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THE PHOTODEGRADATION OF POLY(VINYL CHLORIDE) FILMS

A Thesis

presented for the degree of

DOCTOR OF PHILOSOPHY

in the Faculty of Science of the

University of St. Andrews

by

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August 1972

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



(ii)

DECLARATION

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

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

William Gibb

(iii)

CERTIFICATE

I hereby certify that William Gibb 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

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Summary

Poly(vinyl chloride) films have been carefully prepared in order to be as pure as possible, and then irradiated in an atmosphere of nitrogen, mainly using a 500 W medium pressure mercury lamp which gives a polychromatic source of ultraviolet radiation. The reaction has been followed in two ways. First by trapping and recording the evolved hydrogen chloride, and second by following the ultraviolet and visible spectra of the degraded films.

Within a fairly rigid experimental set-up the following parameters have been varied - film area and thickness, light intensity and temperature, the sample, the distribution of the radiation, and the atmosphere.

The formation of a 'protective barrier' at the film surface is proposed to account for many of the experimental findings and a model to explain the build up of the surface layer is suggested.

Chapter 1

Introduction

Poly(vinyl chloride) was first prepared by Baumann in 1872 and further studies were made by Ostromislensky during 1912-1929. Poly(vinyl chloride) was produced commercially in 1927 and world production has since climbed to 3.7 billion tons (1970). Research work and the accompanying literature has similarly increased and is very extensive. Much of this work has been concerned with the thermal and photodegradation of poly(vinyl chloride). Although this polymer has extensive applications it is relatively unstable to heat and light. These two agencies are particularly damaging for this polymer as very low extents of degradation can bring about considerable changes in the physical properties of the material, and in particular cause discolouration. As the polymer is heated to around 200^oC during processing, and is exposed to sunlight during outdoor use, degradation will occur. In order to combat this stabilisers have been developed. The discovery of a successful stabiliser depends on an understanding of the mechanisms involved in degradation, and it is to this end that much research has been directed. Despite the large volume of this research the degradation mechanisms are not yet fully understood.

A. Radiation Induced Degradation

A wide range of high polymers, or plastics, have been discovered and modified to meet man's increasing demand for a variety of materials. Many of these materials, and in particular poly(vinyl chloride), have extensive applications out-of-doors where they are

subjected to potentially damaging ultraviolet radiation from the sun. The situation is made worse by the presence of oxygen which generally assists degradation. Degradation leads to the deterioration of the material's physical properties and possibly to its ultimate destruction.

1. Experimental Methods

As already stated this problem of polymer degradation has been extensively studied. Two broad techniques can be applied.

The first technique, natural weathering, involves measuring the effect of the sun directly. Selected samples, usually films, are placed at various outdoor sites and any change in their properties followed over a period of time. The sites chosen can be varied throughout the world to give different amounts of sunshine and humidity. This technique is largely applied by the plastics industry as it gives direct analysis of material behaviour, under the conditions to which it will be subjected. However, the period of weathering required will certainly be many months and possibly years. Consequently, accelerated tests have been derived to simulate the sun's effect.

The second technique then involves accelerated degradation tests carried out using either ultraviolet light or high energy radiation. A large range of ultraviolet lamps are available and can be used to simulate the spectral distribution of the sun, though this simulation may sometimes be very approximate. However any ultraviolet source will produce radiation of the same approximate energy as the sun. Hence similar processes can occur within the irradiated polymer. The accelerated degradation is brought about by the increased intensity of the artificial source. High energy radiation sources are more hazardous to use and bear less resemblance

to natural conditions. However this technique is useful for accelerated tests and in many cases produces similar results.

The commonest sources of ultraviolet light are mercury vapour lamps. The low pressure lamp gives a monochromatic source of 253.7 nm radiation. Medium pressure lamps provide radiation at a number of wavelengths in the 230-450 nm region. Individual lines can be isolated by filters. High pressure lamps provide high intensity radiation throughout the same region. These and other ultraviolet radiation sources such as xenon lamps, hydrogen lamps etc. have been described in detail¹. The intensity of the incident radiation can be monitored using either uranyl oxalate actinometry^{1,2}, or the more rapid ferrioxalate method³. Thermopiles are also widely used, but require calibration.

High energy radiation can be obtained from a cobalt-60 gamma ray source, or by the use of high energy electrons supplied, for example, by a Van der Graff generator.

Once a radiation source is chosen two experimental approaches can be followed. One approach is to devise a series of experiments aimed at solving one specific problem caused by degradation. The other approach is more general and involves conducting a range of experiments to determine what exactly has occurred during degradation. This hopefully leads to the elucidation of a degradation mechanism, and hence a better understanding of the processes involved and their possible control. This thesis is concerned with the second approach. Various parameters can be varied within an experimental framework; for example temperature, atmosphere, radiation intensity, and most important the sample used.

There are three considerations concerning the sample used - the actual polymer, the form in which it is used, and the possibility of

the presence of additives. Many of the properties of the polymer used will depend on its method of preparation. The polymerisation temperature will affect the molecular weight, and additives used during polymerisation may also be present as impurities. Bulk polymerised samples should be the purest with residual initiator the only, but sometimes important, impurity.

The polymer can be irradiated in three forms; as a film, as a powder, or in solution. Solution work, which is largely confined to thermal degradation, is useful because it affords the possibility of concentration variation. Work using polymer films is particularly interesting because of its relevance to actual outdoor applications. Complications from surface effects and diffusion of small volatile molecules are introduced.

A wide variety of additives can be studied. These additives may be introduced during polymerisation and may be separate molecules (e.g. initiator) or functional groups within the polymer chain (e.g. end groups, unsaturation). Such impurities are often unavoidable and their concentration may be unknown. Quantitative studies can be made by adding known amounts of certain compounds in order to ascertain their effect. Examples are photosensitisors, radical scavengers, plasticizers and peroxides.

The atmosphere in which the degradation is carried out can also be varied. Oxygen has a large affect on the photodegradation of many polymers. This can easily be studied in air, oxygen, or oxygen-nitrogen mixtures. It is often desirable to conduct the experiment in the absence of oxygen and two techniques can be used. The degradation can be carried out, either in an inert atmosphere (e.g. nitrogen), or under vacuum.

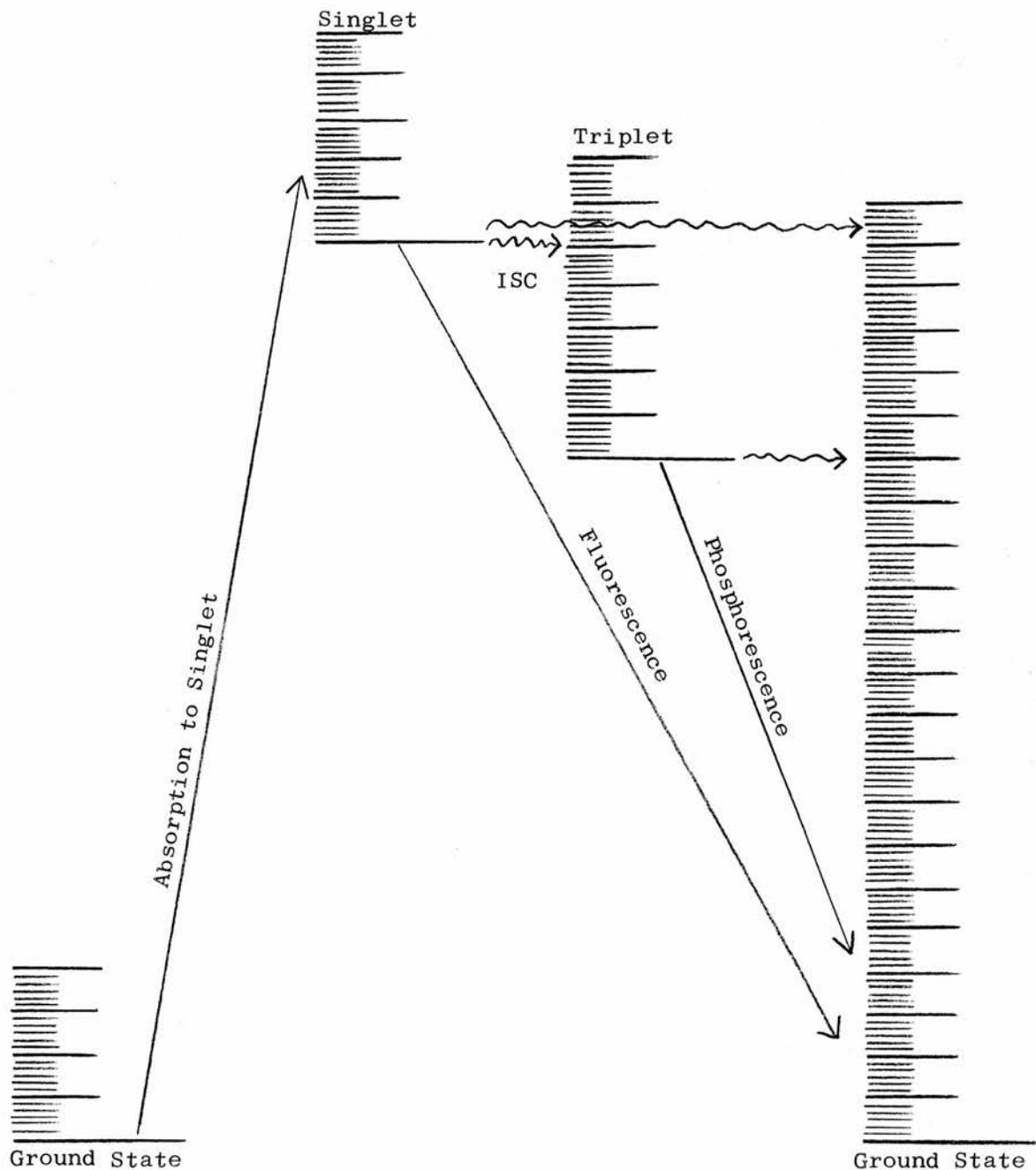
2. Irradiation Processes

Similar reactions have been observed during degradation using ultraviolet and high energy radiation. Absorbed energy leads to radical formation via bond homolysis. These radicals can then undergo a number of reactions leading to cross-linking, main chain scission, unsaturation, and the formation of small molecular fragments. The fundamental difference between these two sources is the energy of the radiation. The high energy of a gamma ray, for example, can give rise to many reactive intermediates and hence many products, leading to complications in analysing the overall reaction. The limited energy of the ultraviolet radiation gives greater selectivity and thus easier analysis. Complications can arise however due to attenuation of the ultraviolet radiation by the absorbing substance. The processes brought about by ultraviolet radiation are now discussed in more detail.

Following the absorption of a photon, two types of reaction are possible - primary and secondary. Primary reactions involve the immediate effect of the light on the absorbing molecule. Most organic molecules lie in a singlet ground state and absorption of a photon raises the molecule to an excited singlet state. Several possibilities now exist. The molecule may revert to the ground state by emission of a photon (fluorescence), or by radiationless transitions and the generation of heat. Intersystem crossing (ISC) can lead to a lower energy triplet state. Again reversion to the ground state can occur by photon emission (phosphorescence), or heat. These processes are shown in Figure 1. Bond dissociation can occur in the singlet or triplet state if the molecules possesses sufficient energy.

Figure 1

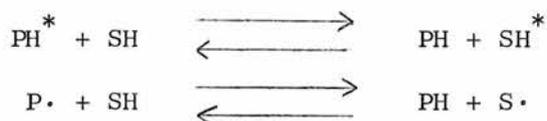
Excited States and Photophysical Transitions between these States



Solid lines = radiative transitions
Wavy lines = radiationless processes

Secondary reactions concern the molecules, atoms, and in particular radicals, produced by the primary process. There are three possibilities. Energy transfer can occur leading to possible bond rupture at a different site to the original absorption. Atoms or radicals can react by a number of pathways to give stable products. Excited molecules may react directly with other molecules to give products.

Photolytic reactions can also be classified as direct or indirect. Direct reactions result from photon absorption followed by bond homolysis and product formation. In indirect reactions impurities or additives, present as separate molecules or other functional groups in the polymer chain, become involved. These indirect reactions may lead to the same products as the direct reactions and may involve energy transfer or free radical processes:-



As shown the reactions can occur in either direction. The most obvious and important indirect reaction involves atmospheric oxygen. Examples of other important impurities are peroxides, residual solvent in polymer films, sensitizers, and unsaturation in the polymer chain.

For most polymers, the main degradation pathway involves radical formation and its subsequent reactions. It is therefore important to further discuss these reactions. The following are the possibilities - chain scission, cross-linking, side chain reactions, rearrangement, reaction with impurities, and elimination reactions leading to unsaturation. Chain scission and cross-linking cause the larger fundamental changes in the physical properties of degraded

polymers. Chain scission can either lead to large fragments or depolymerisation, an important reaction for many polymers (e.g. polymethacrylates, polystyrene).

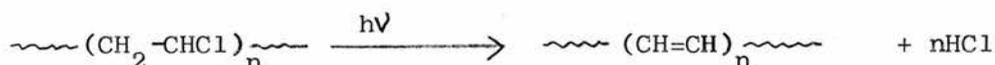
The elimination of a small molecule leading to unsaturation is the main degradation pathway for poly(vinyl halogens). For example poly(vinyl bromide) eliminates hydrogen bromide and poly(vinyl chloride) hydrogen chloride. It is this reaction occurring during the photodegradation of poly(vinyl chloride) that is studied in this thesis.

Impurities will play an important role in the degradation of any polymer and, as stated, oxygen is an example. Oxygen can apparently act as a chain scission inhibitor (poly(methyl methacrylate)), accelerator (polystyrene), or have no effect (poly(α -methyl styrene)). It will also bleach polyenes in for example degraded poly(vinyl chloride).

B. Poly(Vinyl Chloride) Degradation

1. General

The work to be described in this thesis deals exclusively with photodegradation. However it is relevant to also consider thermal degradation in a review of past work. There has been a larger amount of work carried out to investigate thermal degradation which is very similar to photodegradation, giving the same main products. Both forms of degradation give rise to unsaturation in the polymer chain accompanied by elimination of hydrogen chloride. The unsaturation takes the form of conjugated polyenes which appear coloured if $n > 7$:-



Under extreme conditions other products are possible, as will be described later. Impurities in the sample and the presence of oxygen can give rise to other minor products derived from the virgin polymer or the degraded material.

A study of thermal degradation will produce results and mechanisms which may be applicable to photodegradation. It is important however to be aware of the fundamental difference between it and photodegradation. Thermal degradation involves a homogeneous system in which heat can reach all possible reaction sites. In photodegradation a photon must be absorbed by a suitable chromophore. Reaction can then occur at that site or nearby through energy transfer. Photodegradation depends on the number and location of such chromophores.

It is also useful to consider work using high energy radiation. As explained there is a large energy difference between this and ultraviolet radiation; but, as with thermal degradation, the results and mechanisms are similar.

2. Apparatus

The understanding of any chemical reaction depends on the monitoring of the reaction products. For poly(vinyl chloride) there are two main products which can be followed. The only direct quantitative measurement that can be made is the amount of hydrogen chloride evolved. The usual method for monitoring hydrogen chloride is to sweep the evolved hydrogen chloride using a carrier gas (e.g. nitrogen, air etc.) into distilled water. The changing concentration of the resulting solution can be followed using pH or conductivity measurements, or by titrating the hydrogen chloride against weak alkali,

usually sodium hydroxide (manually or automatically). When degradation is carried out under vacuum the evolved hydrogen chloride is trapped and the volume present measured directly or by pressure. More recently developments in mass spectroscopy have allowed its use for monitoring evolved hydrogen chloride. This technique has the advantage that it will detect any other volatile product.

The polyenes, and many other minor products, can be monitored spectroscopically. The most useful tool available for polyene measurement is ultraviolet and visible spectroscopy. In this way the reaction can be followed and the concentration and distribution of the polyenes calculated. Infra-red spectroscopy is useful for identifying minor products, for example carbonyl groups from oxygenated products. Infra-red and nuclear magnetic resonance spectroscopy are also useful for structural determinations. Electron spin resonance spectroscopy has been widely used to prove the presence of radicals, and in some cases identify them.

3. Mechanism

It is convenient to consider the three stages of the degradation reaction - initiation, propagation and termination.

(a) Initiation

Since Marvel and co-workers⁴ pioneering work in 1939 it has been known that poly(vinyl chloride) has a linear 1,3-dihalide structure. Kenyon⁵, and Reinisch and Gloria⁶ observed that saturated alkyl chlorides show no ultraviolet absorption above 220 nm. Work on model compounds has shown that saturated alkyl chlorides are also very stable thermally. Chytrý, Obereigner and Lím⁷ studied the thermal degradation of a number of possible models for poly(vinyl chloride), and found activation energies for 2-chlorobutane,

2,4-dichloropentane and 2,4,6-trichloroheptane of 49.3, 48.9 and 50.8 Kcal mol⁻¹ respectively. Asahina and Onozuka⁸ found values for 2-chloropropane and 2,4-dichloropentane of 42.4 and 69.9 Kcal mol⁻¹ respectively. Chytrý attributed the considerable difference between these results to the different experimental conditions. Asahina and Onozuka also found threshold temperatures (the temperature at which degradation commences) of 340°C and 360°C for 2-chloropropane and 2,4-dichloropentane, to be compared with a value of around 150°C for poly(vinyl chloride). Activation energies for the thermal degradation of poly(vinyl chloride) have been obtained by many workers. Values obtained under a nitrogen atmosphere lie in the range 23-36 Kcal mol⁻¹ 9-20,68. This value is lowered when oxygen is present^{18,19}. It should be noted that samples and conditions varied considerably.

Thus poly(vinyl chloride) will photodegrade when saturated alkyl chlorides show no absorption in the ultraviolet above 220 nm, and thermally degrade at a considerably reduced activation energy. It has been universally recognised that impurities must be present in any poly(vinyl chloride) sample for degradation to occur, under these conditions.

Braun²¹ suggested the following possible irregularities as initiation sites for thermal degradation:-

1. Branch points with tertiary chlorine.
 2. Chain ends with initiator fragments, or unsaturated end groups.
 3. Random unsaturation with allylic chlorine.
 4. Oxidation structures.
 5. Head-to-head units.
1. Many other researchers, investigating thermal degradation,

have suggested tertiary chlorine atoms as a possible initiation site^{17,22-24,68}. Cotman²⁵ pioneered a hydrogenation technique for determining the number of branches present in a poly(vinyl chloride) sample, and calculated there were twenty branches per molecule. This technique was used by Boccato, Rigo, Talamini and Zilio-Grandi²⁶ who found that, over a range of polymerisation temperatures from 25-50°C, there was approximately one branch per sixty carbon atoms (equivalent to 20-30 branches per molecule, depending on molecular weight). Braun²¹ suggested that tertiary carbon atoms were relatively unimportant initiation sites. Baum and Wartman²² chlorinated poly(vinyl chloride) to remove unsaturation. The chlorinated sample was degraded and it was concluded that tertiary chlorine atoms could cause initiation. Bengough and Onozuka²³ attempted to differentiate between allylic and tertiary chlorine by exchange by metal carboxylates. They concluded that allylic chlorine was more reactive than tertiary. Drusedow and Gibbs²⁴ suggested that tertiary chlorines may be split out during polymerisation as hydrogen chloride to give allylic chlorines for further initiation.

2. Many authors, again studying thermal degradation, have suggested that initiation occurs at the poly(vinyl chloride) chain ends^{14,15,17,22,23,27,68}, and an inverse proportionality between molecular weight and rate of degradation has been found^{27,68}. Bengough²⁸ stated that allylic end groups will be formed during polymerisation by transfer to monomer. Carrega, Bonnebat and Zednik²⁹ showed by exhaustive hydrogenation that there existed one allylic end group per polymer molecule. Initiator fragment end groups may also be present as initiators for degradation^{14,15,17,22,68}. Baum and Wartman²² concluded that, although as already mentioned

tertiary chlorine initiation was possible, most of the hydrogen chloride was derived from end group initiation, despite there being about forty times more branches than allylic end groups. Braun²¹ observed that work with model compounds has shown that random allylic chlorine (i.e. within the chain) was more reactive than an allylic end group. Asahina and Onozuka⁸, and Chytrý, Obereigner and Lím⁷ found that 4-chloro-2-hexene was more reactive than 3-chloro-1-pentene. Braun²¹ also observed that, if initiation occurred at the chain ends, then so also should the polyenes. However oxidative degradation resulted in a large molecular weight change, suggesting polyenes in the middle of the chain.

3. Braun²¹ has found a relationship between random unsaturation and thermal stability. A plot of the number of double bonds (found by oxidative cleavage followed by molecular weight determination) versus the rate of dehydrochlorination was shown. Reinisch and Gloria⁶ also suggested that random unsaturation from polymerisation and thermal treatment acted as the initiator for photodegradation.

4 and 5. Other possible initiation sites exist and Braun²¹ mentioned oxidation structures and head-to-head units. He stated that to date there had been no experimental proof of the existence of head-to-head units, and that the elimination of hydrogen chloride from such a unit would result in an unreactive double bond with no allylic chlorine. The possibility of catalyst residues (from polymerisation), especially peroxides, acting as initiators has also been suggested^{6,14,24,27}. Geddes²⁷ showed that dicumyl peroxide, benzoyl peroxide, cumene hydroperoxide, and hydroperoxide structures could all cause acceleration of dehydrochlorination. Arlman¹⁴ found that the rate of dehydrochlorination was doubled when 1%

benzoyl peroxide was present.

Except for Reinisch and Gloria the above researchers were considering thermal degradation. However all the above possibilities with the exception of tertiary chlorine atoms can act as chromophores, and hence sites of initiation. Some other suggestions have been made by researchers working on photodegradation. Golub and Parker³⁰ observed that even in very pure poly(vinyl chloride) there existed enough unsaturation for initiation. They also observed that, when working with cast films, residual solvent would surface to initiate decomposition (in their case methyl ethyl ketone). Kamal, El-Kaissy and Aredessian³¹ studied the effect of residual solvent and found a connection between degradation and the amount of solvent remaining (tetrahydrofuran and dichloroethane). Kenyon⁵ suggested that ketonic impurities could act as initiators. He studied the degradation of sec-butyl chloride in the presence of acetone as initiator and found the rate of degradation was proportional to the concentration of acetone. Owen and Bailey³² used benzophenone as a photosensitiser to initiate degradation.

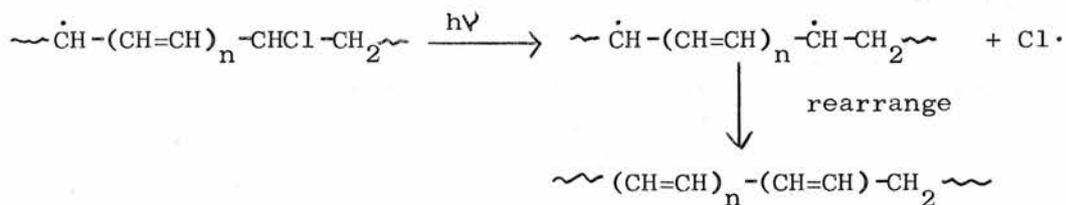
(b) Propagation

Three propagation mechanisms have been proposed for the dehydrochlorination of poly(vinyl chloride) - ionic, radicals, and unimolecular elimination. The following suggestions were made by researchers considering thermal degradation. Marks, Benton and Thomas¹² suggested an ionic mechanism to explain the action of stabilisers. Braun²¹ also discussed the possibility of an ionic mechanism. Arlman¹⁴, and Kelen, Bálint, Galambos and Tüdős¹³ favoured a unimolecular elimination of hydrogen chloride. Geddes²⁷ proposed this as an initiation mechanism. Many other researchers

Lawton and Balwitt³⁶ have found evidence for radicals I, II, III and IV by electron paramagnetic resonance spectroscopy in γ -irradiated poly(vinyl chloride). Ohnishi, Nakajima and Nitta³⁷, and Bovey³⁸ have similarly found radical II. Reinisch, Gloria and Androes³⁹ also found allyl and polyenyl radicals in photodegraded poly(vinyl chloride).

Liebman, Reuwer, Gollatz and Nauman¹⁷ found radicals were present during thermal degradation. This was confirmed by Bamford and Fenton⁴⁰ who discovered that when poly(vinyl chloride) was thermally degraded in tritium labelled toluene, tritium was incorporated into the polymer chain by abstraction.

Miller³⁵, who studied the γ -irradiation of poly(vinyl chloride), suggested the main primary radical process was the rupture of a C-Cl bond to give radical III above. He also pointed out that work on aliphatic chlorides has shown that the chlorine radical was more likely to abstract hydrogen from a methylene group than a CHCl group (6 above) Reinisch, Gloria and Androes³⁹ however stated that abstraction is a fast, non-selective process. The radical produced will depend on relative abundance rather than the kinetics of abstraction. They also suggested that a bi-radical could be formed:-



This polyene now had no allylic chlorine but could be attacked by further chlorine radicals. Geddes²⁷ also discussed transfer and suggested that transfer reactions were open to chlorine radicals and mobile macroradicals (possibly from low molecular weight poly(vinyl chloride)).

Palma and Carezza¹⁸ subjected poly(vinyl chloride) to heat and γ -irradiation simultaneously, and concluded from their results that the same radical mechanism applied in each case.

(c) Termination

Winkler³³ suggested the following possible termination steps:-

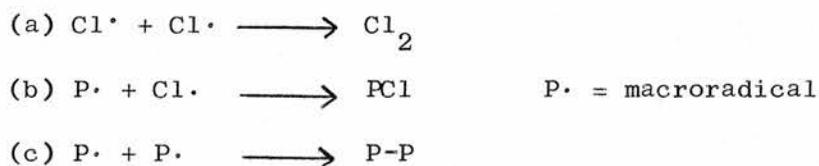
- (1) Chlorine radical abstracts a tertiary hydrogen.
- (2) Chlorine radical abstracts hydrogen from another molecule.
- (3) The poly(vinyl chloride) radical reacts with oxygen.
- (4) The poly(vinyl chloride) radical or the chlorine radical react with another radical.

The four possibilities shown all stop one chain but (1), (2) and (3) can start another. Geddes²⁷ suggested that transfer ((2) above) would control polyene length. He also observed that the chlorine radical might abstract a tertiary hydrogen ((1) above) leading to an unreactive radical $\sim\text{CH}_2-\overset{\cdot}{\text{C}}\text{Cl}-\text{CH}_2\sim$. Bengough and Varma⁹ suggested polyenes were kept short by chain irregularities; either head-to-head units or tertiary chlorines caused by pendant $-\text{CH}_2\text{Cl}$ groups. Braun²¹ however stated that structural irregularities were not sufficient to account for the limit in polyene length. He suggested that when the polyene was sufficiently long the energy absorbed was delocalised by resonance and hence allylic activation ceased. This would explain why poly(vinyl bromide) gave longer polyenes. The C-Br bond is weaker than the C-Cl bond and therefore needs less energy to break it. Arlman¹⁴ also suggested increasing delocalisation caused termination. Lawton and Balwitt³⁶, as already described, studied γ -irradiated poly(vinyl chloride) by electron paramagnetic resonance spectroscopy. They showed that the polyenyl

radical was very stable and only decayed by 10% in 1800 hours at room temperature.

Reinisch, Gloria and Androes³⁹ suggested a similar mechanism for the photodegradation of poly(vinyl chloride). When the polyene reaches a certain length, the light absorbed will not be of sufficient energy to break the next allylic C-Cl bond. Kelen, Bálint, Galombos and Tüdös¹³ suggested that polyene length was limited by the length of 'a priori' given sequences. These were sequences in the polymer chain along which allylic activation could propagate unhindered. Alternatively, the series of allyl activated degradation steps ended by a special reaction step which interrupted the propagation of activation.

The combination of two radicals ((4) above) has been suggested by many authors as a termination step. Stromberg, Strauss and Achhammer²⁰ stated the three possibilities:-



Reaction (c) leads to the formation of a cross-link. This cross-linking reaction is very important in many polymers, including poly(vinyl chloride), and has been the subject of many investigations^{15,24,27,31,33,34,40-45}. The extent of cross-linking has been measured in three ways. Sobue, Tabata and Tajima⁴² irradiated poly(vinyl chloride) films at 253.7 nm and determined the gel fraction (insoluble portion) by soaking the degraded material in cyclohexanone for one week at 30 or 50°C. Kamal, El-Kaissy and Aredession³¹ irradiated films at 280-300 nm and determined the gel fraction by refluxing the degraded material in tetrahydrofuran for

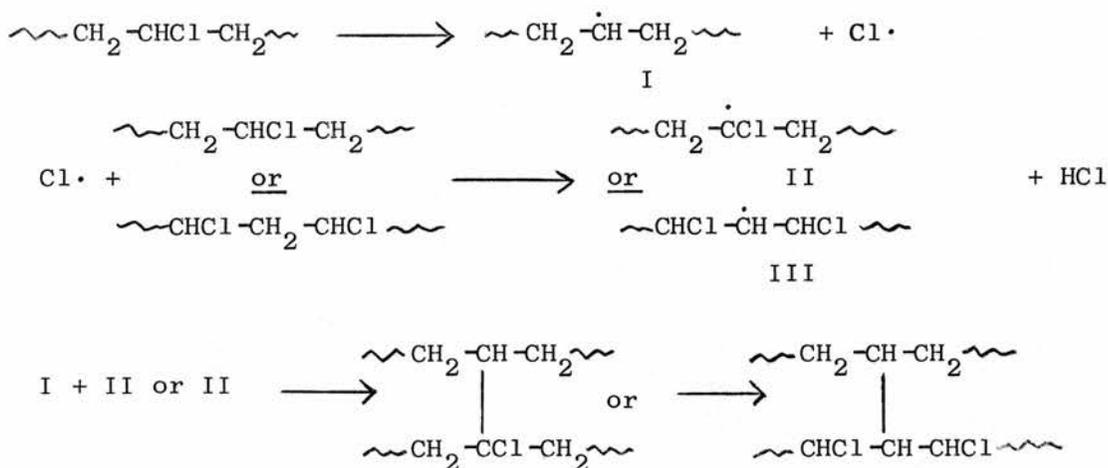
eight hours. Bengough and Sharpe⁴⁵ thermally degraded poly(vinyl chloride) solutions and determined the gelation point. This was assumed to have been reached when a 90° tilt gave no movement of the solution. Drusedow and Gibbs²⁴, and Wippler and Gautron⁴³ measured the change in intrinsic viscosity and hence molecular weight. This technique will also reveal chain scission by a lowering of molecular weight. Taylor⁴⁴ found that initially cross-linking and scission could occur in thermal degradation, but eventually cross-linking would predominate. Drusedow and Gibbs²⁴ found a similar result for thermal degradation in air (i.e. oxygen present). Baum and Wartman³⁴ observed cross-linking when poly(vinyl chloride) was thermally degraded in nitrogen, and chain scission and cross-linking in oxygen. Talamini and Pezzin¹⁵ observed that the molecular weight of a sample thermally degraded in nitrogen increased. When degradation took place in oxygen, however, it was initially decreased followed by an increase.

Drusedow and Gibbs²⁴ suggested four possible cross-linking mechanisms:-

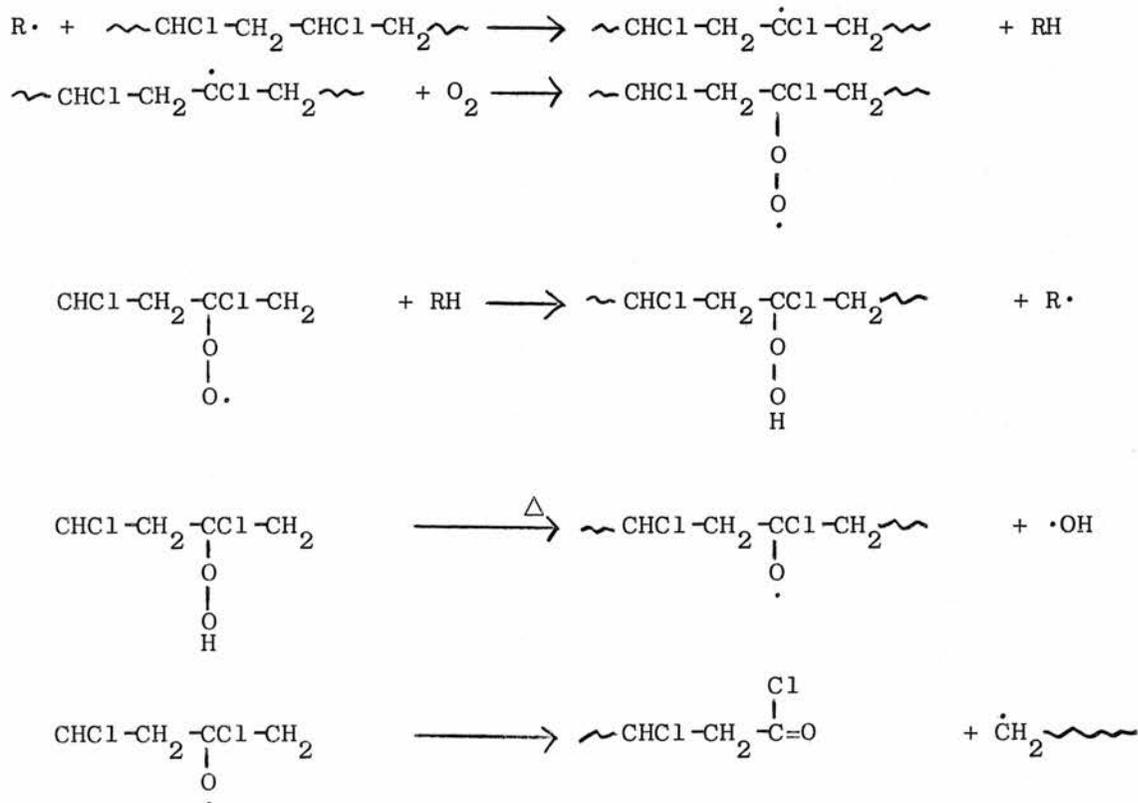
- (1) Co-polymerisation between polyenes.
- (2) Chain transfer between polyene and segment of normal polymer chain.
- (3) Diels Alder type reaction.
- (4) Cross dehydrochlorination between highly active chlorine atoms on one chain and hydrogen atoms on another.

They state that (1) and (3) are highly unlikely, (2) is possible but (4) is most likely. Winkler³³ favoured (4) above, and also suggested the direct combination of two polymer radicals; or that a polymer radical could add to the conjugated unsaturation of

another chain in a similar manner to the addition to butadiene in synthetic rubber preparation. Lawton and Balwitt³⁶ put forward the following mechanism for radical combination:-



Chain scission appears to occur only when oxygen is present and Winkler suggested the following mechanism involving oxygen:-



4. Other Results

The final section of this review is concerned with results not discussed in the preceding three sections. The subjects to be considered are:-

- (a) The role of hydrogen chloride as a catalyst.
- (b) The nature and distribution of the polyenes produced by dehydrochlorination.
- (c) The role of oxygen.
- (d) The possibility of other products.
- (e) The significance of wavelength in photodegradation.
- (f) The possibility of a surface reaction in the photodegradation of films.

(a) Hydrogen Chloride Catalysis

There appears to be more disagreement in this facet of poly(vinyl chloride) degradation than any other. Many authors^{10,12,18,27,34,46,47} investigating the thermal degradation of poly(vinyl chloride) have shown that hydrogen chloride is a catalyst, others that it is not^{14,15,24,48}. Several techniques have been employed to show hydrogen chloride is a catalyst. Braun and Bender¹⁰ degraded in solution and found that the rate of dehydrochlorination was faster when nitrogen was passed over the solution than when it was passed through it. In the latter case the hydrogen chloride is quickly removed from the solution. They also found that addition of hydrogen chloride to the carrier gas caused acceleration. Luther and Krueger⁴⁶ degraded in vacuo and found that the rate of dehydrochlorination was proportional to the concentration of hydrogen chloride.

breakdown. If however a molecular elimination mechanism were occurring then reversible addition of hydrogen chloride in a different orientation might cause catalysis.

(b) Polyenes

As already stated the degradation of poly(vinyl chloride) can be followed by observing the ultraviolet and visible spectrum of the polyenes produced. Many researchers⁴⁹⁻⁵⁵ have prepared and recorded the spectra of various polyenes, $-(CH=CH)_n-$, and recorded λ_{\max} and ϵ (the molar extinction coefficient) values for $n = 2-11$. These values have been used to indicate the polyenes present in degraded poly(vinyl chloride) by identifying the maxima present in the spectra. The spectra obtained vary considerably as to the amount of fine structure present. Golub and Parker³⁰, Kelen, Bálint, Galambos and Tüdös¹³, and Marks, Benton and Thomas¹² observed no well defined peaks. Marks, Benton and Thomas¹² suggested that this was because four polyenes of the same length are possible, given by the formula $RR'C=CH-(CH=CH)_{n-2}-CH=CR''R'''$. The shift from the parent polyene for one, two and three of the Rs = H would be 5, 10 and 15 nm respectively.

Some fine structures have been observed by several authors^{9,21,27,56}. Matsumoto, Mune and Watatani⁵⁶ found maxima at 240, 275, 288, 309, 322, 339, 365, 387, 410 and 432 nm. They attributed these maxima to polyenes up to $n = 9$. Bengough and Varma⁹ found maxima at 364, 388, 414, 436, 458 and 480 nm. Jaffe Orchin⁵⁷ pointed out that the presence of a cis linkage in the polyene will cause a reduction in the intensity of the absorption and a slight downward shift (5-10 nm). A new cis peak will also be observed at a shorter wavelength. (e.g. 340 nm in 9-cis- β -carotene).

Geddes²⁷ has studied the discolouration reaction very extensively. Fine spectra of pressed films, thermally degraded at 150°C in a nitrogen atmosphere, were obtained by heating until only 50 ppm hydrogen chloride were lost. He obtained maxima at 286.5, 312, 326, 346.5, 369, 394, 420, 445.5, 466 and 486 nm, and observed that there was absorption above 500 nm suggesting polyenes with $n > 20$. A maximum absorption was obtained at around 500 nm giving an average polyene length > 10 . The actual average polyene length was determined from molecular weight changes brought about by ozonisation, and found to be about 14. This value was higher than others reported^{9,12,58} where higher degradation temperatures were employed. Geddes considered this was very reasonable as chain transfer, the polyene length determining reaction, would be favoured at higher temperatures. He also pointed out that the history of the polymer sample will affect the distribution of the polyenes. Thallmeier and Braun⁵⁹ found that for powder samples on increasing temperature or time of degradation there was a shift in the polyene sequence lengths towards shorter sequences. However for foils they found a definite shift towards longer sequences.

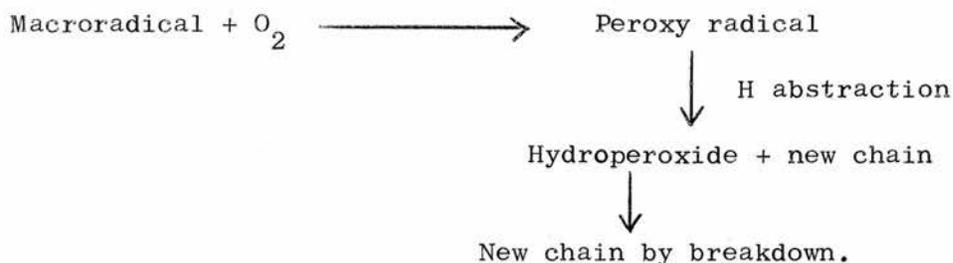
(c) Oxygen

A great deal of work has been done to study degradation in the presence of pure oxygen or air. It has already been seen that oxygen reduces the activation energy in thermal degradation^{18,19}, and promotes chain scission^{24,33,34}. It will be seen in section (d) that the presence of oxygen can lead to extra volatile products⁶². Two other important effects have been observed. Oxygen increases the rate of dehydrochlorination^{6,10,15,24,27,33,34}, and causes bleaching^{10,15,24,34,60} (i.e. attacks polyenes, breaking

up the conjugation and hence destroying the colouration it causes). Acceleration is generally attributed to the ability of oxygen to attack the polymer chain or the polyenes giving fresh reaction sites.

Aitchison⁶⁰ degraded poly(vinyl chloride) using high energy electrons and observed that oxygen caused bleaching, and that ozone was even more effective. Reinisch and Gloria⁶ observed acceleration due to oxygen in photodegradation. They degraded poly(vinyl chloride) films in an oxygen atmosphere using ultraviolet light at 435 nm ($65.7 \text{ Kcal mol}^{-1}$). As this is not enough energy to break the C-Cl bond they concluded that the oxygen must have entered into an exothermic reaction.

Baum³⁴ found that thermal degradation was much faster in air, and even more so in pure oxygen, than in nitrogen. He also found that, if a sample which had already been degraded in nitrogen, was then heated in oxygen rapid bleaching occurred accompanied by faster dehydrochlorination. He observed that photodegradation gave a similar result with carbonyls, hydrogen chloride and water as products. Talamini and Pezzin¹⁵ also observed acceleration and bleaching due to oxygen in thermal degradation. They found that if a varying amount of oxygen was added to the carrier gas, nitrogen, the rate of dehydrochlorination was proportional to the percentage of oxygen present. Geddes²⁷ found acceleration due to oxygen, but it was not a lasting effect. If a sample was degraded alternatively in nitrogen, oxygen, and nitrogen again there was acceleration when the oxygen was present but the reaction proceeded at the original rate when nitrogen was reintroduced. He proposed the following mechanisms to account for the acceleration caused by oxygen:



(d) Other Products

Under certain extreme conditions products other than polyenes, hydrogen chloride and simple oxygen derivatives (e.g. carbonyls) have been found. Reinisch, Gloria and Wilson⁶¹ monitored the volatile products of degradation induced by polychromatic ultraviolet radiation using a mass spectrometer, and found only hydrogen chloride. Kwei⁶² however obtained several other volatile products using 253.7 nm radiation in pure oxygen. Initially only carbon dioxide was produced followed by hydrogen, methane, carbon monoxide and eventually hydrogen chloride.

Stromberg, Strauss and Achhammer²⁰ studied the thermal degradation of poly(vinyl chloride) over a wide range of temperatures. They found that up to 280-350°C, depending on the sample, hydrogen chloride is almost the only product. Above 350°C there are many other products, either aliphatic or aromatic hydrocarbons. Benzene was the most abundant product in this group, formed it was assumed by a cyclisation of one end of a conjugated chain. Blyumenfel'd, Pudov and Neiman⁶³ also found benzene in the thermal degradation of poly(vinyl chloride) and suggested a similar cyclisation mechanism.

(e) Wavelength

It has been seen in the section on initiation that degradation

will occur if chromophores are present which can absorb light of sufficient energy to break the C-Cl bond, the dissociation energy of which lies in the region 78-82 Kcal mol⁻¹ ^{64,65}. This is reduced to about 60 Kcal mol⁻¹ for an allylic C-Cl bond⁶⁴. Reinisch, Gloria and Androes³⁹ suggested a resonance energy of 12 Kcal mol⁻¹ giving a higher value of about 70 Kcal mol⁻¹ for the allylic C-Cl bond. Golub and Parker³⁰ quoted a value of 76 Kcal mol⁻¹ for the C-Cl bond which is equivalent to radiation of wavelength 376 nm. In agreement with Kenyon⁵, they observed that no degradation occurs at wavelengths greater than 340 nm. Evidently more energy is needed for the degradation of poly(vinyl chloride) than is sufficient to simply break the C-Cl bond.

Kenyon⁵ first studied the effect of different wavelengths on the photodegradation of poly(vinyl chloride) powder. He found the following rates of hydrogen chloride evolution in the stated wavelength regions:-

λ (nm)	340 → visible	300 → visible	280 → visible	235 → visible
Hydrogen Chloride	0	10	16	110
(m eq.g ⁻¹ hr ⁻¹)				

Kenyon concluded that the rate of dehydrochlorination was wavelength dependent. Reinisch, Gloria and Wilson⁶¹ obtained a similar result with a cut-off at 332 ± 9 nm and a maximum ΔO.D./photon at 253.7 nm (Optical density, O.D., is a measure of the polyenes produced and here of dehydrochlorination). However they found a decrease in ΔO.D./photon at shorter wavelengths, e.g. 238 nm. They attributed this to the distribution of the dienes, trienes and tetraenes absorbing the light. Golub and Parker³⁰ showed that quantum yield was independent of wavelength. They suggested that Kenyon had

failed to consider that poly(vinyl chloride) absorbs more light at shorter wavelengths.

Petit and Zaitoun⁶⁶ irradiated thin films in the presence of oxygen and found 302.3 nm radiation particularly damaging. Reinisch, Gloria and Wilson⁶¹ compared monochromatic and polychromatic rates of dehydrochlorination. They found that polychromatic radiation is ten times as efficient as monochromatic, and suggested a synergistic effect.

