HIGH MOLECULAR WEIGHT AND POLYMER-BOUND ANTIOXIDANTS

Mohamad Fauzi Yusoff

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Studies in model system and in polypropylene, of a series of sulphur antioxidants of increasing molecular weight and containing the phenolic moiety have furnished evidence for the importance of both the intrinsic antioxidant activity of the additives as well as those of their physical attributes. The latter include: compatibility, solubility and volatility phenomena. While thermal oxidation studies in a liquid substrate (decalin) showed the insignificant influence of the additives' molecular weight over their stabilising activity, studies in polypropylene subjected to enclosed and flowing environments demonstrated markedly different behaviour. Furthermore, the photostabilising performance of the antioxidants and their processing melt behaviour showed considerable variation which were primarily attributable to the physical characteristics of the additives.

Analogous studies were also carried out on a second series of sulphur antioxidants of varying molecular weight but containing the 2-hydroxybenzophenone moiety. Despite their inherent outstanding u.v. screening property and peroxidolytic activity, their limited solubility in polypropylene proved to be their main shortcoming as polymer stabilisers.

Synergistic studies of selected synthesised phenolic (sulphur) antioxidants with a widely-used u.v. stabiliser showed superior synergistic activity in relation to those of commercial phenolic antioxidants. This was rationalised on the basis of the powerful peroxide decomposing activity of the sulphur antioxidants.

Further improvement of antioxidant substantivity and compatibility was investigated on the basis of the possible polymer-binding reactions of selected antioxidants and the simultaneous formation of higher molecular weight derivatives during the melt processing operations. A u.v.-initiated grafting of 3,5-di-tert-butyl-4-hydroxybenzyl mercaptan to polypropylene films was investigated and its application as a polymeric antioxidant masterbatch for virgin polypropylene was also carried out.

High molecular weight antioxidants
Polymer-bound antioxidants
Synergism
Thermal oxidation
Photo-oxidation

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CHAPTER ONE

INTRODUCTION

The versatility, cheapness and ease of processing of polymers have led to their extensive use in a vast array of industrial and domestic(1-3) applications. These advantages are however limited to varying extents by the susceptibility of the polymers to oxidative degradation, primarily by heat and light. Hence, whilst offering satisfactory economic value to the manufacturers and hence to the consumers, polymer articles need to be protected if a reasonable service lifetime is to be expected. This problem can be resolved in one of three ways:

(a) by modifications of polymer composition and structure or changing to polymers that are more resistant to degradation(4-6), eg from polyethylene to polytetrafluoroethylene or poly-p-phenylene,

(b) by the removal of sensitising impurities within the polymers that are known to initiate and accelerate polymer deterioration, eg hydroperoxides(7), carbonyl groups and transition metal ions, and

(c) by the incorporation of chemical additives(8–10) that would inhibit the degradation processes.

Method (a) is not in general a workable solution due to major cost constraints. In addition, the differences in mechancial properties and processing characteristics of modified polymers limit the applicability of this approach. Method (b) is again an impractical one owing to the inherent impossibility of removing all the integral carbonyl and other chromophoric impurities as well as the transition metal ions. Method (c) is therefore the one which is widely adopted in commercial practice in the stabilisation of polymers.

1.1 Polymer Degradation and Antioxidants

It has already been noted that practically all polymers are prone to oxidative degradation. The nature of the degradation reactionsvaries in rate and extent depending on the chemical(11,12) and physical(13,14) structures of the polymers. Molecular weight(15,16), the presence of chemical(7,17–19) and physical(20,21) impurities and the nature of the external environment(22) to which they are exposed all affect the rate of the degradative processes. The presence of labile tertiary hydrogen on the alternate carbon atom in polypropylene, for instance, accounts for its relative vulnerability to thermal as well as photo-oxidation. This is aggravated by the presence of adventitious physical and chemical impurities such as transition metal ions (from polymerisation catalyst residue) and the hydroperoxide/carbonyl groups respectively. The presence of unsaturation and allylic hydrogen in the polymer forms another locus of oxidative breakdown. Hence cis-polyisoprene, polybutadiene etc are highly susceptible to deterioration.

As far as the external environment is concerned, Scott(22) points out that the most important environmental influences, apart from oxygen, which are deleterious to polymer stability are: heat, light, contamination by metal ions, ozone and mechanical deformation.

Oxidation of polymers can primarily be viewed in two principal stages(23). The first is one which is manifested during the processing operations characterised by the high temperature thermal treatment and mechanical shear but only for a comparatively short period. The other occurs during the service life of the fabricated articles subjected to a relatively mild and/or intermittent oxidative attack. These oxidative processes manifest themselves as an adverse effect on the articles' useful properties such as mechanical strength, electrical characteristics, aesthetic appeal etc.

However, the deterioration of polymers can be inhibited by the incorporation of chemical additives, termed antioxidants. Hence the need and importance of antioxidants in conferring stabilisation during processing and longevity of service life cannot be over-estimated. In fact it has been said(24) that the development of the motor car tyre would have probably been impossible but for the discovery of antioxidants.

1.2 Mechanisms of Polymer Breakdown and Antioxidant Action

It is now widely recognised that the breakdown of polymers follows an essentially free-radical chain mechanisms. In spite of the general consensus in this respect, the nature of the initiation step is a subject of controversy. Two major schools of thought are recognised. Both invoke the presence of adventitious thermal and photo-sensitive chemical impurities formed in the polymer either during manufacture or as a consequence of oxidation during high temperature fabrication processes. The first class of sensitising impurities encompasses the macromolecular peroxides, particularly the hydroperoxides, which readily homolyse to give initiating free radicals. The second class comprises the in-chain ketones which are the main derived products formed by the homolysis of hydroperoxides.

1.2.1 Polymeric Hydroperoxides as Initiators

The modern theories of the mechanism of oxidative degradation of polymers are substantially based on studies by Bolland(25) and Bateman(26) in the early part of the 1950's. The free-radical chain mechanism is accepted to apply not only to the olefins for which it was originally developed but also to alkanes(27) and with varying degrees of success to hydrocarbon polymers and other compounds of technological importance(28,29). In all cases, hydroperoxides are considered to play a key role in the initiation steps of the oxidative chain reactions. Chien and Boss(30,31) have also adduced, from polypropylene studies, convincing kinetic evidence that polymeric hydroperoxides are the main precursors for the thermal deterioration of polymers. Mounting evidence provided by Scott and co-workers(32–41), Carlsson and Wiles(42–46), Shelton(47) and Manasek and co-workers(48) further emphasise and lend support to the hydroperoxide theory.

The generalised reaction scheme for the oxidative degradation or autoxidation of polymers is as follows (where RH = polymer):

Initiation Reactions

$$2\mathrm{ROOH} \longrightarrow \mathrm{ROO}\cdot + \mathrm{RO}\cdot + \mathrm{H_2O} \qquad (1)$$

or

$$\mathrm{ROOH} \xrightarrow{h\nu} \mathrm{RO}\cdot + \cdot\mathrm{OH} \qquad (2)$$

$$\left.\begin{array}{l}\mathrm{RO}\cdot \\ \mathrm{ROO}\cdot \\ \cdot\mathrm{OH}\end{array}\right] + \mathrm{RH} \longrightarrow \left[\begin{array}{ll}\mathrm{ROH} & (3) \\ \mathrm{ROOH} + \mathrm{R}\cdot & (4) \\ \mathrm{H_2O} & (5)\end{array}\right.$$

Chain Propagation Reactions

$$\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{ROO}\cdot \qquad (6)$$

$$\mathrm{ROO}\cdot + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R}\cdot \qquad (7)$$

Termination Reactions

$$2\mathrm{ROO}^{\cdot} \longrightarrow \text{Inert products} \qquad (8)$$

It is now generally accepted that photodegradation of polymers involves the same free-radical scheme as the thermal-oxidative degradation(49–52). The main difference lies in the nature and rate of the initiating step which is very much faster in photo-initiation than the bimolecular interaction of hydroperoxides which is the main process involved in thermal initiation.

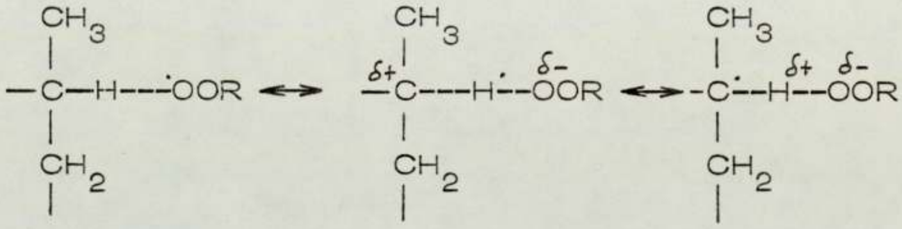
The transition metal ions exert their pro-oxidant effect by forming unstable co-ordination complexes with the macro-alkyl hydroperoxides, followed by electron transfer to generate reactive free-radicals(51). The rate of the two processes,

$$\mathrm{ROOH} + \mathrm{M}^{+} \longrightarrow \mathrm{RO}\cdot + \mathrm{M}^{2+} + \mathrm{OH}^{-} \qquad (9)$$

$$\mathrm{ROOH} + \mathrm{M}^{2+} \longrightarrow \mathrm{ROO}\cdot + \mathrm{M}^{+} + \mathrm{H}^{+} \qquad (10)$$

depends on the redox properties of the metal involved.

At partial pressure of oxygen equivalent to air or higher, the rate of reaction (6) is so fast that the concentration of the alkylperoxy radicals, ROO•, is very much greater than the alkyl radicals, R•. In polypropylene, interaction of the alkylperoxy radicals with the tertiary carbon involves a transition state which is both radical and cationic in character. This is because the methyl group both increases electron density on the carbon atom being oxidised and delocalises the electron by hyperconjugation(38).



$$\begin{array}{l}CH_3\\|\\-C-H---\dot{O}OR\\|\\CH_2\\|\end{array} \longleftrightarrow \begin{array}{l}CH_3\\|\\\overset{\delta+}{-C}---H\overset{\cdot\ \ \delta-}{--OOR}\\|\\CH_2\\|\end{array} \longleftrightarrow \begin{array}{l}CH_3\\|\\-\dot{C}--\overset{\delta+}{H}--\overset{\delta-}{O}OR\\|\\CH_2\\|\end{array}$$

Moreover, alkylperoxy radicals are known to be strongly resonance stabilised and are relatively selective electrophilic species abstracting tertiary bonded hydrogen in preference to secondary or primary hydrogens(53), hence explaining the relative vulnerability of polypropylene to oxidation. In polypropylene, it is suggested(54, 55) that intramolecular propagation of alkylperoxy radicals is the predominant reaction relative to that of the intermolecular, the ratio of the two being of the order of 30:1.

The termination reaction of the oxidative chain reactions involves the annihilation of two alkylperoxy radicals to inert products, reaction (8).

1.2.2 In-chain Ketones as Initiators

The pioneering studies of Charlesby and co-workers(56, 57) has led to considerable interest in the phosphorescence emission from commercial synthetic polymers. For the polyolefins, for instance, the source of the phosphorescence is thought to be due to the presence of impurities in the polymer introduced during the polymerisation and processing stages, since the olefinic structure should not, theoretically, absorb light $>$ 250 nm(58-61).

