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CHEMICAL MODIFICATION OF POLYPROPYLENE

by

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SUMMARY

The modification of polypropylene fibre and film has been achieved by graft copolymerisation of monomer systems, using ultraviolet radiation. Similar attempts with a mechanico-chemical method were unsuccessful. The optimum conditions for grafting were determined using 2-vinyl pyridine as a typical monomer in the presence of a photo initiator, benzophenone. It was found, that the amount of monomer grafted increased with irradiation time, but decreased with increasing concentration of photo initiator. Hence the role of benzophenone as a chain terminator has been demonstrated.

Two stabilisers of the vinyl hindered phenol type were synthesised and in addition a vinyl substituted 2-hydroxy benzophenone was prepared. These monomers were polymerised using free radical techniques and the stability of both the monomer and polymer was determined by the appropriate methods, after blending into polypropylene.

The antioxidant activity of these compounds and their photostability was compared with conventional commercial stabilisers. All the additives at the concentrations used could be solvent extracted.

The thermal and photo oxidative stability of polypropylene has been increased by the grafting of a vinyl antioxidant, particularly 3,5 ditertiary butyl-4-hydroxy benzyl acrylate. This was not affected by solvent extraction. The grafting reaction was influenced by the monomer-benzophenone ratio and reflected in the induction period to oxidation of the polymer film.

Differences in the density of the grafted side chains has been suggested. Possible side reactions have been investigated and termination processes involving benzophenone postulated.

A mechanism for the grafting reaction has been proposed involving the formation of hydroperoxide. Grafting of an ultraviolet absorber was attempted but no increased photostability was observed. This was attributed to a concentration effect of the additive. Graft copolymers of 2-vinyl pyridine and 3,5 ditertiary butyl-4-hydroxy benzyl acrylate with polypropylene were prepared to obtain stability and dyeability. Although the dyeability increased the stability was reduced indicating interference between the materials.

Suggestions for further studies have been proposed.

The work described herein was carried out at the University of Aston in Birmingham between October 1969 and August 1972. It has been done independently and submitted for no other degree.

B W Evans.

October 1972

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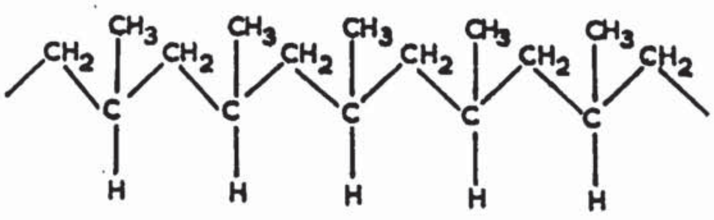
1. INTRODUCTION

Soon after the original patents were filed on polypropylene, it became evident that this new polymer had potential as a fibre forming material offering increased advantages over polyethylene. This optimism, however, was shortlived, and it was not until the early 1960's that polypropylene fibres had made sufficient headway to be a marketable commodity.

The development of polyolefins as textile materials came at a time when other synthetics were already firmly established. Although the polyesters and polyamides were more expensive than polypropylene, the latter had little extra to offer in the way of novel properties to compete with the natural fibres. Progress was further impaired in this field because of the technical problems inherent in polypropylene, limiting its usage to fringe markets where it had a decisive edge over the other synthetics. These problems are heat and light stability, and equally as important in textiles, dyeability.

The chemical structure of polypropylene, being a pure hydrocarbon containing tertiary hydrogen groupings makes it particularly susceptible to oxidation. Isotactic polypropylene has the structure

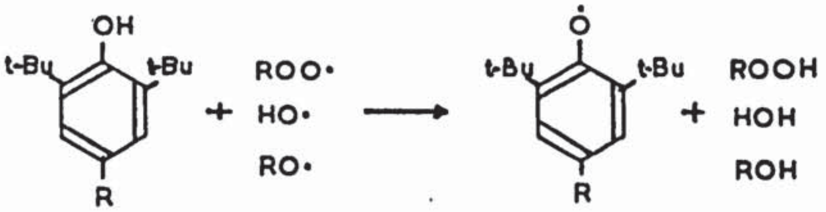


The thermal oxidation of polypropylene has been widely studied and it is now accepted that degradation occurs through the initial formation of hydroperoxides. The characteristic autoxidation of polyolefins is thought to progress by the following scheme[1], where RH represents the hydrocarbon.

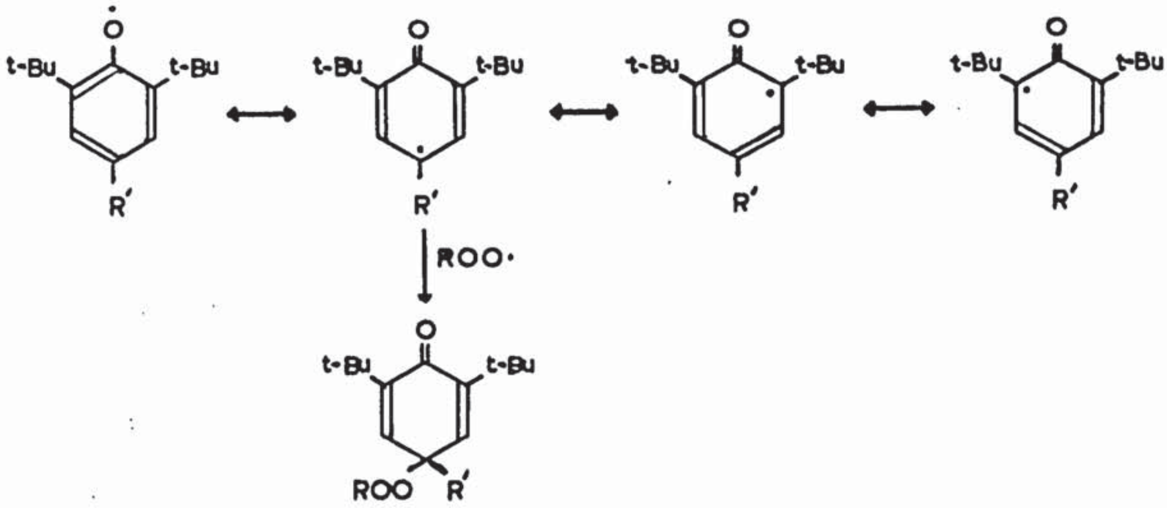
$$\begin{array}{llcll} \text{Initiation} & RH + O_2 & \longrightarrow & \text{free radicals} & (1) \\ \text{Propagation} & R. + O_2 & \longrightarrow & ROO. & (2) \\ & ROO. + RH & \longrightarrow & ROOH + R. & (3) \\ & ROOH & \xrightarrow[\text{light}]{\text{heat or}} & RO. + .OH & (4) \end{array}$$

The chain reaction illustrated by reactions (2) and (3) can be prevented by using a free radical acceptor.

The most important free radical scavengers used in polypropylene are of the hindered phenolic type. These function by a hydrogen transfer process, eliminating active radicals, forming a resonance stabilised phenoxy radical which does not react further with the polymer. The general reaction is as shown.



Resonance stabilisation of the phenoxy radical can then occur, and reaction with a further radical may take place. In theory one mole of stabiliser is capable of eliminating two radical species.



Amine antioxidants function similarly, but their oxidation products tend to be coloured and may be hazardous so are less favoured than the phenolics for polypropylene.

Other types of antioxidant, sulphur compounds, phosphites and metal dithiocarbamates, react by removing the hydroperoxide formed in (3), and decomposing this by a non-radical process[2]. These operate by a different mechanism than the phenols, and the two kinds of antioxidant (peroxide decomposers and radical acceptors), therefore, enhance each other when used together and act synergistically.

In this manner, the oxidation of polypropylene can be retarded both during processing and later in service life.

However, it has been found that the stabilisers could become extracted from the polymer during laundering and drycleaning with the resulting deterioration of the material. This loss of antioxidants could be serious where foodstuffs are involved, since contamination from the film wrapping could occur by leaching. For this reason, legislation exists concerning non-toxic additives in foodstuffs packaging, and phenols are some of the few types accepted for this purpose. There are several approaches to solving the problem of antioxidant loss by volatility and extractability. Studies by Plant and Scott[3] concerning volatility, have shown that for the homologous series I, this decreased with increasing molecular weight of the additive, and the activity of the antioxidant also increased for the series.

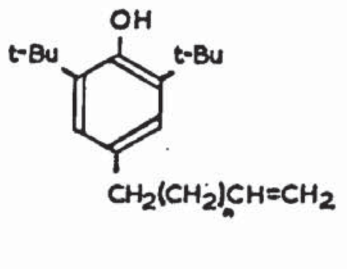
I

Scott has suggested[4] that there is an optimum molecular weight in any class of antioxidant for maximum activity. Below this, losses due to volatilisation may occur, and the compatability of the antioxidant with the polymer may be reduced if this optimum is exceeded. Very little work on the effects of volatility and compatability has been published, but these must play a large part in determining the usefulness of antioxidants.

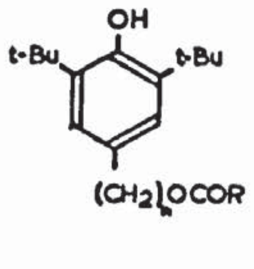
An important industrial objective therefore is to increase further the effectiveness of antioxidants. Several antioxidants of increased molecular weight have been made, but this approach eventually becomes limited. Perhaps the best prospect of reducing the extractability and volatility is to incorporate an antioxidant functional group into a polymer chain. Such polymeric antioxidants may be synthesised by introducing a polymerisable vinyl group into the molecule which does not interfere with its chain breaking activity. Several of these have been made[5,6] and blended into polypropylene prior to processing giving good stability, but these were not chemically combined.

An extension of this idea is the copolymerisation of a vinyl phenol with propylene at the monomer stage, thus incorporating the material ih the polymer backbone. The copolymer is then "diluted" with polypropylene by blending before use. Research has mainly centred around the two types of stabilisers II and III

II



III

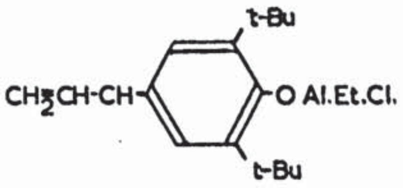


The polymerisation of propylene with Ziegler-Natta catalysts has always been carried out in the absence of polar compounds due to the adverse effect such materials have on the catalyst.

Patton and Horeczy[7] claimed the first successful copolymerisation of propylene with a hindered phenol, using the Ziegler-Natta process. They achieved this, since they found that the steric hindrance around the hydroxyl group nullified the effect of this phenol on the catalyst. They prepared 4-(but-3-enyl)-2,6-ditertiary butyl phenol (II,n=1) and copolymerised this with propylene forming between 0.005-2% by weight of the antioxidant in the total copolymer. The stabiliser was not extracted by methanol and compared favourably on ageing at 150°C with samples containing similar percentages of 4-methyl-2,6 ditertiary butyl phenol which they found to be volatile.

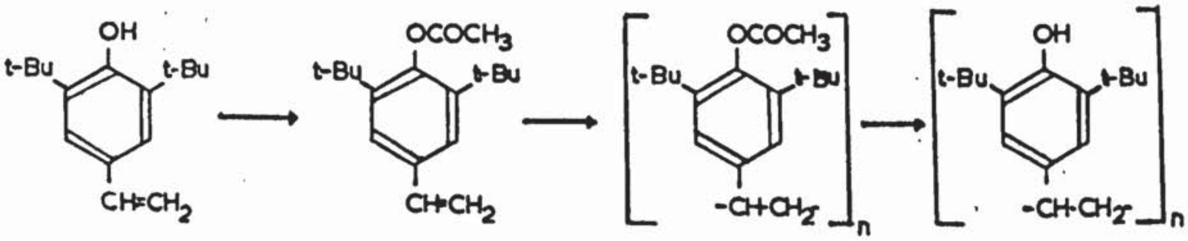
The problem of catalyst deactivation was also overcome by Iwata and Sasaki[8] by substituting the phenol (II) with an aluminium compound. By using this complex (IV) as both monomer and catalyst, copolymerisation with propylene was achieved.

IV



The stability of the material when copolymerised was better than conventional antioxidants, compatability and extraction problems being eliminated. Earlier work by Rocklin and Morris[9] used the hindered phenolic , esters of the benzyl alcohol type as shown in III, (n=1). They noted that the alcohols are relatively polar and therefore of somewhat limited miscibility in non-polar organic substrates. By reacting the 3,5-dialkyl-4-hydroxy benzyl alcohols with organic carboxylic acids, novel esters were produced which retained the desirable antioxidant features and gave enhanced miscibility. Benzoates, palmitates and stearates were made, which were used in vegetable oils and edible fats as antioxidants. The acrylate was also synthesised (III, R=vinyl, n=1), and used without polymerisation in polypropylene at 0.5% concentration by weight and gave oven heat stability at 133°C of two days, together with some UV stability on outdoor exposure. This benzyl acrylate was also copolymerised with styrene to give improved oxidation stability over the pure polymer.

At the beginning of this study little work had been published on the radical polymerisation of vinyl antioxidants since it was known that free radical polymerisation in the presence of a stabiliser would be much reduced, and therefore to form polymers of these compounds was thought impossible. Previously reported polymerisations[10,11] of hindered phenolics have involved blocking the reactivity of the hydroxyl group by acylation, followed by polymerisation, then hydrolysis to regenerate the phenol.

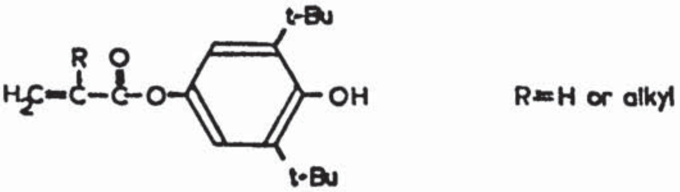


Kleiner[12] however studied a series of vinyl hindered phenols of the ester types (III) including acrylates, methacrylates, fumarates, maleates etc. These were polymerised directly using high molecular weight peroxides such as lauroyl and decanoyl peroxides. Protection of the oxidisable polymer was achieved by blending the polymeric stabiliser into the system either alone or with peroxide decomposers to give synergism. Copolymerisations of several of the crotonates and fumarate derivatives were carried out with amongst others, styrene, vinyl acetate and methyl methacrylates to give increased stability.

All these materials have been introduced into the polymer by preblending or copolymerisation with the monomer, but little work has been done on preformed articles.
In the preparation of textile fabrics and other manufactured products it is frequently desirable to apply finishes or coatings to improve the light stability or anti-static effects of the article.

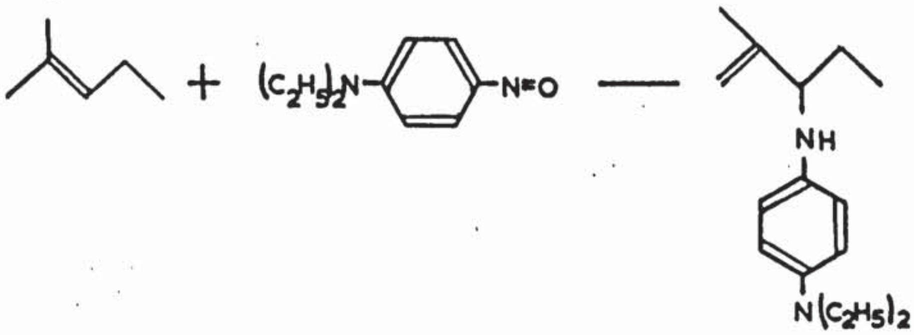
Stiehl[13] synthesised acrylic substituted phenols of the type V for use as antioxidants either as monomers or copolymers with other ethylenically unsaturated compounds.

V



He found that by copolymerising these with a vinylic antistatic agent and surface coating a fabric, then by oven curing, the extractability of the material was much reduced. Although this still occurred, the antistatic and stabilisation properties were enhanced when tested by Xenon arc exposure, laundering and tumble drying. Fabrics coated in this manner even after repeated laundering were still showing good resistance to oxidation whereas conventional stabilisers were leached out.

From copolymerisation and surface coatings, it is only a short progression to chemically bond antioxidants to the polymer chain, and workers at N.R.P.R.A. have reported the incorporation of network bound antioxidants in natural rubber[14]. This was studied using a model compound, 2-methyl-2-pentene, and reacting this with N,N-diethyl-p-nitrosoaniline at elevated temperature. The reaction is illustrated as



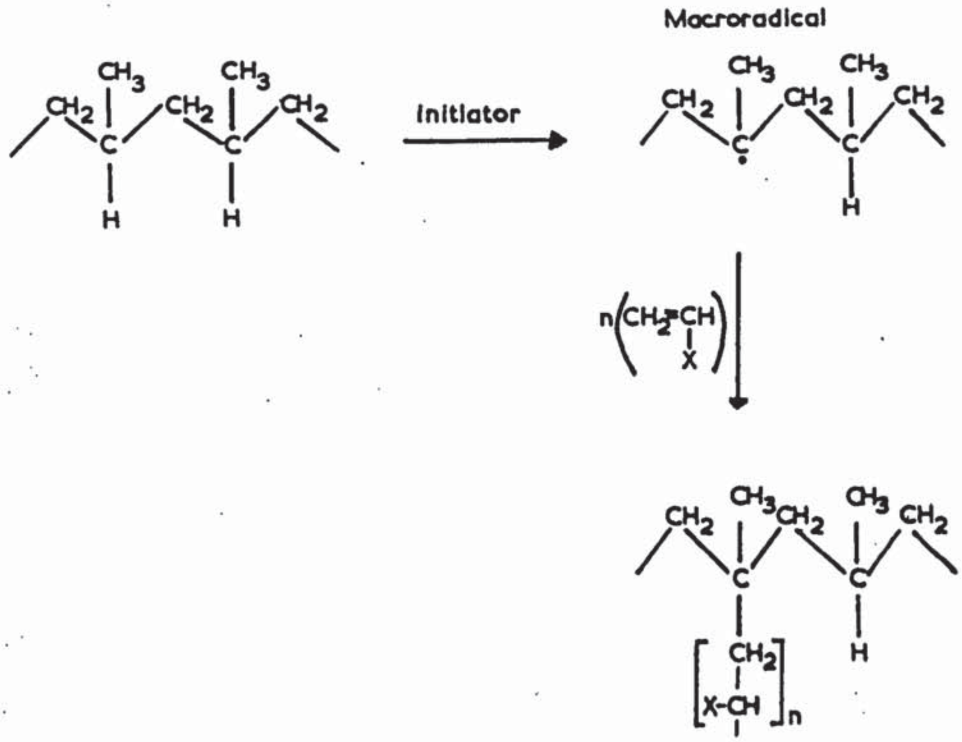
It is thought that an analogous reaction occurs with natural rubber to produce a network bound p-phenylene diamine. Rubber vulcanisates containing this bound stabiliser were oxidised after extraction and compared with known antioxidants. A high retention of activity was found, whereas a marked decrease was observed with conventional materials due to losses on extraction. The limited mobility of the stabiliser due to its attachment to the network did not seem to impair its activity as an antioxidant.

Polypropylene does not have the same chemical structure as natural rubber and consequently a more promising technique for modification in a similar manner would be to graft copolymerise the vinyl stabilisers into the polymer. Losses by volatilisation and solvent extraction would then be much reduced.

Numerous review articles and several excellent books [15,16] have been written on graft copolymers, and the importance of this field of research is amplified by the patent index listed in the most recent study[16].

The formation of graft copolymers by a free radical process firstly requires an active site on the polymers backbone where a monomer or polymer can be induced to graft.

Grafting a polypropylene can be illustrated simply as shown



By a suitable choice of monomer or combination of several monomer systems it should be possible to produce a modified polymer having the desired properties.

Many graft copolymers have not reached commercial fruition, however, and questions arise concerning the advantages of using grafted materials[17], rather than the same blended product.

In the case of polypropylene, being a hydrocarbon the blending of polar materials leads to difficulties due to incompatability with the base polymer. Random copolymers might be used, but the catalyst systems involved in the stereoregular polymerisation of propylene tend to become poisoned by polar materials. These drawbacks can be overcome, but research has tended to favour the modification of the material by grafting, this technique being more flexible in application. Technical problems arise when laboratory experiments are scaled up to production level where cost becomes the predominant factor. Several of the more popular grafting methods such as radiation techniques produce the added complications of possible health hazards to the operator.

A technique which might offer potential economic advantages is the modification of the polymer by grafting, preferably as part of a conventional processing operation, or an alternative inexpensive method which could be adapted to the process. The two techniques studied in this present work are

(a) Mechanico chemical synthesis
and (b) Ultraviolet irradiation

since these were thought to be of possible commercial value.

When polymer molecules are subjected to an applied shear or stress, bond scission results in the formation of free radicals. In the presence of a monomer, polymerisation may produce block copolymers, and if chain transfer processes occur, graft copolymers also form from non-terminal radicals.

Detailed accounts of mechanico chemical processes are available[18,19,20] and more specifically work done on rubber and other polymers using mastication techniques have also been reviewed[21,22].

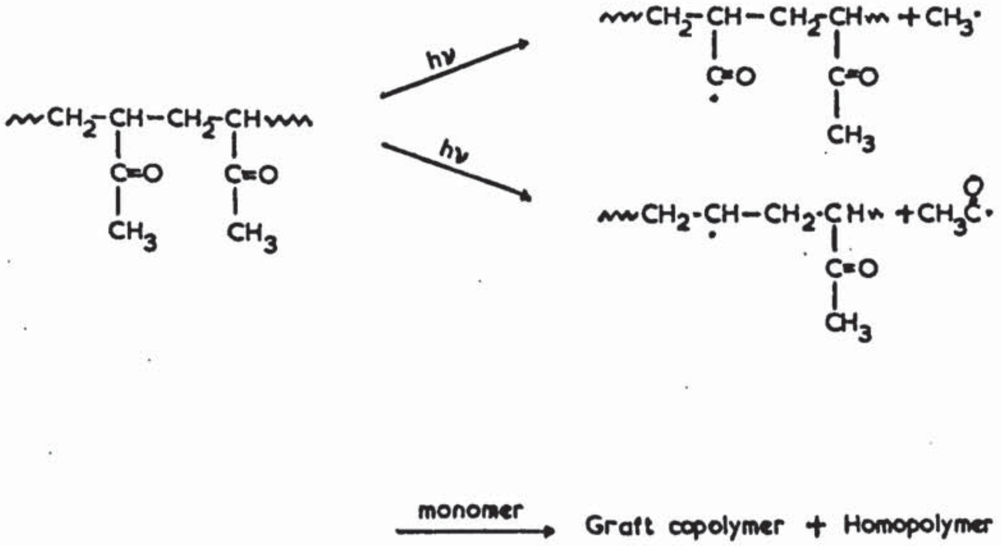
It has been observed using electron spin resonance that during the cold drawing of polymer fibres, free radicals are produced[23,24,25].

These have been observed in nylon[23], polyamides[24], and in various other polymers including polypropylene[25]. Stretching of polymer fibres has been suggested[25] as a useful method of forming graft copolymers, and this process of mechanico chemical synthesis was studied initially.

Ultraviolet radiation also has been used extensively for grafting reactions, and polymerisations[26] and presents an effective way of modifying polymers industrially. It has been frequently used to oxidise film surfaces for printing purposes, and its use for the curing of paint films has been the subject of much discussion, as an alternative to high energy radiation[27].

The early work on copolymerisation using ultraviolet light involved the introduction of labile groups, normally chlorine or bromine[28] into the polymer. These could be removed by photolysis, in the presence of a monomer to form copolymers which were normally block copolymers since the halogens were present as end groupings in the polymer. Miller[29] prepared copolymers of α-chloroacrylonitrile with acrylonitrile and photolysed the chlorine to form a radical site on the backbone. This was done in the presence of acrylamide and resulted in the graft copolymer, poly(acrylonitrile g.acrylamide). This principle is not limited to halogens since it has been found that aliphatic ketones may also be photolysed to produce radicals[30].

Guillet and Norrish[31,32] extended this by UV irradiating a solution of poly(methylvinylketone), with several monomers and interpreted the reaction by the scheme below. Acetaldehyde and methane were formed as well as the graft and homopolymers.



All these polymerisations utilised sites produced by an inherent grouping on the polymer backbone. Few photopolymerisations have been achieved by direct irradiation but Oster and co-workers extended the method by using a photosensitiser. With benzophenone as the photo-initiator they succeeded in grafting acrylamide onto natural rubber[33]. This work was extended, and the effects of different photosensitisers and temperature was studied by Cooper (and co-workers)[34-37] using natural rubber latex.

Oster turned his attentions to other polymers, including polyethylene[38,39], nylon, cellulose, etc. The results of grafting monomers on these materials were included in his patent[39].

Interest in this technique extended to cellulosic materials and photolysis reactions of these polymers were studied[40] using an anthraquinone derivative as a dye sensitiser for the photopolymerisation of the grafting monomers.

Evidence of grafting was obtained from the solubility characteristics of the grafts, and physical mixtures of the two homopolymers. The cellulose, methyl methacrylate system was more recently studied[41] by Japanese workers using other initiators in addition to the phototendering dye described above[40].

There are many ways of photopolymerising vinyl monomers, and the kinetics, methods, and initiating systems for the process are summarised in a review by Oster[26].

Crosslinking reactions can also occur especially with polyethylene[42]. Irradiation leads to free radicals which can recombine or react with oxygen. Recombination leads to crosslinking. Thus

$$2\,-CH_2-\dot{C}H-CH_2- \longrightarrow \begin{array}{c} -CH_2-CH-CH_2- \\ | \\ -CH_2-CH-CH_2- \end{array}$$

This was made use of by Boudevska[43], by first crosslinking, and then grafting polyethylene with methacrylic acid, to prepare films used as separators for alkaline cells. Crosslinking prior to grafting resulted in better materials for preparing membranes of extended cycle life.

Further uses of grafted copolymers will no doubt be found, as the methods of preparing them become more industrially oriented.

SCOPE AND OBJECT OF THE PRESENT WORK

Block and graft copolymers have been known for many years and the principle of having two different segments in the same polymer has been used in the manufacture of polymers with special properties.

Normally modified polymers of this type are made by incorporation of a second monomer at the reaction stage and this involves a separate and generally small scale specialised manufacture. Hence only a small proportion of the very large number of potentially useful copolymers have been developed commercially.

It was proposed to take a small amount of a monomer and introduce this into a large tonnage polymer, e.g. polypropylene, and modify this by a subsequent grafting process, preferably as part of a conventional processing operation. Work has already been done in this area, notably by Watson and his co-workers on the mechanico modification of polymers, and by Oster, on the light sensitised grafting process, and has shown the potential of the techniques. The purpose of the present work was to approach the subject from the standpoint of the graft initiation processes which already exist in polymer fabrication or can be adapted if the process is economically viable.

Two techniques were selected for study; stretching of polypropylene fibre with monomer, and ultraviolet irradiation of the polymer in the presence of the grafting additive. These techniques could provide a useful procedure for introducing modifying groups into the polymer, which might be for example, dyesites, antioxidants and stabilisers, antistatics and water absorbing groups.

Since polypropylene is predominantly unstable to heat and light a primary object of this work was to increase the stability of the polymer using grafted vinyl antioxidants and stabilisers thus reducing additive losses.

It was proposed to explore the described techniques using 2-vinyl pyridine which is useful as a potential dyesite. Once the conditions of grafting had been determined it was proposed that the technique would then be applied to specially synthesised monomers. It was hoped that the results would provide the basis of a commercial process.

CHAPTER II GRAFTING OF POLYPROPYLENE WITH 2-VINYL PYRIDINE

Although polypropylene possesses excellent physical properties of low specific gravity, high mechanical strength etc., it is lacking adhesiveness, printability, dyeability, oil resistance and antistatic properties[44], as can be readily understood from the paraffinic structure. Thus the applicability of this otherwise useful polymer has been greatly restricted. Attempts used to improve the dyeability include the introduction of a dyeable grouping to polypropylene by a chemical reaction[45]. Further, copolymerisation of gaseous propylene with dyeable vinyl compounds has disadvantages in that the stereoregularity of polypropylene is decreased, and the fibre forming properties are reduced. For these reasons the graft copolymerisation methods have proved more popular. Vinyl pyridines have often been used for copolymerisation[46,47] with polyolefins to improve the dyeability, as have their blended polymers[48,49,50]. The polarity of these materials renders the treated polypropylene dyeable with a variety of dyestuffs[51,52].

Other uses of vinyl pyridines have been recently reviewed by Webster[53], but their properties as dyesites has been utilised in this work.

Using 2-vinyl pyridine as the grafting monomer two techniques for the graft modification of polypropylene have been studied. Firstly, mechanico chemical synthesis, by stretching polypropylene fibres in the presence of the monomer, and secondly, ultraviolet irradiation of a heterogeneous system of polypropylene with the grafting monomer. The presence of the vinyl pyridine was detected by its ability to dye the polymer, and the conditions of grafting so elucidated were utilised in the further studies on vinyl stabilisers.

I MECHANICO CHEMICAL GRAFTING

Preparation of samples

Stabilised polypropylene fibre was obtained from I.C.I. Ltd. in the undrawn state, and was Soxhlet extracted in ether for forty-eight hours to remove fibre additives. The skein of fibres containing approximately seventy individual filaments was stored under nitrogen before use.

The 2-vinyl pyridine monomer was obtained from Midland Yorkshire Tar Distillers Ltd., and was vacuum distilled free of inhibitor to give a water white liquid boiling at 58-60^{o}/18mm. The monomer was always freshly distilled and used immediately without storing.

Stretching of polypropylene fibre

The unstabilised polypropylene tow was immersed in 2-vinyl pyridine for several hours, then stretched by hand to a draw ratio of 5 to 1, at approximately 1 metre/sec. The fibre was Soxhlet extracted with ethanol overnight, washed with solvent, then air dried.

The experiment was also carried out in a glove box, under an atmosphere of nitrogen, and the fibre extracted as before. The samples were then dyed.

Dyeing of grafted polymers

The dyes chosen were DYLON[54] multipurpose dyes which can be used for nylon, cotton, wool and polyesters, and require only common salt as a dye assistant. It was thought that these dyes would be effective for vinyl pyridine modified polypropylene.

A stock solution of dye containing 1 gram in 250 ml of water (0.4% concentration) was prepared together with a 10% sodium chloride solution.

Quantities of liquor, dye and assistants used, are normally based on the weight of textile being processed. A "2% dyeing" refers to the use of 2 grams of dye per 100 grams of textile material. To calculate the quantities to be used for dyeing the following formula was useful[55]

$$\text{No. of ml of stock solution required} = \frac{W \times P}{C}$$

where W = Weight in grams of sample to be dyed
P = Percentage of dye or assistant to be used
C = Concentration (%) of stock solution

The dyebath used throughout was

FIBRE	1 gram
DYE	2%
SALT	20%
LIQUOR RATIO	50:1

and the amount of additives required calculated accordingly.

Dyeing was carried out in flasks immersed in a waterbath, the temperature of the bath being raised to boiling over the first thirty minutes, and maintained at this for a further one hour. After this period the fibre was removed and washed with cold water, then dried with hot air. Unstabilised dyed polypropylene fibre was used as a standard each time samples were dyed.

Using DYLON SCARLET, the unstabilised fibre was dyed orange and the grafted material gave the same colouration. The fibres were analysed using the conventional techniques of infra red spectrometry, mass spectrometry, nitrogen analysis, and x-ray crystallography, but no differences were found between the treated and untreated samples. If grafting had occurred the modification was too insignificant to be of commercial importance. It was decided to progress to the study of grafting by ultraviolet irradiation, which has proved successful in the past.

