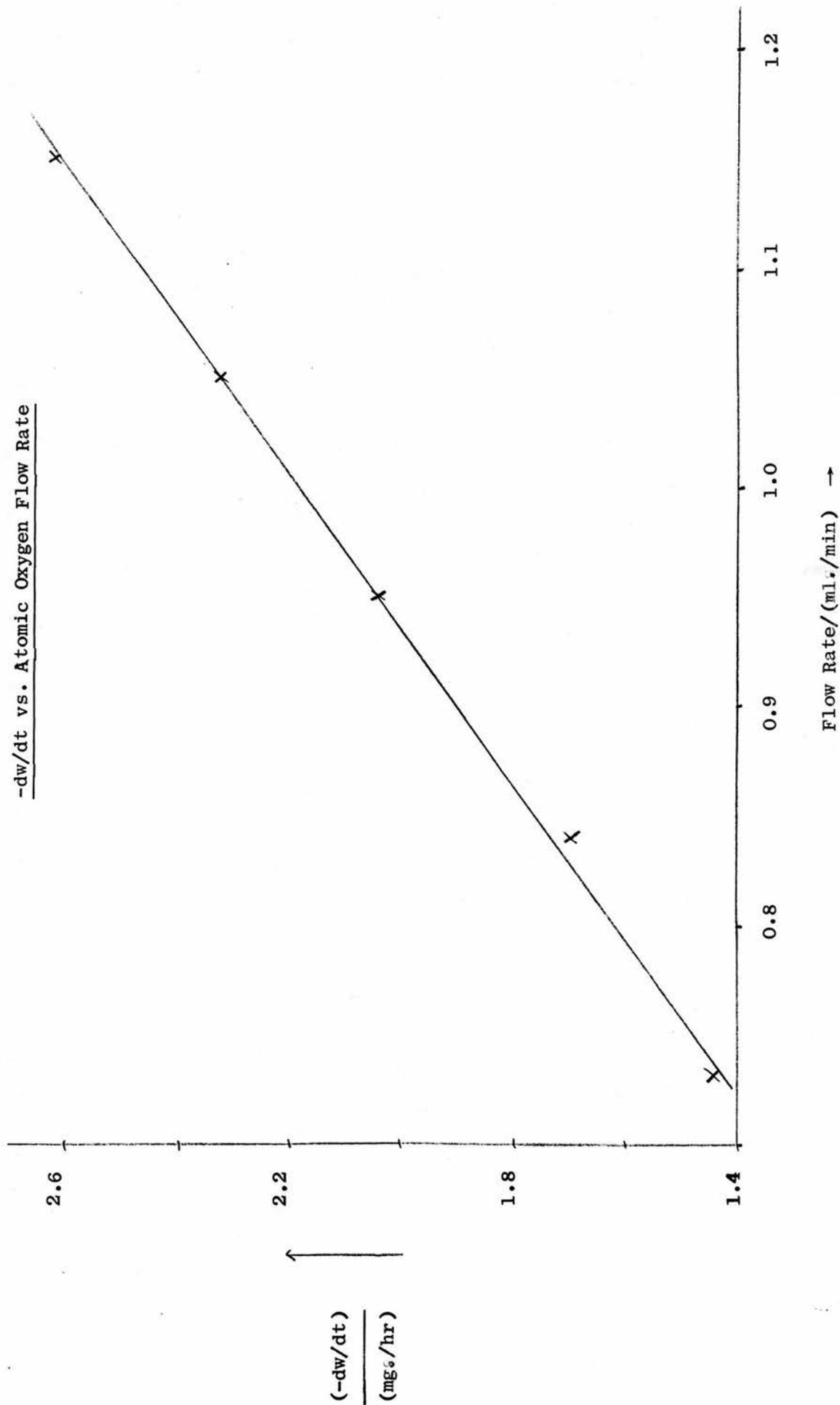


Fig. 11

-dw/dt vs. Atomic Oxygen Flow Rate



flow rate of molecular oxygen was adjusted so that, according to the graph of power input versus molecular oxygen flow rate, the flow rate of atomic oxygen was constant. The following results were obtained:-

Table 18

Molecular Oxygen Flow Rate	Power	Atomic Oxygen Flow Rate	-dw/dt
2.2 ml./min	57 watts	0.73 ml./min	1.4 mg./hr
1.8 ml./min	98 watts	0.73 ml./min	1.4 mg./hr
2.4 ml./min	37 watts	0.73 ml./min	1.4 mg./hr

From the graph of -dw/dt versus atomic oxygen flow rate it is seen that for a flow rate equal to 0.73 ml./min, -dw/dt = 1.4 mg./hr. All the results are, therefore in agreement.

As has already been shown -dw/dt for polystyrene increases with power; it would, therefore, seem reasonable that it should also increase with an increase in the flow rate of molecular oxygen, and hence atomic oxygen, as it does in the case of poly (vinyl chloride). It was, however, decided to check this point experimentally.

As with poly (vinyl chloride), weight loss runs were carried out on polystyrene at various flow rates of molecular oxygen. The following results were observed:-

Table 19

80 Watts

Table 19

<u>Molecular Oxygen Flow Rate</u>	<u>-dw/dt</u>
1.15 ml./min	0.6 mg./hr
0.9 ml./min	1.0 mg./hr
0.65 ml./min	1.25 mg./hr
0.43 ml./min	1.50 mg./hr
0.3 ml./min	1.80 mg./hr
0.23 ml./min	1.75 mg./hr
0.15 ml./min	1.5 mg./hr
0.10 ml./min	0.75 mg./hr

The above, unexpected, results are more clearly illustrated in graph form (Fig. 12), where it is clearly seen that $-dw/dt$ increases with the flow rate of molecular oxygen only up to about 0.3 ml./min where it reaches a peak. After this point any increase in the flow rate of the molecular oxygen causes a decrease in the value of $-dw/dt$.

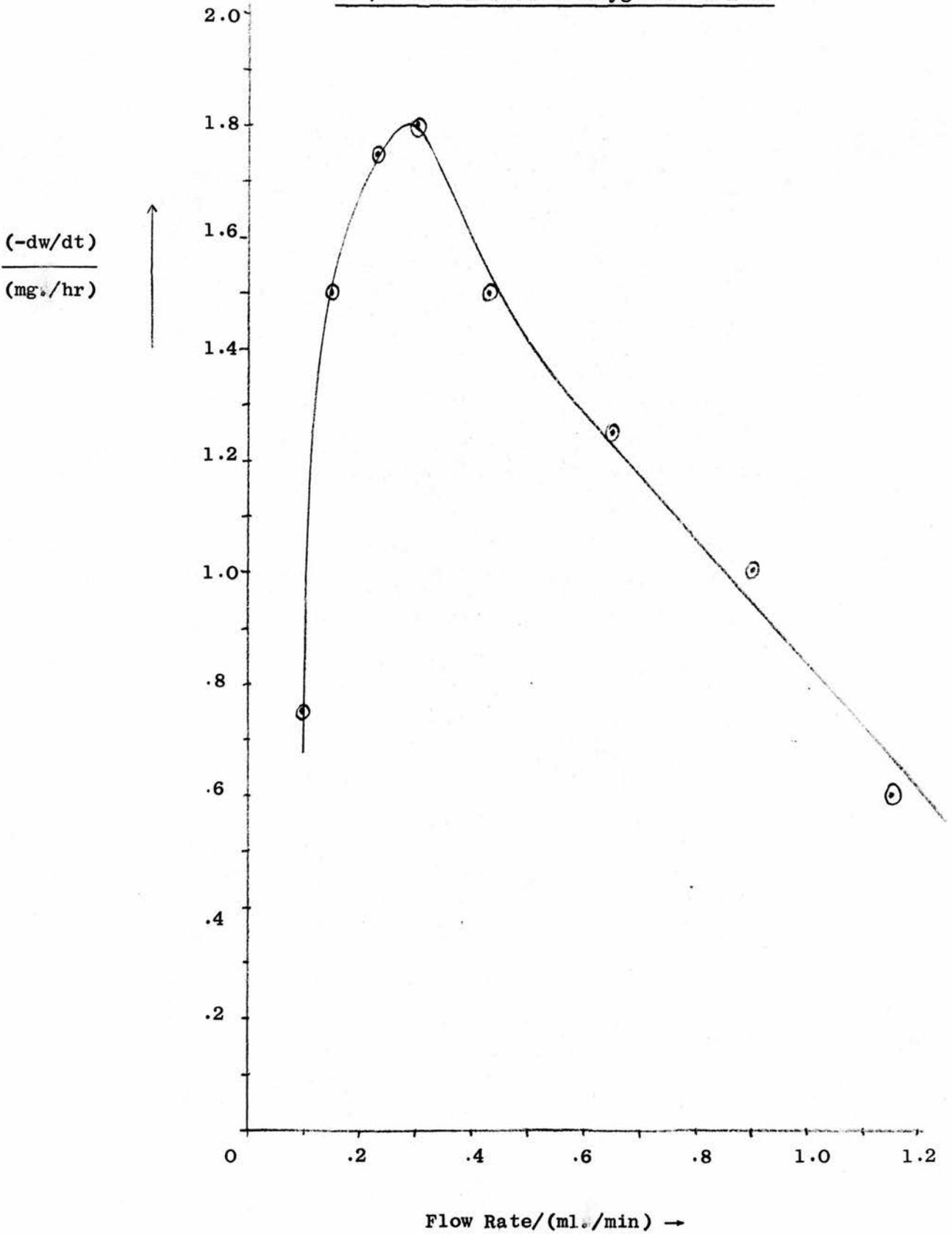
Identification of Products

(a) Gaseous Products

The only products, detected by mass spectrometry and infrared spectroscopy from the discharge and from exposing all the polymers, except poly (vinyl chloride), to active oxygen were, nitrogen dioxide, carbon dioxide, and water vapour. With poly (vinyl chloride) in addition to the above products phosgene was also detected by mass spectrometry.

Fig. 12

-dw/dt vs. Molecular Oxygen Flow Rate



(b) Residual Products

No chemical changes could be detected in the residual polymer films, by any of the methods used.

Relationship between Pressure of Gaseous Products and Time of Exposure

Since the main product of the reaction of polystyrene with atomic oxygen appears to be CO_2 , then it would seem reasonable that the pressure of the CO_2 should bear a relationship to the weight loss of the exposed polystyrene.

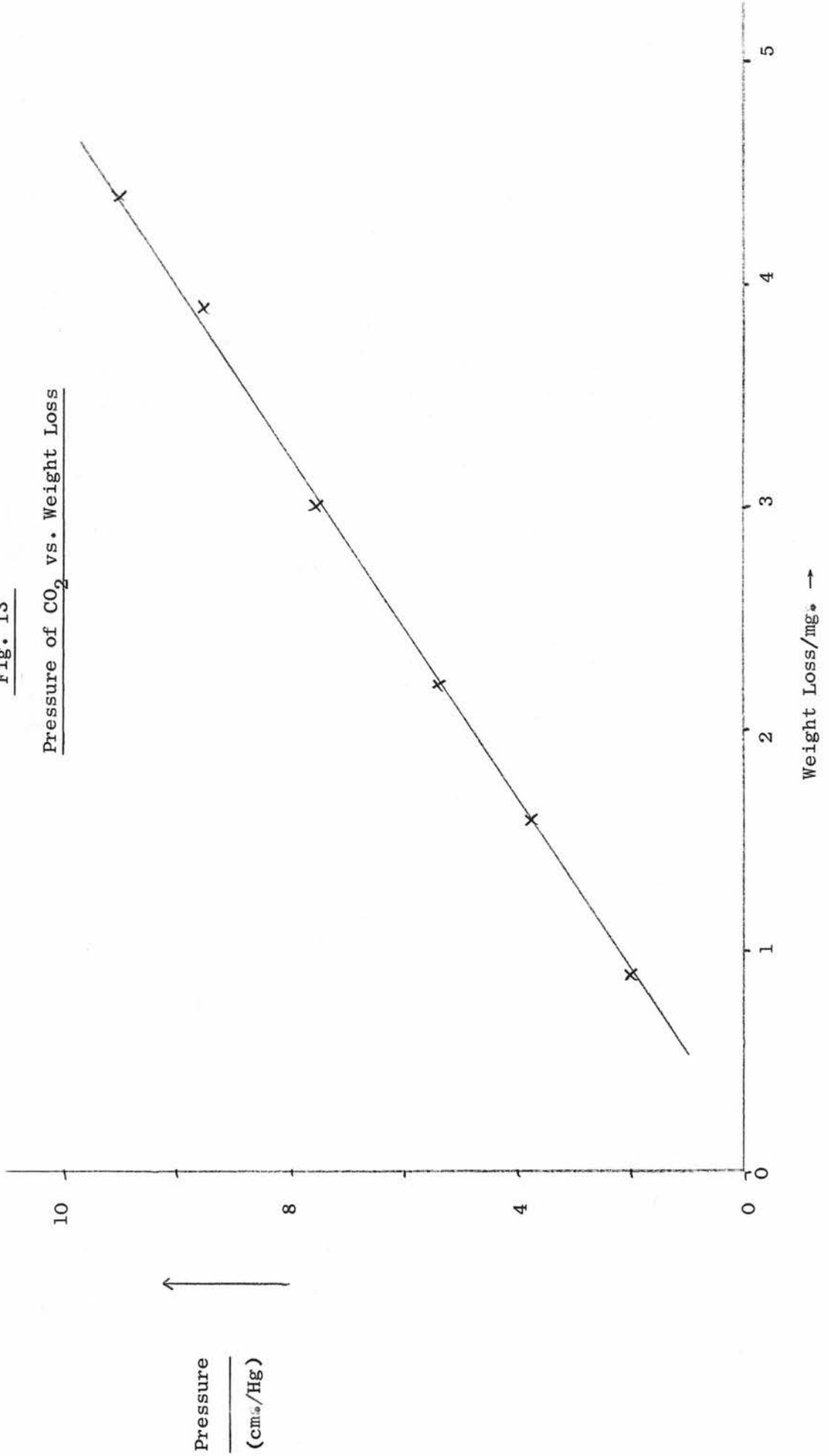
Table 20

Weight of Polymer Film mg	Loss in Weight of Film mg	Total Weight Loss mg	Atmospheric Pressure (Error+.05) P cm/Hg	Height Mercury Column in Manometer h cm./Hg	P-h (Pressure of CO_2) cm./Hg	Total CO_2 Pressure cm./Hg	Time of Exposure hr.
92.5	0.9	0.9	75.5	73.5	2.0	2.0	2
91.8	0.7	1.6	75.1	73.3	1.8	3.8	2
91.2	0.6	2.2	76.3	74.7	1.6	5.4	1.5
90.4	0.8	3.0	76.7	74.5	2.2	7.6	2
89.5	0.9	3.9	76.7	74.75	1.95	9.55	2
89.0	0.5	4.4	76.7	75.2	1.5	11.05	1.5