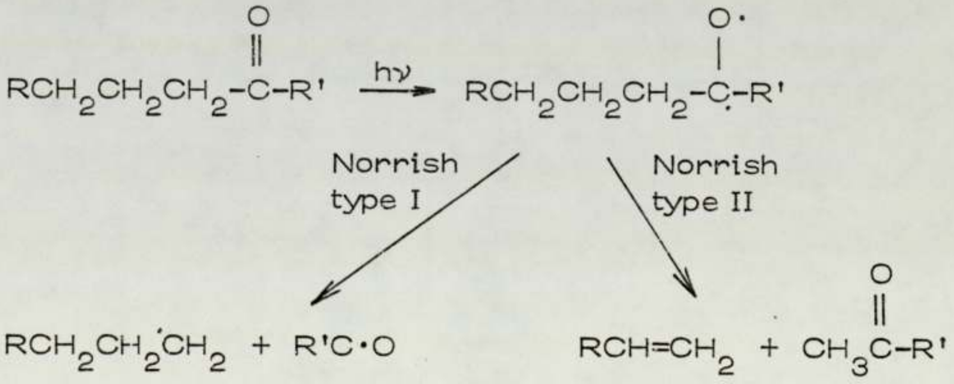
In general, the major emitting species are believed to be the ketonic carbonyl impurities(56, 57). Also since these impurities absorb within the actinic range 290-350 nm, the wavelength range over which many synthetic polymers are susceptible to damage by sunlight, their presence has been thought to be responsible for the photo-initiation processes leading to polymer breakdown(56-58, 62, 63). It has also been indicated(64, 65) that conjugated carbonyl formed as a result of thermal oxidation could be involved in the initiation step during the early stages of photo-oxidation. A relationship has been found between fluorescence intensity due to the conjugated carbonyl initially present in the polymer and the uv lifetime of polypropylene samples(66).

Scott and co-workers(37) show that carbonyl compounds may participate in the photo-initiation processes in extensively oxidised polyolefins which contain a substantial concentration of ketonic carbonyl. However, the evidence is much less unambiguous during the early stages of photo-oxidation and it has been shown that hydroperoxides are the primary initiators(67). In studies on polypropylene, for instance, it has been demonstrated(7) that a plot of initial photo-oxidation rate against initial hydroperoxide concentration shows a linear relationship. No correlation is found between photo-oxidation rate and initial conjugated carbonyl (1685 cm^{-1}) concentration. It is also shown that photo-oxidation rate is only dependent on ketonic carbonyl concentration in so far as carbonyl concentration is related to peroxide concentration.

Many attempts have been made to interpret the phosphorescence spectra of polyolefins in terms of various carbonyl groups and implicate these species in photo-initiation. However, the results from this ultra-sensitive technique appear to be generally inconclusive because of the problems of identification and assigning absolute concentrations to the species.

The dominating importance of hydroperoxides as photo-initiators is further substantiated(7,68) by heating in argon a film of polypropylene which contains a substantial amount of hydroperoxides (33.0 x 10^{-5} g mol/g) and which before this treatment photo-oxidised rapidly. This treatment destroys the hydroperoxides completely with a corresponding increase in the ketonic carbonyl concentration. In spite of the very high concentration of ketonic carbonyl, the photo-oxidation rate of the resulting film is reduced initially to zero.

The known photo-chemistry of aliphatic ketones suggests that triplet carbonyl could undergo both radical and non-radical breakdown processes. These have been invoked to explain the behaviour of carbonyl groups in polymers(69).

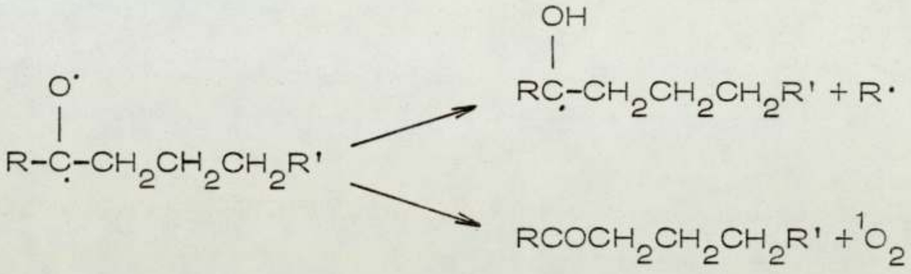


Studies of the quantum yields of the two processes by Hartley and Guillet(70) have shown that Norrish type II breakdown of the carbonyl triplet is favoured relative to Norrish type I homolysis in polymers. Dialkyl ketones with alkyl chains containing 21 carbon atoms or over have a quantum efficiency for the type I elimination of a little over 0.01 compared with 0.06 for type II process. It seems likely for this reason that photo-initiated oxidation will be more important in the later stages of degradation.

It seems clear then that photolysis rather than photo-initiation is the main reaction occurring in polymers containing in-chain ketones. This process has been used to bring about the accelerated photolytic destruction of polymers by the deliberate introduction of carbonyl into the polymer chain during manufacture(71).

1.2.3 Other Possible Initiation Processes

Closely allied to the theory of carbonyl sensitisation process is the role of singlet oxygen(72-76) in the photodegradation of polymers. It is thought that the triplet carbonyl, apart from being able to abstract hydrogen, interacts with molecular oxygen to produce singlet oxygen. This subsequently reacts with vinyl to form hydroperoxides:



$$R-\overset{O^{\cdot}}{\overset{|}{\underset{\cdot}{C}}}-CH_2CH_2CH_2R' \begin{cases} \nearrow RC(\overset{OH}{\underset{\cdot}{\ }})-CH_2CH_2CH_2R' + R\cdot \\ \searrow RCOCH_2CH_2CH_2R' + {}^1O_2 \end{cases}$$

$${}^1O_2 + R''CH_2CH{=}CH_2 \longrightarrow R''CH{=}CHCH_2OOH$$

If the above reactions hold true, then increased concentration of carbonyl in the polymer should lead to a higher rate of photo-initiation. But this is not to be the case as already described.

Other adventitious impurities are also thought to participate in the initiation processes such as the aromatic species(56,57), trienes(77) and oxygen-polymer charge transfer complexes(78,79). There is no direct evidence to support these claims and the findings thus obtained are more implied than conclusive.

1.2.4 Mechanisms of Antioxidant Action

It is apparent from the general reaction scheme that inhibition to polymer oxidation can be achieved in three principal ways:

(i) by scavenging the reactive radicals formed, thus terminating the kinetic chain; reactions (6) and (7),

(ii) by the prevention of the initiation reactions through metal ion chelation, reactions (9) and (10) and decomposing the hydroperoxides to non-radical products, reactions (1) and (2), and

(iii) by preferentially absorbing the deleterious effect of uv light by suitable compounds that are uv screeners, reaction (2).

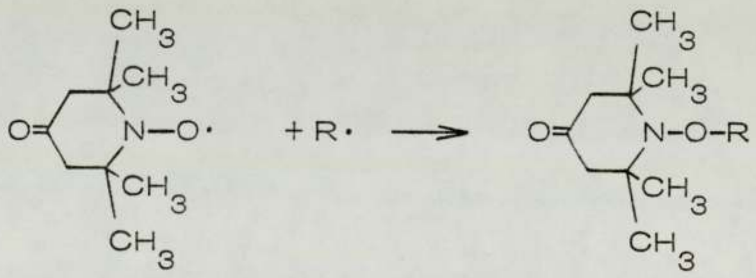
In fact these three methods have been achieved in practice by the use of chain-terminating antioxidants, preventive antioxidants and uv absorbers respectively. Generally they are termed antioxidants.

(a) Chain-terminating antioxidants

Included under the class of the chain-terminating antioxidants are essentially the alkylated hindered phenols and the secondary amines. They function by making available free hydrogen to react with the propagating peroxy radicals, ROO·, thereby terminating the chain reactions(80-82).

$$ROO\cdot + AH \longrightarrow ROOH + A\cdot \qquad (11)$$

The antioxidant radical, A·, thus formed is relatively inert due to stabilisation through resonance. Other types of chain-terminating antioxidants, but of lesser importance, function by the free radical trap(83,84) and the electron donor(85,86) mechanisms. An instance of the former is the rapid reaction of 2,2,6,6-tetramethyl-4-piperidine nitroxide with the alkyl radicals to give stable molecular product,



while examples of the latter have been proposed(86) to be as follows:

$$RO_2^{\cdot} + Ar\ddot{N}R_2 \longrightarrow RO_2{:}\,^{-}Ar\dot{N}R_2^{+}$$

$$RO_2\cdot + Co^{2+} \longrightarrow RO_2\overset{-}{:}\ Co^{3+}$$

From reaction (11) it is evident that phenolic antioxidants function in a sacrificial role. Although the kinetic chain is interrupted by the antioxidants, hydroperoxides are still being formed slowly which make chain-breaking antioxidants palliative in their role. The antioxidant activity of this class of compound is a composite function of the ability of the phenol or amine to release hydrogen atoms to the alkylperoxy radicals and the resulting aryloxy radical to react with the oxygen and the polymer(87a).

$$ROO\cdot + AH \longrightarrow ROOH + A\cdot \qquad (12)$$

$$A\cdot + O_2 \longrightarrow AOO\cdot \qquad (13)$$

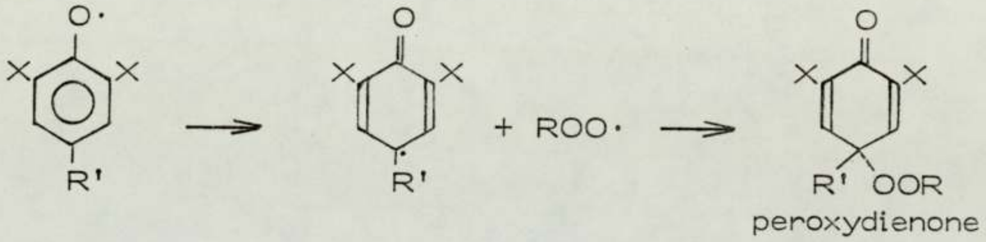
$$AOO\cdot + RH \longrightarrow AOOH + R\cdot \qquad (14)$$

$$A\cdot + RH \longrightarrow AH + R\cdot \qquad (15)$$

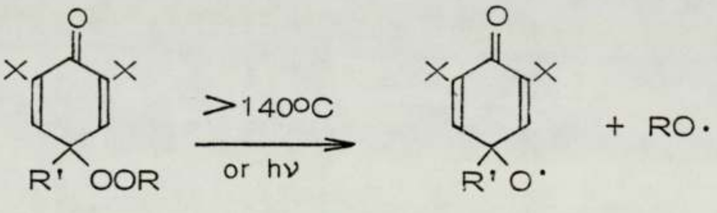
The rates of the above reactions depends on the steric environment of the aryloxyl oxygen. In addition, the ease of hydrogen abstraction by alkylperoxy radical, reaction (12), is increased by electron-releasing groups in the aromatic ring. But the same electronic characteristics favour the direct attack of oxygen on the phenolic hydrogen which is a potential chain-initiating reaction,

$$AH + O_2 \longrightarrow A\cdot + HOO\cdot \qquad (16)$$

Phenolic antioxidants generally contain the seeds of their own destruction as the following reaction shows:



At temperatures above 140°C, or on exposure to uv light(87b), the peroxydienone decomposes rapidly to give new initiating radicals which make phenolic antioxidants relatively inefficient at high temperatures,



Despite these fundamental problems, antioxidants of this class are widely used in the thermal stabilisation of polymers. One of their notable successes is when used in synergistic mixtures with peroxide decomposing antioxidants(88,89).

(b) Preventive antioxidants

Further inhibition to polymer oxidation can be achieved by reactions which involve the annihilation of the hydroperoxides and preventing their decomposition into reactive radicals. This class of preventive antioxidants include metal ion deactivators and peroxide decomposers. The former functions by deactivating the metal ions thereby eliminating the catalytic activity(51,90) of the ions in the decomposition of the hydroperoxides. The deactivation processes can be achieved in one of three ways:

(i) by complexing the metal ions to their maximum co-ordination number by various ligands(91-93),

(ii) by stabilising one valence state at the expense of the other(94) and

(iii) by forming an insoluble product(95), eg FeS.