II GRAFTING BY ULTRAVIOLET RADIATION

An initial study was made using a 2-kilowatt Philips high pressure mercury lamp emitting in the range 2800Å into the visible region. Samples of polypropylene fibre, immersed in vinyl pyridine were irradiated in pyrex tubes at a distance of 25cm from the lamp for a period of 4 hours. The lamp was without water cooling and the solutions of vinyl pyridine became dark and viscous and were quite warm after irradiation. The fibres were ethanol extracted and dyed with a range of DYLON tints. They were successfully dyed black, red, blue and yellow whereas untreated fibre dyed green, orange, pale blue, and straw coloured respectively.

It was, therefore, decided to study the technique of grafting by ultraviolet radiation as a possible commercial method.

EXPERIMENTAL

1. U.V. CABINET

Polymerisations, and ageing tests were carried out using the same series of lamps for both. The equipment was supplied by CIBA-GEIGY LTD. and consisted of a cylindrical metal cabinet with thirty, 20watt lamps mounted around the periphery. The lamps were alternating equal numbers of fluorescent sunlamps and blacklamps, the spectral characteristics approximating to that of sunlight. The distribution of ultraviolet radiation is as shown in figure I and compared with that of sunlight[56]. In order to maintain a constant spectral intensity the lamps were changed in strict rotation, one lamp being replaced every three days.

The fluorescent sunlamp has less intensity than sunlight at the higher wavelengths and much more intensity below 3130Å. Since the emission extends to shorter wavelengths than sunlight, ageing tests on clear plastics are harsher. Quartz glass facilitates the use of this higher energy for polymerisation purposes.

FIGURE I

SPECTRAL DISTRIBUTION OF FLUORESCENT AND BLACK LAMPS COMPARED WITH SUNLIGHT

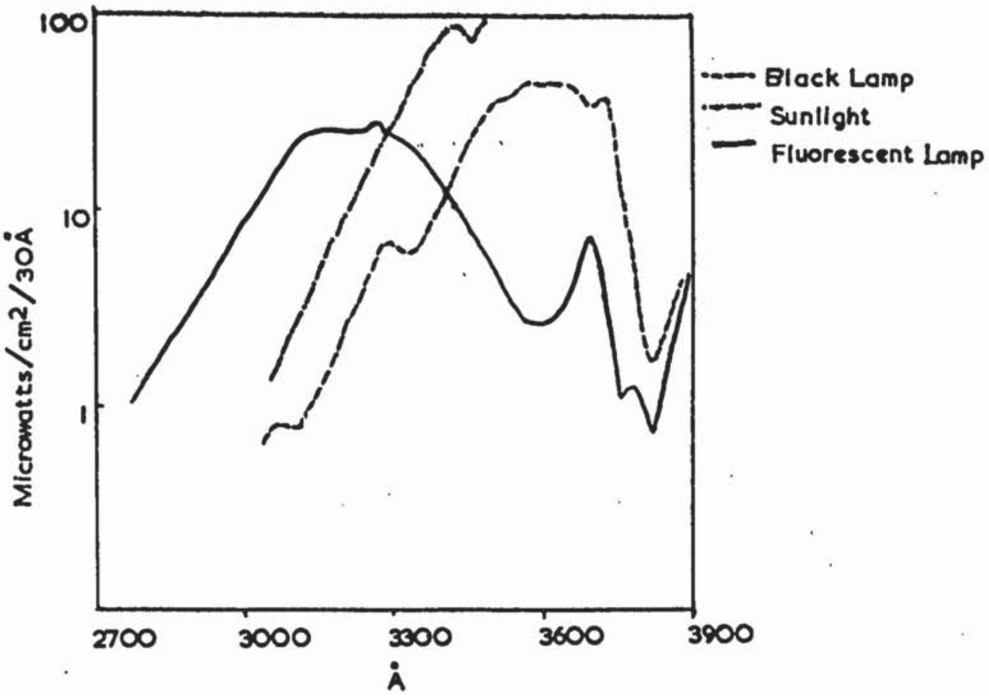
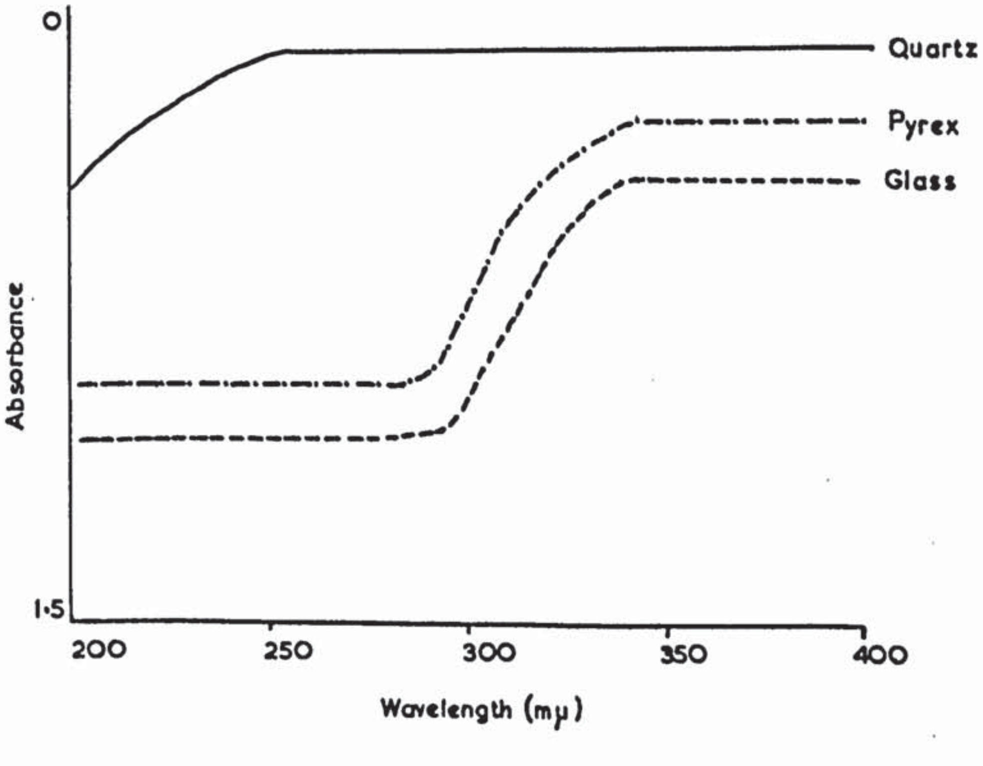


FIGURE II

U.V. TRANSMISSION OF QUARTZ, PYREX & GLASS



The ultraviolet transmission characteristics of quartz tubes are shown in Figure II. This is compared with pyrex, and soda glass, and shows that quartz transmits throughout the scanning range, but the others only begin transmission at wavelengths above 300mμ.

Quartz tubes, (100x 15 x 1mm) were used for the sample solutions, and were sealed with rubber stoppers.

The sample tubes were mounted on the circumference of a motor driven wheel which was concentric with the cabinet, and could be rotated at constant velocity. The distance of the samples from the lamps was 15cms and the tubes were secured by means of clamps. To avoid any variation in intensity throughout the length of ultraviolet source (lamps were 2 ft. long) the samples were mounted in the same position each time, exposed to the upper half of the lamps. The temperature inside the open-ended cabinet was 33 ± 2^{o}C.

The 1g samples of polypropylene fibre immersed in 10mls 2-vinyl pyridine monomer were irradiated for various periods of time. The fibre was removed, Soxhlet extracted with ethanol overnight and then dried.

2. ANALYSIS OF FIBRE SAMPLES

The grafted fibres were analysed both qualitatively and quantitatively using infra-red and ultraviolet spectroscopy respectively.

INFRA-RED SPECTROSCOPY

Infra-red spectra were recorded on a Perkin Elmer

PE 457 infra-red spectrometer.

Fibre spectra are very difficult to obtain because of the nature of the sample. Direct measurement of fibre samples held between sodium chloride plates produces a diffuse and broad spectrum with little definition, and grinding with KBr to form a disc produces similar traces. Most fibres have been characterised spectroscopically by using reflectance techniques such as attenuated total reflectance (ATR). The sample is wrapped around a thallium iodide/bromide trapezoid crystal and clamped between two metal plates and the assembly placed in the infra-red beam. The band intensity of the spectra were weak, but could be improved by backing the sample with rubber pads, and reclamping the plates. The rubber pads distributed the load provided by the pressure plates, thus increasing the contact between the fibre and the crystal. Spectra of polypropylene fibre obtained by this technique however were still ill defined and the method was abandoned. Spectra were obtained by an alternative method, however.

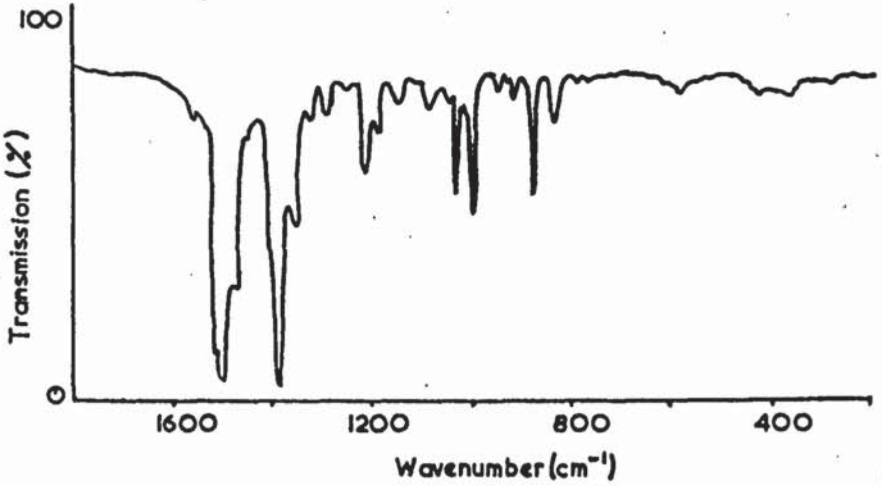
A small amount of polypropylene fibre was finely chopped and placed in a disc mould normally used with potassium bromide. A pressure of fifteen tons was applied for two minutes under vacuum and a thin fibre "film" was obtained. Infra-red measurements were made on this sample resulting in excellent spectra, with sharp and clearly defined peaks. Samples were prepared of the grafted fibre and the spectra showed additional bands at 1585cm^{-1} and 1565cm^{-1} which are characteristic of the pyridine ring system.

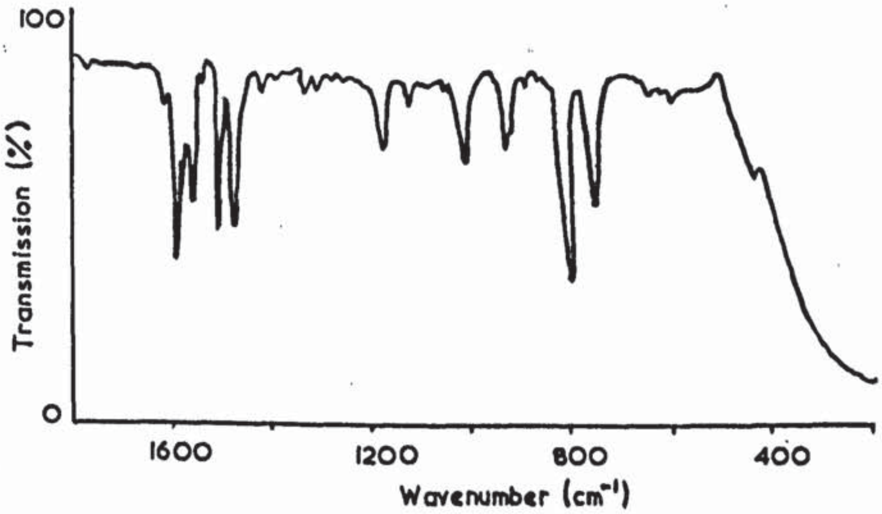
Infra-red spectra of polypropylene fibre, vinyl pyridine, and poly(propylene graft-vinyl pyridine) are illustrated in Figure III.

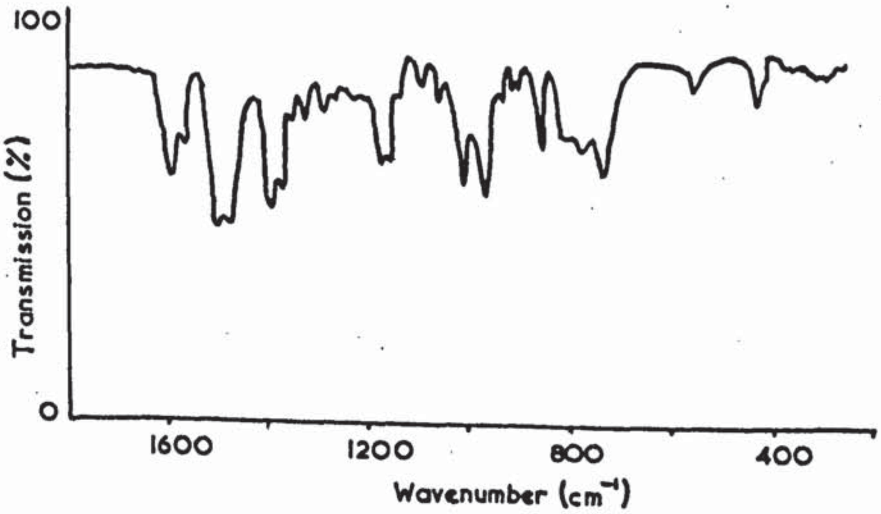
The vinyl pyridine must be grafted, since prolonged extraction with ethanol did not reduce the intensity of the pyridine ring bands in the infra-red spectrum.

FIGURE III

INFRA RED SPECTRA OF (a) POLYPROPYLENE FIBRE (b) VINYL PYRIDINE AND (c) POLYPROPYLENE, VINYL PYRIDINE







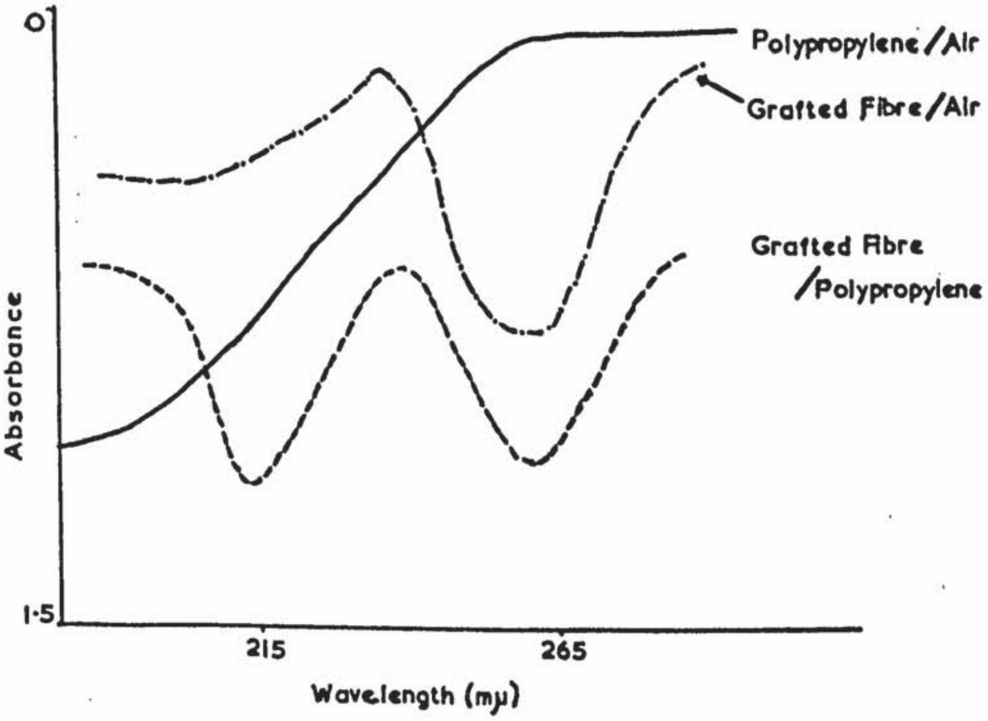
ULTRA VIOLET SPECTROSCOPY

Spectra were recorded on a Perkin Elmer PE 137 ultraviolet spectrometer.

The same fibre disc was used for both infra-red and ultraviolet spectroscopy. U.V. Spectra were obtained of the modified fibre, using air as the reference material, and later polypropylene fibre was used of a similar thickness for this purpose. The spectra obtained for polypropylene fibre, and the grafted sample are shown in Figure IV.

UV SPECTRA OF POLYPROPYLENE MODIFIED FIBRES

FIGURE IV



Two maxima were observed at λmax 215mμ and 265mμ. Ultraviolet spectra of polyvinyl pyridine in ethanol gave maxima of 212mμ and 265mμ. The broad peaks are, therefore, characteristic of polyvinyl pyridine absorbances.

Difficulties occurred in producing a reference disc of the same transparency and path length as the sample and, therefore, quantitative measurements were impractical.

By dissolving the sample in a suitable solvent, and measuring the absorbance, however, the method was made quantitative.

Polypropylene is insoluble in most solvents, but decalin is often used for this purpose at elevated temperatures.

The grafted copolymers showed reluctance to dissolve in this solvent due to the polar nature of the modifying polymer, and calibration in decalin proved difficult because of the insolubility of polyvinyl pyridine.

A standard calibration curve was obtained by dissolving polyvinyl pyridine in trichloroethylene (0.146g/10ml). This gave a single sharp maximum at 275mμ, and on dilution a straight line relationship was found. This line did not pass through the origin and had the equation

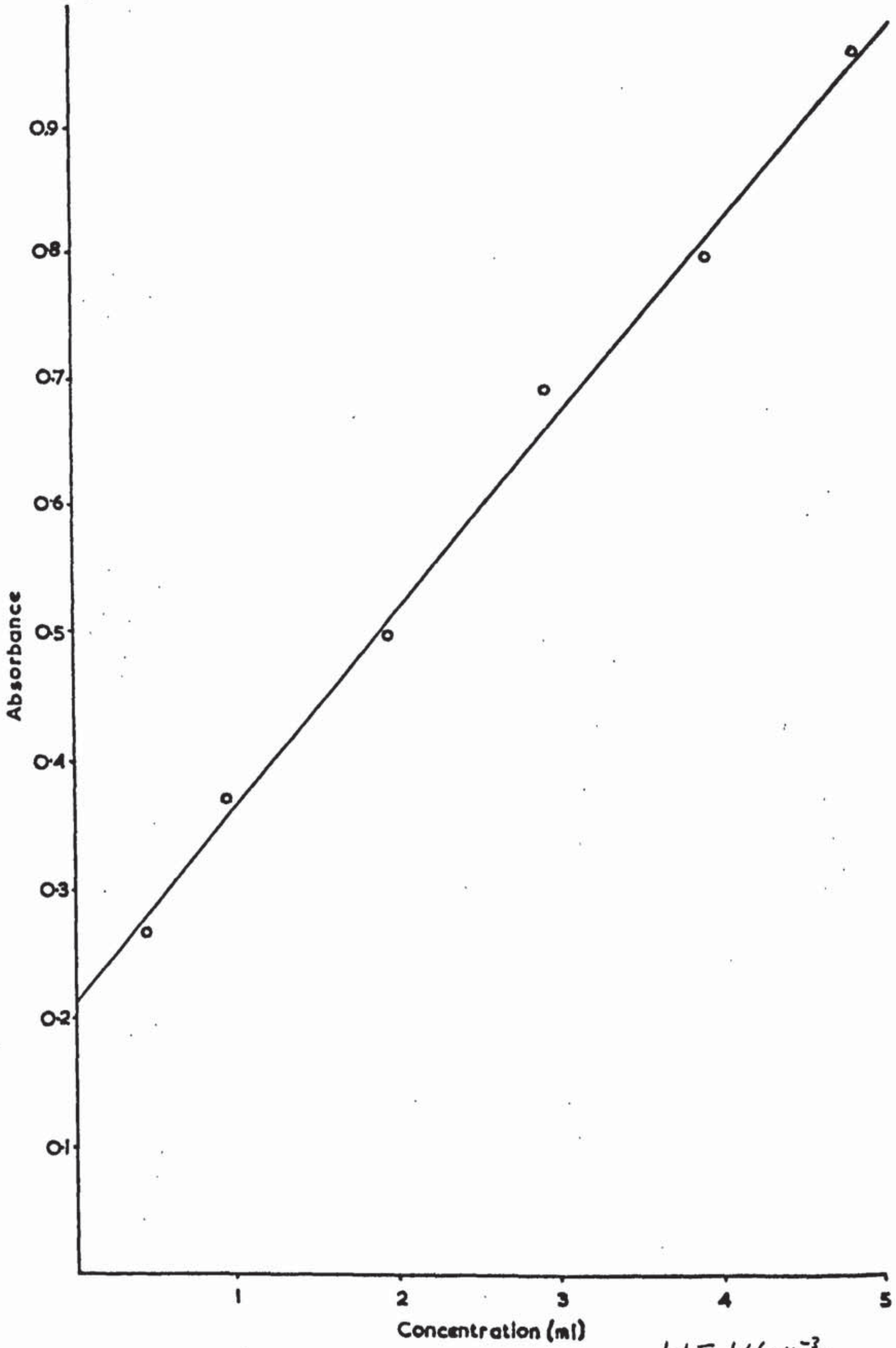
$$A = 0.15C + 0.208$$

where A = absorbance, and C = concentration

This is shown in Figure V

FIGURE V

CALIBRATION CURVE OF POLYVINYL PYRIDINE IN TRICHLOROETHYLENE



1ml ≡ 1.46x10^{-3}g

A known weight of the modified fibre was dissolved in trichlorethylene at the boiling point of the solvent and made up to a 10ml solution. The U.V. 1cm cells were preheated in the solvent and the spectra obtained at approximately 80°C, using hot trichlorethylene as a reference. After a short time the polypropylene began to precipitate as the cells cooled, and spectra were therefore recorded within this period, normally two minutes. From the calibration curve the weight of polyvinyl pyridine in the sample was determined and expressed as a percentage of the total sample weight.

$$\text{Thus \% Polyvinyl pyridine} = \frac{\text{Weight of polyvinyl pyridine}}{\text{Weight of sample}} \times 100$$

By this technique small amounts of sample could be used for the detection of the graft, provided the absorbance exceeded 0.208. This could be achieved by dissolving a suitable weight of fibre. The sources of error may be the difference of path length in the two cells due to expansion on heating. The cells used were a matched pair, and it was hoped that this would have a compensatory effect.

A graph of the percentage of polyvinyl pyridine determined by ultraviolet spectroscopy versus irradiation time is shown in Figure VI and can be seen to be virtually linear with increasing time of exposure.

FIGURE VI

PERCENTAGE OF GRAFTED POLYVINYLPYRIDINE AS A FUNCTION OF IRRADIATION TIME

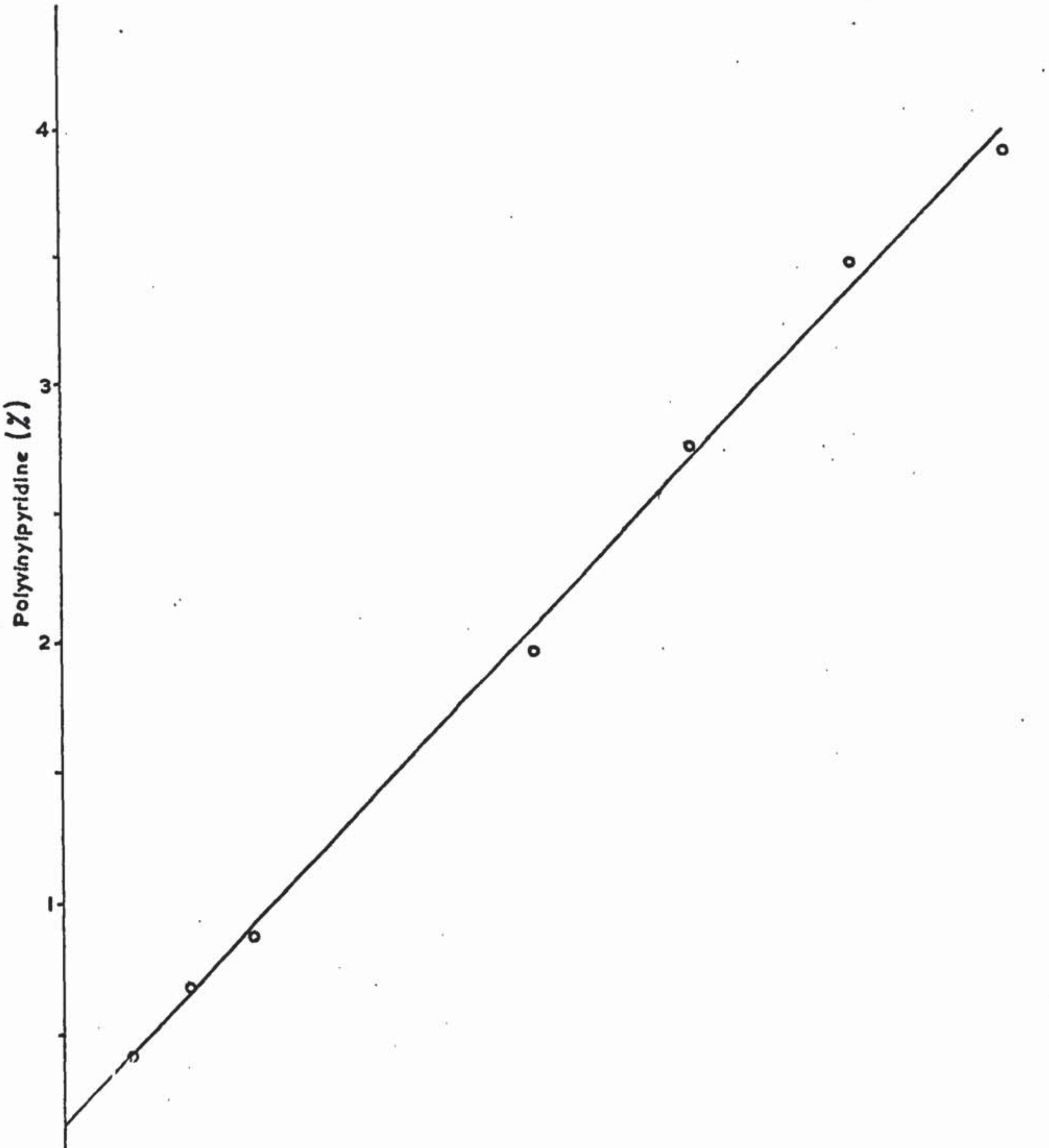


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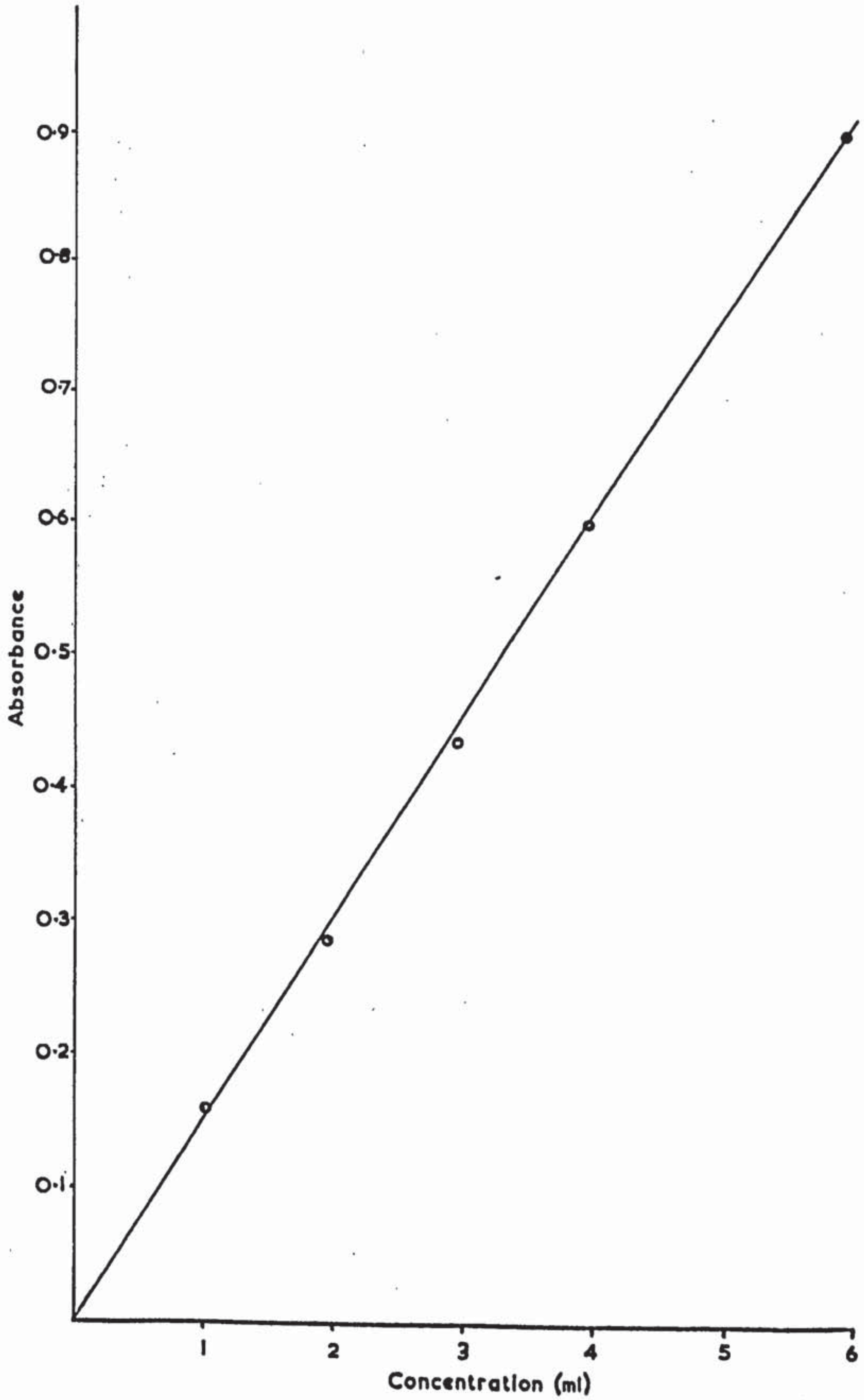
FIGURE VII

CALIBRATION OF DYESTUFF



1ml = $1{\cdot}4 \times 10^{-5}$g

VISIBLE SPECTROSCOPY

The grafted fibres were also dyed using DYLON scarlet, and quantitative data obtained.

Solid dyestuff was dissolved in water at a concentration of 0.014 x 10^{-3} gram/ml and a calibration curve obtained as shown in Figure VII, using λ max 495mμ in the visible region.

A straight line through the origin of equation

$A = 0.153C$ was obtained,

A = absorbance at 495mμ and C = concentration of dyestuff.

Because hot water does not remove the dyestuff even after prolonged boiling, the dyed samples were extracted with various solvents and the spectra measured. The absorption maxima are shown in Table I for the extracted dye.