Total pressure of CO_2 was plotted against the total weight loss of the polystyrene (Fig. 13). As expected a straight line graph was obtained.

Fig. 13

Pressure of CO₂ vs. Weight Loss



Molecular Weight Changes of Polystyrene with Exposure.

Before Exposure

Table 21

Conc. ⁿ	$\eta_{sp} = \frac{(t-t_0)}{t_0}$	$\eta_{sp/C}$
0.1%	0.0794	0.7940
0.2%	0.1651	0.8255
0.3%	0.2554	0.8513
0.4%	0.3485	0.8713

On plotting this the intercept $[\eta]$ was obtained

$$[\eta] = 0.77 = KM^{\alpha} \quad \underline{M = 209,400}$$

After Exposure

Table 22

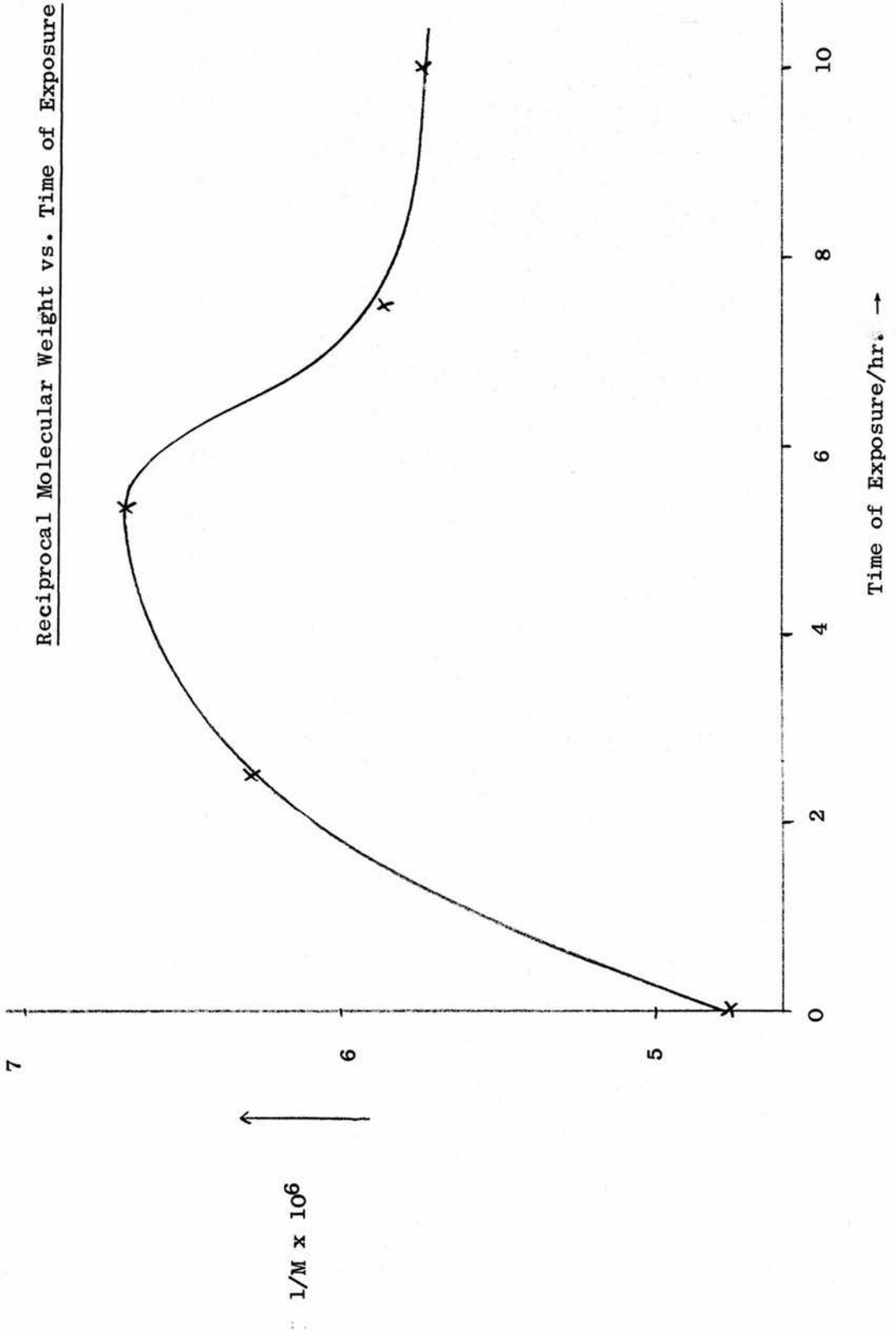
Time of Exposure	$[\eta]$	Molecular Weight M
2.5 hr.	0.614	161,100
5.0 hr.	0.59	149,600
7.5 hr.	0.664	170,600
10.0 hr.	0.674	174,200

On plotting $1/M$ versus Time of Exposure (Fig. 14) it is clearly seen that the molecular weight of the polymer decreased for about the first four hours, after which, on further exposure the molecular weight increased slightly and then leveled off.

In order to check as to whether any residual solvent trapped in the polymer film was having an effect on the molecular weight, the experiment was repeated using films of polystyrene produced by pressure and heat.

Fig. 14

Reciprocal Molecular Weight vs. Time of Exposure



It was found that even after 24 hours exposure no changes in the molecular weight of the polystyrene could be detected.

On observing this it was decided that the molecular weight of a freshly cast film of polystyrene should be placed in a vacuum oven at 40° C and its molecular weight recorded regularly over a period of about a fortnight. The following results were observed.

Table 23

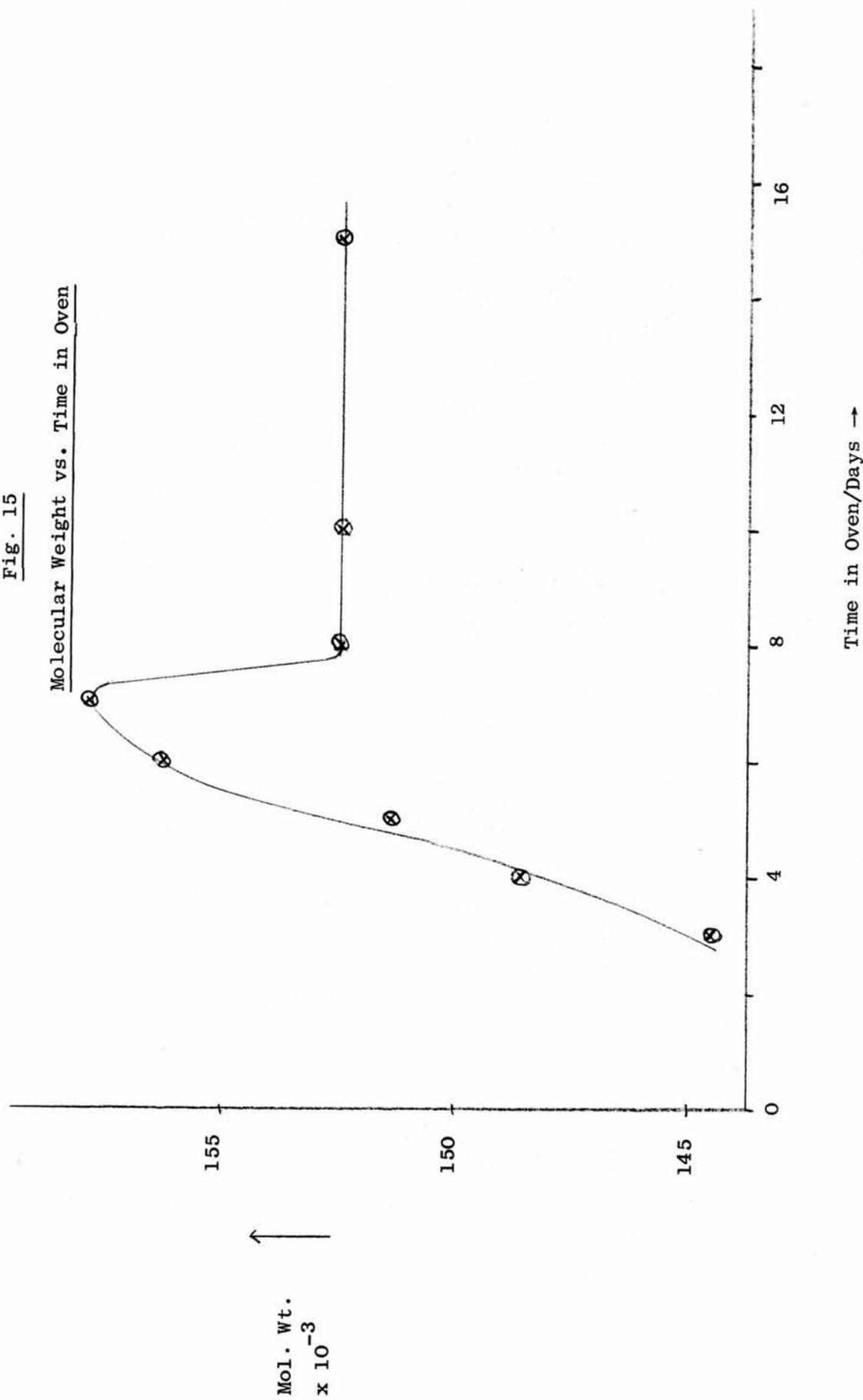
<u>Days in Vacuum Oven</u>	<u>Molecular Weight</u>
3	144,500
4	148,600
5	151,300
6	156,200
7	157,900
8	152,400
10	152,400
15	152,400

On plotting Molecular Weight versus Time in Oven (Fig. 15) it can be seen that the molecular weight of the polystyrene increases as the film dries out, until after seven days it has reached a peak; whereafter it decreases sharply and then levels off; never having reached the molecular weight of the original polystyrene.

It was decided that the above results should be compared with those for another polymer under the same conditions. The polymer chosen was poly (ethyl methacrylate), since it dissolves readily in acetone which evaporates quickly to leave a film. In this case the molecular weight was not actually calculated, but the efflux

Fig. 15

Molecular Weight vs. Time in Oven



times give a good indication as to how it is changing.

Efflux Time of Precipitated Poly (ethyl methacrylate) = 191.2 sec.

Table 24

<u>Days in Vacuum Oven</u>	<u>Efflux Time</u>
3	187.2 seconds
4	189.4 seconds
5	189.4 seconds
6	188.8 seconds
7	188.6 seconds
10	184.3 seconds

On plotting the above flow times against Time in Oven it can be seen that after four to five days in the oven the molecular weight reaches a peak, and that thereafter it begins to drop. The results are in agreement with those obtained for polystyrene.

A sample of powdered poly (ethyl methacrylate), used to make the film, was also placed in the vacuum oven. It was found that even after a week there was no change in the molecular weight.

Thermal Stability After Exposure

Using a Stanton Massflow Thermobalance a direct plot of film weight versus temperature was obtained. From this the change in rate of weight loss with temperature was recorded.