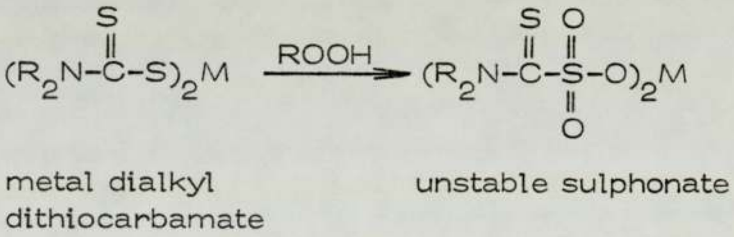
The peroxide decomposers can be broadly classified into three categories:

(1) metal dialkyl dithiocarbamate, eg ZnDEC,

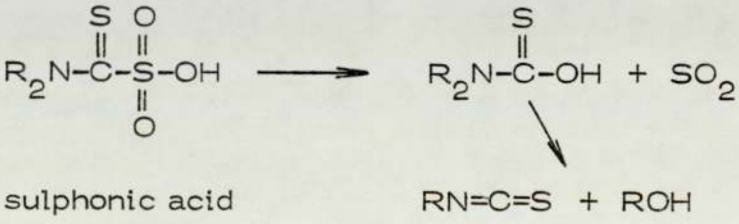
(2) cyclic phosphite esters, eg catechol phosphite, and

(3) mono and disulphide compounds, eg dilaurylthiodipropionate.

Numerous papers have been published by Scott and co-workers(87,96-102) on the mechanisms of the three types of peroxide decomposers. In the case of the metal dialkyl dithiocarbamates, for example, it is now unequivocally recognised that they destroy the hydroperoxides by ionic - generally Lewis acid catalysed - reactions through the evolution of sulphur dioxide or sulphur trioxide,



$$(R_2N-\overset{S}{\overset{\|}{C}}-S)_2M \xrightarrow{ROOH} (R_2N-\overset{S}{\overset{\|}{C}}-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-O)_2M$$

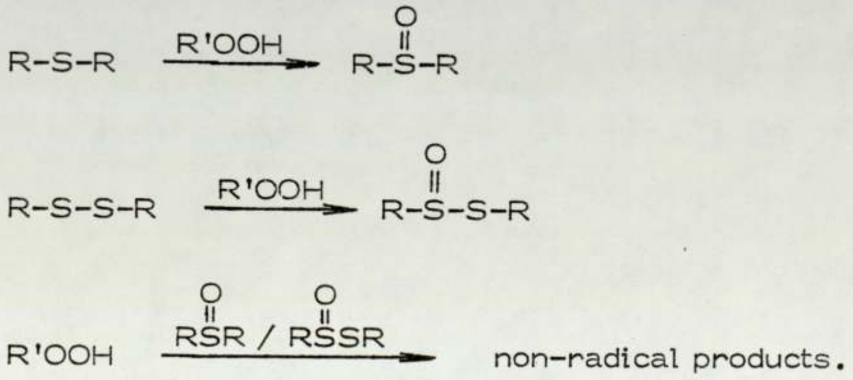


$$R_2N-\overset{S}{\overset{\|}{C}}-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-OH \longrightarrow R_2N-\overset{S}{\overset{\|}{C}}-OH + SO_2 \searrow RN=C=S + ROH$$

It has recently been shown by Husbands(120) that sulphur trioxide is an effective catalyst for the decomposition of cumene hydroperoxide to give phenol and acetone and functions as a Lewis acid.

The action of the cyclic phosphite esters is remarkably similar in many ways to the behaviour of the dithiocarbamates(99–102).

Many alkyl and aryl monosulphides and disulphides inhibit polymer oxidation. The inhibitory effect of these sulphides is only achieved after a certain amount of oxygen has been absorbed by the polymer substrate(103) thereby giving the well-known pro-oxidant effect. Studies at MRPRA(104–107) showed that the reaction of monosulphide and disulphide with hydroperoxide resulted in the formation of sulphoxide and thiosulphinate respectively and reactions of these with hydroperoxides were thought to lead to non-radical products.



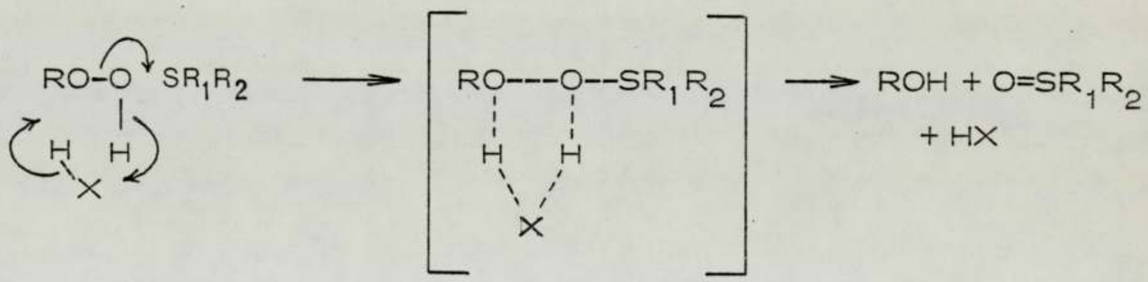
$$\text{R-S-R} \xrightarrow{\text{R'OOH}} \text{R-}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{-R}$$

$$\text{R-S-S-R} \xrightarrow{\text{R'OOH}} \text{R-}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{-S-R}$$

$$\text{R'OOH} \xrightarrow{\text{R}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{R} \,/\, \text{R}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{SR}} \text{non-radical products.}$$

Direct addition of the sulphoxides (or the thiosulphinate) appeared to immediately inhibit the oxidation of squalene(104) in contrast to the delayed stabilisation observed with the corresponding sulphides.

Bateman and Hargrave(108) in an earlier study of the oxidation of cyclohexenyl methyl sulphide with cyclohexenyl and t-butyl hydroperoxides in a hydrocarbon solvent, proposed the following mechanism to account for the formation of the sulphoxides, where HX may be an acid catalyst, solvent or hydroperoxide itself, in which case a second order reaction is seen:



Although the inhibitory effect of the sulphoxides and thiosulphinate are observed at much lower concentrations than the sulphides from which they are derived, the period of time in which they remain active is considerably reduced. This reflects the instability of these compounds, which appears to be positively related to their inhibitory action(109). But there is a limit to the parallalism, since a compound that is too unstable will not exist long enough to provide adequate protection. It is for this reason that the parent mono and disulphides may be preferable as practical antioxidants which will function as a reservoir from which the active inhibitor can be generated.

Three factors(110) appear to contribute to the observed behaviour of organic sulphides as peroxide decomposers:

(i) ease of oxidation to the mono-oxy derivatives,

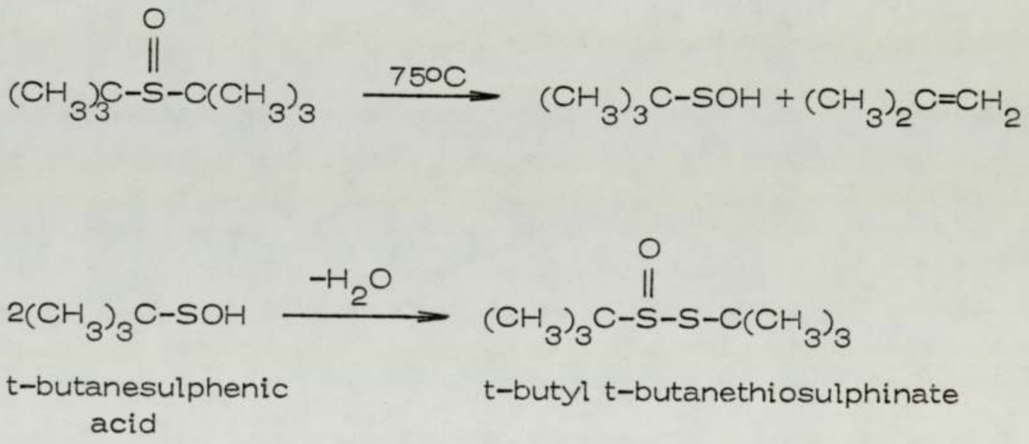
(ii) the intrinsic inhibitory power of the sulphoxides, and

(iii) the optimum stability of the sulphoxide.

This involves achieving a compromise between the instability required for efficient activity and stability of the derivatives to persist long enough to function as preventive antioxidants.

Further detailed and critical studies by Marshall(111) suggest that the sulphoxides are not themselves the effective antioxidants but rather they are the precursors to the more reactive constituents that consume the hydroperoxides. It was shown that in studies on the decomposition of tetralin hydroperoxide by dilauryl sulphinyldiproprionate a significant induction period was observed.

Earlier workers(112–114) had shown that sulphoxides with one or more hydrogens on a carbon β to the sulphur atom undergo decomposition at moderate temperatures to give olefins. Colclough and Cuneen(105) in subjecting di-tert-butyl sulphoxide to thermolysis at 75°C, was able to detect, apart from the olefins the presence of tert-butanethiosulphinate. They postulated sulphenic acid being the responsible intermediate in the formation of the thiosulphinate,



$$(CH_3)_3C-\overset{O}{\overset{\|}{S}}-C(CH_3)_3 \xrightarrow{75^oC} (CH_3)_3C-SOH + (CH_3)_2C{=}CH_2$$

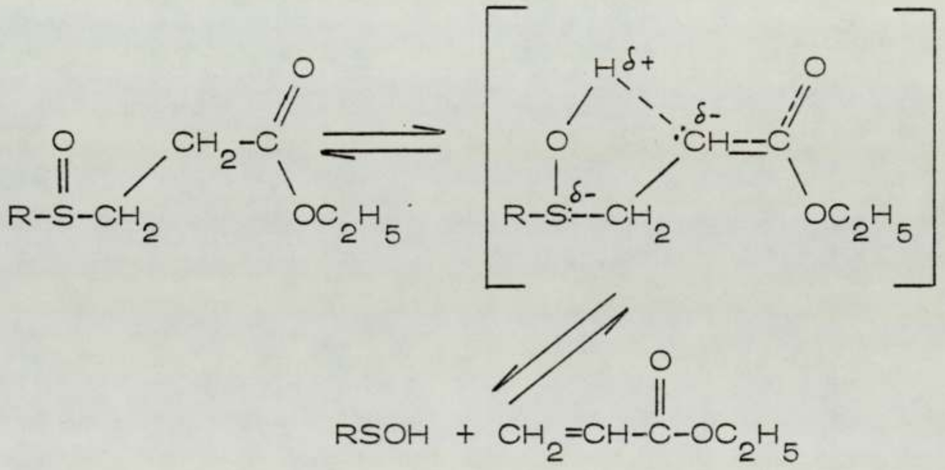
$$2(CH_3)_3C-SOH \xrightarrow{-H_2O} (CH_3)_3C-\overset{O}{\overset{\|}{S}}-S-C(CH_3)_3$$

t-butanesulphenic acid

t-butyl t-butanethiosulphinate

It seems likely then that the sulphenic acid and its oxidation products play a vital role in the peroxide decomposition reactions. It has also been shown(112, 115) that the relative ease of sulphoxides decomposition and hence their inhibitory activity is a strong function of their steric environment.

Di-tert-butyl sulphoxide, for example, decomposes 93 times faster than that of methyl t-butyl sulphoxide under similar conditions. β-ketonic sulphoxide shows even greater reactivity. β-sulphinylpropionate, for instance, thermolyses 15,000 faster than that of di-n-propyl sulphoxide. This increased reactivity has been rationalised in terms of the activating effect of the carbonyl in stabilising the developing carbanion in the transition state as the hydrogen on the adjacent carbon is being transferred to the sulphinyl oxygen,



It was also shown(115) that electron-attracting groups attached to the aromatic ring of the phenyl t-butyl sulphoxides increase the ease of decomposition of the sulphoxides while electron-donating groups tend to prevent the decomposition.