TABLE I

ABSORPTION MAXIMA OF SOLVENT/DYE SOLUTIONS

Ethanol	485 mμ
Benzene	460 mμ
Carbon Tetrachloride	460 mμ
Trichloroethylene	475 mμ
Acetone	495 mμ

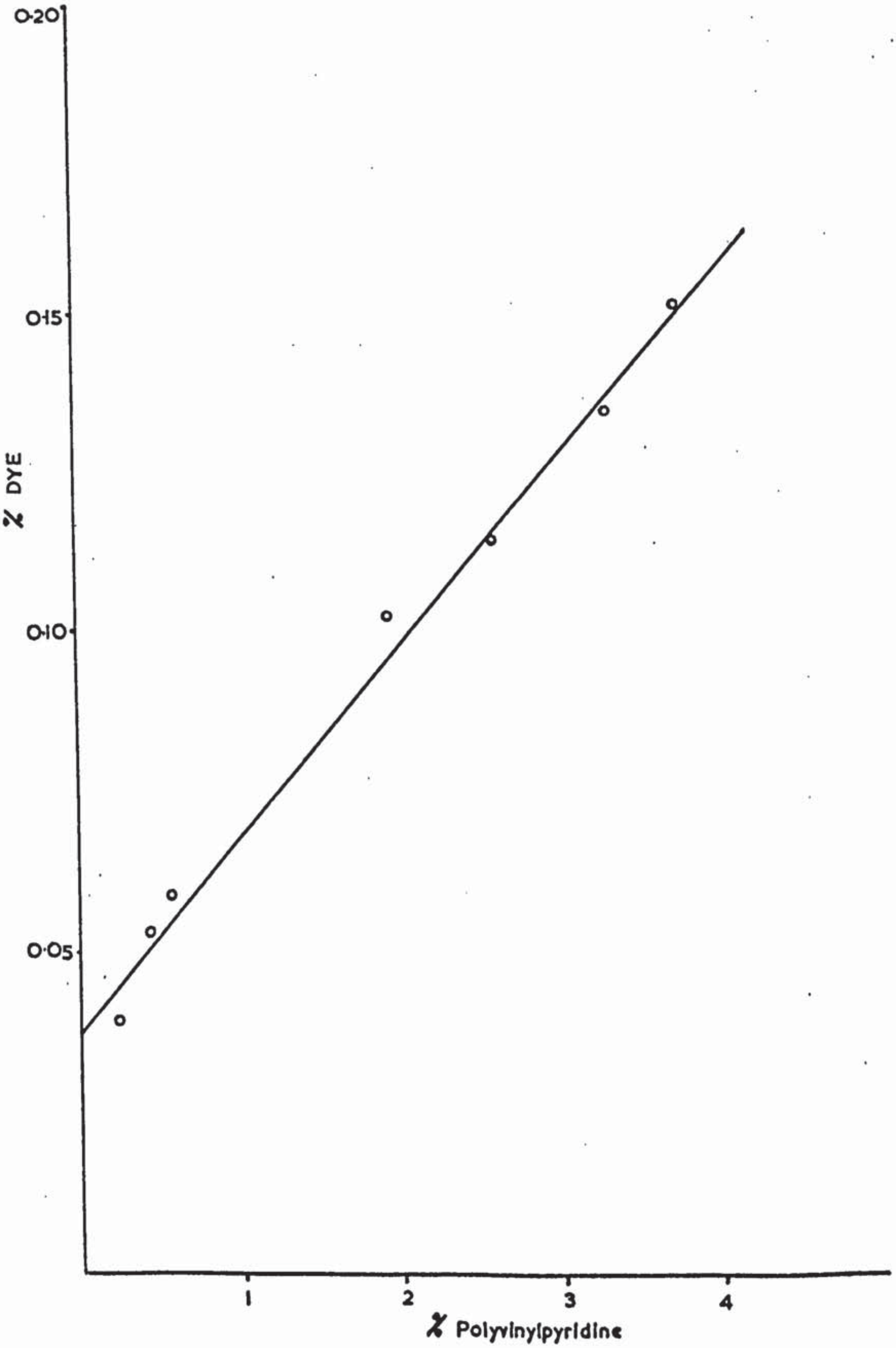
None of the solvents used would dissolve the dye in its solid state, however, and acetone was chosen for quantitative measurements since the absorption maximum at 495 mμ was the same as that for the water/dye calibration.

Known weights of dyed fibre were treated with hot acetone and the solution of extracted dye made up to 10ml. A visible spectrum was obtained, and the concentration of dyestuff determined from the calibration. The amount was expressed as a percentage increase in weight, similar to that of polyvinyl pyridine grafted fibre.

Figure VIII illustrates a graph of the percentage dyestuff plotted against the percentage of polyvinyl pyridine in the grafted fibre.

FIGURE VIII

PERCENTAGE DYESTUFF AS A FUNCTION OF THE PERCENTAGE OF GRAFTED POLYVINYLPYRIDINE



This is linear, but does not go through the origin since unmodified polypropylene does dye to a small extent with these dyes. The amount of dyeing is, therefore, proportional to the amount of vinyl pyridine grafted onto the fibre.

GRAFTING OF POLYPROPYLENE FILM

Grafting reactions were also carried out using 0.001 inch thickness polypropylene film. The film was obtained from I.C.I. Ltd. and was extracted for forty-eight hours with ether before use, under nitrogen (white spot).

ULTRAVIOLET IRRADIATION IN AIR

Samples of film (0.1gram) were immersed in 10ml of vinyl pyridine in sealed quartz tubes, and were irradiated for various periods. The films were removed after this time, extracted with ethanol, and analysed as previously described for polypropylene fibres. Grafting increased with irradiation time and the results are shown in Table II.

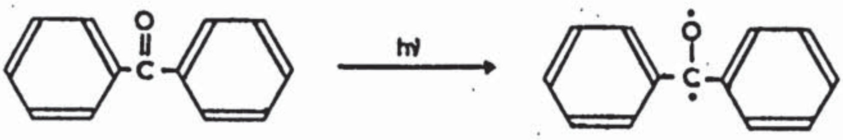
TABLE II

POLYPROPYLENE FILM GRAFTED WITH VINYL PYRIDINE IN AIR

Irradiation Time (hrs)	% PVP
5	3.0
16	9.4
24	11.5
40	15.6
48	19.3

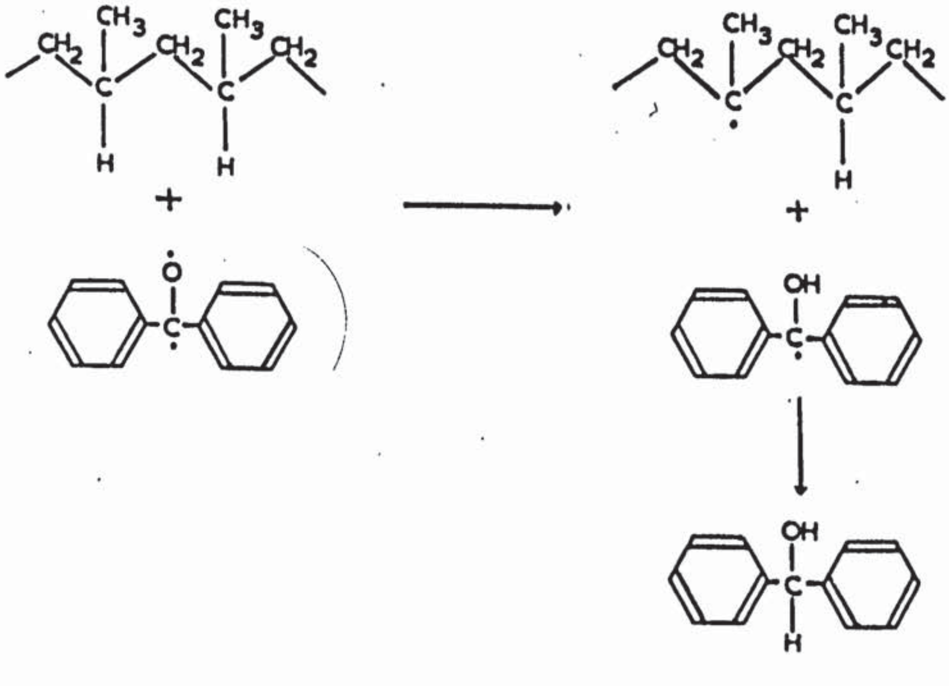
EFFECT OF A PHOTOINITIATOR

Further studies were carried out using benzophenone as a photoinitiating system. Unlike aliphatic carbonyl compounds, which tend to homolyse to give free radicals on irradiation with ultraviolet light, benzophenone is activated to a diradical.



In the presence of polypropylene, this excited species can hydrogen abstract from the polymer backbone forming a macro radical and benzhydrol, by further abstraction.

Thus



In the presence of a vinyl monomer this macro radical can initiate polymerisation to form a grafted copolymer.

Irradiation of vinyl pyridine, polypropylene systems was done at two concentrations of photoinitiator. Vinyl pyridine solutions containing 1% and 5% benzophenone (wt/volume) were used, and the films analysed, giving the data in Table III.

TABLE III

EFFECT OF A PHOTOINITIATOR ON THE GRAFTING OF VINYL PYRIDINE

Irradiation Time (hrs)	1% Benzophenone	5% Benzophenone
5	3.4	0.9
12	5.7	2.4
15	7.3	2.8
20	9.6	-
25	-	2.7
36	12.1	3.3

Increasing the concentration of the photoinitiator decreases the amount of grafting. The reaction was repeated under nitrogen, the air being expelled from the system by continuously purging the solutions with oxygen free nitrogen for four hours. Irradiation was done on a 1% benzophenone vinyl pyridine solution with the film immersed as before. The analysis of the films is shown in Table IV.

TABLE IV

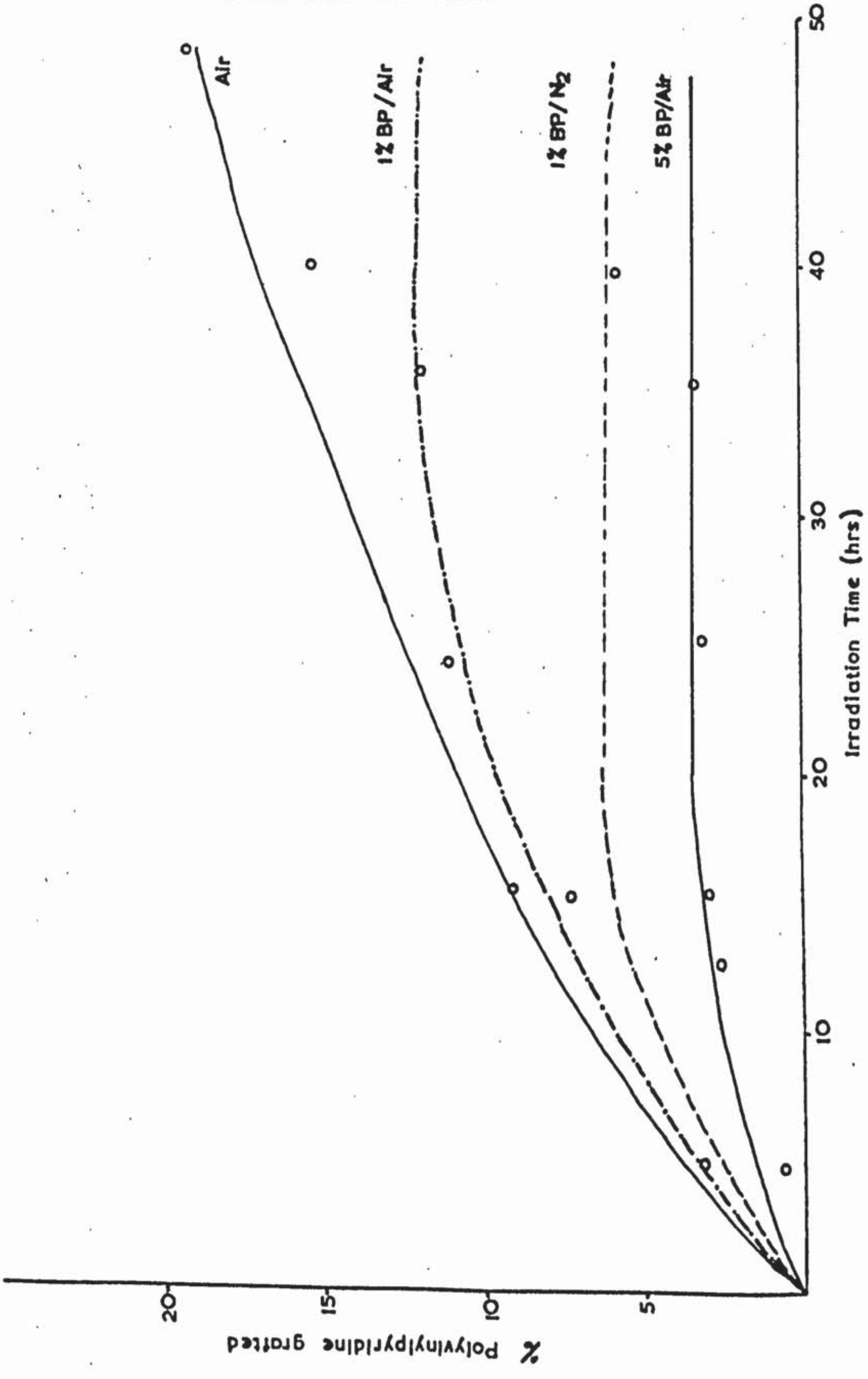
IRRADIATION OF VINYL PYRIDINE UNDER NITROGEN 1% PHOTOINITIATOR

Irradiation Time (hrs)	%PVP
5	1.5
16	5.9
20	6.1
24	6.0
40	6.4

The results of the grafting reactions are illustrated in Figure IX.

FIGURE IX

GRAFTING OF VINYLPYRIDINE ON TO POLYPROPYLENE FILM UNDER VARIOUS CONDITIONS



These results will be discussed later.

During the graft copolymerisation of polypropylene with vinyl pyridine, homopolymerisation of the monomer occurs. This is indicated by an increase in viscosity of the solution, and polymer formed can be precipitated in petroleum spirit. In the early stages of the reaction the precipitated polymer tends to be colloidal, and this method was therefore not used to follow homopolymerisation since weighings were inaccurate.

It was decided to monitor the homopolymerisation by solution viscosity.

MEASUREMENT OF VISCOSITY

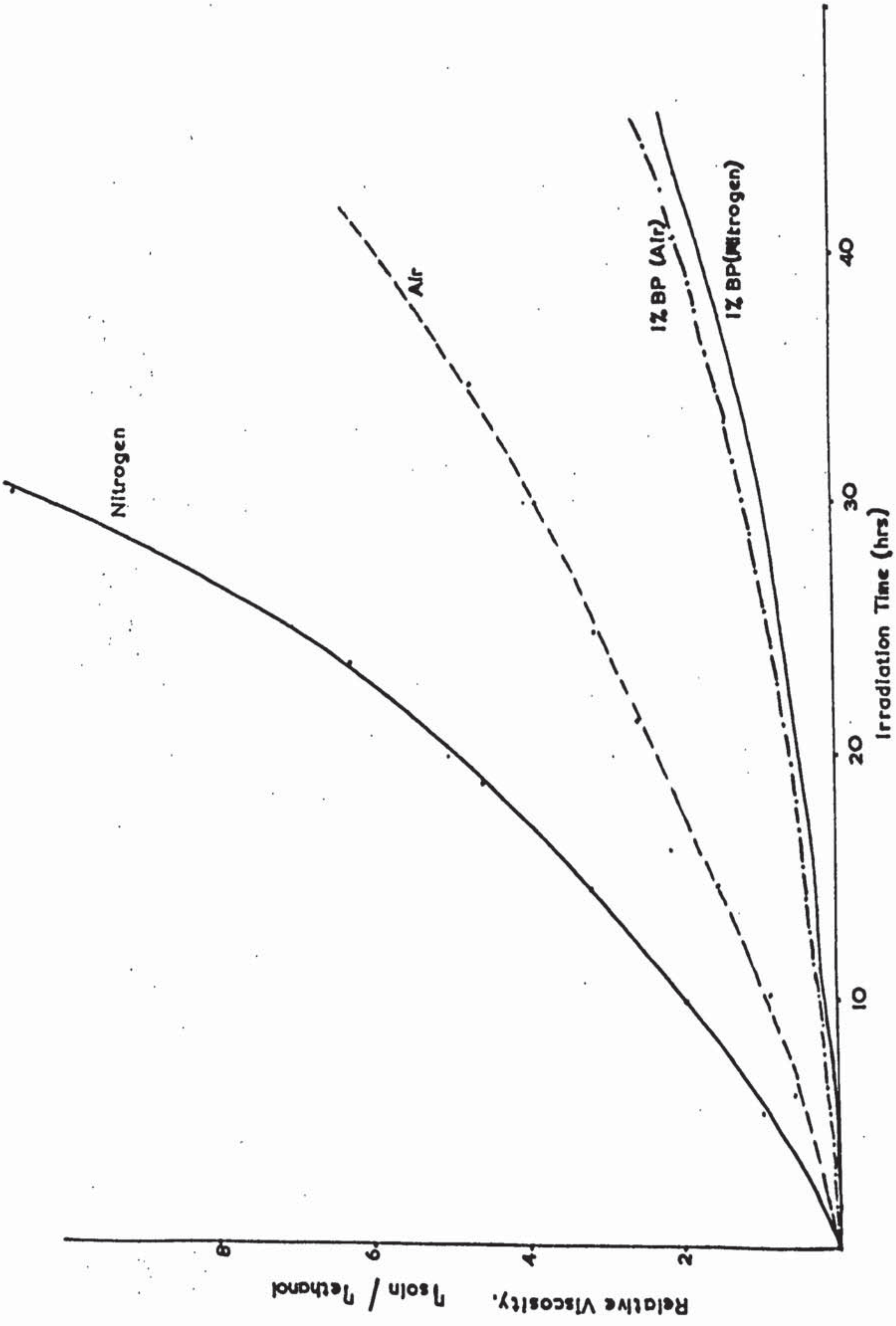
The vinyl pyridine solutions after irradiation were quite viscous and coloured and the flow times of these solutions were often in excess of ten minutes. To overcome this 5ml of the viscous solutions were made up to 20ml with ethanol and the flow times of these solutions were measured in an Ubbelohde viscometer and a relative viscosity of these determined.

All the polymerisations were done alone and in the presence of 0.1g of polypropylene film, but no difference was observed in the viscosity, under the two sets of conditions.

Reactions were done in air, nitrogen, and with benzophenone and the results are shown in Figure X.

FIGURE X

RELATIVE VISCOSITIES OF IRRADIATED VINYLPYRIDINE



Solid polymers were obtained from the vinyl pyridine irradiated solutions but only slight turbidity occurred with the benzophenone system on precipitation in petroleum spirit.

From the figure it appears that oxygen has an inhibiting effect on the polymerisation but in the presence of benzophenone this effect is much greater.

The influence of benzophenone on the polymerisation was therefore studied.

EFFECT OF BENZOPHENONE CONCENTRATION

Samples of polypropylene film and vinyl pyridine were irradiated with various concentrations of benzophenone for eighteen hours. The flow times of the irradiated solutions were measured without added solvent in an Ubbelohde viscometer. Polymer was isolated by precipitation in petroleum spirit and the molecular weight measured using ethanol solutions.

The figures are shown in Table V.

For comparison figures are included for the unirradiated solutions after storing in the dark for eighteen hours.

TABLE V

FLOW TIMES OF IRRADIATED SOLUTIONS CONTAINING BENZOPHENONE

	% B.P.	Flowtime (secs.)
	0.0	405.0
	0.5	84.2
	1.0	60.3
	2.5	56.7
	5.0	49.2
No Irradiation	0.0	220.0
	0.5	218.0

Molecular weights of the polymers precipitated from the above solutions were determined from the Mark-Houwink expression

$$[\eta] = KM^a$$

where $K = 12.2 \times 10^{-5}$ and $a = 0.73$
for polyvinyl pyridine in ethanol[57].

The molecular weights of the polymers were found to be in the range $1.7 - 1.83 \times 10^5$ for all the solutions irradiated. It would seem therefore that only the high molecular weight material was precipitated in petroleum spirits.

The benzophenone appears to terminate the reaction in some manner but only on irradiation, since the flow time of the unirradiated samples are virtually identical.

Therefore the active species must be formed during the irradiation process.

From a consideration of the kinetics of free radical polymerisation, the degree of polymerisation can be defined as

$$\overline{DP} \propto \frac{\text{Rate of propagation of polymer chains}}{\text{Rate of termination of polymer chains}}$$

$$\overline{DP} = \frac{K_p\,[M.]\;[M]}{K_c\,[M.]\;[M\cdot]}$$

K_p	is the rate constant for propagation
K_c	is the rate constant for termination by combination
$[M]$	is the monomer concentration
$[M\cdot]$	is the concentration of growing polymer radicals

In the presence of an added radical terminator, the expression $K_c[M.]^2$ will be small and therefore

$$\overline{DP} \propto \frac{[M\cdot]\;[M]}{[T]\;[M\cdot]}$$

where $[T]$ is the concentration of the added terminator.

$$\overline{DP} = K\,\frac{[M]}{[T]}$$

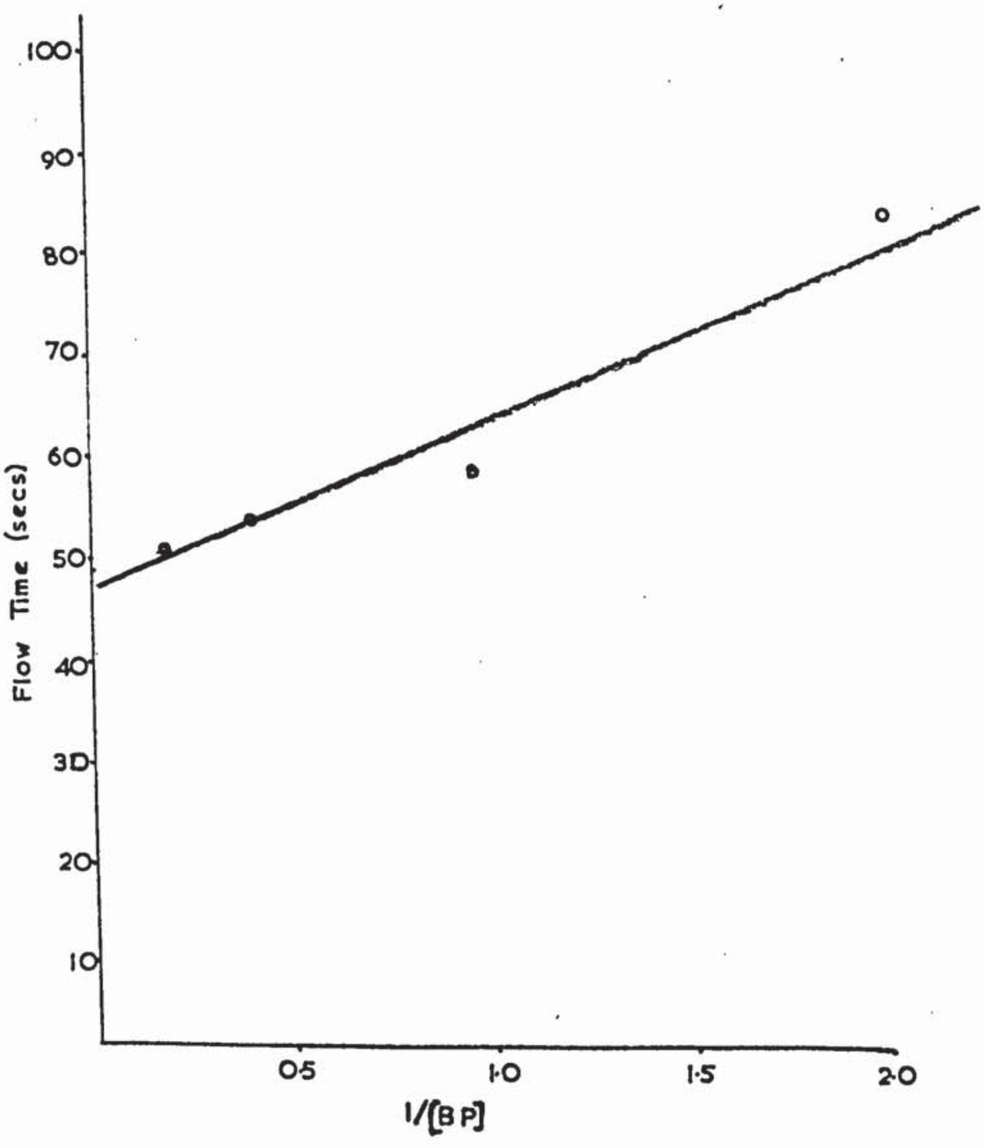
Therefore if a chain terminator is present a graph of $\overline{DP}$ versus $\frac{I}{[T]}$ at a fixed concentration of monomer should approximate to a straight line.

Assuming that the flow time of the solutions is proportional to the degree of polymerisation, a graph of flowtimes versus reciprocal benzophenone concentration is shown in Figure XI.

This linearity suggests that benzophenone in irradiated vinyl pyridine solutions functions as a chain terminator.

FIGURE XI

FLOW TIME AS A FUNCTION OF RECIPROCAL BENZOPHENONE CONCENTRATION IN IRRADIATED VINYLPYRIDINE SOLUTIONS



DISCUSSION

The graft modification of polypropylene with 2-vinyl pyridine has been achieved using ultraviolet radiation. The failure of the mechanico chemical technique is probably due to an insufficient formation of active free radicals capable of initiating a vinyl polymerisation. If grafting has occurred the amount is too insignificant to be of commercial importance since the dyeability of the material was similar to the unmodified polymer.

The use of benzophenone as a photoinitiator lowers the degree of grafting of the uninitiated polymerisation but the film product obtained is much better. In the absence of benzophenone, grafting of polypropylene with vinyl pyridine in air produces films which feel leathery to the touch and are slightly opaque. This must be a function of the length of grafted side chain, and the distribution of these grafted segments in the polymer. The presence of a photoinitiator causes hydrogen abstraction[33] from the backbone of the polypropylene forming a radical site capable of initiating a graft. With vinyl pyridine irradiated with the film only, the sites on the backbone must be formed by a chain transfer reaction, terminating the growing homopolymer by hydrogen abstraction. Studies of the polymerisation reaction in the presence of benzophenone have shown that a termination process is occurring producing oligomers of vinyl pyridine with some long chain polymers. The termination process with vinyl pyridine alone is probably by combination of radicals forming long chain polymer. It is reasonable to assume that the lengths of the grafted side chains are similar to the length of the polymer chains formed in the solution, and therefore these long and randomly distributed grafts may cause the changes in surface properties observed.

Increasing the concentration of benzophenone in the polymerising system probably increases the number of grafting sites on the polypropylene film but also increases the rate of termination. This results in shorter chains grafted, but more frequently distributed. Overall, the degree of grafting is lowered but the film is still capable of being dyed.

Two types of grafting can therefore be distinguished;

(a) long and infrequently grafted side chains
and (b) short but frequently distributed grafted material

The reaction of polypropylene film with vinyl pyridine in the presence of the photoinitiator produces grafted films of the second type, the overall degree of grafting being lowered as the concentration of initiator increases. Grafting of the film under an inert atmosphere with benzophenone produces a lower amount of grafted copolymer than in air. Since the concentration of initiator is the same, similar numbers of grafting sites should be produced at similar irradiation times, resulting in the same amount of grafting. This is not found to be the case, however, therefore oxygen must be playing some part in the reaction.

After hydrogen abstraction has occurred by benzophenone, two alternative reactions are possible. Firstly, direct grafting of the monomer can be initiated forming side chains of copolymer, or secondly, reaction with oxygen to form the alkyl peroxy radical shown below.

$$\mathrm{RH} \xrightarrow{\text{Benzophenone}} \mathrm{R.} \qquad (1)$$

$$\mathrm{R.} + \text{Monomer} \longrightarrow \text{Grafted copolymer} \qquad (2)$$

$$\mathrm{R.} + \mathrm{O_2} \longrightarrow \mathrm{ROO.} \qquad (3)$$

The alkyl peroxy radical can then further hydrogen abstract to form the hydroperoxide which can be photolysed to alkoxy and hydroxyl radicals.

$$\mathrm{ROO.} + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R.} \qquad (4)$$

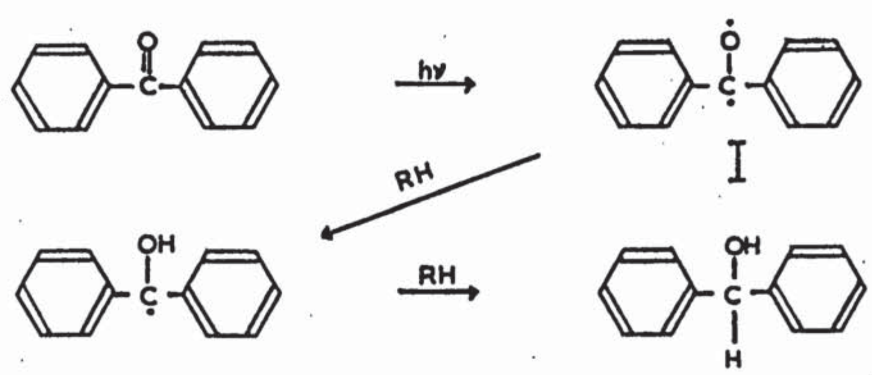
$$\mathrm{ROOH} \xrightarrow{h\nu} \mathrm{RO}\cdot + \cdot\mathrm{OH} \qquad (5)$$

The alkoxy radical can then initiate further grafting with monomer.

$$\mathrm{RO.} + \text{Monomer} \longrightarrow \text{Grafted copolymer} \qquad (6)$$

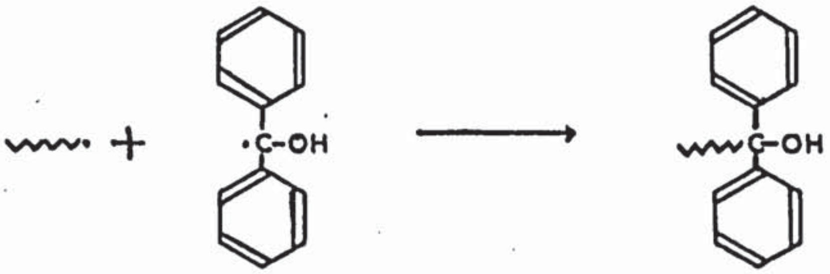
Reactions under nitrogen giving grafting would be restricted to step (2), whereas similar reactions under air, produce increased possibilities for grafting, by steps (4) and (5).

The termination reactions involving benzophenone are in doubt. Hydrogen abstraction processes form the intermediate benzhydrol radical before further abstraction to yield benzhydrol itself.



Benzhydrol Radical **Benzhydrol**

This radical can be resonance stabilised by the phenyl groupings and may terminate by radical combination shown below.



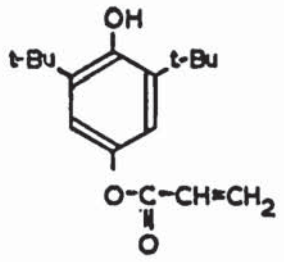
In the absence of polypropylene termination still occurs on irradiation and the diradical I is probably involved, since there is no source of active hydrogen to form the benzhydrol radical.

Termination reactions with benzophenone only occur on irradiation with ultraviolet light, since the presence of benzophenone in vinyl pyridine solutions without radiation does not prevent the homopolymerisation (Table V).