(i) Before Exposure

Initial weight $W_0 = 17 \text{ mg.}$

w = weight at $T^{\circ} \text{C}$

Table 25

$-dw/dt$	Temperature $T^{\circ}C$
0.046 mg/hr	355.7
0.076 mg/hr	361.8
0.226 mg/hr	376.3
0.358 mg/hr	381.5
0.446 mg/hr	385.5
0.688 mg/hr	392.9
0.595 mg/hr	399.1
0.485 mg/hr	400.0

Table 26

Weight of Film w mg	w/wo	$T^{\circ}C$
16.6	0.975	348.0
16.3	0.960	359.25
15.6	0.918	370.5
14.6	0.855	376.75
12.5	0.735	382.0

(ii) After 4 hours Exposure

$w_0 = 17.6$ mg.

Table 27

$-dw/dt$	Temperature $T^{\circ}C$
0.055 mg./hr	356.25
0.110 mg./hr	364.0
0.257 mg./hr	372.75
0.365 mg./hr	378.28
0.685 mg./hr	388.75
0.296 mg./hr	400.0

Table 28

Weight of Film w mg	w/wo	$T^{\circ}C$
17.1	0.970	345.0
16.8	0.955	354.5
16.1	0.915	364.0
15.4	0.875	369.0
14.2	0.805	375.0
12.6	0.715	380.0
11.0	0.625	383.5

(iii) After 8 hours Exposure

wo = 15.4 mg.

Table 29

<u>-dw/dt</u>	<u>Temperature T^oC</u>
.042 mg./hr	345.7
.085 mg./hr	362.0
.187 mg./hr	370.5
.288 mg./hr	375.5
.337 mg./hr	377.5
.468 mg./hr	383.3
.539 mg./hr	389.1
.321 mg./hr	400.0

Table 30

<u>Weight of Film w mg</u>	<u>w/wo</u>	<u>T^oC</u>
14.8	0.96	350.5
14.6	0.95	355.75
14.3	0.93	361.0
13.8	0.895	366.0
12.2	0.79	374.0
10.2	0.665	381.5

(iv) After 12 hours Exposure

wo = 18.7 mg.

Table 31

<u>-dw/dt</u>	<u>Temperature T^oC</u>
.034 mg./hr	348.5
.076 mg./hr	358.5
.188 mg./hr	367.6
.330 mg./hr	376.3
.476 mg./hr	382.1
.692 mg./hr	385.4
.575 mg./hr	400.0

Table 32

<u>Weight of Film w mg</u>	<u>w/wo</u>	<u>T^oC</u>
17.9	0.955	351.5
17.5	0.935	360.25
17.0	0.910	369.0
16.0	0.855	374.0
14.3	0.765	379.0
11.3	0.605	382.5

Graphs of $-dw/dt$ versus $T^{\circ}C$ and w/wo versus $T^{\circ}C$ were then

plotted (Figs. 16,17).

It is seen from the graphs that all the runs with exposed films give points which virtually all lie on the same curve, which in turn is quite distinct from the curve obtained by plotting points from a run with a film of unexposed polystyrene. The graphs show clearly that after irradiation the polystyrene decomposes more quickly than a non irradiated sample.

Contact Angle Measurements

A typical enlarged photograph of a droplet of purified water on the surface of a polymer film is shown in Fig. 18. From such a photograph measurements of the contact angle were taken and recorded against time of exposure.

The following table is a list of the various polymers used and how their contact angles with water change with exposure to active oxygen.

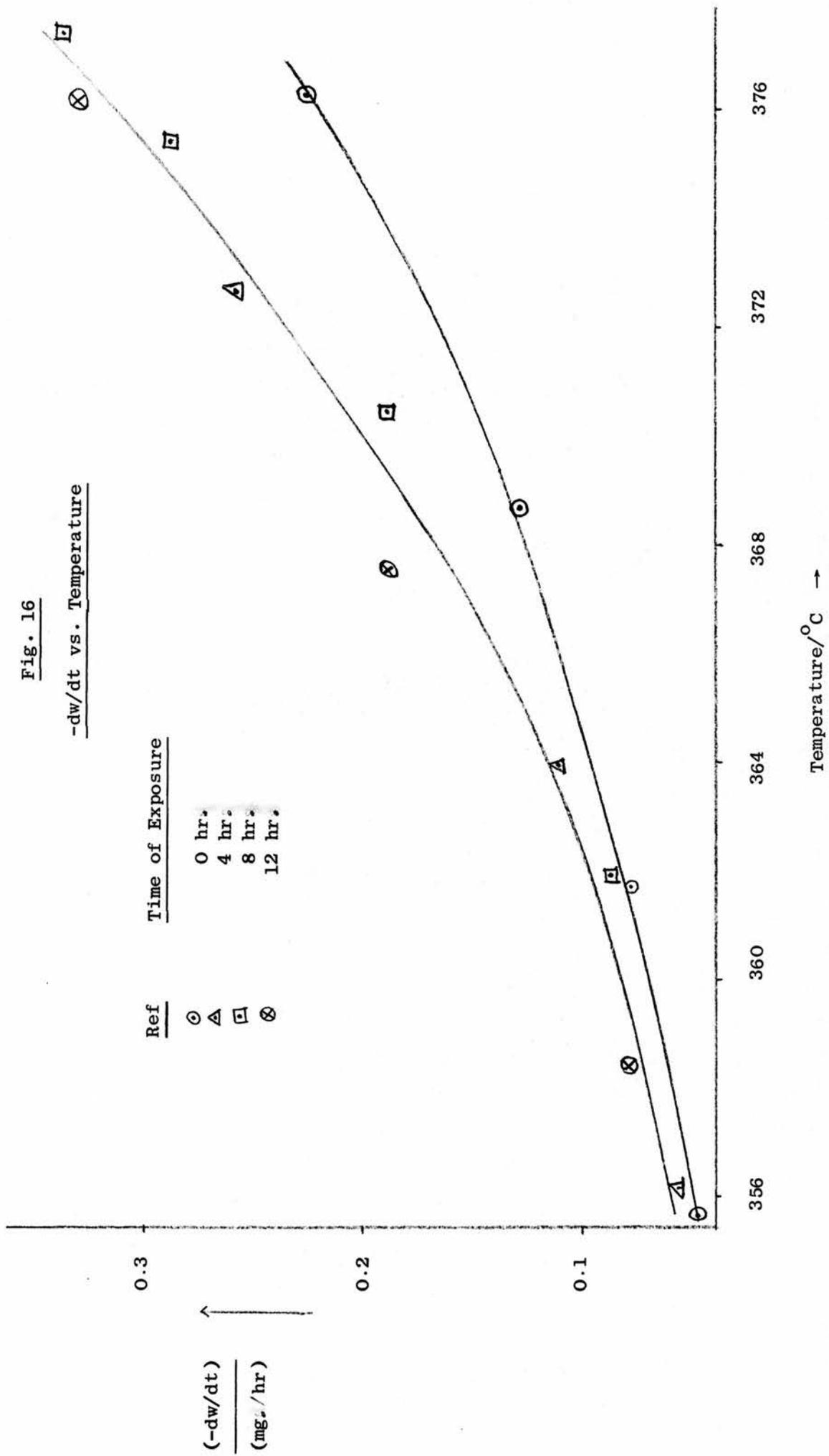
Table 33

Time of Exposure	Polymers				
	Polystyrene	Polyethylene Terephthalate	Poly (vinyl chloride)	Polyacrylo nitrile	Nylon-66
	CONTACT	ANGLES			
0.0 hr.	89°	92°	90°	67°	54°
0.5 hr.	62°	47°30'	61°	47°	40°
1.0 hr.	51°	31°30'	46°	35°	29°
1.5 hr.	43°	26°	38°30'	27°	27°
2.0 hr.	38°20'	25°30'	33°20'	22°	26°
2.5 hr.	35°	23°30'	32°30'	19°30'	26°

Using the above results a graph of Contact Angle versus Time of

Fig. 16

$-\frac{dw}{dt}$ vs. Temperature



Ref	Time of Exposure
○	0 hr.
△	4 hr.
□	8 hr.
⊗	12 hr.

$\frac{(-dw/dt)}{(mg./hr)}$

Temperature/°C →

Fig. 17

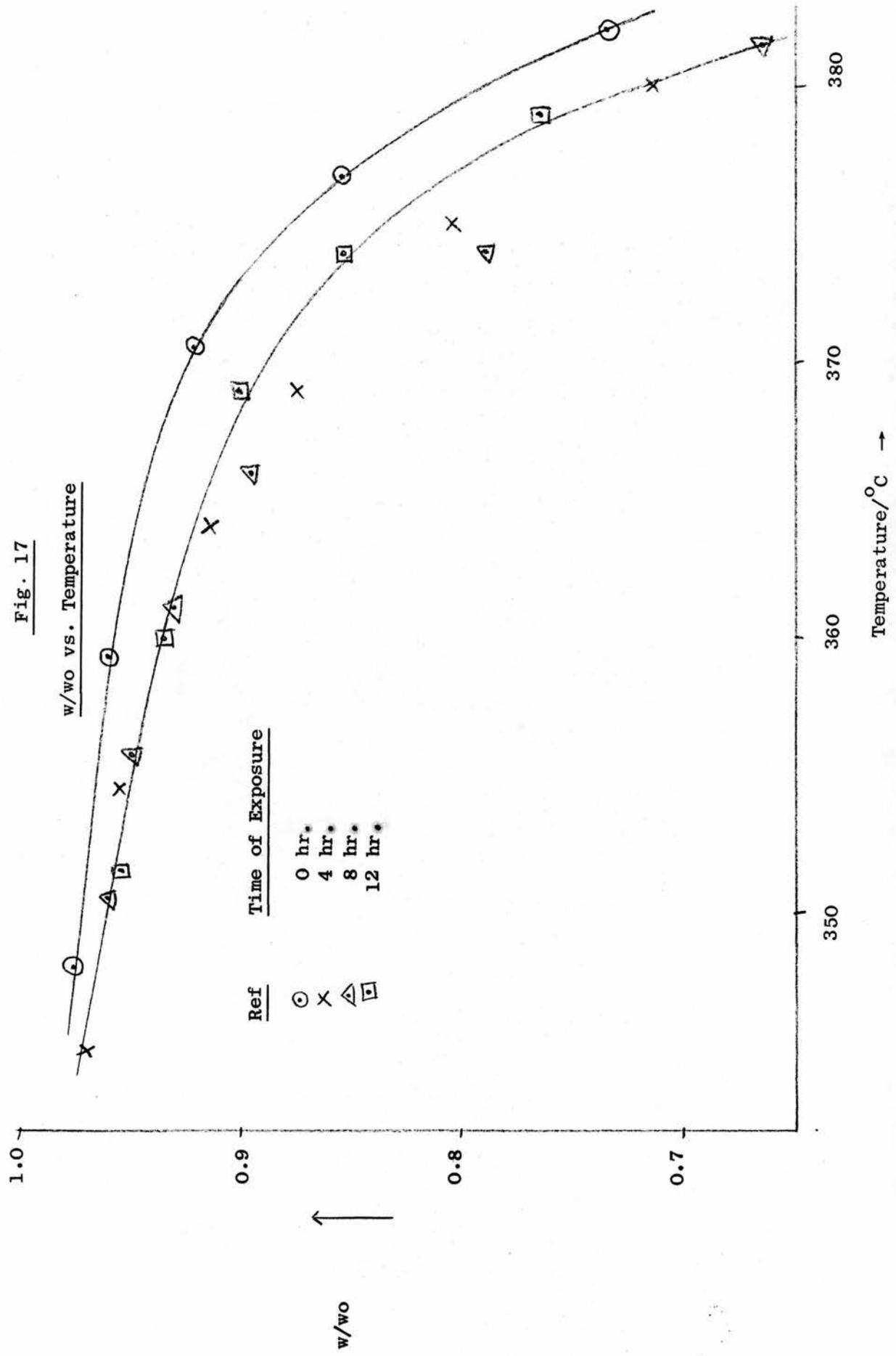
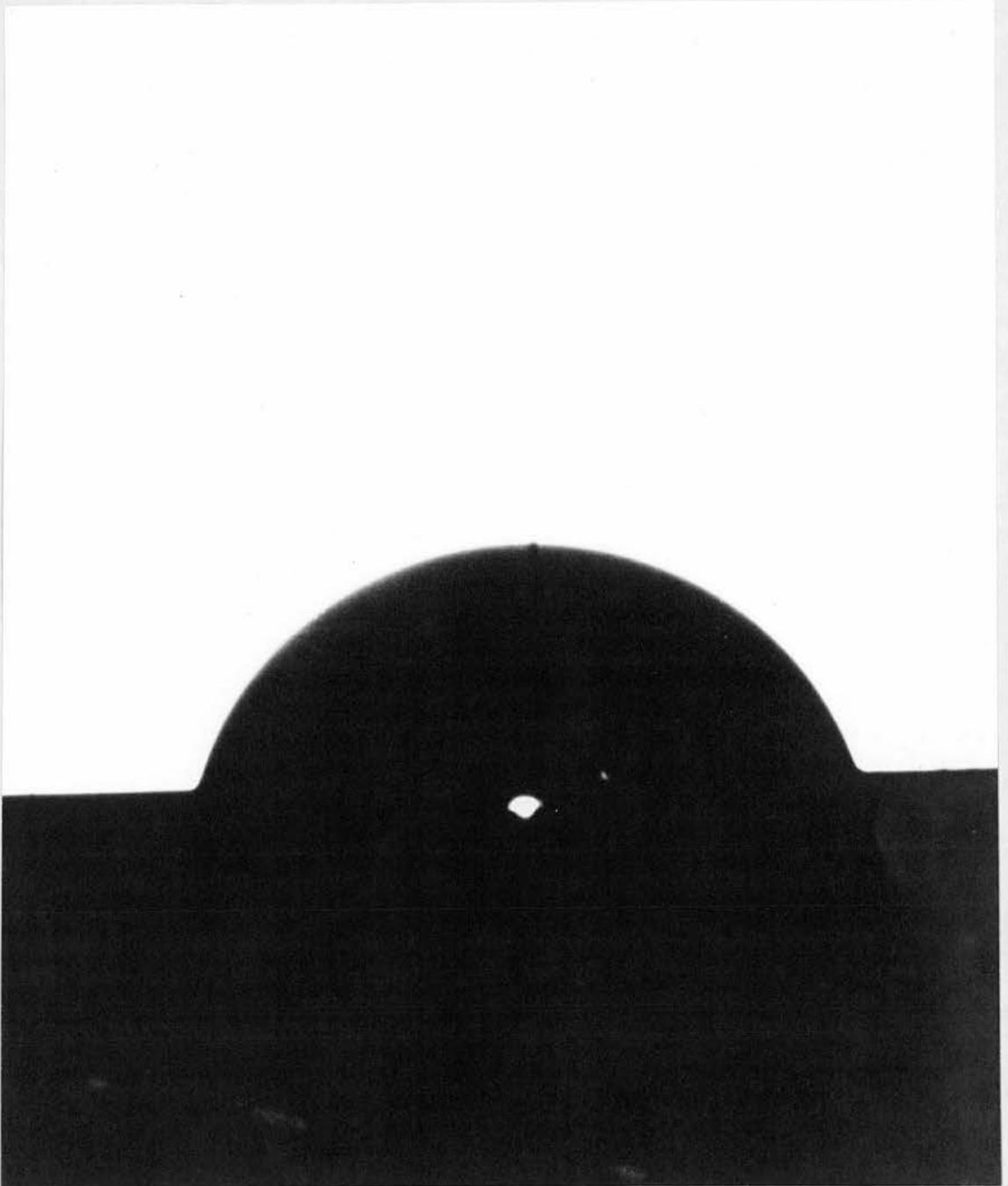