Recent studies by Armstrong, Plant and Scott(116,117) have thrown much light on the mechanisms of sulphur antioxidants particularly the thiodipropionate esters,

$$(ROCOCH_2CH_2)_2S$$

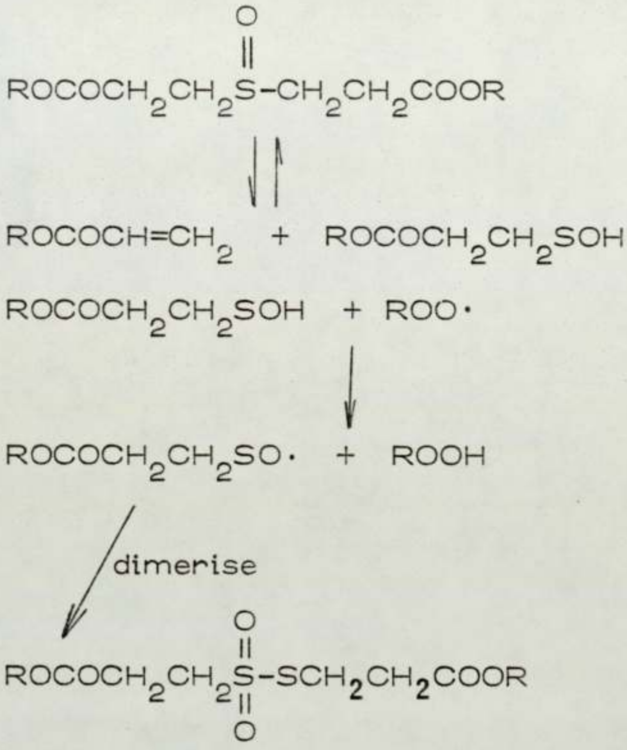
Three distinct mechanisms have been proposed to account for the observed chemical reactions of the antioxidant behaviour:

(1) a radical trapping process involving sulphenic acid formed by the breakdown of the sulphoxides,

(2) a radical generating reaction, thereby giving the pro-oxidant effect, and

(3) a Lewis acid catalysed destruction of the hydroperoxides by the further oxidation products of the sulphenic acid.

Mechanisms (1) is accounted for by the following reaction scheme:



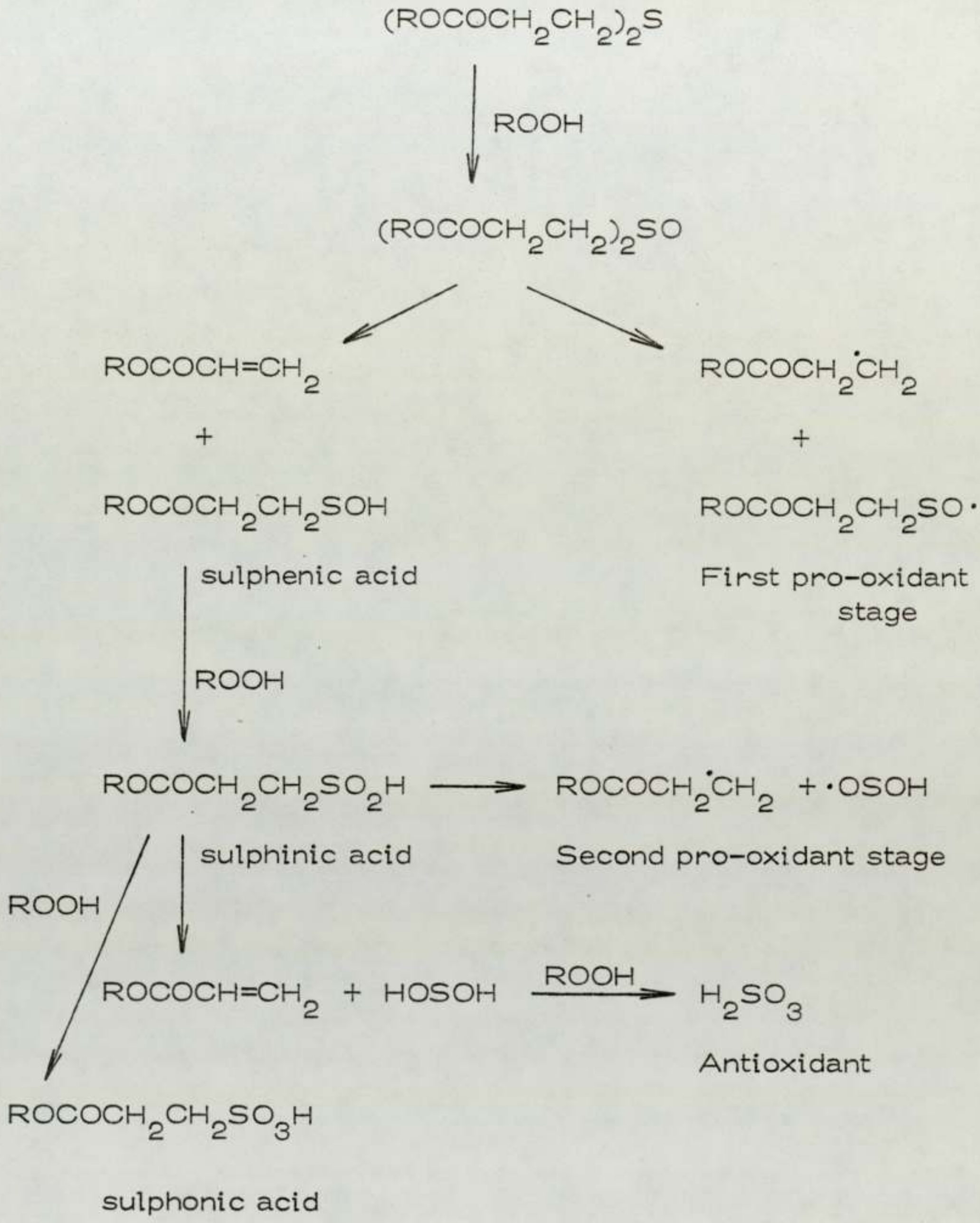
$$ROCOCH_2CH_2\overset{O}{\overset{\|}{S}}-CH_2CH_2COOR \rightleftharpoons ROCOCH{=}CH_2 + ROCOCH_2CH_2SOH$$

$$ROCOCH_2CH_2SOH + ROO\cdot \longrightarrow ROCOCH_2CH_2SO\cdot + ROOH$$

$$ROCOCH_2CH_2SO\cdot \xrightarrow{\text{dimerise}} ROCOCH_2CH_2\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-SCH_2CH_2COOR$$

The sulphenic acid is therefore behaving as a classical chain-breaking antioxidant and the sulphinyl radical thus formed is very stable and cannot continue the kinetic chain reaction. It is removed by dimerisation(118).

Using oxygen absorption techniques, Scott(97) explained the pro-oxidant and antioxidant reactions of dilaurylthiodipropionate by the following reactions:



Subsequent publication by Armstrong and Scott(116) showed that the reaction between the derived sulphenic acid and hydroperoxide also contributed to the pro-oxidant effect.

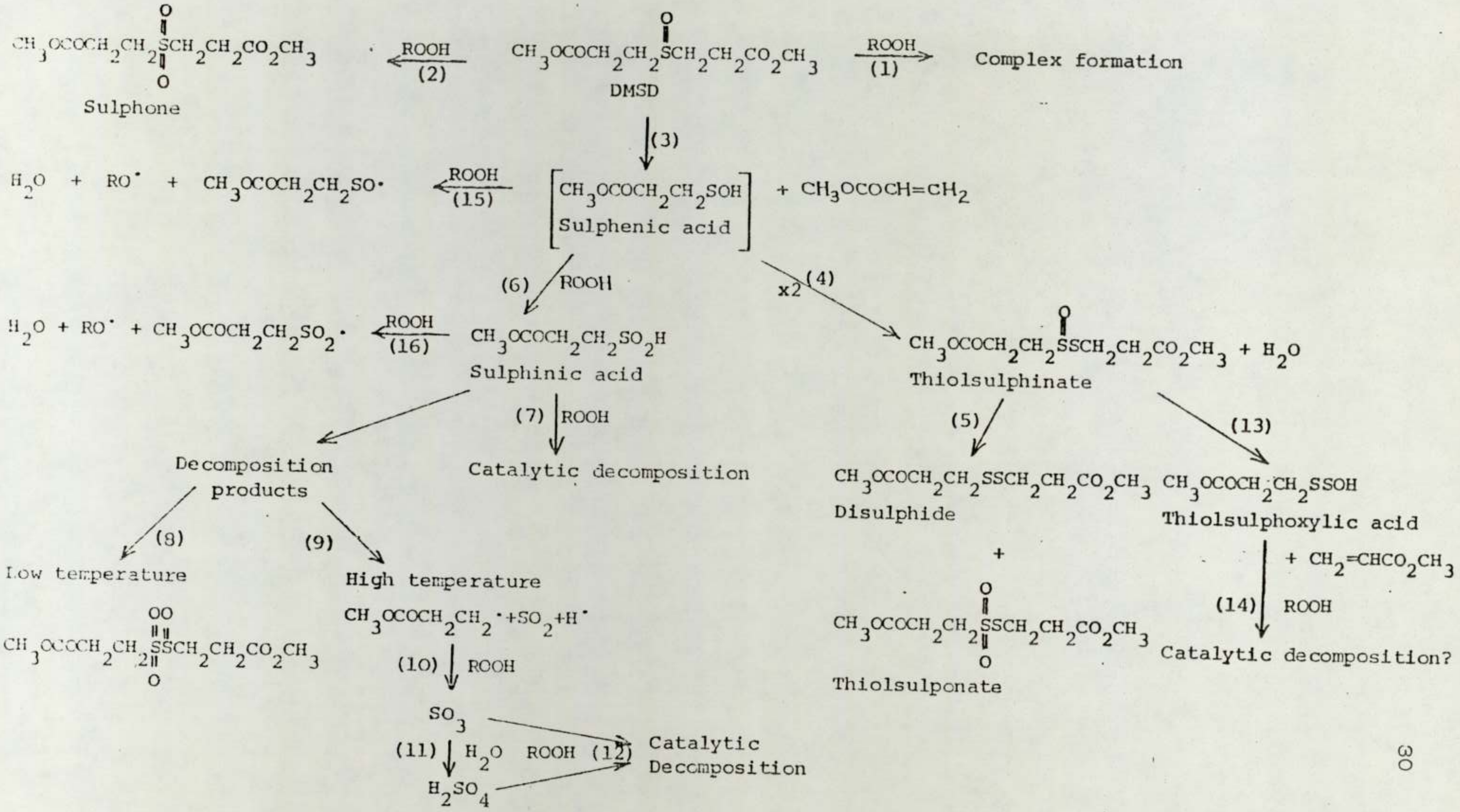
$$ROCOCH_2CH_2SOH + R'OOH \longrightarrow R'O\cdot + H_2O + ROCOCH_2CH_2SO\cdot$$

The picture emerging of the mechanism of antioxidant action is much less unambiguous. A number of possible products of the sulphoxide/ hydroperoxide systems were examined(119) including sulphonic acid and sulphur dioxide. Armstrong concluded that the peroxide decomposing ability of the sulphonic acid, for instance, was not sufficient to explain the activity of its parent sulphoxide. A comparison of sulphur dioxide with the thiodipropionate in decalin showed that at similar molar concentration, the antioxidant efficiency as measured by the induction period to oxygen absorption was very similar. However, there was one notable difference between the two. While the SO_2 had no effect on the linear rate of oxidation at the end of the induction period, the ester did. In addition, the inhibitory effect of the latter increased with increased concentration suggesting that other sulphur compounds besides SO_2 were involved in their antioxidant function.