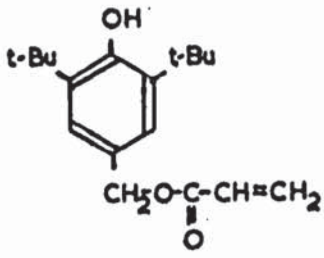
Further studies on this termination are necessary to ascertain the exact role played by benzophenone.

CHAPTER III SYNTHESIS AND CHARACTERISATION OF VINYL SUBSTITUTED COMPOUNDS FOR USE AS BOUND STABILISERS AND ANTIOXIDANTS

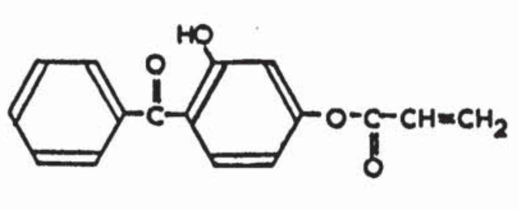
The following compounds were synthesised to determine their potential as bonded stabilisers in polypropylene. These compounds have been previously prepared, but used only as monomeric or polymeric additives and no attempt has been made to chemically combine them directly to a polymer.



3,5 ditertiary butyl-4-hydroxy phenyl acrylate



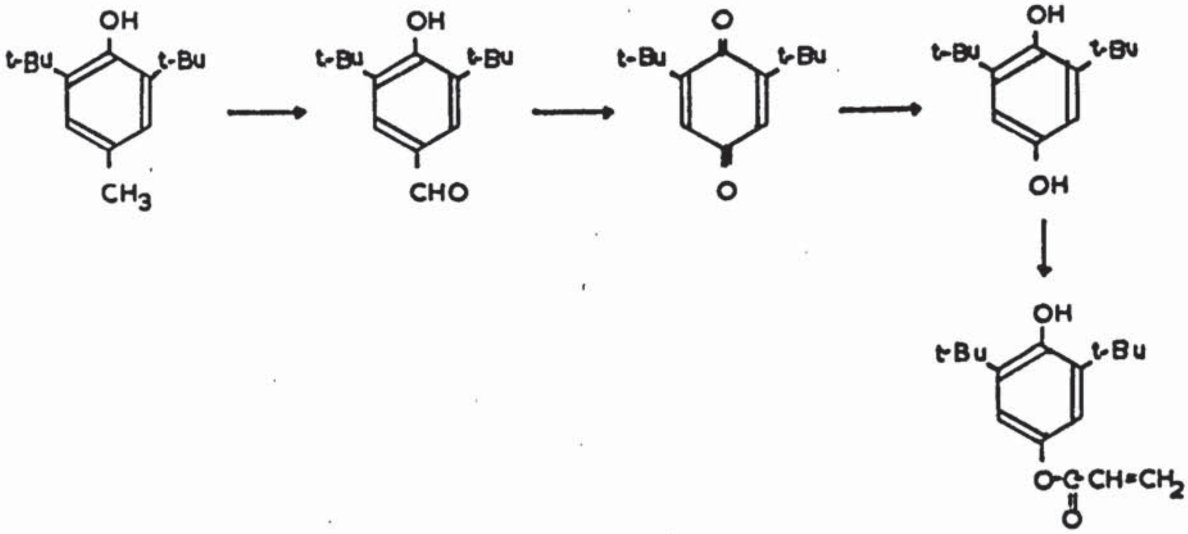
3,5 ditertiary butyl-4-hydroxy benzyl acrylate



4-benzoyl-3-hydroxy phenyl acrylate

A. SYNTHESIS OF 3,5 DITERTIARY BUTYL-4-HYDROXY PHENYL ACRYLATE

The following reaction scheme was used;



1. Preparation of 2,6-ditertiary butyl benzoquinone

The method of Coffield[58] was used to prepare 3,5 ditertiary butyl-4-hydroxy benzaldehyde, and the 2,6 ditertiary butyl benzoquinone was obtained from this by oxidation.

Thus, 128g (0.8M) of bromine was added dropwise to a stirred solution of 44.6g (0.2M) of 2,6 ditertiary butyl-4-methyl phenol (I.C.I. Ltd.) in 600ml of tertiary butyl alcohol at 25°C. The temperature rose, and after the addition of bromine, stirring was continued for a further hour. The mixture was cooled and the yellow crystalline product filtered off. This was washed with 10% sodium thiosulphate solution, then with distilled water and dried in a vacuum desiccator. The product was an off-white crystalline solid, melting at 189°C. The yield was 43g (91%) of 3,5 ditertiary butyl-4-hydroxy benzaldehyde.

The aldehyde was characterised by infra-red spectroscopy (I.R.) and nuclear magnetic resonance spectroscopy (N.M.R.)

<u>I.R. data</u>

phenolic O-H	3450cm^{-1}
carbonyl	1670cm^{-1}

<u>N.M.R.</u> (CCl_4)

aldehydic proton	0.2τ	(singlet)
aromatic protons	2.3τ	(singlet)
phenolic proton	4.3τ	(singlet)
tertiary butyl proton	8.6τ	(singlet)

The aldehyde (30g) was dissolved ih 5% caustic soda solution (640ml) and 91ml of 6% hydrogen peroxide solution added dropwise over one hour. The temperature was maintained at 50-60°C, and throughout the addition air was bubbled through the mixture. A deep yellow crystalline solid was precipitated. This was filtered, dried and recrystallised from methanol as yellow-orange prisms (10.5g) melting at 65.5°C.

I.R. data

C-H aromatic	3010cm^{-1}
C-H aliphatic	2900cm^{-1}
Carbonyl	1660cm^{-1}

N.M.R. (CCl_4)

aromatic protons	3.5τ	(singlet)
tertiary butyl protons	8.6τ	(singlet)

2. Preparation of 2.6 ditertiary butyl-4-hydroxy phenol

2,6 ditertiary butyl benzoquinone was dissolved in isopropanol and concentrated hydrochloric acid, to give a yellow solution. Zinc dust was added and a rapid effervescence occurred. When the solution was colourless, sodium bicarbonate was added to decompose any excess acid, and the solids were filtered off. The isopropanol solution was rotary evaporated to yield a white solid. This was recrystallised from petroleum ether, and a white crystalline solid was obtained melting at 101°C (Literaature 99-101°C)[59].

I.R. data

free phenolic O-H	3640cm^{-1}
hydrogen bonded O-H	3500-3100cm^{-1}

N.M.R. (CCl_4)

aromatic proton	3.3τ	(singlet)
phenolic proton	5.4τ	(singlet)
tertiary butyl protons	8.6τ	(singlet)

N.M.R. (Acetone)

Solvent shift showing paraphenolic proton at 3.37τ (singlet) also.

3. Preparation of acryloyl chloride

Acrylic acid (Koch-Light) was freshly distilled free of stabilisers before use, and then reacted with an equimolar quantity of thionyl chloride. The mixture was heated strongly, and a lacrymatory colourless liquid was distilled from the reaction at 77°C. The acryloyl chloride, was sealed in a glass phial before use. Infra-red data was difficult to obtain because of hydrolysis to acrylic acid.

4. Reaction of 2,6-ditertiary butyl-4-hydroxy phenol with acryloyl chloride

The method of Stiehl[13] was used for the preparation of the 3,5 ditertiary butyl-4-hydroxy phenyl acrylate. 22.2g (0.1M) of 2,6 ditertiary butyl-4-hydroxy phenol and 20.2g (0.2M) of triethylamine were dissolved in 150ml of tetrahydrofuran, under nitrogen (white spot grade), and stirred with cooling in ice until a clear solution was obtained. Over a period of ten minutes 9.1g (0.1M) of acryloyl chloride was added and stirring continued for one hour. The triethylamine hydrochloride was filtered, and the filtrate poured into an excess of water to give an oil. This oil slowly solidified over a period of days to give an orange solid. After several recrystallisations from ethanol, a white solid, 3,5 ditertiary butyl-4-hydroxy phenyl acrylate was obtained melting at 102-103°C.

I.R. data

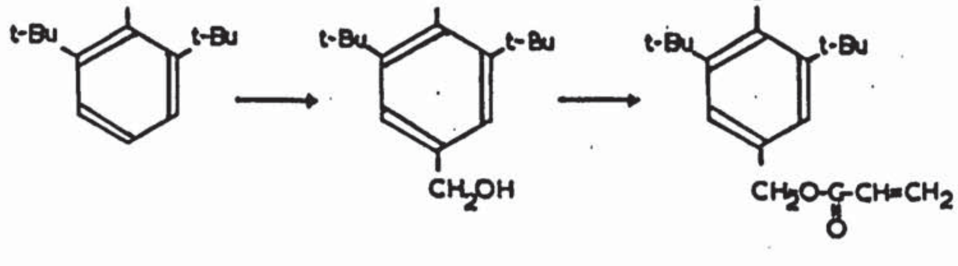
phenolic O-H	$3500cm^{-1}$
ester carbonyl	$1730cm^{-1}$
vinyl double bond	$1650cm^{-1}$

N.M.R. ($CDCl_3$)

aromatic proton	3.2τ	(singlet)
vinyl protons	3.4-4.2τ	(multiplet)
phenolic proton	5.0τ	(singlet)
tertiary butyl protons	8.6τ	(singlet)

B. SYNTHESIS OF 3,5 DITERTIARY BUTYL-4-HYDROXY BENZYL ACRYLATE

This was prepared according to the following scheme;



1. Preparation of 3,5 ditertiary butyl-4-hydroxy benzyl alcohol

The 2,6 ditertiary butyl phenol was used as obtained from CIBA-GEIGY Ltd. without further purification.

The method was followed directly as described by Shell International Research[60].

53.5 parts by volume of a 7.5% solution of formaldehyde in tertiary butyl alcohol, 50 parts of a 500g/litre solution of 2,6 ditertiary butyl phenol in tertiary butyl alcohol and 14 parts of a 50g/litre solution of potassium tertiary butoxide in the same solvent were mixed at 20°C and stirred under nitrogen (white spot grade) for thirty minutes. The mixture was then poured into ice water and two layers formed, the upper organic layer solidifying. The solids were washed with water, stirred with isopentane, filtered and air dried. A sparkling crystalline white solid of 3,5 ditertiary butyl-4-hydroxy benzyl alcohol was obtained melting at 137°C.

I.R. data

free phenolic OH	$3580 cm^{-1}$
Hydrogen bonded OH	$3500 cm^{-1}$

N.M.R. (CCl_4)

aromatic protons	2.9τ	(singlet)
phenolic proton	4.9τ	(singlet)
methylene protons	5.5τ	(singlet)
tertiary butyl protons	8.6τ	(singlet)

N.M.R. (benzene)

Solvent shift showing aliphatic alcoholic proton at 8.6τ (singlet) also.

2. Reaction of 3,5 ditertiary butyl-4-hydroxy benzyl alcohol with acrylic acid

This reaction yielding 3,5 ditertiary butyl-4-hydroxy benzyl acrylate was carried out as described by Rocklin and Morris[9].

A mixture of 47.2g (0.2M) of 3,5 ditertiary butyl-4-hydroxy benzyl alcohol and 130ml of acrylic acid was warmed gently until complete solution was achieved. A further 10ml of acrylic acid containing one drop of concentrated sulphuric acid was added and the solution allowed to remain at room temperature for six hours. The solution was then poured into water and the organic phase extracted with ether, and the excess acrylic acid removed with aqueous sodium bicarbonate. The ether phase was dried over magnesium sulphate, filtered and evaporated. The residue was recrystallised from petroleum ether to give 19.9g of 3,5 ditertiary butyl-4-hydroxy benzyl acrylate, melting at 67.5-69°C.

I.R. data

free phenolic OH	3640cm^{-1}
ester carbonyl	1830cm^{-1}
vinyl double bond	1640cm^{-1}

N.M.R. (CCl_4)

aromatic protons	2.9τ	(singlet)
vinylic protons	$3.6-4.5\tau$	(multiplet)
phenolic proton	4.8τ	(singlet)
methylene protons	5.0τ	(singlet)
tertiary butyl protons	8.6τ	(singlet)

C. SYNTHESIS OF 4-BENZOYL-3-HYDROXY PHENYL ACRYLATE

This was prepared by the method of CIBA Ltd.[61] using the following reaction;

The 2.4 dihydroxy benzophenone was used as received from Koch-Light Ltd. without further purification.

64.2 parts of 2,4 dihydroxy benzophenone were dissolved ina lye prepared from 12 parts of caustic soda and 200 parts of methanol. The solvent was removed by rotary evaporation and the monosodium compound dried, and suspended in 500 parts of absolute benzene. Acryloyl chloride (27 parts) was added dropwise with stirring and cooling, and the mixture stirred for a further hour. After a short period of heating, the sodium chloride was removed and the benzene distilled off under vacuum. The acrylic ester formed as an oily residue which crystallised on the addition of aqueous ethanol. Further recrystallisation gave 51 parts (64%) of 4-benzoyl-3-hydroxy phenyl acrylate as yellow lustrous crystals melting at 80°C.

I.R. data

hydrogen bonded OH	3400cm^{-1}
ester carbonyl	1750cm^{-1}
aromatic carbonyl	1640cm^{-1}

U.V. (acetone)

λ_{max} 335mμ

N.M.R. (CCl_4)

phenolic proton	-2.2τ	(singlet)
5 aromatic protons	2.3-2.6τ	(multiplet)
3 aromatic protons	3.2-3.7τ	(multiplet)
vinyl protons	3.1-4.0τ	(multiplet)

POLYMERISATION OF THE SYNTHESISED VINYL COMPOUNDS

The molecular weights and molecular weight distributions were determined by gel permeation chromatography (g.p.c.) using polymethyl methacrylate as a standard. This work was carried out by Dr. J.M. Evans at R.A.P.R.A., Shawbury.

1. Preparation of Poly 3,5 ditertiary butyl-4-hydroxy phenyl acrylate

2.76g (0.01M) of the monomer were dissolved in 20ml of benzene and 0.03g (0.002M) azobisisobutyronitrile added as initiator. The whole was refluxed with stirring under nitrogen (white spot). After eight hours a further 0.015g initiator was added and the reaction left for a further sixteen hours. The product was rotary evaporated to yield a white solid.

Polymerisation was confirmed by an infra-red spectrum showing disappearance of the vinylic absorption of the monomer. The N.M.R. spectrum became broader, and additional peaks appeared at 7.6-8.4τ typical of $CH-CH_2$ aliphatic resonance, with a corresponding decrease at 3.4-4.2τ.

Thermogravimetric analysis (t.g.a.) showed an increase of weight loss from 100°C for the monomer, to 250°C for the polymer.

Polymer characteristics from g.p.c. were

$$Mn = 2982$$

$$Mw/Mn = 1.51$$

2. Preparation of Poly 3,5 ditertiary butyl-4-hydroxy benzyl acrylate

Polymerisation of this monomer was carried out as described above and a white solid was obtained.

I.R. data

broad phenolic OH	3640cm^{-1}
ester carbonyl	1830cm^{-1}
vinyl double bond	absent

N.M.R. ($CDCl_3$)

aromatic proton	2.8τ	(broad singlet)
phenolic proton	4.8τ	(broad singlet)
methylene protons	5.0τ	(broad singlet)
$CH-CH_2$ protons	7.4-8.4τ	(broad multiplet)

Thermogravimetric analysis showed an increase in decomposition temperature from 100°C for the monomer to 225°C for the polymer.

Polymer characteristics from g.p.c. were Mn = 9415, Mw/Mn = 3.64.

3. Preparation of Poly-4-benzoyl-3-hydroxy phenyl acrylate

Polymerisation was carried out as previously described for the other monomers, and a yellow solid product was eventually obtained. The infra-red spectrum was uninformative since the double bond of the vinyl group was masked by the carbonyl of the benzophenone at 1640cm^{-1}.

The N.M.R. spectrum showed broad peaks, the 3.1-4.0τ vinyl resonance disappearing and peaks appearing at 7.1-7.9τ of the aliphatic $CH-CH_2$ resonance.

The stability of the polymer was much increased by t.g.a. to 300°C compared with 65°C for the monomer. The number average molecular weight Mn was 9914, and a molecular distribution of 4.36 was found from g.p.c.

PREPARATION OF 3,5 DITERTIARY BUTYL-4-HYDROXY BENZYL STEARATE

Although this compound does not contain a vinyl group it was synthesised for use as a comparative antioxidant and has been included here for completeness.

The preparation used was as described by Rocklin and Morris[9]. 23.6g (0.1M) of 3,5 ditertiary butyl-4-hydroxy benzyl alcohol were reacted with 28.4g (0.1M) of stearic acid in dioxane containing 2ml of concentrated sulphuric acid. The mixture was allowed to stand for twelve hours, then diluted with a litre of water, and the solid precipitate filtered off. The solid was dried after washing to yield 50g of a waxy orange precipitate of 3,5 ditertiary butyl-4-hydroxy benzyl stearate. The melting point was difficult to assess but a value of 58°C was obtained using differential thermal analysis.

I.R. data

phenolic OH	3640cm^{-1}
carbonyl	1700cm^{-1}

N.M.R. ($CDCl_3$)

aromatic protons	2.9τ	(singlet)
phenolic proton	5.0τ	(singlet)
methylene protons	5.6τ	(singlet)
tertiary butyl protons	8.6τ	(singlet)
stearyl protons	7.7-7.9τ	(multiplet)
	8.8τ	(singlet)
	9.2τ	(multiplet)

INSTRUMENTAL TECHNIQUES

The infra-red spectra were recorded on a PERKIN ELMER 257 infra-red spectrophotometer.

Ultraviolet spectra were recorded on a PERKIN ELMER 137 spectrophotometer.

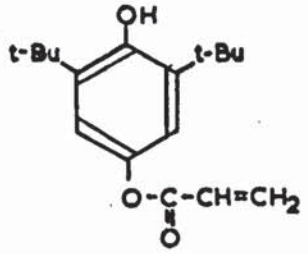
Nuclear magnetic resonance spectra were recorded on a PERKIN ELMER R10 (60M/c/sec) instrument. Tetramethylsilane was used as a reference.

Thermogravimetric analysis and differential thermalanalysis of the samples were determined using a DuPont 900 Thermal analyser.

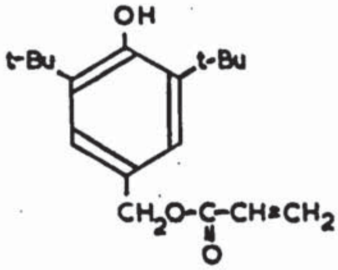
ABBREVIATIONS

The following abbreviated forms have been adopted for the various compounds used in this work.

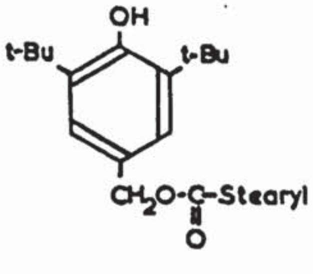
DBPA 3,5 ditertiary butyl-4-hydroxy phenyl acrylate



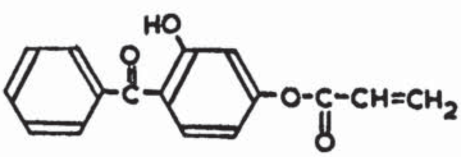
DBBA 3,5 ditertiary butyl-4-hydroxy benzyl acrylate



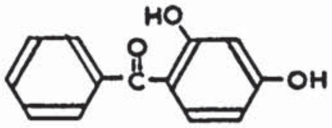
DBBS 3,5 ditertiary butyl-4-hydroxy benzyl stearate



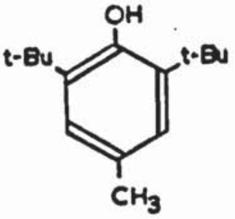
BHPA 4-benzoyl-3-hydroxy phenyl acrylate



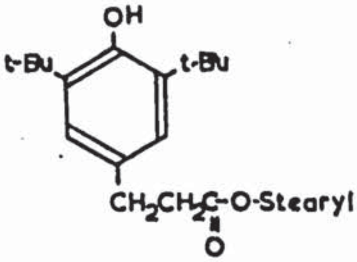
DHBP   2,4 dihydroxy benzophenone



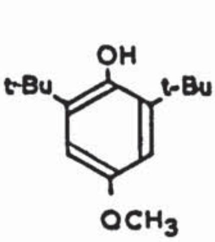
TOPANOL OC   2,6 ditertiary butyl-4-methyl phenol



IRGANOX 1076



TOPANOL 354   2,6 ditertiary butyl-4-methoxy phenol

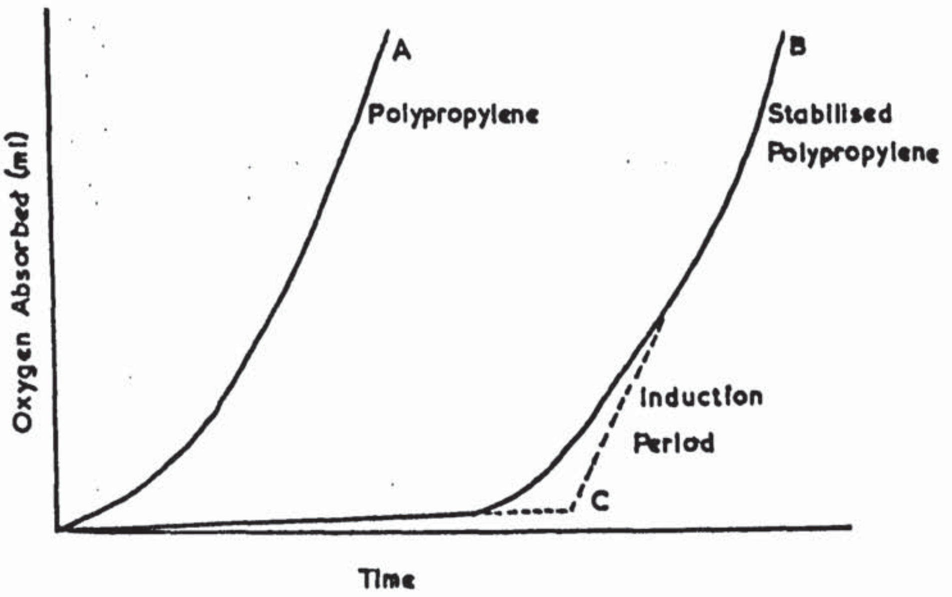


These abbreviations will be used throughout, where appropriate.

CHAPTER IV EVALUATION OF ANTIOXIDANT ACTIVITY

The effective of the synthesised monomers and polymers as antioxidants was determined using the technique of oxygen absorption. The oxidation of polypropylene is autocatalytic, and a graph of oxygen absorbed with time at elevated temperatures produces the trace A shown in the figure I below.

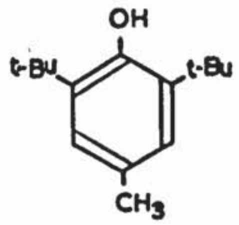
Figure I



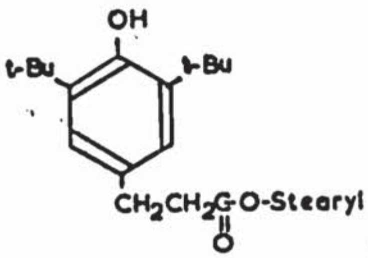
When a stabiliser is incorporated into the polymer system, the oxidation is retarded and an induction period occurs as defined above at C. At this stage, the stabiliser has been exhausted and the oxidation proceeds at a similar rate as for the unstabilised polymer, giving curve B. The induction period can be used as a measure of the relative activity of antioxidants.

The induction periods of the synthesised antioxidants were measured firstly in decalin, which oxidises quite readily. This determined whether the systems were antioxidants, since the introduction of acrylic groupings and subsequent polymerisation reactions may have affected the activity of the hindered phenol.

Secondly, the compounds were used in polypropylene to assess whether they were stabilisers for this polymer or not. For comparison purposes, two commercial antioxidants were also used. These are shown below.

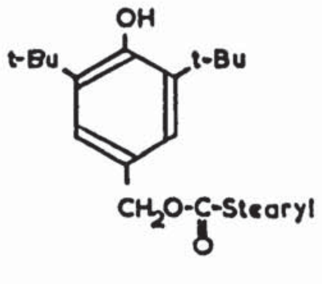


TOPANOL OC (I.C.I. Ltd.)



IRGANOX 1076 (CIBA-GEIGY Ltd.)

A further long chain hindered phenol was prepared having the structure



to study the effect of increased chain length on the activity of the ester as an antioxidant.

PREPARATION OF POLYMER FILMS

1. Impregnation of polypropylene with antioxidant

Several methods have been used to introduce antioxidants into polymers. On a large scale this has been achieved by ball milling or tumbling. The dispersion of the antioxidant throughout the polymer is very important, and since only small quantities of additive were used in this study it was decided to use the technique of solvent evaporation.

One hundred gram of unstabilised polypropylene powder (I.C.I. Ltd. HF 20C/CV 170) were shaken with a solution of the antioxidant (2×10^{-4} mole/100g polymer) dissolved in dichloromethane (50-100ml). After shaking several minutes, the polymer suspension was rotary evaporated at ambient temperature. Frequent additions of solvent were made during evaporation to wash stray polymer back into the bulk. Tumbling was continued for one hour after total evaporation of the solvent. The stabilised polymer samples were stored in the refrigerator prior to use.

2. Film Formation

The blended polypropylene powder (5g) wqs pressed between stainless steel plates (12" x 12") at 180°C for three minutes. The press had electrically heated plattens and could be water cooled. The pressure used was 25 tons/sq. in. on a 6 inch diameter ram which produced films varying in thickness from 0.005 inch to 0.008 inch. Films of 0.005 inch thickness only were used for oxidation studies.

DETERMINATION OF INDUCTION PERIOD

The equipment used for the measurement of the induction period was devised in this department[62] and is illustrated in Figure II. The system was completely flushed with oxygen for several minutes and the reaction vessel A, (containing solution or film as appropriate) then immersed in a thermostated oil bath. The lagged reservoir, B, connected to the reaction vessel by capilliary tubing, C, dipped into a beaker containing di-n-butyl phthalate, which is an involatile fluid. The beaker was supported on a 6 x 2 x $^1/16$" steel plate, which was rigidly fixed at one end, the flexible part being allowed to bend under the weight of the filled beaker. Two strain gauges (Phillips type PR 9810F) were bonded to each side of the clamped plate with an epoxy adhesive (Araldite). These were electrically connected to a recorder to form the four arms of a Wheatstone bridge circuit, the pairs of strain gauges (S_1 and S_3) and (S_2 and S_4) being on the same side of the steel plates. The circuit is shown in Figure III. A D.C. 3 volt supply was used throughout, and P consisting of a 2MΩ and 25KΩ potentiometer in series was introduced to enable the recorder to be adjusted to zero.

As oxygen was absorbed by the sample in A, an equal volume of liquid was removed from the beaker into the lagged reservoir. The steel plate began to unbend due to the decrease in weight thus altering the resistance of the strain gauges. This was recorded as an oxidation curve on a Leeds and Northrup "Speedomax" recorder, the trace being similar to that shown earlier in Figure I. The system was, therefore, completely automated.

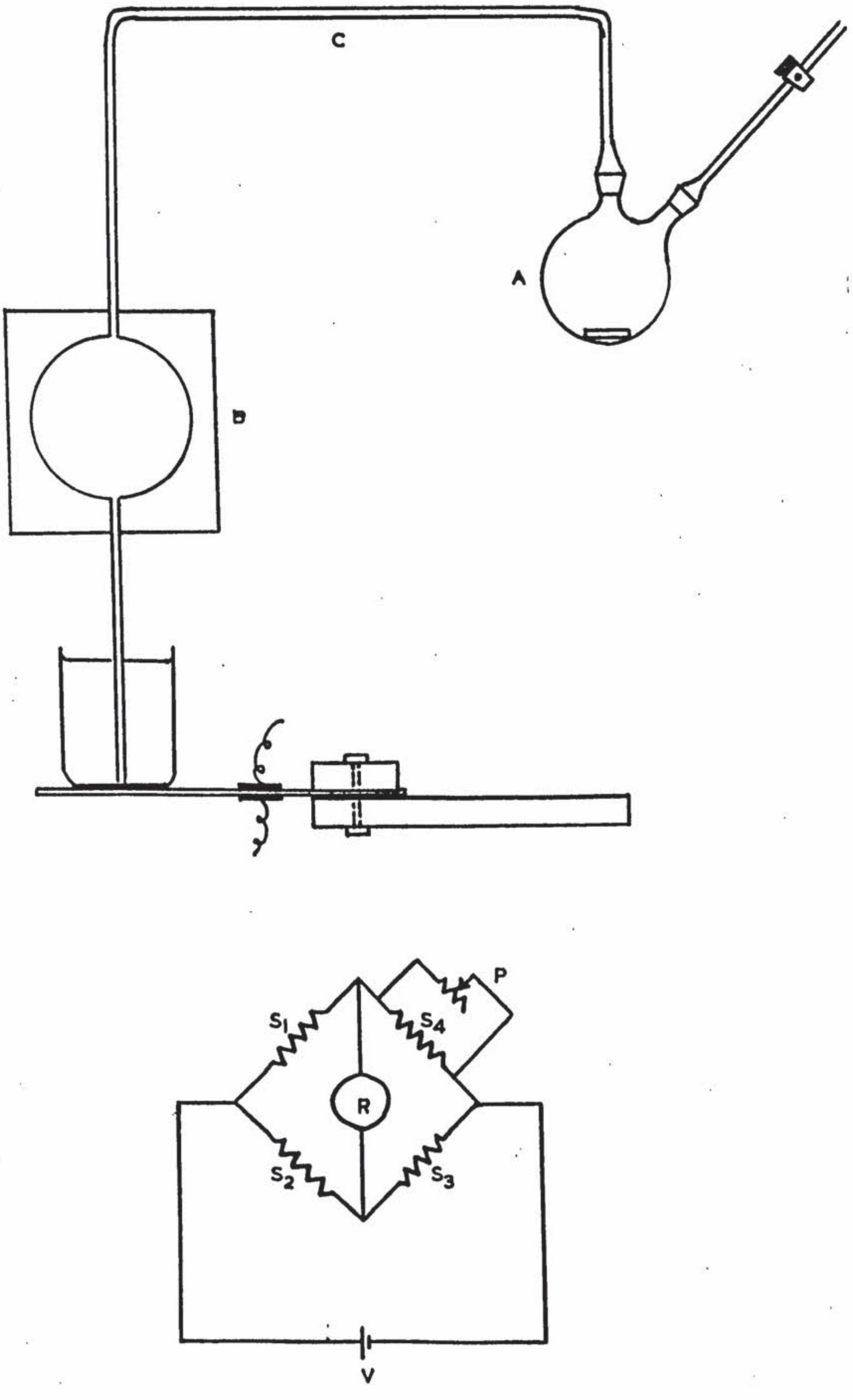


FIGURE II

ANTIOXIDANT ACTIVITY IN DECALIN

The antioxidant was dissolved in freshly distilled decalin at a concentration of 2×10^{-4} mole per 100ml decalin. The solution was constantly stirred during the oxidation, which was carried out in a thermostated bath at 120°C. The induction periods for the various stabilisers are shown in Table I.