Fig. 18

Droplet of Water on Polymer Surface



Exposure was plotted for the various polymers. (Fig 19)

From the graph it is seen that the greatest change in contact angle, and therefore in the surface of the polymer, occurs in the first hour.

Table 34

	Polystyrene	Polyethylene Terephthalate	Poly(vinyl chloride)	Polyacrylo nitrile	Nylon 66
Change in Contact Angle in 1st hour	48°	60°30'	44°	32°	25°
Total Change in Angle	54°	68° 30'	57°30'	47°30'	28°
Percentage Change in 1st hour	89%	88%	77%	67%	89%

The experiment was then repeated, this time titrating out the atomic oxygen with NO₂ in order to see whether singlet oxygen had any effect on the surface of the polymer film.

It was found that even after several hours exposure there was no change in the contact angle of water with a film of polystyrene, indicating that the singlet oxygen had no effect on the polymer surface.

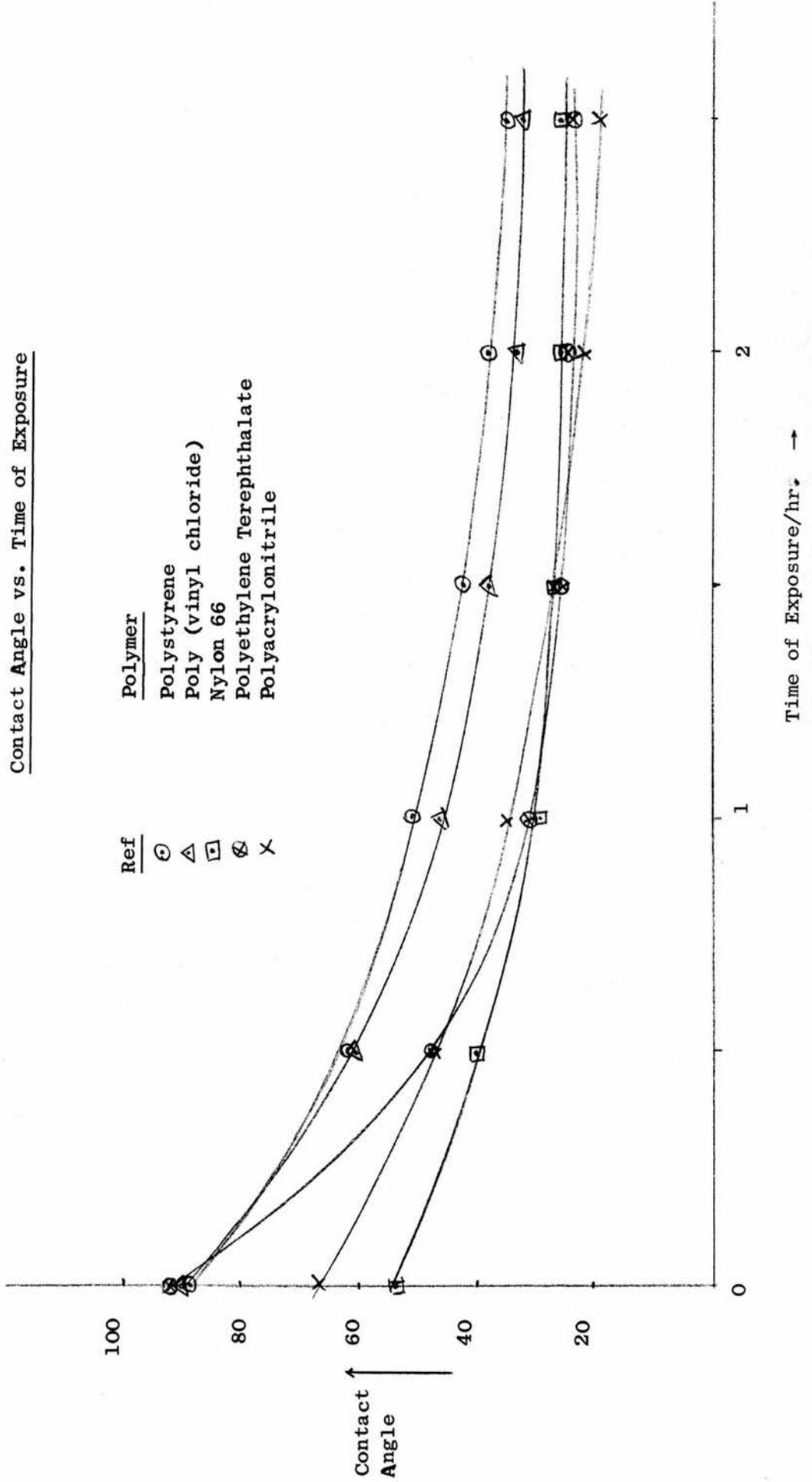
Introduction of Monomer to an Exposed Film of Poly (vinyl chloride)

An infrared spectrum of poly (vinyl chloride) has peaks at 1780 and 1725 cm⁻¹ due to the presence of solvent, tetrahydrofuran, trapped in the film. These peaks are denoted A and B respectively and are in the ratio A:B = 1.4:1.

After exposure of the polymer film to active oxygen, followed by methyl methacrylate, another infrared spectrum was obtained. This spectrum showed a new peak at 1640 cm⁻¹ (C) and an increase in the

Fig. 19

Contact Angle vs. Time of Exposure



Ref
○ △ □ ◇ ×

Polymer
Polystyrene
Poly (vinyl chloride)
Nylon 66
Polyethylene Terephthalate
Polyacrylonitrile

Contact Angle ↑

Time of Exposure/hr. →

size of peak B.

The following ratios were then observed:-

$$A:B:C = 2.1:2.3:1 \text{ and } A:B = 1:1.3$$

The peak at 1640 cm^{-1} is due to the presence of double bonds. These exist only in the methyl methacrylate. The increase in the size of peak B, 1725 cm^{-1} , could be due to the presence of the ester which exists in both the monomer and in poly (methyl methacrylate).

Therefore either monomer or polymer or both are present. To resolve this the film was then soaked in methanol for several hours, which should have removed any monomer present. On examining the infrared spectrum, however, it was seen that there was little change:-

$$A:B:C = 2.4:2.8:1 \text{ and } A:B = 1:1.7$$

The film was then heated in a vacuum oven at 110°C for $2\frac{1}{2}$ hours, and a further infrared spectrum obtained. On examining the spectrum it was seen that peak C was greatly reduced in size whereas there was no change in peak B, therefore, poly (methyl methacrylate) is present.

If heating had converted the methyl methacrylate trapped in the film, to polymer then peak B would have increased in size.

This did not occur, therefore both monomer and polymer must have been present before heating.

From the infrared spectrum of the poly (vinyl chloride) removed from the vacuum oven, the following ratios were observed:-

$$A:B:C = 5.1:6.1:1 \text{ and } A:B = 1:1.16$$

A sample of poly (vinyl chloride) was then exposed to monomer for half an hour without any previous irradiation, and its infrared spectrum examined. No change was observed, i.e. neither methyl methacrylate nor poly (methyl methacrylate) were present.

Modification of Inert Surfaces By Treatment with Active Oxygen

(i) Glass

Table 35

	Treatment	Contact Angle with water
(a)	None	42°0'
(b)	Active O ₂ for 4 hours	13°50'
(c)	Active O ₂ for 4 hours followed by exposure to methyl methacrylate for ½ hour	63°30'
(d)	Mixture of Active Oxygen and methyl methacrylate vapour	65°40'
(e)	As in (c) followed by washing with chloroform	73°0'
(f)	Active O ₂ for 4 hrs. followed by exposure to Acrylic Acid for ½ hour.	33°

To check that the increase in contact angle is not merely caused by adsorbed monomer on the surface of the glass, a piece of glass was soaked in monomer for ½ hour, and then washed with chloroform and dried. The contact angle with water was then measured. No change was observed, therefore the above observed changes are not due to adsorbed monomer.

(ii)

Table 36

Sample	Contact Angle with water
Poly (methyl methacrylate) Film	68°20'
Glass coated with thin film of poly (methyl methacrylate)	64°0'
Stainless steel coated with thin film of poly (methyl methacrylate)	71°

(iii) Stainless Steel

Table 37

Treatment	Contact Angle with water
(a) None	80°0'
(b) Active O ₂ for 2 hrs	21°0'
(c) Active O ₂ for 2hrs followed by exposure to methyl methacrylate for ½ hour.	37°0'
(d) As in (c) followed by washing with CHCl ₃	58°30'

Polymer Solutions

Polystyrene in Toluene

For polystyrene in toluene at 30°C $\gamma = 2.73$ (P.47)

0.2%

$t_c(\text{toluene}) = 176.1$ seconds

Table 38

Efflux Time Seconds	Total Time of Exposure	Molecular Weight
205.2	0 hours	204,700
205.3	½ hr	206,300
205.4	1 hr	207,000
205.5	1½ hr	208,000
205.6	2½ hr	208,700
205.7	3½ hr	209,600
205.7	4½ hr	209,600

0.4%Table 39

Efflux Time Seconds	Total Time of Exposure	Molecular Weight (M)
236.6	0 hr.	201,400
236.7	$\frac{1}{2}$ hr.	201,800
236.9	$1\frac{1}{2}$ hr.	202,700
237.1	$2\frac{1}{2}$ hr.	203,500
237.2	$3\frac{1}{2}$ hr.	204,000
237.3	$4\frac{1}{2}$ hr.	204,400
237.3	$5\frac{1}{2}$ hr.	204,400