Subsequent work by Husbands(120) has further disentangled the complexities of the sulphoxides interaction with hydroperoxides. Detailed studies were made on the dimethylsulphinyldipropionate (DMSD) to which the following reaction schemes have been proposed as shown in Scheme 1.

Reaction (1) involves direct antioxidant activity by DMSD in the form of deactivation of the hydroperoxide by complex formation. However as also conclusively shown by Armstrong(117, 119), this is a relatively minor effect in the overall antioxidant activity of DMSD. Reaction (2) is the oxidation to produce the sulphone, which again represents intrinsic antioxidant activity of the DMSD molecule. It occurred to a minor extent. Reaction (3) is the thermal decomposition of DMSD to produce methyl acrylate and presumably a sulphenic acid. Although the acid has not been absolutely indentified, subsequent reaction products have, which lead to the conclusion that the sulphenic acid is an extremely reactive intermediate in the decomposition process. Reaction (4) is the bimolecular production of thiosulphinate with the elimination of water. Subsequent reaction of the thiosulphinate by reaction (5) yields disulphide and thiosulphonate. Reaction (6) is the direct oxidation of the sulphenic acid to the sulphinic acid. The resultant acid is capable of catalytic hydroperoxide decomposition by reaction (7). At low temperature, this decomposition is thought to involve the formation of sulphinyl sulphone by reaction (8). At no time is SO_2 detected as a by-product.

Scheme 1   The reaction between DMSD and hydroperoxide (from Dr Husbands' work, reference 120)



The decomposition of the sulphinic acid at elevated temperatures has been shown to occur by a homolytic process producing sulphur dioxide, reaction (9), which is the precursor to an even more powerful catalytic hydroperoxide decomposer than the sulphinic acid. It is also concluded that the high activity is associated with the oxidation to sulphur trioxide by reaction (10) followed by reaction with water to produce sulphinic acid, reaction (11). The active catalyst for the decomposition here is either sulphur trioxide or sulphuric acid or more likely a combination of the two. The experimental evidence suggests that sulphur dioxide is only involved in the stoichiometric reaction with hydroperoxide. The catalytic process is shown as reaction (12).

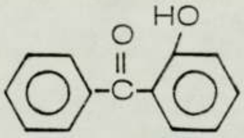
The production of the secondary acidic species derived from the thermal decomposition of the thiosulphinate, reaction (13), was postulated to account for the unusually high activity of thermally decomposed solutions of DMSD. The occurrence of methyl methacrylate in the decomposition products of the thiosulphinate both at high and low temperatures strongly suggests that the acidic species is the thiosulphoxylic acid and that this is in fact the catalytic species involved in the decomposition of hydroperoxides by reaction (14). Reactions (15) and (16) account for the pro-oxidant as mentioned earlier.

(c) Uv Stabilisers

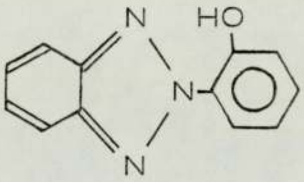
To complement the protection afforded by the chain-terminating and preventive antioxidants, light stabilisers are also incorporated into polymer articles exposed to outdoor environments. Basically they can be divided into three general types according to their mode of action(121). The first type is the one whereby the additive itself absorbs most of the uv light and thereby leaving little to be absorbed by the polymer. Such an additive is generally called 'uv absorbers'. Alternatively, an additive which itself absorbs little or no uv light may interact with a photo-excited group in a manner that transfers the excitation energy to the additive. This type of light stabiliser is usually called the excited state quenchers. In both cases, the additive must be able to dispose of its excitation energy in a harmless manner before it undergoes some irreversible photochemical reaction which would destroy its effectiveness. The third functions by decomposing the hydroperoxides which has already been discussed at length in the preceding section.

(1) Uv Absorbers

The main classes of compound contained in this category are the 2-hydroxybenzophenones (I) and the 2-hydroxybenzotriazoles (II) and the salicylates (III)



(I)



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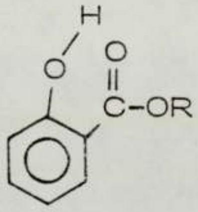
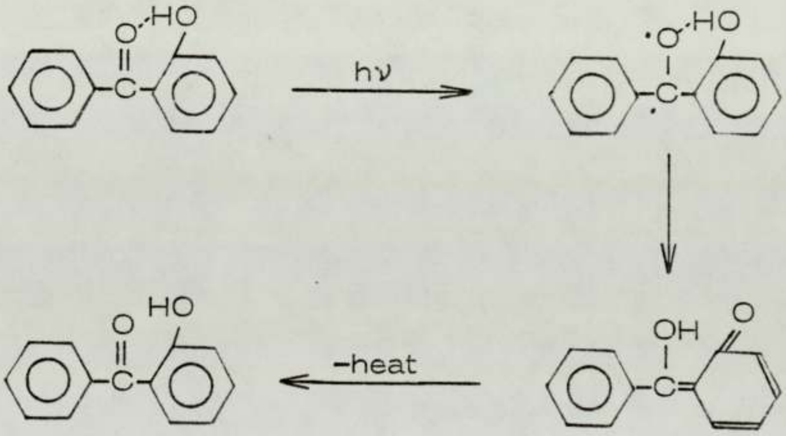


(III)

These were believed originally to function entirely as uv screening agents(51, 122–124). It was thought that, like pigments such as carbon black or titanium dioxide, they had the ability to absorb uv light and dissipate this as thermal rather than chemical energy. Subsequent work has demonstrated that this class shows some ability to behave by the chain-breaking mechanism(33, 125, 126) and also to quench triplet states(127–129). However, there is little doubt that uv screening is one, and probably the most important of their functions so that they prevent or reduce the rate of formation of initiating free radicals in the polymer. It has been postulated(51) that the ability of the 2-hydroxybenzophenone, for example, to effectively absorb the electromagnetic energy without the formation of free radicals, is related to the possibility of hydrogen bond formation which permits energy transfer and leading to enolic quinone formation.



(2) Excited state quenchers

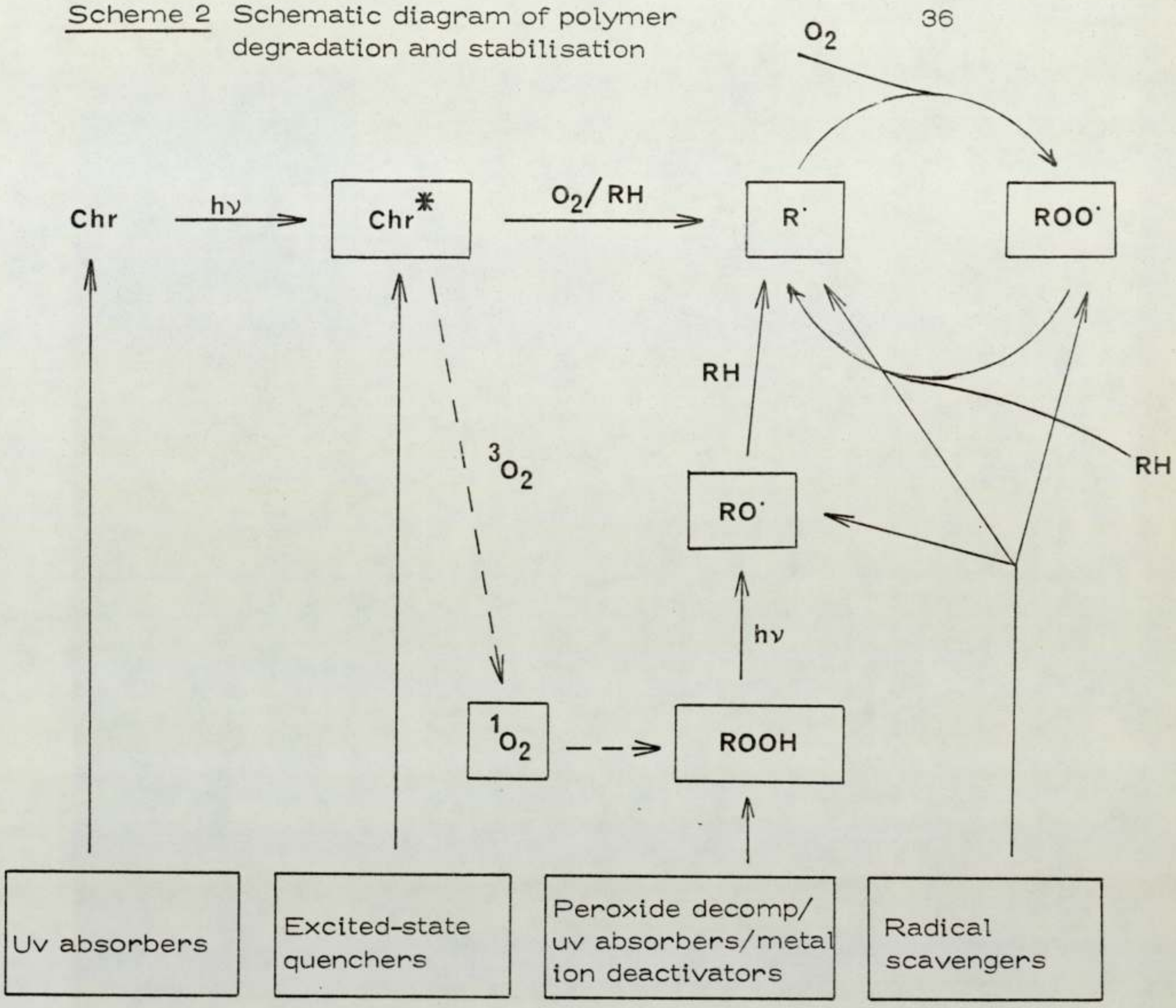
The suggestion that some uv stabilisers may function by deactivating photo-excited states of molecules, particularly of triplet carbonyl and singlet oxygen, arose largely as a result of fundamental photochemical studies in model systems and many attempts have been made to invoke this mechanism to explain the activity of a variety of photo-stabilisers(130-135). Many effective uv stabilisers are indeed efficient quenchers of photo-excited states(133) but so are many more which are not. The transition metal acetyl acetonates, for instance, are quenchers of triplet carbonyl but are among the most powerful photo-activators known(33).

(3) Peroxide decomposers

Notable examples in this class of uv stabilisers are the metal dithiocarbamates(136-138), the dithiophosphates(39, 125) and the cyclic phosphate esters(100, 139) which have been shown to possess high activity as both thermal and uv stabilisers.

Thus oxidation of polymers by the free-radical chain mechanism can be inhibited at several stages in the reaction. This can be depicted by the following schematic diagram(135) (slightly adapted), where Chr = chromophore:

Scheme 2 Schematic diagram of polymer degradation and stabilisation



1.3 Synergistic Behaviour of Antioxidants

Most antioxidants generally exhibit synergism. Synergism can be defined as the co-operative action of the antioxidants such that the overall protective effect is greater than the sum of the two or more individual effects taken independently.

Scott(140) distinguishes two mechanistically distinct types of synergistic behaviour:

(1) homosynergism - this arises from two antioxidants of unequal reactivity but operating by the same mechanism, and

(2) heterosynergism - this is derived from the co-operative effect of two or more antioxidants acting by different mechanisms.

Homosynergism is exhibited by, for instance, two different chain-breaking antioxidants possessing different reactivities towards peroxy radicals. A combination of 2-isopropyl-4-methyl phenol and 2,6-ditertiary-butyl-4-methyl phenol shows homosynergism. The latter is called the inhibitor regenerator since it provides a constant reservoir of hydrogen atoms for the regeneration of the former active antioxidant (due to less steric hindrance) hence greatly lengthening the lifetime of polymer articles.