TABLE I

INDUCTION PERIODS TO OXIDATION IN DECALIN OF 2×10^{-4} MOLE/100ml ANTIOXIDANT AT 120°C

Additive	Induction period (hours)	Melting point (°C)
None	2	-
DBBA	102	68
Poly DBBA	100	-
DBPA	98	102
Poly DBPA	62	-
Topanol OC	345	70
Irganox 1076	133	52
DBBS	138	58

ANTIOXIDANT ACTIVITY IN POLYPROPYLENE

Stabilised polypropylene film (lgram) of thickness .005 inch was cut into thin strips and oxidised as shown in A, Figure II. The induction period was determined using the same additive concentration of 2×10^{-4} mole/100g polypropylene as used in the decalin studies. The stabilised films were acetone extracted in a Soxhlet for forty-eight hours and the induction periods of these extracted films also measured. The results are illustrated in Table II.

TABLE II

INDUCTION PERIODS OF POLYPROPYLENE STABILISED FILMS AT 120°C AT CONCENTRATION 2×10^{-4} MOLE STABILISER/100g POLYMER

Additive	Induction Period (Hours) Unextracted	Induction Period (Hours) Extracted
None	2	2
DBBA	28	2
Poly DBBA	35	2
DBPA	34	2
Poly DBPA	29	2
Topanol OC	115	2
Irganox 1076	2985	2
DBBS	130	2

The polymeric additives were incorporated at 2×10^{-4} mole/100g polypropylene based on monomeric molecular weight.

OVEN AGEING OF POLYPROPYLENE

The stabilised polypropylene films were aged in a Wallace oven at 120°C in a forced draught of air (0.5 cu ft/hour). The failure point was taken as embrittlement, on flexing the film through 180°C. Table III shows the relative stabilities of 0.005 inch thick polypropylene blended films.

TABLE III

EMBRITTLEMENT ON OVEN AGEING AT 120°C OF POLYPROPYLENE FILM CONTAINING 2×10^{-4} MOLE ADDITIVE/100g POLYMER

Additive	Embrittlement Times (Hours)
None	7
DBBA	20
Poly DBBA	18
DBPA	18
Poly DBPA	17
Topanol OC	11
Irganox 1076	>1000
DBBS	244

DISCUSSION

Evaluation of antioxidants using accelerated ageing tests is no substitute for actual service conditions, and predictions of polymer lifetimes during service from such data should be viewed critically and objectively. Because a stabiliser is excellent when tested under one set of conditions, this does not imply that it can be used universally. Increasing the temperature by 20°C can reduce a good antioxidant to one of mediocre performance. Most antioxidants become less effective at higher temperatures, but considerations such as volatility, mobility and compatability must be taken into account and an effort made to rationalise them.

Gordon[63] has shown that antioxidants can be arranged in several orders of effectiveness depending on the type of testing employed. Oven ageing data for example varies with sample thickness, and some stabiliser systems are more susceptible to increases than others. Accelerated test conditions are valuable tools, however, if used with some reservation.

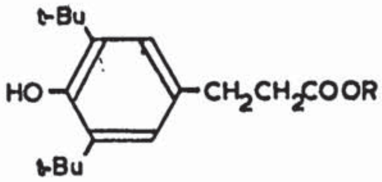
The oxidation of decalin, a pure hydrocarbon, in a sealed system of oxygen begins after two hours at 120°C. The induction periods can be extended by dissolving an antioxidant in the system and the results are as shown in Table I under the conditions stated.

Since the oxidation was carried out in solution, under an atmosphere of oxygen, the results should indicate the true antioxidant behaviour, the factors of volatility, compatability, and mobility being eliminated.

Scott[64] studied the effect of the molecular weight of additives on their induction period in decalin using the homologous series shown, under the conditions stated in Table IV.

TABLE IV

INDUCTION PERIODS IN DECALIN AT 140°C AT CONCENTRATION OF 2×10^{-3} MOLE/100ml DECALIN



R	Induction Period (Hours)
Methyl	27
Hexyl	24
Lauryl	22
Stearyl	18

At a concentration of 2×10^{-4} mole/100ml decalin, at the same temperature the stearyl antioxidant gave an induction period of ten hours[65].

Lowering the temperature by 20°C to 120°C (Table I) the same stabiliser gives an induction period of 133 hours. This illustrates the decrease in effectiveness with increasing temperature shown by most antioxidants.

Scott found a slight decrease in antioxidant activity with increasing molecular weight. Comparisons on this basis, of the stabilisers in Table I are not too revealing as they do not represent a homologous series. However, the inherent antioxidant behaviour of all the additives studied was good, the Topanol OC being quite remarkable.

The two long chain stearyl compounds show similar activity, which could be expected since their structures are not too dissimilar.

Studies of the blended antioxidants in polypropylene (Table II) show a marked decrease in activity over that in decalin. Again, using a sealed oxygen system, the volatility effect of the antioxidant is eliminated. The results reflect the compatability of the additives with respect to polypropylene.

The long chain additives are more effective, and Irganox 1076 shows a remarkable induction period illustrating its great compatability with the polymer. The synthesised monomer and polymer additives show a low activity and are similar to each other in effectiveness. Acetone extraction of the material reduces the stability to that of the unstabilised polypropylene. Even the polymeric additives were removed, and the induction period of the Irganox 1076 sample fell dramatically. This result is important when we consider the activity of the grafted antioxidants, after acetone treatment.

Oven ageing of the films (0.005") in a stream of air at 120°C (Table III) shows once again the importance of compatability. The two commercial stabilisers illustrate the opposite effects under the conditions of the test. The activity of Topanol OC falls from 115 hours in oxygen to 11 hours in an air oven. Similarly the synthesised additives show reduced activity. This may be attributed to stabiliser losses due to volatility.

Plant and Scott[3] using torsional braid analysis, oven aged fibre braids containing the stabilisers shown in Table IV. The stearyl additive showed an activity of 9,800 hours, compared with the methyl derivative of 25 hours at 100°C.

On oven ageing films at 120°C (Table III) the stearyl antioxidant showed stability of greater than 1000 hours, the final figure probably being much greater. The activity of the synthesised stearyl compound DBBS on oven ageing (244 hours) is probably similar to that in oxygen (130 hours), the increase being due to circulating air through the oven and not oxygen.

CHAPTER V(I) GRAFT MODIFICATION OF POLYPROPYLENE WITH ANTIOXIDANT MONOMERS

Although the activity of the synthesised stabiliser monomers and polymers was low in comparison with the conventional antioxidants, it was decided to graft the monomers into polypropylene. The extractability of the stabilisers would, therefore be reduced and compatability effects would be limited since the compounds would be grafted, and therefore an integral part of the polymer unlike the blended additives.

1. Preparation of samples

The antioxidant monomers used were all solids, and the grafting was therefore carried out in a solution, using benzene as the solvent. The monomers were normally made up in 100ml of benzene, and because the concentration of the monomer was often less than 10g per 100ml benzene the irradiation times were longer than those used for 2-vinyl pyridine. Benzophenone was again used as the photoactivator.

Thus, 0.1g unstabilised polypropylene film (.005") was immersed in a benzene solution of the monomer and benzophenone, stoppered in a quartz tube and irradiated for a known period of time. Normally six solutions were irradiated simultaneously.

After irradiation the film samples were washed with benzene to remove residual solution and then Soxhlet extracted in acetone for forty-eight hours. Acetone is a solvent for both the monomeric and polymeric stabilisers and removes all non-grafted material. The films were then dried in a vacuum dessicator before use.

2. Characterisation of grafted films

The induction periods of the films were determined as described earlier in a closed oxygen system and the results are as shown in the various tables and graphs. The following studies were carried out using 3,5 ditertiary butyl-4-hydroxy benzyl acrylate monomer (DBBA) at the concentrations stated.

A. Effect of Irradiation Time on Induction Period

Benzene solutions (100ml) containing 5g DBBA and 1g benzophenone were irradiated for various periods of time in the presence of 0.1g polypropylene film. The induction periods were determined and are shown in Table I.

TABLE I

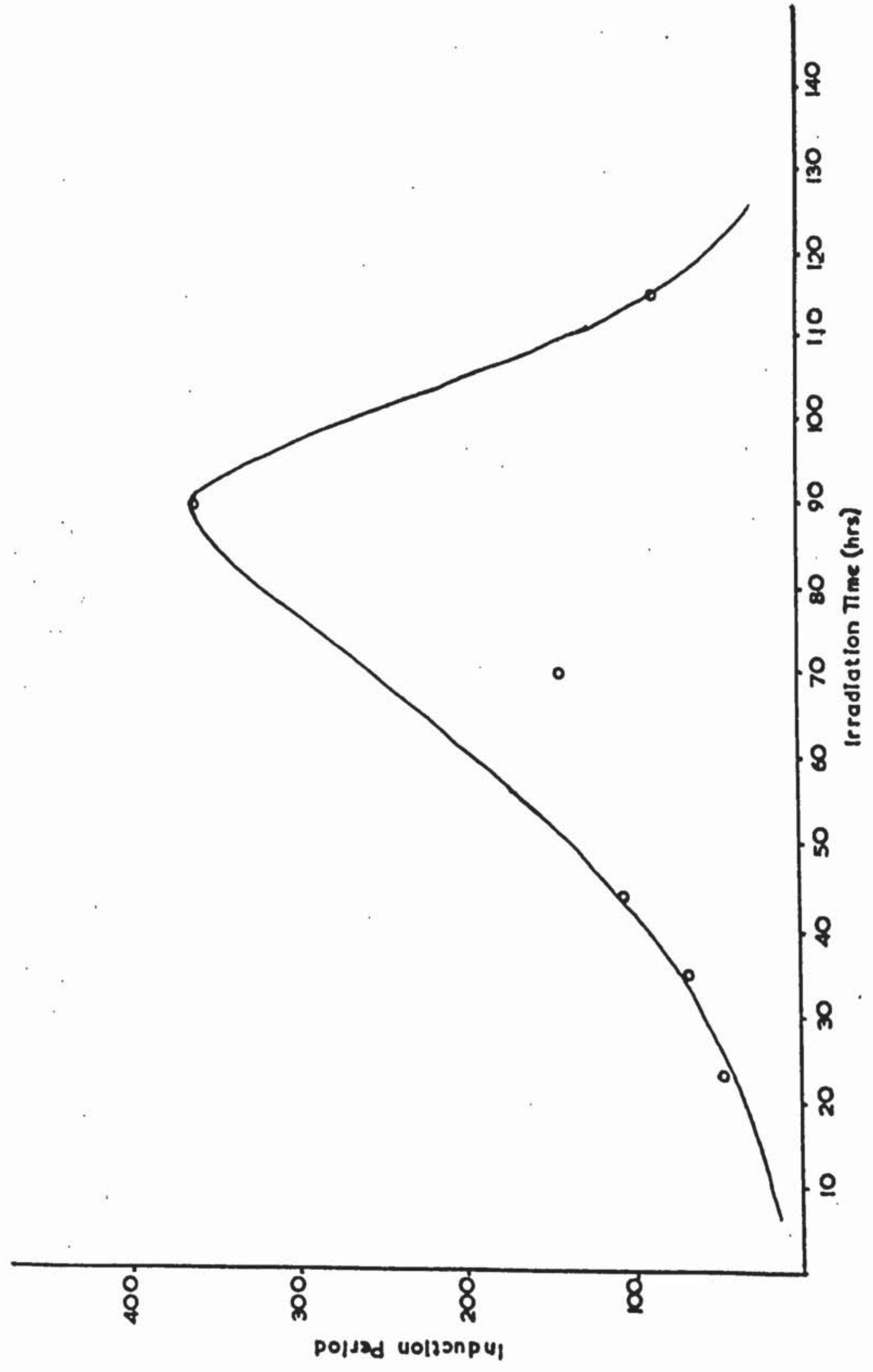
INDUCTION PERIODS OF POLYPROPYLENE FILM GRAFTED WITH DBBA AT A CONCENTRATION OF 1% BENZOPHENONE AND 5% MONOMER

Irradiation Time (Hours)	Induction Period (Hours)
24	50
36	73
45	110
70	140
90	366
126	87

These results are illustrated graphically in Figure I.

FIGURE I

INDUCTION PERIOD VS. IRRADIATION TIME OF GRAFTED POLYPROPYLENE FILM USING A SOLUTION OF 5% DBBA AND 1% BENZOPHENONE



B. Effect of Monomer Concentration on Induction Period

The monomer concentration of DBBA was varied and samples were irradiated for ninety hours at a fixed concentration of benzophenone. The induction periods were measured and are shown below.

TABLE II

INDUCTION PERIODS OF GRAFTED POLYPROPYLENE FILM IRRADIATED FOR NINETY HOURS WITH A SOLUTION OF 1% BENZOPHENONE AT VARIOUS CONCENTRATIONS OF DBBA

Monomer Concentration (g/100ml Benzene)	Induction period (Hours)	Monomer/Benzophenone Molar Ratio
10	342	6.28
5	366	3.14
2.5	550	1.57

C. Effect of benzophenone concentration

2.5g of DBBA monomer were irradiated for ninety hours with polypropylene in benzene (100ml) with various concentrations of benzophenone. The induction periods are shown in Table III and graphically in Figure II.

TABLE III

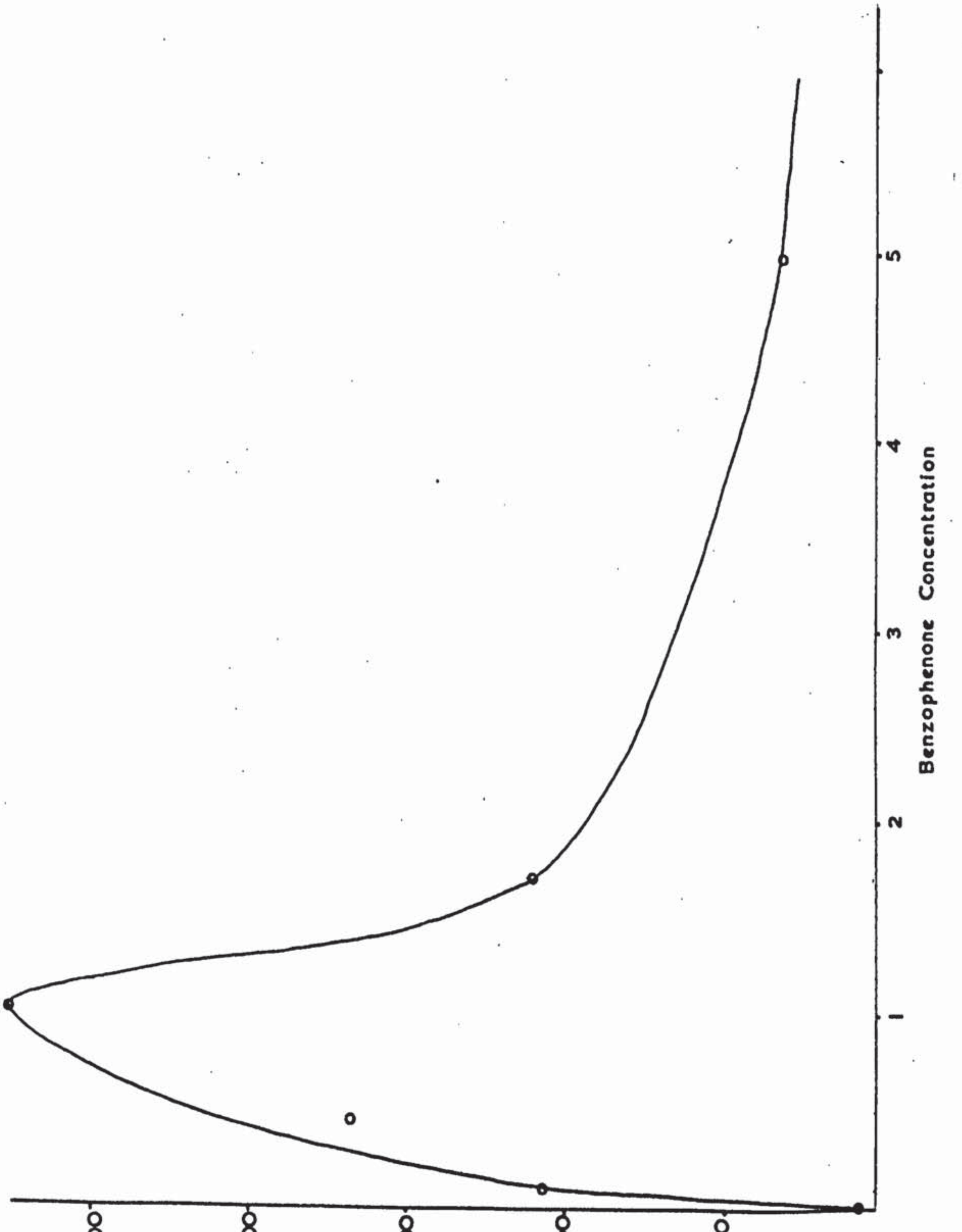
INDUCTION PERIODS OF POLYPROPYLENE FILMS GRAFTED WITH 2.5g DBBA SOLUTIONS AT VARIOUS CONCENTRATIONS OF BENZOPHENONE IRRADIATION TIME, NINETY HOURS

Benzophenone Conc$^{n.}$ g/100ml	Induction Period	Monomer/Benzophenone Molar Ratio
0	16	
0.1	215	15.7
0.5	330	3.14
1.0	550	1.57
1.7	220	0.92
5.0	66	0.314

FIGURE II

INDUCTION PERIOD OF GRAFTED POLYPROPYLENE FILM VS. BENZOPHENONE CONCENTRATION IN THE DBBA MONOMER SOLUTION

Fixed monomer concentration 2.5g/100ml. Irradiation time 90 hours



D. Effect of nitrogen on Induction Period

A solution of 5g of monomer and 1g of benzophenone in benzene (100ml) was irradiated with polypropylene film for ninety hours, after the system had been purged with white spot nitrogen for four hours. The film was acetone extracted and the induction period measured, the results being as shown below, in Table IV.

TABLE IV

IRRADIATION UNDER NITROGEN

Monomer (gram)	Benzophenone (gram)	Induction Period (Hours)	Monomer/Benzophenone Molar Ratio
5	1	172	3.14

E. Grafting of polypropylene with 3.5 ditertiary butyl-4-hydroxy phenyl acrylate

6.72g of 3,5 ditertiary butyl-4-hydroxy phenyl acrylate were made up in a solution of 1g benzophenone in 100ml benzene and irradiated for ninety hours. The films were then extracted and an induction period of 18 hours was determined.

ANALYSIS OF GRAFTED FILMS

1. U.V. Analysis

A calibration curve was plotted for DBBA (0.103g polymer) using ultraviolet spectroscopy of a solution of this polymer in trichloroethylene. A straight line was obtained showing good correlation and this is shown in Figure III. Some grafted films were analysed and the results are shown in Table IV, for two of the systems irradiated under the experimental conditions shown in Table II.

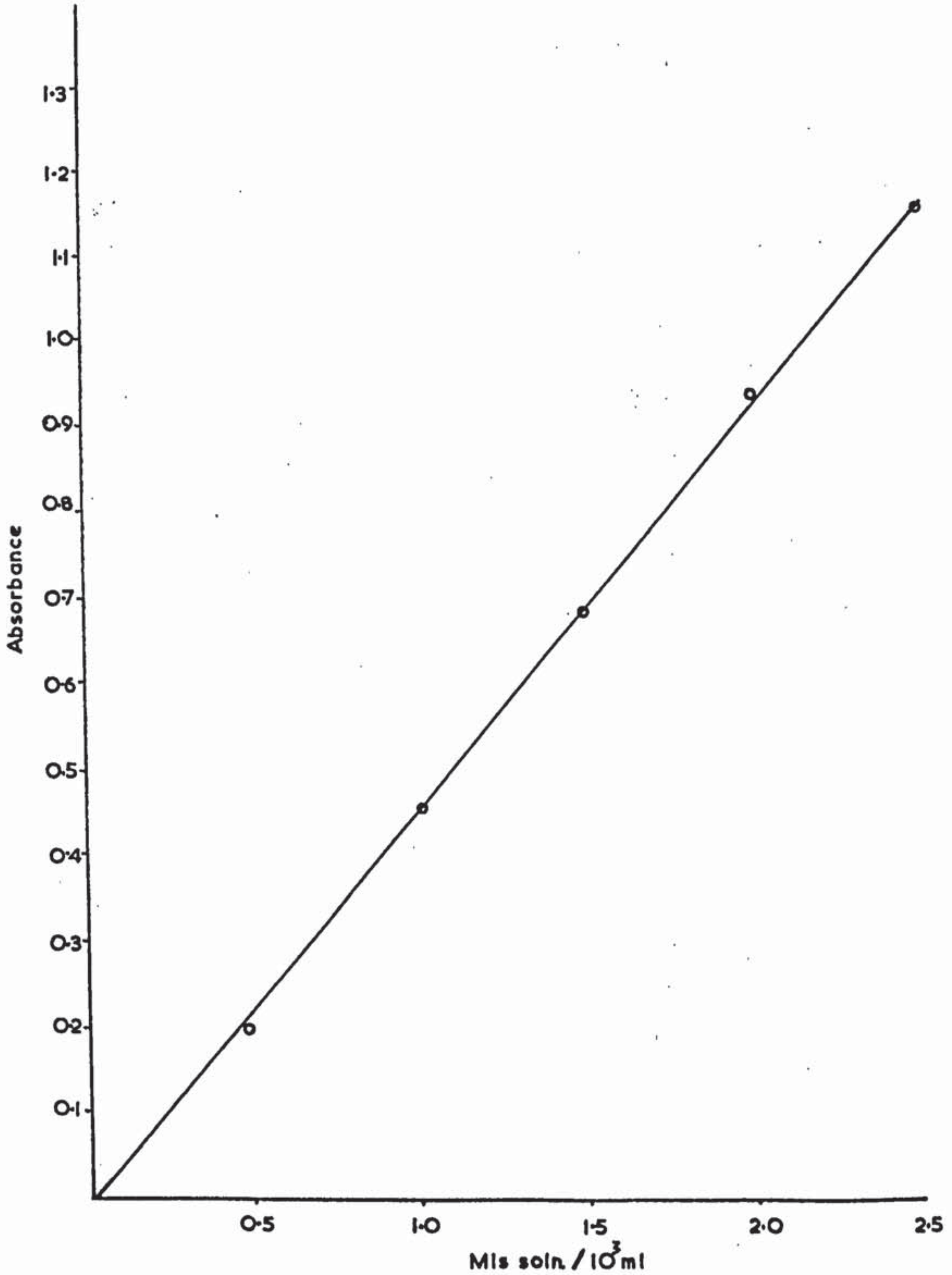
TABLE V

ANALYSIS OF DBBA GRAFTED FILMS

Monomer	Benzophenone	% Grafted polymer present	Moles/100g Polypropylene
2.5	1	0.092	3.18×10^{-4}
10	1	0.089	3.02×10^{-4}

FIGURE III

U.V. CALIBRATION CURVE FOR 0.103g 3,5 DITERTIARY BUTYL-4-HYDROXY BENZYL ACRYLATE IN TRICHLOROETHYLENE



2. Oven Ageing

Samples of film which had been irradiated with various concentrations of DBBA at a fixed benzophenone concentration (1%) (Table II) were aged in a Wallace oven under a forced draught of air at 120°C. All the films yellowed and embrittled. The ageing times are shown in Table VI.

TABLE VI

OVEN AGEING OF GRAFTED FILMS

Monomer concentration in irradiated system (g/100ml)	Ageing time (Hours)
2.5	240
5	240
10	240

DISCUSSION

The variation of induction period to oxidation has shown several interesting phenomena. Evidence for grafting is based predominantly on the induction period after acetone extraction of the film. Extraction of films blended with the polymeric stabilisers, has shown that the activity of the films reverts to that of the unstabilised polypropylene. It is, therefore, unlikely that the lengthy induction periods of the grafted material is due to incomplete extraction.

The grafting would seem to be a surface phenomenon since U.V. analysis of the films grafted with DBBA (TableV) indicate a similar concentration to those of the blended materials (viz 2 x 10^{-4} mole/100g polypropylene), yet the antioxidant activity is ten times greater. Increase of the monomer concentration from 2.5 to 10% in the grafting solution, at constant concentration of photoinitiator results in a reduction of stability of two hundred hours (Table II). Analysis of these two films by ultraviolet spectroscopy shows that they have a similar concentration of graft of 3 x 10^{-4} mole per hundred grams of polypropylene. The variation of induction period in these films must, therefore, be a function of the grafted chain length. For the same concentration of benzophenone (1%) irradiated for ninety hours, a similar number of radical sites should be formed on the polypropylene backbone. The increase in monomer concentration should result in an increased grafted chain length, and it would appear that this length is important regarding stability of the polymer on oxidation.

It can be concluded that the shorter the grafted chain length of the antioxidant, the better becomes the stability.

This same effect is reflected in Table III.

Keeping the monomer concentration fixed at 2.5g/100ml benzene the benzophenone concentration was varied and the samples irradiated for ninety hours. The induction period increased with photoinitiator concentration to a maximum at approximately 1% initiator then decreased as the concentration was raised above this figure.

The monomer-benzophenone molar ratio appears to be the significant factor since the induction period of irradiating 5g monomer with 1g benzophenone, in 100ml benzene compares favourably with that of a solution of 2.5g monomer with 0.5g in the same amount of solvent. (Table II and Table III), the molar concentrations being equal.

The benzophenone is again acting as a chain terminator similar to the irradiation of vinyl pyridine. At low concentrations of initiator a small number of sites are found on the polymer backbone and the chain length of the polymerising monomer increases. At higher concentrations the number of polymer radical sites increases and the termination reactions also become greater resulting in shorter grafted chains causing increased effective stabilisation. As the monomer/initiator rates falls below unity, polymerisation becomes difficult due to the much increased termination reaction and consequently the induction period is reduced. It is therefore not the amount of grafting which determines the stability of the films, but the density of the graft.

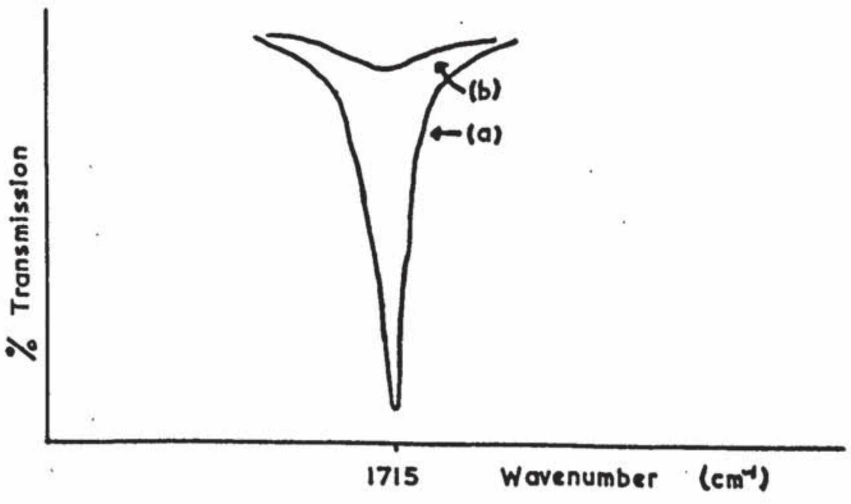
Irradiation of the monomer in the absence of benzophenone shows stability of only 16 hours (Table III) indicating that initiation by other processes play only a small part in the grafting reaction. The variation of induction period with irradiation time was also studied using a solution of 5g monomer and 1g benzophenone in 100ml benzene. Increasing irradiation time, increased the period to oxidation, again to a maximum before the stability decreased (Figure I). This stability decrease is probably due to the onset of degradation of the polymer film. When polypropylene is irradiated alone in a quartz tube, and in benzene for 130 hours, the degradation in benzene is much reduced. This is illustrated by the relative amounts of carbonyl formed after this irradiation time and is as shown in Figure IV.

FIGURE IV

RELATIVE AMOUNTS OF CARBONYL FORMED DURING IRRADIATION OF POLYPROPYLENE FILM FOR 130 HOURS

(a) in air

(b) in benzene



Irradiation in benzene limits the amount of air available for oxidation of the polypropylene film.

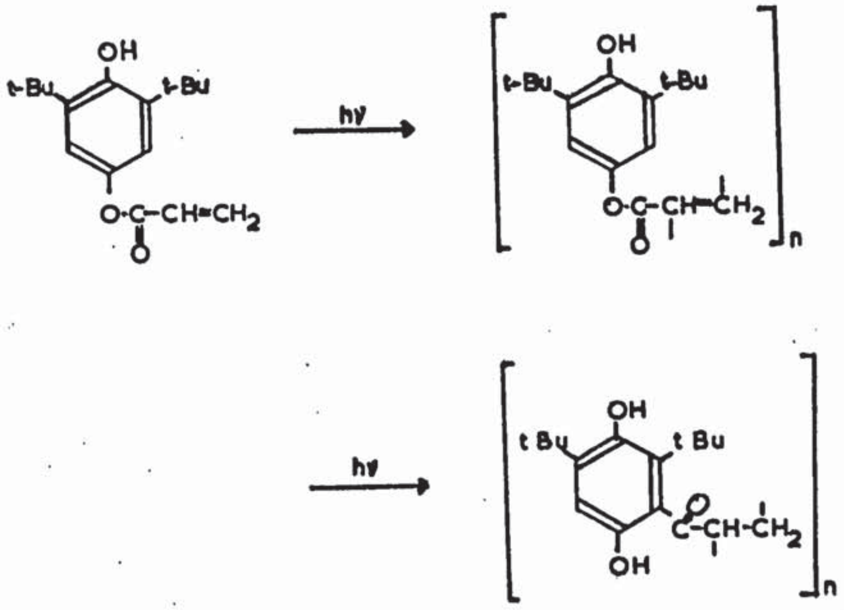
Eventually the degradation reaction becomes more predominant than the grafting process, indicated by the reduction in stability on measuring the induction period.

When the grafting process is carried out under nitrogen, the induction period of the films falls to approximately one half of that in air. (Table IV). For the same concentration of benzophenone and monomer irradiated under the same conditions the expected stability should be the same. This is not found to be the case and oxygen must therefore play some part in the process. As in the case of vinyl pyridine graft copolymerisation the formation of hydroperoxides and subsequent photolysis reactions must be responsible for the more efficient grafting of the antioxidant monomer, resulting in the greater stability when irradiated in air.

The graft copolymerisation of 3,5 ditertiary butyl-4-hydroxy phenyl acrylate was disappointing, an induction period of 18 hours only being obtained for the conditions shown in E. For this reason the grafting reactions were evaluated using the second monomer DBBA as described.

The reasons for this low stability were not pursued but it may be that a rearrangement may occur under ultraviolet irradiation, reducing its effectiveness as an antioxidant. The Fries photochemical rearrangement is well known and polymerisation followed by such a rearrangement may not be improbable.

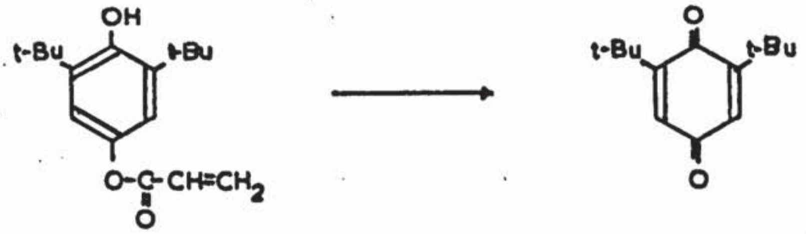
Thus

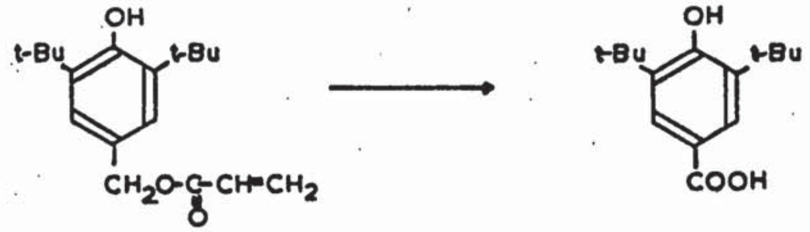


Further investigations with this material may provide an answer to the low stability of this antioxidant on grafting.