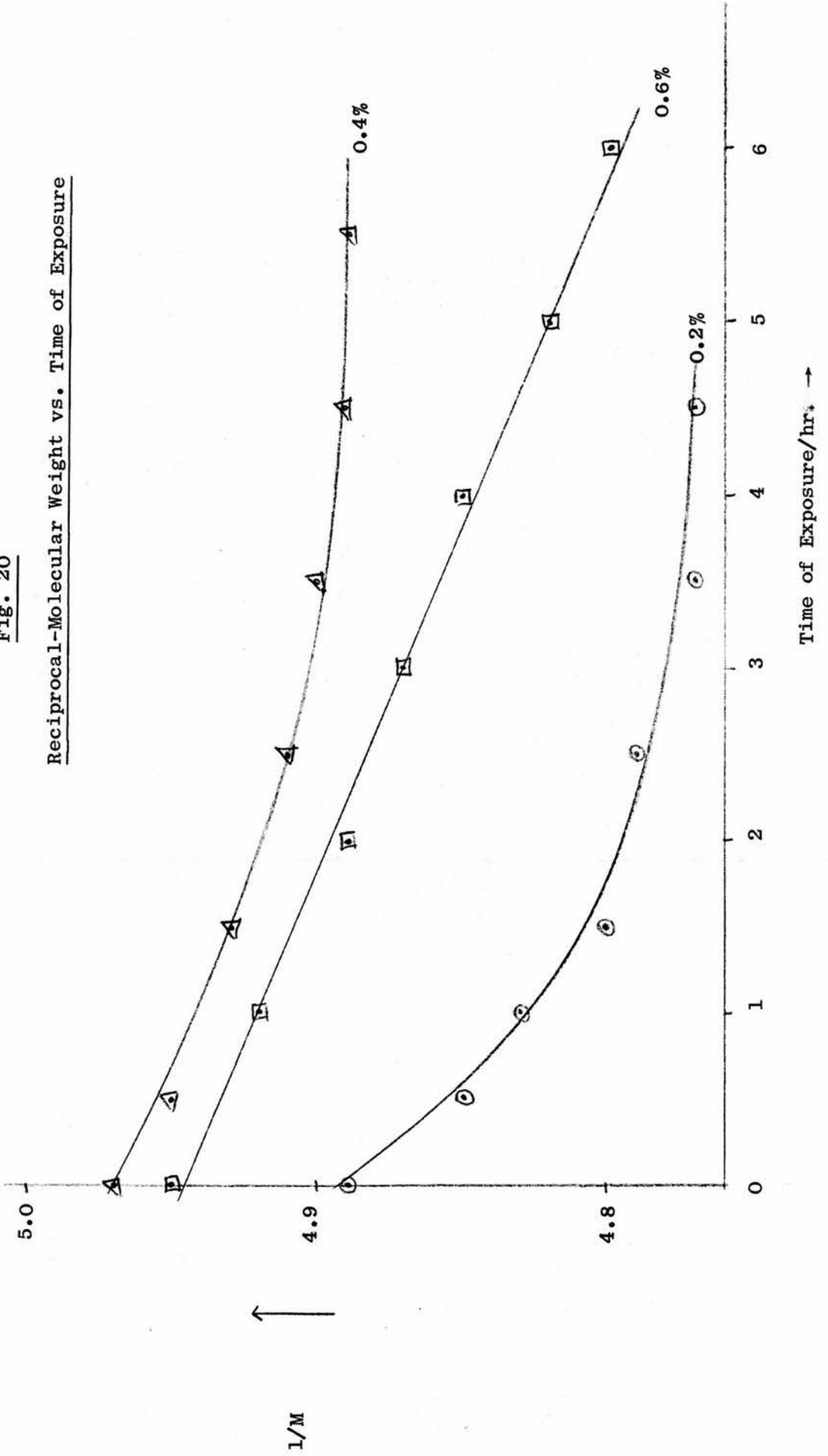
0.6%Table 40

Efflux Time Seconds	Total Time of Exposure	Molecular Weight (M)
271.85	0 hr.	202,200
272.2	1 hr.	203,200
272.7	2 hr.	204,300
273.1	3 hr.	205,400
273.5	4 hr.	206,300
274.0	5 hr.	207,600
274.4	6 hr.	208,500

The above results were plotted as reciprocal molecular weight (1/M) versus time of exposure (Fig. 20). From the graphs it can be seen that in all cases the molecular weights of the polymer solutions increased, levelling off, in the case of the 0.2% and

Fig. 20

Reciprocal-Molecular Weight vs. Time of Exposure



0.4% solutions, after about 4 hours exposure. With the 0.6% solution the molecular weight was still increasing even after 6 hours exposure.

The experiment was repeated twice, and in both cases the same results were obtained.

Poly (methyl methacrylate) in Toluene at 25°C

In this case the flow rates were used as an indication of changes in molecular weight.

0.2%

Table 41

<u>Efflux Time</u> <u>Seconds</u>	<u>Time of</u> <u>Exposure</u>
198.75	0 min.
199.05	10 min.
199.05	20 min.
199.05	50 min.

Thus the molecular weight increases sharply, compared with polystyrene, but also levels off very much more quickly.

Table 42

0.6%

<u>Efflux Time</u> <u>Seconds</u>	<u>Time of</u> <u>Exposure</u>
226.9	0 hr.
227.6	0.25 hr.
227.7	0.5 hr.
227.8	1.0 hr.
227.85	1.5 hr.
227.9	2.0 hr.
227.95	2.5 hr.
228.0	3.5 hr.
228.05	4.5 hr.
228.10	5.5 hr.
228.15	6.5 hr.

With the 0.6% solution the efflux time initially increases very sharply showing a sharp increase in the molecular weight of the poly (methyl methacrylate). The rate of increase quickly slows down, but, as with the polystyrene, after 6 hours exposure the molecular weight is still increasing.

Polystyrene in CCl₄ at 25°C

0.2%

Table 43

Efflux Time Seconds	Time of Exposure
193.1	0 hr.
193.3	½ hr.
193.5	1 hr.
193.7	1½ hr.
193.7	2 hr.
193.7	2½ hr.

0.4%

Table 44

Efflux Time Seconds	Time of Exposure
222.3	0 hr.
222.5	½ hr.
222.7	1½ hr.
222.9	2 hr.
223.1	2½ hr.
223.2	3 hr.
223.2	3½ hr.

Compared with the polystyrene in toluene the above efflux times

increase and level off more quickly, indicating that the reaction occurs more readily in CCl_4 than in toluene.

With the 0.6% solution it is seen that there is very little difference in the rate at which the efflux time increases when compared with the rate of increase for the toluene solution. As with the polystyrene/toluene solution, after 6 hrs exposure the flow rate is still increasing, and, therefore, the molecular weight is still increasing.

0.6%

Table 45

Efflux Time Seconds	Time of Exposure
255.6	0 hr.
256.1	1 hr.
256.55	2 hr.
257.05	3 hr.
257.55	4 hr.
257.95	5 hr.
258.35	6 hr.

Exposure of Solvent

(a) Without Correction For Evaporation

(i) Toluene 30°C

Table 46

Efflux Time Seconds	Time of Exposure
172.4	0 hr.
173.0	$\frac{1}{2}$ hr.
173.2	1 hr.
173.4	$1\frac{1}{2}$ hr.
173.95	2 hr.
174.3	$2\frac{1}{2}$ hr.

From these results it is seen that toluene reacts very readily with active oxygen.

(ii) Carbon Tetrachloride at 25°C

Table 47

Efflux Time Seconds	Time of Exposure
162.8	0 hr.
163.0	$\frac{1}{2}$ hr.
163.05	$1\frac{1}{2}$ hr.
163.10	2 hr.
163.20	$2\frac{1}{2}$ hr.

From these results it is seen that although carbon tetrachloride reacts with active oxygen it does not do so nearly as readily as toluene.

(b) With Correction for Evaporation

As with the solutions of polystyrene, the solvents were weighed before and after reaction with active oxygen, and any loss was made up by addition of pure solvent.

(i) Toluene at 30°C

Table 48

Efflux Time Seconds	Time of Exposure
172.35	0 hr.
172.40	$\frac{1}{2}$ hr.
172.45	$1\frac{1}{2}$ hr.
172.50	2 hr.
172.53	$2\frac{1}{2}$ hr.
172.56	3 hr.
172.58	$3\frac{1}{2}$ hr.
172.60	4 hr.
172.62	$4\frac{1}{2}$ hr.

Weight correction causes a drastic reduction in the rate of change of efflux time.

(ii) Carbon Tetrachloride at 25°C

Table 49

Efflux Time Seconds	Time of Exposure
162.90	0 hr.
162.95	$\frac{1}{2}$ hr.
163.00	1 hr.
163.02	$1\frac{1}{2}$ hr.
163.03	2 hr.
163.05	$2\frac{1}{2}$ hr.

With carbon tetrachloride correction for evaporation virtually eliminates changes in the efflux time.

Exposure of Monomer

Since exposure of polystyrene solutions to active oxygen brought about an increase in molecular weight it was thought that exposure of monomer might result in polymerisation.

The monomer used was redistilled ethyl methacrylate. The results are as follows:-

Table 50

Efflux Time Seconds	Time of Exposure
183.5	0 hr.
183.8	1 hr.
184.1	2 hr.
186.3	4 hr.
191.0	6 hr.
195.7	7 hr.

An increase in molecular weight is indicated. On evaporation of the reaction mixture there remained a viscous liquid which was thought to be low molecular weight polymer. Infrared spectroscopy confirms that this liquid is in fact poly (ethyl methacrylate).

Thermal Stability After Exposure

The following samples were thermally degraded; (i) Polystyrene precipitated in methanol from a polystyrene/toluene solution before exposure; (ii) Polystyrene precipitated in methanol from a polystyrene/toluene solution after several hours exposure to active oxygen, giving the following results:-

(i) Before Exposure

w₀ at 330°C = 25 mg.

Heating Rate = 1.44°C/min

Table 51

Weight of Polymer w mg	w/wo	Temperature T°C
24.6	.984	355.0
24.0	.96	362.0
23.2	.928	367.0
21.8	.872	371.5
19.4	.776	376.0
16.0	.64	381.0
12.8	.512	384.6
9.2	.368	388.0
5.2	.208	393.0
2.2	.088	398.0
0.8	.032	402.5

(ii) After Exposure

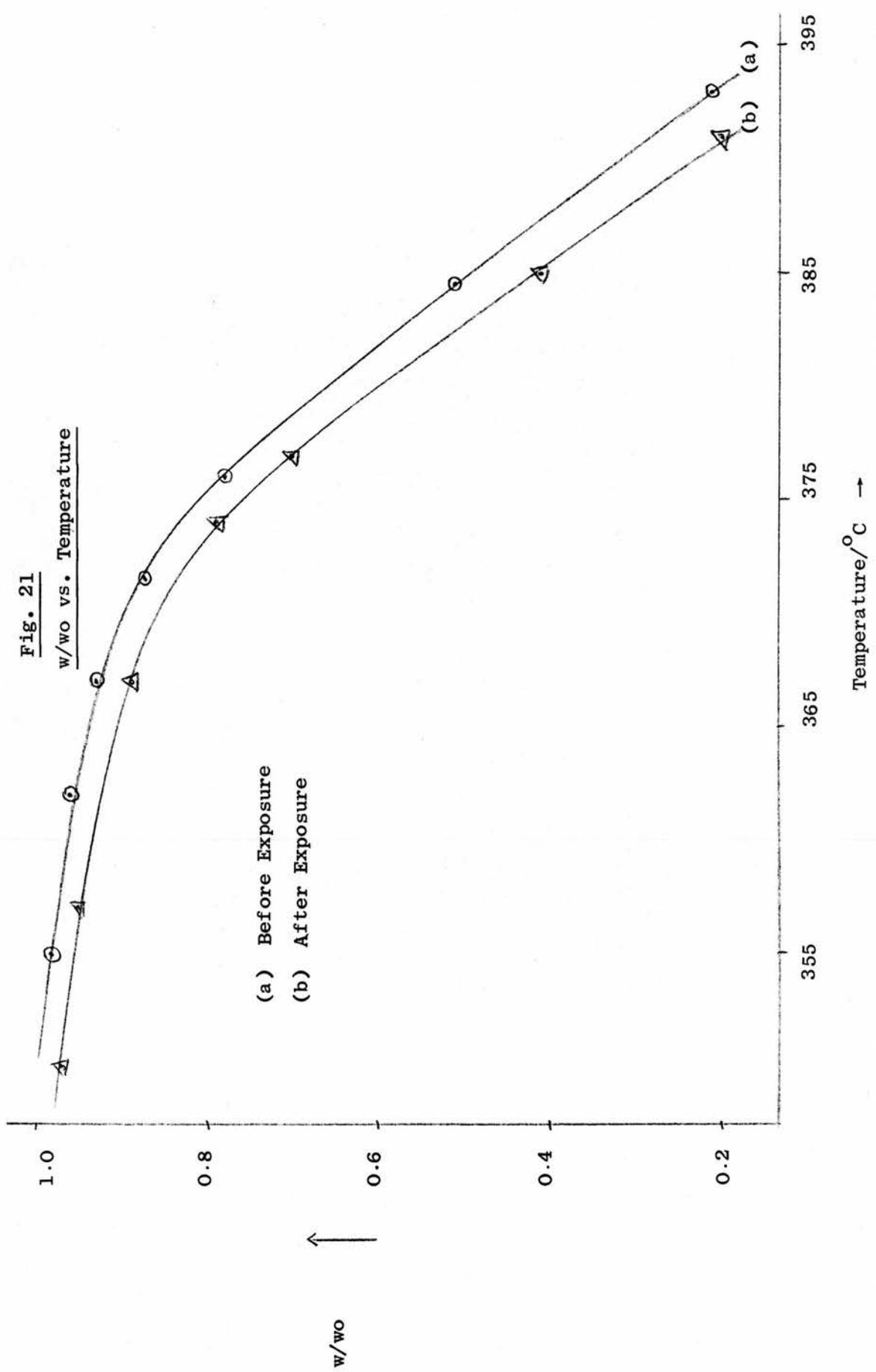
$w_o = 23.6 \text{ mg. at } 330^\circ\text{C}$

Heating Rate = 1.44°C/min

Table 52

Weight of polymer w mg	w/w _o	Temperature T ^o C
22.9	0.970	350
22.4	0.949	357
21.0	0.890	367
18.6	0.788	374
16.6	0.703	377.2
13.3	0.564	381
9.6	0.407	384.6
7.0	0.297	388
4.6	0.195	391.2
2.8	0.119	395
1.2	0.051	402
0.7	0.030	412

On plotting w/w_o vs T^oC it can be concluded that after exposure polystyrene is thermally less stable (Fig. 21).