Heterosynergism comprises combinations of antioxidants in which the various components react at different stages in the oxidation scheme. These synergistic systems may be composed of a chain-terminating antioxidant with either a peroxide decomposer or a uv absorber with a chain-terminating antioxidant, for example, would bring about a reduction in the rate of radical formation and hence the chain-terminating antioxidant would be consumed more slowly(141).

In another combination, comprising a peroxide decomposer and a chain-terminator, each component will reinforce the other. The peroxide decomposer limits the accumulation of hydroperoxide, the chain-terminator is thus preserved and its reactivities to inhibit the kinetic chains results in a lower rate of degradation, thereby extending the usefulness of the peroxide decomposer(142-144).

Another important aspect of synergism, known as autosynergism occurs when two kinds of antioxidant activities are associated in the same molecule(140). This explains for example, the greater effectiveness of amine antioxidants than the phenolics due to their additional ability to complex metal ions, ie amines have a dual functionality of a chain-breaker as well as metal-ion deactivator.

1.4 Need for Physical Retention of Antioxidants within the Polymer System

Although the understanding of the chemistry of the antioxidants' intrinsic behaviour has reached a considerable level of sophistication, it has become apparent over recent years that their physical parameters need also be put in perspective if a realistic approach to the antioxidants' technological effectiveness is to be made.

Three main factors(145) need to be taken into consideration when evaluating antioxidant effectiveness under conditions of service:

(1) the antioxidant's inherent behaviour which is determined primarily by the chemical nature of the antioxidant function,

(2) the microenvironment of the antioxidant in the polymer; this governs the compatibility and ease of migration of the antioxidant, and

(3) the rate of loss of antioxidant from the polymer through volatilisation, extraction, etc.

Hence physical factors which are expected to be important include the antioxidant's volatility, compatibility, migration and solubility(145-147) with the host polymer. Emanuel(148) has even suggested that antioxidant compatibility with the polymer and its volatility are probably more important than the observed effectiveness of the antioxidant in model liquid phase system. It has also been shown(145) that the poor performance of some alkylated hindered phenols as uv stabiliser results in part not only from their photodestruction and formation of sensitising products but also from their relatively low solubility and ease of physical loss.

With the widening use of polymers in many and varied applications, requiring resistance to aggressive environments, the compatibility and extractability factors of the antioxidants are indeed the dominating requirements which must be considered. Instances of polymer articles which come under this jurisdiction are gaskets, radiator hoses, household pipings and sealings. Unquestionably, the antioxidants should not leach out into the liquid medium if they are to provide effective protection to the articles. Basically, two main approaches have been made to prevent or minimise physical loss of antioxidants from the polymer substrates:

(1) increasing the molecular weight of the antioxidant so as to effectively lower the volatility and/or immobilise the antioxidant molecule within the polymer matrix, and

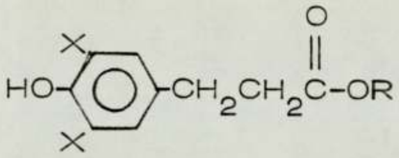
(2) chemically binding the antioxidant to the polymer backbone.

1.5 High Molecular Weight Antioxidants

It is to be expected on the basis of theoretical considerations that increasing the molecular weight of antioxidants should bring about a reduction in their volatilities. Spacht et al(149) carried out basic studies in this area and as expected, volatilities of neat antioxidants decrease with increasing molecular weight. They extended(150) their work to natural rubber gumstock and found that 2,6-di-t-butyl-4-methyl phenol is lost 20 times faster than 2-benzyl-4-methyl-6-t-butyl phenol (at 1 phr concentration) during the curing operation. Their earlier work(149) showed that the vapour pressure of the former is 24 times that of the latter at 100°C. This conclusively shows that molecular weight is indeed an important parameter in determining antioxidant volatility. They also showed(150) that sample thickness obeys an inverse relationship with antioxidant loss and that a significantly higher loss of antioxidant is noted with increasing initial concentration.

Hawkins et al(151) used a number of phenolic and amine antioxidants to test their evaporation property in low density polyethylene. The process of evaporation was carried out by subjecting the individual polymer films containing the antioxidants to a flowing nitrogen atmosphere at 105°C for a fixed period of time. Oxygen absorption tests were then carried out on the 'evaporated' films and they found that higher molecular weight antioxidants performed better, as reflected by the longer induction period. Extraction experiments consisting of placing polymer films in a Dewar flask filled with distilled water at room temperature, were also carried out and again it was shown that antioxidant activity after the extraction process was directly related to the molecular weight of the antioxidant.

Studies on the antioxidant volatility in a pure state and in polypropylene using a series of thiodipropionate and di-t-butyl phenol antioxidants were made by Plant and Scott(145).
Antioxidants used were:

Antioxidant function	Side chain R	Molecular Weight
$(ROCOCH_2CH_2)_2S$	Methyl	206
	Hexyl	346
	Lauryl	514
	Stearyl	702
	Methyl	292
	Hexyl	362
	Lauryl	446
	Stearyl	530

It was demonstrated that the antioxidant volatilities show a strong dependence on molecular weight at various temperatures. In polypropylene, the behaviour of this series of antioxidants was studied by measuring the induction period derived from the torsional braid test in an air-flowing atmosphere at 100°C. Again the induction periods show an increase with increasing molecular weight. This evidence strongly suggests the acute dependence of antioxidant effectiveness on molecular weight.

In a separate study, Evans and Scott(152) further emphasised the positive relationship between antioxidant effectiveness and molecular weight as demonstrated by the better performance of 3,5-di-t-butyl-4-hydroxy-benzyl stearate than 3,5-di-t-butyl-4-hydroxybenzyl acrylate.

Latos and Sparks(153) carried out some work on water leaching of antiozonants in an attempt to evaluate the factors which affect the retention of antiozonants and hence their effectiveness in rubber stocks. They found that the molecular weight of an additive is also an important factor in determining the amount of additive leached out. In the field of uv absorbers, DeCroes and Tamblyn(154) carried out an elegant study on low density polyethylene and demonstrated the superior performance during photo-oxidation of the higher molecular weight 2,2'-dihydroxy-benzophenones by varying the alkoxyl group in the 4 position.

In an attempt to obtain a high molecular weight antioxidant, an antioxidant-monomer, 3,5-di-t-butyl-4-hydroxybenzyl acrylate was polymerised so that the antioxidant-polymer was formed(152). Surprisingly, it was found that the effectiveness of the antioxidant-polymer in polypropylene does not reflect its non-volatility characteristics in an air-flowing atmosphere. It was postulated that this may result from its almost complete lack of solubility and compatibility in the polymer since the melting point of the antioxidant-polymer (ca 225°C) is well above tne temperature used for processing and compression moulding of the polymer (180°C). The important inference that emerges from this evidence is that high molecular weight is not the only criterion in determining the degree of physical retention and effectiveness of antioxidants. Other equally important factors such as solubility and compatibility need also to be considered. In fact Evans and Scott(152) pointed out that there is a limit to antioxidant effectiveness as molecular weight increases due to compatibility and mobility limitations.

A limited amount of information is available on the compatibility of antioxidants with polymers and the attendant relationship between compatibility and the antioxidant activity. Difficulties arise in defining the precise meaning of compatibility of an additive in low concentrations with a polymer particularly when the latter exhibits a crystalline structure. Nevertheless, attempts have been made by several workers in this direction.

Ambrovic and Mikovic(155) in their study of antioxidant compatibility used differential thermal and enthalpic analyses of first-order transitions on polypropylene containing various phenolic antioxidants and uv stabilisers of the alkoxy-substituted benzophenones. They concluded that the bis-phenolic antioxidants exhibit greater compatibility with the more ordered regions of polypropylene than those of the monophenolics. It was also shown that the compatibility of the uv stabilisers increases as the alkoxy side chain is lengthened. They suggested that antioxidants could be divided into two groups: those which dissolve in the crystalline regions and thereby decrease the melting point of the polymer; and those which dissolve only in the amorphous regions of the polymer and thus do not decrease the melting point.

However, the high concentrations of antioxidants which were used by Ambrovic and Mikovic (10%) may cast some doubt on the validity of the conclusions due to the possible modification of the crystal structure of the substrate polymer. It is not clear that a similar situation will exist at the technologically acceptable levels of addition of antioxidants (0.1-0.3%).

An investigation by Parrini and Corrieri(156) which attempted to overcome some of the above limitations, was based on the principle(157) that a compatible diluent decreases the rate of crystallisation of a crystalline polymer and that the decrease is proportional to the amount of the diluent present. Insoluble substances such as pigments can increase the rate of crystallisation by nucleation(158). Using the dilatometric technique, it was found possible to separate compatible and incompatible additives at concentrations below 1%. Using this technique, Parrini et al(159) investigated the compatibility of a series of alkoxy-substituted benzophenones in polypropylene (at less than 2% concentration), and in contrast to Ambrovic and Mikovic's findings(155) they found that the compatibility of the additives with polypropylene remains consistently similar as the length of the alkoxy side chain is increased. They offered no explanation for the phenomenon but presumably the large concentration difference of the additives used does contribute to the anomaly.

Frank and Lehner,(160) in attempting to make a direct determination of antioxidant distribution in polypropylene as a measure of compatibility by a uv microscopy technique, showed that a benzotriazole derivative resides predominantly in the non-crystalline region. It was suggested that this behaviour should generally be applicable to other additives in a crystalline polymer. Recently a similar finding was made by Billingham et al(161) in their studies on a nickel-containing additive in polypropylene using uv as well as fluorescence microscopy.

Thus the compatibility of an antioxidant with a crystalline polymer can probably be considered in terms of the degree of interaction between the additive and the less ordered regions of the polymer matrix. In polypropylene, both the inter-spherulitic amorphous regions and the intra-spherulitic areas of low crystallinity between the individual crystallites seem to be capable of retaining the antioxidants. Fortuitously the accumulation of antioxidants in the amorphous phase of the polymer matrix appears to be advantageous since Hawkins and Winslow(162-165) have demonstrated that the major oxidation reactions occur primarily in the less ordered areas.

Newland(166) quantified the degree of compatibility of a series of alkoxy-substituted hydroxybenzophenones in polypropylene by measuring the time which elapsed before a visible exudation of the antioxidants to the polymer surface occurred. The exudation time was not found to be simply related to the chain length of the alkoxy substituents; in the series up to the octadecoxy derivative, the heptoxy and dodecoxy-substituted stabilisers were found to exhibit the longest exudation times by two orders of magnitude. These findings are perhaps not unexpected in that the assessment of compatibility using the criterion of exudation time will be complicated by the rate of diffusion or migration characteristics of the stabilisers in the polymer.

The diffusion of large molecules through highly crystalline polymers has been reported by several workers(167–172). They showed that the rate of diffusion of an additive tends to decrease with increase in polymer crystallinity and diffusant molecular weight. It has been suggested(167,170) that the additives tend to diffuse solely through the less ordered regions, and the crystalline structures of the polymer impose an extremely tortuous path upon the diffusant. The technological implication of these findings is that the effectiveness of high molecular weight antioxidants is inversely related to their migration characteristics and that higher molecular weight antioxidants will offer better physical retention within the polymer matrix.

Chien and Boss(172) carried out an elegant study on stabilisation reactions by diffusion and demonstrated that the kinetics of the reactions of 2,6-di-t-butyl-4-methylphenol in squalene and polypropylene are similar. They pointed out that this is indicative of the fact that the reaction between the antioxidant and the peroxy radical of the polymer is thus not controlled by diffusion phenomena. Hawkins and his co-workers(162–175) also provided evidence that the immobility of an antioxidant need not necessarily preclude its stabilising activy so that a high molecular weight antioxidant is not disadvantageous provided the compatibility criterion is met.