(f) Surface Reaction

Golub and Parker³⁰ found that when a poly(vinyl chloride) film was irradiated with ultraviolet light the rate of dehydrochlorination decreased with time. This was in contrast to γ -irradiation which gave the same initial rate of dehydrochlorination but continued at a faster rate. They suggested that the relatively lower energy ultraviolet radiation was harmlessly dissipated through intramolecular energy transfer to the polyene system. This effect would not be seen initially as the number of double bonds would be insufficient to make any important contribution to the "internal protective" mechanism. Reinisch, Gloria and Wilson⁶¹ found a similar falling off in the rate of dehydrochlorination and attributed it to the effect of the polyenes on the surface acting as an energy sink. They found that film thickness had no effect on the rate of degradation and concluded that the reaction was confined to a surface layer. Sobue, Tabata and Tajima⁴² irradiated poly(vinyl chloride) using 253.7 nm radiation and found that the gel content (insoluble portion) was proportional to the time of irradiation. A plot of film thickness versus %gel content, after a given time, showed a curve which suggested the true gel

content was constant for a given dose at any thickness. This indicated that a surface reaction was occurring. Hintzenstern⁶⁷ studied the natural weathering of industrial poly(vinyl chloride) and found that a surface layer was formed independent of film thickness.

Price and Fox⁶⁹ studied the effect of ultraviolet radiation on the surface of various organic coatings, including poly(vinyl chloride). They showed that changes occur at the surface by measuring the changes in the wettability of the surface by various solvents. This was done by measuring the contact angle.

C. Purpose of the Investigation

Many different samples have been degraded under a wide variety of conditions and this has led to varied, and sometimes conflicting, results. This thesis is concerned with the photodegradation of poly(vinyl chloride) films. Samples were kept as pure as possible and an inert atmosphere (nitrogen) was used. It was hoped that, by studying the simplest possible system, a basic understanding of the processes and mechanisms involved might be obtained. It should then be possible to apply the results to more complicated systems, in particular where commercial samples containing various additives are studied.

Chapter 2

Experimental

1. Polymer

Powdered poly(vinyl chloride) samples were supplied by B.P. Chemicals International Limited. All the samples were bulk polymerised and contained no impurity other than residual initiator. Further purification was considered unnecessary.

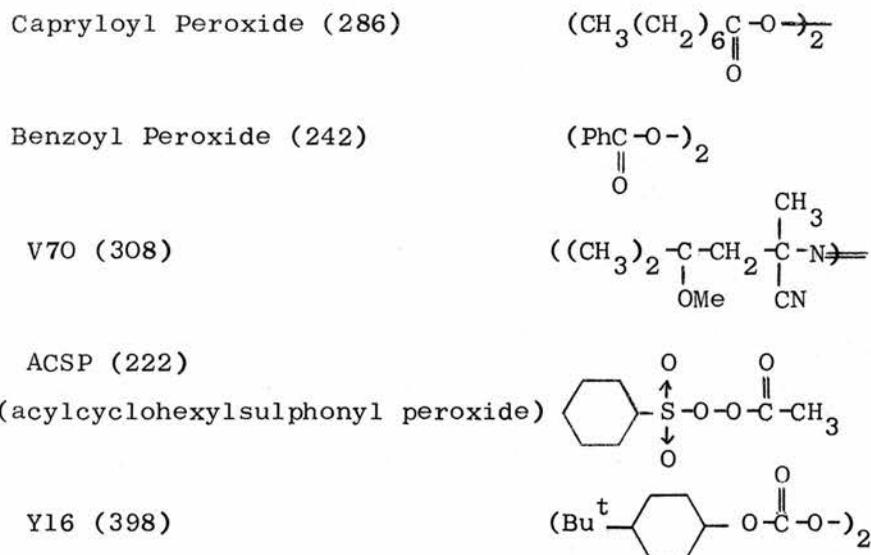
The main sample used throughout this work was JLB 956. This material, and two other samples JLB 958 and JLB 960 used to study molecular weight variation, were pure and contained a minimal amount of residual peroxide. These three samples JLB 956, 958 and 960 had number average molecular weights (M_n) of 39,200, 48,800 and 56,100 respectively.

A further set of samples were supplied prepared using different initiators, in varying concentrations, and with a range of M_n values. A complete list of these samples, their polymerisation details and M_n values are shown in Table 1. These details and the rate coefficients for decomposition (k_d), from which the percentages of residual initiator were calculated, were supplied by B.P.

Table 1

Sample JLB-	Initiator	Concen. (wt %)	Reaction Time (hr)	Polym Temp (°C)	Conversion (%)	Residual Initiator (wt %)	Initiator (mol %)	Mn $\times 10^3$
1026	Capryloyl Peroxide	0.5	5	54	57	0.45	0.10	42.0-45.0
1027	Capryloyl Peroxide	2.0	2.5	54	77	1.90	0.42	
1028	16	0.1	4.33	54	69	0.042	0.0067	
1029	16	0.4	1.25	54	56	0.31	0.049	
1030	Benzoyl Peroxide	1.0	4	54	26	0.95	0.24	
1031	Benzoyl Peroxide	4.0	5.75	54	68	3.69	0.95	
1035	ACSP	0.03	2	54	62	0.0001	v. small	
1036	ACSP	0.06	3.5	40	56	0.007	v. small	
1037	ACSP	0.09	5	30	39	0.021	0.006	
1038	Capryloyl Peroxide	0.5	2	65	56	0.41	0.09	
1039	70	0.2	4	40	19	0.11	0.002	42.4
1040	70	0.3	7.75	30	18	0.24	0.048	67.7
1041	16	0.1	4	65	29	0.0006	v. small	32.9

The initiator formulae and molecular weights are as follows:-



It should be noted that, because of its instability, ACSP is used as a 29% solution in dimethyl phthallate (DMP). The concentrations in Table 1 refer to ACSP only.

2. Film Preparation

Films were prepared by casting from an approximately 10% solution of poly(vinyl chloride) in tetrahydrofuran. The following technique was used in order to obtain the purest possible sample. The tetrahydrofuran was distilled over calcium hydride in a nitrogen atmosphere immediately prior to use. A weighed amount of poly(vinyl chloride) powder was slowly added to the tetrahydrofuran, which was swirled to aid dissolution. This solution was placed on a shaker until dissolution was complete (10-15 minutes). The solution was then poured into a plate-glass boat (approx. 12 cm square) which was floating in a dish containing mercury. The dish was housed in a dessicator containing silica gel and

flushed with oxygen-free nitrogen (see Figure 2).

A film formed after 5-7 hours. This film was peeled off the glass plate, stapled to a piece of cardboard (to prevent wrinkling and curling during further removal of tetrahydrofuran), and placed in a vacuum oven at room temperature. The film was allowed to dry for at least 30 days.

Further removal of tetrahydrofuran from poly(vinyl chloride) films has been achieved by placing them above refluxing methanol⁷⁰, or shaking them in methanol at room temperature³². For the work reported in this thesis these techniques were found to have no beneficial effect on the films, and in some cases caused cloudiness.

Loaded films, that is films containing a known amount of some chemical additive were also prepared. Benzoyl peroxide and acenaphthene were the principal additives used. The recrystallised material was dissolved in the freshly redistilled tetrahydrofuran to which the poly(vinyl chloride) was then added. When the film formed the additive was assumed to be homogeneously dispersed throughout.

Film purity was checked by ultraviolet spectroscopy. This technique detects the presence of any chromophores, particularly those absorbing in the range 230-340 nm, the range throughout which potentially damaging radiation can be absorbed. A typical spectrum of an undegraded poly(vinyl chloride) film (JLB 956) is shown in Figure 3. Comparison with the spectrum of redistilled tetrahydrofuran, shown in Figure 4, indicated that most of the absorption in the region 230-325 nm was probably due to residual tetrahydrofuran. Short polyenes which would absorb in this region (i.e. $n = 1, 2, 3$) may be present. Such structures can be formed during polymerisation.

Figure 2
Film Casting Apparatus

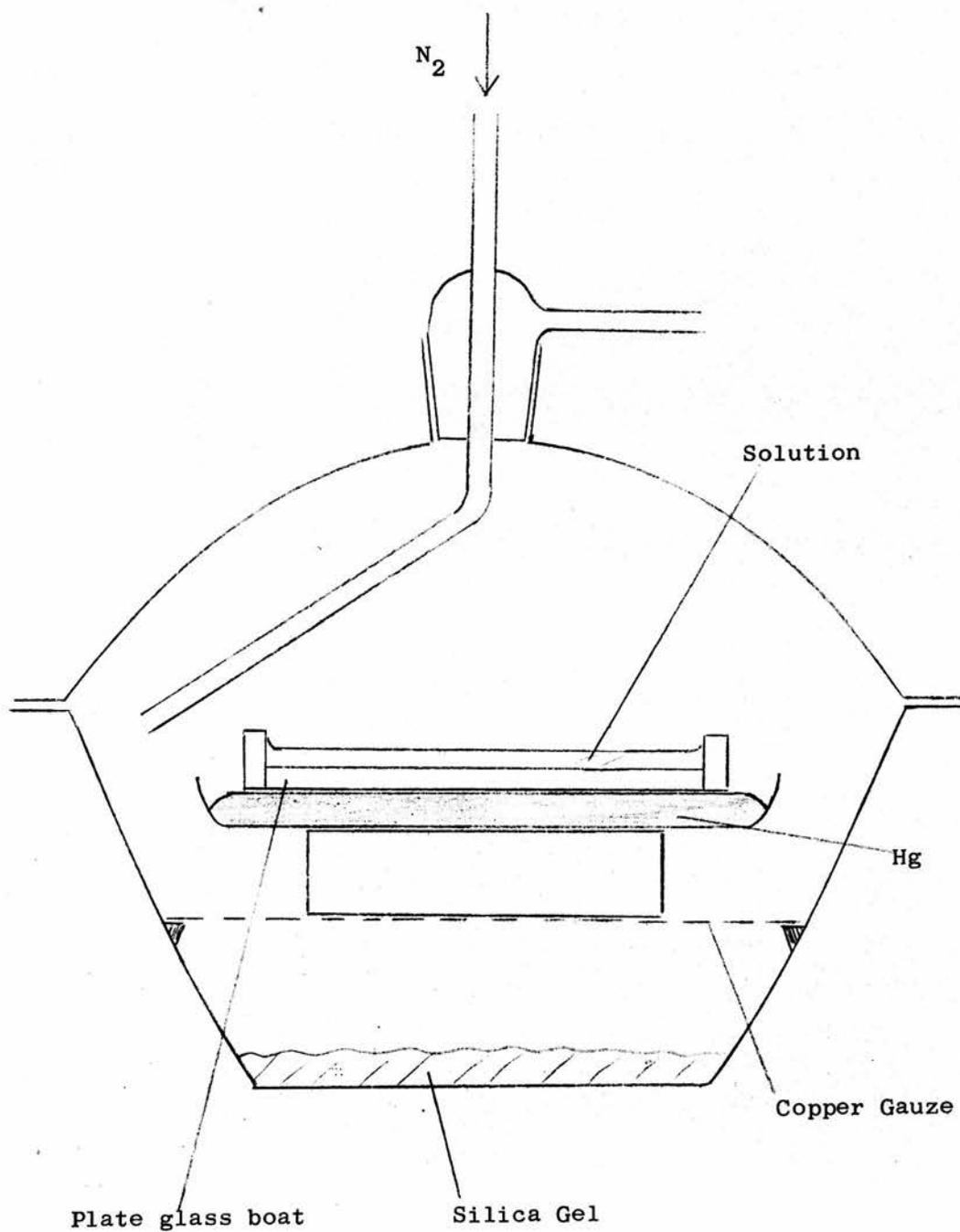


Figure 3

Ultraviolet spectrum of an undegraded film

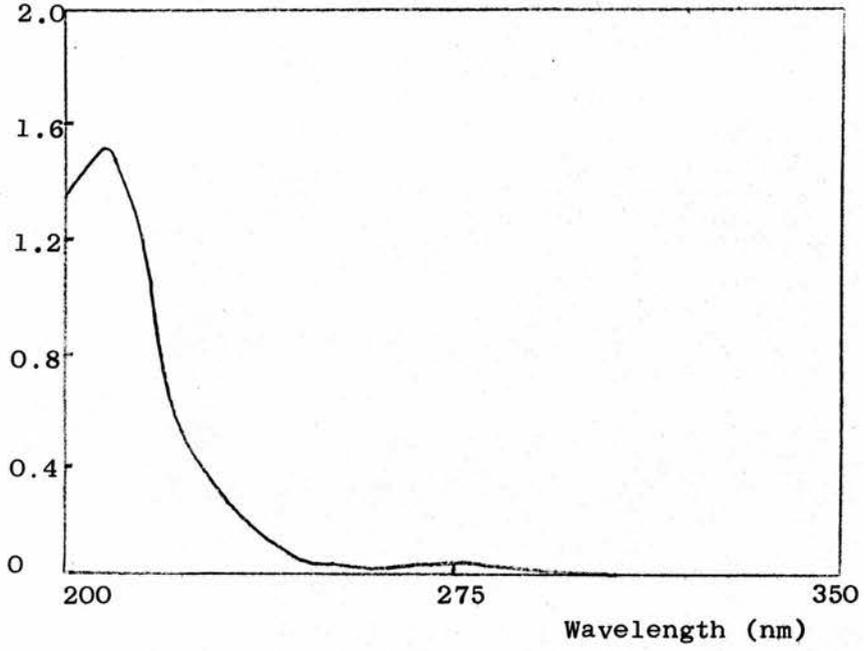
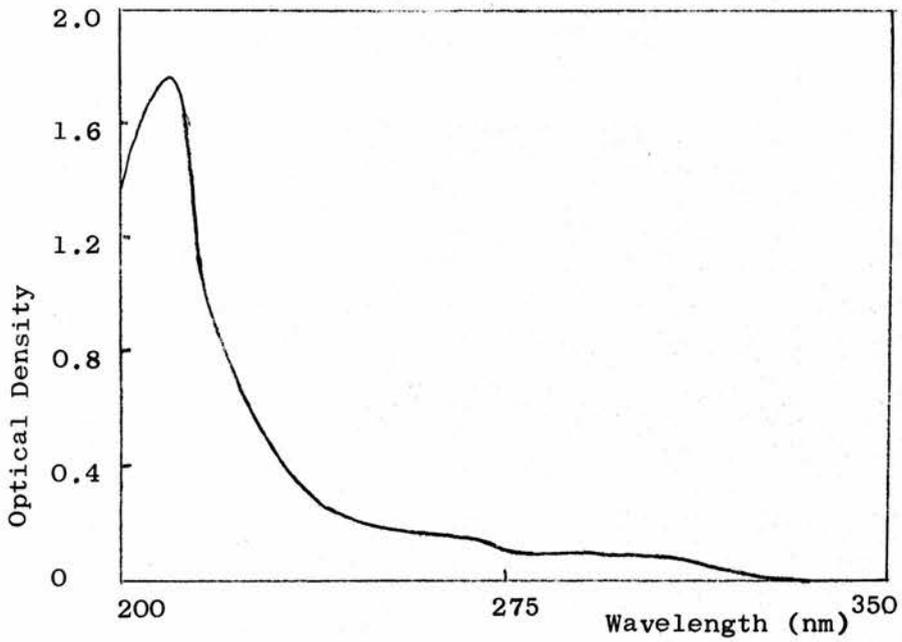


Figure 4

Ultraviolet spectrum of redistilled tetrahydrofuran



The exact amount of tetrahydrofuran remaining in a film which had been dried for over 30 days was not determined. It was estimated to be as much as 5% in some cases.

The film samples containing residual peroxide, and the loaded films were carefully studied and their spectra will be shown later under 'Results'.

Films were also examined by infra-red spectroscopy to check for the presence of carbonyl groups, possibly formed during preparation. In all cases there was some absorption in the region 1700-1800 cm^{-1} but usually it was very slight, with no distinguishable peaks. Residual tetrahydrofuran showed up as a broad, but weak, peak at 1900 cm^{-1} . As with the ultraviolet spectra, specific infra-red spectra will be reported later.

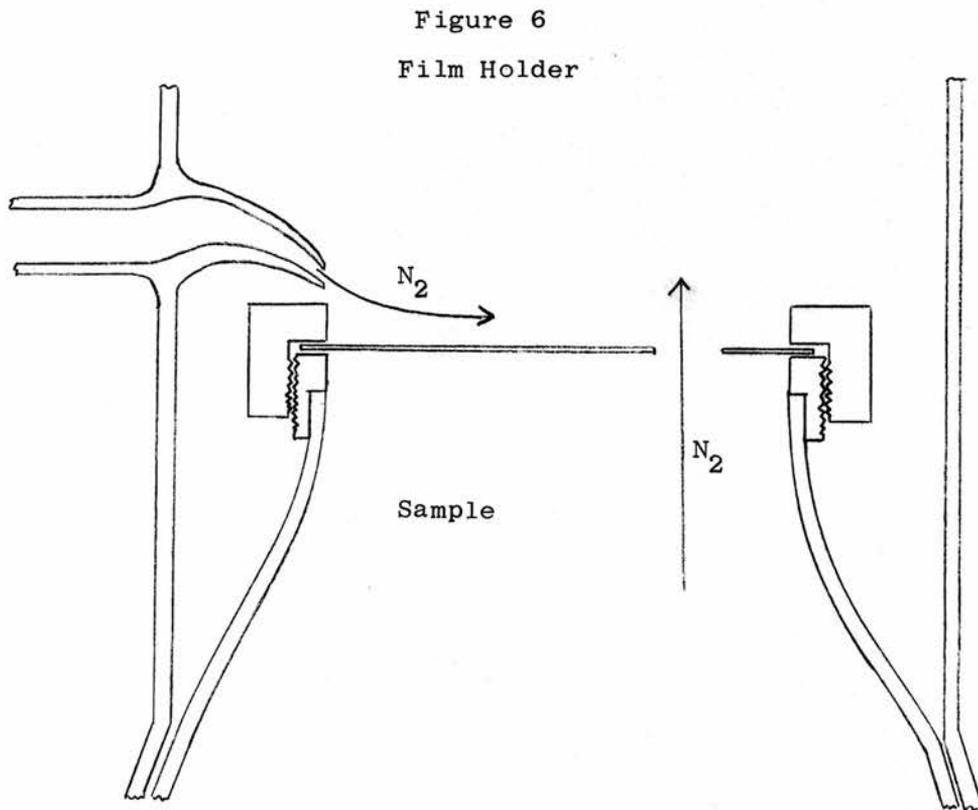
Normally film thickness was around 0.1 mm (100 μ). This thickness was achieved by calculating from the glass boat area and the density of poly(vinyl chloride), 1.40 g cm^{-2} , the weight of powder required for the film. Circular samples for degradation, diameter 3.9 cm, were cut from the film stock and the thickness of individual samples checked by weighing. It was found that for samples (maximum possible seven) from one cast film there was no more than 5% variation in thickness. Because of the presence of residual tetrahydrofuran, the actual thickness measured in this way was slightly inaccurate. This tetrahydrofuran reduced the film density, assumed to be 1.40 g cm^{-2} , from which the thickness was calculated. A typical sample weighs 180 mg of which up to about 10 mg may be tetrahydrofuran. The possible variations in thickness and the amount of residual tetrahydrofuran are in fact unimportant as both these factors are shown later to have no effect on the photodegradation.

3. Apparatus

(a) Photodegradation

(i) Apparatus

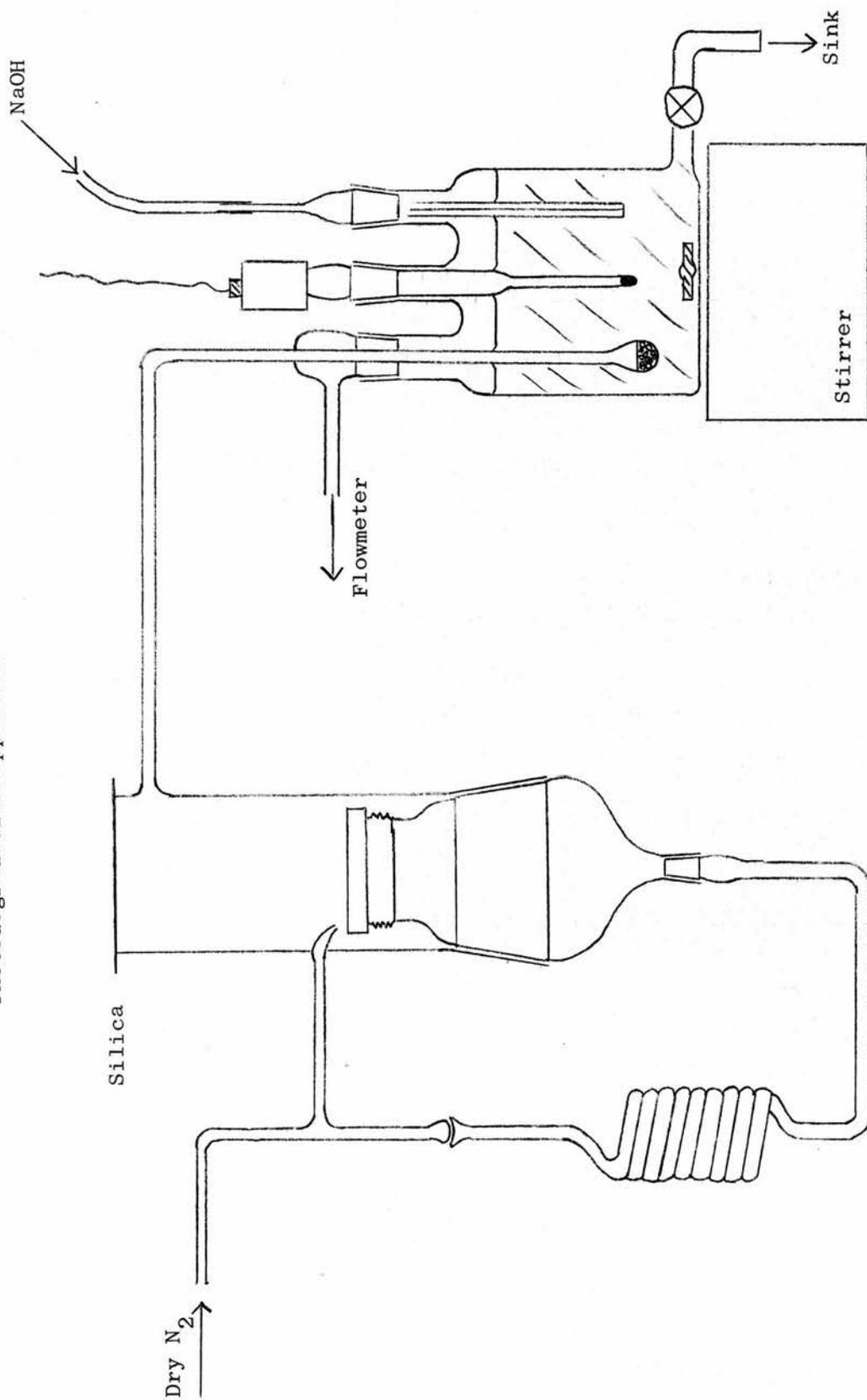
The photodegradation runs were carried out in the apparatus shown in Figure 5, and were normally of seven hours duration. A detail from Figure 5 appears in Figure 6 below, and shows more clearly how the film sample was mounted.



Before mounting, a small hole, diameter 0.6 cm, was punched in the sample to permit nitrogen flow from below. The irradiated film area was 9.34 cm^2 . Except for the actual sample holder, which was stainless steel, all glass apparatus was used. The stainless steel holder and the silica window were bonded to the glass using 'Araldite' adhesive.

Each film sample has two slightly different surfaces - the

Figure 5
Photodegradation Apparatus



side which was against the glass plate during casting and the other side. When two samples, from the same cast film, were irradiated at opposite sides no difference in the dehydrochlorination curves was found. It is therefore irrelevant which side of the sample is irradiated.

(ii) Nitrogen

The nitrogen was first passed through magnesium perchlorate to ensure it was dry. No attempt was made to remove traces of oxygen which may be present. Marks, Benton and Thomas¹² estimated that 'white spot' grade nitrogen contains between 5 and 40 ppm oxygen. The nitrogen then flowed across the film surface through a glass nozzle, and from below through the hole punched in the film. Any hydrogen chloride evolved was rapidly swept into the titration cell through a sintered glass bubbler.

The nitrogen flow rate was controlled by a needle valve and monitored by a calibrated flowmeter. Experiments were conducted to determine a satisfactory rate. It was found that above 50 cc min⁻¹ and up to at least 130 cc min⁻¹ the flow rate had no effect on the dehydrochlorination curve obtained. If the flow rate dropped below 50 cc min⁻¹ a delay in recording the evolved hydrogen chloride was observed. The resultant curve was initially below the one obtained at a higher flow rate and only coincided with it when the reaction had slowed down after a few hours. A flow rate of 70-80 cc min⁻¹ was used throughout the experiments described in this thesis.

(iii) The 'Combi-Titrator'

The reaction was followed using a Metrohm Combi-Titrator 3D. This instrument consists of a pH-meter (type E512), an impulsomat(E473),

and a mechanical burette and recorder (E425). The instrument maintains the solution in the titration cell at a constant, preset, pH by adding sodium hydroxide to neutralise the dissolved hydrogen chloride. The amount of sodium hydroxide added was recorded and gave a direct measure of the hydrogen chloride evolved during the reaction, that is a dehydrochlorination curve. The sodium hydroxide was added via a capillary tube.

The pH was measured using a glass electrode with a calomel electrode as reference. It was decided to trap at a slightly alkaline pH to give the greatest possible hydrogen chloride solubility, and 7.5 was chosen. Marks and co-workers¹² found that hydrogen chloride trapping was quantitative under these conditions. This was checked by placing two titration cells and 'Combi-Titrators' in series. It was found that the amount of hydrogen chloride trapped in the second cell was negligible.

(iv) Carbon Dioxide Removal

Great care was taken to keep oxygen and carbon dioxide out of the system. Carbon dioxide upsets any measurements as it forms a buffer solution in the titration cell. The following precautions were taken:-

(1) The apparatus was kept constantly flushed with nitrogen. The only time it was open to air was when a new sample was placed in the apparatus. This was done the night before a run (approx. 16 hr) so that any oxygen or carbon dioxide introduced would be flushed out.

(2) The titration cell was filled (200 ml) with fresh water before each run. This water was obtained by passing distilled water

down a mixed bed ion-exchange column (BDH, Amberlite monobed resin - MB1). The CO₂-free water thus obtained gave a pH between 6.4 and 6.8, and was made up to 7.5 by adding sodium hydroxide. The system was allowed to settle before a run was started.

(3) The sodium hydroxide was obtained by dilution from an approximately M/20 stock using distilled water. It was passed down an anion-exchange column (BDH, Amerlite resin IRA-400 (Cl)) to remove carbon dioxide. The column was first activated by elution with molar sodium hydroxide. The sodium hydroxide solutions used ranged from about M/200 to M/400. The actual molarity of each solution was determined by titrating it against M/400 potassium hydrogen phthallate using phenolphthalein as indicator. The standardised, CO₂-free, sodium hydroxide was stored in a reservoir supplied with the 'Combi-Titrator'. It was protected from carbon dioxide in the atmosphere by a filter containing 'Carbosorb' soda lime.

(b) Spectra

The ultraviolet and visible spectrum of every degraded sample was recorded immediately after the run was finished. This gave a permanent record of the concentration and distribution of the polyenes produced during degradation. If the spectrum was not recorded immediately, it decayed, presumably through product reaction with oxygen present in the atmosphere. The infra-red spectrum was recorded in certain cases, particularly when compounds which were readily identifiable in the infra-red were present in the sample, e.g. peroxides. All spectra were recorded with air as reference.

A special holder was developed to study photodegradation by

following the ultraviolet and visible spectrum throughout the reaction. This apparatus is shown in Figure 7. The film sample was held, as shown, between the two halves of the apparatus by springs. The whole apparatus, mounted on a wooden stand, fitted into the sample beam of a Unicam SP800 spectrophotometer. Spectra could be taken after time intervals without exposing the sample to oxygen. The apparatus was clamped in position under the lamp, connected to the supply of carrier gas, usually nitrogen, and the four taps opened. After a desired time interval the taps were shut, the gas supply disconnected, and a spectrum recorded. This procedure could be repeated as often as required. The atmosphere could be varied, and irradiation conducted under static conditions by keeping the taps shut. This would permit a build up of evolved hydrogen chloride.

(c) Film Area and Thickness

A series of runs was conducted using samples of varying film area. This variation was achieved by cutting different sized holes in the middle of the film samples, using a range of cork-borers. Areas from the normal 9.34 cm^2 down to 4.31 cm^2 were used.

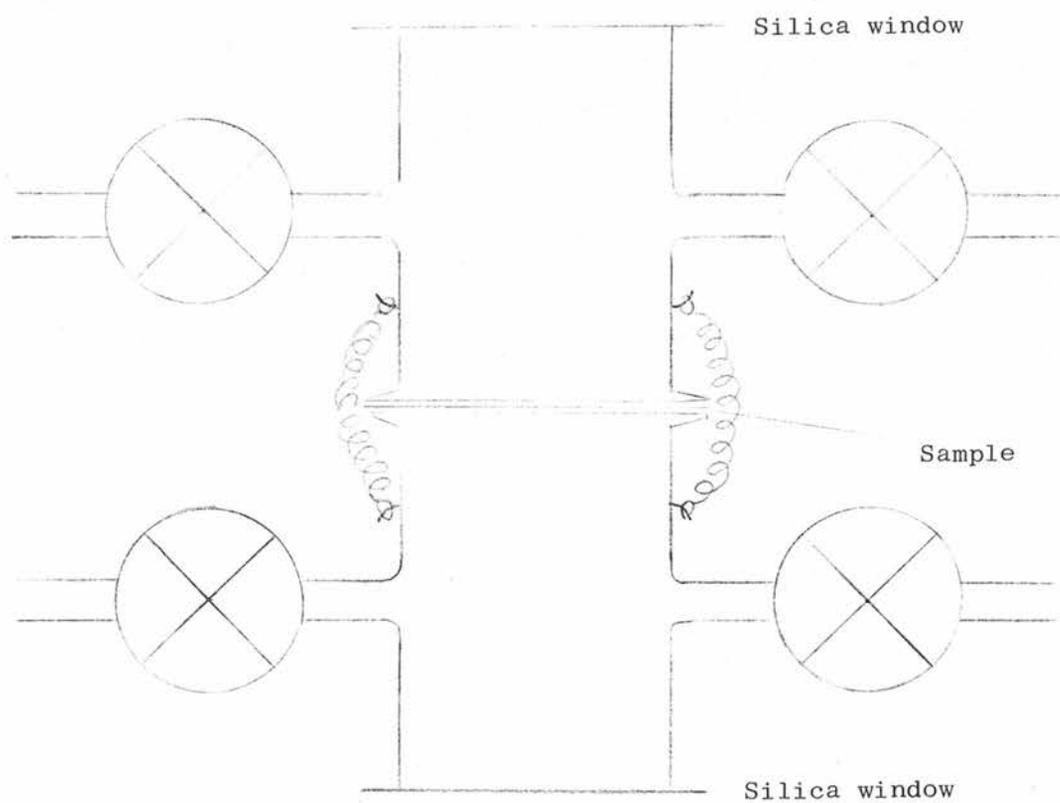
Another series was carried out to study the effect of film thickness. Films of thickness 0.05-0.25 mm were prepared by varying the amount of poly(vinyl chloride) powder used in the film casting.

(d) Temperature

All experiments were conducted at room temperature, 293K, except for two series of runs over a range from 273K to 333K.

Figure 7

Apparatus for studying ultraviolet spectra of degraded films



The temperature was varied by placing the photolysis cell in a water bath (Bath A) as shown in Figure 8. Bath A was connected to a second water bath (Bath B), a standard thermostatted water tank equipped with a pump. The water was pumped up to bath A and returned down an overflow pipe to bath B. A temperature difference of up to three degrees existed between the baths, depending on the water temperature. The temperature of bath A was continuously checked with a thermometer. Before a run was started the water was circulated until bath A reached a constant temperature. Another 15 minutes were allowed for the film sample to reach that temperature.

In order to avoid any cooling inside the apparatus, the nitrogen carrier gas was preheated. This was done by passing the nitrogen through a glass coil (Coil 1 in Figure 8) in bath B and then along lagged glass tubing to the photolysis cell. The nitrogen was cooled again by passing through a second coil (Coil 2 in Figure 8) at room temperature. For the run at 273K the baths were filled with an ice-water mixture.

(e) Thermal Treatment

Normally heating of the poly(vinyl chloride) samples was avoided. However, a set of experiments was conducted to determine the effect of heating samples above their T_g ($\sim 80^\circ\text{C}$), prior to photodegradation. Again the presence of oxygen was avoided by heating the samples under vacuum in the apparatus shown in Figure 9. The samples were placed between two circular stainless steel plates, which were then firmly bolted together. Samples were heated for one hour at a range of temperatures from 100 - 180°C and their weight losses recorded. The ultraviolet spectra of the heated samples

Figure 8
Thermostat System

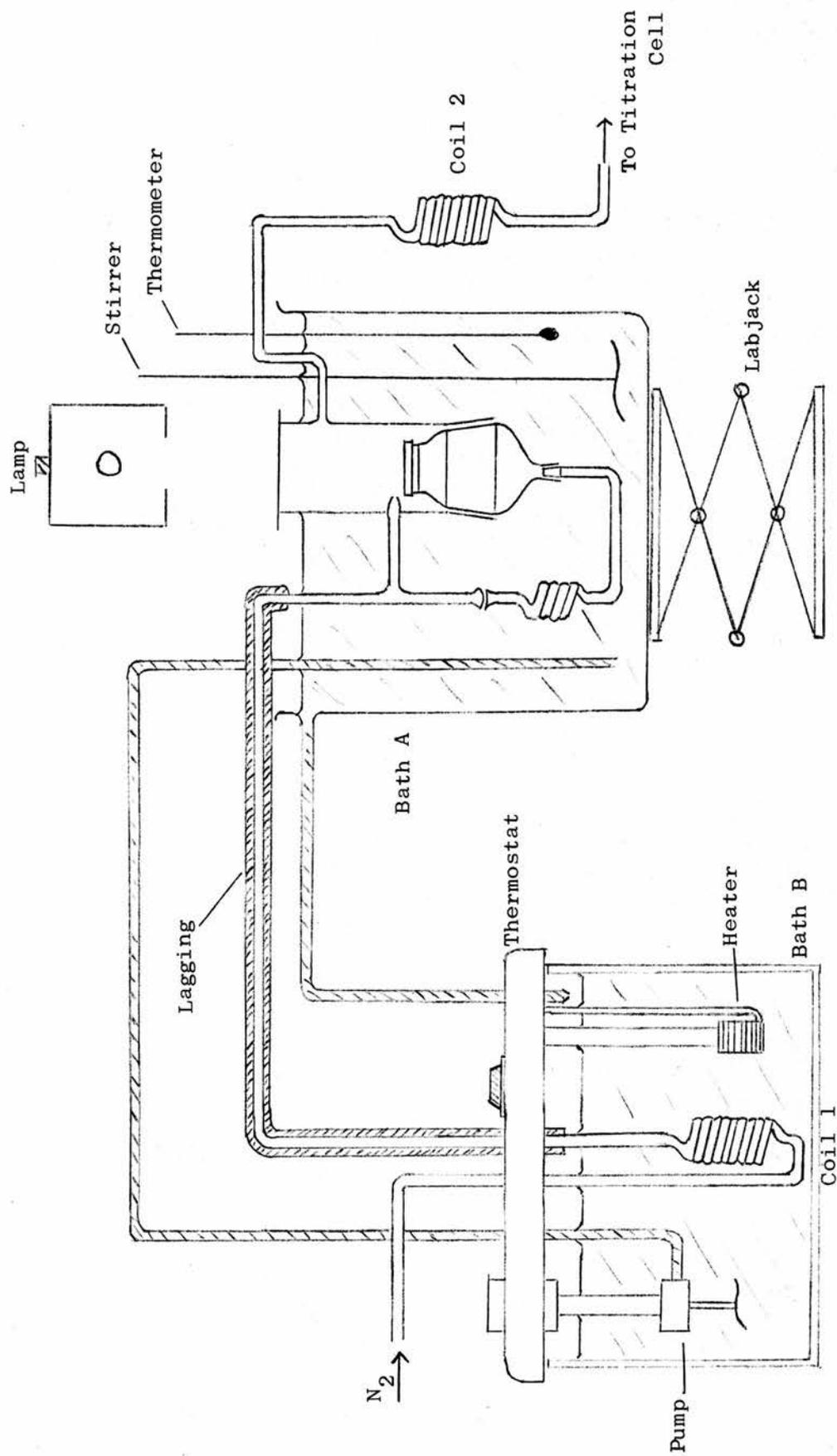
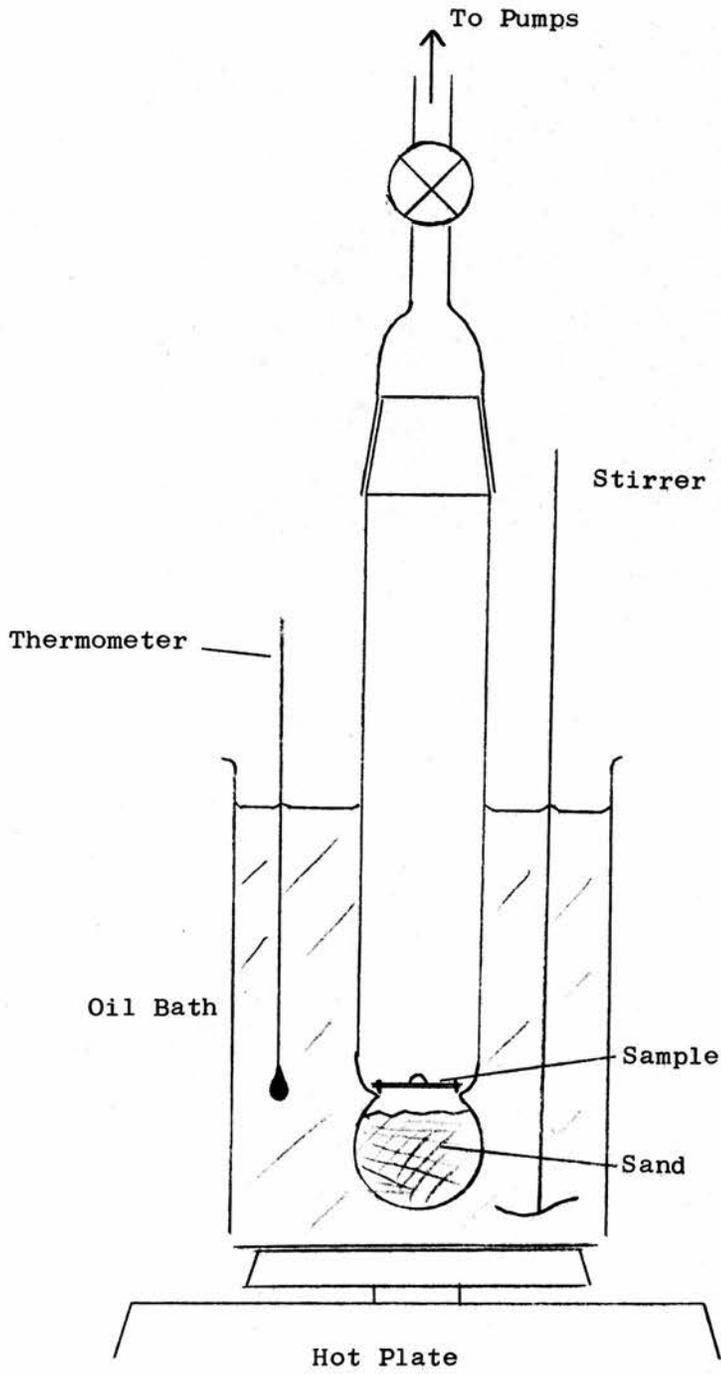


Figure 9

Thermal Treatment Apparatus



were also recorded in order to determine the extent, if any, of thermal degradation.

(f) Ultraviolet Sources

(i) Medium Pressure Lamp

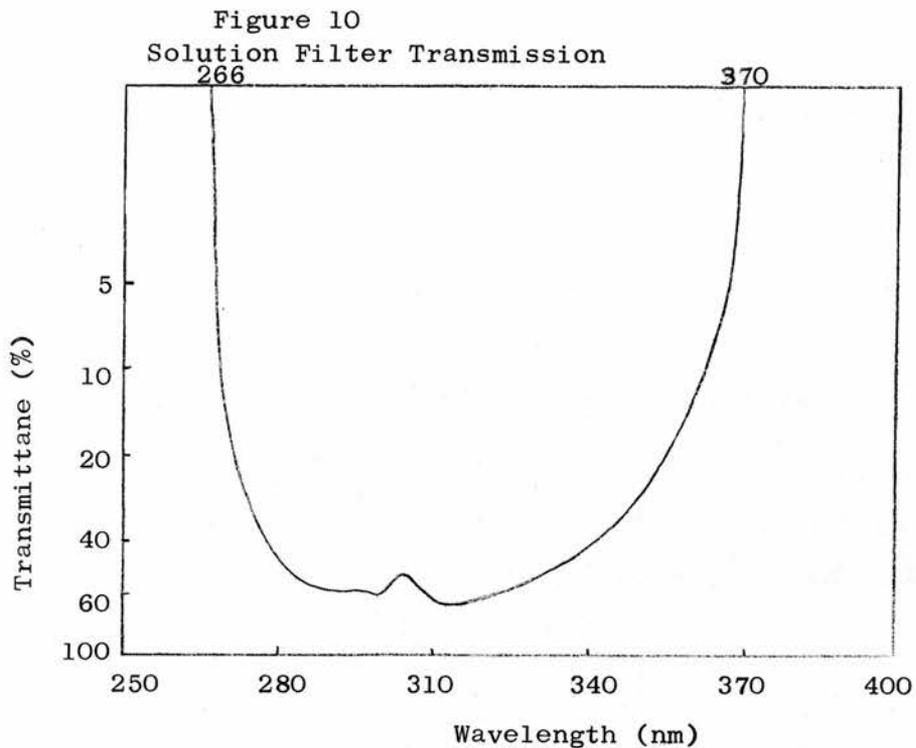
Most runs were conducted using a 500 watt medium pressure mercury lamp (obtained from Engelhard Hanovia Lamps). This lamp emits radiation over a wide range of wavelengths in the ultraviolet and visible, the relative intensities of which are shown in Table 2 (only wavelengths detectable by the actinometer are included i.e. < 450 nm). This data is taken from information supplied by the makers.

TABLE 2

Wavelength (nm)	Intensity (watts per 100 watts loading)
235	0.12
238	0.23
240	0.21
246	0.09
248	0.53
254	0.68
258	0.08
260	0.11
264	0.14
265	0.98
270	0.23
275	0.17
280	0.55
289	0.26
292	0.11
297	0.74
302	1.42
313	2.72
334	0.37
366	4.30
391	0.06
405	1.14
406	0.24
436	2.10

Each arc (type 509/10) has a working life of 1000 hours and the intensity of the emitted light is kept constant by using an intensity stabiliser supplied with the lamp. Actinometric studies showed that the light intensity varied only by about 3%. Normally the intensity was kept constant, but it could be varied by altering the arc-to-sample distance. This technique was used in a series of experiments conducted to determine the effect of intensity variation on the photodegradation reaction.

In order to transmit light in the region 260-370 nm only, a solution filter was used in conjunction with the medium pressure lamp. This filter corresponded to one of a set described by Wladimiroff⁷², and the solution was composed of $200 \text{ g l}^{-1} \text{ CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $100 \text{ g l}^{-1} \text{ NiCl}_2 \cdot 6\text{H}_2\text{O}$ in a mixture of 65% ethanol and 35% water, containing 1 mol l^{-1} hydrogen chloride. A silica cuvette was filled with this solution and irradiated for 10 hours at a range of 10 cm. After this activating treatment the filter gives a constant transmission for at least 100 hours. The range and percentage transmission of the filter are shown by the spectrum in Figure 10.



The cuvette was equipped with a long neck to allow for expansion from heating and cooled by compressed air to keep this to a minimum. It was clamped in position immediately above the silica window on top of the photolysis cell (see Figure 5).

Plate glass and pyrex glass were also used as filters to cut out all light below 325 nm and 295 nm respectively.

(ii) Low Pressure Lamp

Some experiments were carried out using a 125 w low pressure mercury lamp with the glass envelope removed (manufactured by General Electric Company Limited - model No. MVW/U). This lamp gave an approximately monochromatic source at 253.7 nm and the intensity could again be varied by altering the arc-to-sample distance.

(g) Actinometry

Source intensities were initially determined by uranyl oxalate actinometry. However the more convenient potassium ferrioxalate actinometer was mainly used, as described by Hatchard and Parker⁴. The solution used was sensitive up to 450 nm. All light intensities were measured. The medium pressure lamp was used to emit light at a range of intensities from $0.17 - 3.57 \times 10^{16}$ quanta $\text{cm}^{-2} \text{s}^{-1}$, and the low pressure lamp from $2.14 - 5.19 \times 10^{15}$ quanta $\text{cm}^{-2} \text{s}^{-1}$.

4. General

(a) Instruments

Ultraviolet and visible spectra were recorded on a Unicam SP 800B spectrophotometer. Optical density measurements, mainly for actinometry, were made using a Unicam SP500 Series 2 spectrophotometer.

Infra-red spectra were normally recorded on a Perkin-Elmer 257 grating spectrophotometer, but in a few cases a Perkin-Elmer model 621 was used.

(b) Equipment

The silica windows were polished Spectrosil 'B' quality discs, thickness 2 mm, obtained from Thermal Syndicate Limited. These discs showed 100% transmission throughout the ultraviolet and visible spectrum.

A photocell was used to monitor light intensity during one experiment to be described later. This photocell, taken from a Unicam SP500 spectrophotometer, was used in conjunction with a milliammeter.