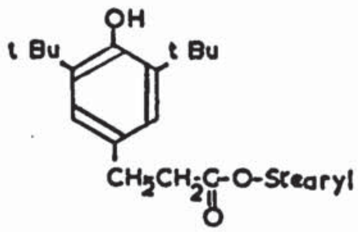
Oven ageing in air of several grafted film samples show degradation at 240 hours with signs of brittleness and yellowing. (Table VI). This figure is much lower than the same induction periods under a closed atmosphere of oxygen as shown in Table II. Degradation of the grafted side chain with subsequent loss by volatilisation may be the reason since in a sealed system the antioxidant will be retained. Oxidation of the stabiliser could account for the stability of the film samples on oven ageing, since low molecular weight stabilisers would be formed which are less effective than the parent antioxidant. Volatilisation of these products would then reduce the stability of the films.

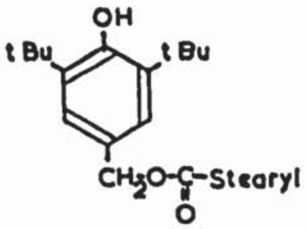
Some possible oxidation products are shown below.





Oxidation of the stearyl compound Irganox 1076 would not be as rapid because of the presence of another methylene grouping in the para position, and the reversal of the ester grouping. Thus 1076 has a greater stabilising effect than the other stearyl compound DBBS which may oxidise more quickly. The structures are shown below.





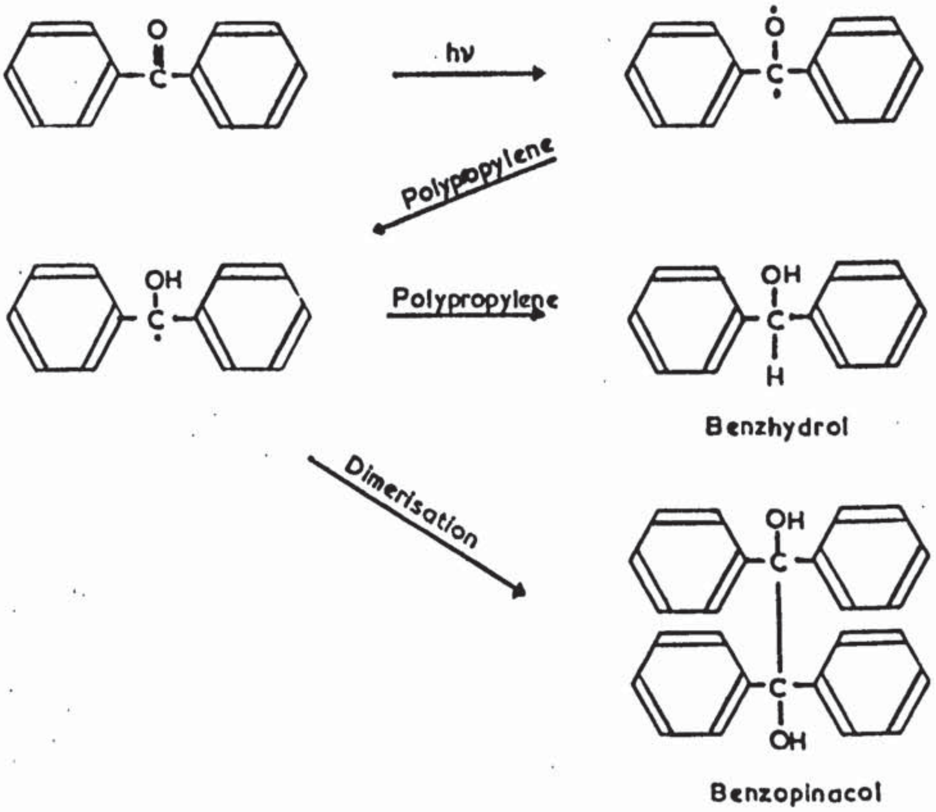
This may explain why 2,6 ditertiary butyl-4-methyl phenol is such a good antioxidant. The activity under both closed systems accelerated tests, (decalin and in the film) is good, but losses in the oven ageing is due to volatility. The para methyl grouping would be more difficult to oxidise, than the benzyl acrylate or benzyl stearate type compounds, where this methylene grouping would be activated more to oxidation because of the presence of ester linkages in the molecule. The low stability of grafted DBPA could therefore be explained by the ease of oxidation to the hydroquinone compound whose antioxidant activity would be much lower.

Further work on the oxidation of these monomeric and polymeric compounds may show that oxidation of the antioxidant and volatilisation of the oxidation products are the key factors in the stabilising efficiency of these compounds.

CHAPTER V (PART II) EFFECT OF THE VINYL ANTIOXIDANT ON THE POLYMERISATION REACTION

Irradiation graft copolymerisation of 3,5 ditertiary butyl-4-hydroxy benzyl acrylate with polypropylene has been achieved, using benzophenone as a photoinitiator. Since the monomer is an antioxidant, and the grafting process occurs by a free radical mechanism, it was decided to study the reaction to determine the role of the monomer functioning as an antioxidant.

Benzophenone acts as a hydrogen abstracting agent from polypropylene on irradiation, and this process should continue even in the presence of stabilisers, to give benzhydrol (or possibly benzopinacol).



However, if a large amount of antioxidant is present, e.g. monomer, during the copolymerisation, relative to the benzophenone, then hydrogen abstraction could occur during irradiation, from the phenol, in addition to that from the polypropylene. This would enhance the benzhydrol formation during the reaction.

To determine whether the antioxidant played any part in the reaction several systems of polymer film, benzophenone and stabiliser were irradiated and the products analysed using gas-liquid chromatography (GLC). Three antioxidant systems were studied; the monomer, 3,5 ditertiary butyl-4-hydroxy benzyl acrylate; 2,6 ditertiary butyl-4-methoxy phenol (Topanol 354 - I.C.I. Ltd.) and 2,6 ditertiary butyl-4-methyl phenol (Topanol OC).

The following solutions were made up, (Table VII), the stabiliser/benzophenone molar ration being fixed at 3.14:1. All figures quoted are in grams and the additives were dissolved in 10mls benzene before irradiation for ninety hours.

TABLE VII

POLYPROPYLENE FILM IRRADIATED WITH VARIOUS STABILISERS IN BENZENE SOLUTIONS CONTAINING BENZOPHENONE

	1	2	3	4	5	6
Irradiated system		Topanol 354		Monomer DBBA		Topanol OC
Polypropylene	0.1	-	0.1	-	0.1	0.1
Benzophenone	0.1	0.1	0.1	0.1	0.1	0.1
Antioxidant	-	0.4075	0.4075	0.5	0.5	0.38

After irradiation the solutions were analysed for benzhydrol using GLC.

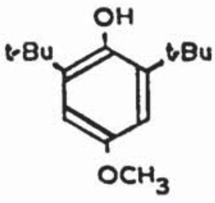
PRODUCT ANALYSIS

Measurements were made on a PYE 104 GAS CHROMATOGRAPH using a flame ionisation detector. The column was a five foot CARBOWAX 20M operating at 240°C and nitrogen was used as the carrier gas.

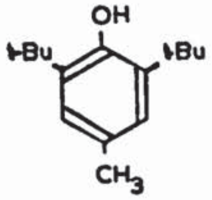
A standard benzene solution containing 1% benzophenone and 1% benzhydrol gave the chromatograph shown in figure V, the retention times being 12 and 24 minutes respectively. Benzopinacol in benzene gave benzophenone and benzhydrol on analysis, and would appear to breakdown on the column. If benzopinacol is a product in these reactions, then it cannot be detected under these conditions, only its breakdown products.

As the yield of benzhydrol was low in these reactions the sensitivity of the instrument was increased by a factor of twenty and the traces of benzhydrol shown in figure V at this sensitivity are actual size.

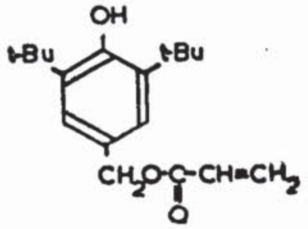
Irradiation of polypropylene film and benzophenone alone in benzene yielded only benzhydrol as the major product, together with unreacted benzophenone. The antioxidant I below yielded benzhydrol on reaction with benzophenone alone, and in the presence of polypropylene the amount was increased.



I



II



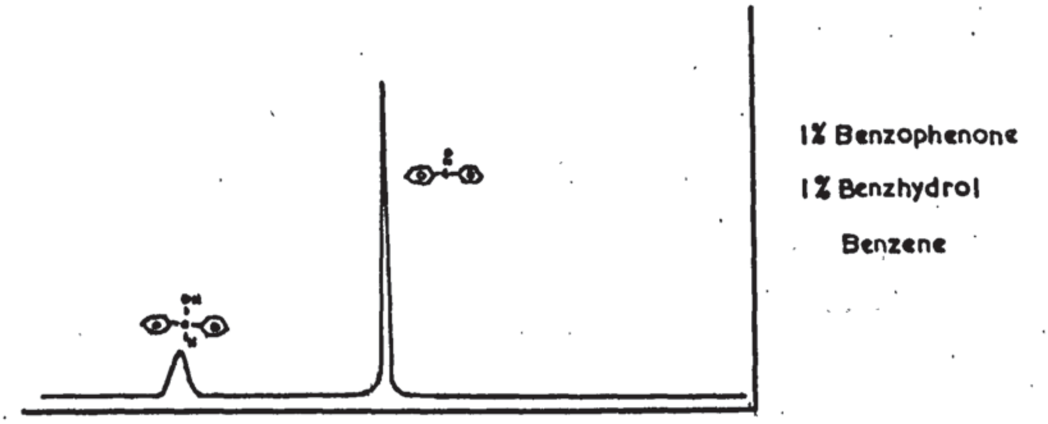
III

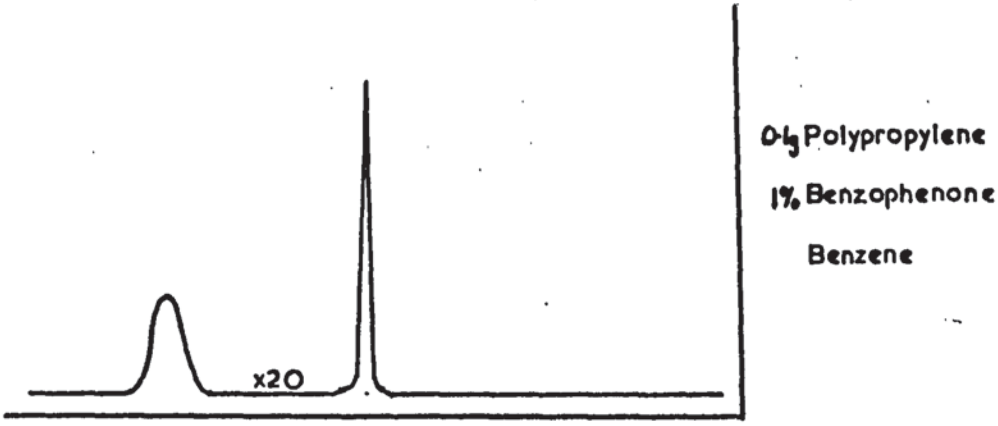
The monomer III showed a little benzhydrol, but this did not increase in the presence of polypropylene.

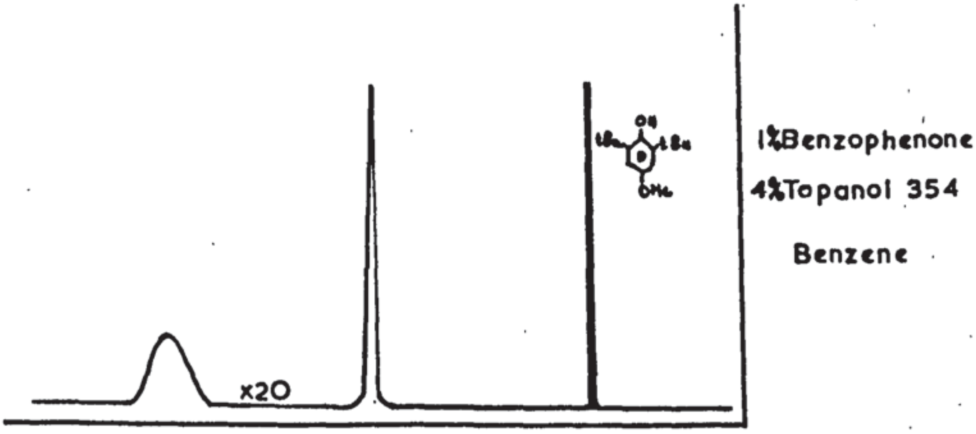
Stabiliser II even in the presence of polypropylene showed little or no benzhydrol formation.

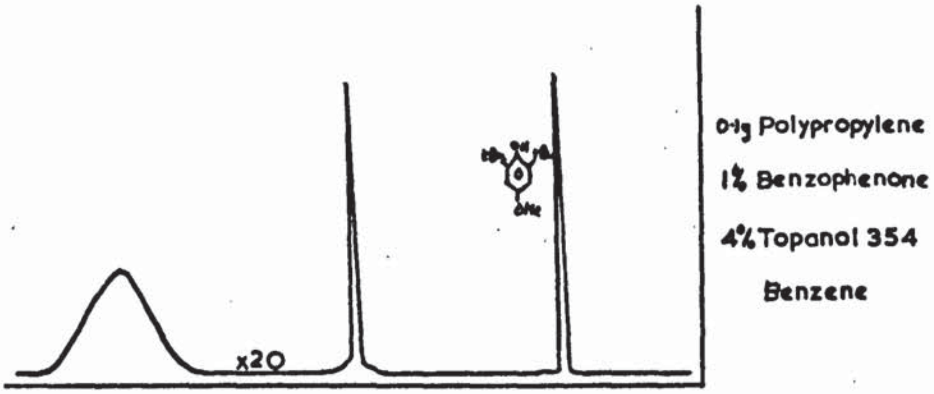
FIGURE V

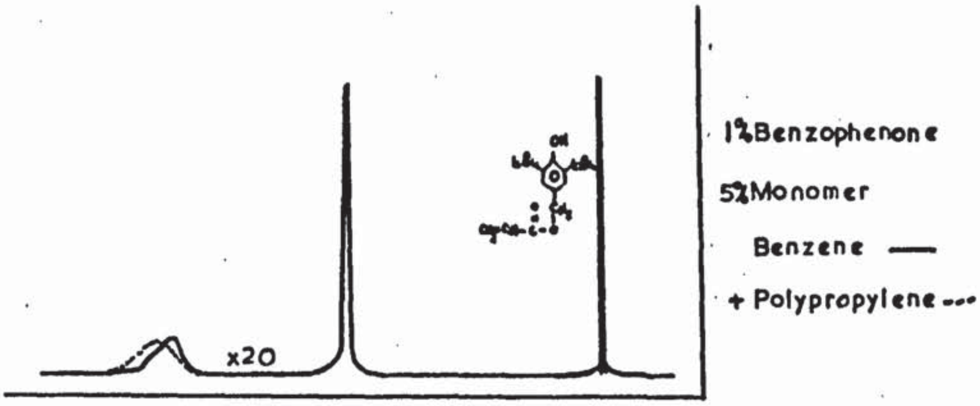
CHROMATOGRAMS

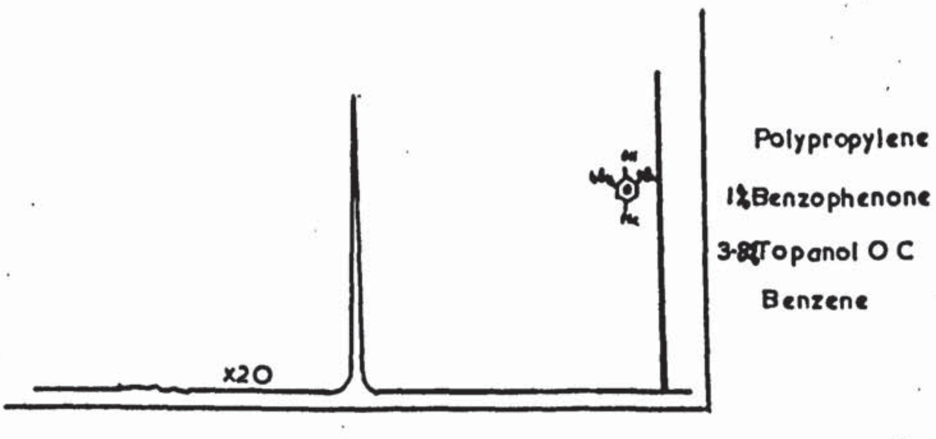







x20
0·1g Polypropylene
1% Benzophenone
4% Topanol 354
Benzene


x20
1% Benzophenone
5% Monomer
Benzene ——
+ Polypropylene ---


x20
Polypropylene
1% Benzophenone
3·8% Topanol O C
Benzene

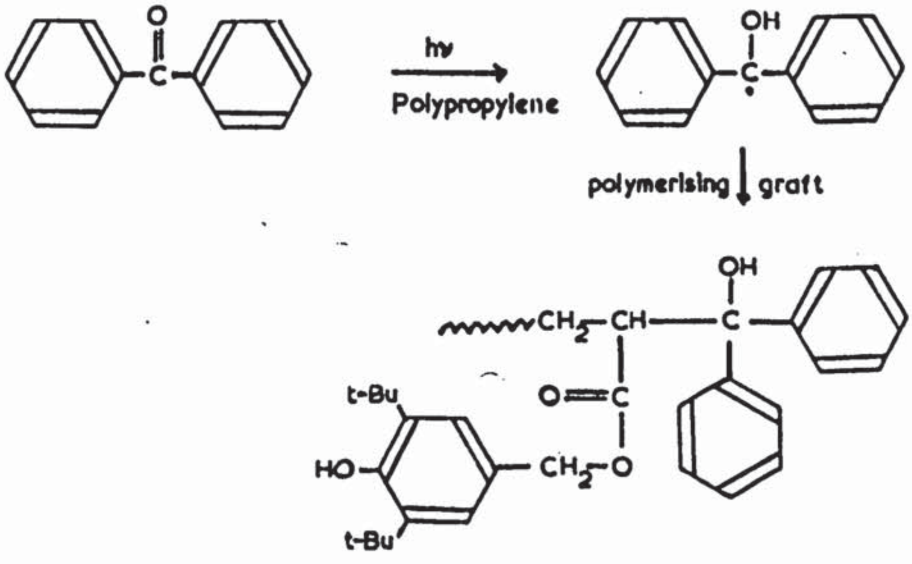
Since all the solutions were irradiated for the same period with the same benzophenone concentration, then in the presence of polypropylene film the same amount of benzhydrol should be formed.

With the methoxy antioxidant I the amount of benzhydrol is increased indicating hydrogen abstraction by the activated benzophenone from the phenol.

Compounds II and III show reduced benzhydrol formation and must therefore interfere with the hydrogen abstraction process.

The first hydrogen abstraction from the polypropylene cannot be impaired since it has been shown earlier that grafting of the monomer occurs by this reaction.

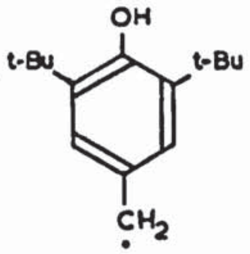
During the irradiation, polymerisation of III will occur and the growing chains are probably terminated in some way by the benzophenone. This would explain the decrease in benzhydrol formation as shown below.



This does not explain the anomolous behaviour of the 4-methyl antioxidant II. Less benzhydrol forms than with III, and since no vinyl group is present no polymerisation can occur, so some other mechanism must be responsible.

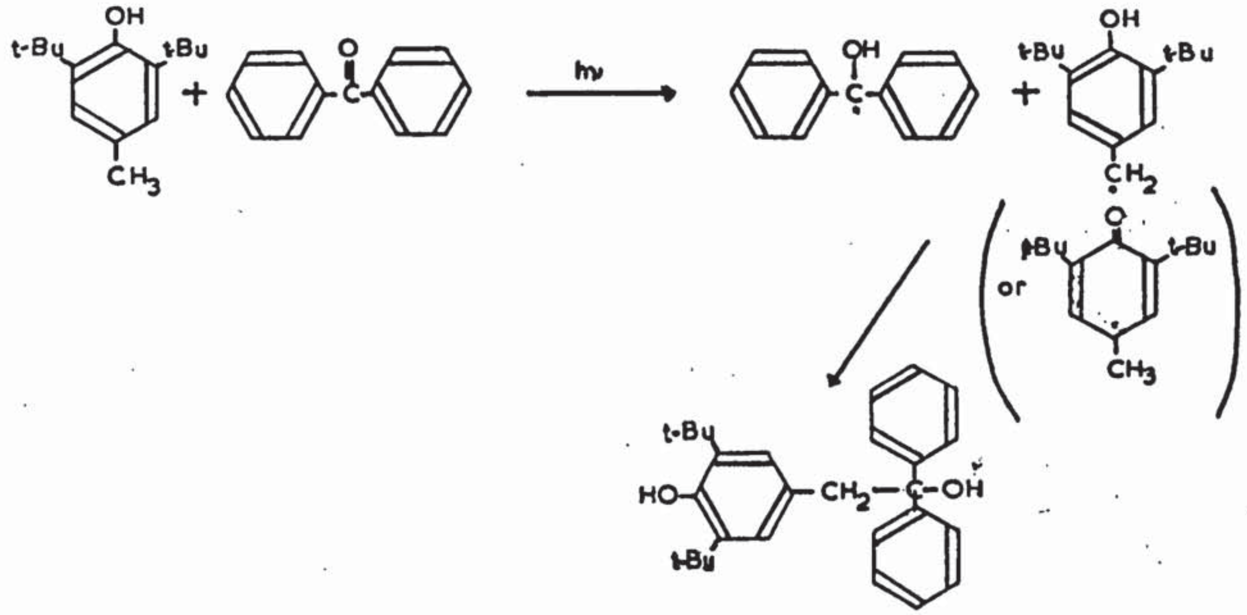
Benzhydrol or its precursor is effectively removed from the system, but only in the presence of two of the antioxidants.

The similarity between them is the presence of the para methylene group which could be a site for hydrogen abstraction, since work has shown[89] that the oxidation of 2,6 ditertiary butyl-4-methyl phenol occurs via the radical IV.



IV

Photolysis of benzophenone in the presence of 2,6 ditertiary butyl-4-methyl phenol could result in a coupled product by the following scheme

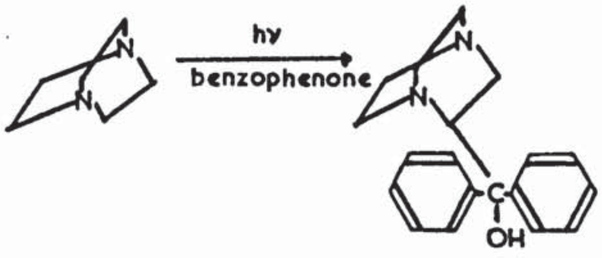


hydrogen abstraction, followed by combination of the radicals.

This compound may be one possibility, a similar process occurring with the monomer system III, DBBA.

Radical coupling of benzophenone has been reported[90] during the photosensitised oxidation of 1,4 diazobicyclo (2, 2, 2,) octane (V). The isolated product was the benzyl alcohol VI*

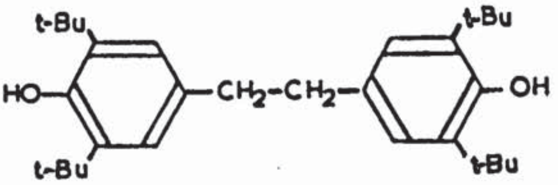
V



VI

The photolysed solution (6), Table VII was reanalysed by GLC at the higher sensitivity of X20. After two and a quarter hours a large broad peak was observed which slowly came off the column over a period of twenty minutes. No other products were observed. The remaining antioxidant solutions were also analysed for this period and the same product was observed but only in the case of the monomer solutions 4 & 5. The methoxy antioxidant I did not produce this long retained product, suggesting that a benzyl grouping was necessary for this to occur.

A sample of the dibenzyl derivative VII was obtained,[91]



VII

and this was found to have a retention time similar to the unknown product from II and III, extending over a period of half an hour.

For two compounds to have a similar lengthy retention time they must be similar in polarity or very close in boiling point. Separation of these two compounds, the dibenzyl adduct VII and a possible coupled product of antioxidant with benzophenone was not practical since the instrument was operating at optimum conditions.

If coupled products were formed in the reaction, VII is one possibility. Formation of benzophenone adducts may also occur but evidence for this so far is limited, and further work needs to be done to clarify the situation.

CHAPTER VI (PART I) ULTRAVIOLET LIGHT STABILISATION OF POLYPROPYLENE

Polypropylene, as a pure paraffinic material would not be expected to absorb radiation from sunlight. However, the polymer is severely affected by ultraviolet light, and the large patent literature existing on the photo stabilisation of polypropylene is evidence enough of the importance attached to this field of research.

The lower photostability of polypropylene compared with polyethylene is attributed to the presence of the labile tertiary hydrogen atom in the repeat unit. Processing of the polymer involves thermal treatment which is sufficient to oxidise the material forming hydroperoxides.[66,67] The presence of these and other chromophoric impurities is thought to be responsible for the initial photodegradation processes in the polymer[68]. The decomposition of polypropylene hydroperoxide has been thoroughly studied[69] and most of the products characterised. The main oxidation products are polymeric ketones, which continue the degradation of the polymer[70] according to the following scheme. The two major ketone products are, I and II.

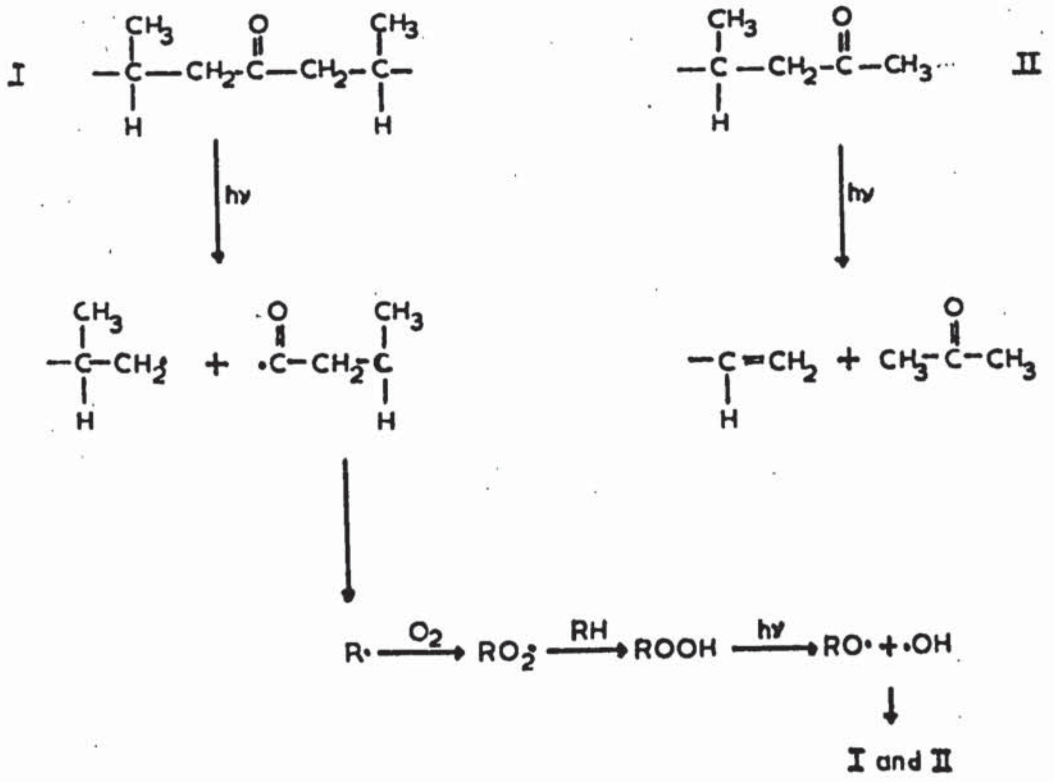
$-\overset{CH_3}{\underset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-$

I

$-\overset{CH_3}{\underset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

II

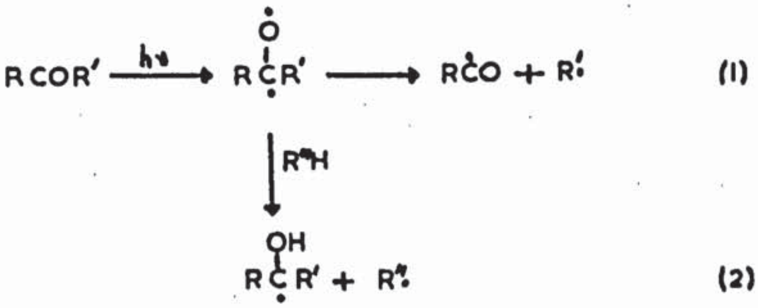
During irradiation these decompose by either a chain scission process in the case of I, or a terminal chain scission to yield small molecular products, from type II ketones.



To prevent this degradation, stabilisers are commonly used, and are of three types. Firstly, a phenolic radical scavenger, which interrupts the kinetic chain process leading to hydroperoxide formation. Secondly, a hydroperoxide decomposer which acts by a non-radical process preventing polymer chain scission, and thirdly, a light stabiliser. There are numerous additives used to improve the photostability of polymers[71]. Photostabilisers may act by an U.V. absorbing process, preventing the radiations from reaching the polymer, or by deactivating the excited chromophore, dissipating the absorbed radiation harmlessly in another form.

Absorption of a photon by a carbonyl group leads to an excited singlet state which either deactivates by fluorescence to the ground state, or stabilises itself by intersystem crossing to a longer lived triplet state.

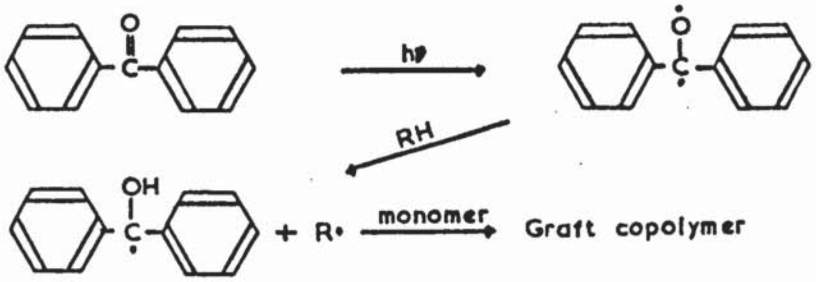
This triplet state can react with the substrate, by hydrogen abstraction in the case of polypropylene, or may breakdown to give radicals.



Reaction (1) is typical of aliphatic carbonyls, (2) being typical of aromatic species.

Reaction (2), hydrogen abstraction from the substrate has been used effectively as a free radical initiator for grafting onto polyolefins[38] using benzophenone. This carbonyl activates by U.V. irradiation, and then hydrogen abstracts from the substrate generating a free radical site on the backbone of the polymer, capable of initiating a radical grafting process.