Chapter 4

Discussion

Relationship between Weight Loss and Time of Exposure to Active Oxygen

From the results (Fig. 5) it can be seen that the weight losses of all the polymers exposed to active oxygen are directly proportional to the time of exposure, $-dw/dt$, varying from 0.15 mgs/hr for polyethylene terephthalate to 2.5 mgs/hr for poly (vinyl chloride).

There are two main factors which affect the oxidation of glass-state polymers (Chapter 1). These are (i) Steric Effects and (ii) Crystallinity.

(i) In the autoxidation of a series of polymers Hansen et al⁴² have shown that the greater the steric hindrance, the more difficult it is for oxidation to take place. Although their work does not directly involve atomic oxygen, it is likely that analogous highly reactive species are involved in the mechanism.

(ii) Researchers at the Bell Telephone Laboratories^{48,49} have shown that crystalline regions within semi-crystalline polymers are less vulnerable to oxidation than the amorphous regions.

Taking these factors into account, it is not surprising that polyethylene terephthalate, which is very crystalline, has the lowest rate of weight loss, and that poly (vinyl chloride), which is only 3-10% crystalline, has the greatest rate of weight loss.

It appears from these results, that crystallinity has a greater effect on oxidisability than steric hindrance, because both polyethylene terephthalate and nylon-66 which are very crystalline have lower rates of weight loss than the amorphous but much more sterically hindered polystyrene.

Steric effects do play a part, however. On comparing the rate of weight loss of polystyrene with the slightly crystalline poly (vinyl chloride) and polyacrylonitrile it is seen that it is less

than that of former and similar to that of the latter.

It may be that, in the case of polystyrene, polyethylene terephthalate, and nylon-66, the reaction is strictly confined to the surface. In the former case by steric hindrance and in the latter cases by the fact that the crystalline regions form impenetrable layers. There is unfortunately no comparable data for weight losses during thermal oxidation.

Relationship between Rate of Weight Loss and Power

Titrating out atomic oxygen with nitrogen dioxide has shown that, of the active species produced, only the atomic oxygen reacts to any extent on the polymer surface.

From a plot of $-dw/dt$ versus power (Fig. 7) it can be seen that the rate of weight loss is directly proportional to the input power.

The likely explanation for this, is that increasing the power to the cavity must cause an increase in the active species produced and therefore an increase in the amount of atomic oxygen reaching the polymer surface. This has in fact been shown to be the case experimentally, when it was seen that increasing the power, while keeping the molecular oxygen flow rate constant, caused the amount of atomic oxygen at the surface of the polymer to increase. (Fig. 9).

It was also observed that, if the power was kept constant and the flow rate of the molecular oxygen increased, then the flow rate of atomic oxygen also increased. (Fig. 8). It would therefore seem reasonable to assume that increasing the flow rate of molecular oxygen would cause an increase in the rate of weight loss of the polymer being exposed.

This was in fact observed in the case of poly (vinyl chloride), where as a final check the polymer was subjected to a discharge

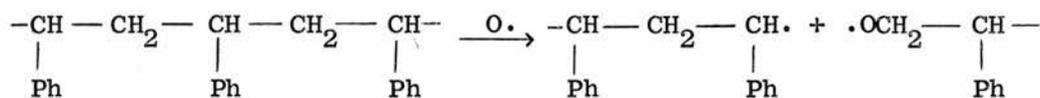
produced by various flow rates of molecular oxygen and various power inputs which, according to previous results (Fig. 9), would give the same flow rate of atomic oxygen. As has already been stated, the rate of weight loss remained constant.

With polystyrene, however, it was found that although the rate of weight loss increased directly with increasing power, suggesting in turn that it would increase with an increase in the amount of atomic oxygen, on increasing the flow rate of molecular oxygen a fall in the rate of weight loss was observed. This result was confirmed on repeating the experiment. On the second occasion a freshly prepared film of polystyrene was used, and the oxygen cylinder was replaced.

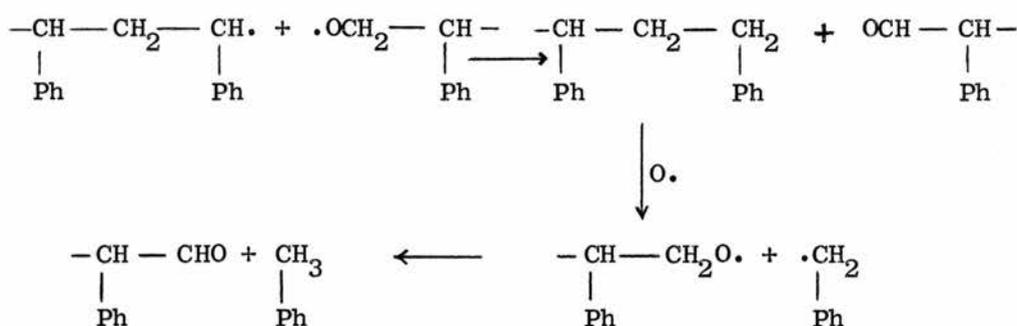
It, therefore, appears that although polystyrene does in fact lose weight at a greater rate on increasing the amount of atomic oxygen, its reaction is pressure dependent.

It is rather difficult to understand the reason for this phenomena. It is possibly connected with the structure of the polystyrene, and therefore with the mechanism of its reaction with atomic oxygen.

The initial step may be one of scission, such as:-



followed by:-



If the next step then involves diffusion of the toluene through the surface layers into the gaseous stream, then it can be seen that at low pressure this step will be enhanced, but, as the pressure is increased it will become more and more difficult. There will therefore be an optimum pressure for $-dw/dt$. Below this pressure the reduction in the concentration of oxygen atoms will cause a decrease in $-dw/dt$ and above it the difficulty of diffusion of the toluene from the polymer will also cause a decrease in $-dw/dt$. This hypothesis fits the facts presented in graph form in Fig. 12.

Products

The fact that no chemical changes could be observed in the residual polymer films, and that the gaseous products detected by infrared spectroscopy and mass spectrometry were CO_2 , H_2O , and also in the cases of polyacrylonitrile and poly (vinyl chloride), NO_2 and COCl_2 respectively, suggests that the polymer surfaces, on exposure to atomic oxygen, break down to give these products.

The fact that COCl_2 is one of the products from the exposure of poly (vinyl chloride) may be the reason for the anomalously high value of $-dw/dt$ exhibited by this polymer. The molecular weight of COCl_2 is much higher than that of any of the other products. Therefore, although $-dw/dt$ for poly (vinyl chloride) is many times larger than that for the other polymers, its rate of reaction in terms of bonds broken may in fact be very similar.

The gaseous products, from the exposure of polystyrene to atomic oxygen, were trapped out and the pressure measured at regular intervals. From the results a straight line graph was obtained, (Fig. 13). This shows that the weight loss of the exposed polystyrene is directly proportional to the pressure of the products,

of which the main one is CO_2 . The formation of CO_2 is, therefore, directly related to the weight loss process.

Although it appears that the polymer surfaces break down leaving no chemical residue, the breakdown need not necessarily be completely to give the final products. It is quite likely, as has already been suggested in the case of polystyrene, that fairly large groups leave the polymer surface and enter the gaseous stream. In the gaseous state these molecules will be very quickly broken down to the final products, by atomic oxygen. Thus in the case of polystyrene it has been suggested that toluene leaves the surface. This is not ruled out by the fact that no toluene is detectable amongst the gaseous products, because in the gas phase, toluene will be broken down to give CO_2 and H_2O , on reacting with atomic oxygen.

Molecular Weight Changes

It is suspected that the reaction of polymers with atomic oxygen is confined to the surface and the few layers below it. If this were the case then the bulk of the polymer should remain unaffected and its molecular weight should not change.

On exposing polystyrene to atomic oxygen for various periods of time, however, and determining its molecular weight by viscometry, it was found that changes had taken place (Fig. 14).

Since this result was not consistent with a surface reaction it was decided that further research concerning molecular weight was necessary. Thus the experiment was repeated, this time using a polystyrene film prepared without solvent (Chapter 2). In this case there was no change in the molecular weight of the polystyrene,

even after 24 hours exposure. The previous changes observed were, therefore, attributed to residual solvent effects.

On this basis, it was decided that the molecular weight of a freshly cast polystyrene film should be regularly determined over a period of several days while it was 'drying out' in a vacuum oven at 40°C, ie. under the conditions a polymer film is normally subjected to before experimentation.

For the first few days in the vacuum oven the film showed an increase in molecular weight as solvent evaporated. After about a week, however, the molecular weight reached a peak, dropped slightly, and levelled off at a value below that for the original polystyrene pellets from which the film was made, (Fig. 15).

Similar results were obtained for films of poly (ethyl methacrylate), (Table 24) although a sample of the powdered polymer, used to make the films, showed no change in molecular weight under the same conditions.

The change in molecular weight is therefore quite definitely a solvent effect and has nothing whatsoever to do with exposure to atomic oxygen. Perhaps the combined effects of heat, although only 40°C, and the swelling caused by solvent, acted together to cause slight degradation of the polymer. Whatever the reason it is not directly concerned with the present research, but is an interesting observation which requires further examination.

In conjunction with the above findings, the fact that polymer films of different thickness, but constant surface area, were found to have constant values for $-dw/dt$ strengthens the suggestion that the reaction of polymers with atomic oxygen occurs on the surface of the polymer.

Thermal Stability After Exposure

With polystyrene the results show, (Figs. 16,17), that although small, there is a definite lowering in the thermal stability of the polymer with exposure to atomic oxygen.

The reason for this is that, even although attenuated total reflection infrared spectroscopy showed no chemical changes on the surface of the polymer, there might in fact be some chemical groups, in small concentration, whose peaks were masked by the stronger spectrum of polystyrene. These groups could be ethers or peroxides, both of which would quickly break up upon heating and thus initiate degradation, even although their concentration was very low.

Contact Angle Measurements

Since the reaction of polystyrene with atomic oxygen occurs entirely on the surface of the polymer, and since it is suspected that this is the major reaction site for all the polymers, then the fact that all the exposed polymers exhibit a decrease in their contact angle with water seems reasonable (Fig. 19). Polyethylene terephthalate, which has the lowest value for rate of weight loss on exposure to atomic oxygen, unexpectedly shows the greatest decrease in contact angle, which after 2½ hours exposure is only 25.5% of the original angle.

It will be easier to discuss the results by referring to the following table:-

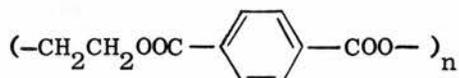
Table 53

Polymer	Percentage of Original Angle		Percentage Change in 1st hour
	After 1 hr	After 2.5 hr.	
Polystyrene	57	39	70
Polyethylene Terephthalate	34	25	88
Polyacrylonitrile	52	29	67
Poly (vinyl chloride)	51	36	76
Nylon-66	54	48	89

On examining this table it can be seen that as well as having the greatest degree of change in contact angle, polyethylene terephthalate along with nylon-66, exhibits almost 90% of this change in the first hour of exposure.

In this short time both nylon-66 and polyethylene terephthalate have lost very little weight on exposure to atomic oxygen, being very crystalline polymers and therefore resistant to oxidation. To explain the rapid degree of change in contact angle, therefore, the chemical structures of these two polymers must be examined:-

(i) Polyethylene Terephthalate



(ii) Nylon 66



Of all the polymers exposed these two are the only ones which have oxygen present in their structure, polyethylene terephthalate in an ester linkage, and nylon 66 in a peptide linkage. It seems very probable, therefore that these linkages are readily broken or further oxidised to form polar groups. The fact that neither of the polymers reacts readily with atomic oxygen suggests that the reaction of these groups contributes nothing towards the breakdown of the polymer. The fact that nylon 66 only shows a 52% decrease in contact angle compared with the 75% decrease in the case of polyethylene terephthalate also suggests that the ester linkage reacts more readily than the peptide linkage, with atomic oxygen, to form a polar group.

Introduction of Monomer to an Exposed Film of Poly (vinyl chloride)

The fact that the reaction of polymers with atomic oxygen is a surface one and probably involves a free radical mechanism led to the premise that if a polymer film treated in this manner was immediately exposed to monomer then the monomer would polymerise on to the surface of the polymer.

The results (pp. 69,70) obtained from exposing a treated film of poly (vinyl chloride) to methylmethacrylate appear to back up this belief. From the infrared data it appears that methyl methacrylate has undoubtedly polymerised directly on to the surface of the poly (vinyl chloride).

Modification of Inert Surfaces by Treatment with Active Oxygen

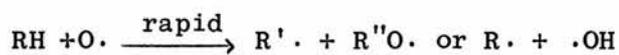
Having obtained positive results on treating exposed polymer films with monomer it was decided to repeat the experiment using inert surfaces such as glass and stainless steel.