(c) Chemicals

Analytical grade chemicals obtained from either Fisons Limited or British Drug Houses Limited were used. The benzoyl peroxide and acenaphthene used for preparing loaded films were recrystallised prior to use.

Oxygen, 'white spot' grade nitrogen, and hydrogen chloride were obtained from the British Oxygen Company Limited.

Chapter 3

Results

1 The Surface Reaction.

It has been suggested that the photodegradation of poly(vinyl chloride) films takes place in a surface layer^{42,61}. It was decided to fully investigate this possibility and the following set of experiments was designed. Unless otherwise stated, a light intensity of 3.57×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$ was used throughout these experiments.

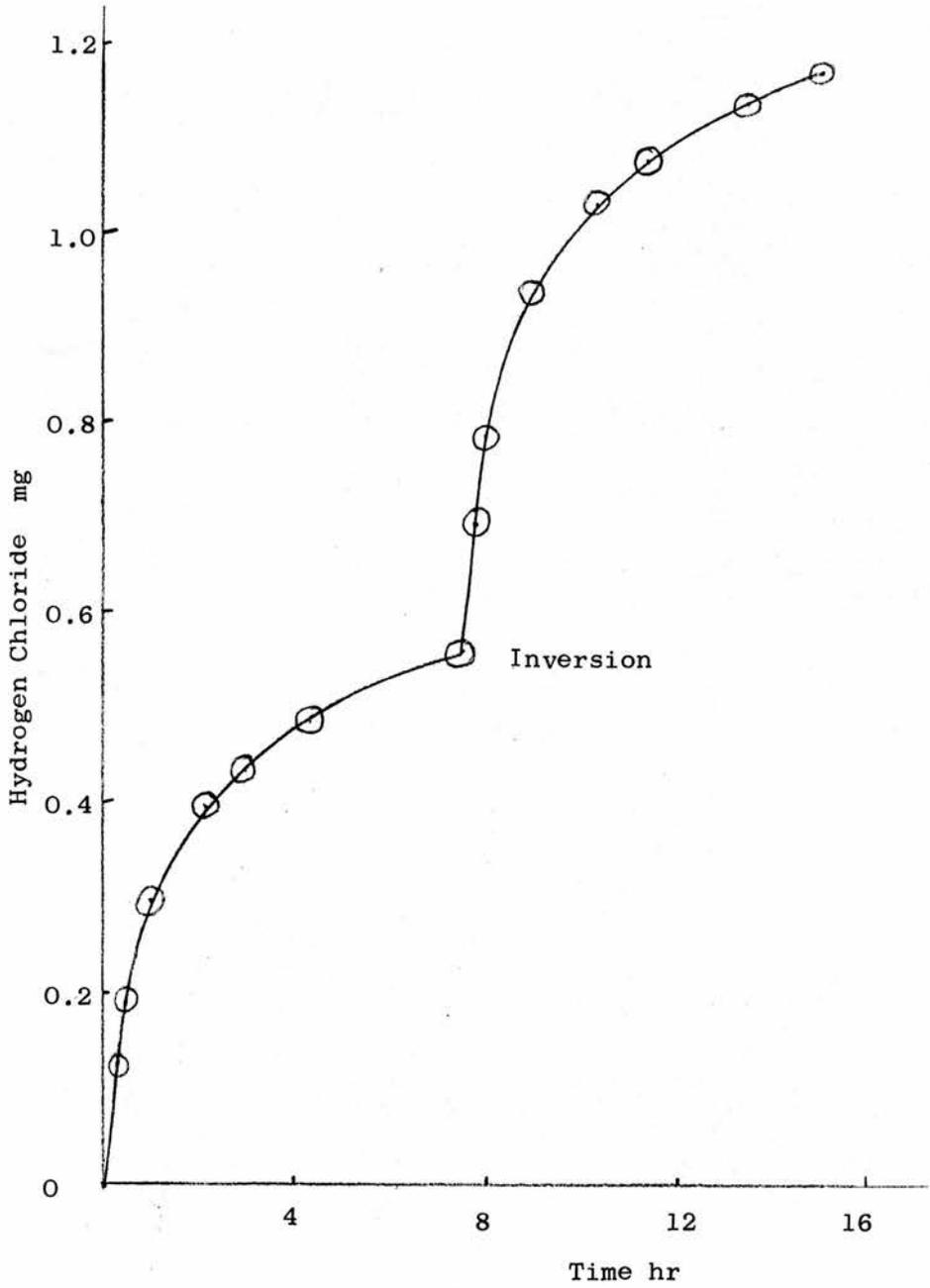
(a) The Dehydrochlorination Curve

It was found that, after an initiation period of a few minutes, hydrogen chloride gas was evolved at a rate increasing up to a maximum of about 1.0 mg hr^{-1} after 15 minutes. After this time the rate of dehydrochlorination steadily decreased until after 7.5 hours it was 0.015 mg hr^{-1} . If irradiation was extended up to 30 hours dehydrochlorination continued at a slow, decreasing rate. All curves obtained throughout this thesis were of this general form although the initiation times, rates of reaction, and inflection points will vary according to conditions, particularly light intensity. It should be noted that degradation can be recorded spectroscopically in under two minutes (see section f(i)). The initiation period was therefore not the time taken for degradation to begin, but the time required for the dehydrochlorination rate to build up to a measurable value, and for the evolved hydrogen chloride to be swept into the titration cell.

Samples were irradiated for 7.5 hr, inverted, and then irradiated for another 7.5 hr. The dehydrochlorination curve is shown in Figure 11. The first part of the curve, up to the point of irradiation, is that obtained for single-surface irradiation experiments. The second part is similar to the first, with a slight increase in the

Figure 11

The dehydrochlorination curve for a film degraded at both surfaces



amount of hydrogen chloride evolved.

(b) Film Thickness

Film samples with a range of thickness, d , from 0.29 to 0.05 mm were prepared. These samples were irradiated for 7.5 hr and each evolved approximately the same amount of hydrogen chloride, (with the exception of the sample with $d = 0.05$ which is anomalous). The weight losses after 7.5 hr, $\Delta W_{7.5}$, and thicknesses are shown in Table 3.

Table 3

$d(\text{mm})$	$\Delta W_{7.5}$ (mg)
0.052	0.603
0.108	0.547
0.177	0.542
0.242	0.538
0.289	0.540

A much thinner sample was prepared at a later date. This sample, $d = 0.013$ mm (13μ), was irradiated for seven hours using a light intensity of 0.88×10^{16} quanta $\text{cm}^{-2}\text{s}^{-1}$, and evolved 0.391 mg hydrogen chloride. This is very close to the ΔW_7 value of 0.389 mg obtained for a normal sample, $d = 0.109$ mm, at the same light intensity.

(c) Film Area

Samples with a range of areas were irradiated for 7.5 hours. The sample areas and $\Delta W_{7.5}$ values are shown in Table 4.

Table 4

Area (cm^2)	$\Delta W_{7.5}$ (mg)
9.34	0.618
7.61	0.519
6.16	0.415
4.31	0.304

A straight line graph was obtained when film area was plotted against $\Delta W_{7.5}$ and this is shown in Figure 12.

(d) Two Samples - Superimposition

Two film samples were placed one on top of the other, so that the lower one was completely covered, and irradiated for 7.5 hr. The upper sample was degraded and gave the normal dehydrochlorination curve, with no extra hydrogen chloride evolved. Analysis of the lower sample by ultraviolet spectroscopy showed that it was not degraded at all, thus indicating that the damaging radiation must all have been absorbed by the upper sample.

(e) Photography

Cross-sections of degraded films were photographed using the following technique. A piece of degraded film was embedded in an epoxy resin, a cross-section microtomed, and then photographed under an optical microscope (magnification 640X). In the first photograph (see Figure 13a) the thin smooth dark band shows the film-resin interface at the undegraded surface. The broader wavy band at the other interface shows the degraded material. In the second photograph (see Figure 13b) both surfaces have been degraded and appear as two broad wavy dark bands. In both cases it can be seen that the degraded material is confined to the surface layer. The same effect was observed when a very thin sample, $d = 13\mu$, was photographed. It was possible to estimate from this photograph that the surface layer was approximately $2-3\mu$, and certainly not more than 5μ , deep.

(f) Light Absorption

The experiments described in this section show how the amount of light absorbed by a degrading sample varied as the irradiation proceeded.

Figure 12

A plot of $\Delta W_{7.5}$ versus film area

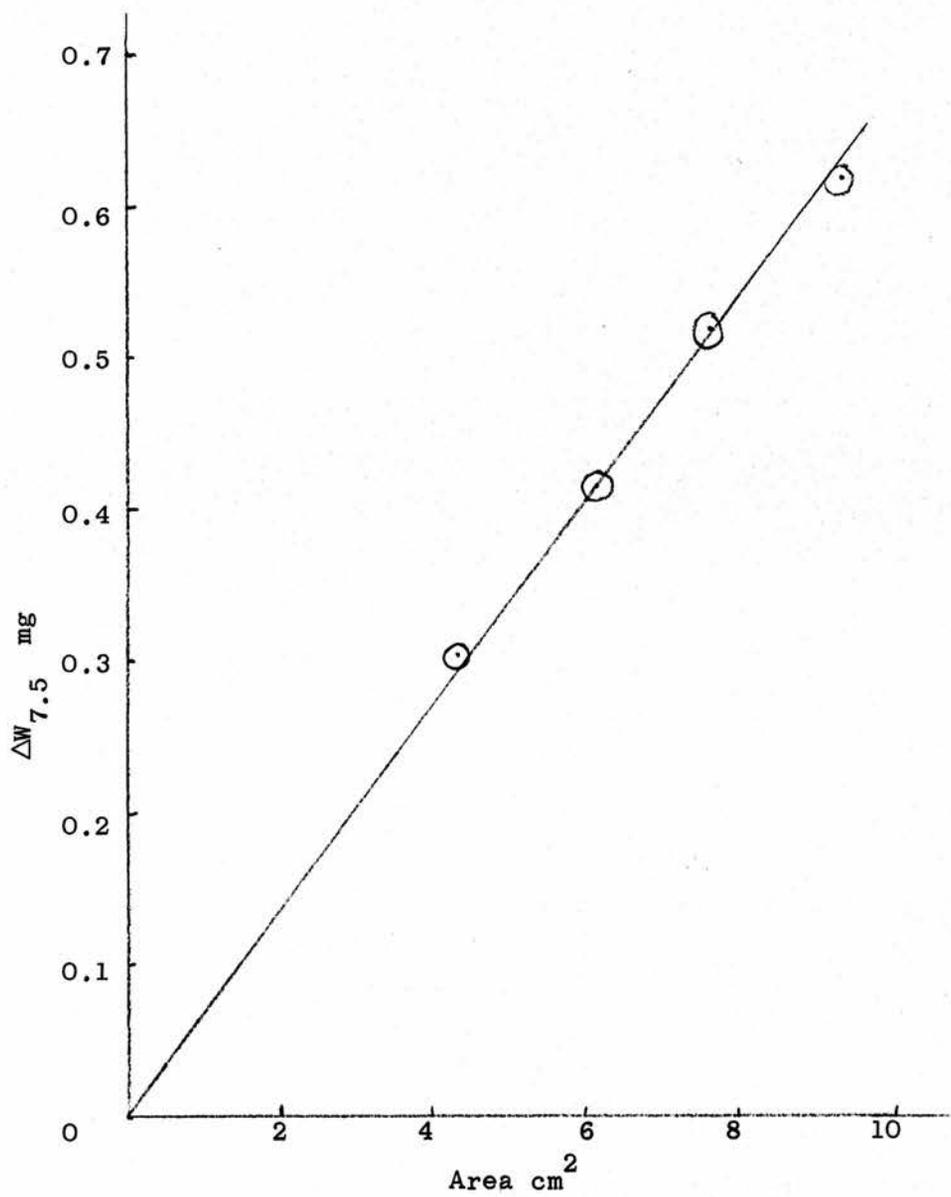
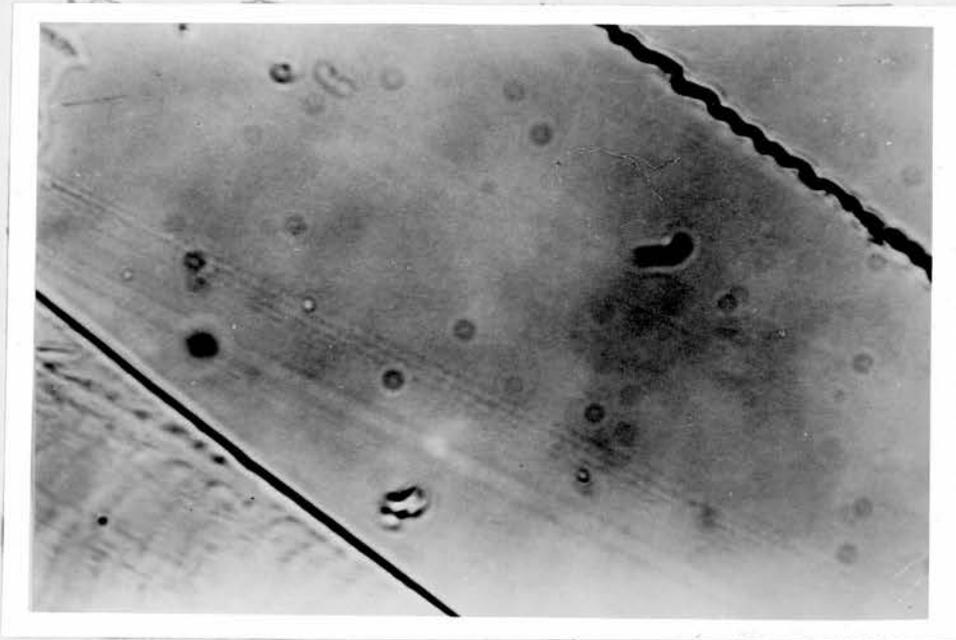


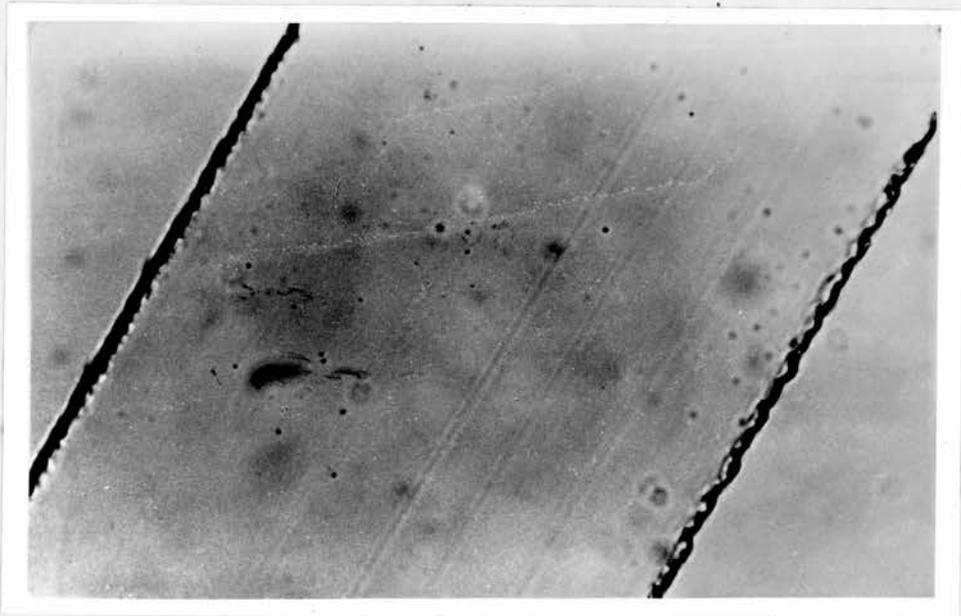
Figure 13

Photographs of cross-sections of films degraded (a) at one surface and (b) at both surfaces (x 640)

(a)



(b)



(i) Ultraviolet and Visible Spectra

Ultraviolet and visible spectra revealed the amount of light that was absorbed by a sample at a given wavelength. For these samples an increase in optical density, most pronounced at around 275 nm, was easily visible after only one minute. A pale yellow colouring was visible to the eye after five minutes, indicating absorption in the visible, and therefore long polyenes. After 7.5 hr the film sample appeared dark yellow. A typical spectrum of a film irradiated for 7.5 hr is shown in Figure 14, and it can be seen that there is no transmission below 275 nm. Absorption extends beyond 600 nm. A more thorough spectroscopic investigation of the dehydrochlorination reaction is reported in section 5.

(ii) Actinometry

The intensity of the light transmitted by a degrading sample was monitored actinometrically as explained. It should be noted that for practical reasons these experiments were conducted in air and consequently values for the light absorbed would be lower than in nitrogen (oxygen bleaches polyenes - see section 7). Table 5 shows the percentage of the incident light transmitted, I_{tr} , and the time of irradiation for a typical sample.

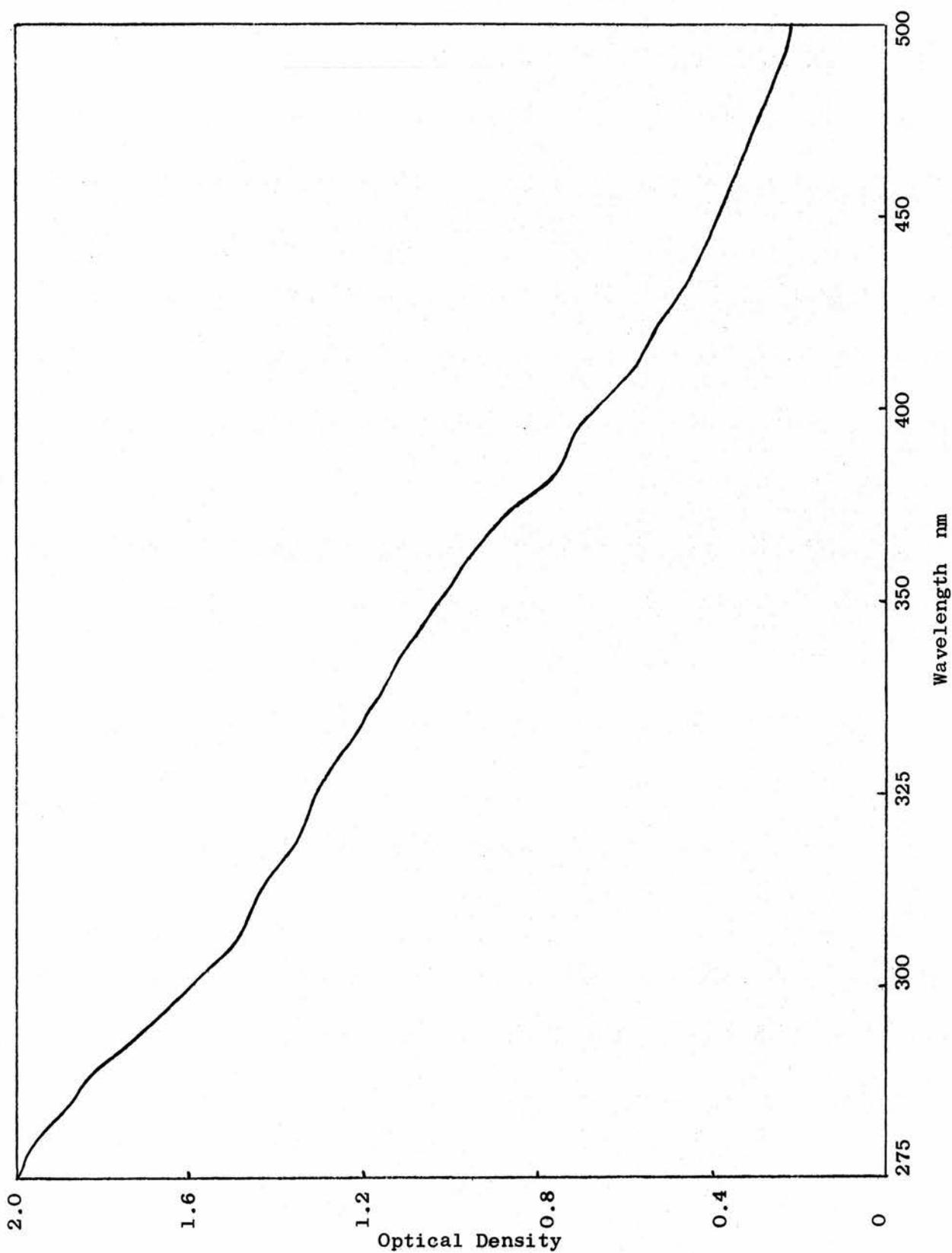
Table 5

t (min)	I_{tr} (%)
0	100
2.5	53
24	11
56	5.1
105	3.7
170	3.1

These values show that the irradiated sample very rapidly absorbed an increasing amount of the incident radiation below 450 nm

Figure 14

The Ultraviolet spectrum of a degraded film



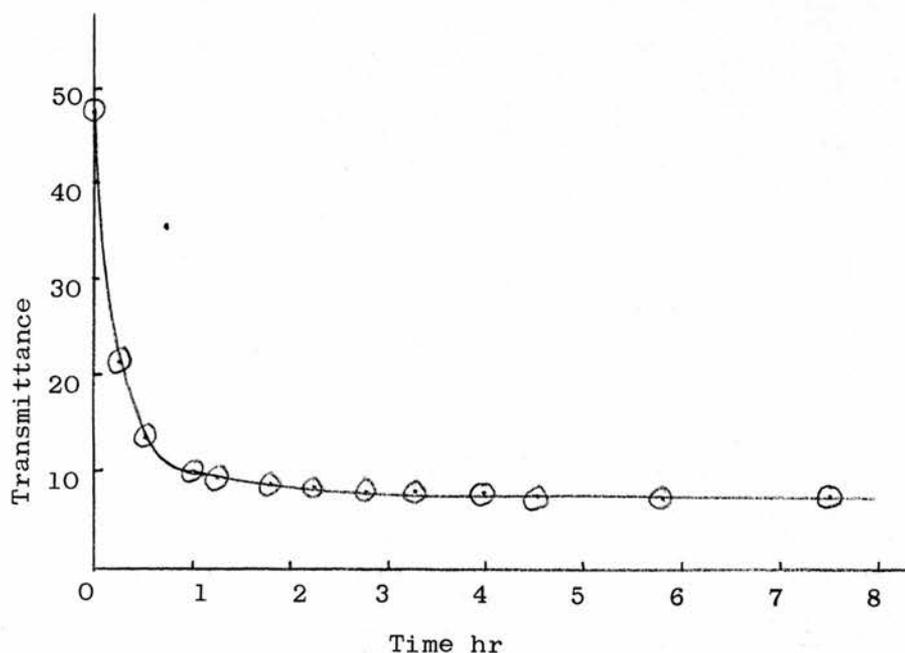
(the actinometer is sensitive to light at wavelengths < 450 nm).

(iii) The Photocell

The same experiment as described in (ii) was conducted using a photocell instead of an actinometer to measure the transmitted light. The curve shown in Figure 15 shows the very rapid fall off in transmitted light intensity. The intensity on an arbitrary scale was measured in milliamps.

Figure 15

Plot of degraded film transmittance versus time



2 Temperature and Light Intensity Variation.

Having established that the reaction was occurring in a surface layer, it was decided to determine the effect of various parameters. This section deals with temperature and light intensity variation.

(a) Temperature

Samples, cut from the same cast film, were irradiated for seven hours at temperatures ranging from 273-333 K. The light

intensity was constant at 3.57×10^{16} quanta $\text{cm}^{-2}\text{s}^{-1}$. The results of two sets of experiments, including the rate, $\Delta W/\Delta t$, of dehydrochlorination, are shown in Tables 6 and 7. It can be seen that the data from the two series are in fair agreement.

Table 6

t (hrs)	T = 303 K		T = 313 K		T = 323 K		T = 333 K	
	W(mg)	$\Delta W/\Delta t$ (mg hr ⁻¹)	ΔW (mg)	$\Delta W/\Delta t$ (mg hr ⁻¹)	ΔW (mg)	$\Delta W/\Delta t$ (mg hr ⁻¹)	ΔW (mg)	$\Delta W/\Delta t$ (mg hr ⁻¹)
0.5	0.171	-	0.162	-	0.196	-	0.217	-
1.0	0.297	0.297	0.295	0.295	0.327	0.327	0.359	0.359
2.0	0.407	0.110	0.423	0.128	0.452	0.125	0.489	0.130
3.0	0.475	0.068	0.495	0.072	0.523	0.071	0.560	0.071
4.0	0.521	0.046	0.546	0.051	0.575	0.052	0.612	0.052
5.0	0.557	0.036	0.589	0.043	0.612	0.037	0.649	0.037
6.0	0.592	0.035	0.623	0.034	0.644	0.032	0.681	0.032
7.0	0.617	0.025	0.651	0.028	0.671	0.027	0.708	0.027

Table 7

t (hr)	T = 273 K		T = 299 K		T = 308 K		T = 318 K		T = 328 K	
	ΔW (mg)	$\Delta W/\Delta t$ (mg hr ⁻¹)	ΔW (mg)	$\Delta W/\Delta t$ (mg hr ⁻¹)	ΔW (mg)	$\Delta W/\Delta t$ (mg hr ⁻¹)	ΔW (mg)	$\Delta W/\Delta t$ (mg hr ⁻¹)	ΔW (mg)	$\Delta W/\Delta t$ (mg hr ⁻¹)
0.5	0.132	-	0.191	-	0.214	-	0.225	-	0.238	-
1.0	0.244	0.244	0.313	0.313	0.330	0.330	0.360	0.360	0.373	0.373
2.0	0.359	0.115	0.429	0.116	0.456	0.116	0.488	0.128	0.495	0.122
3.0	0.414	0.055	0.492	0.063	0.519	0.062	0.552	0.064	0.566	0.071
4.0	0.467	0.053	0.535	0.043	0.562	0.043	0.600	0.047	0.613	0.057
5.0	0.501	0.034	0.568	0.033	0.598	0.036	0.634	0.034	0.650	0.037
6.0	0.524	0.023	0.596	0.028	0.625	0.027	0.661	0.027	0.681	0.031
7.0	0.544	0.020	0.618	0.022	0.647	0.022	0.685	0.024	0.706	0.025

The weight losses for fixed periods of the photodegradation reaction are shown in Tables 8 and 9. For example, ΔW_{1-7} signifies the weight loss between one hour and seven hours irradiation.

Table 8

T(K)	ΔW_{1-7} (mg)	ΔW_{2-7} (mg)	ΔW_{3-7} (mg)
303	0.320	0.210	0.142
313	0.356	0.228	0.156
323	0.344	0.219	0.148
333	0.349	0.219	0.148

Table 9

T(K)	ΔW_{1-7} (mg)	ΔW_{2-7} (mg)	ΔW_{3-7} (mg)
273	0.300	0.186	0.130
299	0.305	0.189	0.126
308	0.317	0.191	0.128
318	0.325	0.197	0.132
328	0.333	0.211	0.140

The activation energy of the reaction can be calculated by the following method. The rate of evolution of hydrogen chloride (HCl) can be written,

$$d(\text{HCl})_a/dt = -k \cdot f(\text{HCl})_a$$

where $(\text{HCl})_a$ is the bound HCl available for photochemical reaction, t is time and k is the rate constant for the degradation reaction.

It follows that,

$$\int [1/f(\text{HCl})_a \cdot d(\text{HCl})_a] = \int -k \cdot dt.$$

$$f'(\Delta W) = -kt + c \quad \text{----- (1)}$$

Since $f'(\Delta W) = 0$ when $t = 0$, $c = 0$. The temperature dependence of k is given by the Arrhenius equation,

$$k = A e^{-E/RT} \quad \text{----- (2)}$$

Substitution of Equ. (2) in Equ. (1) yields:

$$f'(\Delta W) = t \cdot A e^{-E/RT} \quad \text{----- (3)}$$

Taking a constant value for ΔW and hence for $f'(\Delta W)$ equation

(3) can be written,

$$K = t' \cdot A e^{-E/RT} \quad \text{-----} \quad (4)$$

where K is the constant value of $f'(\Delta W)$ and t' is the time taken to reach that value.

Thus,

$$\log K = -\log t' - \log A + E/RT$$

$$\log t' = E/RT - \log AK \quad \text{-----} \quad (5)$$

Hence for a series of runs, and by taking a constant weight loss, a plot of $\log t'$ vs. $1/T$ should yield a straight line with a slope E/R . Two plots, made at $\Delta W = 0.45$ mg, using the data from Tables 6 and 7 are shown in Figure 16. Several values of ΔW were taken and all yielded about the same activation energy. The results from Table 6 gave an activation energy of 12.5 kJ mol^{-1} , and those from Table 7 a value of 15.4 kJ mol^{-1} . Because temperature variation has such a small effect on this reaction, it is difficult to obtain an accurate activation energy. However, it can be deduced from these results that the activation energy is of the order 14 kJ mol^{-1} .

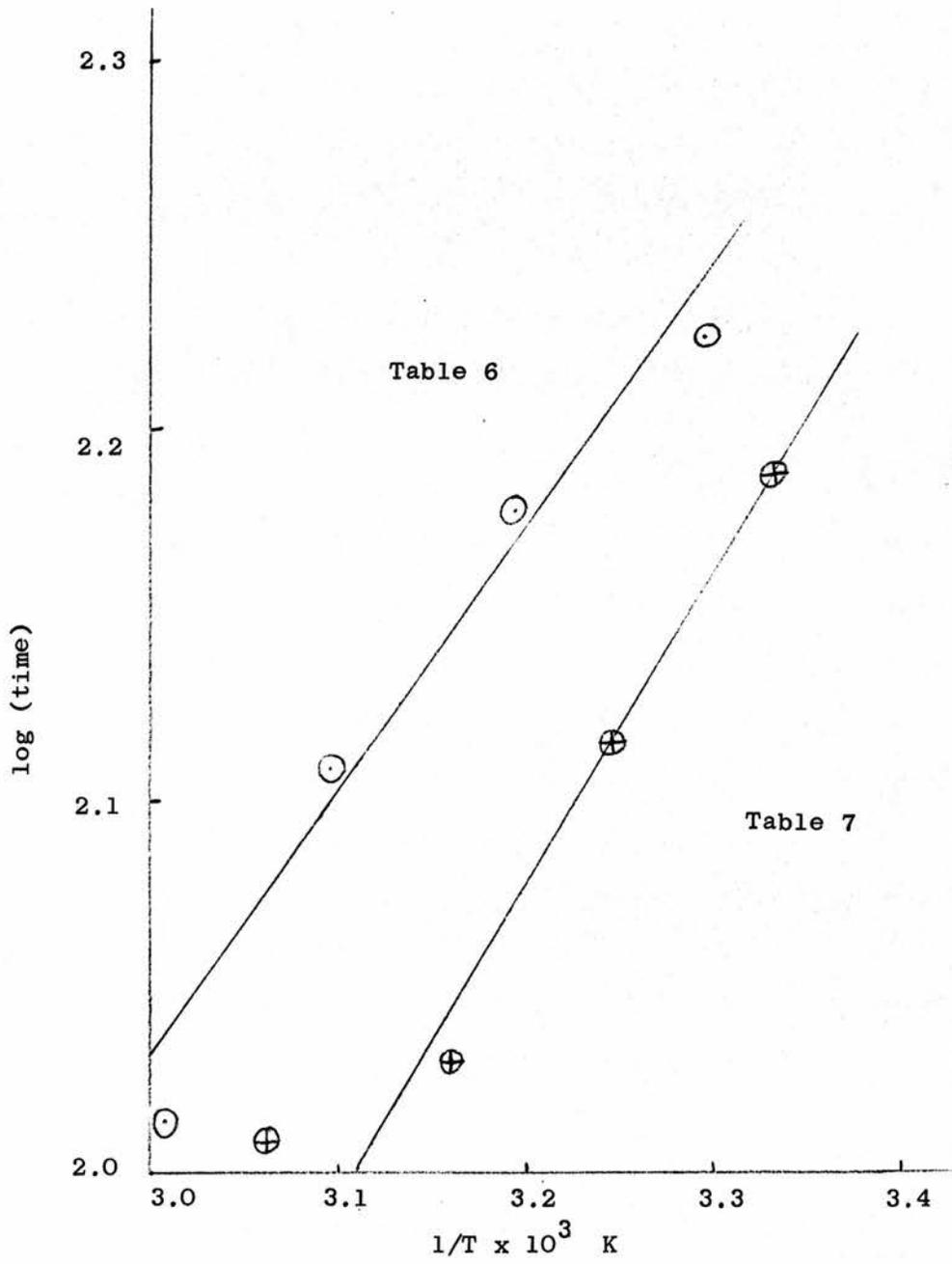
Raising the temperature at which the irradiation was conducted increased the number of long polyenes present in the degraded sample. This could be seen in two ways. First, as the temperature increased the colour of the degraded samples changed from pale yellow to yellow to yellow-brown to brown. Second, the ultraviolet spectra of these samples showed a higher optical density throughout the visible, the higher the degradation temperature. For example optical density values at 550 nm of 0.125, 0.160, 0.170 and 0.195 were obtained for samples irradiated at 303, 313, 323 and 333 K respectively.

(b) Intensity Variation

Samples, again taken from the same cast film, were irradiated for seven hours at different light intensities, at a constant

Figure 16

Activation energy plots



temperature 293 K. The light intensity was varied and determined as reported, and the intensities used are shown in Table 10, where d is the arc-to-sample distance.

Table 10

d (cm)	I_o quanta $\text{cm}^{-2} \text{s}^{-1}$ $\times 10^{16}$	I_o' quanta $\text{cm}^{-2} \text{s}^{-1}$ $\times 10^{16}$
19.6	2.56	2.83
29.6	1.28	1.24
39.2	0.68	0.71
50.1	0.41	0.43

Theoretically the light intensity is proportional to $1/d^2$.⁷³ To minimise scatter due to inherent difficulties in the actinometry measurements, a corrected value for the light intensity, I_o' , was found by plotting I_o , the experimentally obtained value, against $1/d^2$. I_o' at a given d, was read off from the best straight line obtained.

The results of two sets of experiments, including the rate, $\Delta W/\Delta t$, of dehydrochlorination, are shown in Tables 11 and 12. Tables 13 and 14 show the ΔW_{1-7} , ΔW_{2-7} , and ΔW_{3-7} values. The two sets of experiments are in good agreement.

Table 11

I_o' (quanta $\text{cm}^{-2}\text{s}^{-1}$)	2.83×10^{16}		1.24×10^{16}		0.71×10^{16}		0.43×10^{16}	
	ΔW (mg)	$\Delta W/\Delta t$ (mg hr^{-1})	ΔW (mg)	$\Delta W/\Delta t$ (mg hr^{-1})	ΔW (mg)	$\Delta W/\Delta t$ (mg hr^{-1})	ΔW (mg)	$\Delta W/\Delta t$ (mg hr^{-1})
t (hr)								
0.5	0.177	-	0.084	-	0.028	-	0.008	-
1.0	0.283	0.283	0.199	0.195	0.110	0.110	0.048	0.048
2.0	0.385	0.102	0.299	0.104	0.220	0.110	0.149	0.101
3.0	0.435	0.050	0.349	0.050	0.272	0.052	0.203	0.052
4.0	0.473	0.030	0.385	0.036	0.306	0.034	0.238	0.035
5.0	0.499	0.026	0.414	0.029	0.332	0.026	0.266	0.028
6.0	0.519	0.020	0.434	0.020	0.351	0.019	0.287	0.021
7.0	0.538	0.019	0.454	0.020	0.370	0.019	0.305	0.018

Table 12

0.5	0.182	-	0.087	-	0.036	-	0.014	-
1.0	0.290	0.202	0.202	0.202	0.121	0.121	0.057	0.057
2.0	0.384	0.094	0.304	0.102	0.232	0.111	0.158	0.101
3.0	0.436	0.052	0.356	0.052	0.281	0.051	0.226	0.068
4.0	0.469	0.033	0.388	0.032	0.316	0.033	0.266	0.040
5.0	0.495	0.026	0.413	0.025	0.340	0.024	0.291	0.025
6.0	0.515	0.020	0.433	0.020	0.361	0.021	0.312	0.021
7.0	0.535	0.020	0.450	0.017	0.379	0.018	0.332	0.020

Table 13

I_o' (quanta $\text{cm}^{-2}\text{s}^{-1}$) $\times 10^{16}$	ΔW_{1-7} (mg)	ΔW_{2-7} (mg)	ΔW_{3-7} (mg)
2.83	0.255	0.153	0.103
1.24	0.259	0.155	0.105
0.71	0.260	0.150	0.098
0.43	0.257	0.156	0.102

Table 14

I_0' quanta $\text{cm}^{-2} \text{s}^{-1}$ $\times 10^{16}$	ΔW_{1-7} (mg)	ΔW_{2-7} (mg)	ΔW_{3-7} (mg)
2.83	0.245	0.141	0.099
1.24	0.248	0.146	0.094
0.71	0.258	0.147	0.096
0.43	0.275	0.174	0.106

Another set of experiments was conducted under the same conditions, but using a lower intensity arc, and extending the irradiation time up to 30 hours. The dehydrochlorination curves obtained, and the light intensities used, are shown in Figure 17.

Ultraviolet absorption spectra of films irradiated for one hour at different intensities, as shown in Table 10, were also recorded, and are shown in Figure 18.

3 Sample Variation.

As stated most of the work described in this thesis was done using JLB 956 as polymer sample. However other films were obtained from different polymer samples. Alternatively films of JLB 956 were modified either by heat treatment or incorporation of additives. The results of the photodegradation of these samples are reported here.

(a) Peroxide Loaded Films

The poly(vinyl chloride) samples in Table 1 were used to prepare films for degradation. These samples fell into two groups, depending on polymerisation temperature. This section deals with the samples JLB 1026-1031, 1035 which were all polymerised at 54°C and have approximately the same molecular weight. The initiator used, and hence the possible end groups present in the polymer chain, and

Figure 17

The dehydrochlorination curves for samples irradiated for 30 hours at light intensities, I_0 (quanta $\text{cm}^{-2}\text{s}^{-1} \times 10^{16}$) of:-

- A $I_0 = 2.00$
- B $I_0 = 0.88$
- C $I_0 = 0.51$
- D $I_0 = 0.32$

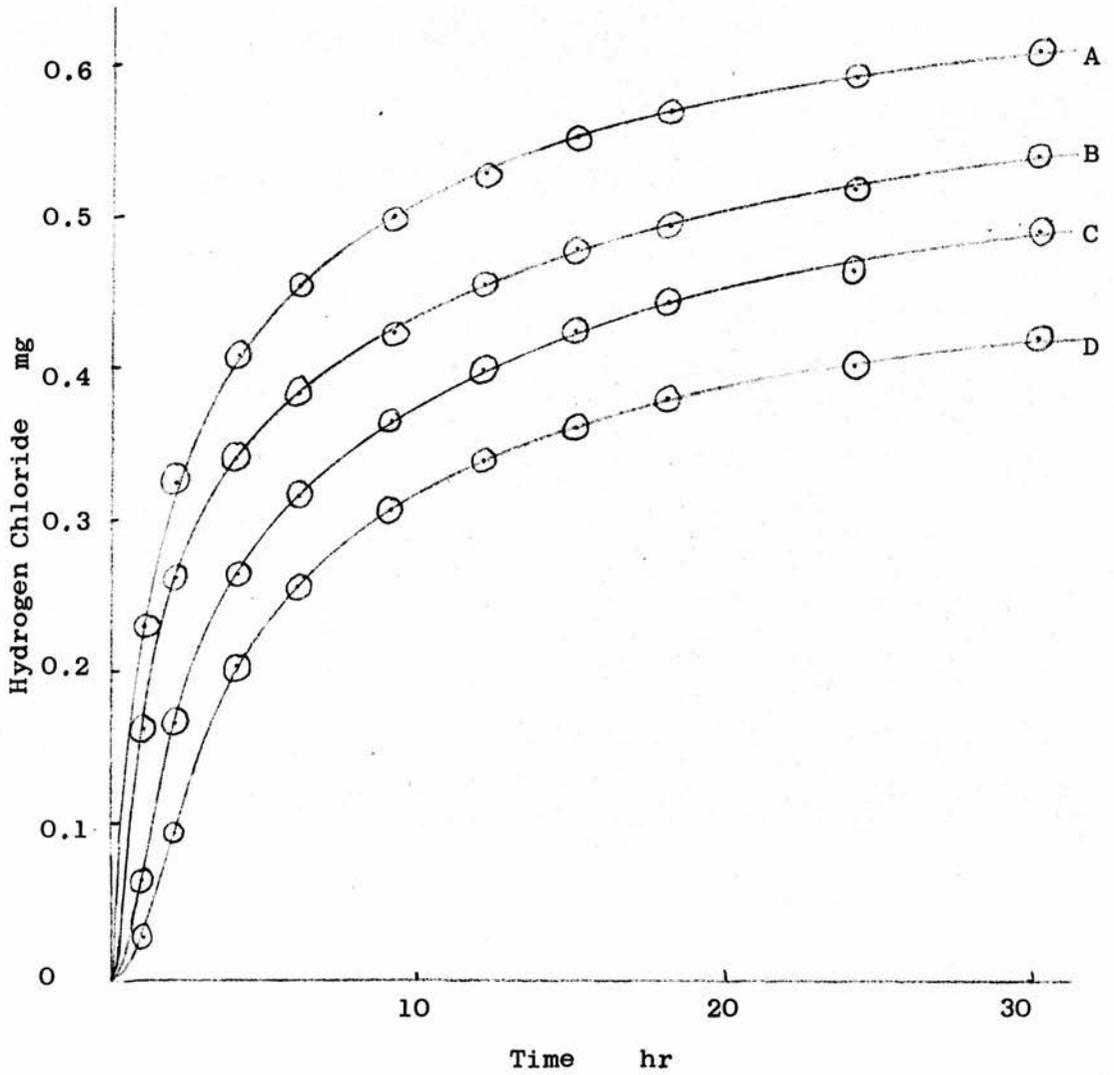
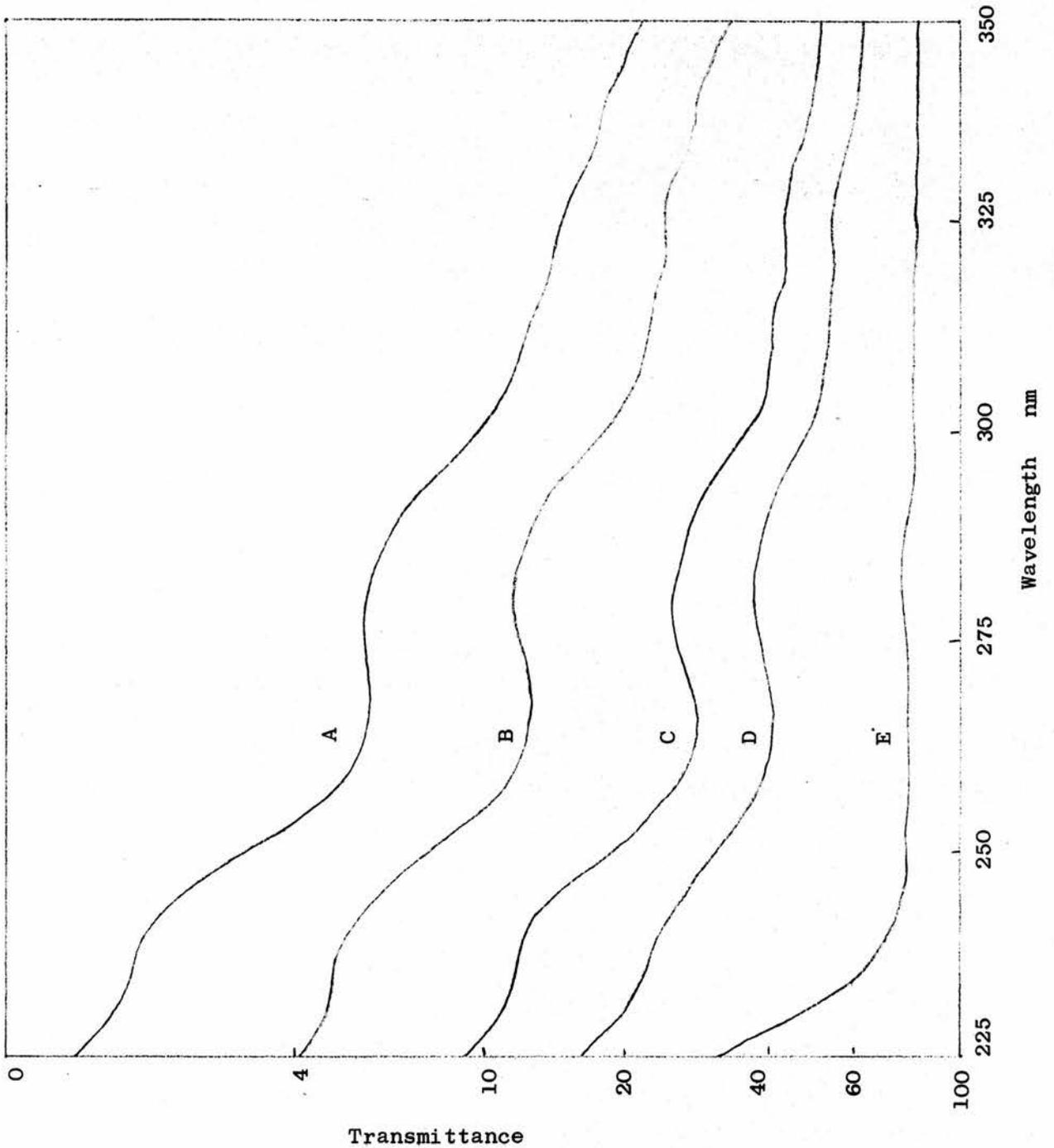


Figure 18

Ultraviolet spectra of film samples irradiated for one hour at light intensities, I_0 (quanta $\text{cm}^{-2} \text{s}^{-1} \times 10^{16}$), of:

- A $I_0 = 2.83$
- B $I_0 = 1.24$
- C $I_0 = 0.71$
- D $I_0 = 0.43$
- E Unirradiated



the amount of initiator used or remaining, had been varied. Section (b) will report the results obtained using samples with different molecular weights.