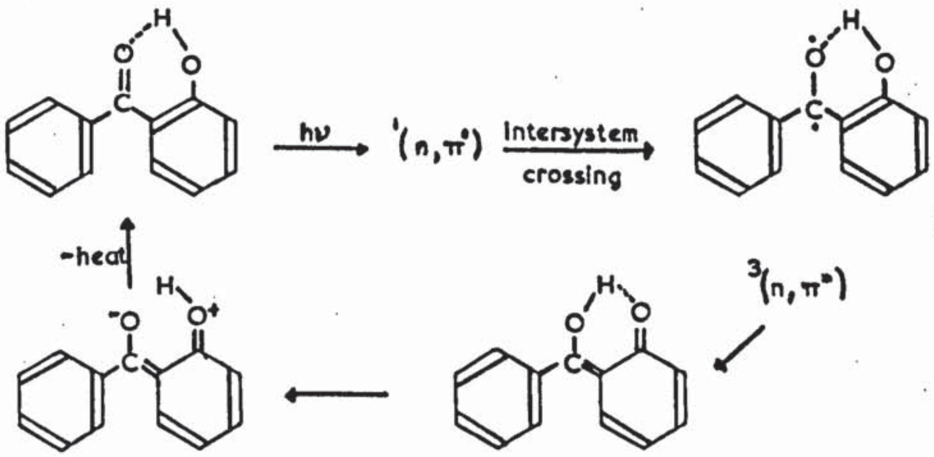
Thus with benzophenone



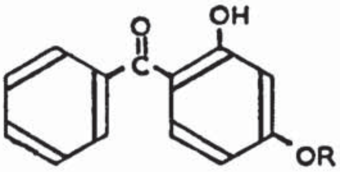
If the aromatic carbonyl is substituted by hydroxyl groupings in the 2 position the molecule acts as a deactivator and stabiliser. Thus 2-hydroxy benzophenones are stabilisers whereas 4-hydroxy substituted compounds are not.

Unlike benzophenone, the 2-hydroxy benzophenones showing similar U.V. absorption characteristics are one of the most important classes of ultraviolet light deactivators presently used[72].

These are thought to act by the following scheme, hydrogen bonding being responsible for the stabilising ability of these materials.



In an attempt to increase the effectiveness of these hydroxy benzophenones substitutes have been introduced at the 4-position, normally in the form of ethers where R =n - alkyl, below.



III

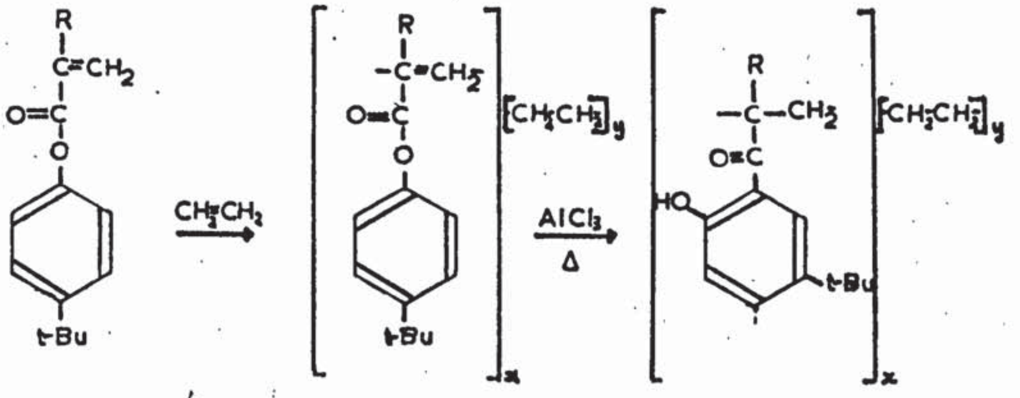
Investigations on substituted hydroxy benzophenones have shown that the length of the alkyl group R is of critical importance[74]. By compatability and diffusion measurements[75,76] it has been shown that in polypropylene for the homologous series III, migration decreases with increasing chain length, and compatability is independent of this length. In polyethylene, compatability was better with longer side chains. As with antioxidants, compatability, volatility and mobility are factors to be considered in synthesising more effective U.V. stabilisers.

The mode of operation of 2-hydroxy benzophenones, is a subject of much research. Guillory and Cook[77] investigated 2-hydroxy 4-n-octyloxy benzophenone and concluded that this acts both as a U.V. screener and an excited state quencher. Carlsson, Wiles and Suprunchuk confirmed this[78], although they suggested that more work needed to be done on these compounds.

Recent research has been concerned with more efficient methods of utilising U.V. stabilisers. This has been approached by either using surface coatings of stabiliser additives or by chemically combining the additive with the polymer. Clearly, surface coatings are subject to effects of volatility and leachability by solvents, and chemical combination would seem to be the better approach.

Early work by CIBA[79] was concerned with new monomeric polymerisable U.V. screening coatings based on 2-hydroxy benzophenones, and these were used as surface treatments. Mainly these were esters and amides based on acrylates and acrylamides. Fertig and co-workers[80] synthesised glycidyl acrylates of 2,4 dihydroxy benzophenone and blended either this monomer, or polymer into polystyrene, polymethyl methacrylate or polyvinyl chloride, and found that the extractability was much reduced. It was thought that some copolymerisation may have occurred during the processing to obtain polymer films.

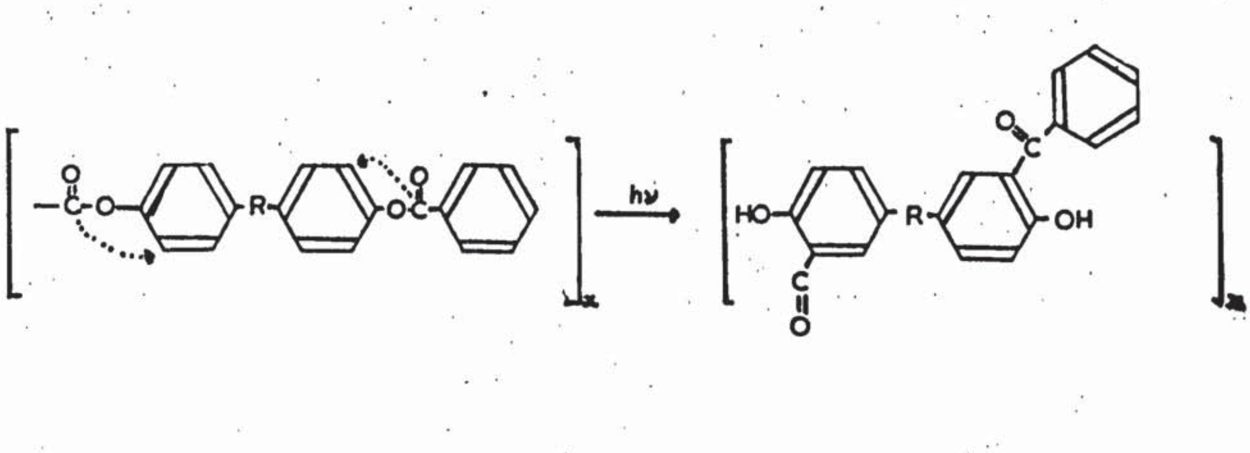
Probably the most novel approach has been by Tocker[81] who copolymerised the acrylate IV with ethylene, and then effected a rearrangement on the copolymer to form a hydroxy benzophenone as part of the material.



IV

By chemically bonding the additive, relatively high concentrations of absorber can be incorporated. This technique avoided loss of the ultraviolet absorber and resulted in better weatherability.

A recent paper[82] utilised this rearrangement, with polyesters as a barrier coating which rearranged under the influence of ultraviolet light to form polymeric hydroxy benzophenones.



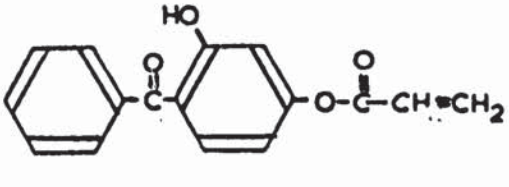
As the surface material degraded, new polyester was exposed which rearranged to give added protection. The polyesters had to be modified slightly by varying R, to increase their solubility in common solvents, but were used as transparent ultraviolet barrier coatings on several polymers, including polypropylene, with good effect.

In thin polypropylene films, (22μ) it has been[83] shown that photo-oxidation is confined to a surface layer of the polymer. The degradation is initiated by chromophores present in this layer[84], and this prompted research into the effectiveness of additives applied to the surface. The conclusion reached showed that best effects were achieved by incorporating a low percentage of the stabiliser throughout the bulk of the film, and a higher concentration as a surface layer. This would lead to some cost saving since better stabilisation could be achieved using less material, but utilising it where it would be most effective, on the surface.

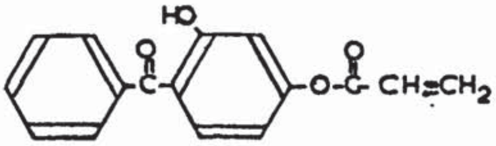
In the same manner in which the vinyl antioxidants have been grafted, as described earlier, it was decided to incorporate an U.V. stabiliser and assess its effectiveness as a bonded additive.

The compound selected was the substituted 2 hydroxy benzophenone V ..

V



V



whose synthesis has been described in Chapter II.

By grafting this monomer it was hoped that extraction problems and possible volatility effects would be overcome.

ASSESSMENT OF DEGRADATION

1. Infra-red measurements

During the photo-oxidation of polypropylene, polymeric ketone products form and these can be monitored effectively using infra-red spectroscopy. By measuring the intensity of the carbonyl bond as a function of irradiation time the degradation of the polymer can be followed quantitatively.

From Beer Lamberts Law

Absorbance, $A = \log_{10} \frac{Io}{I} = \varepsilon cl$

where Io is the intensity of radiation effectively entering the sample

I is the intensity of radiation before leaving the sample

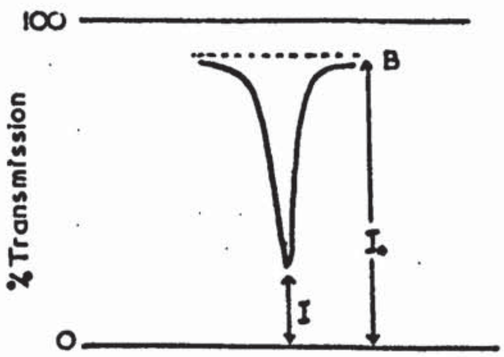
ε is the extinction co-efficient

c is the concentration of the absorbing material

and l is the pathlength of radiation within the sample

Where the spectra are obtained, measured on transmission paper, the value of A can be found as illustrated in figure I.

Figure I



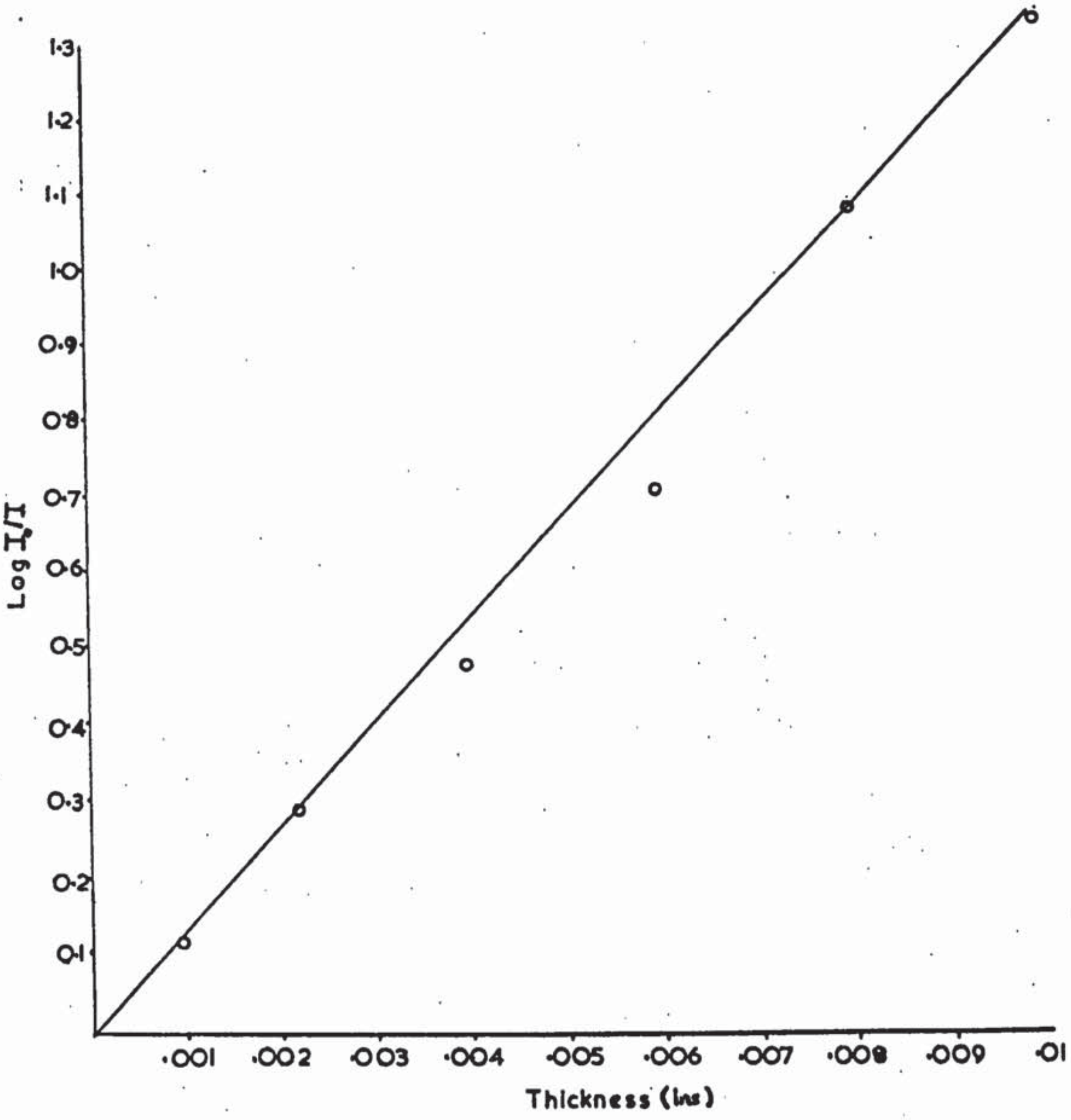
The absorbance A is calculated as defined above.

Generally, difficulties, occur in measuring the thickness of the sample. This can be overcome by using an internal standard, whose concentration is known and is constant. Re-writing the Beer-Lambert expression

$$\frac{A}{A'} = \frac{\log_{10} I_0/I}{\log_{10} I_0'/I'} = \frac{\epsilon c l}{\epsilon' c' l} = \frac{\epsilon c}{\epsilon' c'}$$

where the primed samples refer to the internal standard. The internal standard chosen was the 2720cm^{-1} polypropylene band which was a convenient measure of film thickness. This absorbance was calibrated against films of known thickness, determined by a micrometer. The calibration is shown in Figure II.

FIGURE II



CALIBRATION OF INTERNAL STANDARD

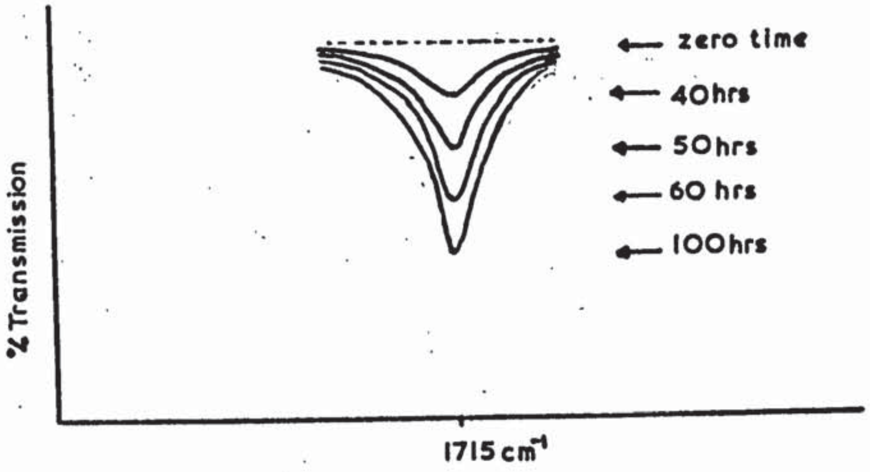
The absorbance of the carbonyl band was measured at 1715cm^{-1}.

The value of $\frac{A1715}{A2720}$ will be referred to throughout as the CARBONYL INDEX.

The variation of carbonyl intensity with irradiation time is shown in Figure III.

Figure III

INCREASE OF CARBONYL INTENSITY WITH IRRADIATION TIME



Spectra were recorded on transmission paper, since calculations on logarithmic paper, although involving less computation, could lead to errors unless reflection effects from the film are taken into account[85]. Often the baseline B (figure I) may not be horizontal. To determine I_0, a sloping baseline is drawn so as to join neighbouring minima of the absorption curve. The infra-red spectra were recorded on a Perkin Elmer 457 spectrophotometer, the data being processed on a computer to obtain the carbonyl index directly for each system studied.

2. Determination of Embrittlement Times

The film samples (0.005") were fixed in cardboard holders mounted on the rotating wheel, at a distance of 15cms from the source and irradiated in the ageing cabinet previously described. Brittleness in the samples was detected by flexing the films through 180^{0}C and failure under this test represented the embrittlement time.

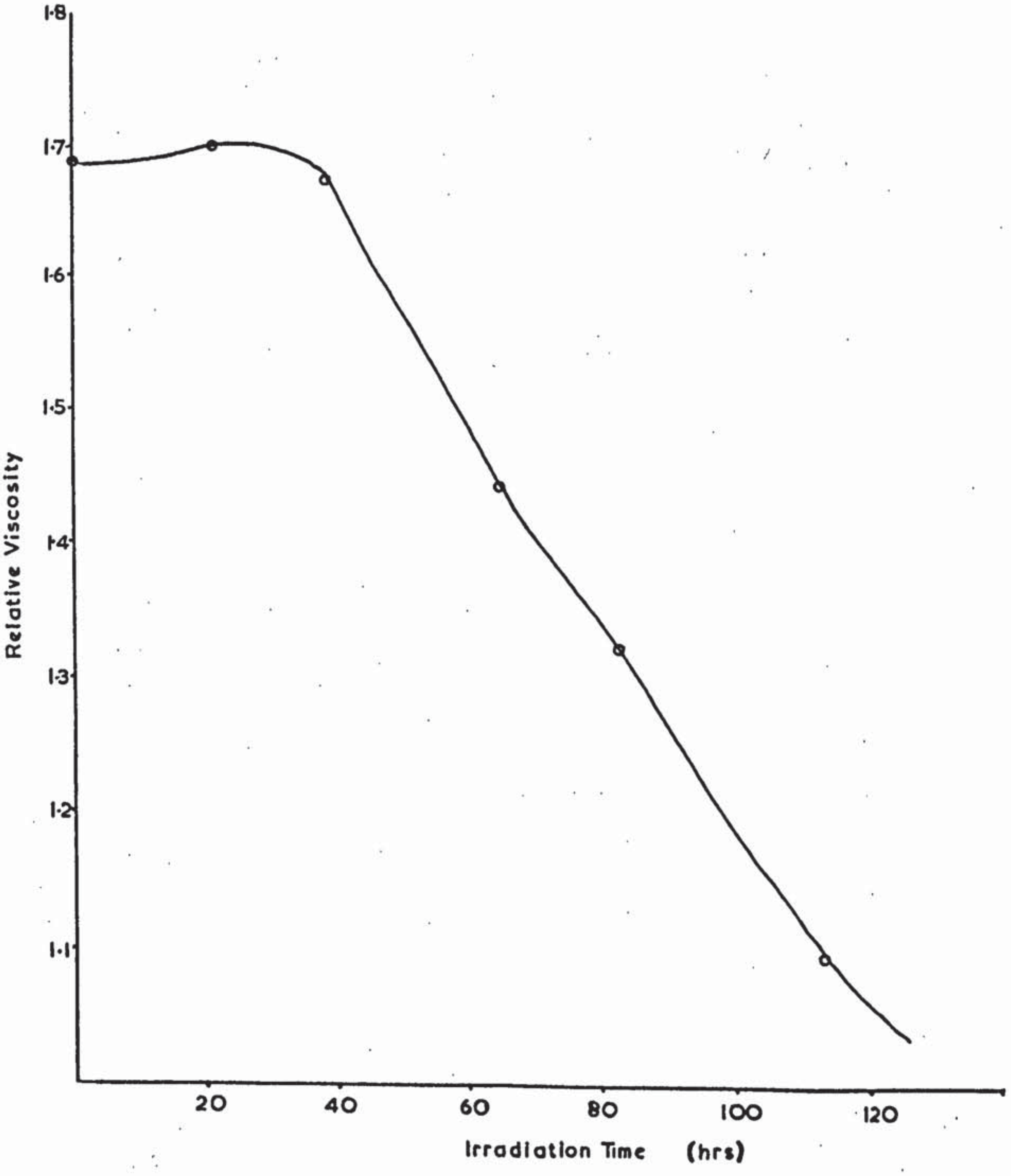
3. Measurement of Molecular Weight

The degradation of a 0.005 inch film of polypropylene was followed by measuring the solution viscosity in decalin after various irradiation times. Single point viscosity measurements were taken of a 0.4% solution of film in decalin at 135^{0}C in an Ubbelohde viscometer. The results are illustrated in figure IV. This technique was only used for unstabilised polypropylene. Once degradation occurs, the chain scission process is quite rapid. The measurements required several polymer film samples and since this is a destructive technique, the same sample could not be used for further irradiations.

It was felt that the information obtained could not add to the data found from carbonyl index, and since the same film sample could be used continuously in the latter technique, infra-red measurements were used throughout.

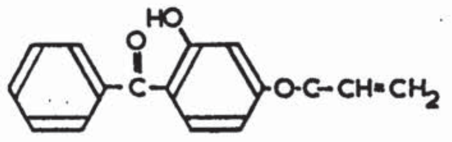
FIGURE IV

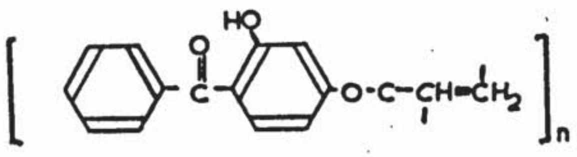
U.V. DEGRADATION OF POLYPROPYLENE FILM AS A FUNCTION OF VISCOSITY (0.4% SOLUTION POLYMER IN DECALIN AT 135°C

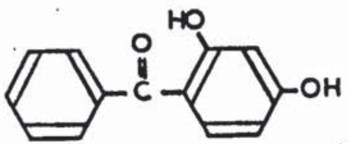


ULTRA VIOLET DEGRADATION STUDIES

The ultraviolet absorbers examined were synthesised as described earlier and are shown below


BHPA


Poly BHPA


DHBP

The 2,4 dihydroxy benzophenone, DHBP, was obtained from Koch-Light Laboratories, and was used for comparison purposes without further purification. These compounds were incorporated into polypropylene powder at several concentrations by solvent evaporation, and films were pressed to 0.005 inch thickness as before.

The thermal (phenolic) stabilisers were irradiated also but only at a concentration of 2×10^{-4} mole per hundred gram of polypropylene. Carbonyl index and embrittlement times were determined and these are shown in Figures V, VI, VII, VIII, IX and Tables I and II.

A sample of polypropylene film containing 1% benzophenone was prepared, and this was irradiated also. The embrittlement time is included in Table I, and the carbonyl index illustrated in Figure V.

TABLE I

U.V. EMBRITTLEMENT TIMES OF U.V. STABILISED POLYPROPYLENE

Additive	Embrittlement time concentration (mole/100g polymer)		
	$2x10^{-4}$	$1x10^{-3}$	$5x10^{-3}$
BHPA	62	107	174
Poly BHPA	70	130	174
DHBP	70	107	130
Benzophenone	-	-	18

TABLE II

U.V. EMBRITTLEMENT TIMES OF THERMALLY STABILISED POLYPROPYLENE
CONCENTRATION $2x10^{-4}$ MOLE/100g POLYMER

Additive	Embrittlement Time
None	64
DBBA	86
Poly DBBA	86
DBPA	63
Poly DBPA	63
Topanol OC	110
Irganox 1076	153
DBBS	170

LEGEND OF FIGURES

Carbonyl index vs irradiation time

Figure V	Unstabilised polypropylene and polypropylene blended at 1% concentration with benzophenone.
Figure VI	Polypropylene stabilised with BHPA.
Figure VII	Polypropylene stabilised with Poly BHPA.
Figure VIII	Polypropylene stabilised with DHBP.
Figure IX	U.V. irradiation of polypropylene with thermal stabilisers.

FIGURE V

UNSTABILISED POLYPROPYLENE AND POLYPROPYLENE BLENDED AT 1% CONCENTRATION WITH BENZOPHENONE. CARBONYL INDEX vs IRRADIATION TIME