Although the only method of examination used after treatment of the surfaces was to measure their contact angles with water, the results (Page 71) definitely indicate that this method enables monomers to be polymerised directly on to the surface of glass and stainless steel.

This could prove to be quite a useful method of surface modification. For example, the strength of polymer fibres bonded together by a resin could be greatly increased if before bonding the fibres were first treated with atomic oxygen, and acrylic acid subsequently polymerised directly on to the surface, thus enabling the resin to actually form a chemical bond with the fibres.

Reaction Mechanism

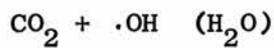
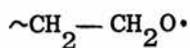
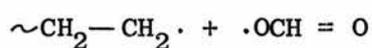
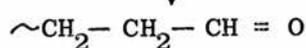
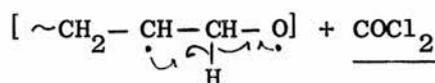
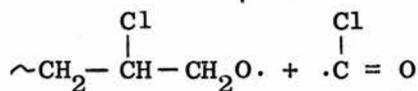
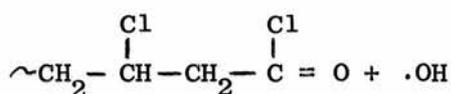
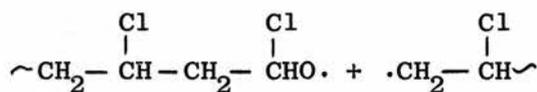
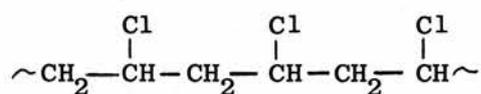
The first step appears to be (P. 25):-



e.g. poly (vinyl chloride)

Products:- CO_2 , H_2O , $COCl_2$

Possible Mechanism



SOLUTIONS

Having established that the reaction of polymer films with atomic oxygen is confined to the surface, and having examined this in detail, it was then decided, that in order to obtain further information, it would be necessary to study the reaction of polymers, in solution, with atomic oxygen.

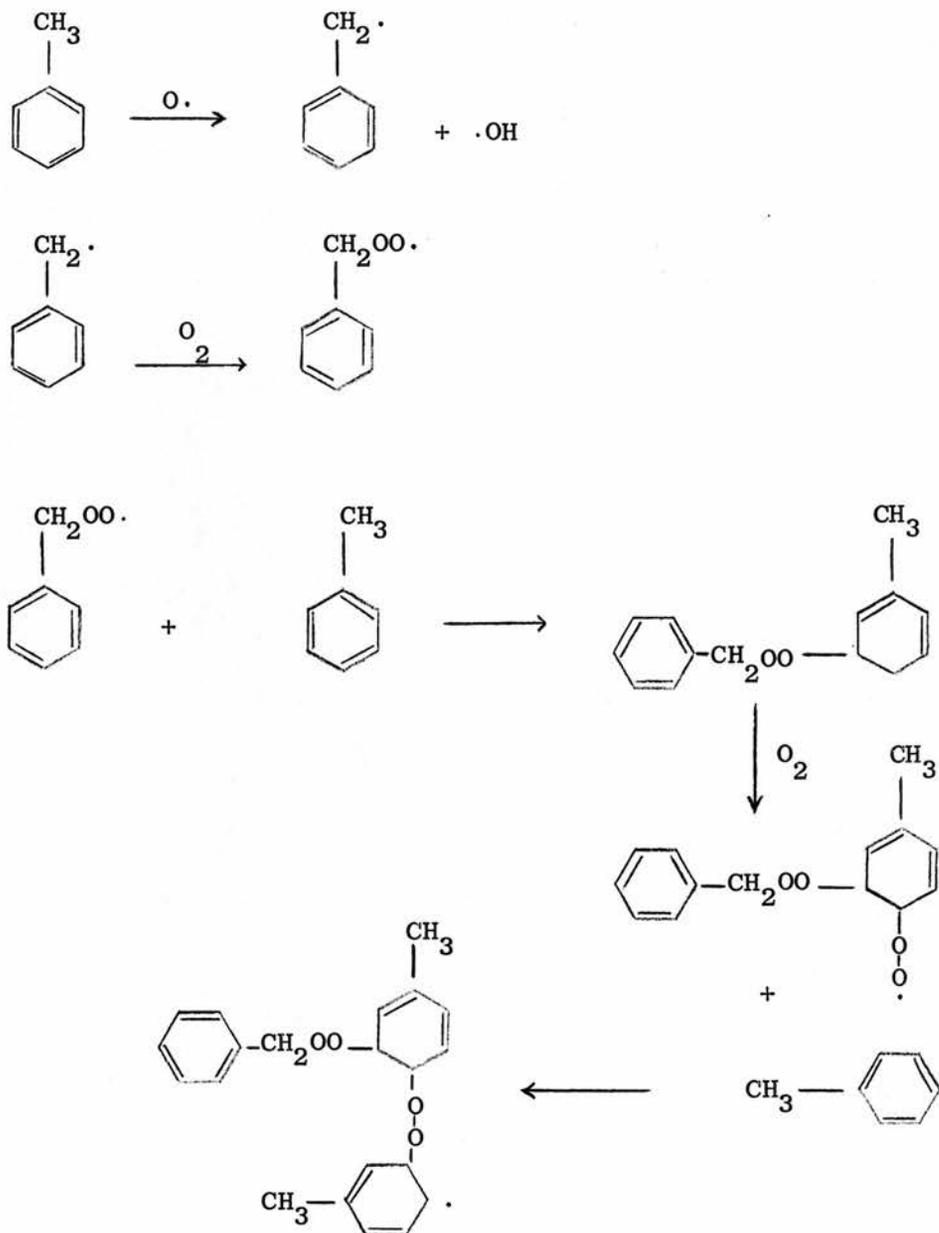
Since under normal conditions for thermal oxidation either scission or cross-linking can occur, separately or in competition it was decided to follow any such changes in the polymer solutions by viscometry. In all cases it was found that on exposing the polymer solutions to active oxygen an increase in molecular weight was observed. Therefore cross-linking must have occurred.

The results for dilute solutions (P.P. 72-74) indicated that the rate of the reaction increased on changing from toluene to carbon tetrachloride. Therefore, either the solvent participates in the reaction mechanism of cross-linking, or else competes with the polymer for atomic oxygen. The former postulation is ruled out by the fact that concentrated solutions in either solvent have similar rates, which suggests that the reaction is one of competition, and that if the polymer concentration is increased its chances of reacting with the active oxygen rather than the solvent are also increased.

To test this theory the solvents were exposed to atomic oxygen and their efflux times measured. The results indicate that toluene does in fact react much more readily with the atomic oxygen than the carbon tetrachloride. (P.P. 76,77). It may be that the increase in the molecular weight is due to the formation of low molecular weight polymer formed by linking of toluene molecules. In the case

of carbon tetrachloride the changes are probably due to impurities such as chloroform, which is very difficult to remove.

A possible mechanism for linking of toluene molecules is:-



If this is the case then it is likely that the low molecular weight polymer is involatile and therefore its concentration will increase as the reaction proceeds and toluene evaporates. It was

therefore decided to repeat the runs with weight corrections for evaporation. This time the changes in efflux time were extremely small especially with the carbon tetrachloride.

The reaction mixture was subjected to g.l.c. after exposure. No change was observed. This however does not rule out the fact that low molecular weight polymer could have been trapped on the column.

Since it was suspected that low molecular weight polymer was being formed on exposure of toluene to atomic oxygen it was decided to treat methyl methacrylate in the same way. In this case the production of low molecular weight polymer was verified by infrared spectroscopy.

With the polystyrene solutions it is seen that in the case of the 0.4% and 0.2% solutions the molecular weights increased initially with exposure, but eventually levelled off. The 0.6% solution continued to increase in molecular weight up to the experimental time limit.

If N_0 = Number of moles of polymer

then $N_0 - N_t$ = number of cross links; where N_t = number of moles after t hours exposure.

$$N_0 = \frac{W_0}{P_0} \quad \text{where } W_0 = \text{initial weight of polymer} \\ \text{and } P_0 = \text{Number average molecular weight initially.}$$

$$N_t = \frac{W_t}{P_t} \quad \text{where } P_t = \text{molecular weight at time } t$$

$$\therefore \frac{N_0 - N_t}{N_0} = (W_0/P_0 - W_0/P_t)/N_0 = (1 - \frac{P_0}{P_t}) = \text{number of cross links per mole.}$$

The results will be clearer if the number of cross links per mole is plotted against the time of exposure

0.2%

Table 54

Time of Exposure hours	$(1 - P_g/P_t) \times 10^3$
0.5	7.8
1.0	10.1
1.5	15.8
2.5	19.2
3.5	23.4
4.5	23.4

0.4%

Table 55

Time of Exposure hours	$(1 - P_o/P_t) \times 10^3$
0.5	2.0
1.5	6.4
2.5	10.3
3.5	12.7
4.5	14.7
5.5	14.7

0.6%

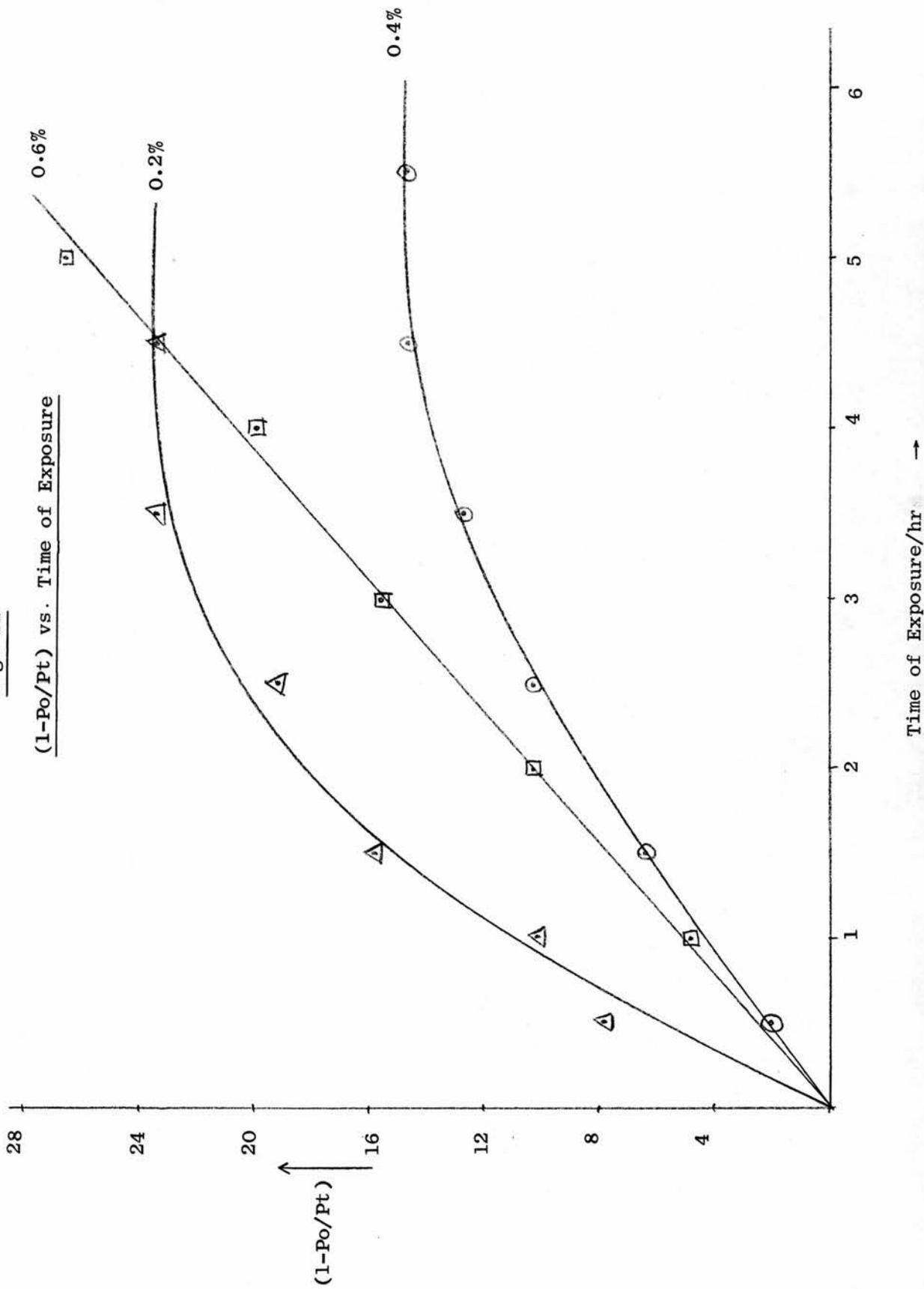
Table 56

Time of Exposure hours	$(1 - P_o/P_t) \times 10^3$
1	4.9
2	10.3
3	15.6
4	19.9
5	26.6
6	30.2

From the graph (Fig. 22) it can be seen that the 0.2% solution appears to stop cross-linking after about 4 hours, the 0.4% after

Fig. 22

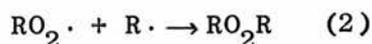
$(1-P_o/P_t)$ vs. Time of Exposure



about 5 hours and that after 6 hours the 0.6% solution continues to cross-link.