It is convenient to consider each peroxide, benzoyl, capryloyl and Y16, separately.

(i) Benzoyl Peroxide

This peroxide differs from the others to be discussed in that it shows strong absorption in the ultraviolet. The ultraviolet spectrum of benzoyl peroxide in n-heptane is in Figure 19 and shows absorption maxima at 229, 276 and 284 nm with molar extinction coefficients of 25,590, 2021 and 1632 $\text{l mol}^{-1} \text{cm}^{-1}$ respectively.

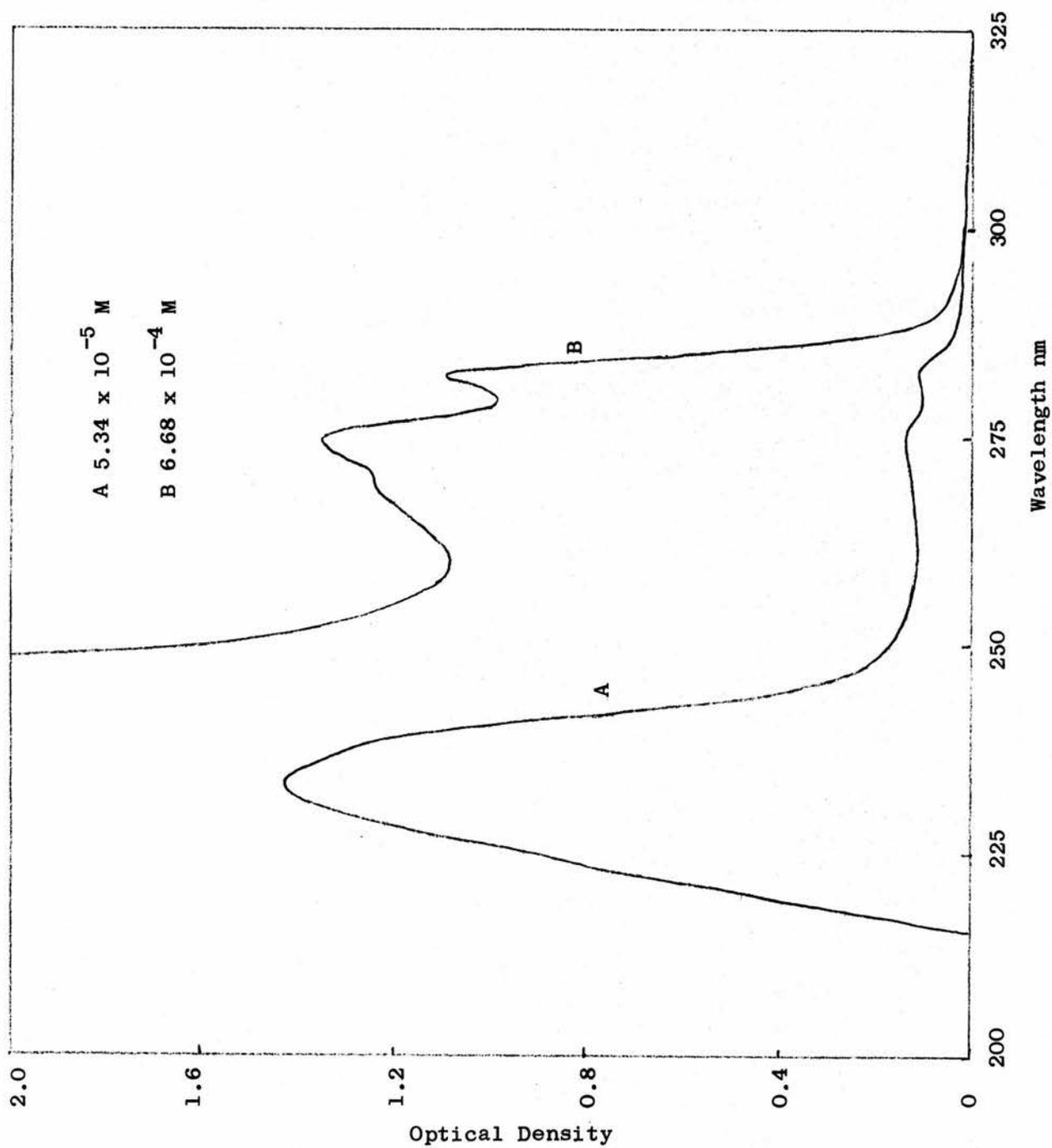
Two types of benzoyl peroxide containing films have been studied. First there were the two samples, JLB 1030 and 1031, polymerised using excess benzoyl peroxide as initiator. Second there was a range of samples prepared by adding recrystallised benzoyl peroxide to JLB 956, the standard poly(vinyl chloride) sample. All the samples, and a reference sample of pure JLB 956, were irradiated for seven hours using a light intensity of 0.88×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$. The film sample details and ΔW_7 values are shown in Table 15.

Table 15

Polymer	Film (code)	Benzoyl Peroxide (mol %)	ΔW_7 (mg)
JLB 956	44	0	0.389
JLB 956	P/1	0.025	0.378
+	P/2	0.25	0.282
Bz_2O_2	P/3	1.25	0.208
JLB 1030	P/8	0.24	0.291
JLB 1031	P/9	0.94	0.246

Figure 19

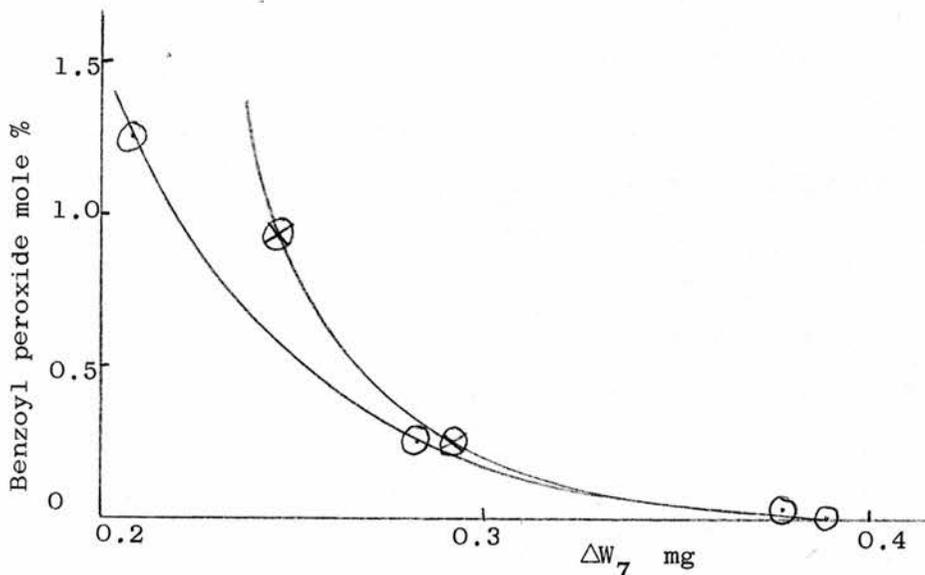
Ultraviolet spectrum of benzoyl peroxide in methanol



It can be seen that benzoyl peroxide reduced the amount of degradation that occurred in seven hours. Figure 20 shows a plot of ΔW_7 versus mole % benzoyl peroxide present in the film.

Figure 20

Plots of ΔW_7 v mole % benzoyl peroxide



This plot suggests that the artificially loaded samples degrade to a lesser extent than the samples polymerised using benzoyl peroxide.

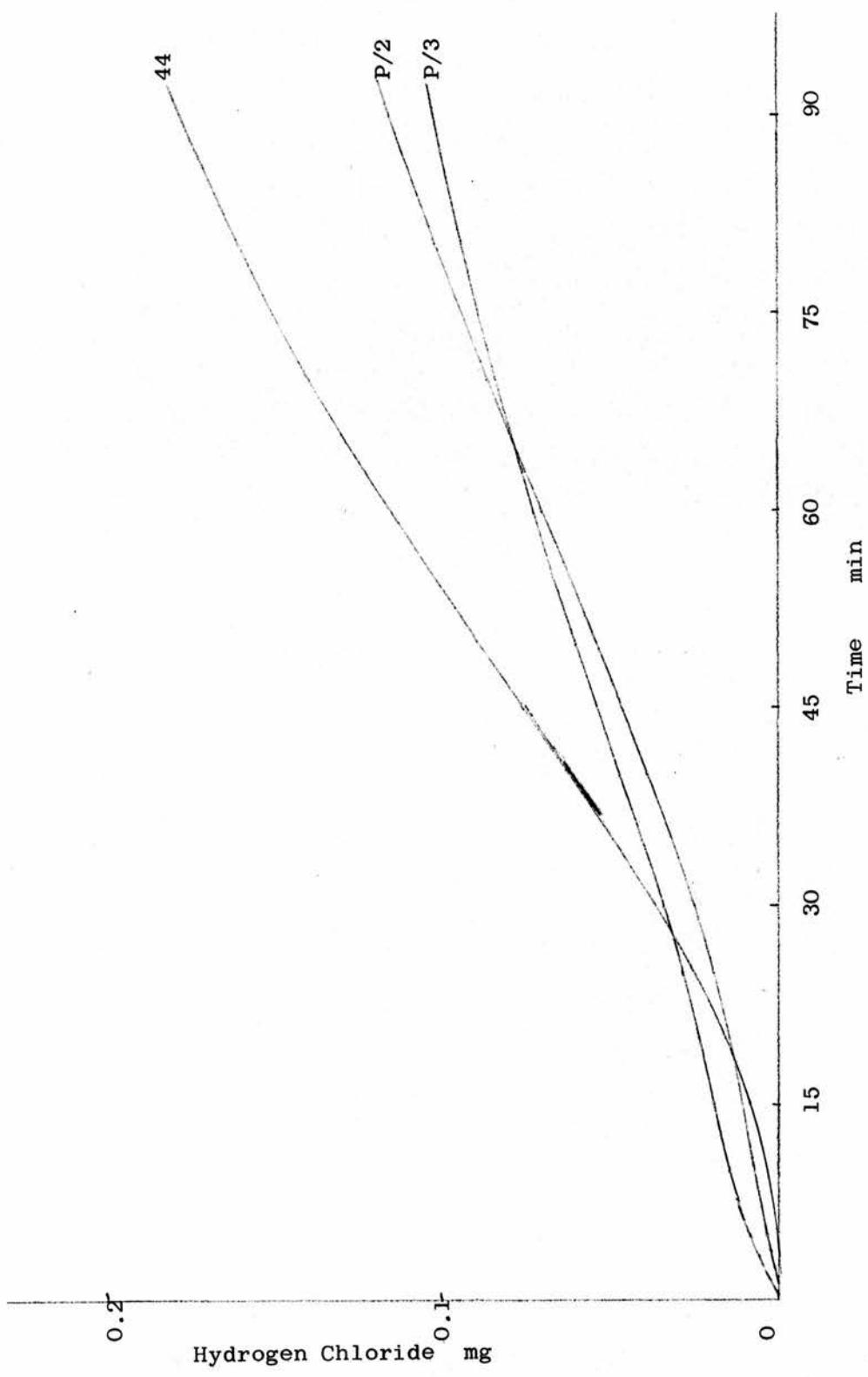
When the early part of the reaction was studied in more detail it could be seen that, although the sample containing most benzoyl peroxide degraded least in seven hours, it in fact was initially fastest. Correspondingly the other samples lay in between. This is shown by the early stages of the dehydrochlorination curves for films 44, P/2 and P/3 shown in Figure 21. The same effect is shown by films P/8 and P/9. The dehydrochlorination curves for films 44 and P/1 are virtually coincident.

Spectral Analysis: These samples were examined by ultraviolet and infra-red spectroscopy before and after degradation. The ultraviolet spectra of the two types of samples were the same with films

Figure 21

Dehydrochlorination curves of benzoyl peroxide loaded films

(films 44, P/2 and P/3 contain 0, 0.25 and 1.25 mol % benzoyl peroxide respectively)



P/3 and P/9 showing a complete cut-off at 287 nm. The benzoyl peroxide peaks at 276 and 284 nm can be seen in Film P/2. Figure 22 shows the ultraviolet spectra of films P/1, P/2 and P/3 before irradiation.

The infra-red spectra of all these samples showed the characteristic benzoyl peroxide doublets at 1785, 1760 cm^{-1} and 1695, 1680 cm^{-1} , their intensities being proportional to the amount of peroxide present. The only other benzoyl peroxide peak which was not obscured by the poly(vinyl chloride) spectrum appeared at 785 cm^{-1} . The two samples P/8 and P/9 showed an additional very strong absorption at around 1715 cm^{-1} . This must have been due to some compound formed during polymerisation.

The ultraviolet spectra of all these samples taken after irradiation were very similar showing a cut-off at around 290 nm and a large hump between 300-350 nm with a peak at 325 nm. (Film P/1 does not contain enough benzoyl peroxide to have any visible effect.) A typical example, P/3, is shown in Figure 23. Film P/1 gives a very similar spectrum and the same optical density at 325 nm, 1.35.

The infra-red spectra of all the samples taken after irradiation showed the two doublets and the 785 cm^{-1} singlet reduced in intensity. The samples P/2 and P/3 showed a new very strong absorption at 1715 cm^{-1} . For P/8 and P/9 this peak, which had already been present, was considerably enlarged. A new small peak is also visible at 1620 cm^{-1} , when sufficient benzoyl peroxide is present, that is in films P/3 and P/9. The relevant region of a typical spectrum, film P/9, is shown in Figure 24.

In order to help identify the reaction products, a solution of benzoyl peroxide in cyclohexane was irradiated. The ultraviolet

Figure 22

Ultraviolet spectra of benzoyl peroxide loaded films before irradiation (Films P/1,2,3 contain 1.25, 0.25 and 0.025 mol % benzoyl peroxide respectively)

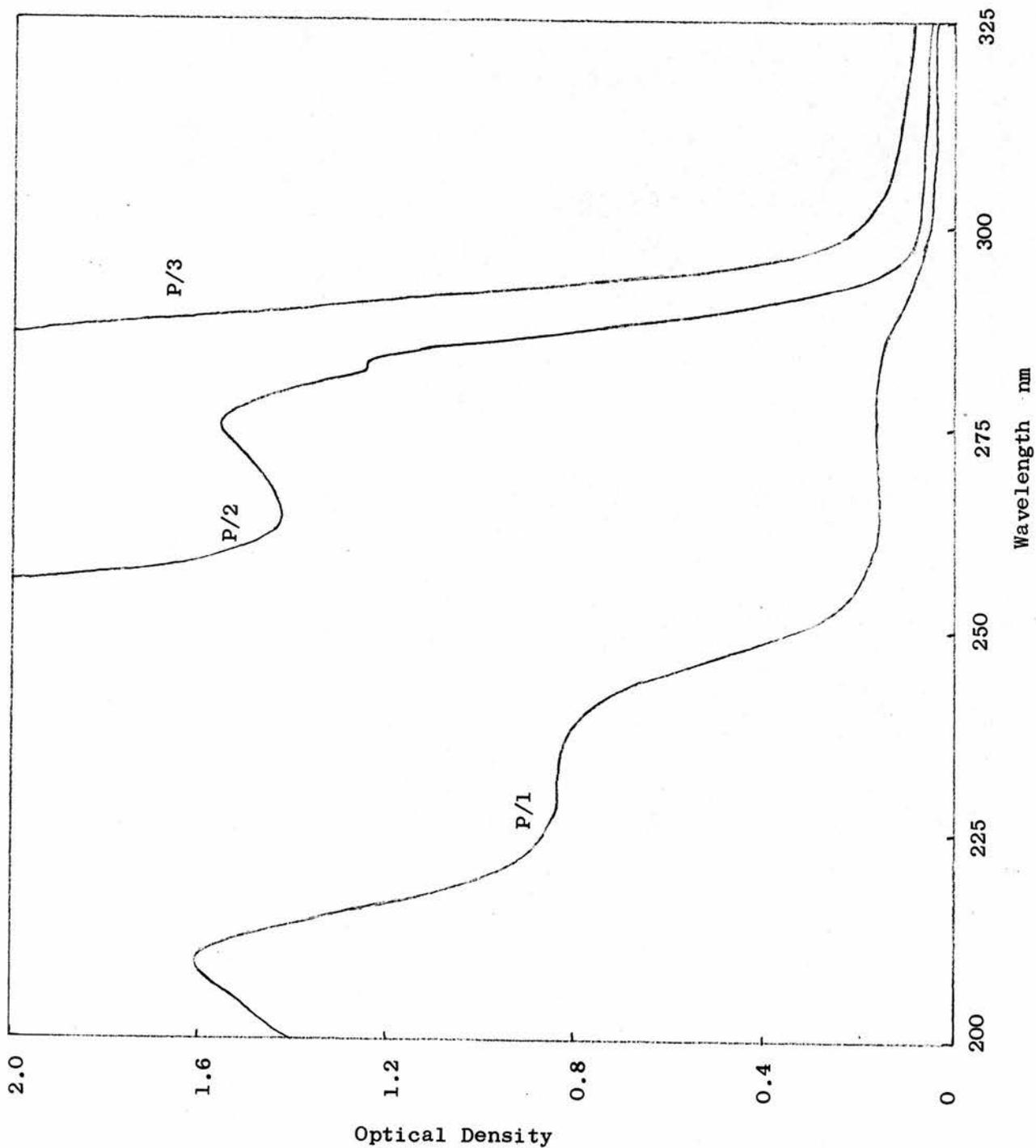


Figure 23

Ultraviolet spectrum of a typical benzoyl peroxide containing film after irradiation

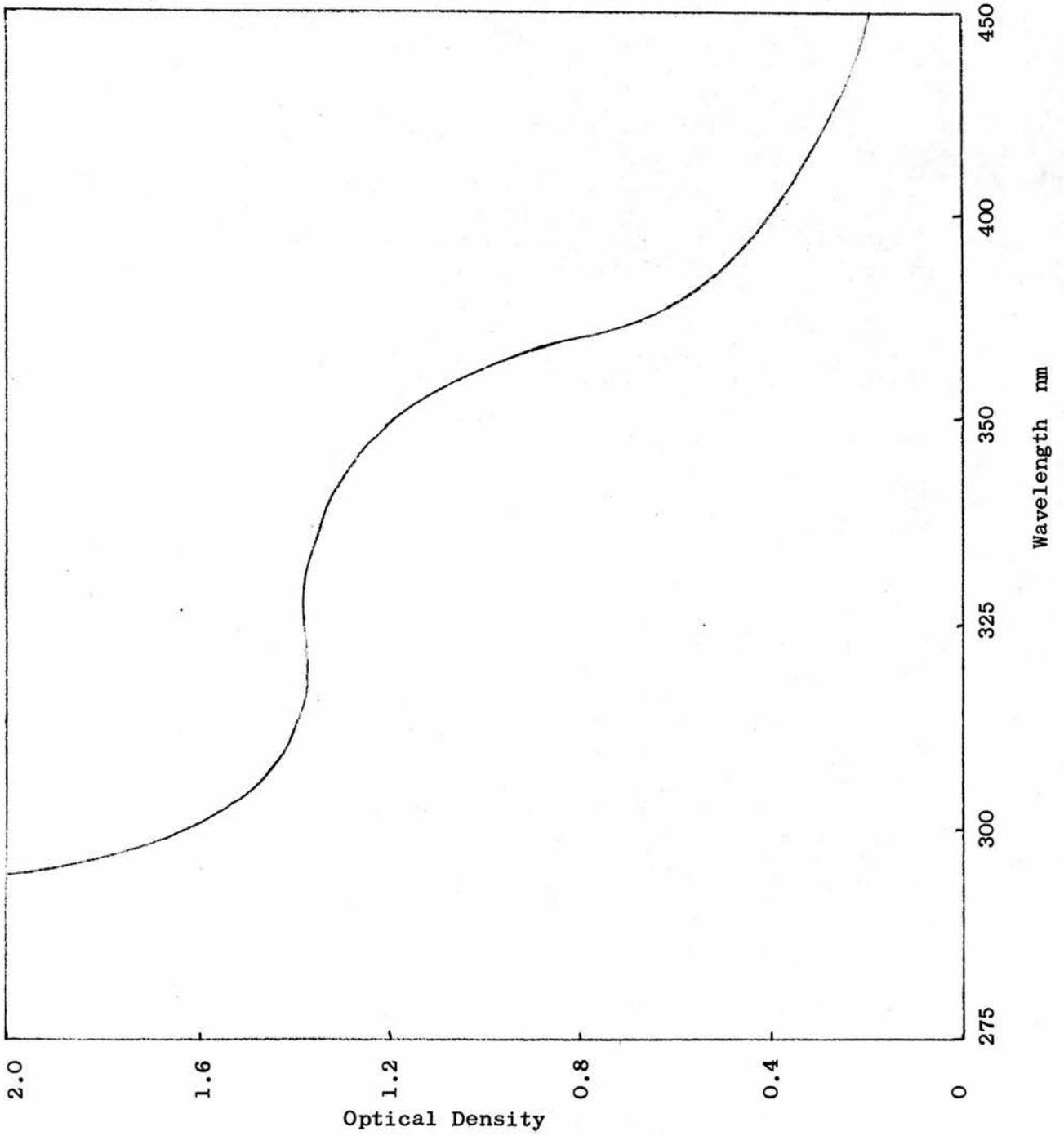
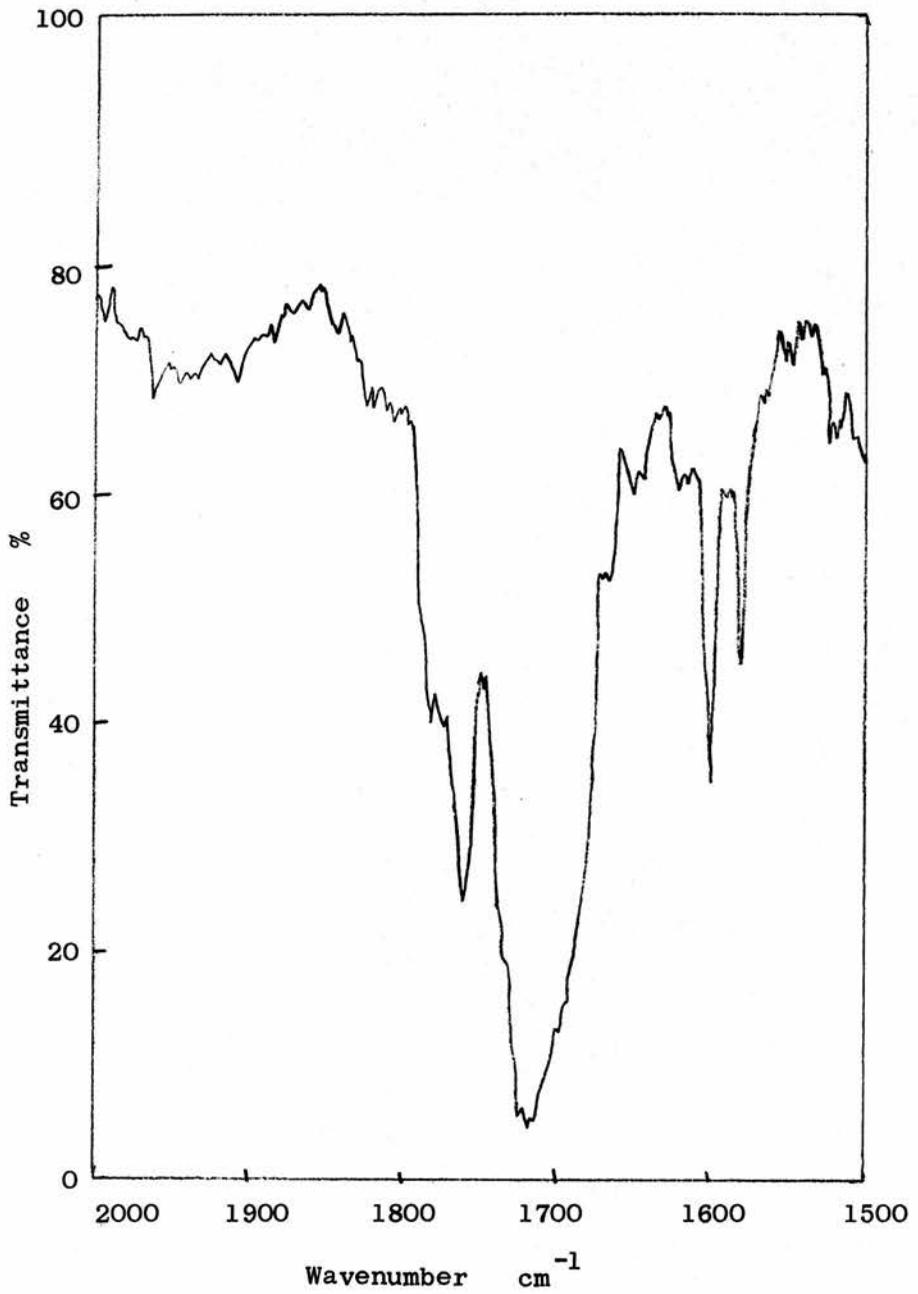


Figure 24

Infra-red spectrum of a typical benzoyl peroxide containing film after irradiation



spectra taken after 5, 10 and 30 minutes showed a build up of the same hump at 325 nm as appeared for the loaded films. This indicated that the compound causing this absorption was not related to the poly(vinyl chloride). The infra-red spectrum of benzoyl peroxide (as a nujol mull) irradiated for five minutes showed new peaks at 1690 and 1630 cm^{-1} . A further experiment was conducted. A sample of P/9 which had been degraded for seven hours was placed in methanol. Any methanol-soluble products or substances present in the film, but not chemically bound to the polymer chain, should be dissolved out of the film. The ultraviolet spectrum of the methanol extracts showed peaks at 229, 275 and 282 nm consistent with benzoyl peroxide, and a peak at 204 nm probably due to tetrahydrofuran. A very slight absorption between 300-350 nm was visible but no peaks or humps. The ultraviolet spectrum of the film showed a small change from the one taken before methanol treatment. The intensity of the hump at 325 nm was slightly reduced.

(ii) Capryloyl Peroxide

This material is a straight chain aliphatic peroxide and shows virtually no absorption in the ultraviolet. The only peak has a $\lambda_{\text{max}} = 228 \text{ nm}$ with an extinction coefficient of $236.6 \text{ l mol}^{-1} \text{ cm}^{-1}$. The two samples JLB 1026, 1027 were irradiated using light intensities of 0.88 and $1.00 \times 10^{16} \text{ quanta cm}^{-2} \text{ s}^{-1}$. The residual peroxide present and ΔW_7 and $\Delta W_7'$ values are shown in Table 16.

Table 16

Polymer Sample (JLB-)	Code	Residual Peroxide (mol %)	ΔW_7 (mg)	$\Delta W_7'$ (mg)
956	-	0	0.389	0.421
1026	P/4	0.10	0.413	0.425
1027	P/5	0.42	0.441	0.468

These results suggest the residual peroxide causes acceleration of the dehydrochlorination reaction, proportional to the amount present.

Spectral Analysis: The ultraviolet spectra for both samples before and after irradiation were similar to the reference sample.

The infra-red spectrum of pure capryloyl peroxide shows a doublet at 1810, 1790 cm^{-1} . This doublet was not observed in the film samples, suggesting that the amount of capryloyl peroxide remaining in the sample was much smaller than calculated.

Pure capryloyl peroxide was irradiated and examined by infra-red spectroscopy. There was, as expected, no difference between the spectra recorded before and after irradiation. This is in contrast to benzoyl peroxide which can absorb light and decompose.

(iii) Y16

This material is another aliphatic peroxide and again shows virtually no absorption in the ultraviolet. The only peak has a $\lambda_{\text{max}} = 228 \text{ nm}$ with an extinction coefficient of $109.4 \text{ l mol}^{-1} \text{ cm}^{-1}$. The two samples JLB 1028, 1029 were irradiated at a light intensity of $0.88 \times 10^{16} \text{ quanta cm}^{-2} \text{ s}^{-1}$, and again at a later date of $1.00 \times 10^{16} \text{ quanta cm}^{-2} \text{ s}^{-1}$. The polymer details, and ΔW_7 and $\Delta W_7'$ values are shown in Table 17.

Table 17

Polymer Sample (JLB-)	Code	Residual Peroxide (mol %)	ΔW_7 (mg)	$\Delta W_7'$ (mg)
956		-	0.389	0.421
1028	P/6	0.0067	0.419	0.449
1029	P/7	0.049	0.449	0.445

For these samples the amount of residual peroxide was negligible. The slight acceleration was probably caused by something else, although the ΔW_7 of 0.449 for JLB 1029 appears rather high.

Spectral Analysis: Again the ultraviolet spectra before and after irradiation were similar to the reference sample. The infra-red spectra of the film samples did not show the characteristic Y16 peak at 1800 cm^{-1} .

(b) Molecular Weight

The results of the photodegradation of a range of samples of varying molecular weight are reported here. A light intensity of $1.00 \times 10^{16} \text{ quanta cm}^{-2} \text{ s}^{-1}$ was employed. Four initiators were used to prepare these samples - capryloyl peroxide, Y16, V70 and ACSP. Also, as far as possible, samples containing similar amounts of residual initiator were compared e.g. JLB 1026 and 1038. The sample details and ΔW_7 values are shown in Table 18.

Unfortunately the ACSP containing samples, which show the greatest molecular weight spread, also contain dimethyl phthalate. This material absorbs in the ultraviolet and the spectra of the three films M/4, M/5 and M/6 can be seen in Figure 25. The slight discolouration of film M/6, and its ultraviolet spectrum before

Figure 25

Ultraviolet spectra of film samples containing dimethyl phthalate
(See Table 18 for significance of film codes M/4,5,6)

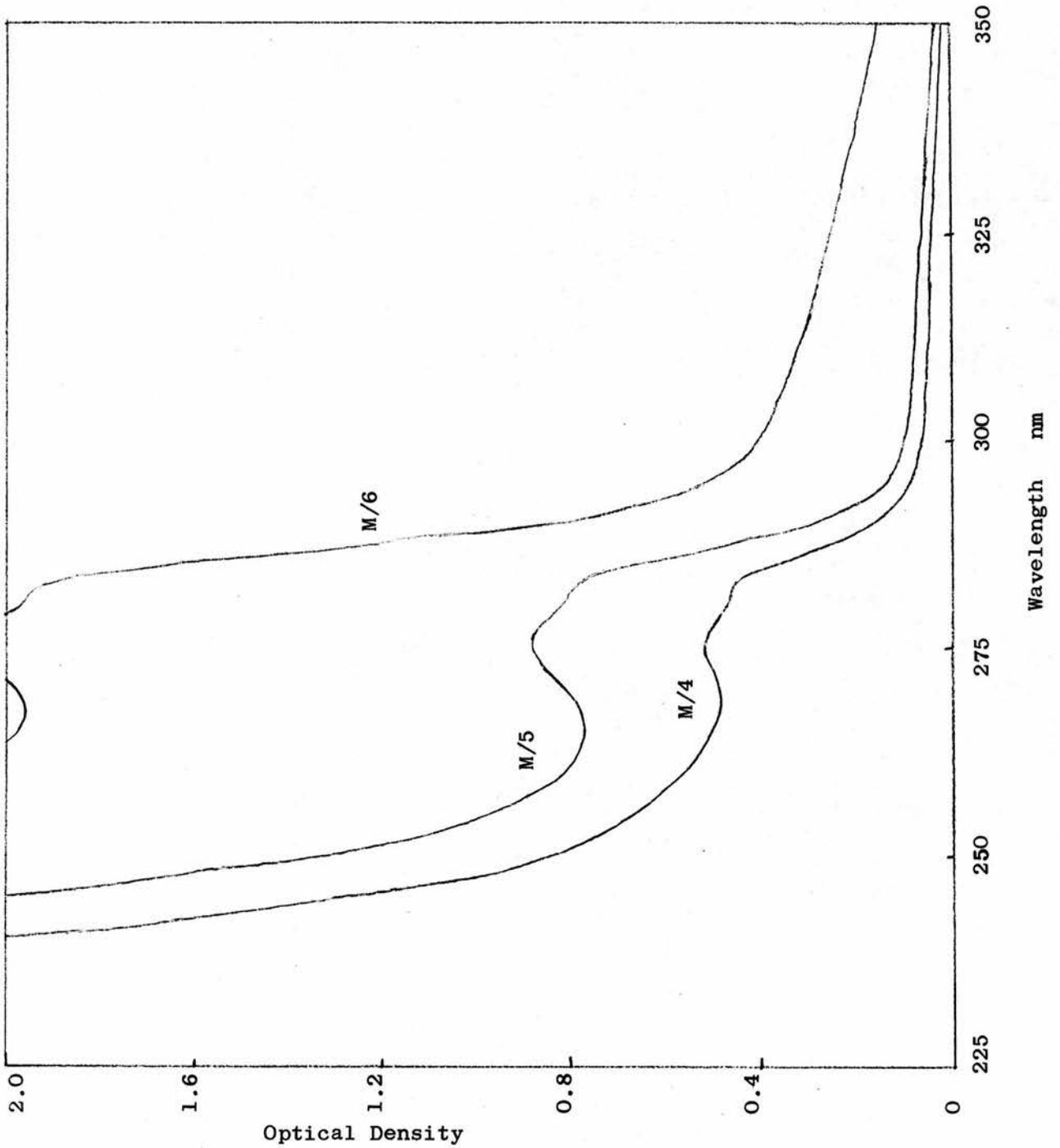


Table 18

Polymer Sample (JLB-)	Initiator	Code	Residual Initiator (mol %)	ΔW_7 (mg)	Molecular Weight $\times 10^3$
1026	Capryloyl Peroxide	P/4	0.10	0.425	43.5
1038		M/7	0.09	0.416	29.8
1028	Y16	P/6	0.0067	0.449	43.5
1041		M/11	0.00009	0.465	32.9
1039	V70	M/9	0.022	0.434	42.4
1040		M/10	0.048	0.409	67.7
1035	ACSP	M/4	0.00008	0.377	43.5
1036		M/5	0.0055	0.371	61.6
1037		M/6	0.0179	0.348	90.0
956	-	-	-	0.421	39.2

irradiation, indicate that this sample was degraded to a small extent before irradiation. In common with capryloyl peroxide, Y16 and V70, ACSP itself shows virtually no ultraviolet absorption. The result was that, as with benzoyl peroxide containing films, these films degraded less than the reference to an extent roughly proportional to the amount of dimethyl phthalate present, (0.023, 0.056 and 0.069 mol % respectively). Any effect due to molecular weight variation was total obscured.

Infra-red spectroscopic analysis of these films before irradiation showed, by comparison with the spectra of pure dimethyl phthalate and ACSP in dimethyl phthalate, peaks at 1725, 1600 and 1575 cm^{-1} due to dimethyl phthalate and at 1770 cm^{-1} due to ACSP. Spectra taken after irradiation showed no change. The ultraviolet spectra of these films recorded after irradiation showed a very strong broad hump with $\lambda_{\text{max}} = 325 \text{ nm}$, similar to that observed for benzoyl peroxide containing films. For film M/4 the optical density at 325 nm was 1.9 and films M/5 and M/6 showed cut-offs at 350 and 355 nm respectively (cf. Figure 23).

V70 is an azo initiator (see Page 31), again virtually transparent in the ultraviolet, showing two very weak peaks at $\lambda_{\max} = 230$ and 340 nm with extinction coefficients of 78.3 and $92.2 \text{ l mol}^{-1} \text{ cm}^{-1}$ respectively. The ultraviolet spectra of films M/9 and M/10 before and after irradiation are identical to the reference. The infra-red spectrum of the pure V70 shows no absorption in the region $1500\text{-}2000 \text{ cm}^{-1}$.

These results were complicated by the possible presence of different residual initiators and end groups. Films were therefore prepared from JLB 956, 958 and 960 which are known to contain a negligible amount of peroxide. Samples were again irradiated for seven hours at a light intensity of $1.00 \times 10^{16} \text{ quanta cm}^{-2} \text{ s}^{-1}$ and the results appear in Table 19.

Table 19

Polymer Sample (JLB-)	Molecular Weight $\times 10^3$	ΔW_7 (mg)
956	39.2	0.424
958	48.8	0.431
960	56.1	0.449

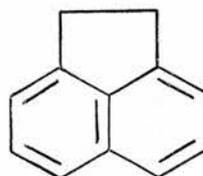
These results suggest that ΔW_7 is definitely not inversely proportional to molecular weight.

(c) Acenaphthene

When it had been observed that benzoyl peroxide caused retardation of the dehydrochlorination because of its ultraviolet absorbance, it was decided to prepare films containing another ultraviolet absorber and acenaphthene was chosen. This material absorbs over a wide range of wavelengths in the appropriate region of the spectrum and the λ_{\max} and ϵ values are shown in Table 20 along with its formula

Table 20

λ_{\max} (nm)	ϵ ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)
211	20,500
229	97,000
244	1,400
279	5,800
289	6,500
300	4,200
307	2,800
311	1,100
317	840
321	1,700



Acenaphthene

Firstly, by adding recrystallised acenaphthene to JLB 956, a film was prepared containing 2 mole % acenaphthene. The ultraviolet spectrum of this film showed a cut-off at 325 nm. A sample was irradiated for seven hours at a light intensity of 0.88×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$ and compared with the results shown in Table 15 for benzoyl peroxide containing films. A ΔW_7 value of 0.265 mg was obtained compared with, for example, 0.208 mg for a film containing 1.25 mol % benzoyl peroxide. It was also found by studying the early part of the dehydrochlorination curve that, as for benzoyl chloride loaded films, the reaction was initially faster than the reference.

It was then decided to prepare a set of samples containing a range of acenaphthene concentrations. These samples were irradiated at a light intensity of 1.00×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$ and later at 1.03×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$. Their ΔW_7 and $\Delta W_7'$ values, and the amount of acenaphthene present are shown in Table 21.

Table 21

Code	Acenaphthene (mol %)	Series 1	Series 2
		ΔW_7 (mg)	$\Delta W_7'$ (mg)
L/2	2.0	0.317	-
L/3	1.0	0.343	0.355
L/4	0.5	0.399	0.412
L/5	0.2	-	0.435
Reference	-	0.421	0.424

After the first set of results it was found that the early part of the reaction showed a different pattern from the benzoyl peroxide films. In this case the loaded films all started faster than the reference but film L/4 was fastest, as is shown by the dehydrochlorination curves in Figure 26. Film L/5 was prepared to give another result between L/4 and the reference, and it was found that film L/5 was initially slower than L/4, but was faster than the reference and remained so. This is shown more clearly by the graphs in Figure 27 of the weight losses after 15 minutes and seven hours, $\Delta W_{0.25}$ and ΔW_7 versus the mole % acenaphthene present.

Spectral Analysis: The ultraviolet spectra of films L/3, 4, 5 are shown in Figure 28 and the acenaphthene peaks can clearly be seen. After irradiation these samples exhibit a cut-off at 325 nm. The infra-red spectra of these samples showed characteristic acenaphthene peaks at 1600 and 795 cm^{-1} which were unaffected by irradiation.