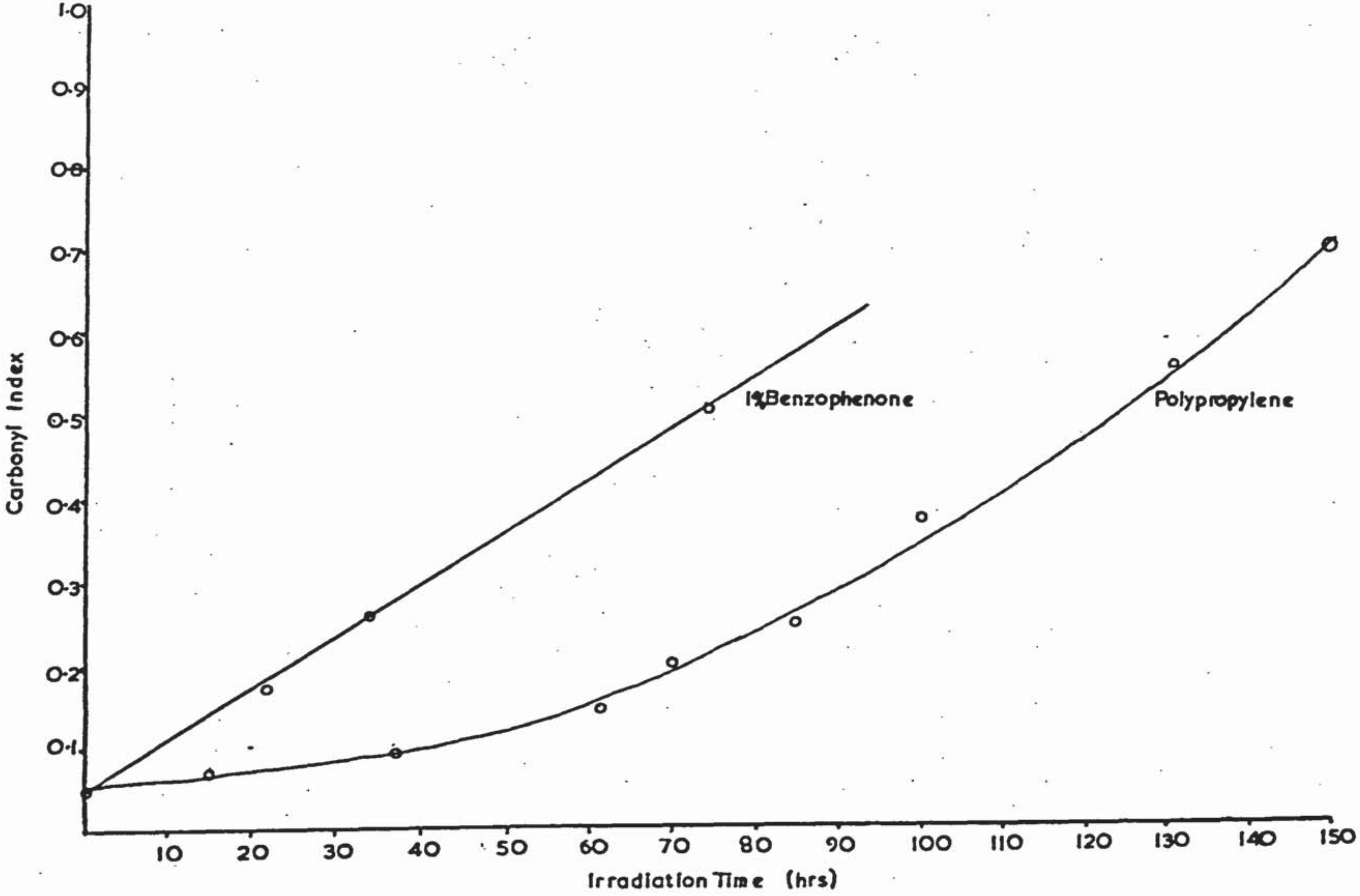


FIGURE VI

POLYPROPYLENE STABILISED WITH BHPA

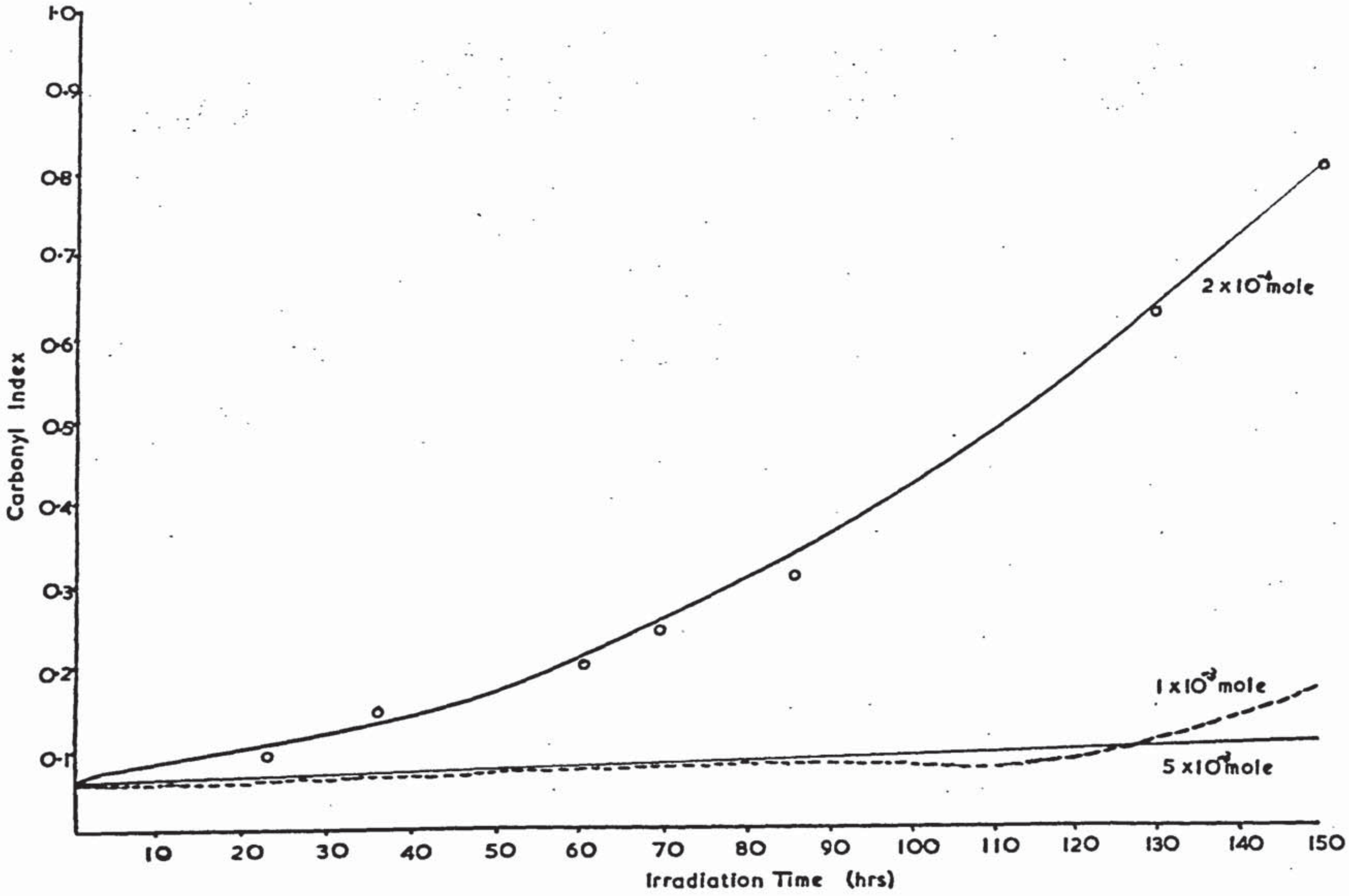


FIGURE VII

POLYPROPYLENE STABILISED WITH POLY BHPA

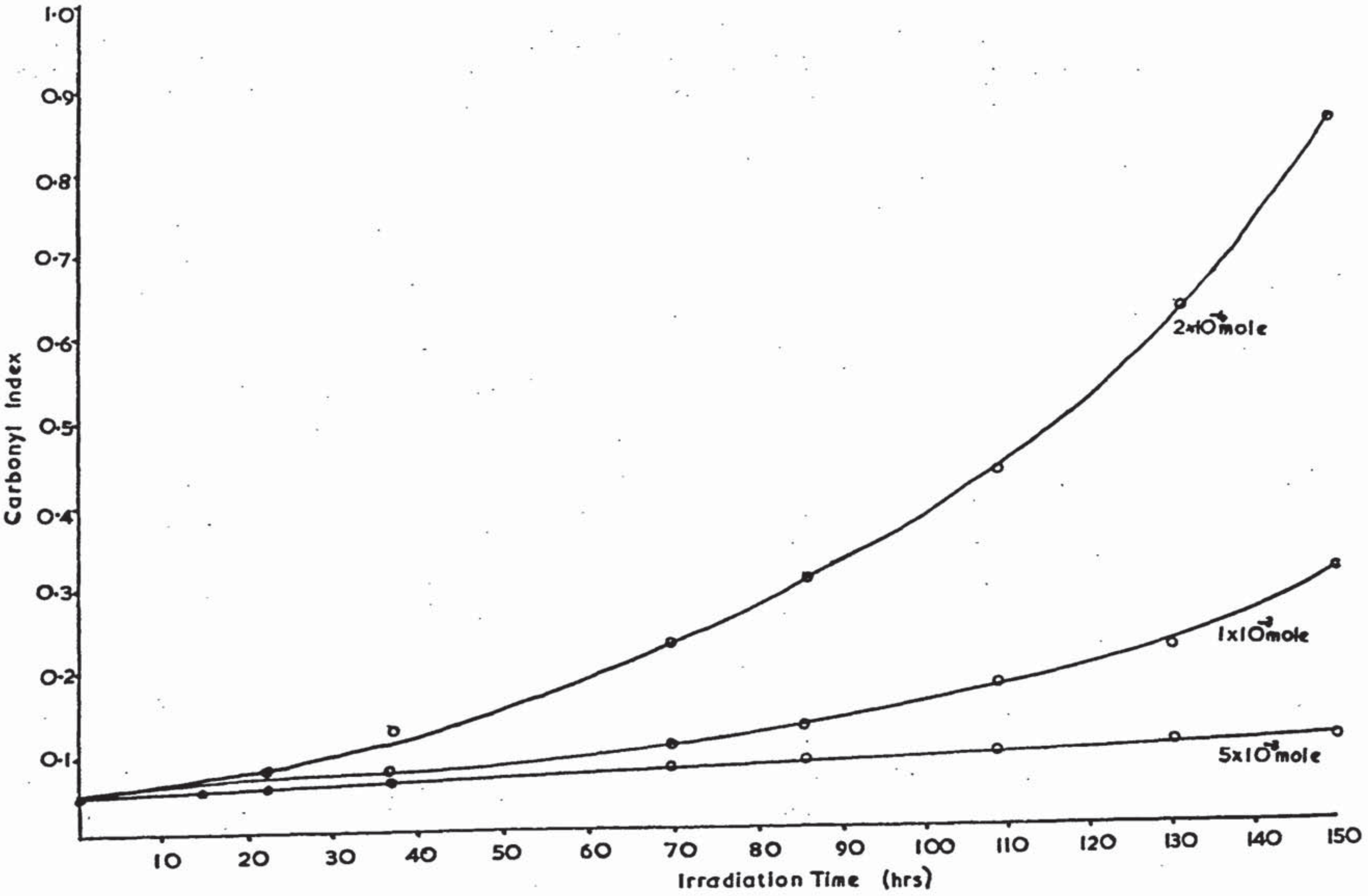


FIGURE VIII

POLYPROPYLENE STABILISED WITH DHBP

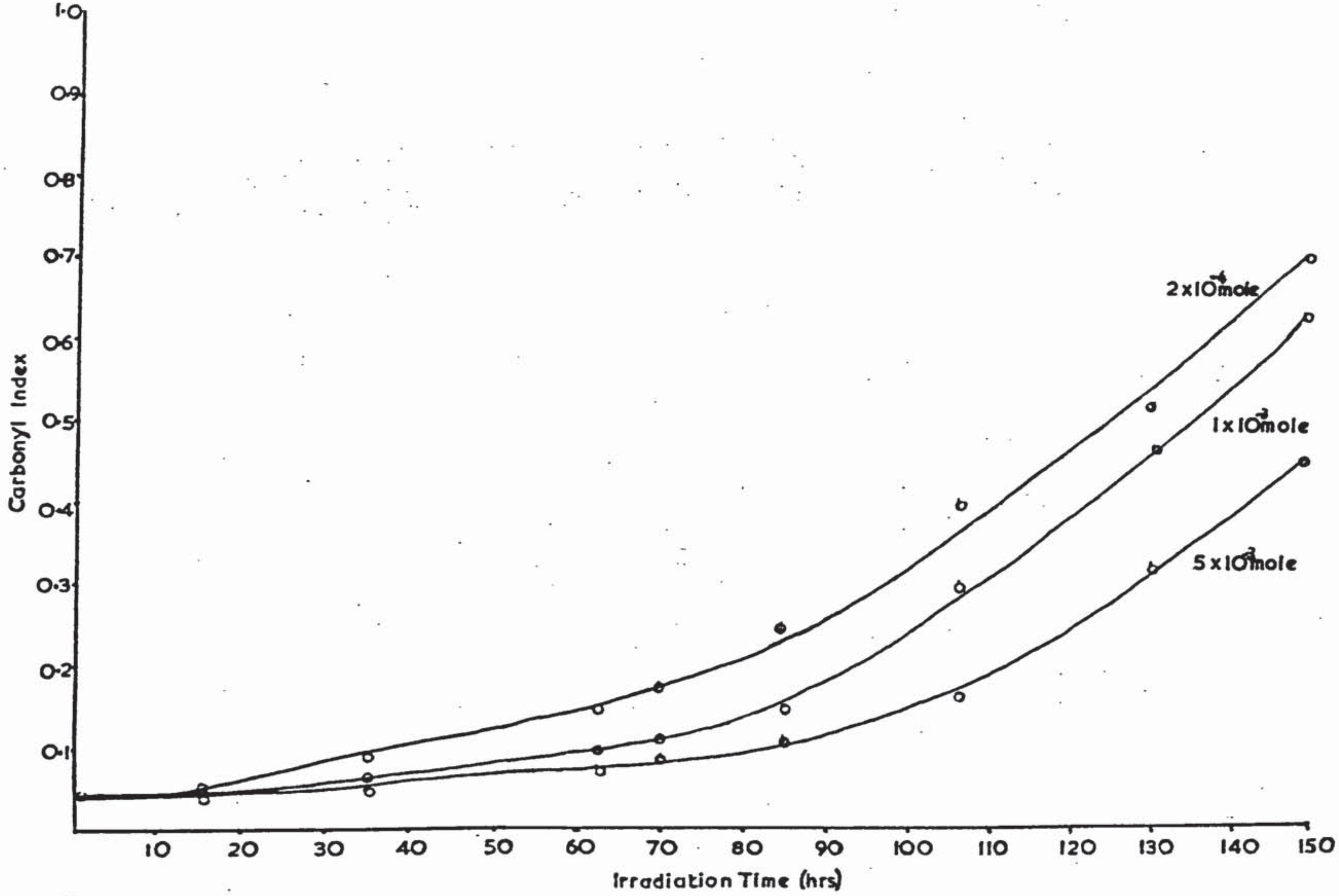
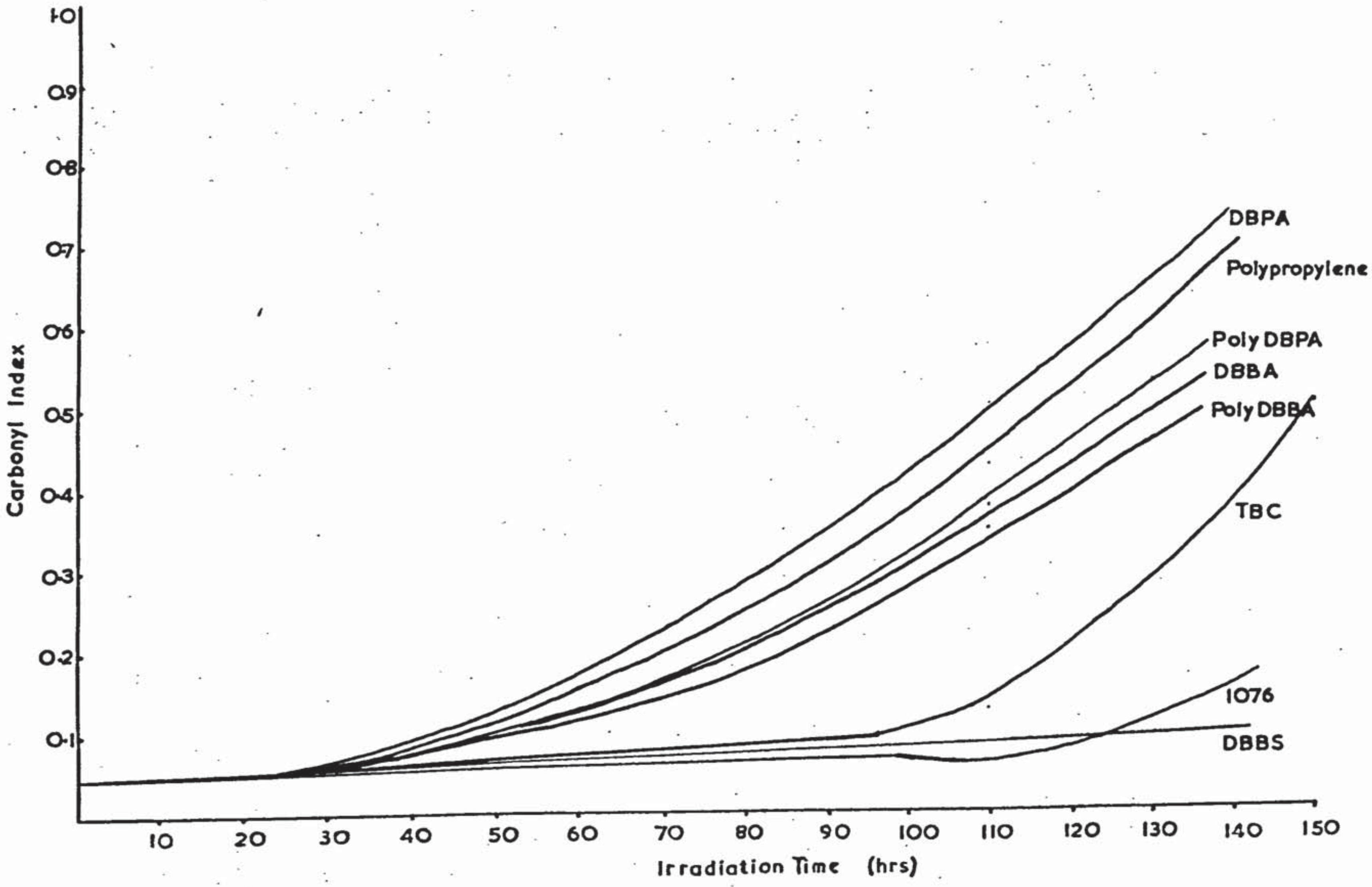


FIGURE IX

U.V. IRRADIATION OF POLYPROPYLENE WITH THERMAL STABILISERS



DISCUSSION

All the ultraviolet absorbers used were ineffective at a concentration of 2×10^{-4} mole/100g polymer, since the carbonyl index curves are the same as for the unstabilised polypropylene. The stabilising efficiency seems to be concentration dependent, and all show greater effectiveness with increasing concentration. The thermal stabilisers also improve the ultraviolet stability, their mechanism of stabilisation being as kinetic chain breaking compounds,

$$\left.\begin{array}{lcl} R. + O_2 & \longrightarrow & ROO. \\ ROO. + RH & \longrightarrow & ROOH + R\cdot \end{array}\right\} \begin{array}{l}\text{kinetic}\\ \text{chain}\\ \text{reaction}\end{array}$$

where AH represents the antioxidant, then

$$ROO. + AH \longrightarrow ROOH + A\cdot$$

the radical A$\cdot$, further reacting to give non-radical products.

The hydroperoxides formed, still undergo photolysis, but the propagation process becomes retarded when these additives are present.

The increased stability with the long chain antioxidants Irganox 1076 and DBBS could be due to their increased compatability with the polymer.

The failure of the hydroxy benzophenones at low concentrations is not totally unexpected since they function essentially as absorbers. Ambrovic[86] in studies of the homologous series of 4-alkoxy hydroxy benzophenones (III) reported that 2,4-dihydroxy benzophenone was only slightly soluble in polypropylene and found similar to previous workers [75,76] that the effectiveness improved as the chain length of the substituents increased.

It has been shown[87] that a correlation exists between the chemical shift of the 2-hydroxy grouping, in the N.M.R. and the activity of the compound as an U.V. stabiliser. The more effective these compounds were as U.V. stabilisers the greater was the negative shift of the hydroxy proton resonance.

However, increased hydrogen bonding cannot be the total explanation for the potential activity since 2-hydroxy-4-methoxy benzophenone and 2-hydroxy-4-dodecyl benzophenone have a similar chemical shift. It is known that the latter longer chain compound is a much better stabiliser than the 2-hydroxy-4-methoxy derivative. This has been attributed in polyethylene to an increase in compatability[87]. Other factors must also contribute to the overall picture however. Leitman[88] and co-workers found that intermolecular bonding could also influence the activity of these hydroxy benzophenones by affecting the intramolecular bond strength responsible for the stabiliser activity.

Carlsson and co-workers[78] reported that 4-methoxy 2-hydroxy benzophenone was highly volatile and completely sublimed from the polypropylene film during the first forty hours of irradiation. This explains the better stabilisation achieved with the 4 dodecyl hydroxy compound therefore. Much more work will be required to evaluate systems fully.

Comparing embrittlement times in Table I, there is little to choose between the additives at any of the concentrations used. The value for benzophenone blended at one percent concentration is included to illustrate the increased stabilisation of 2 hydroxy substitution.

A better comparison of these additives at various concentrations can be seen in the carbonyl index plots. Stabilisation with DHBP even with increasing concentration, shows little change in the rate of carbonyl build up in the polymer. The rate of carbonyl formation for both the monomer and polymer systems is much reduced at the higher concentrations. A minimum concentration must therefore exist before a measurable difference in stability occurs and since these additives are more effective on the surface[78] higher loadings are necessary for bulk blending of the polymer.

An attempt was therefore made to graft the acrylic ultraviolet stabiliser onto the surface of polypropylene.

GRAFTING OF 4-BENZOYL-3-HYDROXY PHENYL ACRYLATE

A solution of 10g of 4-benzoyl-3-hydroxy phenyl acrylate and 1g of benzophenone in 100ml benzene was irradiated for ninety hours with 0.1g of polypropylene film. After this period the film was acetone extracted for forty-eight hours, then U.V. degraded and the carbonyl build up recorded. The trace was identical to that of unstabilised polypropylene.

Analysis of the film by ultraviolet spectroscopy on dissolving in trichloroethylene revealed nothing.

Either the grafting was too low to detect, or none had occurred. Since at low concentration of the additive, the rate of carbonyl formation is the same as polypropylene (figures VI and VII) low grafting could be the reason.

It was concluded that large amounts of grafted co-monomer would be needed to give the same effect as the blended counterpart.

CHAPTER VI (PART II) PHOTOSTABILITY OF VINYL PYRIDINE AND CO-POLYMERS

Since vinyl pyridine can be successfully grafted to polypropylene film, it was decided to assess the U.V. stability of these films, to see if any increase in stability could be achieved with this monomer. The blended thermal antioxidants also showed U.V. activity and since grafting of the U.V. absorber (BHPA) proved disappointing an attempt was made to copolymerise the vinyl antioxidant DBBA with vinyl pyridine to obtain both increased stability and dyeability.

1. Photostability of vinyl pyridine grafted films

Several film samples grafted with vinyl pyridine were prepared using various concentrations of benzophenone initiator, by irradiating solutions for eighteen hours. The films were ethanol extracted and the carbonyl index followed with increasing irradiation time. All the samples showed an increased rate of carbonyl formation over polypropylene although the embrittlement times were the same.

The results are illustrated in figure X.

2. Copolymerisation of vinyl pyridine with DBBA antioxidant

Polypropylene film was irradiated in a benzene solution (100ml) containing 2.5% DBBA, 5% vinyl pyridine and 1% benzophenone for ninety hours. The following samples were irradiated simultaneously;

Polypropylene film in 1% benzophenone/benzene solution

Polypropylene film with 5% vinyl pyridine/1% benzophenone/benzene solution

Polypropylene film with 2.5% DBBA/1% benzophenone/benzene solution

All the films were extracted for forty-eight hours in benzene and vacuum dried. The vinyl pyridine grafted films were dyed with DYLON scarlet, but only dyed slightly pink, polypropylene film dyeing orange. The The films were degraded by U.V. irradiation and the carbonyl index monitored. The results are shown in Figure XI and the embrittlement times in Table III.

Oxygen absorption of the vinyl pyridine/DBBA grafted film in a closed oxygen atmosphere gave an induction period of only 36 hours.

TABLE III

EMBRITTLEMENT TIMES OF GRAFTED FILMS

System	Embrittlement
Film/1% benzophenone solution	18
Film/1% benzophenone/5% vinyl pyridine	44
Polypropylene	63
Film/1% benzophenone/5% vinyl pyridine/2.5% DBBA	115
Film/1% benzophenone/2.5% DBBA	158

FIGURE X

POLYPROPYLENE GRAFTED FILMS OF VINYL PYRIDINE AT VARIOUS CONCENTRATIONS OF BENZOPHENONE IRRADIATED FOR 18 HOURS

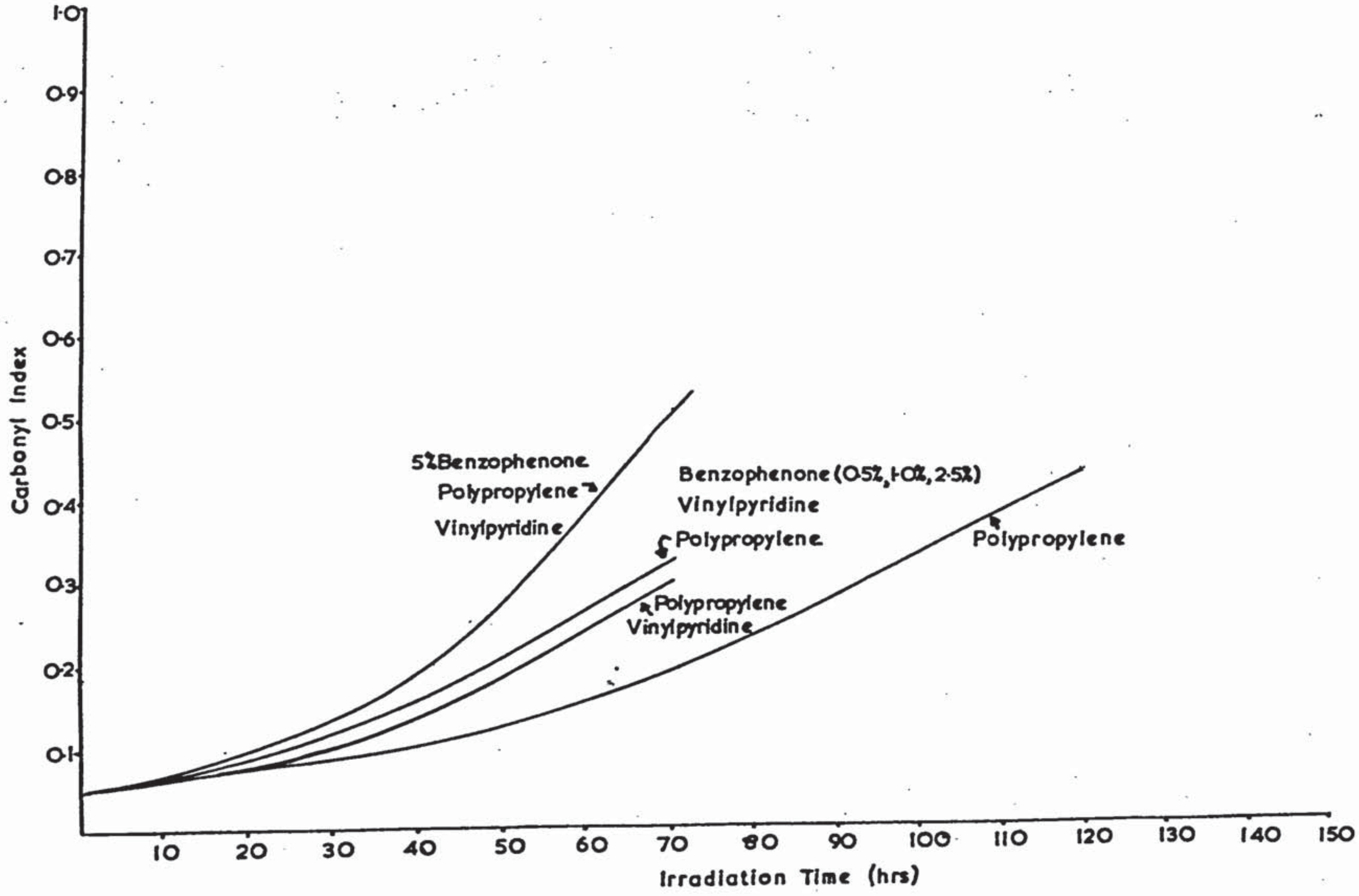
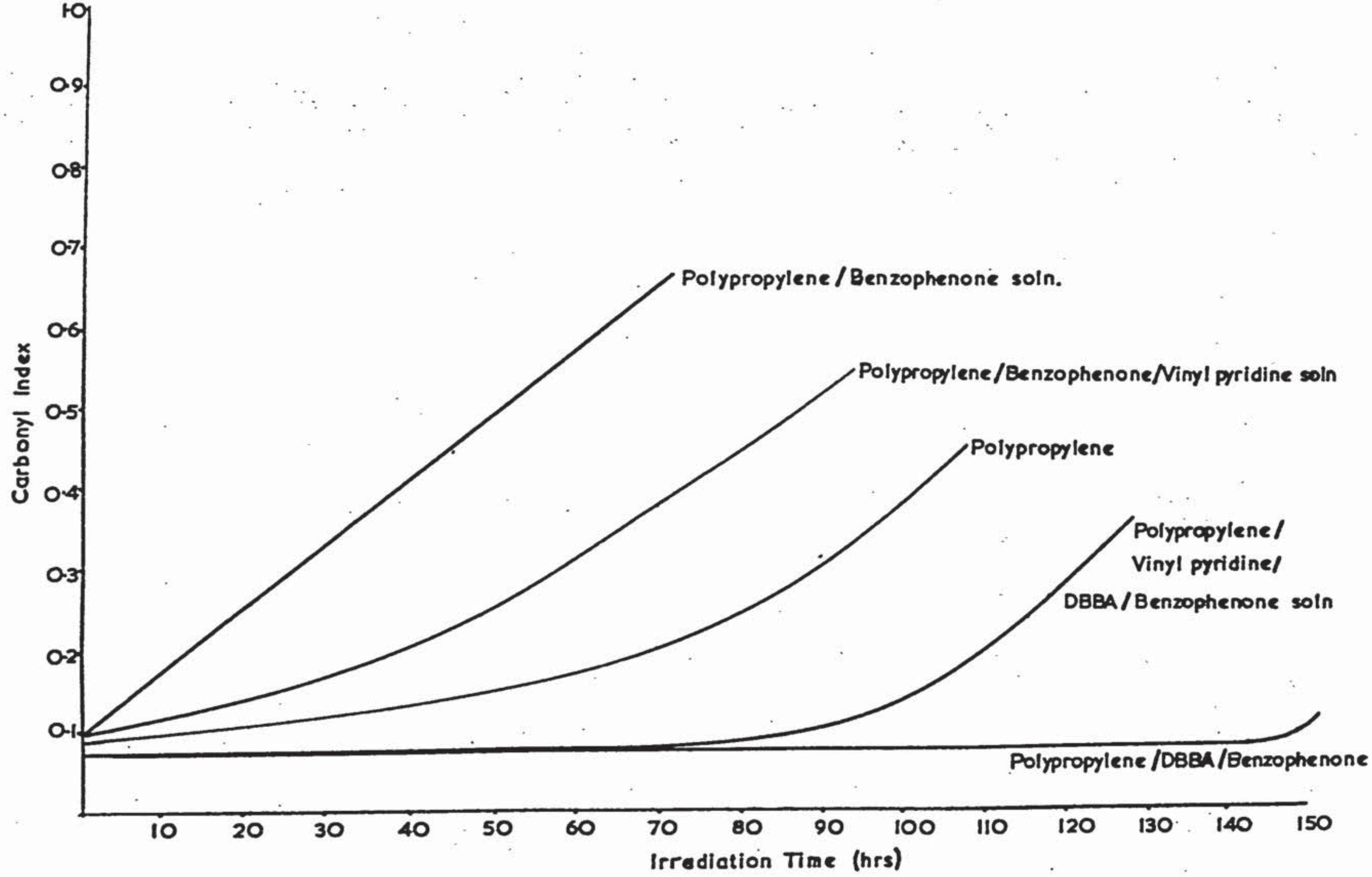


FIGURE XI

GRAFTING POLYPROPYLENE WITH VINYL PYRIDINE/DBBA BY IRRADIATION FOR 90 HOURS



DISCUSSION

The polypropylene, benzophenone irradiated film (figure XI) shows immediate carbonyl build up, due to photolysis of hydroperoxides formed during the hydrogen abstraction process. The presence of grafted vinyl pyridine reduces the stability of the film, as reflected in the embrittlement time, and degrades faster than polypropylene itself.

The introduction of the antioxidant into the system improves the U.V. stability of the total film, but the presence of the vinyl pyridine must interfere in some way with the activity of the stabiliser. Grafting the antioxidant alone, is better than blending either the monomeric or polymeric form into the film. Since the material is grafted near the surface of the film the initial oxidation can be prevented, increasing the lifetime of the film. The only added advantage of grafting vinyl pyridine is the increase in dyeability of the film. Incorporation of more vinyl pyridine with the antioxidant would only increase the carbonyl formation degrading the film faster. Similarly the thermal oxidation stability of vinyl pyridine/antioxidant grafted films shows the same effect. Since grafting of an U.V. stabiliser seems ineffective alone, it may be possible to copolymerise this with the thermal antioxidant and assess whether there is any enhancement of properties, i.e. synergism. This could be a useful study for further work.

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The grafting of polypropylene film with 3,5 ditertiary butyl-4-hydroxy benzyl acrylate has produced a bonded antioxidant system which is non-extractable. The important feature of the grafting process was the ratio of the monomer to the initiator since optimum conditions were achieved for oxidation stability by varying this ratio in the initial irradiated system. The role of benzophenone as a terminator has shown that the stability of the grafted film is a function of the density of grafting and not the total antioxidant content. A suitable method for determining the chain length of the grafted monomer would be useful to show this since the density of the side chains can only be inferred.

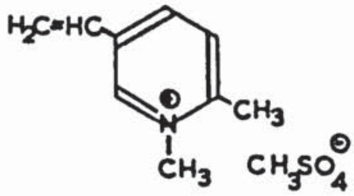
Similarly, the presence of air in the irradiated systems enhances the final stability of the grafted film to oxidation and this suggests the formation of hydroperoxide groups. Subsequent photolysis of these species produces further grafting sites and therefore the grafting density increases.

Pre-oxidation, followed by grafting, may provide further information on the part played by oxygen under the conditions used in this study. Although the antioxidant becomes bonded to the film, thus reducing the extractability, volatilisation of the antioxidant may still occur during degradation. Oven ageing of the samples has shown that this is probably the case. Studies on the oxidation stability of the polymeric and monomeric antioxidants may show that more volatile products are formed which can be easily lost. This may reveal evidence as to the reason for the poor stability obtained on grafting 3,5 ditertiary butyl-4-hydroxy phenyl acrylate, DBPA.

The graft copolymerisation of the U.V. stabiliser BHPA was also disappointing, although a significant amount would need to be grafted to produce favourable stability since the activity was concentration dependent. Possible synergism may be achieved by copolymerising BHPA with DBBA although this would depend on the reactivity ratios of the two systems. This is probably the case with the copolymerisation of vinyl pyridine with DBBA, vinyl pyridine probably predominating in the overall composition of the copolymer, causing the lowering of the thermal and U.V. stability of the system.

Other monomer systems could also be used to produce other properties absent in polypropylene.

A brief study was carried out on the graft copolymerisation of 1,2 dimethyl-5-vinyl pyridinium methyl sulphate (DMVPMS) (Midland Yorkshire Tar Distillers) below, with polypropylene, by grafting in a solution of 1% benzophenone in methanol.



The system was irradiated for eighteen hours, and extracted with water which is a solvent for the polymer.

The wettability of the polymer was determined by measuring the contact angle of a droplet of water on the surface of the film. The angle measured was 90^{o} for polypropylene and 65^{o} for the treated material, indicating modification. Polypropylene can therefore be modified with this material to produce a hydrophilic film. By a suitable choice of monomer, this technique of UlV. grafting may be widely applied to produce the desired properties in polypropylene.

From a commercial aspect, the main drawback of this technique is the time scale involved, especially with the vinyl antioxidant monomers. By increasing the power of the lamps used, this may be overcome, but it is more likely that better results could be achieved with a much lower wavelength, and therefore a higher energy source.

A balance would have to be achieved between the oxidation of the polymer film, and the desired amount of grafting.

Further studies with this technique should prove rewarding.

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