High molecular weight antioxidants, therefore, not only provide low volatility but also offer better retention within the polymer matrix through low mirgration characteristics. However, the molecular weight of the antioxidant has a limiting value above which physical retention and chemical activity are impaired through antioxidant/polymer incompatibility.

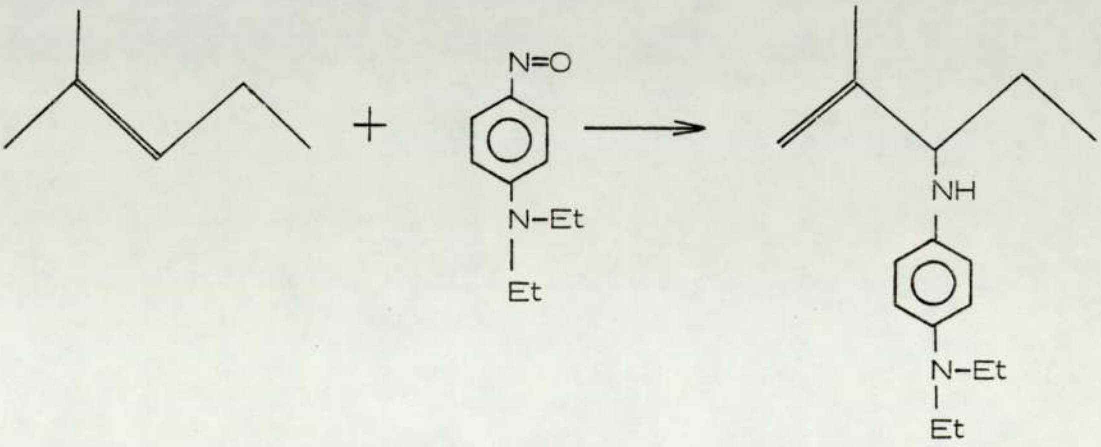
1.6 Polymer-bound Antioxidants

Seven distinct approaches have been made by recent researchers to chemically bind antioxidants to the polymer backbone. These will be briefly discussed in the following sections.

(1) Use of nitroso compounds

Cain et al(174) have probably made an important contribution in this field. They showed that during vulcanisation, nitroso compounds are successfully bound to natural rubber as evidenced by the high antioxidant activity after the azeotrope extraction process. The compounds used were: N,N-diethyl-p-nitrosoaniline, p-nitrosodiphenyl amine and p-nitrosophenol. It is also apparent from the results that the reduction in antioxidant mobility due to the chemical binding in the network chain does not significantly decrease the antioxidant effectiveness. Even though the process is technologically attractive and requiring no deviation from standard compounding practice, the discolouration imparted to the gum vulcanisate can be a disadvantage in some applications. They suggested that structural variations of the nitroso compounds would remedy the problem. The binding reactions have also been successfully carried out with SBR, NBR and chloroprene rubber(175).

Based on model compound studies on 2-methyl pentene(174,176), N,N-diethyl-p-nitrosoaniline is thought to undergo the following reaction during the vulcanisation of natural rubber:



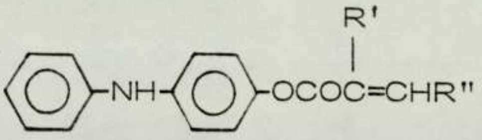
Recently Fedorova and Kavum(177), using p-nitrosodiphenyl amine on unfilled natural rubber and utilising the techniques of stress relaxation and fatigue lifetime, arrived at similar conclusions.

(2) Use of polymerisable compounds

Polymerisable compounds containing antioxidant function which have been grafted to polymers include 3,5-di-tert-butyl-4-hydroxybenzyl acrylate (DBBA), 3,5-di-tert-butyl-4-hydroxy phenyl acrylate (DBPA) and N-(4-anilinophenyl)acrylamide. Cooray(178) and Amarapathy(179) have carried out a detailed investigation of the grafting reactions of DBBA with natural rubber latex. Reaction variables such as temperature, pH, soap concentration and initiator type and concentration which, in combination would effect optimisation of the grafting reactions were established. Even after being subjected to an azeotrope extraction, the polymer was found to possess a high degree of antioxidant retention as indicated by the oxygen absorption and stress relaxation tests. The masterbatch technique was successfully developed and highlighted the possible commercial exploitation of the process.

Evans and Scott(152) using a similar antioxidant (DBBA), found that grafting could also be effected on a polypropylene artefact by uv light with benzophenone being used as an initiator. It was shown that the polypropylene film imparts a much improved oxidative resistance after acetone extraction.

Meyer et al(180, 181), in an attempt to form a polymer-bound antioxidant, successfully copolymerised monomeric antioxidants of the general type,



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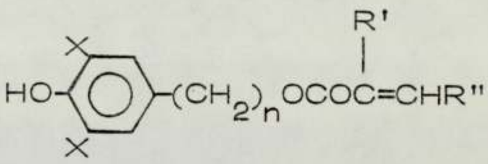
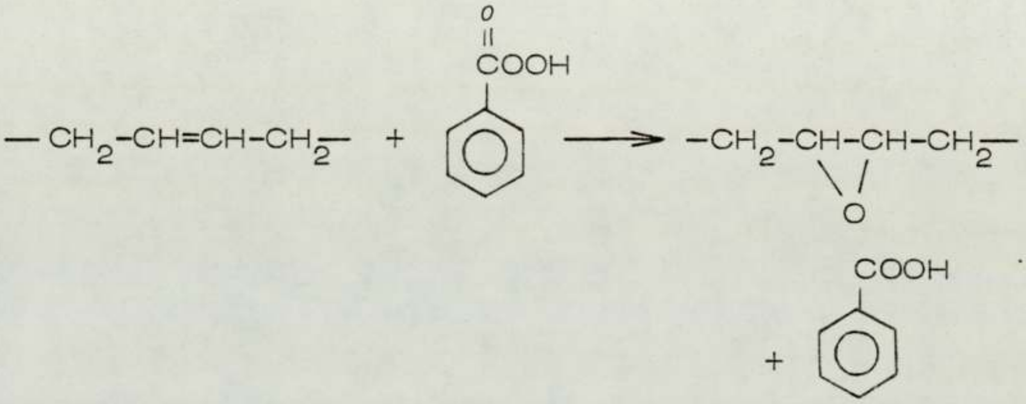


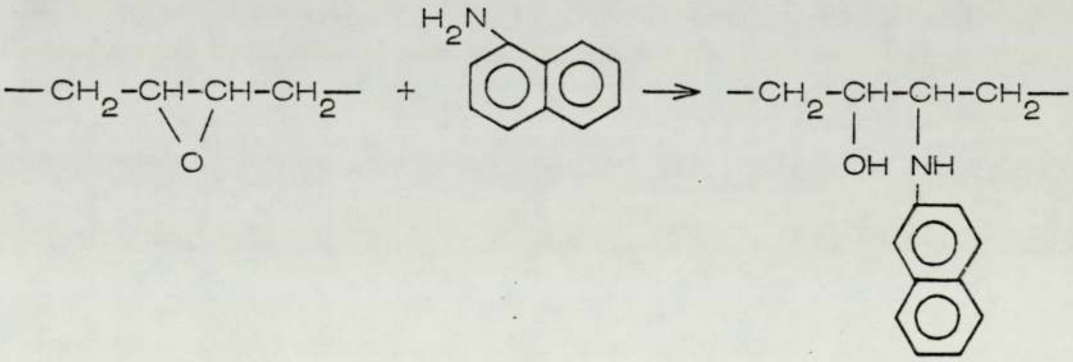
with SBR and NBR emulsions. It was demonstrated that the antioxidants retain their normal protective characteristics in the copolymerised form and are not removed by solvent extraction nor by volatilisation. Kline and Miller(182) obtained similar results on their work on SBR emulsion systems.

(3) Epoxy modification of polymer chains

The principle of the process, which has been utilised by Kirpichev et al(183), requires introducing reactive epoxy groups into the polymer (polybutadiene) chain and reacting the modified rubber with suitable antioxidant such as β-naphthylamine to form a polymer-bound antioxidant. Epoxidation of the polymer was achieved by a reaction with a perbenzoic acid:



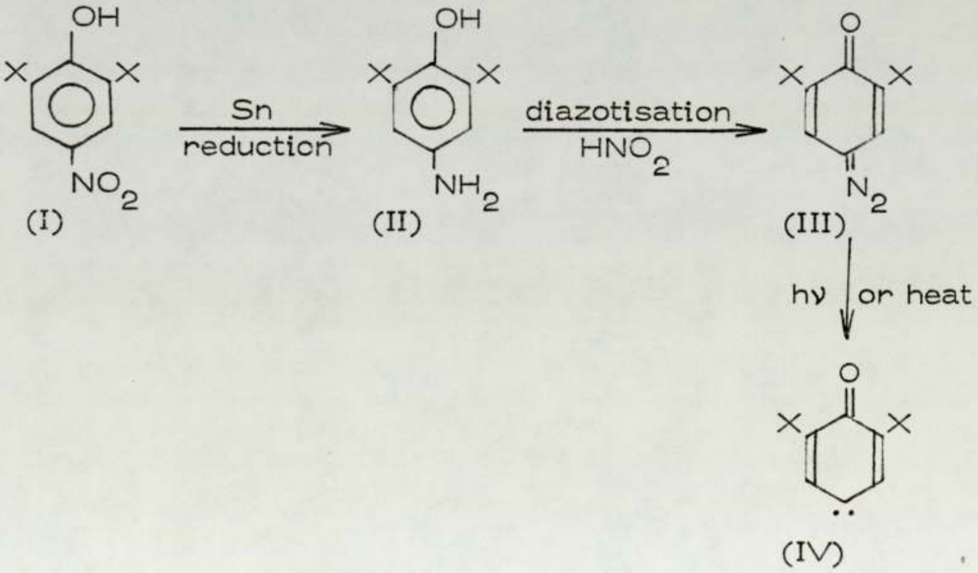
The resultant modified chain, under suitable reaction conditions and with phenol as catalyst, reacts with β-naphthylamine to produce a network-bound antioxidant,



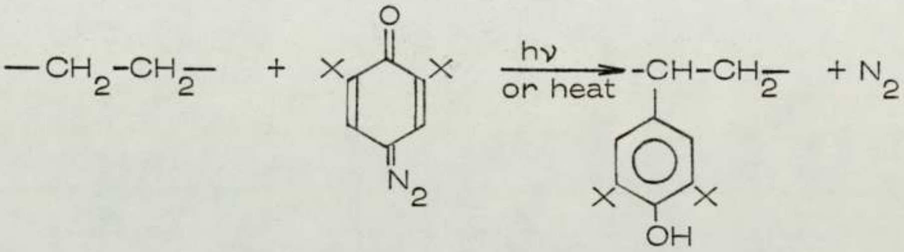
The binding reaction was demonstrated by uv and ir spectral evidence. In their subsequent work,(184) they also showed the successful binding of p-aminodiphenylamine to the epoxidised polybutadiene. These workers were mainly involved with the kinetics and activation energies of the reactions and avoided the actual oxidative study of the modified polymer. It is to be expected however that the modified polymer will exhibit superior oxidative properties.