(d) Phenyl Benzoate

After the results obtained using benzoyl peroxide loaded films had been analysed it was decided to prepare a film containing phenyl benzoate. It has been shown that phenyl benzoate is a product of benzoyl peroxide irradiation⁷⁴, and it was hoped that

Figure 26

Dehydrochlorination curves for acenaphthene loaded films (L/2,3,4 represent films containing 2.0, 1.0 and 0.5 mol % acenaphthene respectively)

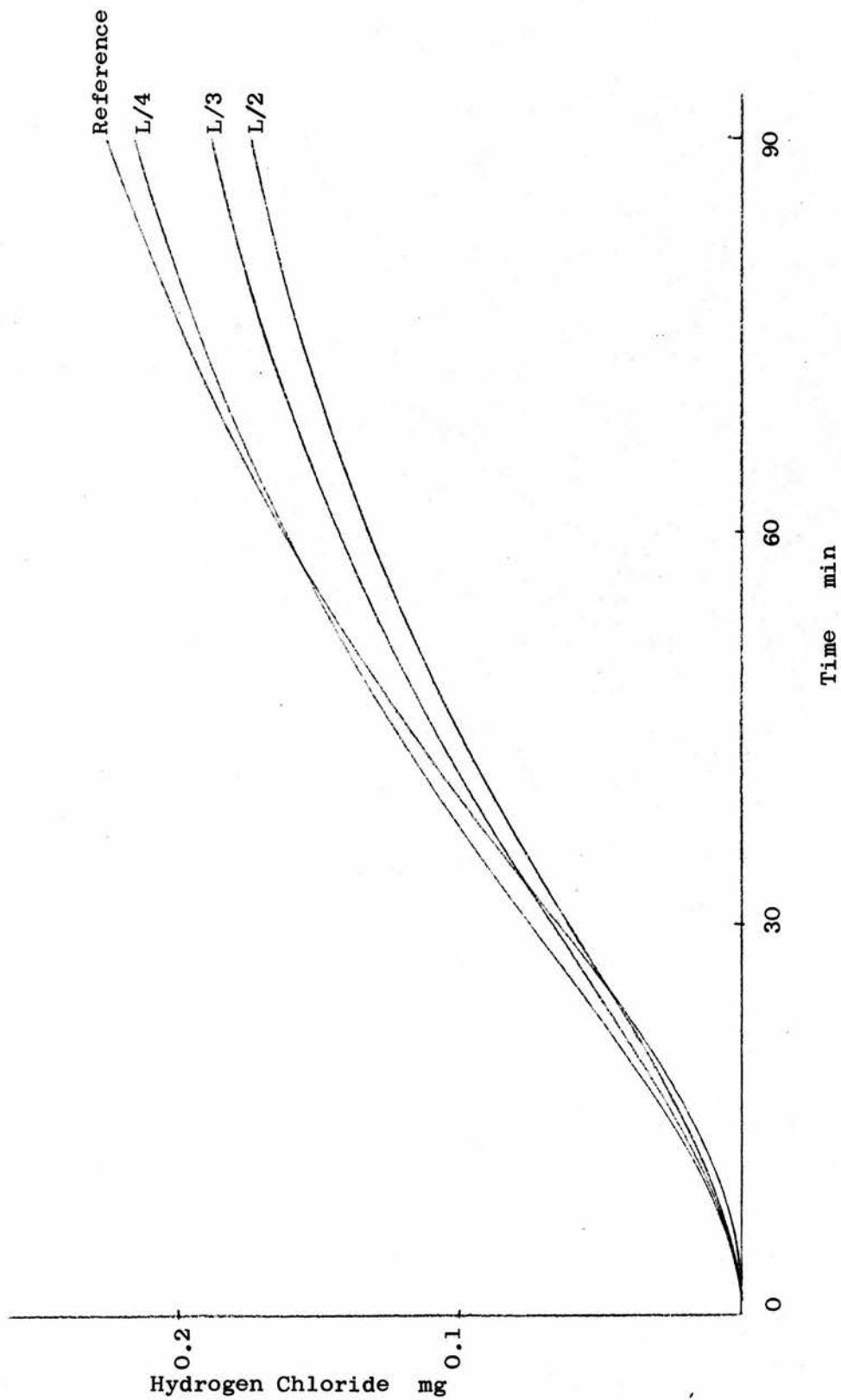


Figure 27

Plots of ΔW_7 and $\Delta W_{0.25}$ versus mol % Acenaphthene present for acenaphthene loaded films

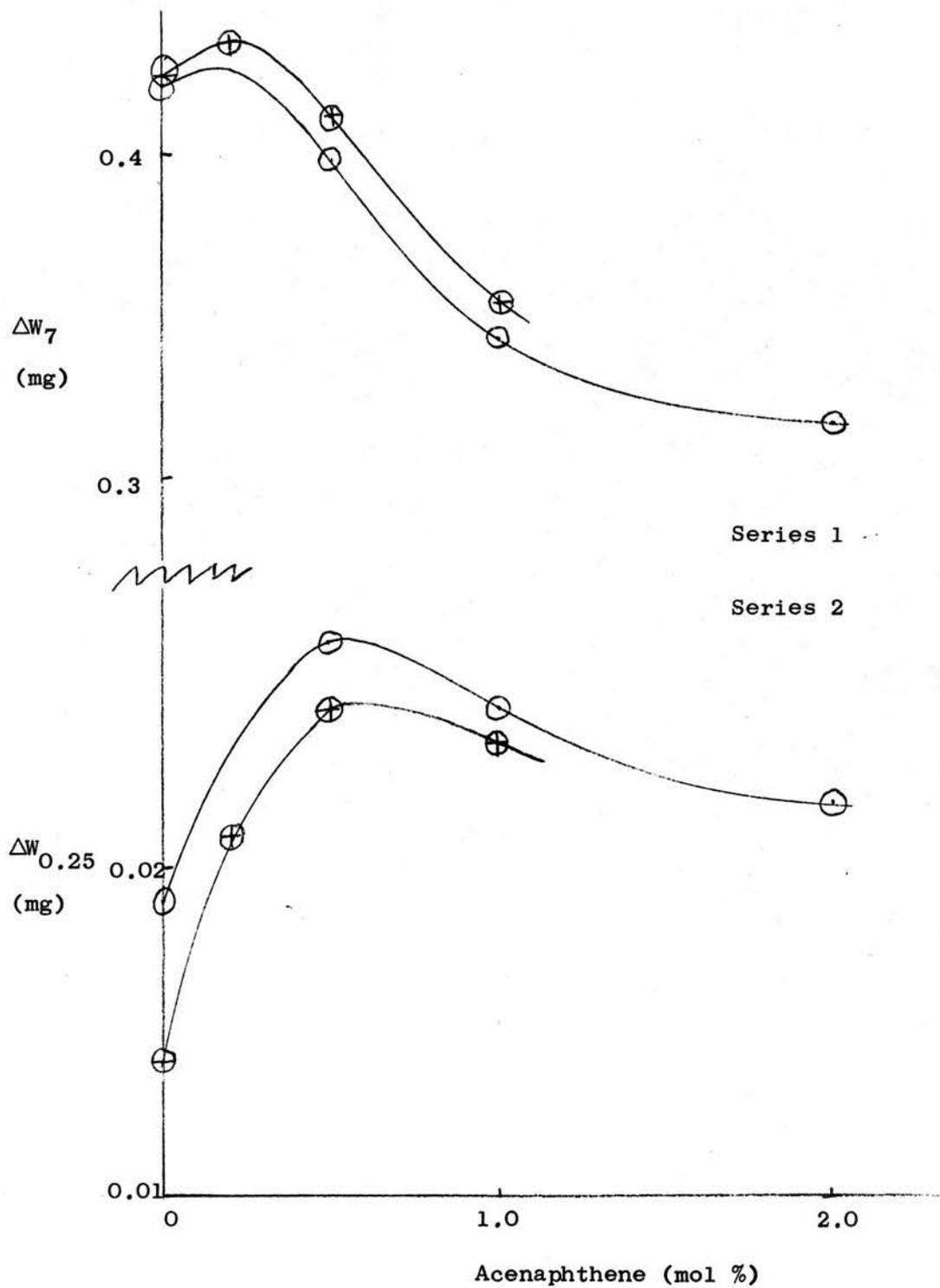
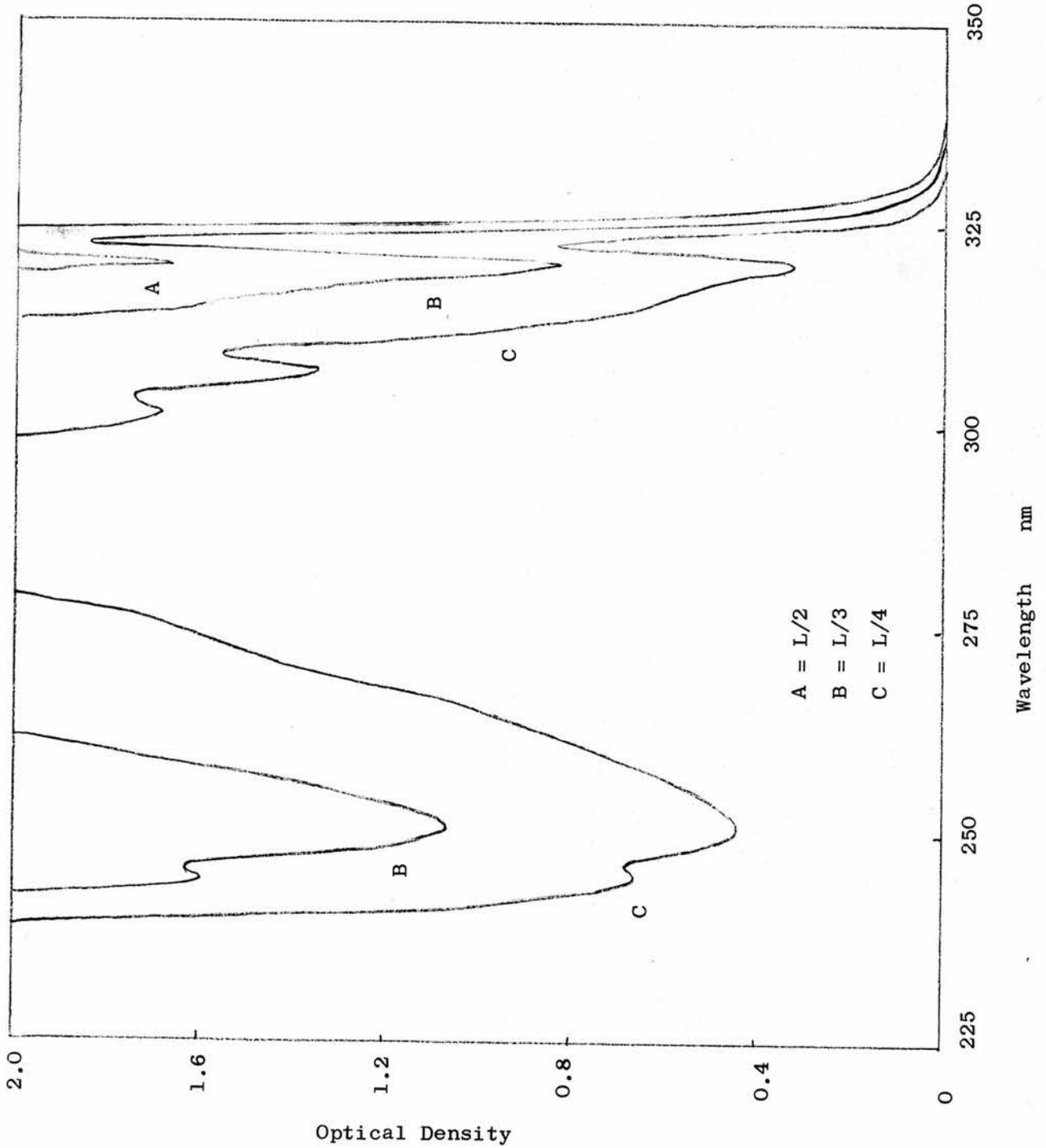


Figure 28

Ultraviolet spectra of acenaphthene loaded films before irradiation
(L/2,3,4 represent film containing 2.0, 1.0 and 0.5 mol % acenaphthene respectively)



irradiation of a film containing phenyl benzoate might help to elucidate the products of the irradiation of benzoyl peroxide loaded films. The ultraviolet spectrum of pure phenyl benzoate in methanol appears in Figure 29 and shows $\lambda_{\text{max}} = 230 \text{ nm}$ with an extinction coefficient of $14,000 \text{ l mol}^{-1} \text{ cm}^{-1}$.

A film containing 1 mole% phenyl benzoate was prepared and irradiated for seven hours at a light intensity of 1.03×10^{16} quanta $\text{cm}^{-2} \text{ s}^{-1}$. The weight of hydrogen chloride evolved in seven hours was 0.271 mg compared with a reference of 0.424 mg. A comparison with the data in Table 15 shows that phenyl benzoate is as effective a dehydrochlorination suppressor as benzoyl peroxide. The reaction was again initially faster than the reference.

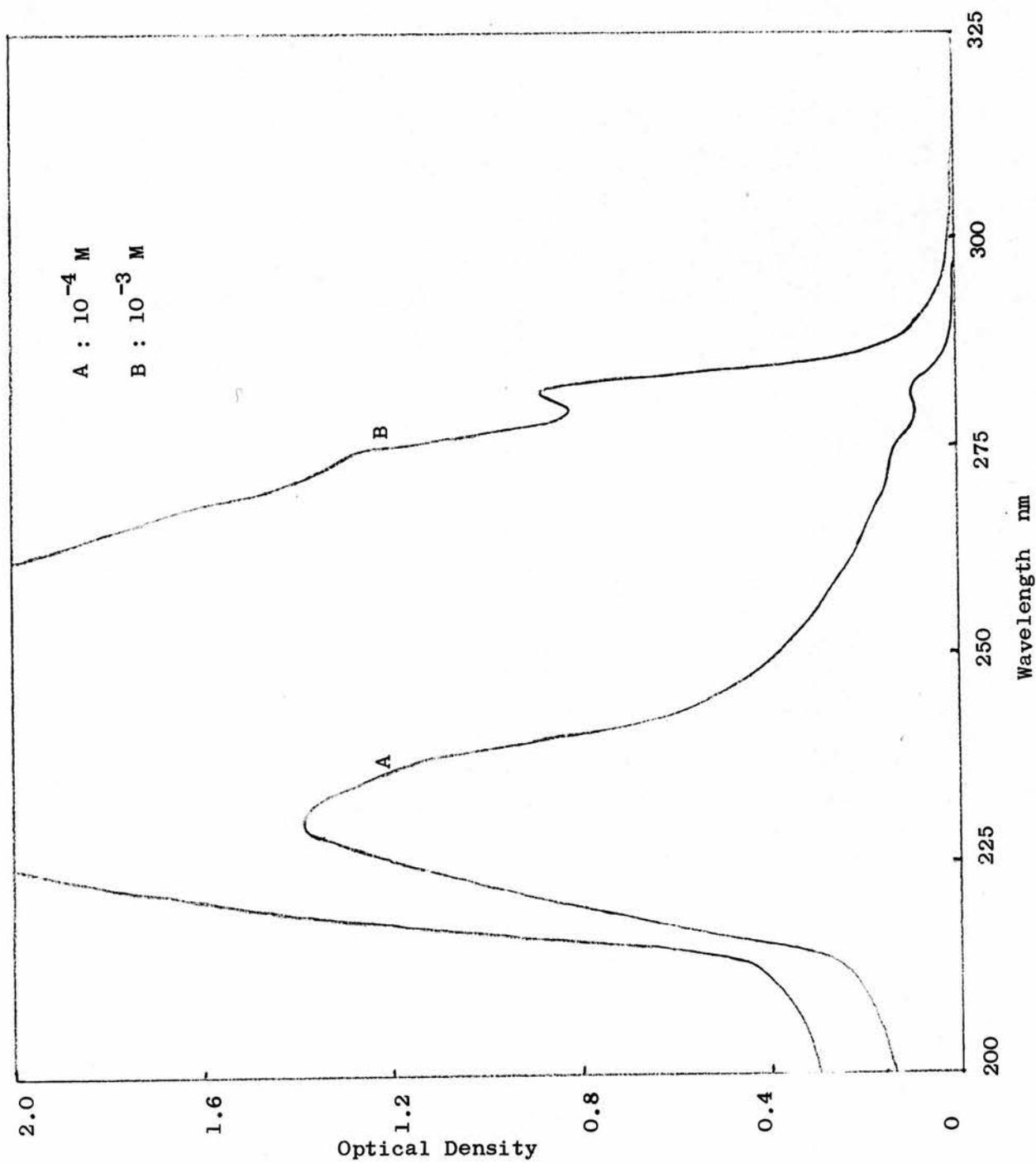
The ultraviolet spectrum of the film before irradiation showed a cut-off at 287 nm. The ultraviolet spectrum after irradiation was very similar to the one obtained for benzoyl peroxide loaded films, see Figure 23, except that the hump was at 335 nm instead of 325 nm. The optical density at the peak was 1.90 against the 1.36 for the benzoyl peroxide loaded films. The infra-red spectrum before irradiation showed a strong characteristic phenyl benzoate absorption at 1735 cm^{-1} , and a medium peak at 1590 cm^{-1} . After irradiation the intensity of these peaks was slightly reduced and a new weak peak appeared at 1620 cm^{-1} .

(e) Tetrahydrofuran

As tetrahydrofuran was present in all the film samples studied it was important to determine whether it could effect the degradation reaction. Samples containing different amounts of tetrahydrofuran were irradiated. This was achieved by altering the amount of drying the films received. It should be noted that a film

Figure 29

Ultraviolet spectrum of phenyl benzoate in methanol



which has received zero days drying in the oven has been about sixteen hours in the degradation apparatus, during which time some tetrahydrofuran could evaporate.

The samples were irradiated for seven hours at a light intensity of 1.24×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$ and their ΔW_7 values and drying times are shown in Table 22.

Table 22

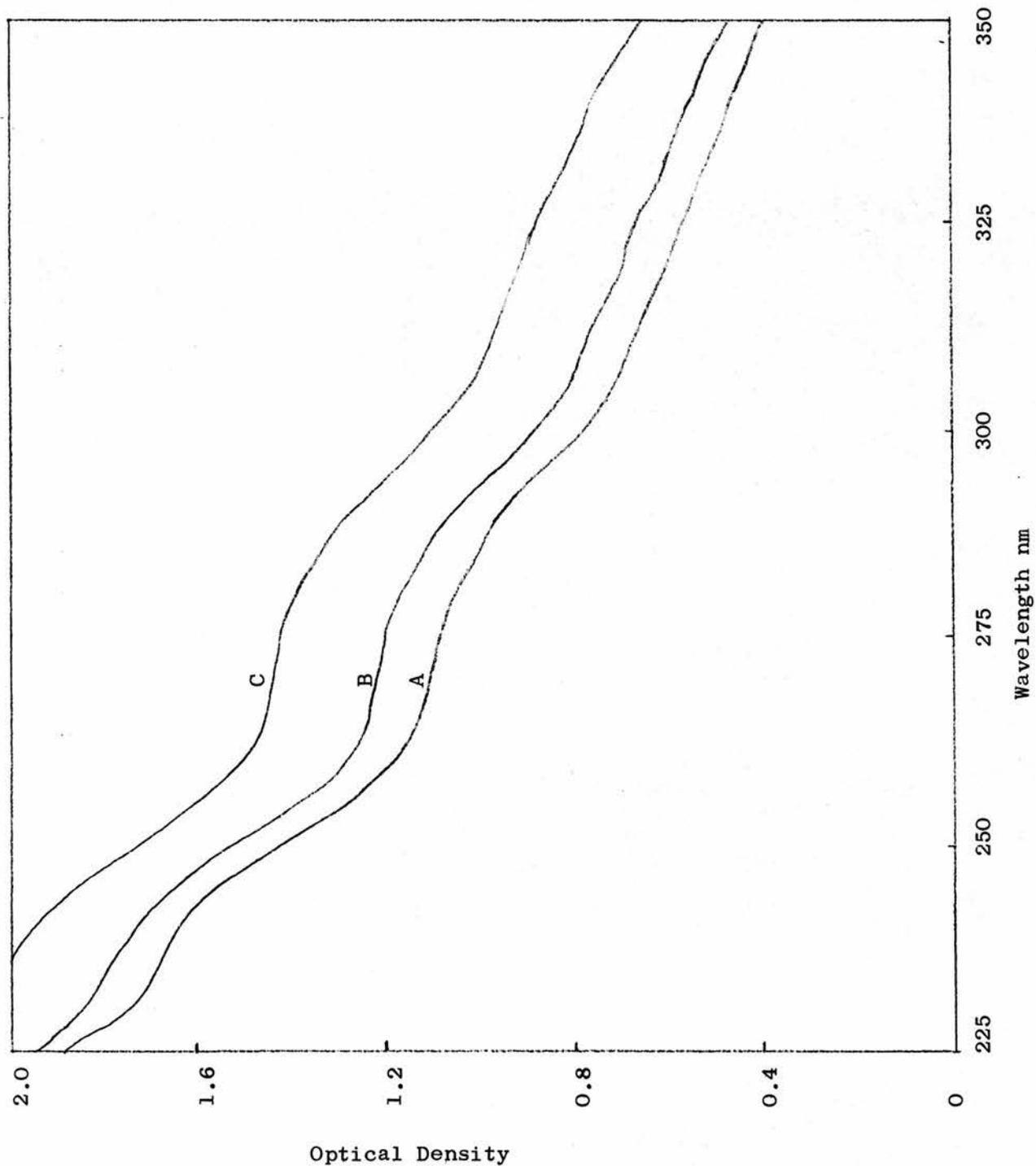
Sample	Drying Time (days)	ΔW_7 (mg)
A	0	0.458
B	1	0.454
C	7	0.458
D	17	0.454

The concentration of tetrahydrofuran present has no effect on the amount of hydrogen chloride evolved. The infra-red spectra of these films showed a broad peak at 1900 cm^{-1} due to tetrahydrofuran and this could be seen to be reduced by drying. The peak was not large enough however to permit quantitative measurements. Each film sample was weighed before irradiation to check the film thickness. However, as stated earlier, for any film casting the thickness was not perfectly uniform and the sample weight could vary by about 5% or up to nearly 10 mg. Any quantitative measurement of the amount of solvent present was therefore meaningless because of this large potential error.

The ultraviolet spectra of these films taken after irradiation showed that, although the same amount of dehydrochlorination had occurred, the area under the ultraviolet spectrum was less, the greater the tetrahydrofuran concentration. This is shown by the ultraviolet spectra of films A, B and C in Figure 30. Film D gave a spectrum

Figure 30

Ultraviolet spectra of degraded film samples containing different amounts of tetrahydrofuran (for significance of letter code see Table 22)



only slightly above Film C indicating that very little further tetrahydrofuran removal had occurred between 7-17 days.

(f) Thermal Treatment

Prior to being irradiated for seven hours, film samples, taken from the same cast film, were heated for one hour over a range of temperatures, using the apparatus described. A light intensity of 0.88×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$ was employed. Table 23 shows the temperature at which the samples were heated, the weight loss during heating, the ΔW_7 value for the photodegradation, and the optical density of the degraded films at 450 nm, OD_{450} .

Table 23

Film Sample	Heating Temperature ($^{\circ}\text{C}$)	Weight loss during heating (mg)	ΔW_7 (mg)	OD_{450}
1	Untreated	-	0.398	0.22
2	115	7.6	0.407	0.44
3	123	-	0.432	0.51
4	138	9.8	0.415	0.60
5	160	12.0	0.441	0.66
6	175	10.7	0.483	0.59

The ultraviolet spectra obtained after heating but before irradiation showed that no thermal degradation occurred until a temperature of 160°C had been reached. Thermal degradation did occur in samples 5 and 6 and comparison with photodegradation results suggests that the weight loss caused would have been < 0.1 mg. The large weight loss resulting from heating must have been due to loss of solvent, tetrahydrofuran.

The ultraviolet spectra obtained after irradiation show that thermally treated samples exhibited a shift in polyene distribution towards longer sequences. Samples 2-4 show a small increase in ΔW_7

but a large change in OD_{450} . The large increases in the ΔW_7 values only occurred when thermal degradation had taken place. The ultraviolet spectra of samples 1-5 are shown in Figure 31. Sample 6 for some unknown reason lost less solvent than sample 5 but the rough correlation between solvent loss and OD_{450} still exists.

4 Source Alterations.

As explained most experiments were conducted using the unfiltered medium pressure lamp. However different sources were used and the results obtained are now reported. They are divided into two sections - (a) experiments using a low pressure lamp and (b) experiments using a medium pressure lamp in conjunction with various filters.

(a) The Low Pressure Lamp

This source is approximately monochromatic⁶⁵, emitting light at a wavelength of 254 nm, and was used to compare the relative effectiveness as degraded agents for poly(vinyl chloride) of poly- and monochromatic sources.

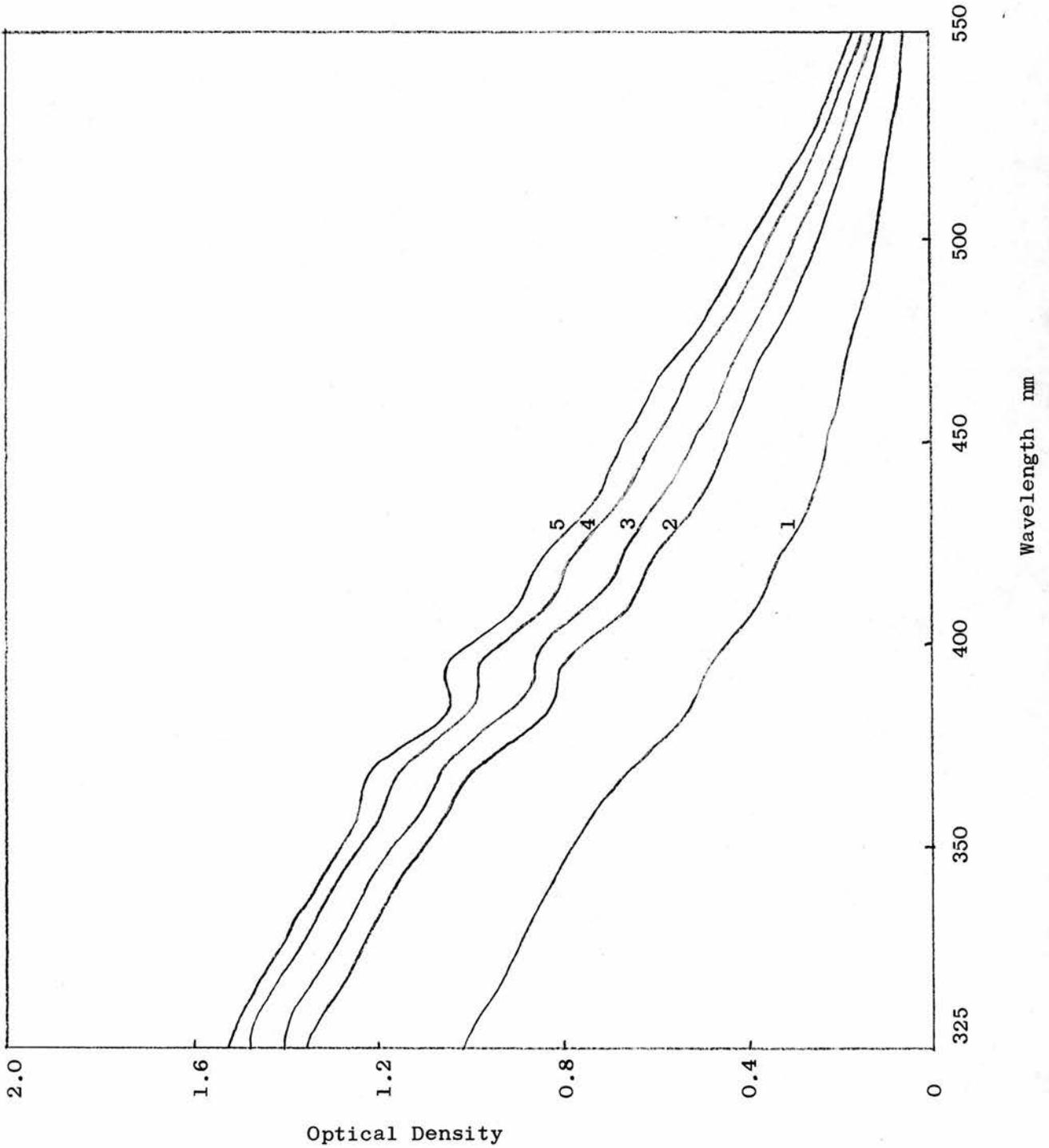
Film samples, from the same cast film, were irradiated for 30 hours at three different light intensities, and the results, including ΔW_7 and ΔW_{30} , are shown in Table 24. The results obtained for a run using the medium pressure lamp are also shown for comparative purposes.

Table 24

	I_0 (quanta $cm^{-2} s^{-1}$) $\times 10^{15}$	ΔW_7 (mg)	ΔW_{30} (mg)
Low Pressure	2.15	0.057	0.402
	3.20	0.084	0.569
	5.19	0.198	0.741
Medium Pressure	5.10	0.336	0.494

Figure 31

Ultraviolet spectra of film samples thermally treated, and then photodegraded (for significance of number code see Table 23)



The dehydrochlorination curves obtained were of the same general shape as for polychromatic degradation; that is the rate increases up to a maximum and then steadily falls off. In detail however there are considerable differences. The initiation time (time taken for dehydrochlorination to reach a measurable value) was larger and the inflection point was reached after a longer time, and at a higher ΔW value, in the monochromatic case. The dehydrochlorination curves for the mono- and polychromatic irradiations, at light intensities of 5.19 and 5.10×10^{15} quanta $\text{cm}^{-2} \text{s}^{-1}$ respectively, are shown in Figure 32 and illustrate these differences. It can be seen that, at the same light intensity, the monochromatic irradiation gives a much greater evolution of hydrogen chloride in 30 hours.

It had been found that films containing benzoyl peroxide or acenaphthene degraded less than a reference when subjected to polychromatic irradiation. Samples containing these additives were irradiated using the monochromatic source at an intensity of 3.2×10^{15} quanta $\text{cm}^{-2} \text{s}^{-1}$ and the sample details and results are shown in Table 25.

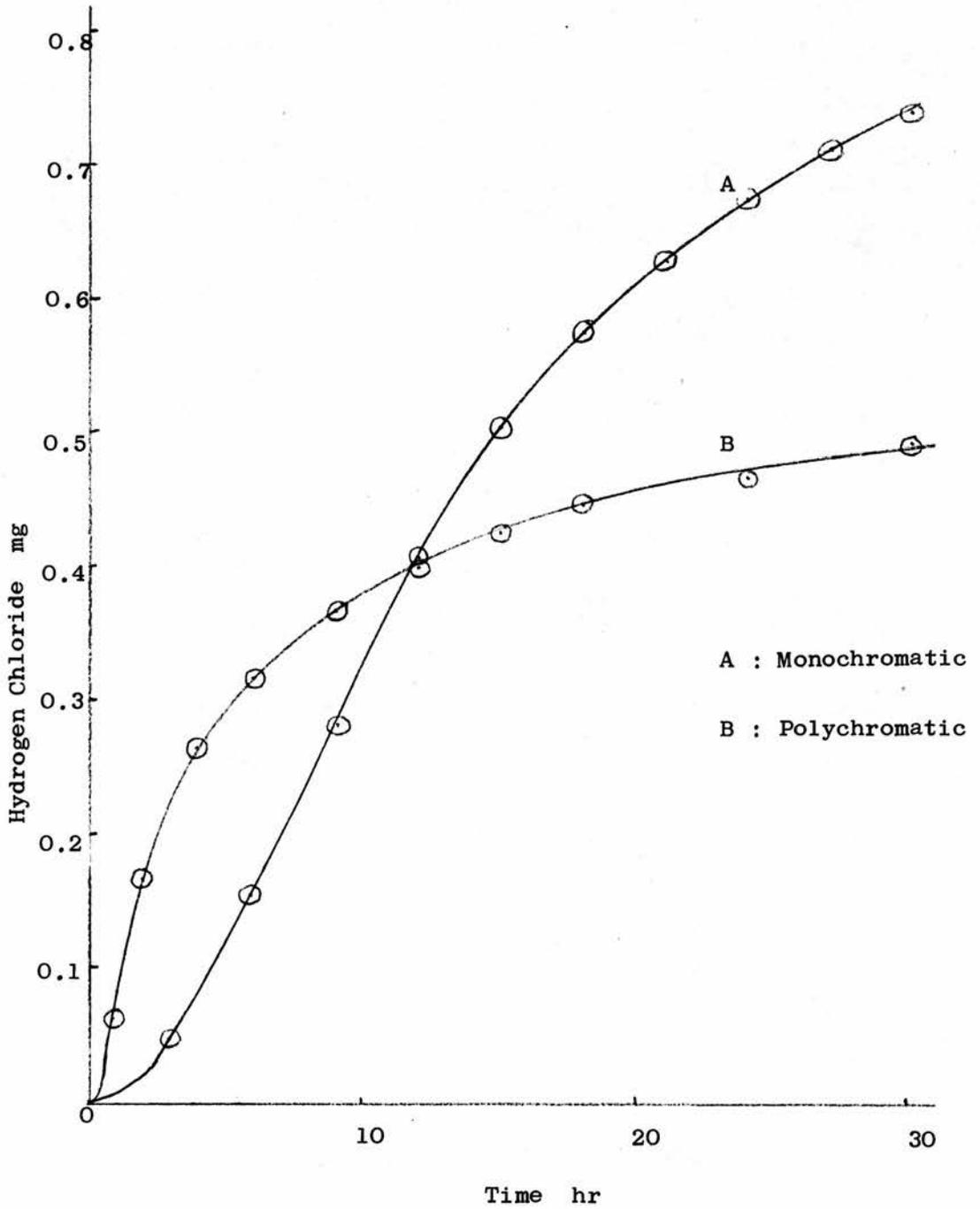
Table 25

Additive	Code	Mol %	ΔW_{30} (mg)
-	-	-	0.569
Benzoyl peroxide	P/8	0.24	0.225
Acenaphthene	L/3	1.00	0.370

The same effect occurs here as for polychromatic irradiation. As before, the loaded films start off faster than the reference, but exhibit a greater proportional retardation, especially the benzoyl peroxide loaded film.

Figure 32

Dehydrochlorination curves for film samples irradiated at the same intensity using low and medium pressure lamps, emitting mono- and polychromatic irradiation



(b) Filters

When film samples were irradiated for seven hours through a plate-glass filter, cut-off 325 nm, or a pyrex filter, cut-off 295 nm, no degradation was observed. The ultraviolet spectra of the samples before and after irradiation were identical.

Films were next irradiated through the solution filter described in Chapter 2. This filter transmitted light in the region 266-370 nm. A sample was irradiated for seven hours through this filter at a light intensity of 2.21×10^{15} quanta $\text{cm}^{-2} \text{s}^{-1}$. The amount of hydrogen chloride evolved in that time was too small to be recorded by the 'Combi-titrator'. The ultraviolet spectra of the sample recorded before and after irradiation showed that degradation had occurred but that it was very slight indeed. The change in optical density at 275 nm was about 0.02, equivalent to the change brought about by unfiltered light intensity of 1.24×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$ in about one minute.

Benzoyl peroxide loaded films absorb strongly in the region 266-287 nm and therefore might be expected to degraded under these conditions. Film P/9, containing 1.25 mol % benzoyl peroxide, was irradiated through the solution filter. Degradation did occur, though not to a very large extent, and it ceased after about $2\frac{1}{2}$ hours when $\Delta W = 0.057$ mg.

By increasing the arc-to-sample distance to 70 cm a comparable unfiltered light intensity of 1.47×10^{15} quanta $\text{cm}^{-2} \text{s}^{-1}$ was obtained (i.e. all wavelengths present). A sample irradiated at this intensity gave a normal dehydrochlorination curve and $\Delta W_7 = 0.176$ mg.

The ultraviolet and infra-red spectra of the benzoyl peroxide loaded film showed the same peaks after irradiation as were obtained after unfiltered irradiation.

It was next considered possible that a film already degraded polychromatically might further degrade when irradiated through the solution filter. A sample was irradiated for one hour at an unfiltered light intensity of 2.03×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$. The system was kept closed and four hours allowed for the hydrogen chloride present in the system to be swept clear. The sample was then irradiated through the solution filter for five hours, during which time it evolved only about 0.007 mg hydrogen chloride. However marked changes were observed in the ultraviolet and visible spectra of this sample. Figure 33 shows the spectra taken after polychromatic irradiation (1 hr) and after further filtered irradiation (5 hr). It can be seen that, after the filtered irradiation, there is a reduction in the optical density in the 240-370 nm region, accompanied by a slight increase below 250 nm and above 370 nm.

5 Spectral Data.

This section is concerned with the extra information that can be derived from a close study of the ultraviolet and visible spectra. Firstly to understand the results it is necessary to tabulate the λ_{max} and ϵ values for the polyenes produced by degradation, and they are shown in Table 25. These values were arrived at by averaging values in the literature for degraded poly(vinyl chloride) and various model compounds^{9,27,49-56}.

The ϵ values in particular are very speculative. It has however been shown that ϵ is proportional to n . The polyenes with $n > 4$ all show four peaks and λ_{max} for the most intense, usually the longest wavelength, peak is shown below. All these peaks have been shown to

Figure 33

Ultraviolet spectra of a film irradiated polychromatically for one hour, and through the solution filter for a further five hours

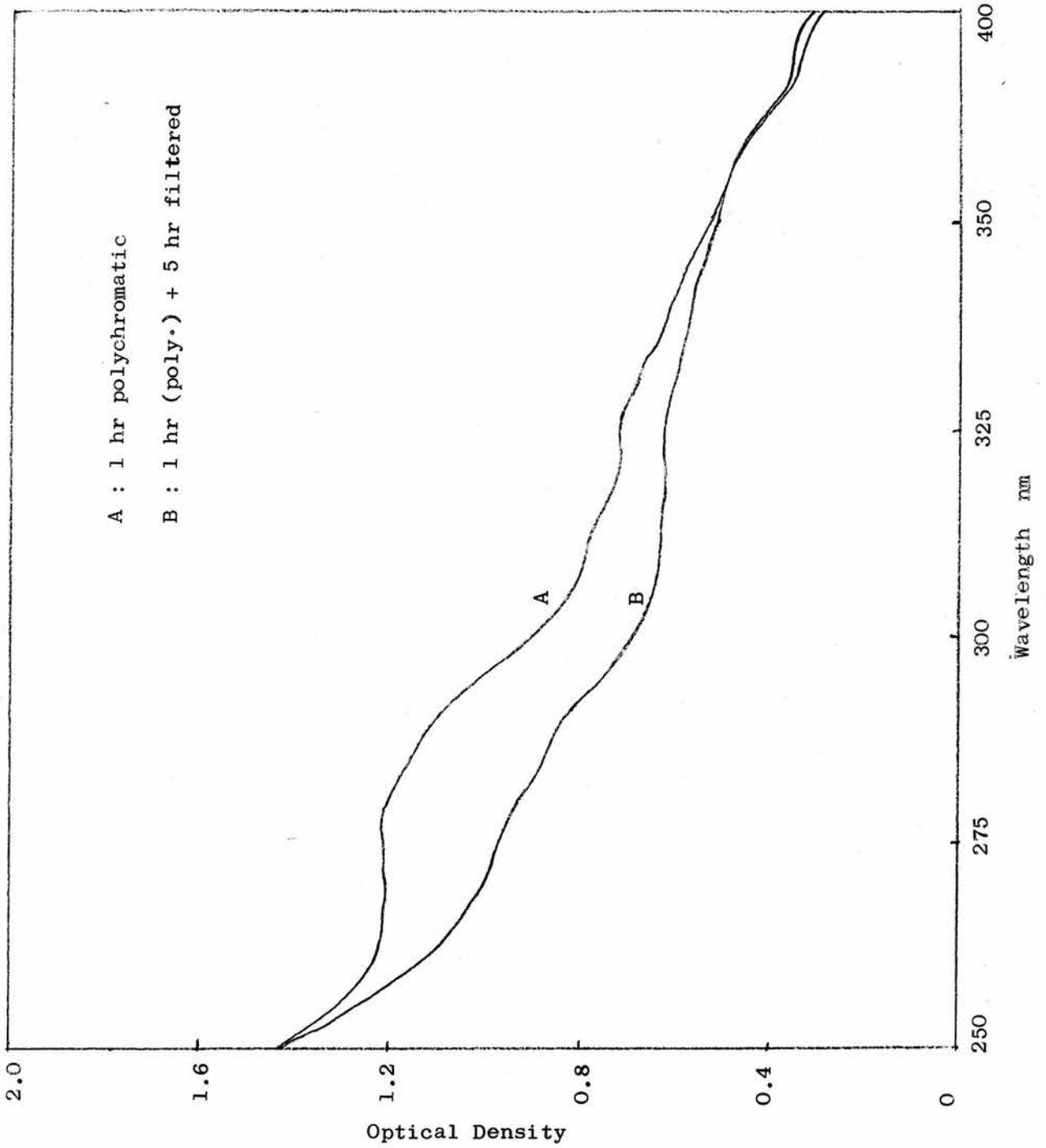


Table 26

n	λ_{max} (nm)	ϵ (l mol ⁻¹ cm ⁻¹)
1	< 200	-
2	240	20,000
3	278	30,000
4	305	40,000
5	325	50,000
6	360	60,000
7	390	70,000
8	410	80,000
9	430	90,000
10	450	-
11	470	-
16	500	200,000 ?

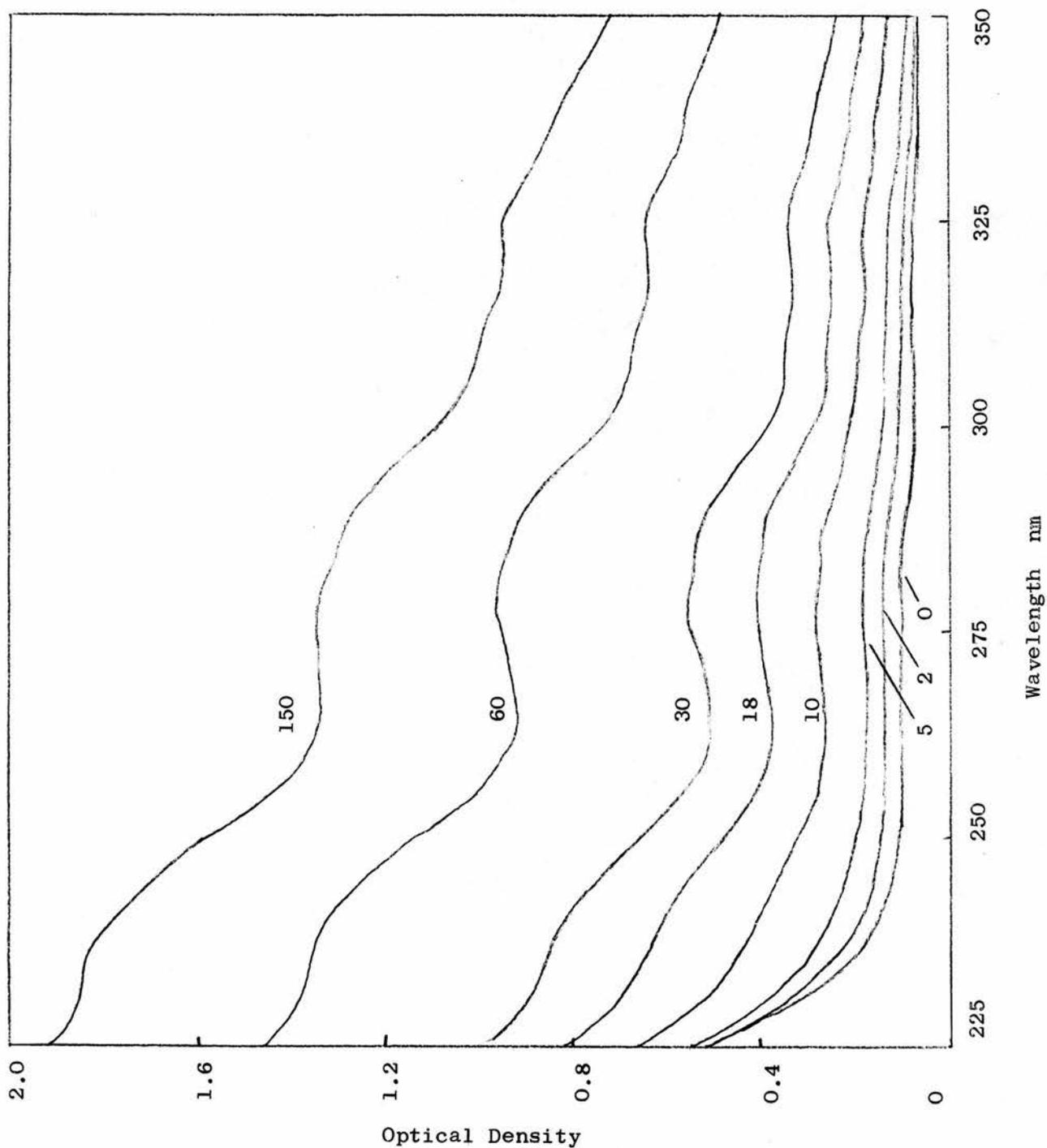
obey the Lewis-Calvin relationship, $\lambda^2 = kn$, up to about $n = 7$. After that there is a fall off in λ ^{50,54,55}.

Spectra have been obtained after successive time intervals using the cell described. A series of spectra obtained by irradiating a standard sample for $2\frac{1}{2}$ hours at a light intensity of 1.24×10^{16} quanta cm⁻² s⁻¹ are shown in Figure 34. Other films made from different polymer samples have been examined this way. Film P/5 (JLB 1027) and film P/7 (JLB 1029) gave identical spectra to those shown in Figure 34. Films P/2, P/3 and P/9 containing varying amounts of benzoyl peroxide gave a series of spectra showing the build up of the large hump at 325 nm discussed earlier (page 59). The series obtained for film P/3 is shown in Figure 35.

A standard sample was also irradiated in a static atmosphere by keeping the taps shown in Figure 7 shut. This permitted a build up of evolved hydrogen chloride. Comparison with Figure 34 shows that the reaction was suppressed. The optical densities at 278 nm after 30, 60 and 150 minutes were 0.48, 0.70 and 1.16 respectively against 0.55, 0.96 and 1.35 for the sample continuously flushed

Figure 34

Ultraviolet spectra of a film sample irradiated for 0, 2, 5, 10, 18, 30, 60 and 150 minutes



with nitrogen. In a further experiment a sample was irradiated in an atmosphere of hydrogen chloride with the taps shut. This sample gave optical densities of 0.23, 0.30 and 0.41 after 30, 60 and 150 minutes irradiation. Clearly the reaction was severely suppressed.

A series of spectra was also obtained using the low pressure lamp at a light intensity of 5.19×10^{15} quanta $\text{cm}^{-2} \text{s}^{-1}$. These are shown in Figure 36 and indicate that there is a similar polyene distribution to that obtained in the medium pressure case. This is confirmed by the calculation shown below.

The build up of polyenes of a given length can be demonstrated graphically. A series of spectra were obtained from the irradiation of a standard sample, using the medium pressure lamp, and the change in optical density at 240, 278, 325, 390 and 470 nm, corresponding to absorption by polyenes with $n = 2, 3, 5, 7$ and 11 , plotted against time up to seven hours. These plots are shown in Figure 37 and are similar in shape to the overall dehydrochlorination curve.

These spectra can be examined further to give an approximation to the polyene distribution in the film. Consider the absorptions at 278, 325, 390 and 430 nm caused by polyenes of length 3, 5, 7 and 9 double bonds. The change in the optical density, OD, after a given time of irradiation, from the OD at $t = 0$, can be found from the spectrum taken after that time. Now $OD = \sum_n \epsilon_n C_n d$, and as d is constant and $\epsilon_n = n \epsilon_g$ (where ϵ_n and C_n are the extinction coefficient and concentration of a polyene length n , and ϵ_g is a constant), then $C_n = \frac{OD}{n \cdot \text{constant}}$. The relative concentration of the polyenes can now be obtained by dividing the change in optical density at a given wavelength, ΔOD , by the appropriate n , and then dividing throughout by the values obtained for $n = 9$, i.e. C_9 , this being the smallest C value. The results calculated using the spectra discussed above are shown in Table 27. C represents relative concentrations.