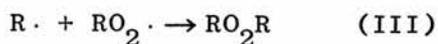
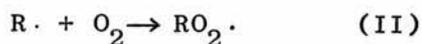
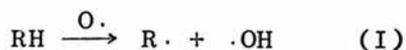
It is therefore necessary to examine the various reactions which can occur. Before doing this however, consider the results for the thermal stability of a sample of polystyrene after exposure in solution. Using a Stanton Massflow Thermobalance it was found that samples precipitated from exposed solutions proved to be thermally less stable than a sample from an untreated solution. This leads to the conclusion that cross-linking is occurring via an ether or peroxy group, which will break on heating and initiate degradation.

Thus of the two reactions which can occur to give the observed increase in molecular weight:-



(1) is ruled out since it would cause an increase in the thermal stability, which is the opposite of what is observed.

It is, therefore, assumed that on exposure of polymer solutions to atomic oxygen the following reactions occur:-



With toluene as solvent it will compete with the polymer for the oxygen atoms.



toluene. The fact that the 0.4% solution takes longer to level off than the 0.2% solution is due to the fact that the greater concentration of polymer reduces the competing effect of toluene with the result that reactions (I) and (II) occur to a greater extent than reactions (IV) and (V).

Similarly with the 0.6% solution, the concentration of polymer is sufficient to lessen the competing effect of toluene such that after 6 hours the molecular weight of the polymer is still increasing. It will eventually level off when the concentration of molecular oxygen in solution has been sufficiently reduced.

On switching from toluene to carbon tetrachloride, as solvent, similar results are observed. In this case the rates of reaction of the 0.2% and 0.4% solution are much faster than in toluene, and quickly level off (Tables 43,44). This is due to the fact that carbon tetrachloride does not compete as readily as toluene, with the polymer, for the atomic oxygen. Therefore more of the atomic oxygen is available for reactions (I), (II) and (III), with the result that they will occur more rapidly. Since the concentration of the 0.6% solution appears to be great enough to render the effect of solvent competition negligible, it is not unexpected to find that the rate of the reaction of the 0.6% solution in carbon tetrachloride is similar to that in toluene.

With a solution of poly (methyl methacrylate) it is seen that even although the solvent is toluene, the rate of the reaction, i.e. the rate at which the efflux time increases, is faster than the rate for a solution of polystyrene in carbon tetrachloride (Tables 41,42). The reason for this may be that the ester group in the poly (methyl methacrylate) is very susceptible to attack by atomic oxygen and renders the effect of any competition, by solvent or impurities negligible. This suggestion is strengthened by the fact that in

contact angle measurements it was found that polymers such as poly ethylene terephthalate and nylon 66 which have oxygen in their structures react very rapidly with atomic oxygen.

In conclusion it appears that in the solid state the reaction with atomic oxygen is mainly confined to the surface of the polymer, especially in the case of crystalline polymers. Although there are no major chemical changes, the changes in contact angles suggest that some chemical change has taken place, increasing the polarity of the surface. This method of treatment improves the bonding of the surface and can in fact be used to polymerise monomer directly on to the surface.

There are unfortunately no rates available for the thermal oxidation of the polymers with which the results could be compared. There are plans, however, to investigate this at a later date in this laboratory.

Studying the products is of no real help in determining the mechanism, since any large molecules leaving the polymer surface will be very quickly oxidised further in the gaseous state, by atomic oxygen.

In the case of solutions the mechanism is different. Instead of breakdown, cross-linking occurs, and the rate of the reaction is faster than in the solid phase.

It appears that the reaction is dependent upon the concentration of molecular oxygen absorbed in the solution. Future work will involve repeating the solution experiments, varying the concentration of the absorbed oxygen.

BIBLIOGRAPHY

- (1) C.C. Davis and J.T. Blake, 'Chemistry and Technology of Rubber', Reinhold, New York, 1937.
- (2) R.B. Mesrobian and A.V. Tobolsky, J. Polym. Sci, 2, 463 (1947).
- (3) R. Criegee et. al. Ber. 72, 1799 (1939).
- (4) E.H. Farmer and A. Sundralingham. J. Chem. Soc. 1943, 125.
- (5) G. Chevanne and O. Miller, Bull. Soc. Chim. Belg. 40, 611 (1931).
- (6) F.F. Rust U.S. Pats. 2,396,206 and 2,396,217.
- (7) P. George and A.D. Walsh. Trans. Faraday Soc. 42, 94 (1946).
- (8) J.L. Bolland and G.Gee Trans. Faraday Soc. 42, 236, 244 (1946)
- (9) N. Uri 'Autoxidation and Antioxidants' P.P 65-77, Wiley (Interscience).
- (10) E.T. Denisov, Dokl. Akad. Nauk, SSSR 130, 1055 (1960).
- (11) G.A. Russell, J. Am. Chem. Soc. 78, 1041 (1956).
- (12) J.A. Howard and K.U. Ingold Can. J. Chem. 45, 785 (1967).
- (13) D. Barnard et. al. 'The Chemistry and Physics of Rubber-Like Substances', MacLaren, London 1963, P.593.
- (14) J. Coryl-Lacau Rev. Gen. Caoutchouc, 30, 819 (1953). 31, 473 (1954).
- (15) L. Bateman, Quart. Rev. (London) 8, 147 (1954).
- (16) B.S. Middleton and K.U. Ingold, Can. J. Chem., 45, 192 (1967).
- (17) L. Dulog, E. Radlmann, and W. Kern, Makromol Chem. 60, 1 (1963).
- (18) F.R. Mazo, J. Amer. Chem. Soc. 80, 2465, 2497 (1958) also 80, 2480, 6701.
- (19) A.A. Miller and F.R. Mayo. J. Am. Chem. Soc. 78, 1017 (1956).
- (20) D.E. Van Sickle, F.R. Mayo, E.S. Gould and R.M. Arluck. J. Am. Chem. Soc. 89, 967 (1967).
- (21) A.P. Zeelenberg and A.F. Bickel, J. Chem. Soc. (1961), 4014.
- (22) L. Bateman, Quart. Rev. (London) 8, 147 (1954).
- (23) G.A. Russell, J. Am. Chem. Soc. 79, 3871 (1957).
- (24) G.A. Russell, J. Am. Chem. Soc. 77, 4583 (1955).
- (25) J. A. Howard and K.U. Ingold, Can. J. Chem. 45, 793 (1967).
- (26) T.G. Traylor and G.A. Russell, J. Am. Chem. Soc. 87, 3698 (1965).

- (27) C.E. Boozer, B.W. Ponder, J.C. Trisler and C.E. Wightman III, *J. Am. Chem. Soc.* 78, 1506 (1956).
- (28) A.A. Zavitsas and S.Seltzer, *J. Am. Chem. Soc.* 86, 1265 (1964).
- (29) J.A. Howard and K.U. Ingold, *Can. J. Chem.* 44, 1119 (1966).
- (30) D.G. Hendry and G.A. Russell, *J. Am. Chem. Soc.* 86, 2368 (1964).
- (31) C. Walling and P.J. Wagner, *J. Am. Chem. Soc.* 86, 3368 (1964).
- (32) P. Gray, and A. Williams *Chem. Rev.* 59, 239 (1959).
- (33) P. Kabasakalian and E.R. Townley, *J. Am. Chem. Soc.* 84, 2723 (1962).
- (34) J.K. Kochi, *J. Am. Chem. Soc.* 84, 1193 (1962).
- (35) J.A. Howard and K.U. Ingold, *Can. J. Chem.* 43, 2729 (1965).
- (36) B.S. Middleton and K.U. Ingold *Can. J. Chem.* 45, 192 (1967).
- (37) G.A. Russell, *J. Am. Chem. Soc.* 78, 1047 (1956).
- (38) H.H.G. Jellinek, 'Styrene, Its Polymers, Copolymers, and Derivatives', Reinhold, New York (1952).
- (39) A. Voltinov, P. Kobeko and F. Marcy, *J. Phys. Chem. (USSR)* 16, 106 (1942).
- (40) U.M. Yur'ev, A.N. Pravedrikov, and S.S. Medvedev, *Dokl. Akad. Nauk SSSR*, 124, 335 (1959).
- (41) Bartlett and D.H. Reid, *Chem. Ind. (London)*, 1504, (1956).
- (42) R.H. Hansen, W.M. Martin, and T. de Benedictis, *Trans. Inst. Rubber Ind.* 39, T301 (1963).
- (43) A.T. Betts, and N. Uri, *Nature*, 199, 568 (1963).
- (44) R. Hiatt and T.G. Traylor, *J. Am. Chem. Soc.* 87, 3768 (1965).
- (45) N.T. Notely, *Trans Faraday Soc.* 58, 66 (1962) and 60, 88 (1964).
- (46) L. Reich and S. Stivala, *Rev. Makromol. Chem.* 1, 249 (1966).
- (47) L. Dulog, E. Radlmann and W. Kern, *Makromol Chem.*, 60, 1 (1963).
- (48) J.P. Luongo. *J. Polym. Sci.*, B1, 141 (1963).
- (49) F.H. Winslow. C.J. Aloiso, W.L. Hawkins, W. Matreyck and S. Matsuoka, *Am. Chem. Soc., Div. Polym. Chem., Preprints* 4, nos. 2, 706 (1963).
- (50) C.S. Foote, *Science*, 162, 963 (1968).
- (51) C.S. Foote, *Accounts. Chem. Res.* 1, 104, (1968).

- (52) K. Gollnick, *Advan. Chem. Ser.*, 77, 78 (1968).
- (53) K. Gollnick, *Advan. Photochem*, 6, 1 (1968).
- (54) A.U. Khan and M. Kasha, *J. Chem. Phys.*, 39, 2105 (1963); 40, 605 (1964).
- (55) A.U. Khan and M. Kasha, *Nature*, 204 (1964).
- (56) C.S. Foote and S. Wexler, *J. Am. Chem. Soc.* 86, 3879 (1964).
- (57) E. McKeown and W.A. Waters, *J. Chem. Soc. B*, 1040 (1966).
- (58) R.J. Cvetanovic, *J. Chem. Phys.* 23, 1208 (1955).
- (59) P.A. Leighton, 'Photochemistry of Air Pollution', Academic Press Inc., New York, N.Y. 1961 P.103.
- (60) R.J. Cvetanovic, *J. Chem. Phys.* 23, 1375 (1955).
- (61) C.A. Arrington, W. Brennen, G.P. Glass, J.V. Michael, and H. Niki, *J. Chem. Phys.*, 43, 525 (1965).
- (62) G.B. Kistiakowsky and G.G. Volpi, *J. Chem. Phys.*, 27, 1141 (1957).
- (63) R.H. Hansen, J.V. Pascale, T. de Benedictis and P.M. Rentzepis, *J. Polym. Sci*, A, 3, 2205 (1965).
- (64) S.J. Arnold, M. Kubo and E.A. Ogryzlo, *Advan. Chem. Ser.*, 77, 133 (1968).
- (65) M.L. Kaplan and P.G. Kelleher, *J. Polym. Sci. B*, 9, 565 (1971).
- (66) K. Gollnick, *Advan. Photochem.* 6, 1, (1968).
- (67) E.J. Corey and W.C. Taylor, *ibid*, 86, 3881 (1964).
- (68) S.J. Arnold, E.A. Ogryzlo, and H. Witzke, *J. Chem. Phys.*, 42, 1837 (1965).
- (69) A.M. Fallick, B.H. Makar, and R.J. Myers, *J. Chem. Phys.*, 42, 1837, (1965)
- (70) A. Nickon and W.L. Mendelson. *J. Am. Chem. Soc.*, 87, 3921 (1965)
- (71) K. Gollnick and G.O. Schenck, *Pure Appl. Chem*, 9, 507 (1964)
- (72) D.R. Kearns, W. Fenical and P. Radlick, *Ann. N.Y. Acad. Sci.* 171, 32 (1970).
- (73) D.R. Kearns, W. Fenical, and P. Radlick, *J. Amer. Chem. Soc.* 91, 7771 (1969).
- (74) D.B. Sharp, Abstracts, 138th National Meeting of the American Chemical Society, New York, N.Y. Sept. 1970. Abstract 79.
- (75) D.R. Kearns, W. Fenical, and P. Radlick, *J. Am. Chem. Soc.* 91, 3396 (1969).

- (76) P.D. Bartlett, G.D. Mendenhall, and A.P. Schaap, International Symposium on Singlet Oxygen, New York Acad. of Sci, New York Oct. 23, 1969.
- (77) Hake and Phelps, Phys. Rev., 1963, 131.
- (78) H.P. Frank, J. Polym. Sci., 7, 567 (1951).
- (79) K. Patterson, thesis.
- (80) S.H. Maron, J. Appl. Polym. Sci. V, 282 (1961).
- (81) H. Draeger, Chem. Abs., 64, 7374h.