Figure 36

Ultraviolet spectra of a film sample monochromatically irradiated using the low pressure lamp for 0, 2, 4, 6.7, 11.5, 19.25, 26.25, 35.25 and 51.8 hours

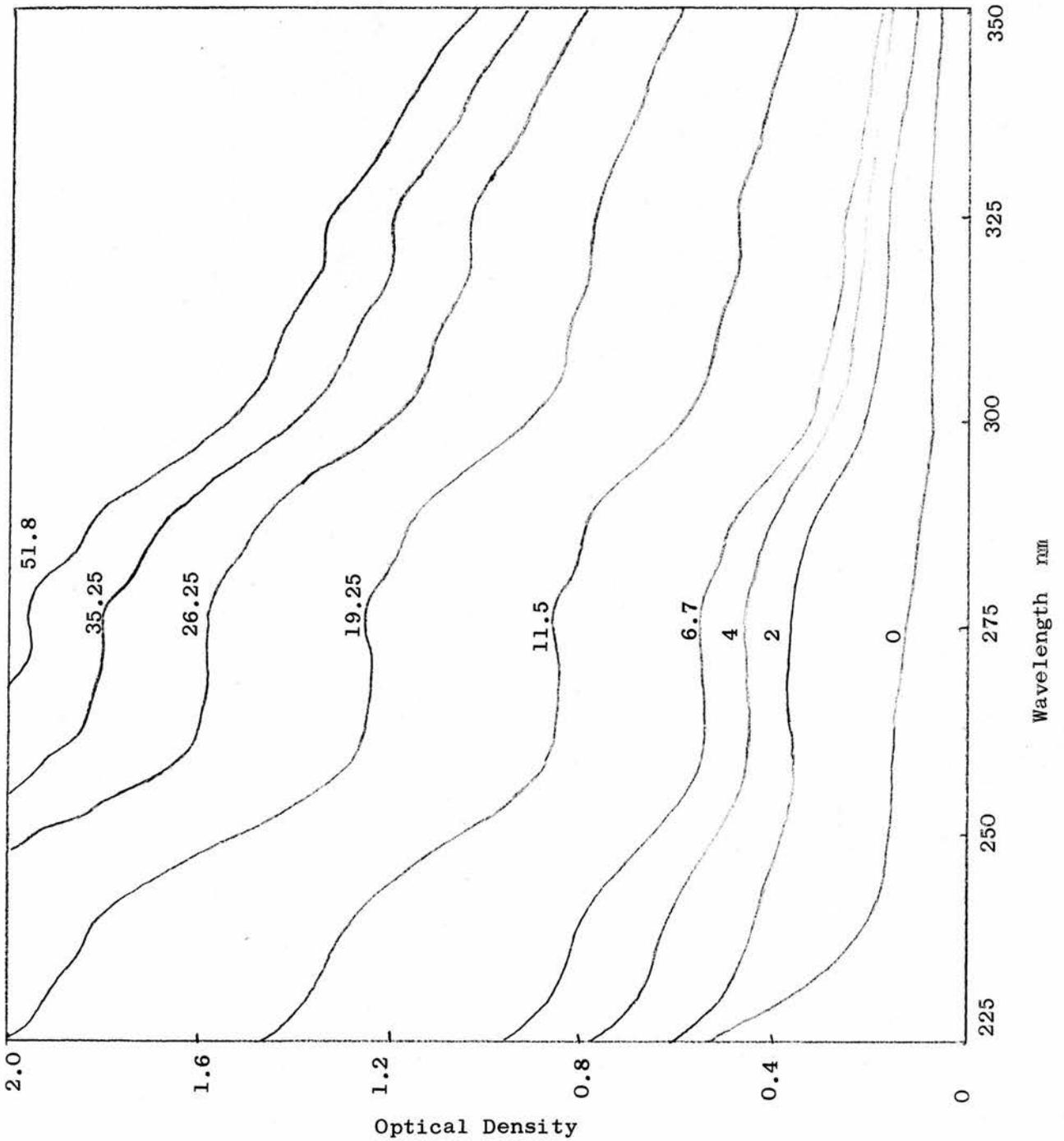


Figure 37

Plots of OD_{λ} versus time (λ is shown on the curve)

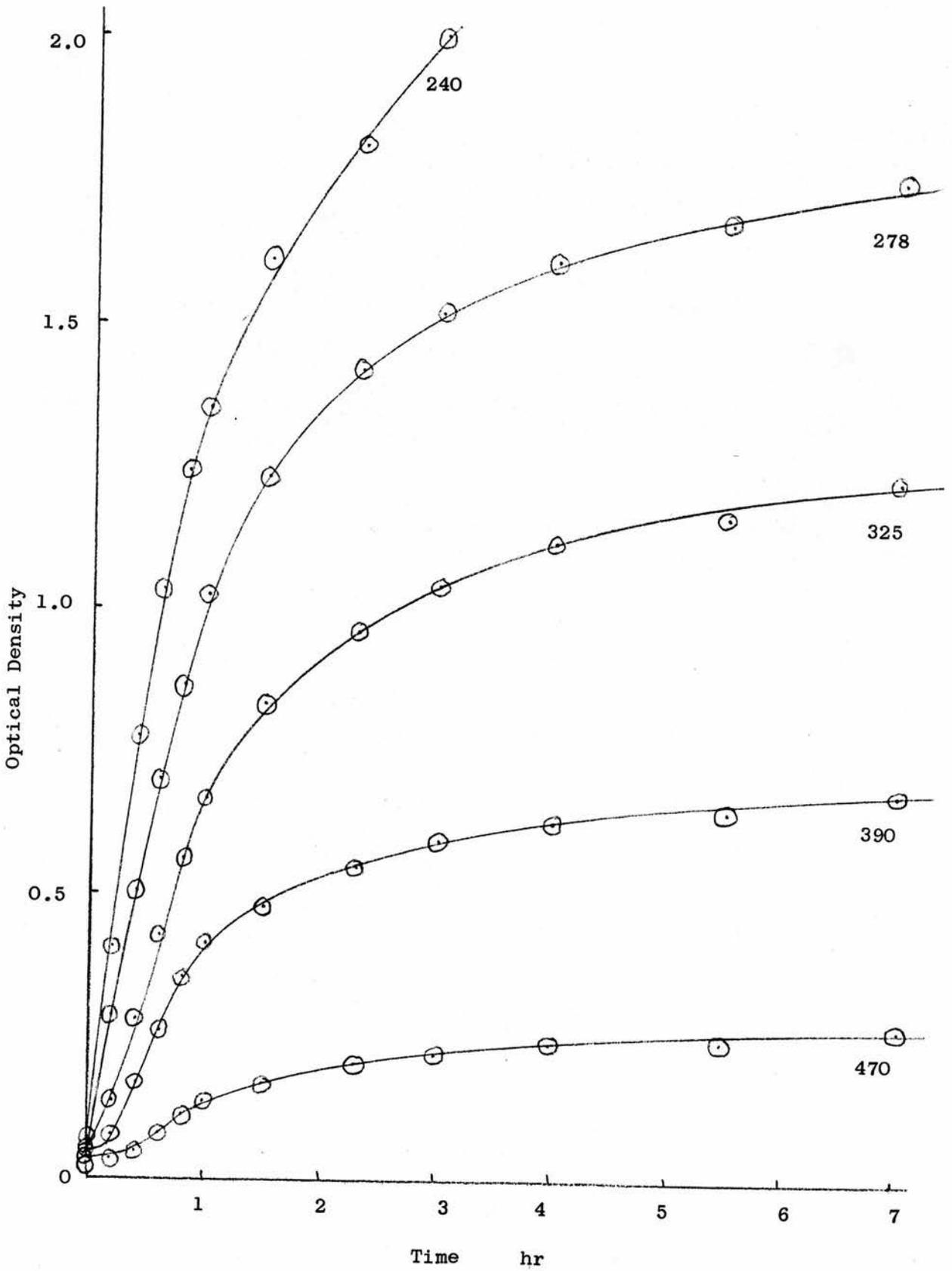


Table 27

t (hr)	ΔOD_{278}	C_3	C_3/C_9	ΔOD_{325}	C_5	C_5/C_9	ΔOD_{390}	C_7	C_7/C_9	ΔOD_{430}	C_9	C_9/C_9
0.2	0.230	77	77.0	0.110	22	22.00	0.035	5	5.00	0.010	1	1.00
0.4	0.445	148	24.67	0.255	51	8.50	0.125	18	3.00	0.055	6	1.00
0.6	0.640	213	16.38	0.400	80	6.15	0.220	31	2.38	0.115	13	1.00
0.8	0.805	268	13.40	0.535	107	5.35	0.310	44	2.20	0.180	20	1.00
1.0	0.965	322	13.41	0.645	129	5.38	0.370	53	2.21	0.215	24	1.00
1.25	1.145	382	13.64	0.780	156	5.57	0.410	59	2.11	0.255	28	1.00
1.5	1.175	392	13.52	0.805	161	5.55	0.435	62	2.14	0.265	29	1.00
2.3	1.360	453	13.32	0.930	186	5.47	0.505	72	2.12	0.305	34	1.00
3.0	1.465	488	13.19	1.010	202	5.46	0.550	79	2.14	0.335	37	1.00
4.0	1.555	518	12.95	1.085	217	5.43	0.580	83	2.08	0.360	40	1.00
5.5	1.670	540	13.17	1.130	226	5.51	0.595	85	2.07	0.365	41	1.00
7.0	1.710	570	13.26	1.195	239	5.56	0.635	91	2.12	0.390	43	1.00

It can be seen that after about one hour relative concentrations C_3/C_9 , C_5/C_9 , C_7/C_9 and C_9/C_9 are constant. Averaging the values obtained after one hour a mean $C_3:C_5:C_7:C_9$ ratio of 13.3:5.5:2.1:1 is obtained.

The results obtained using the data shown in Figure 36, where the low pressure lamp was used, are shown in Table 28.

Table 28

t (hr)	ΔOD_{278}	C_3	C_3/C_9	ΔOD_{325}	C_5	C_5/C_9	ΔOD_{390}	C_7	C_7/C_9	ΔOD_{430}	C_9	C_9/C_9
6.67	0.448	148	37.00	0.190	38	9.50	0.080	11	2.75	0.035	4	1.00
11.50	0.760	253	18.07	0.415	83	5.93	0.225	32	2.29	0.125	14	1.00
19.25	1.140	380	13.57	0.720	144	5.14	0.410	59	2.11	0.255	28	1.00
26.25	1.480	493	13.32	0.970	194	5.24	0.550	79	2.14	0.335	37	1.00
35.25	1.700	567	12.60	1.130	226	5.02	0.640	91	2.02	0.405	45	1.00
51.84	1.850	617	11.87	1.260	252	4.85	0.725	104	2.00	0.470	52	1.00

In this case a similar distribution is obtained, although after 50 hours it is still shifting in favour of longer sequences.

The ultraviolet spectra of degraded films can also, within limits, be used to measure the amount of dehydrochlorination that has occurred. There exists a relationship between the weight loss in a given time, ΔW_t , and the optical density at a given wavelength OD_λ , or the area under the spectrum, A, recorded after that time. This relationship only holds for one film sample. It has already been seen in section 3(e) that, for example, different amounts of tetrahydrofuran in a film will lead to different spectra for the same weight loss.

This relationship can be illustrated by considering the data from section 2(b), and in particular Table 11. Samples, taken from one cast film, were irradiated at different intensities to give ΔW_7 values of 0.538, 0.454, 0.370 and 0.305 mg. The areas under the ultraviolet spectra between 275-700 nm were 353, 313, 287 and 277 units respectively, and the OD_{325} values 1.45, 1.29, 1.20 and 1.11 respectively. The curves obtained when ΔW_7 was plotted against OD_{325} or A showed that they are related. Similar curves can be obtained from plots using OD at any wavelength or A between any two wavelengths. In this case as the highest intensity spectrum exhibited a cut-off at 275 nm this figure was taken as the lower limit for the area calculated.

The same principles can be applied to the data from a series of spectra obtained for one run. For example Table 29 shows the weight of hydrogen chloride evolved after a given time, ΔW_t , (taken from the run at $I_0 = 2.83 \times 10^{16}$ quanta $\text{cm}^{-2} \text{s}^{-1}$ in Table 11), the optical densities at 275 and 325 nm, and the areas under the spectra between 250-450 nm, taken from a series of spectra obtained at the same light intensity.

Table 29

t (min)	ΔW (mg)	OD ₂₇₈	OD ₃₂₅	A
10	0.028	0.68	0.44	121
15	0.069	0.90	0.61	178
20	0.111	1.08	0.745	219
30	0.178	1.28	0.900	264
45	0.240	1.47	1.040	305
60	0.283	1.575	1.115	329
90	0.345	1.70	1.210	356
120	0.385	1.78	1.260	373

Plots of ΔW versus OD₂₇₈ and OD₃₂₅ are shown in Figure 38. The curves obtained are very similar to the one obtained for a plot of ΔW versus A.

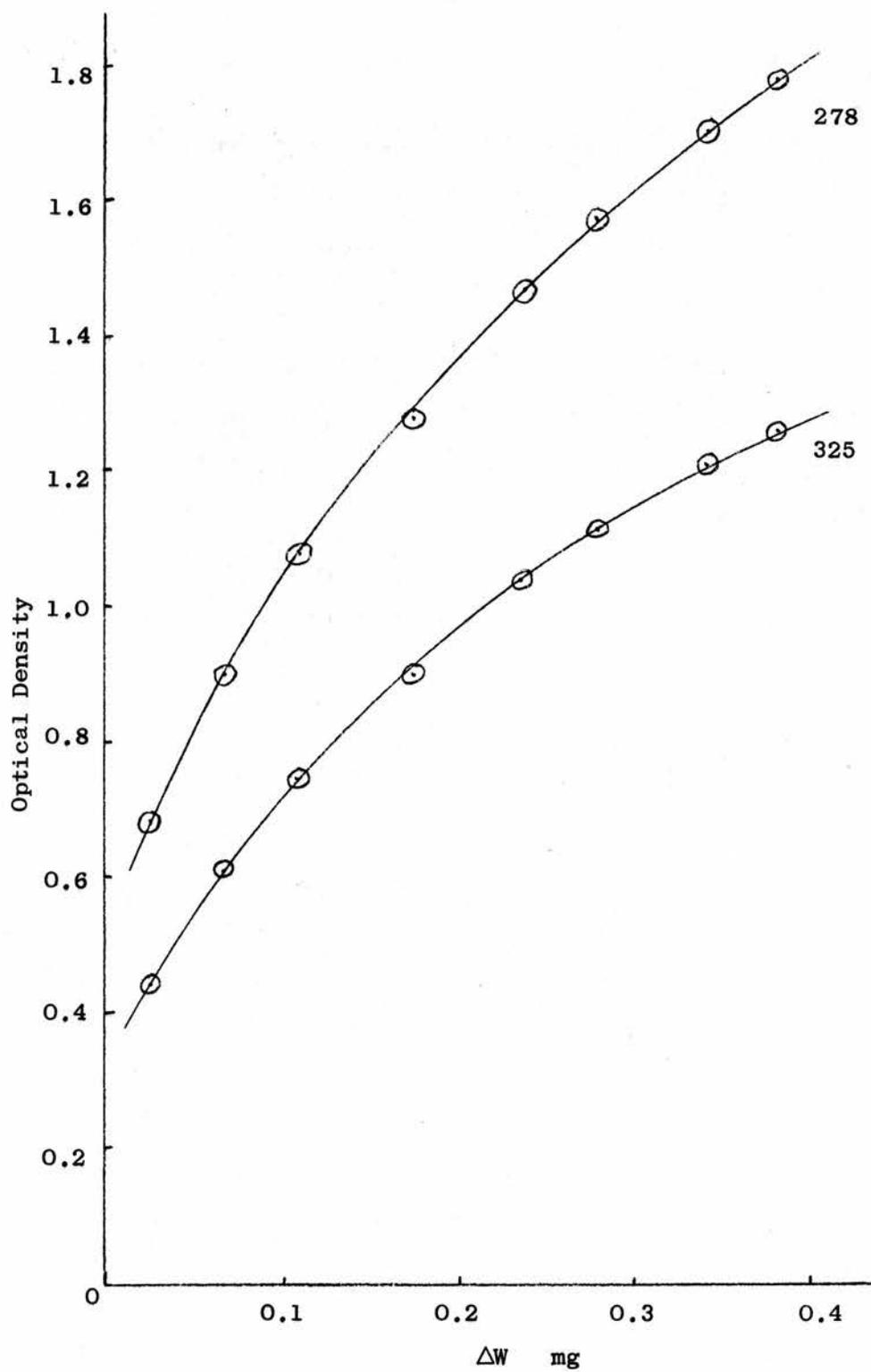
Lastly this relationship will still hold for results obtained using the same sample, but different lamps - medium and low pressure. That is, after the same weight loss, the spectra obtained for two samples irradiated using the two lamps are the same. This confirms what has already been stated, that the low and medium pressure lamps give approximately the same polyene distribution.

6 Stopping and Starting Reactions.

A number of experiments have been conducted to determine the effect of irradiating a sample for a period of time, stopping the irradiation, and then restarting it later. This procedure will give an indication of the occurrence of a dark reaction. It has already been seen that there are two ways of following degradation; monitoring the evolved hydrogen chloride and following changes in the ultraviolet spectra.

Figure 38

Plots of ΔW versus optical density at 278 and 325 nm



The following experiments were conducted using a light intensity of 3.57×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$. A sample was irradiated for two hours, during which time 0.447 mg hydrogen chloride were evolved, and irradiation stopped. During the next 2 hours a further 0.046 mg hydrogen chloride were trapped. The rate of dehydrochlorination was 0.087 mg hr^{-1} when irradiation was stopped and 0.056 mg hr^{-1} when it was subsequently restarted. The reaction proceeded as normal after restarting. Another sample was irradiated for four hours, evolving 0.551 mg, irradiation stopped and a further 0.014 trapped during the next $2\frac{1}{2}$ hours. These results suggest that either a dark reaction was occurring or there was a delay in trapping the evolved hydrogen chloride.

A sample was irradiated for one hour and its ultraviolet spectrum recorded. Another sample was irradiated for one hour, the irradiation stopped, and the system flushed with nitrogen for a further six hours. Extra hydrogen chloride was collected but the spectrum then recorded was identical to the one recorded immediately after irradiation ceased. The extra hydrogen chloride trapped during further flushing must have been produced by photochemical reaction during the first hour. Similarly the hydrogen chloride collected after two and four hours irradiation described above was the result of a trapping delay. The amount of hydrogen chloride recorded depended on the rate of reaction when irradiation ceased.

These results mean that during the early part of the reaction dehydrochlorination was in fact faster than observed. When the reaction started to slow down dehydrochlorination was then slower than observed because hydrogen chloride formed earlier was only just being collected. The apparent dehydrochlorination rate of 0.087 mg hr^{-1} when irradiation was stopped after two hours was therefore higher than

the true value. As it has been shown that no dark reaction took place, the true rate was probably close to the rate at which the reaction restarted, 0.056 mg hr^{-1} (this value is probably a little low for the same reasons). These effects are exaggerated by the high light intensity used and the resulting high initial rate of dehydrochlorination.

7 Oxygen.

The role of oxygen in the photodegradation of poly(vinyl chloride) has not been studied in great detail. However a few experiments have been conducted and these are reported in two parts - (a) dehydrochlorination measurements and (b) spectral studies.

(a) Dehydrochlorination Measurements

Samples, taken from the same cast film, were irradiated for seven hours at light intensities of 2.83, 1.24, 0.71 and 0.43 quanta $\text{cm}^{-2} \text{s}^{-1}$ in an atmosphere of oxygen, and gave ΔW_7 values of 1.278, 0.974, 0.739 and 0.523 mg respectively. The dehydrochlorination curves obtained, and a reference curve obtained at $I_0 = 2.83 \times 10^{16}$ quanta $\text{cm}^{-2} \text{s}^{-1}$ in a nitrogen atmosphere, are shown in Figure 39. Comparison with the results in Tables 11 and 12 (Section 2(b)) shows that ΔW_7 at all intensities has approximately doubled, the increase being greater the higher the light intensity. However, although it slows down, the initial reaction was faster in nitrogen than oxygen.

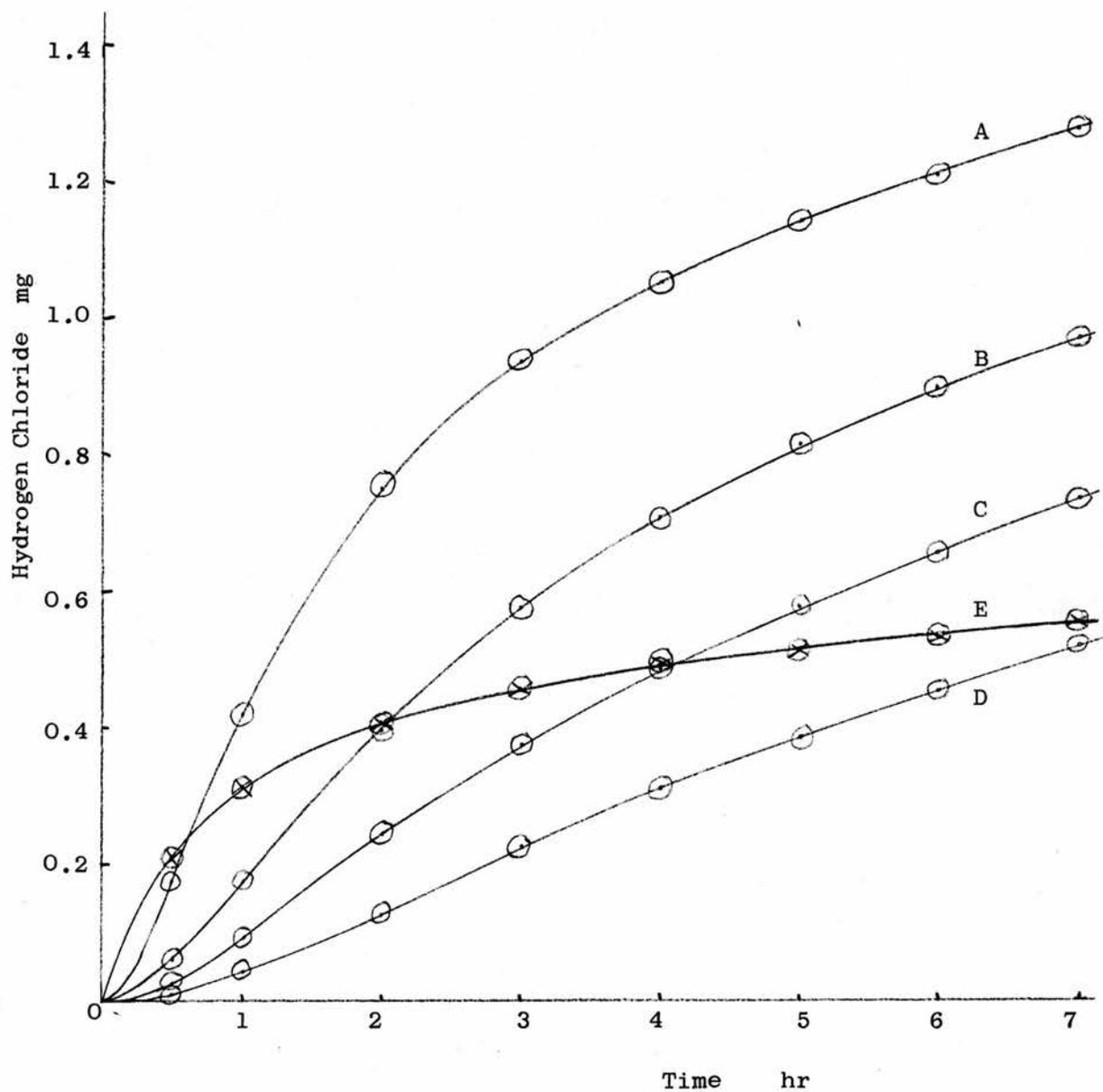
(b) Spectral Measurements

Oxygen caused bleaching. A comparison of the spectra obtained for films irradiated at a light intensity of 2.83×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$ showed $\text{OD}_{325} = 1.45$ in nitrogen and 0.93 in oxygen although the relative ΔW_7 values were 0.538 and 1.278 mg.

Figure 39

Dehydrochlorination curves for samples irradiated for seven hours - (a)
 Curves A → D in oxygen (b) Curve E in nitrogen - at light
 intensities, I_0 (quanta $\text{cm}^{-2} \text{s}^{-1} \times 10^{16}$) of:-

A : $I_0 = 2.83$
 B : $I_0 = 1.24$
 C : $I_0 = 0.71$
 D : $I_0 = 0.43$
 E : $I_0 = 2.83$



A series of spectra, similar to those shown in Figure 34 obtained in nitrogen, were recorded in oxygen at the same light intensity of 1.24×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$. The bleaching effect was clearly visible and OD_{275} values of 0.23, 0.32 and 0.43 were recorded after 15, 30 and 60 minutes against 0.36, 0.55 and 0.96 in nitrogen. The same sort of results were obtained using the low pressure lamp.

The polyene distribution in a sample degraded in oxygen was calculated as described on page 75 and the results are shown in Table 30. Because OD_{430} is so small the concentration of polyenes with $n = 7$ is taken as one for comparative reasons.

Table 30

t (min)	ΔOD_{278}	C_3	C_3/C_9	ΔOD_{325}	C_5	C_5/C_9	ΔOD_{390}	C_7	C_7/C_9	ΔOD_{430}	C_9	C_9/C_9
15	0.115	38	38.0	0.050	10	10.0	0.010	1	1.00	0	0	
30	0.200	67	33.5	0.075	15	7.5	0.015	2	1.00	0	0	
60	0.310	103	25.75	0.110	22	5.5	0.030	4	1.00	0.005	0.5	
120	0.450	150	25.00	0.160	32	5.33	0.045	6	1.00	0.010	1	

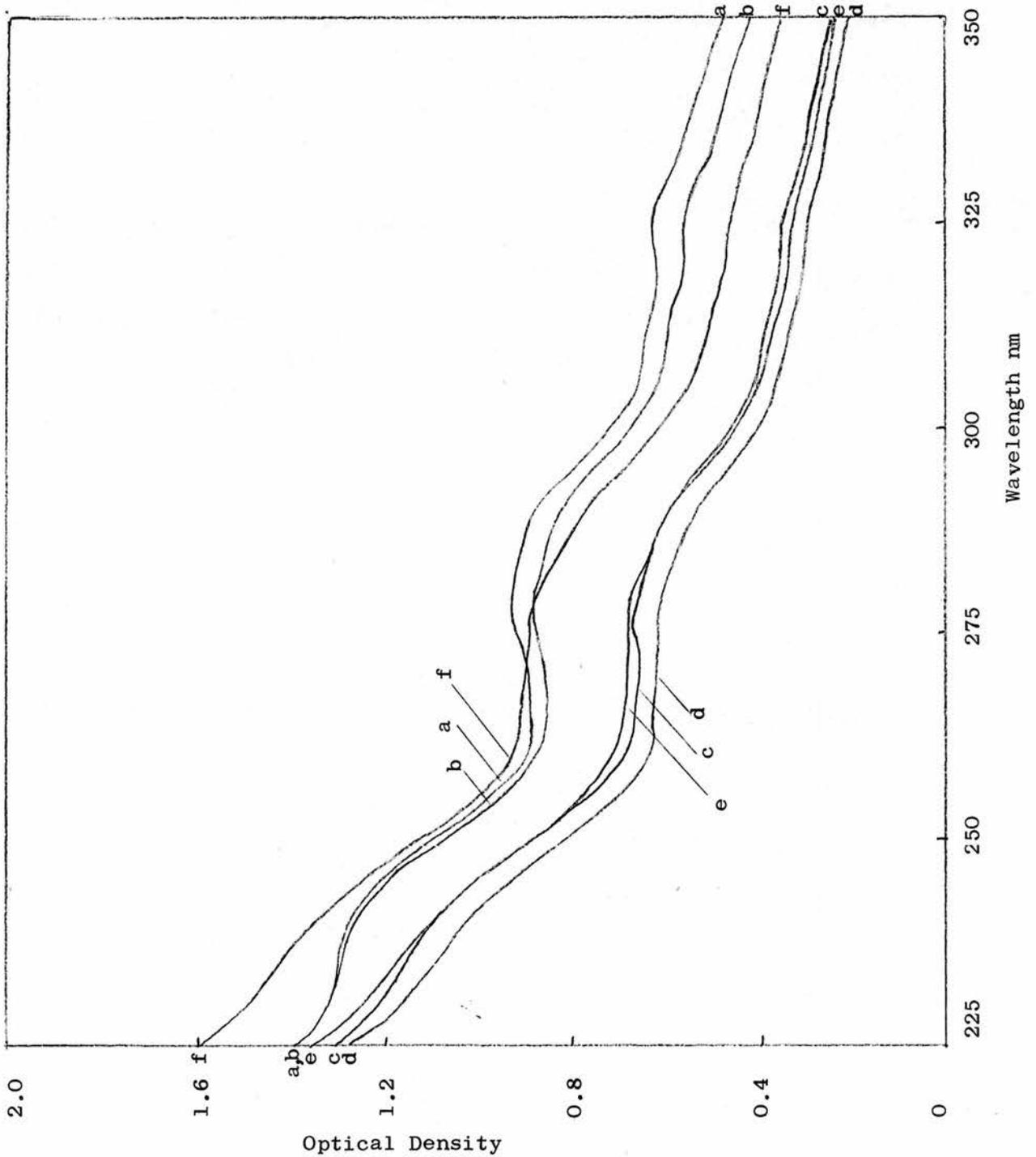
This table clearly illustrates the vast difference between irradiation in nitrogen and oxygen. After two hours in oxygen 150 x as many trienes as nonaenes are present compared with 13 x in nitrogen (see Table 27).

The effect of oxygen on a sample already degraded in nitrogen was also investigated spectroscopically. A sample was irradiated in nitrogen for one hour at a light intensity of 1.24×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$, and the ultraviolet spectrum recorded. Further spectra were recorded after the system had been flushed with oxygen for 15 minutes and then after 5, 20, 60 and 210 minutes irradiation in oxygen. The spectra obtained are shown in Figure 40.

Figure 40

Ultraviolet spectra of a film sample:-

- (i) irradiated in nitrogen for 60 mins - a
- (ii) flushed with oxygen for 15 mins - b
- (iii) irradiated in oxygen for a further 5, 20, 60, 210 minutes - c, d, e, f respectively



The polyene distribution was again calculated as already described and the results are shown in Table 31.

Table 31

t	ΔOD_{278}	C_3	C_3/C_9	ΔOD_{325}	C_5	C_5/C_9	ΔOD_{390}	C_7	C_7/C_9	ΔOD_{430}	C_9	C_9/C_9
60 (N ₂)	0.810	270	15.00	0.535	107	5.94	0.280	40	2.22	0.160	18	1.00
15 (O ₂ unirr)	0.770	257	21.42	0.465	93	7.75	0.270	31	2.58	0.110	12	1.00
5 (O ₂)	0.550	183	36.60	0.265	53	10.60	0.100	14	2.80	0.045	5	1.00
20 (O ₂)	0.500	167	60.29	0.210	42	15.16	0.070	10	3.61	0.025	2.77	1.00
60 (O ₂)	0.565	188	42.34	0.240	60	13.51	0.090	13	2.93	0.040	12	1.00
210 (O ₂)	0.760	253	21.67	0.355	71	6.08	0.185	26	2.23	0.105	4.44	1.00

It can first of all be seen that the presence of oxygen caused bleaching without ultraviolet irradiation. This effect had been observed before in films irradiated for seven hours and then stored in the dark. It was for this reason that spectra were taken immediately after a run was completed. This effect was accelerated when irradiation was restarted, and a shift towards shorter sequences can be seen. However after 3½ hours irradiation in oxygen the polyene distribution had almost returned to that found after irradiation in nitrogen. This is in contrast to the results in Table 30 when all the irradiation was conducted in oxygen.

Lastly the infra-red spectra of films degraded in oxygen show peaks at 1770 and 1720 cm⁻¹ due to carbonyl compounds.

Chapter 4

Discussion

1 The Surface Reaction

It has been suggested that the photodegradation of poly(vinyl chloride) films is confined to a surface layer^{42,61}. The results discussed in this section show conclusively that this is the case.

The results indicated that film thickness had no effect on the rate of degradation and that the amount of degradation was proportional to film area. Both these conclusions indicate a surface reaction. The irradiation of a film sample at each surface clearly showed two separate, but similar reactions occurring at these surfaces. The photographic evidence also showed that degradation was confined to a thin surface layer and that this layer appeared to be less than 5 μ deep.

It is postulated that a surface layer is formed because of the build up of a 'protective barrier'. A similar effect was suggested by Golub and Parker³⁰, and Reinisch, Gloria and Wilson⁶¹. It has been seen in the introduction that once initiation has occurred further degradation of the poly(vinyl chloride) depends upon the absorption of damaging radiation by the polyenes already formed. During the first few seconds of irradiation a very small number of polyenes are probably formed throughout the film. However when the incident radiation strikes the film surface it will be absorbed by the first chromophore it encounters, and hence a polyene build up near the surface will result. The effect will be very rapidly magnified as the greater the surface concentration of polyenes the more light will be absorbed at the surface and thus the more polyenes will form there.

The light absorption experiments reported in section 1(f) of

chapter 3 showed that there was a very rapid rise in the amount of light absorbed by the irradiated film. For example, the results in Table 5 indicate that after about an hour only 5% of the incident light below 450 nm was transmitted. But this figure is in fact too high for two reasons. First it is only light below a certain threshold wavelength that can product degradation. Kenyon⁵ proposed a maximum wavelength of 340 nm as being capable of degrading poly(vinyl chloride), and Reinisch and co-workers⁶¹ obtained a similar result. The results obtained in this work using plate-glass and pyrex filters, and a filtered source which only transmitted light between 266-370 nm, suggest that the samples used here will only degrade if light of a wavelength < 266 nm is present. (These particular results are discussed in more detail in section 5(a).) Second for experimental reasons these results were obtained in air, and consequently the conjugation length of the polyenes will be reduced by bleaching and hence less absorption will occur.

This figure of 5% will then be much smaller if only light of a wavelength < 266 nm instead of < 450 nm is considered and the run is conducted in nitrogen. The curve shown in Figure 15 also indicates a rapid build up of light absorption.

A clearer view of this phenomenon can be obtained from the result reported in section 1(d) of Chapter 3. It was found that if two samples were placed one on top of the other and irradiated the lower sample was not degraded at all within spectroscopically measurable limits. This indicates that all the damaging radiation is absorbed by the top film before degradation can occur to any measureable extent in the bottom film.

It is possible now to interpret the nature of the 'protective barrier' mentioned before and to account for the shape of the

dehydrochlorination curve. A polyene gradient will exist throughout the surface layer. Near the top of this layer where there is a relatively high concentration of polyenes a large proportion of the light will be absorbed but there will be very few available sites for reaction as they are nearly all gone. Lower down in the layer there are many sites for reaction but very little light penetrates. Initially then as the polyenes layer is building up the reaction will accelerate, but as reaction sites become depleted a steady deceleration will occur. A theoretical model to explain the build up of the polyenes at various depths in the film is described and discussed in detail in Chapter 5. This model goes some way towards explaining how such a surface layer as described here could be formed. It is difficult however to explain the shallowness of the layer and its apparently sharp limits shown by the photographs in Figures 13a and 13b.

Having shown the existence of a surface layer and suggested reasons for its occurrence, it is possible to make some other observations. It is now evident that this reaction, unlike thermal degradation, is heterogeneous and hence a kinetic analysis of the reaction is virtually impossible. Because the products of the reaction form sites for further light absorption the nature of the reaction is constantly changing. Also because film thickness, and hence the weight of material under a given area, has no effect on degradation the term "percentage degradation" is meaningless.

It was observed that when a film was irradiated for 7.5 hr, inverted, and irradiated for a further 7.5 hr a slight increase in the amount of dehydrochlorination at the second surface was obtained - 0.601 mg versus 0.556 mg at the first surface. It is possible that when irradiation is commenced at the second surface there are two sites for reaction. A surface layer similar to the one at the first

surface is formed, but some reaction can occur at the opposite surface where there are polyenes to absorb light and reaction sites available. This second reaction site could produce the extra hydrogen chloride evolved during the second irradiation.

The presence of a surface layer containing a lot of polyenes will produce a strain in the film surface. This strain causes a rippling of the surface at the degraded side of the film, visible in Figure 13a. The non-degraded side is comparatively smooth. In Figure 13b, where degradation has occurred at both surfaces the rippling can also be seen at both surfaces. Van Krevelen and Hoftyzer⁷⁵ have calculated the density of polyene to be 0.87 g cm^{-3} . The density of poly(vinyl chloride) lies in the region $1.37\text{-}1.41 \text{ g cm}^{-3}$, and therefore although obviously not all the poly(vinyl chloride) is converted to polyene, a considerable change in density will have occurred at the surface.

2 Temperature and Intensity Variation

The results obtained show that there is an increase in the rate of dehydrochlorination with increasing temperature and the reaction has an activation energy of 14 kJ mol^{-1} . This value agrees well with Reinisch and Gloria's³⁹ experimental value of 18 kJ mol^{-1} and their theoretical value, predicted from consideration of an energy diagram. They suggested this was consistent with reaction via an excited state singlet. The increase in the rate of reaction is most marked during the first hour and thereafter the rate becomes almost independent of temperature. Individual $\Delta W/\Delta t$ values in Tables 6 and 7 appear to indicate that the rate is constant after one hour. However a close inspection of the ΔW_{1-7} , ΔW_{2-7} and ΔW_{3-7} values in Tables 8 and 9 shows that temperature is having an effect, albeit very slight.

The results also indicate that there was a shift towards longer

polyenes at higher temperatures. This effect was also observed when thermally treated films or films containing different amounts of tetrahydrofuran were irradiated. It is postulated that tetrahydrofuran can reduce the polyene conjugation length. The higher the temperature the less tetrahydrofuran will remain in the film and the less will be the reduction in polyene conjugation length. This effect is discussed in full in section 3(c).

As expected intensity has a large effect on the rate of dehydrochlorination but this effect only lasts about one hour, and thereafter the rate apparently becomes independent of intensity. This is shown by the ΔW_{1-7} , ΔW_{2-7} and ΔW_{3-7} values in Tables 13 and 14 which are constant.

The intensity dependence of the reaction during the early stages can be illustrated in two ways - (a) by plotting the weight loss after half an hour, $\Delta W_{0.5}$, against the square root of the absorbed light intensity, $I_a^{\frac{1}{2}}$, or (b) by plotting the inverse of the time taken to reach the inflection point, t_{inflec}^{-1} , against $I_a^{\frac{1}{2}}$. The results discussed in section 1, suggest that at $I_0 = 3.57 \times 10^{16}$ quanta $\text{cm}^{-2}\text{sec}^{-1}$ complete absorption of the damaging radiation is virtually instantaneous. It is highly probable then that at the intensities considered here absorption is complete after half an hour, or at the inflection point, so that I_0 is equivalent to the light absorbed, I_a . In fact I_a is equal to that proportion of the incident light absorbed below 340 nm, i.e. the potentially damaging radiation. Bearing in mind that the actinometer is only sensitive up to 450 nm and utilizing the lamp's light distribution data shown in Table 2 it is found that 55% of the light is emitted below 340 nm. I_a is therefore equal to $0.55 I_0$ once absorption is complete. The $\Delta W_{0.5}$, t_{inflec}^{-1} , and $I_a^{\frac{1}{2}}$ values for the

two sets of experiments are shown in Table 32.

Table 32

$\Delta W_{0.5}$ (mg)		t_{inflec}^{-1} (min ⁻¹)		$I_a^{\frac{1}{2}}$ x 10 ⁸
1st set	2nd set	1st set	2nd set	
0.177	0.182	0.071	0.071	1.24
0.084	0.087	0.038	0.036	0.82
0.028	0.041	0.024	0.021	0.62
0.008	0.014	0.016	0.014	0.49

Straight line graphs are obtained by plotting $\Delta W_{0.5}$ and t_{inflec}^{-1} against $I_a^{\frac{1}{2}}$ and these are shown in Figures 41 and 42. If the weight loss after a period of time longer than one hour is plotted against $I_a^{\frac{1}{2}}$ a straight line is not obtained.

The reaction must now be considered as taking part in two stages. First a relatively fast stage dependent on temperature and intensity and second a slower stage virtually independent of temperature and independent of intensity. An explanation of this phenomenon can be obtained by considering the surface layer formed during degradation. The weight of hydrogen chloride evolved after infinite time, ΔW_{∞} , at a given intensity can be approximately estimated by extrapolation of the curves shown in Figure 17. These limiting values suggest that the depth of the surface layer is dependent on the intensity of irradiation. This is reasonable because during the first few minutes, or more probably seconds, of irradiation the polyene barrier will be formed at the film surface. When the light is more intense it will penetrate further to form polyenes at initiation sites deeper into the film, and hence a deeper surface layer (the nature of these initiation sites will be discussed later).

Using these ΔW_{∞} values it is now possible to calculate the percentage decomposition after one hour, $\Delta W_1 / \Delta W_{\infty} \times 100$, and the

Figure 41

A Plot of $I_a^{1/2}$ versus $\Delta W_{0.5}$

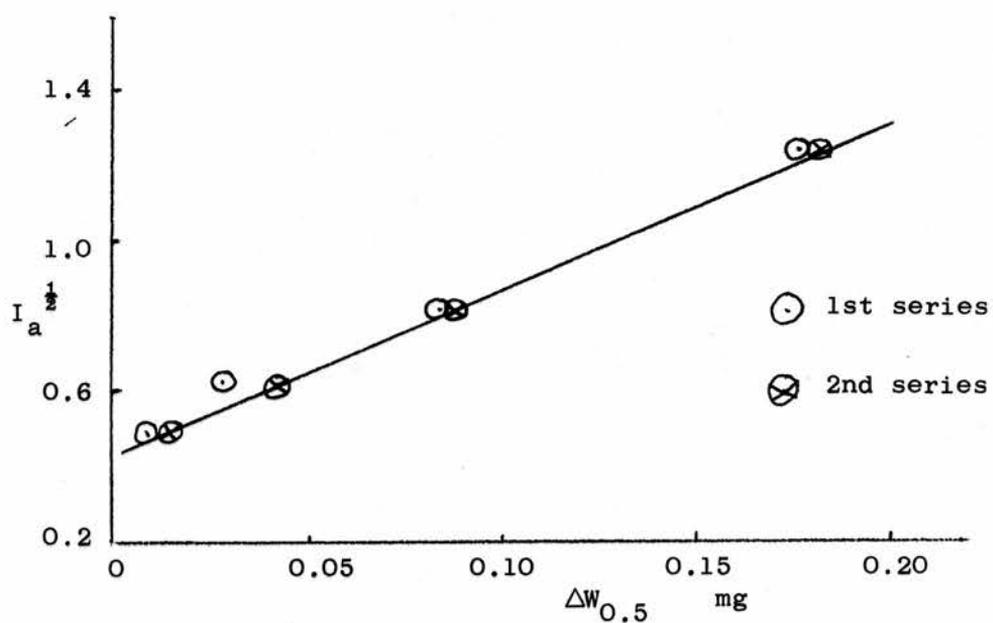
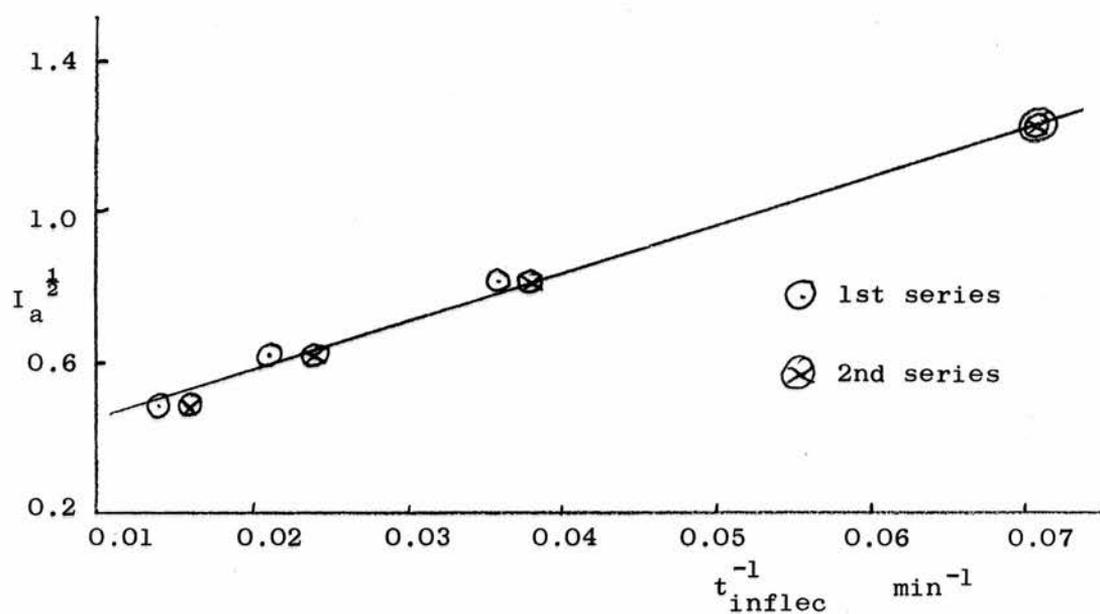


Figure 42

A Plot of $I_a^{1/2}$ versus t_{inflec}^{-1}



results using the ΔW_1 values from Table 9 and the I_0 values are shown in Table 33.

Table 33

I_0 (quanta $\text{cm}^{-2} \text{s}^{-1}$ $\times 10^{16}$)	ΔW_1 (mg)	ΔW_∞ (mg)	$(\Delta W_1 / \Delta W_\infty \times 100)$
2.83	0.283	0.80	35
1.24	0.195	0.74	26
0.71	0.110	0.68	16
0.43	0.048	0.62	8

It can be seen that, although there is the compensating factor of a slightly smaller ΔW_∞ in the less intense case, the actual percentage decomposition is far smaller.

The absorption spectra shown in Figure 18 indicate that the amount of light absorbed, given by the area under the spectrum, is much greater when the lamp intensity is greater. As stated if the results from section 1(f) are taken into account the light below 340 nm, Kenyon's⁵ limiting value for the photodegradation of poly(vinyl chloride), and certainly below 266 nm, the possible limiting value for this work, all the available light is absorbed before one hour's irradiation is completed. However the amount of light absorbed in the most intense case will still be approximately 7 x as great as in the least intense case, (this being the relative intensity ratio, and the distribution of the different wavelengths being the same). The spectra do show that there is the same polyene distribution at each intensity so that any differences in behaviour cannot be attributed to this.

It is likely then that the second stage of the reaction is controlled, not by a chemical process, but by the availability of

the hydrogen chloride. Considering the two extreme cases, in the more intense case although a lot more potentially damaging light is absorbed approximately 35% of the available hydrogen chloride has already evolved. However in the less intense case, less light is absorbed but only 8% of the available hydrogen chloride has evolved. Similarly the other two examples lie in between. If these two factors cancel out then the rate of reaction will become independent of intensity. Because this 'availability' will be relatively unaffected by temperature the dehydrochlorination reaction will be almost independent of temperature as has been observed.

It should be pointed out that for convenience the reaction has been described as occurring in two distinct stages. In fact there is no dividing line but rather a merging of the two. When 'availability' becomes the rate determining factor the reaction starts to slow down, i.e. at the inflection point. This occurs, not after one hour, but after a time depending on intensity. For example the t_{inflec} values for the first set of experiments were 14, 26, 42, and 71 minutes at I_0 values of 2.83, 1.24, 0.71 and 0.43×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$ respectively. This means that after half an hour the runs at the two highest intensities are no longer intensity dependent. It is perhaps fortuitous that the data for these runs results fit the $\Delta W_{0.5}$ versus $I_a^{1/2}$ plot shown in Figure 41, but it does indicate that there is no sudden change in the nature of the dehydrochlorination reaction.

The relationship between $\Delta W_{0.5}$ and $I_a^{1/2}$ has shown an intensity dependence during the first hour. An attempt was now made to find a relationship to describe the second stage of this reaction. At a given intensity it has been established that I_a is constant and that 'availability' controls the rate of reaction. This reasoning would

predict a possible inverse relationship between rate of reaction and extent of reaction. It was therefore decided to plot the rate of reaction, dW/dt , against the inverse of the weight loss. The dW/dt values used are not those shown in Table 11 (average rates over an hour found by subtraction of ΔW_t values) but slopes calculated by drawing tangents to the dehydrochlorination curves at the appropriate times. This was done after 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.5 hours. However, as it has been shown that a higher ΔW_∞ is found at a higher intensity a more accurate representation of 'availability' can be found by considering the fraction of the available hydrogen chloride that has already evolved. dW/dt was therefore plotted against the inverse of the fraction gone, $1/F$, where F is calculated using the ΔW_∞ values shown in Table 33 and the ΔW values in Table 11. The graphs obtained at the four light intensities, 2.83, 1.24, 0.71 and 0.43×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$, are shown in Figure 43.

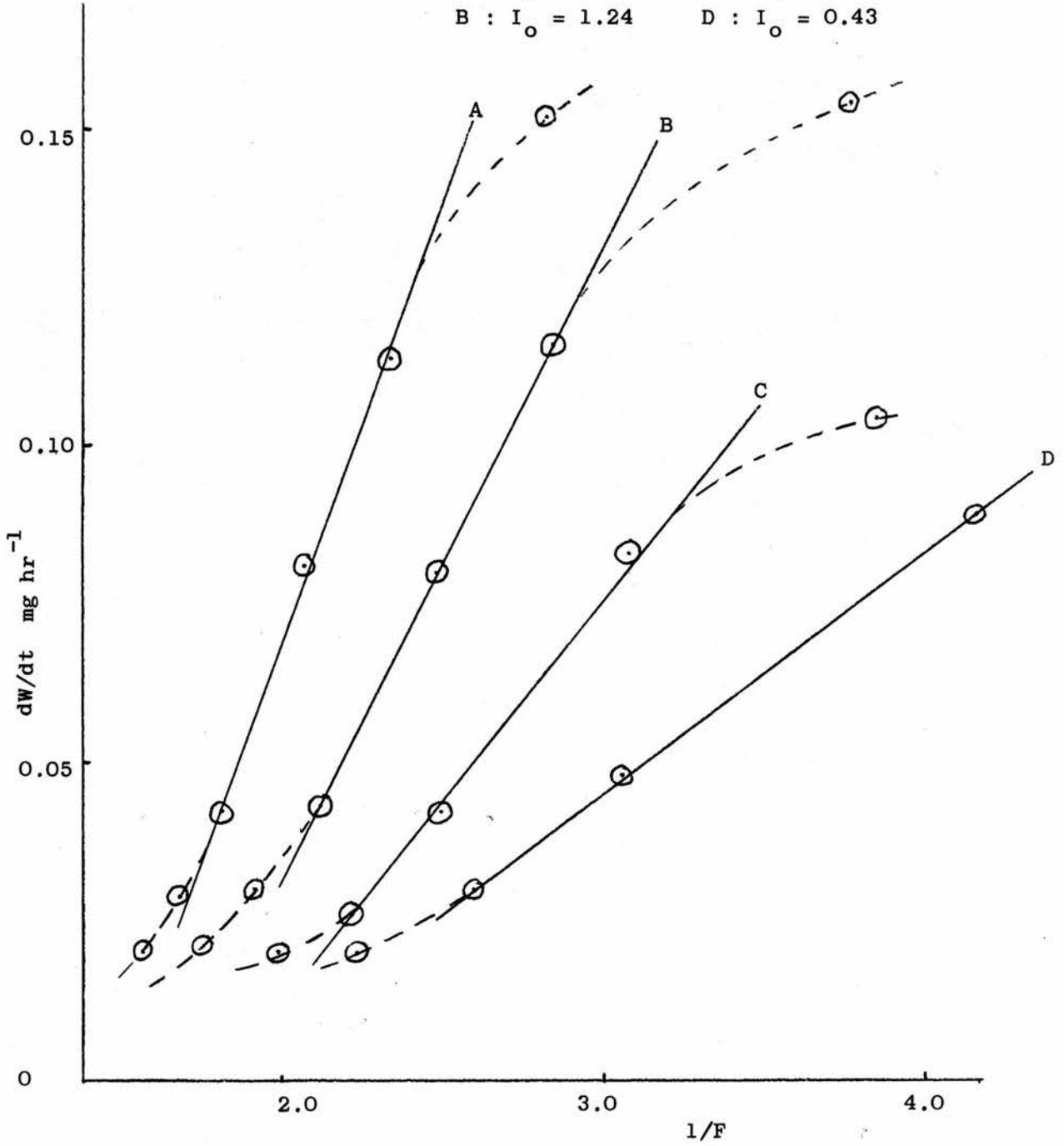
These graphs are approximately linear over a central portion of the reaction. The relationship does not hold for $t < t_{\text{inflec}}$. This is reasonable because 'availability' is not controlling the reaction until t_{inflec} is reached. The relationship does not at high t either. At high conversion it is possible that the 'availability' problem becomes so acute that dW/dt is proportional to, not $1/F$, but $1/F^2$. Indeed a plot of dW/dt versus $1/F^2$ is linear at high t . In general then it is probable that dW/dt is proportional to $1/F^n$ where n is unity up to a certain t value and then increases with t .

Further information can be obtained from these graphs. It has already been observed that after the first hour, or more accurately 71 minutes i.e. when t_{inflec} has been reached at all intensities, the dehydrochlorination curves are approximately superimposable. That is, after this time, the rate of reaction is the same at the four

Figure 43

Plots of dW/dt versus $1/F$ at light intensities I_0 (quanta $\text{cm}^{-1}\text{s}^{-1}$
 $\times 10^{16}$) of:-

A : $I_0 = 2.83$ C : $I_0 = 0.71$
B : $I_0 = 1.24$ D : $I_0 = 0.43$



intensities. However if the same F , and hence $1/F$, value is taken different rates are obtained. For example at $1/F = 2.6$, $dW/dt = 0.151$, 0.091 , 0.049 and 0.029 at $I_o = 2.83$, 1.24 , 0.71 and 0.43×10^{16} quanta $\text{cm}^{-2} \text{s}^{-1}$ respectively. These values obey the relationship $(dW/dt)_F \propto I_o^{1/2}$ and hence $(dW/dt)_F \propto I_a^{1/2}$. This is to be expected because at constant F , the availability of hydrogen chloride at each intensity is the same and therefore a higher I_a value will lead to a faster rate of reaction.

In conclusion the reaction occurring after inflection can be described by the two equations:-

$$(dW/dt)_t = \text{constant}$$

$$(dW/dt)_F = k \cdot I_a^{1/2}$$

3. Sample Variation

It has been shown that the reaction is confined to a surface layer and that its very early stages determine the characteristics of the dehydrochlorination reaction. The purpose of this section is to try and determine what controls or is responsible for the initiation of the reaction. It was with this in mind that the various samples, polymerised using different initiators and whose molecular weights and end groups were also different, were studied. The most significant results were in fact obtained when samples containing an ultraviolet absorber were irradiated and it is these results which are discussed first.

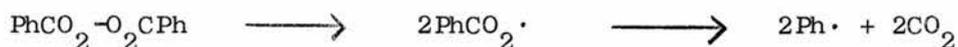
(a) Samples Containing Additives Absorbing in the Ultraviolet

(i) Benzoyl Peroxide

The first samples that were studied were the two types of benzoyl peroxide loaded films. The results show that in all cases the

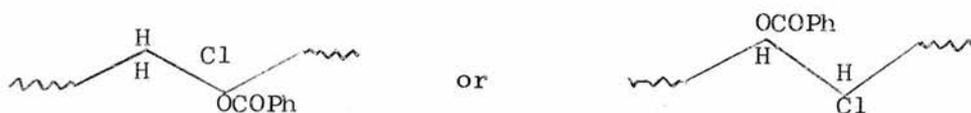
rate of reaction is initially faster than a standard but eventually becomes slower. The higher the concentration of the peroxide the faster was the initial reaction and the lower the ΔW_7 value. This effect can be rationalised by considering the early stages of the reaction and the 'protective barrier' produced.

Benzoyl peroxide is known to decompose when heated or subjected to ultraviolet light and the thermal decomposition in solution is particularly well documented⁷⁶. The peroxide decomposes in two stages by a first order process:-



The ultraviolet spectra of benzoyl peroxide and a film containing benzoyl peroxide (Figures 19 and 22) show that benzoyl peroxide will absorb radiation in the region 215-287 nm. The polychromatic source used emits light in this region, though it should be noted not below 235 nm (see Table 2), and when a sample is irradiated the light will be absorbed by the peroxide which will decompose to give radicals. The more peroxide that is present the more radicals will be produced. These radicals will initiate poly(vinyl chloride) degradation at many more sites than in the reference sample causing an initial acceleration in the rate of dehydrochlorination. This will result in the more rapid formation of a protective polyene barrier which will consequently be less deep than normal but denser in polyenes. Unreactive products of the benzoyl peroxide decomposition which absorb ultraviolet light will add to the 'barrier'. The formation of a more effective 'protective barrier' will result in a lower ΔW_7 value. The more peroxide that is present the more effective will be the 'barrier' formed and the lower ΔW_7 . The actual mechanism of initiation is discussed later.

benzoates e.g.



It can now be seen why this peak was already present in the films cast from polymer synthesised using benzoyl peroxide as indicator. During polymerisation benzoate radicals are formed which will react in the same way as above to form poly(vinyl chloride)benzoate.

Benzoyl peroxide irradiated as a nujol mull showed new peaks in the infra-red at 1690 cm^{-1} , benzoic acid, and at 1630 cm^{-1} (weak). This peak at 1630 cm^{-1} probably corresponds to the one at 1620 cm^{-1} found in the degraded films. The compound responsible for this absorption is not known. No phenyl benzoate was observed but Haas⁷⁴ postulated a strong cage effect to account for the products when polymer is present. It is possible that phenyl benzoate will not be formed in the absence of the polymer matrix.

Examination of the ultraviolet spectra before and after irradiation does not add much to an evaluation of the products. It was reported in the results that a broad hump, shown in Figure 23, is formed during degradation and the build up of this hump is shown in Figure 35. The intensity of the hump appears to be unaffected by the amount of benzoyl peroxide present. The results of irradiated pure benzoyl peroxide and of extracting a degraded film with methanol suggest the compound(s) responsible for this absorption are products of benzoyl peroxide decomposition and not connected with the poly(vinyl chloride). However most of the reasonable possibilities, for example phenyl benzoate and dibenzyl, absorb below 300 nm and to obtain absorption at 325 nm two conjugated chromophores are generally required (see Page 100).

(ii) Acenaphthene

When it was observed that benzoyl peroxide loaded films degraded to a lesser extent than a reference, it was decided to investigate the possibility that any ultraviolet absorber would have the same effect and acenaphthene was chosen as an example. The results indicate that acenaphthene does have a similar effect with three outstanding differences. First the acenaphthene is not as effective as benzoyl peroxide with 2 mole % giving a similar retardation to 0.25 mole % benzoyl peroxide. Second the infra-red spectra before and after irradiation indicate that the acenaphthene is unaltered by the irradiation and therefore that it is not participating in a chemical reaction. Third the early stages of the dehydrochlorination curves show a different pattern to those obtained for benzoyl peroxide loaded films. In this case all the acenaphthene loaded films are initially faster than the reference but there is an optimum amount of acenaphthene giving the fastest initial reaction - about 0.5 mole %. As before though, the more acenaphthene that is present the lower is the ΔW_7 value obtained, except that a very small amount appears to produce a slightly higher ΔW_7 than the reference.

Clearly the acenaphthene plays a different role to benzoyl peroxide. Benzoyl peroxide causes the initial acceleration by decomposing to form radicals. Acenaphthene however acts in two ways, initially as a photosensitizer and then as a blocking agent. The initial acceleration is caused by the acenaphthene absorbing light and transferring energy to neighbouring polymer chains. At first sight it appears that the film containing 0.5 mole % is initially faster than the films containing 1.0 and 2.0 mole% acenaphthene. In fact these films are already slowing down because of the blocking effect. All three samples are in the early stages equally faster

than the sample containing 0.2 mole% (the dehydrochlorination curves are coincident for about 5 minutes). The film containing 0.2 mole % is in turn faster than the reference. This can be explained by considering the actual amount of damaging radiation that is absorbed by the varying amounts of acenaphthene. It is known from Beer's Law that:-

$$I_a = I_o (1 - 10^{-\epsilon cl})$$

The fraction of light absorbed, I_a/I_o , is then given by:-

$$I_a/I_o = 1 - 10^{-\epsilon cl}$$

Now consider film L/2 which contained 2 mole % acenaphthene. From the film dimensions, c can be calculated to be 0.5 mol l^{-1} . As degradation is confined to a surface layer the l value to be used is not the film thickness but the depth of this layer. A value 0.001 cm is used.

The value of ϵ to be used is less obvious. It is probable though that the greatest portion of the light for initiation will be absorbed at that wavelength which exhibits a relatively high ϵ value, assuming the lamp emits light at that wavelength and also that it is below 340 nm. The wavelength chosen is 280 nm at which ϵ for acenaphthene is $5,800 \text{ l mol}^{-1} \text{ cm}^{-1}$.

$$\text{Now } \epsilon cl = 5,800 \times 0.5 \times 0.001 = 2.9.$$

The I_a/I_o values for all the films can now be tabulated and are shown in Table 34.

Table 34

Film	ϵcl	$10^{-\epsilon cl}$	I_a/I_o
L/2	2.9	0	1.00
L/3	1.45	0.04	0.96
L/4	0.725	0.19	0.81
L/5	0.29	0.51	0.49

It can now be seen that films L/2,3,4 absorb roughly the same amount of the incident light at 280 nm, but film L/5 absorbs considerably less. Films L/2,3,4 will therefore be photosensitized to about the same extent with film L/5 less.

Once a few polyenes have been formed the photosensitizing role of the acenaphthene will become insignificant as it is far easier for the polyenes to further react by normal routes. The acenaphthene now becomes a trap for the ultraviolet light and it adds to the 'protective barrier' formed by the polyenes on the surface. This effect causes the rapid deceleration and eventually the low ΔW_7 value. The more acenaphthene that is present the greater will be this blocking effect.

The results in Table 34 might suggest that as films L/2,3,4 absorb the same amount of light they will be equally retarded. However an examination of the relevant ϵ values shows this is not the case. The calculation in Table 34 was made at 280 nm where $\epsilon = 5,800 \text{ l mol}^{-1} \text{ cm}^{-1}$. But propagation will largely occur by polyenes absorbing light, not acenaphthene, and this can occur at any wavelength between 235-340 nm. Now at 254 nm, for example, ϵ for acenaphthene is $1,600 \text{ l mol}^{-1} \text{ cm}^{-1}$. If the same calculation as before is made using this ϵ value I_a/I_o values of 0.84, 0.60, 0.37 and 0.17 are found for films L/2,3,4,5 respectively. Hence over a range of wavelengths with different ϵ values, mostly considerably smaller than $5,800 \text{ l mol}^{-1} \text{ cm}^{-1}$, 2 mole % acenaphthene (L/2) will be a more effective blocking agent than 1 mole % (L/1) etc.

The result obtained for film L/5 indicates that it was faster than the reference throughout the run. This cannot be explained by the arguments proposed, which suggest it should have been slower than the reference after an initial acceleration. This anomaly could be due to experimental error as the differences are very small.

It is probable that, as for benzoyl peroxide loaded films, the initial acceleration causes the formation of a shallower surface layer than usual. By the same arguments as were put forward for benzoyl peroxide loaded films, this would help the retardation effect. The acceleration during the first few minutes is not however as great in this case.

(iii) Dimethyl Phthallate

Dimethyl phthallate was present in the films prepared using ACSP as initiator because of the unstability of ACSP which is used as a 29% solution in dimethyl phthallate. These films had been prepared in an attempt to study the dependence on molecular weight, but the effect of having an ultraviolet absorber present obscures any trend and as previously retardation is observed. The infra-red spectra before and after irradiation suggest that the dimethyl phthallate does not decompose, so that the retardation mechanism would be similar to that for acenaphthene loaded films. However the ultraviolet spectrum after irradiation shows a hump at 325 nm, presumably similar to that observed for benzoyl peroxide loaded films, but more intense. This suggests that the dimethyl phthallate must have reacted in some way.

(iv) Phenyl Benzoate

As Haas⁷⁴ had shown that phenyl benzoate was a product of the decomposition of benzoyl peroxide suspended in a poly(vinyl chloride) film, a film containing this material was prepared and irradiated.

Again retardation is observed with phenyl benzoate approximately as effective as benzoyl peroxide. 1 mole % phenyl benzoate gave $\Delta W_7 = 0.271$ mg against a reference of 0.424 mg compared with 0.282 and 0.389 mg for benzoyl peroxide. Examination of the infra-red spectrum showed that the amount of phenyl benzoate present in the film was slightly decreased after irradiation, indicating that its mode

of action is probably in between those of benzoyl peroxide and acenaphthene. If the material is decomposing some radicals will be produced but almost certainly not as many as for benzoyl peroxide.

The similarity to benzoyl peroxide loaded films is extended in that the weak peak at 1620 cm^{-1} in the infra-red, and the hump at 335 nm in the ultraviolet, slightly shifted from 325 nm in this case, are both observed in these films. The nature of the compound(s) absorbing at 325 nm in the ultraviolet is however unknown. This 'hump' is observed when films containing benzoyl peroxide, dimethyl phthallate or phenyl benzoate are irradiated, and it appears to be unrelated to the polymer. It is possible that derivatives of benzophenone are responsible for this absorption as benzophenone itself shows a broad peak at 333 nm with $\epsilon = 30,000 \text{ l mol}^{-1} \text{ cm}^{-1}$.

This result confirms that the products of the decomposition of benzoyl peroxide will add to the effectiveness of the 'protective barrier' by absorbing incident light as suggested.

(b) End groups and Residual Initiators

The results obtained for the film samples with different end groups and with different molecular weights, i.e. different numbers of end groups, are discussed here. In some cases these samples also contain significant amounts of residual initiator.

Initiation will be discussed in detail later and it is sufficient at this point to mention the following relevant possibilities. Residual peroxide can break down to give radicals which will initiate dehydrochlorination. This can happen very easily during thermal degradation, but in photodegradation the initiator can only decompose by direct absorption of light or as a result of energy transfer. It has been shown that capryloyl peroxide, V70, Y16 and ACSP do not absorb

to any significant extent in the ultraviolet, particularly above 235 nm. However it is possible that they could decompose by energy transfer from another chromophore. This is most likely to occur when polyenes have formed and can act as sensitizers for initiator breakdown. This will not then be an initiation, but rather a propagation process. The inability of capryloyl peroxide to decompose by direct absorption of ultraviolet light was illustrated when it was irradiated as a nujol mull and no change was observed in the infra-red spectrum.

Initiation could possibly occur by absorption of light at the chain ends. These chain ends may be initiator fragments, probably ester groups. Esters however generally absorb below 220 nm and therefore will have no effect when the lamp emits no light < 235 nm. Ketonic end groups which will absorb in the right region are very unlikely.

The other important type of end group is a β -chloroalkene formed through termination by transfer during polymerisation²⁸. Allylic end groups have been suggested as initiators by many workers^{14,15,17,22,23,27,68} but all were studying thermal degradation. As before initiation can only occur here if the end group can absorb light in the region 235-266 nm. The available evidence suggests that monoenes cannot generally absorb above about 230 nm and that any absorption above 200 nm will be very weak indeed. For example, oct-3-ene shows λ_{\max} at 185 nm ($\epsilon = 8,000 \text{ l mol}^{-1} \text{ cm}^{-1}$) but no absorption above 230 nm⁷⁷. Oleic acid shows λ_{\max} at 185 nm ($\epsilon = 8000 \text{ l mol}^{-1} \text{ cm}^{-1}$) with $\epsilon = 16 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 230 nm and $7 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 240 nm⁷⁷. This example is exceptional because butene, pentene and cyclohexene show no absorption above 210 nm⁷⁸. It is almost certain then that allylic end groups cannot cause initiation, although it should be noted that there are models and that within a polymer different

behaviour may be observed.

The actual results obtained are not very clear and any changes are comparatively small and subject to a large proportional experimental error. The results obtained using capryloyl peroxide containing films suggest residual peroxide can have an accelerating effect. However the infra-red spectra show that the calculated amounts of peroxide are obviously incorrect. Any acceleration might be due to a small amount of peroxide, undetectable by infra-red spectroscopy. However, as stated it could only react as a result of energy transfer to give a higher ΔW_7 .

The Y16 containing films, which are calculated to contain virtually no residual peroxide (confirmed by spectroscopy) show similar results. A slightly higher ΔW_7 is observed than for the reference. It is possible that the the result for P/7 in the first series (see Table 17) is incorrect and that the ΔW_7 values for P/6 and P/7 are the same, as shown by the second series. The small increase over the reference is relatively insignificant and could be due to very minor differences between films.

The results obtained using different molecular weight samples were shown in Tables 18 and 19. Again no very significant changes can be observed. It has been found for thermal degradation that the rate of dehydrochlorination is inversely proportional to molecular weight^{27,68}. The films containing V70 suggest this to be true here, but the opposite is shown by P/6 and M/11 and by the results in Table 19.

The results from this section are disappointing and inconclusive, though they do suggest end groups will have little effect on photodegradation.

(c) Tetrahydrofuran Variation

Sample variation was achieved in two other ways, apart from those discussed to date. Section 3(e) of the Results reported the degradation of samples containing varying amounts of tetrahydrofuran and section 3(f) the degradation of thermally treated samples, in which the amount of tetrahydrofuran also varied.

The results in section 3(e) show that as expected the amount of tetrahydrofuran present in a film does not have any effect on the extent of degradation. This is in marked contrast to the results found by Kamal, El-Kaissy and Aredessian³¹. These workers photodegraded poly(vinyl chloride) containing varying amounts of tetrahydrofuran, monitored by the intensity of "the characteristic absorption band at 280 nm", and concluded that the extent of degradation was proportional to the amount of tetrahydrofuran present. The extent of degradation was however monitored by observing the ultraviolet spectra. There are two important points to make here. First pure tetrahydrofuran does not absorb at 280 nm as suggested, and in fact does not absorb much above 260 nm. What these authors have presumably monitored is the amount of quinol present which is used as a tetrahydrofuran stabiliser. This has been confirmed by running spectra of pure and stabilised tetrahydrofuran. Quinol could well initiate dehydrochlorination by absorbing light at 280 nm and a varying amount might alter the extent of degradation. However the second point is that the results found in this work show that it is not accurate to monitor dehydrochlorination by observing the ultraviolet spectrum when varying amounts of tetrahydrofuran are present.

It has been shown that, although the same amount of hydrogen chloride has evolved, different ultraviolet spectra are obtained for samples containing different amounts of tetrahydrofuran (Figure 30).

It can be seen that the more tetrahydrofuran is present the less is the observed absorption at all wavelengths. Tetrahydrofuran somehow decreases absorption without affecting dehydrochlorination.

Matsumoto, Mune and Watatani⁵⁶ have shown that tetrahydrofuran can decolour thermally degraded poly(vinyl chloride) and that the reaction is assisted by air and light. However this decolouration was achieved by dissolving the degraded material in tetrahydrofuran. Also the proposed mechanism involved oxygen and the formation of tetrahydrofuran hydroperoxide. The situation here is clearly very different and the chemical involvement of the tetrahydrofuran very unlikely.

A possible explanation for the observed results involves the tetrahydrofuran acting as a plasticizer. For a polyene, length n , to form the polymer chain must be planar for n units, otherwise conjugation and the consequent allylic C-Cl activation will be lost. However once formed this polyene may be under considerable strain and the plasticizing action of the tetrahydrofuran will permit rotation of the C-C bonds in the polyene. This rotation may lead to a loss of planarity and a reduction in the conjugation length.

It could be argued that if the plasticizing action of the tetrahydrofuran produces loss of planarity in the polyene, why not in the poly(vinyl chloride) as well? The answer here lies in the different glass-rubber transition temperatures, T_g . The T_g of poly(vinyl chloride) is 85°C , whereas for example poly(1,3-butadiene) is -58°C and polyisoprene is -67°C ⁷⁹. Rotation is therefore far more difficult for the pure poly(vinyl chloride) because of the bulky chlorine atoms.

This plasticizing ability of tetrahydrofuran will apply to polyenes of all lengths but in particular to the longer polyenes which

are under greater strain. Also the longer polyenes will produce maybe two or more short polyenes in different planes. The proportion of shorter polyenes should therefore increase and this is observed if the calculation on page 75 is made. The $C_3:C_5:C_7:C_9$ ratios for the films dried for 0, 1 and 7 days in the vacuum oven are 31.4:10.0:2.6:1, 27.3:9.3:2.6:1 and 19.1:7.2:2.3:1 respectively. These ratios show that the more tetrahydrofuran is present the higher the proportion of short polyenes.

This ability of tetrahydrofuran to reduce the polyene conjugation length is confirmed by two other sets of results. First it was reported that the samples photodegraded over a range of temperatures, from 0-65°C, showed greater ultraviolet absorption the higher the degradation temperature. As tetrahydrofuran is a fairly volatile solvent, b.p. = 65°C, prolonged heating at these temperatures above 30°C will remove residual tetrahydrofuran. The result will be that the sample degraded at a lower temperature will contain more tetrahydrofuran and hence will show reduced absorption. It should be noted that all samples, even after prolonged drying, contain considerable amounts of tetrahydrofuran which can be removed by heating. This is proved in the thermal treatment experiments discussed below, where higher temperatures are employed (100-180°C).

Second the same effect is observed for the samples which have received thermal treatment prior to photodegradation. The results in Table 23 show that only when the sample has been thermally degraded, before irradiation, is a significant increase in the extent of photodegradation, given by ΔW_7 , observed. This is to be expected because thermal degradation will produce polyenes homogeneously dispersed throughout the sample which will then act as sites for further propagation by photolysis. This may lead to the production

of a slightly deeper surface layer because of the ready absorption of light at extra sites deeper into the film.

Large changes are however observed in the ultraviolet spectra of the photodegraded samples even in the cases where a very small change in ΔW_7 has been observed e.g. sample 4 in Table 23 (ΔW_7 for sample 3 appears to be anomalous). It can be seen that there is a reasonable correlation between tetrahydrofuran removal, or treatment temperature, and the optical density at 450 nm, OD_{450} . There will be a slight increase in OD_{450} due to the extra dehydrochlorination after high temperature thermal treatment. This will however be small as, for example, in a normal run an evolution of 0.030 mg hydrogen chloride between 5.5 and 7.0 hours irradiation is only accompanied by an increase in OD_{450} of 0.03. It appears that in this case tetrahydrofuran again acts to reduce polyene conjugation length and the more tetrahydrofuran remains in the film, the less will be the absorption throughout the ultraviolet and visible.

As before the effect of tetrahydrofuran on polyene distribution can be seen by calculation of the ratio $C_3:C_5:C_7:C_9$. Table 35 shows the calculated C_3/C_9 , C_5/C_9 , C_7/C_9 and C_9/C_9 values for the film sample 1-5 obtained from the spectra shown in Figure 31.

Table 35

Sample	C_3/C_9	C_5/C_9	C_7/C_9	C_9/C_9
1	16.83	6.83	2.34	1.00
2	10.85	4.67	1.96	1.00
3	8.93	4.09	1.79	1.00
4	7.95	3.79	1.78	1.00
5	7.55	3.60	1.77	1.00

It can be seen that, starting with the untreated sample 1, a steady shift in distribution in favour of longer polyenes is observed

as tetrahydrofuran is removed. Sample 5 contains about half as many trienes as sample 1, compared to nonaenes. These results are consistent with the proposed ability of tetrahydrofuran to act as a plasticiser. When most of the tetrahydrofuran is removed, as in sample 5, the long polyenes which are formed during photodegradation will remain planar.

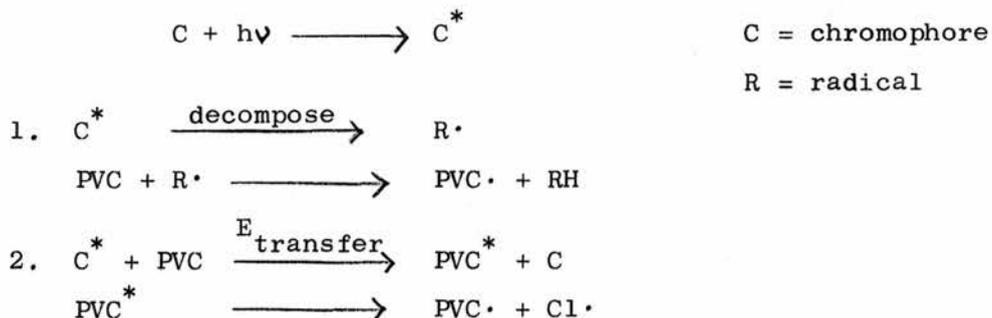
4. Mechanism

A fairly comprehensive account of the mechanism of poly(vinyl chloride) degradation was given in the introduction. This section discusses in more detail those mechanisms which are apposite to photodegradation under the conditions described. It is convenient to divide this section into initiation, propagation and termination.

(a) Initiation

The initiation of photodegradation requires some compound or functional group to absorb light with the right energy to do one of two things. First the absorbing species can decompose to give radicals which can then abstract hydrogen from a polymer chain to give a macroradical. Second it can act as a photosensitiser, producing a radical by transferring to the poly(vinyl chloride) sufficient energy to break the C-Cl bond. The energy required will be less if there are allyl C-Cl groups available.

These processes can be shown schematically as follows:-

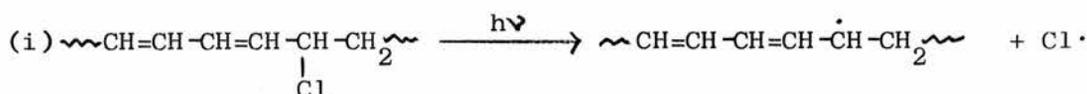


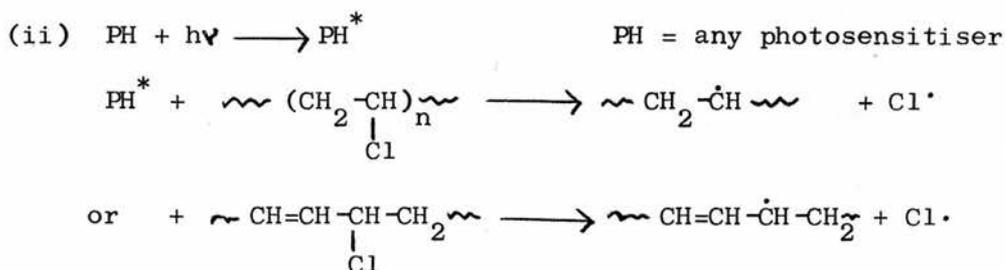
The actual possibilities are as follows. Residual peroxide can act as an initiator of type 1 above, if it can absorb ultraviolet light e.g. benzoyl peroxide. Other chromophoric additives can initiate degradation by either route 1, e.g. phenyl benzoate, or route 2, e.g. acenaphthene. Owens and Bailey³² have shown that benzophenone can initiate poly(vinyl chloride) photodegradation (type 2), and Kenyon⁵ has shown that acetone can initiate degradation by decomposing to form methyl radicals (type 1).

However these are exceptional circumstances and the problem is to determine what causes initiation in the relatively pure reference samples. The ultraviolet spectra taken before irradiation show that these films, despite all the precautions taken, are not perfectly transparent in the region 235-266 nm. It was reported in the introduction that many workers studying thermal degradation favoured chain ends as sites for initiation. However the results discussed in section 3(b) suggest that as initiation centres for photodegradation these sites are not feasible. Braun²¹ favoured single double bonds randomly dispersed throughout the polymer chain, but these sites are unlikely for the same reason - they cannot absorb damaging radiation.

It is suggested that the likeliest initiation sites are unsaturation already present in the film or trace impurities acting as photosensitisers e.g. ketonic groups, quinol, or even tetrahydrofuran which shows some absorption around 250 nm.

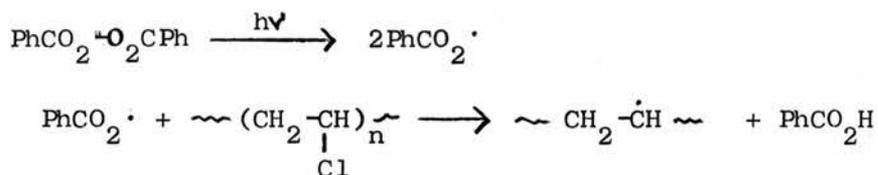
The mechanisms can now be shown in more detail:-





(i) is an internal and (ii) an external sample of type 2 above. In (i) no energy transfer is required because the chromophore is present in the poly(vinyl chloride) chain. Both reactions are very similar to propagation and are explained more fully in that section.

(iii) This third mechanism probably does not apply to the pure film but is type 1 described earlier. Benzoyl peroxide is used as an example:-



There are two more points to make before proceeding to propagation. The existence of unsaturation in the poly(vinyl chloride) is not proven but it is possible it might arise during polymerisation. One possible mechanism to produce unsaturation would be similar to (iii) above, except that the initiator radical is produced thermally. The ultraviolet spectrum of a reference sample before irradiation suggests from its broad shape, that what little absorption there is below 300 nm could be due to dienes and trienes.

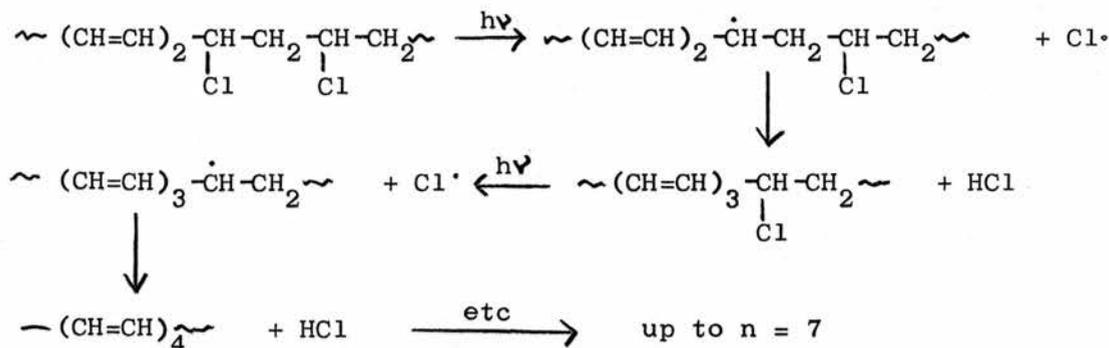
It should also be noted that a very low concentration of initiator is required because once a few polyenes are formed they will act as chromophores for further degradation.

(b) Propagation

There are two basic propagation mechanisms, examples of each having been seen in section (a).

(i) Stepwise dehydrochlorination

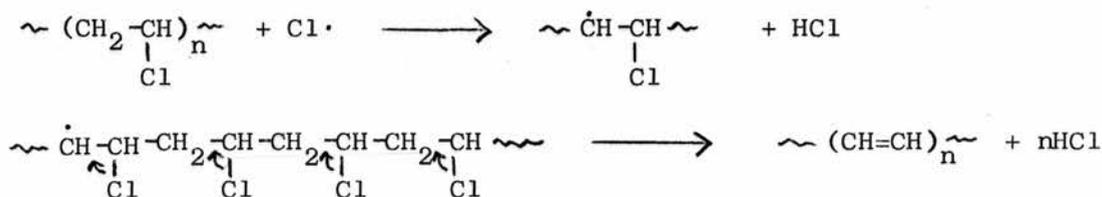
In this case a radical pair is formed and subsequently the polyene lengthens one double bond at a time i.e. stepwise:-



This reaction can only continue until $n = 7$, because after this time the light absorbed will not be of sufficient energy to break the allylic C-Cl bond. This mechanism has been proposed before³⁹.

(ii) 'Unzipping'

In this case some small radical, usually $\text{Cl}\cdot$ (or for example $\text{PhCO}_2\cdot$ in initiation as shown), abstracts a hydrogen atom from a poly(vinyl chloride) molecule giving a radical which unzips to give a long polyene. This is the mechanism proposed by Winkler³³, and drawn out in full in the introduction. It can also be shown as follows:-



This mechanism will produce the very long polyenes which are obviously present in the degraded polymer, as shown by the absorption in the visible region up to around 600 nm corresponding to $n = 20-25$.

This chlorine radical is produced by transfer from another chain and can be the result of breakdown of mechanisms (i) or (ii). The following possibilities for the cessation of dehydrochlorination along a poly(vinyl chloride) chain are as follows:-

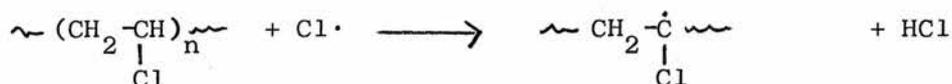
1. Stereochemical considerations - the polymer chain goes out of plane so that a conjugated polyene will not be formed by further dehydrochlorination

2. A branch or pendant $-\text{CH}_2\text{Cl}$ is reached

3. A head-to-head linkage.

As branches are comparatively rare²⁵, and head-to-head units unknown²¹, the stereochemistry of the polymer matrix probably determines the transfer step. This chain transfer step will also determine the average polyene length. The relative numbers of the different polyenes have been calculated (see page 76) and the results are discussed more fully later. They show that the shorter the polyene the more abundant it is, suggesting that transfer is very common.

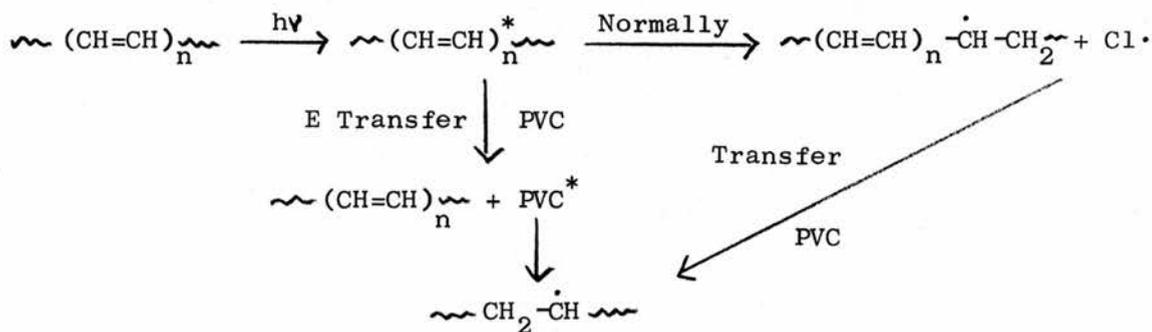
There is another possibility when transfer occurs. Instead of abstracting the methylenic hydrogen in poly(vinyl chloride) the chlorine radical may abstract a tertiary hydrogen giving a relatively unreactive macroradical:-



This is then in effect a termination mechanism. Reinisch and co-workers³⁹ pointed out that the abstraction reaction is very fast and non-selective. The tertiary hydrogen is 1.5 x as reactive as the secondary, and the allylic is 0.7 x the secondary. The type of radical produced will therefore depend on relative abundance rather than the kinetics of abstraction.

There are two other mechanistic possibilities. (i) Transfer caused by the macroradical, instead of the chlorine radical, abstracting a hydrogen atom from a nearby chain. This would be difficult for steric reasons but Geddes²⁷ suggested it might be open to mobile radicals possibly from low molecular weight poly(vinyl chloride).

(ii) Energy transfer followed by C-Cl bond rupture is possible but again unlikely as hydrogen abstraction is easier. This reaction would be as follows:-



N.B. PVC could be replaced by another polyene in the above scheme.

In the same way that transfer via a chlorine radical will reduce polyene length, energy transfer as shown here will also reduce polyene length.

It should be noted that as reported in the introduction all the postulated radical species have been found by electron spin resonance measurements^{36,37}.

(c) Termination

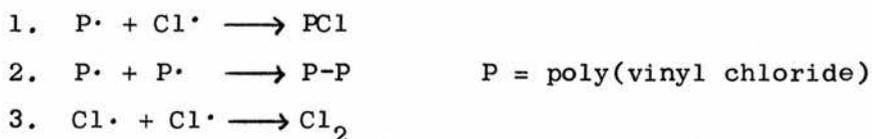
The following possibilities exist:-

(i) Abstraction of a tertiary hydrogen to give an unreactive radical (see section (b) above).

(ii) Many polyenyl radicals live on because of their high resonance stability. This is probably what happens to the

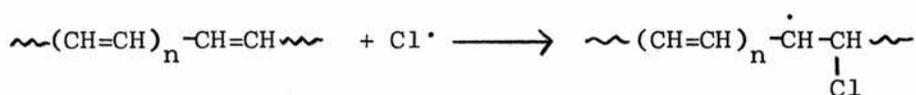
macroradical left behind when transfer occurs. This high stability was confirmed by Lawton and Balwith³⁶ who found by electron spin resonance spectroscopy that in γ -irradiated poly(vinyl chloride) polyenyl radicals only decay 10% in 1800 hours at room temperature.

(iii) The combination of two radicals will cause termination and there are three possibilities:-



Reaction 1 may occur, but 2 is probably commonest and gives rise to a cross-link. Chlorine has never been found by any workers, presumably because when a chlorine radical is formed it will immediately abstract a hydrogen atom from nearby. The chance of another chlorine atom being near at hand is remote and even if chlorine did form it would immediately be broken up again by the ultraviolet light.

(iv) The reversible addition of a chlorine atom to a polyene will remove a reactive radical and produce a comparatively unreactive polyenyl radical. This radical may not react again giving termination by route (ii) above:-



Poutsma⁸⁰ has studied the free radical chlorination of alkenes. Generally speaking at room temperature addition is favoured against abstraction. For example addition is 10 x faster than abstraction for 2-butene. However addition is reversible whereas abstraction is not. He also found that the low activation energies for abstraction and addition, $< 1 \text{ kcal mol}^{-1}$, had two effects. First addition to butadiene was no faster than the statistical twice that for 1-butene. Normally allylic activation makes the diene much more reactive.

Second as already observed it accounts for the lack of selectivity of the abstraction reaction. It is difficult to extend these results to polyenes within a polymer matrix, but it is clear that addition could have an important retarding effect on dehydrochlorination.

5 Source Variation

A monochromatic source, emitting light at 253.7 nm, and the polychromatic source in conjunction with filters were used to obtain some information about the wavelength dependence of this reaction.

(a) Filters

The use of glass and pyrex filters to cut out all light below 325 and 295 nm respectively showed that light of a lower wavelength than 295 nm is necessary to cause degradation. The results obtained using the solution filter, which only permitted transmission in the region 266-370 nm, showed that only a very small spectroscopically measureable amount of degradation has occurred in seven hours. It can be calculated that the change in optical density of 0.02 is equivalent to a weight loss of approximately 0.0005 mg. This vast reduction in the rate of reaction is brought about by excluding the higher energy radiation in the region 235-266 nm. It cannot be attributed to the reduction in intensity to 2.21×10^{15} quanta $\text{cm}^{-2} \text{s}^{-1}$ because a polychromatic run at $I_0 = 1.47 \times 10^{15}$ quanta $\text{cm}^{-2} \text{s}^{-1}$ gave a normal dehydrochlorination curve with $\Delta W_7 = 0.175$ mg.

This result is in contrast to Kenyon's⁵ and Reinisch, Gloria and Wilson's⁶¹ who found a limit of 340 nm for photodegradation. The difference must lie in the purity of the samples examined. The samples used here showed no absorption above 295 nm before irradiation and would therefore not absorb light at > 295 nm. Absorption in the

region 266-295 nm is very slight and obviously not sufficient to initiate a significant amount of degradation. There is more absorption in the region and this light is required to degrade the samples.

If this explanation is complete then a film which does absorb strongly above 266 nm should degrade as normal. However this is not found to be the case. The benzoyl peroxide loaded films irradiated through the solution filter initially degraded as expected, presumably via peroxide breakdown and radical attack on the poly(vinyl chloride). The reaction was not however sustained suggesting that for prolonged dehydrochlorination the high energy radiation is required. Similarly it might be expected that a film already polychromatically degraded, and therefore containing trienes and tetraenes which will absorb above 266 nm, might continue to degrade when irradiated through the filter. Again this was not observed to any significant extent.

This effect is more difficult to rationalise. It suggests that in the absence of this high energy radiation the polyenes alone cannot support degradation and that fresh reaction sites are created by impurities, which as stated only absorb below 266 nm in these samples. This though cannot be the whole story because the benzoyl peroxide loaded film still contains plenty of species which absorb above 266 nm, including undecomposed benzoyl peroxide, and yet the reaction ceases in this case after a relatively small amount of degradation. The explanation for this could again lie in the nature of the surface layer created. If, as in the polychromatic case, the presence of the benzoyl peroxide very rapidly creates a narrow, polyene dense, surface layer the reaction will very quickly slow down as before. But in this case the 'protective barrier' has much less damaging

radiation to block because the most reactive radiation below 266 nm is excluded. It could be then that after about 2 hours reaction, and a weight loss of 0.057 mg, the 'protective barrier' is completely effective.

One curious effect that irradiation through the filter, after polychromatic irradiation, does have is to alter the polyene distribution. The ultraviolet spectra shown in Figure 33 indicate that, after irradiation through the filter, the absorption in the region 250-370 nm is reduced accompanied by an increase above 370 and below 250 nm. As there is very little accompanying hydrogen chloride evolution this reaction must involve some kind of rearrangement of the polyenes with $n = 3-6$ to give longer polyenes and dienes. This rearrangement reaction must be easier than further degradation which appears to only occur if higher energy radiation is present. It suggests that if over a much longer time scale degradation could be achieved using light in the region 266-370 nm the resultant polyene distribution would be shifted towards the visible when compared with that obtained using unfiltered radiation.

(b) Monochromatic

The results show that basically the degradation process follows a similar course to that for polychromatic irradiation. The reaction commences at an increasing rate, rises to a maximum at the inflection point and then falls off. In detail however the dehydrochlorination curves for runs A and B shown in Figure 32, illustrate the differences between the two. The two runs were conducted at the same incident light intensity.

It can be seen that the polychromatic run started off much faster and reached a higher maximum rate, at 0.3 mg hr^{-1} after about

seven hours. It is these rates that should be considered when comparing the relative effectiveness of the two types of irradiation. After inflection it is the blocking effect which controls the reaction.

Examining the emitted light of the two sources it is apparent that the actual effective light intensity in the polychromatic case is less than in the monochromatic. The actinometer is sensitive to light up to 450 nm. The data in Table 2 shows that only 55% of the calculated light intensity is below 340 nm, and 18% below 266 nm. Yet despite this the polychromatic run is, from the maximum rates, about 7 x faster than the monochromatic.

Now the results using the filters indicated that degradation could not occur at a significant rate unless light at a wavelength < 266 nm was present. However it seems here that if this light is present then the lower energy radiation can assist degradation by a synergistic effect. A possible explanation for this effect is as follows. It has been experimentally found that light in the region 266-370 nm can redistribute the polyenes already present to produce dienes and polyenes with $n > 7$ from polyenes with $n = 3-6$. The dienes produced will be very reactive to light in the region 235-266 nm and thus a reactive site has been recreated. In this way the lower energy, longer wavelength, light will assist polychromatic degradation by re-creating the more reactive dienes. This then indicates that light up to 370 nm may be able to assist in polychromatic degradation, although this is not proven. The dienes produced by the observed redistribution may only come from say trienes and tetraenes in which case only light up to about 340 nm can assist degradation. It is convenient then to accept Kenyon's limiting wavelength for photodegradation of 340 nm.

Reinisch and co-workers⁶ found a polychromatic quantum yield 10 x that for monochromatic, and proposed a synergistic effect. If there were no such effect there would be very little difference between the two sources as far as effective light was concerned except that the monochromatic source would be about 5 x more intense. Alternatively it would require the use of light between 235-266 nm instead of monochromatic light at 253.7 nm to cause a 35 x increase in the rate of dehydrochlorination and this is not practicable.

As it is now apparent that polychromatic light up to say 340 nm assists the degradation of these poly(vinyl chloride) samples the increased rate of reaction can be readily understood. The monochromatic radiation at 253.7 can only be absorbed by dienes and trienes. The polychromatic radiation can however be absorbed by polyenes up to $n = 7$. It seems that this synergistic effect and the increased number of available chromophores is sufficient to produce a rate of dehydrochlorination 15 x (7 x from rates, and twice because only 55% of the light is < 340 nm) faster than occurs during monochromatic irradiation.

Going back to Figure 32, it can be seen that despite, or rather as will be seen because of, this much faster maximum rate of dehydrochlorination, after 30 hours the sample irradiated monochromatically has evolved 0.741 mg in comparison with 0.494 mg in the polychromatic case. The explanation for this phenomenon again lies in the nature of the 'protective barrier' formed on the film surface. It has been shown before how, in the polychromatic case, the rapid increase in the rate of degradation is accompanied by the build up of a 'polyene barrier' which becomes effective after a certain time interval, t_{inflec} , (depending on I_0) and causes the subsequent fall off in the dehydrochlorination rate.

In the monochromatic case there are two differences. First

the reaction starts off more slowly and the polyene barrier takes longer to form. For this reason the light will have penetrated deeper, for longer, and a deeper surface layer will be formed. This will be the opposite of the effect observed for benzoyl peroxide loaded films where the very rapid reaction caused the formation of a dense shallow polyene layer. The greater depth of the surface layer means that at a comparable weight loss there will be more sites available for reaction (cf. Table 33 - ΔW_{∞} , and hence $\Delta W_t / \Delta W_{\infty} \times 100$, will be relatively high here).

Second, as stated only dienes and trienes can absorb at 253.7 nm so that the effectiveness of the polyene layer to block damaging radiation is reduced. In the polychromatic case only 18% of the incident light would be absorbed by dienes and trienes, this being the percentage of the light emitted in the range 235-266 nm. However in the monochromatic case all the incident light is at 253.7 nm and must therefore be absorbed by dienes and trienes. Hence for an effective block 5 x as many dienes and trienes are required.

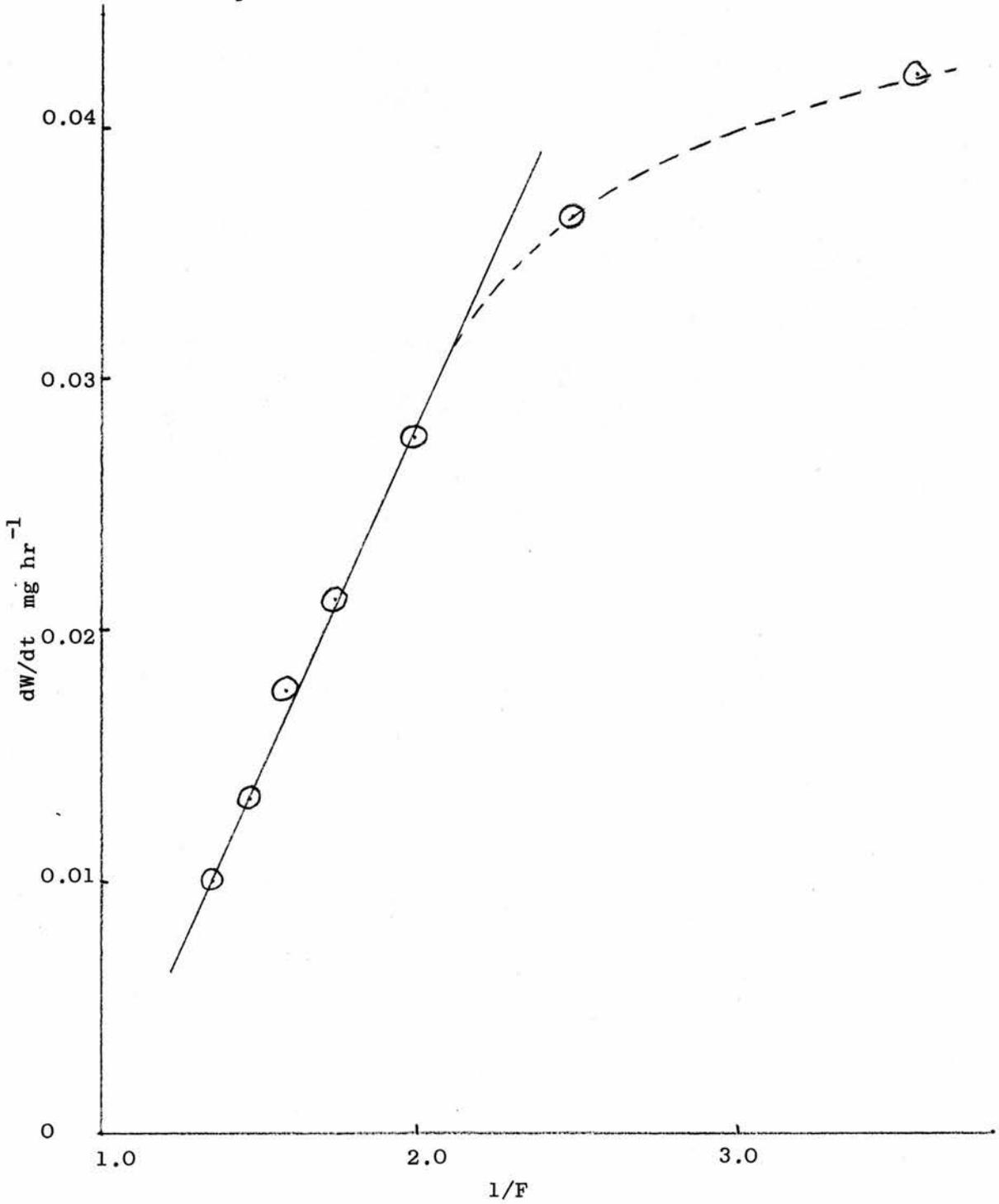
It can be seen then that the same processes operate in each case, but that the distribution of light in the polychromatic case causes the observed differences. The similarity can be further illustrated by plotting the rate of reaction, dW/dt , against the fraction of the available hydrogen chloride evolved, and this plot is shown in Figure 44 for $I_0 = 5.19 \times 10^{15}$ quanta $\text{cm}^{-2} \text{s}^{-1}$. ΔW_{∞} is estimated to be 1.0 mg at this intensity. As for polychromatic irradiation a straight line is obtained, cf Figure 43, thus indicating the similar role of 'availability' in each case.

The results also showed that, as for polychromatic irradiation, the presence of an ultraviolet absorber, benzoyl peroxide or

Figure 44

A plot of dW/dt versus $1/F$ for monochromatic irradiation

($I_0 = 5.19 \times 10^{15}$ quanta $\text{cm}^{-2} \text{s}^{-1}$)



acenaphthene, caused a considerable retardation of dehydrochlorination. This retardation appears to be proportionally greater than was observed in the polychromatic case. The calculation on page 97 showed that the acenaphthene film (L/3) will absorb 96% of the light at 253.7 nm and a similar calculation for the benzoyl peroxide loaded film (P/8) shows it will also absorb most of the light (at 253.7 nm $\epsilon = 1990$ l mol⁻¹ cm⁻¹). It is reasonable then that the presence of these additives will have a large effect. The mechanisms involved will be as described for polychromatic irradiation.

6 Spectral Data

This section discusses the results shown in section 5 of Chapter 3. These results help to elucidate four facets of the photodegradation - (a) the polyene distribution, (b) the relationship between spectra and weight loss, (c) hydrogen chloride catalysis, and (d) further comparison between mono- and polychromatic irradiation.

(a) Polyene Distribution

The series of spectra obtained (see Figure 34) for polychromatic irradiation of a standard sample in nitrogen and the subsequently calculated relative polyene concentrations (see Table 27) show that the shorter the polyene the more abundant it is. This is in contrast to the results obtained for thermal degradation. Geddes²⁷ found an absorption maximum at 500 nm indicating an average polyene length of 14. Other workers^{9,12,58} have found a slightly lower value around 10. Geddes attributed his high average polyene length to the low temperature of degradation employed giving a low rate of transfer.

The main difference between thermal and photodegradation is that thermal degradation occurs above the T_g, and photodegradation below it.

The comparative fluidity of the polymer molecules during thermal degradation will permit rotation of the C-C links in the polymer chain. Thus it will be much easier to form the long polyenes observed in thermally degraded poly(vinyl chloride). In photodegradation no rotation is possible and the high rate of transfer will be caused by the chain reaction reaching the end of a planar portion of the poly(vinyl chloride) chain. This has already been discussed in section 4(b).

The calculations in Table 27 also showed that initially short polyenes are favoured but after about one hour the polyene distribution is constant, ($C_3:C_5:C_7:C_9 :: 13.3:5.5:2.2:1$). It is curious that even after seven hours irradiation the same proportion of the longer polyenes is being produced. It might be expected that at high conversion it would be difficult to form a long polyene because of the scarcity of a suitable undegraded section of polymer chain. There are however three ways in which long polyenes could still be produced. First they could come from further reaction of an existing polyene or the linking of two existing polyenes. Second they would be produced by the redistribution brought about by light in the region 266-370 nm. Third they could be formed at fresh sites at the bottom of the protective barrier where an unzipping reaction could continue unhindered along a chain. These routes to long polyenes would offset the restrictions imposed by high conversion.

It has been shown that a high rate of transfer brought about by structural limitations keeps the average polyene length short. Initially the short polyenes are favoured to an even greater extent and the high proportion of trienes say is steadily reduced during the first hour until a constant value is reached. Transfer was

presumably easier at that stage when, apart from structural limitations, the main consideration in the dehydrochlorination chain reaction was which hydrogen atom was nearest to the newly formed chlorine radical. It could be the next hydrogen atom on the chain from which the chlorine radical had evolved, or a hydrogen atom on a neighbouring chain. When more polyenes have been formed and 'availability' starts to control the reaction, the hydrogen atoms on other chains will become scarcer. Hence transfer for this reason will be reduced, and a lower proportion of short polyenes will result.

(b) Spectra and Weight Loss

The results obtained show that for a given cast film the area under the ultraviolet spectrum, or the optical density at a given wavelength, OD_{λ} , is related to the weight loss, but this is not a linear relationship. It was shown that it holds for samples, from the same cast film, irradiated at different intensities, or for one sample over a series of time intervals. This is to be expected as the area, or OD_{λ} , is a measure of the polyenes produced, or of the number of one particular polyene, and it has been shown that this is not affected by intensity or time, after about one hour.

It is important to note that it is very dangerous to compare different samples. It has been shown, for instance, that samples containing different amounts of tetrahydrofuran do not give the same spectrum after the same weight loss.

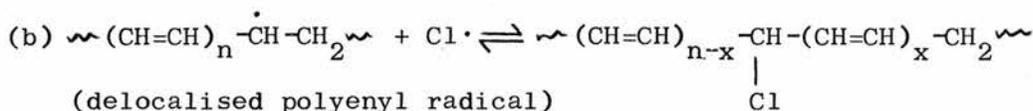
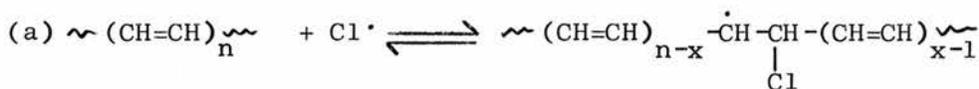
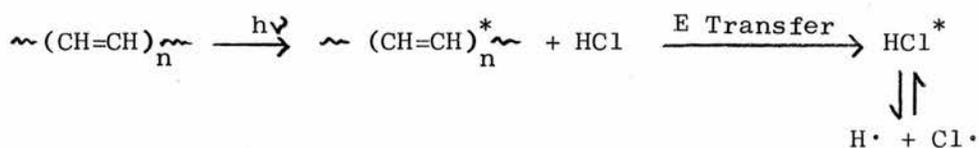
(c) Catalysis

The results showed that, when a series of spectra were obtained using the cell shown in Figure 7, keeping the taps shut so that there would be a build up of evolved hydrogen chloride, the

reaction was apparently suppressed. A great deal of work has gone into determining whether hydrogen chloride is a catalyst for thermal degradation (see Introduction). It would appear that the opposite is occurring here for photodegradation. This is confirmed by the result obtained when the cell was filled with 100% hydrogen chloride and the dehydrochlorination reaction was apparently severely suppressed.

It is possible however that the dehydrochlorination is not being suppressed but that discolouration is. It has just been shown that ultraviolet spectra may not always be a good measure of dehydrochlorination. Obviously a combination of the two is possible, so that dehydrochlorination is reduced, but so is discolouration, and hence the reduction is not as large as the spectra suggest.

The mechanism of this reaction is not known. The following two possibilities exist. First the hydrogen chloride gas could be an ultraviolet filter, absorbing the damaging light. This however is impossible because the cell filled with hydrogen chloride showed no absorption. Second the hydrogen chloride may reduce the polyene conjugation length by a reversible addition reaction as suggested in section 4 (c) (iv). The feasibility of this reaction was discussed in that section and it was concluded that it was a reasonable possibility:-



Both reactions break up long polyenes. The hydrogen chloride concentration in the film is increased by a partial pressure of hydrogen chloride above the film, i.e. no sweeping, or an atmosphere of hydrogen chloride.

If reactions of this type do account for the observed reduction in absorption the actual amount of dehydrochlorination would be as great as usual, if not greater because of the breakdown of the 'protective barrier'. In this way the effect would be similar to oxygen which causes increased dehydrochlorination but reduced discolouration (see section 7).

(d) Mono- and Polychromatic Irradiation

A comparison of the polyene distributions obtained for mono- and polychromatic irradiation (see Tables 27 and 28) shows that the results are similar. In both cases short polyenes are initially favoured, but a shift towards longer polyenes is observed. However, whereas polychromatic irradiation produces a constant distribution after one hour, in the monochromatic case the distribution is still altering, albeit very slightly, in favour of longer polyenes after 50 hours. It is possible that because of the deeper surface layer produced, the restrictions imposed by high conversion are not as severe here as in the polychromatic case. It is possible that if in the monochromatic case the irradiation time was extended a constant distribution would be obtained.

7 Oxygen

It was not the purpose of this work to study the photo-oxidation of poly(vinyl chloride) in any detail. A few experiments have been conducted for comparative purposes. It was observed in the Introduction that oxygen causes an increase in the rate of

dehydrochlorination and also causes bleaching. Both these effects have been observed here. However the mechanisms of the acceleration is a little different in this case.

Comparison of the dehydrochlorination curves obtained in oxygen and nitrogen at the same light intensity, curves A and E in Figure 39, shows that in fact the reaction in nitrogen is initially faster than in oxygen. The rapid acceleration in the rate of reaction in nitrogen is brought about by the formation of polyenes which in turn absorb to give more polyenes. In oxygen however polyene formation is restricted by the growing polyenyl radical reaction with oxygen, so that the concentration of polyenes does not increase so rapidly. However for the same reason a 'protective barrier' is not formed as quickly or effectively. Hence eventually more dehydrochlorination is obtained, in fact about twice as much depending on intensity.

Intensity has more effect in oxygen than nitrogen. It can be seen that the curves in Figure 39 are not superimposable after one hour or any other time interval, but are diverging. In this case the calculation and conclusions shown on page 89 do not apply. That is the availability of reaction sites is not exactly offset by the absorbed light intensity. The bleaching of the polyenes will produce a deeper surface layer and hence more available reaction sites, so that the greater light intensity is manifested as greater hydrogen chloride evolution.

The series of ultraviolet spectra obtained and the polyene distribution calculation (see Table 30) show how the polyene length is reduced by oxygen. It can be seen that $C_3:C_5:C_7:C_9$ which was 13.3:5.5:2.2:1 in nitrogen is 150:32:6:1 in oxygen after two hours. The exact mechanism of the bleaching reaction is not discussed here. Several authors^{24,33,34} have shown that oxygen promotes chain scission

and a mechanism has been proposed by Winkler³³. Oxygen may also react with polyenes without causing scission but breaking the conjugation i.e. bleaching. The infra-red spectra show that carbonyl compounds are produced as Winkler's mechanism proposes.

Lastly it has been shown how oxygen can bleach a sample which has already been degraded in nitrogen. It is interesting that the oxygen can cause bleaching even in the dark. This will be due to stable polyenyl radicals reacting with oxygen. The polyene distribution calculations, Table 31, for the sample degraded in nitrogen, exposed to oxygen, and then irradiated in oxygen show that there is the expected shift towards shorter polyene sequences, and after 20 minutes irradiation in oxygen a $C_3:C_5:C_7:C_9$ ratio of 60.3:15.2:3.6:1 is obtained. This ratio does not favour the trienes as much as that obtained for irradiation in oxygen alone, but is tending that way. However after this maximum the ratio tends back towards the value observed in nitrogen alone. This is curious and suggests that once the 'polyene barrier' is formed in nitrogen it cannot be totally broken down to give a similar situation to that in oxygen alone. The less deep surface layer that is formed in nitrogen will prevail even in oxygen and will therefore produce a similar polyene distribution.

Chapter 5

The Model

The calculation that follows was designed to try to explain the build up of a surface layer of polyenes. For simplicity sake it is necessary to consider a monochromatic source, e.g. the low pressure mercury lamp emitting at 253.7 nm, and one polyene which will absorb at this wavelength, a triene.

The film is 0.1 mm or 100 μ thick and is split into 100, 1 μ thick, layers. These layers are labelled $n = 1, 2, 3, 4, \dots, 100$, and the optical densities, OD, in these layers at time t are $OD(1, t)$, $OD(2, t)$, $OD(3, t) \dots OD(100, t)$, i.e. $OD(n, t)$. Time is divided into 100 units. Therefore the optical densities in layer n at these times are $OD(n, 0)$, $OD(n, 1)$, $OD(n, 2) \dots OD(n, 100)$.

The initial optical density for the whole film is found from the ultraviolet spectrum and is given by $OD(\text{init})$. It is assumed that this is entirely due to trienes homogeneously dispersed throughout the film. Therefore:-

$$OD(1, 0) = OD(2, 0) = OD(3, 0) \dots = OD(100, 0) = \frac{OD(\text{init})}{100}$$

Now Beer's Law states that:-

$$OD = \log I_0 / I$$

where I_0 is the incident light intensity and I the transmitted light intensity.

Let $I(1, 0)$, $I(2, 0)$, $I(3, 0) \dots$ etc be the intensities of the light transmitted by layers 1, 2, 3, ... etc at $t = 0$, and let I_0 the incident intensity at $t = 0$ be denoted by $I(0, 0)$. Then as $OD(1, 0) = OD(2, 0) \dots$ etc:-

$$OD(n, 0) = \log \frac{I(0, 0)}{I(1, 0)} = \log \frac{I(1, 0)}{I(2, 0)} = \log \frac{I(2, 0)}{I(3, 0)} \dots$$

The light absorbed by each layer can now be calculated.

Consider layer 1. The antilog of OD(1,0) gives $\frac{I(0,0)}{I(1,0)}$.

Taking I(0,0) as 1 then I(1,0) can be found as a fraction of the incident light intensity. Now the light absorbed by layer 1, during time unit 1, IA(1,1) is given by I(0,0) - I(1,0), and is again a fraction of the incident light intensity.

Now consider layer 2. The antilog of OD(2,0) gives $\frac{I(1,0)}{I(2,0)}$, and as I(1,0) is known from layer 1, I(2,0) can be found and hence IA(2,1) which equals I(1,0) - I(2,0).

In general the antilog of OD(n,t) gives $\frac{I(n-1,t)}{I(n,t)}$. I(n-1,t) is known from the layer above, and hence I(n,t) is found and IA(n,t), equal to I(n-1,t) - I(n,t).

The light absorbed by each layer during time interval t is now known. It is assumed that this light absorbed by the trienes will be used to make more trienes. This is not an accurate reproduction of the experimental facts. The trienes will react to give tetraenes and longer polyenes and may form some trienes by transfer reactions. However only one polyene is being considered here and in fact at the same time some dienes are forming trienes. The trienes then are being used to represent all polyenes so that the fact that trienes will not generally produce trienes is unimportant.

The number of trienes produced during time t is found by multiplying IA(n,t), the fraction of I₀ absorbed during time t, by I₀ and Ø, the quantum yield of hydrogen chloride, HCl, and dividing by 3. That is:

$$P3E(n,t) = IA(n,t) \times I_0 \cdot \text{Ø}/3$$

where P3E(n,t) is the number of molecules of triene produced in layer n during time t.

A correction factor to account for 'availability' must now be introduced. The number of trienes produced is multiplied by

$\frac{P3(\infty) - P3(n,t-1)}{P3(\infty)}$, where $P3(\infty)$ is the maximum number of trienes that can be produced in one layer, and $P3(n,t-1)$ is the number of trienes already present in layer n at time t . In practice it was found that a better fit was obtained if this expression was cubed. It can then be seen that:-

$$P3EC(n,t) = P3E(n,t) \times \left(\frac{P3(\infty) - P3(n,t-1)}{P3(\infty)} \right)^3$$

where $P3EC(n,t)$ represents the corrected number of molecules of triene produced in layer n during time t .

The number of trienes produced is then added to the number that was already present to give the new total, $P3(n,t)$ i.e.

$$P3(n,t) = P3(n,t-1) + P3EC(n,t)$$

This number $P3(n,t)$ can now be converted back into an optical density to give $OD(n,t)$. Now

$$OD(n,t) = \epsilon \cdot C(n,t) \cdot l$$

In this expression ϵ is taken to be 30,000, l is the thickness of one layer i.e. 10^{-4} cm, and C is calculated as follows

$$x \text{ molecules} = \frac{x}{6.023 \times 10^{23}} \text{ moles}$$

Consider 1 cm^2 of film. Then $V = 10^{-7}$ litres

$$\therefore C = \frac{x \times 10^7}{6.023 \times 10^{23}} \text{ mol l}^{-1}$$

$$\begin{aligned} \text{Therefore } OD(n,t) &= \epsilon \cdot C(n,t) \cdot l \\ &= 30,000 \times P3(n,t) \times \frac{10^{-16}}{6.023} \times 10^{-4} \\ &= \underline{P3(n,t) \times 4.981 \times 10^{-17}} \dots \dots \dots (1) \end{aligned}$$

To illustrate the last three steps consider layer 1 during time

1. $IA(1,1)$ has been calculated and hence $P3E(1,1) = IA(1,1) \times I_0 \cdot \theta/3$.

$P3E(1,1)$ is now found as follows:-

$$P3EC(1,1) = P3E(1,1) \times \left(\frac{P3(\infty) - P3(1,0)}{P3(\infty)} \right)^3$$

P3(1,0) is found from OD(init) using expression (1) above.

$$\text{i.e. } P3(1,0) = \frac{OD(1,0)}{4.981 \times 10^{-17}} = \frac{OD(\text{init})}{100 \times 4.981 \times 10^{-17}}$$

It should also be noted that P3(1,0) = P3(2,0).....

Then

$$P3(1,1) = P3(1,0) + P3EC(1,1)$$

and hence,

$$OD(1,1) = \frac{P3(1,1) \times 4.981 \times 10^{-17}}$$

Now consider time unit 2 for layer 1. The antilog of OD(1,1)

gives $\frac{I(0,1)}{I(1,1)}$ and hence I(1,1) as a fraction of I_0 .

$$IA(1,2) = I(0,1) - I(1,1)$$

$$P3E(1,2) = IA(1,2) \times I_0 \cdot \emptyset/3$$

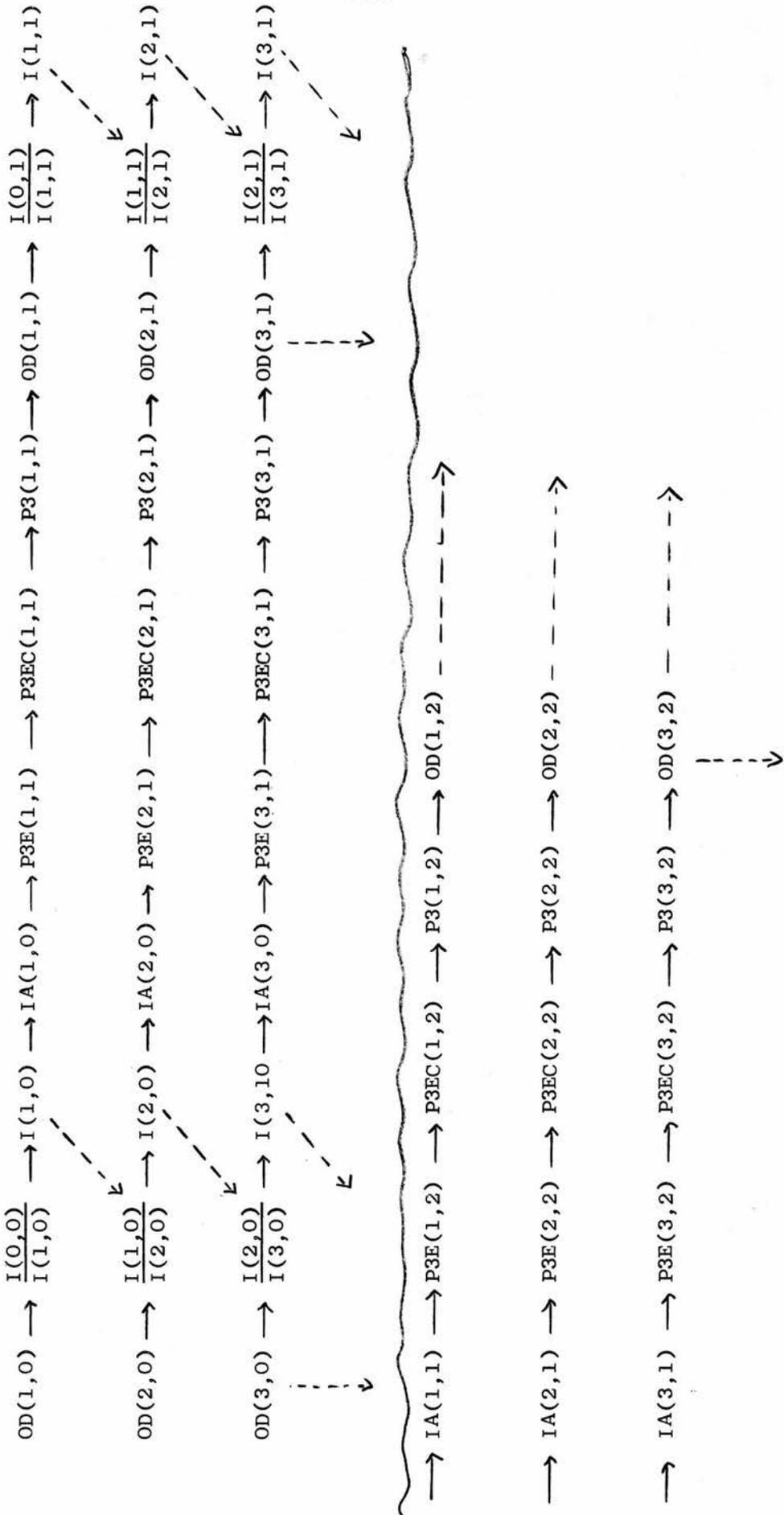
$$P3EC(1,2) = P3E(1,2) \times \left(\frac{P3(\infty) - P3(1,1)}{P3(\infty)} \right)^3$$

N.B. P3(1,1) is known from the preceding time interval.

$$P3(1,2) = P3(1,1) + P3EC(1,2)$$

$$OD(1,2) = \frac{P3(1,2) \times 4.981 \times 10^{-17}}$$

This calculation is continued for 100 time units and down through 100 layers A diagrammatic summary is shown below:-



The calculation was made using a computer and P3E, P3EC, P3 and OD were printed out for each level at each time interval along with running totals for each time interval.

The only data required are values for OD(n,0), and hence P3(n,0), P3(∞) and $I_0 \cdot \phi / 3$. OD(init) is 0.15 at 253.7 nm and therefore OD(n,0) is 0.0015 and P3(n,0) = 3.01×10^{13} molecules. P3(∞) is chosen as 2.857×10^{15} and $I_0 \cdot \phi / 3$ as 1.2×10^{15} , in order to give the best fit with experimental data.

Figure 45 shows plots of OD versus time using OD values (a) calculated from the model using time intervals of $\frac{1}{2}$ hour i.e. covering 50 hours, (b) obtained from the experimentally found spectra shown in Figure 36 (see Page 75). It can be seen that the curves are nearly superimposable indicating that the model gives a good approximation to the experimental results.

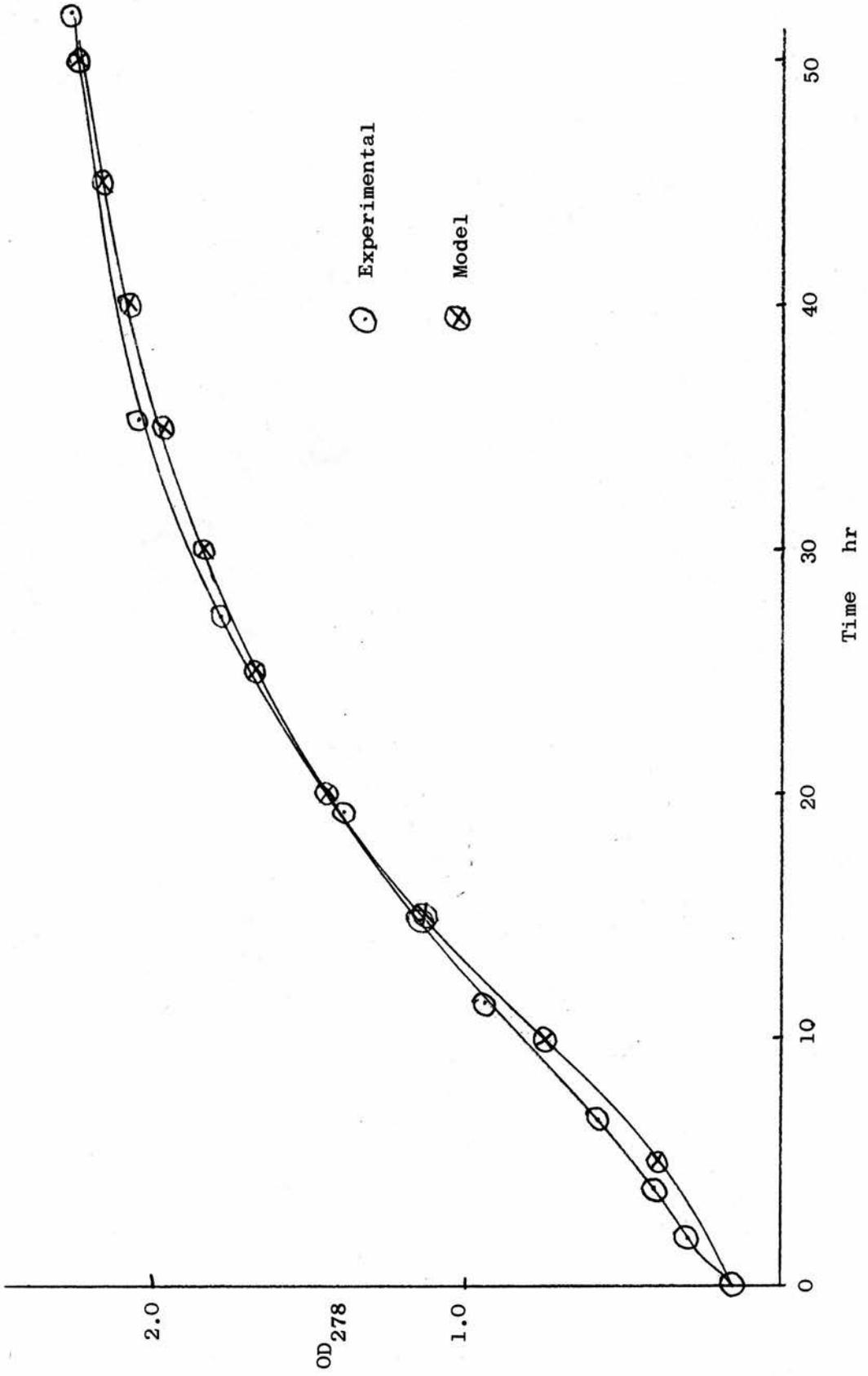
Having found the value of $I_0 \cdot \phi / 3$ which gives the best solution then ϕ can be calculated. The calculation has been fitted to experimentally found optical densities where $I_0 = 5.19 \times 10^{15}$ quanta $\text{cm}^{-2} \text{s}^{-1}$.

$$\begin{aligned} I_0 &= 5.19 \times 10^{15} \\ &= 5.19 \times 10^{15} \times 60 \times 30 \\ &= 9.342 \times 10^{18} \text{ quanta cm}^{-2} \text{ per } \frac{1}{2} \text{ hr} \\ I_0 \cdot \phi / 3 &= 1.2 \times 10^{15} \\ \therefore \phi &= \frac{3.6 \times 10^{15}}{9.342 \times 10^{18}} = 0.00039 \end{aligned}$$

The ϕ value is the quantum yield of hydrogen chloride from trienes only and holds throughout the reaction. The retardation effect is accounted for by the 'availability' correction factor, not a changing ϕ . Reinisch, Gloria and Wilson⁶¹ showed that the polychromatic ϕ for their experimental conditions was reduced from

Figure 45

Comparative plots of OD_{278} , found experimentally and by the Model, versus time



0.09 to 0.025 in $2\frac{1}{2}$ hours. It was however probably not the actual ϕ that changed but the 'availability'.

This ϕ value can now be checked. Consider the situation between 6 and 9 hours irradiation when the rate of reaction is a maximum.

$$\begin{aligned} \text{Rate} &= 0.045 \text{ mg hr}^{-1} \\ &= 0.0225 \text{ mg } \frac{1}{2}\text{hr}^{-1} \\ &= \frac{0.0225 \times 10^{-3} \times 6.023 \times 10^{23}}{36.5} \\ &= 3.71 \times 10^{17} \text{ molecules HCl } \frac{1}{2} \text{ hr}^{-1} \end{aligned}$$

But film area = 9.34 cm^2

$$\therefore \text{Rate} = \frac{3.71 \times 10^{17}}{9.34} = 3.97 \times 10^{16} \text{ molecules } \frac{1}{2} \text{ hr}^{-1} \text{ cm}^{-2}$$

However only a fraction of these molecules come from trienes. Between 6 and 9 hours 0.106 mg hydrogen chloride are evolved. For the same period of time from the computer read out:-

$$\begin{aligned} P3 &= 0.445 \times 10^{16} \text{ molecules triene} \\ &= 1.335 \times 10^{16} \text{ molecules HCl} \\ &= \frac{1.335 \times 10^{16} \times 36.5 \times 10^3}{6.023 \times 10^{23}} \\ &= 8.09 \times 10^{-4} \text{ mg cm}^{-2} \end{aligned}$$

Total hydrogen chloride evolved = 0.106 mg

$$= \frac{0.106}{9.34} = 0.0113 \text{ mg cm}^{-2}$$

$$\therefore \text{Hydrogen chloride from trienes} = \frac{8.09}{1.13} \times 10^{-2}$$

$$= \underline{0.072 \times (\text{total HCl})}$$

Now rate of HCl production = $3.97 \times 10^{16} \text{ molecules } \frac{1}{2}\text{hr}^{-1}$

$$\begin{aligned} \therefore \text{Rate of HCl production from trienes} &= 0.072 \times 3.97 \times 10^{16} \\ &= 2.82 \times 10^{15} \end{aligned}$$

All the incident light is absorbed at this stage of the reaction and therefore:-

$$\text{Light absorbed} = I_a = 9.342 \times 10^{18} \text{ quanta cm}^{-2} \frac{1}{2} \text{hr}^{-1}$$

$$\therefore \phi = \frac{2.82 \times 10^{15}}{9.342 \times 10^{18}} = 0.00030$$

This figure agrees well with the 0.00039 found by the model.

Now that the fraction of the hydrogen chloride produced by the trienes is known an overall monochromatic quantum yield can be found.

$$\begin{aligned} \phi_{\text{MONO}} &= 0.00039 \times \frac{1}{0.072} \\ &= 0.0054 \end{aligned}$$

This value is of the same order as the 0.009 found by Reinisch and co-workers⁶¹.

Having tested the significance of the best value found for $I_0 \phi / 3$, the value for $P3(\infty)$ is examined. A value of 2.857×10^{15} was found to give the best fit if the correction factor was cubed. Now consider the total hydrogen chloride available in a 1μ layer:-

$$\begin{aligned} \text{Weight} &= pV = 1.4 \times 10^{-4} \text{ g in a } 1 \text{ cm}^2 \text{ area} \\ W &= \frac{1.4 \times 6.023 \times 10^{23} \times 10^{-4}}{62.5} \quad (\text{Density of poly(vinyl chloride) taken as } 1.4) \\ &= 1.35 \times 10^{18} \text{ molecules HCl} \end{aligned}$$

The number of molecules available for trienes:-

$$\begin{aligned} &= 1.35 \times 0.072 \times 10^{18} \\ &= 9.72 \times 10^{16} \end{aligned}$$

\therefore The total number of molecules of triene possible

$$\begin{aligned} &= \frac{9.72}{3} \times 10^{16} \\ &= \underline{3.24 \times 10^{16}} \end{aligned}$$

But $P3(\infty) = 2.857 \times 10^{15}$ i.e. only $\frac{2.857}{32.4} = 0.088$ or approximately 1/10th of the apparently available trienes are in reality available. If the cubed factor is not introduced an even smaller $P3(\infty)$ is needed

to give a good fit and maybe only 1/15th of the trienes become available. Which is the correct answer is not clear though the smaller fraction does seem less likely. Also the cubed factor can possibly be justified because three units are needed to form a triene. Maybe if tetraenes were considered the factor would have to be raised to the power 4.

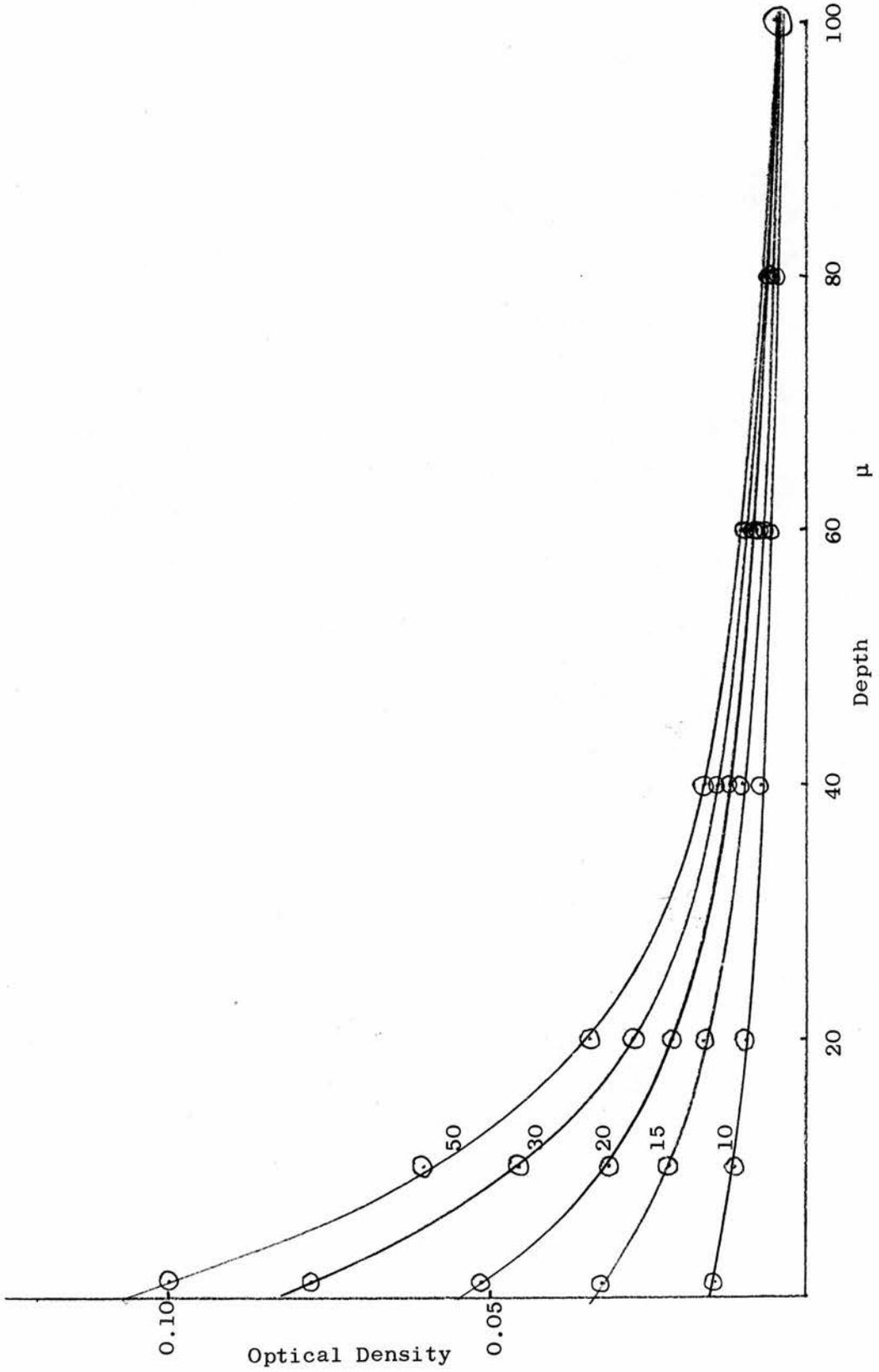
This factor must be connected with the geometry or structure of the polymer and may be a measure of the number of planar units of the type $\sim (\text{CH}_2 - \underset{\text{Cl}}{\underset{|}{\text{CH}}})_3$, as planarity is a condition for a conjugated polyene.

It has now been shown that the model can be made to fit experimental data. The individual changes in optical density in each layer, and hence the polyene build, can now be examined. Figure 46 shows plots of optical density versus film depth at various times.

These plots clearly show an exponential polyene distribution and the build up of a surface layer. They do not show as sharp a cut-off as is observed in the photographs in Figure 13a and 13b, but this model is only an approximation and it does give a good indication of how a surface layer is formed.

Figure 46

Plots of optical density versus depth at the times (hr) as shown on the curves



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