(4) Use of a reactive carbene derivative of an antioxidant

Kaplan et al(185, 186) found that nitrophenol (I), after undergoing a series of reactions under specified controlled conditions, results in the formation of a reactive intermediate known as a carbene, a species with a divalent carbon atom (IV),



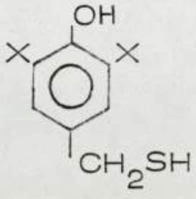
It is known that carbenes can insert themselves into C–H bonds and it is this reaction which has been exploited by these workers to produce a polymer-bound antioxidant in LDPE, polypropylene and polyoxymethylene, eg:



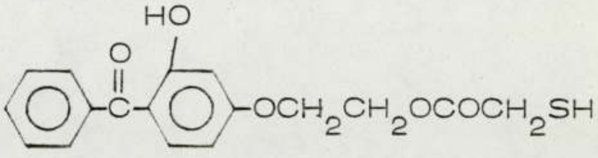
It is evident that this work has potential commercial advantage in that the binding of the antioxidant could be achieved during any heat treatment in the conventional processing of polymers (eg extrusion, calendering or even vacuum forming). They convincingly showed the superiority of the antioxidant-bound polymer from oxygen absorption studies.

(5) Use of mercapto compounds

Little work has been done with mercapto compounds apart from the studies which have been carried out by W S E Fernando(187), Kularatne(188a) and M R N Fernando(188b) on ABS and natural rubber latices. They showed the superior performance of polymers containing I and II to oxidative degradation even after



(I)

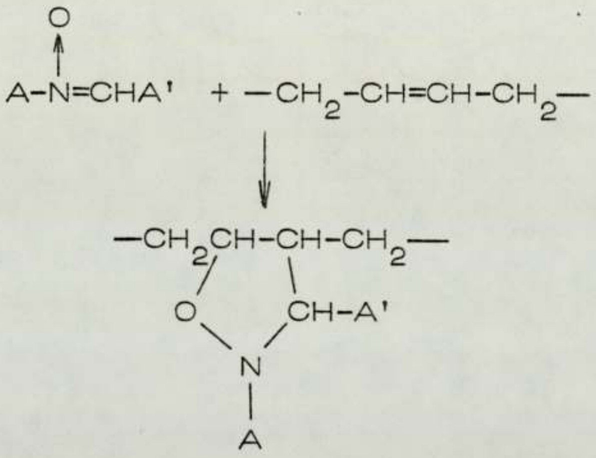


(II)

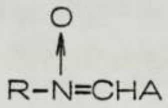
solvent extraction due to the binding of the additives to the polymer backbone as well as the operation of autosynergism of the bound additives. Recently Cooray and Scott(189) have demonstrated that antioxidant of type I became bound to PVC during melt processing, simultaneously lowering the discolouration imparted to the processed polymer. This finding is potentially important since PVC, despite its versatility and cheapness, suffers discolouration during processing due to dehydrochlorination with concomittant conjugated double bonds formation. In all cases, reaction of the thiyl radicals with the double bond is thought to play the key role in the binding reactions.

(6) Use of nitrone compounds

The 1,3-cycloaddition of nitrones to the double bonds in elastomers provides a general technique for introducing an antioxidant group (A or A') into a rubber molecule. This technique has been successfully applied to cis-polybutadiene and cis-polyisoprene during vulcanisation using a variety of curing systems(190-192).



Amine and phenolic nitrones of the structure,

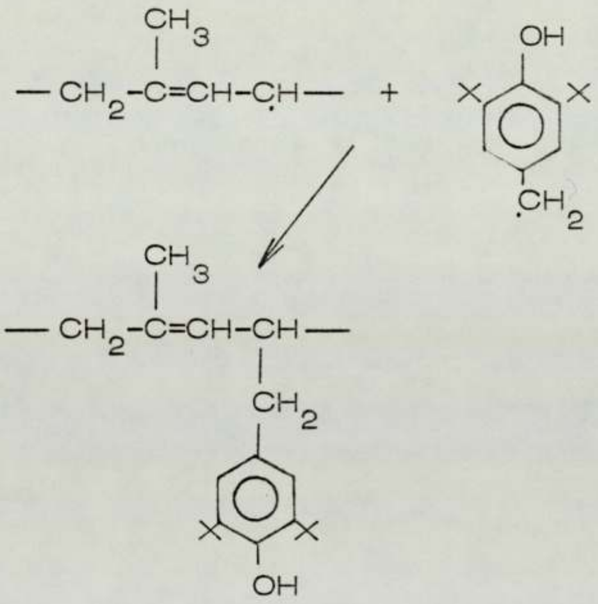


$$R\text{-}\overset{\overset{O}{\uparrow}}{N}\text{=CHA}$$

were found to react readily with rubber during vulcanisation to give a superior antioxidant-bound polymer under aggressive environments.

(7) Use of benzyl radicals

Recently, Kularatne and Scott(193) demonstrated a radical-radical coupling of a benzyl radical containing an antioxidant function with an allylic carbon of natural rubber latex to obtain a bound antioxidant imparting excellent oxidative resistance to



the polymer after solvent extraction even though the percentage bound is of the order of 11% based on the original amount of antioxidant added (2 phr). With the cheapness of the antioxidant which is readily available on the market and with the ease of effecting the binding reaction (using the tert-butyl hydroperoxide/ tetraethylene pentamine initiator system) the process is certainly attractive and feasible for commercial exploitation especially in the manufacture of rubber gloves, prophylactics and ladies stockings.

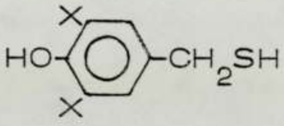
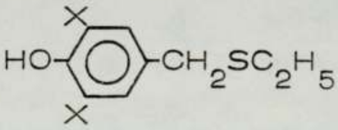
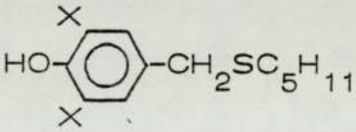
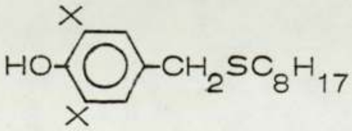
1.7 Aim and Scope of Project Work

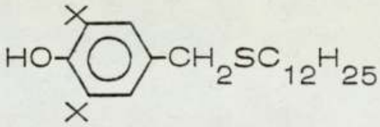
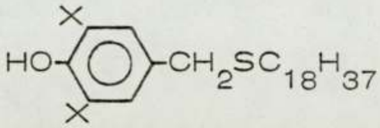
Over recent years there has been an increasing trend towards the use of high molecular weight antioxidants in polyolefins in an attempt to enhance the additives' substantivity within the polymers. This is evidenced by the use of three industrially important antioxidants, viz: Topanol CA (ICI, Mwt = 542), Irganox 1076 (Ciba-Geigy, Mwt = 530) and Irganox 1010 (Ciba-Geigy, Mwt = 1176). The current literature indicates that considerable efforts are being made to produce still higher molecular weight antioxidants for many polymers.

The purpose of the present investigation was to gain a further insight into the relationships between antioxidants' molecular weight and their stabilising activity in polymers under practical technological applications. This is based on the premise that the net performance of any antioxidant in polymeric substrate is a function of not only its intrinsic chemical activity but also of its physical characteristics. These include compatibility, solubility, and volatility phenomena. It was therefore desirable to assess the individual contributions made by these factors.

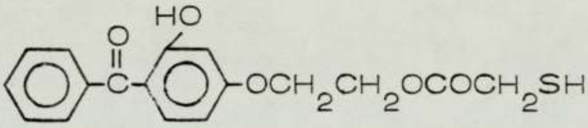
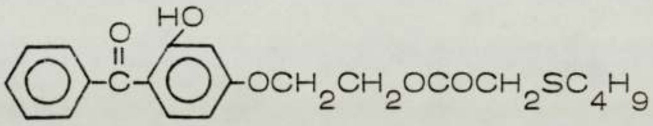
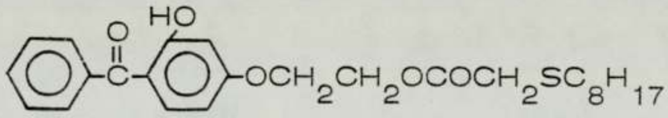
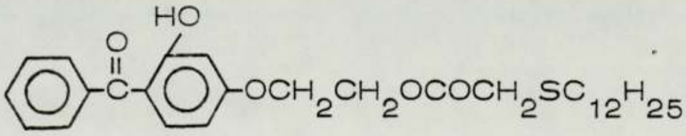
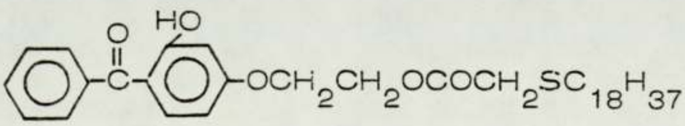
In order to evaluate the effects of the individual parameters towards the overall stabilisation of polypropylene, the following two series of antioxidants and uv stabilisers of increasing molecular weight based on sulphur compounds were selected for synthesis:

(1)

Antioxidant Series	Code to be used
	BHBM (AOS-H)
	AOS-C2
	AOS-C5
	AOS-C8

	AOS-C12
	AOS-C18

(2)

Uv-stabiliser Series	Code to be used
	UVS-H
	UVS-C4
	UVS-C8
	UVS-C12
	UVS-C18

It was proposed initially to determine the activity of the antioxidants in a liquid hydrocarbon substrate using a restricted atmospheric environment in an attempt to assess their inherent chemical activity in the absence of any physical constraints. The antioxidant performance in polypropylene was then to be monitored at elevated temperatures under two sets of conditions: evaluations being carried out in a restricted environment in order to elicit the additive-polymer compatibility influence and simultaneously suppressing the volatility effects, and in a flowing atmosphere where volatilisation would become apparent. In addition, the solubility measurements of antioxidants in a liquid hydrocarbon solvent should provide supportive indication of the degree of the antioxidant compatibility within the polymer system. The synthesised compounds were to be compared with commercially available antioxidants and uv stabilisers, viz: n-octadecyl-3-(3',5'-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076, Ciba-Geigy), 2,6-di-tert-butyl-4-methylphenol (Topanol OC, [TBC], ICI) and 2-hydroxy-4-octyloxybenzophenone (Cyasorb UV531,[HOBP], Cyanamid Inc).

Furthermore, the photo-stability of polypropylene films containing various antioxidant systems was to be assessed, and related to their varying processing melt treatments which were always involved in the fabrication processes.

Synergistic studies of the synthesised phenolic (sulphur) antioxidants, typified by 3,5-di-tert-butyl-4-hydroxybenzyl mercaptan (BHBM) and 3,5-di-tert-butyl-4-hydroxybenzyl lauryl sulphide (AOS-C12) with the commercial UV531 would also be made. Their performance would be compared with those exhibited by Irganox 1076 and Topanol OC (TBC).

Further improvement of antioxidant substantivity and compatibility would be investigated on the basis of the possible binding reactions of TBC and BHBM with the polymer and the simultaneous formation of higher molecular weight antioxidant derivatives during the melt processing operations. A uv-initiated grafting of BHBM to polypropylene films was also to be studied both in oxygen and nitrogen atmospheres and its application as a polymeric antioxidant masterbatch for virgin polypropylene was to be investigated.

CHAPTER TWO

EXPERIMENTAL

2.1 General Experimental Techniques

2.1.1 Materials: Sources and Purification Methods

The purification of the reagents used in the present work were substantially based on the methods described by Weissberger(194). The literature values were quoted either from the 'Handbook of Chemistry and Physics'(195) or the 'Dictionary of Organic Compounds'(196).

(a) Polypropylene - Unstabilised polypropylene in powder form (Propathene HF 184/CV 170) was supplied by Imperial Chemical Industries Limited and was stored in sealed containers in a refrigerator (-15°C).

(b) Phenolic antioxidants - Two commercial antioxidants were used: one is a long-chain monophenol, n-octadecyl-3-(3'-5'-di-tertiarybutyl-4-hydroxyphenyl)propionate being marketed by Ciba-Geigy Limited under the trade name of

Irganox 1076; and the other is a relatively low molecular weight monophenol, 2, 6-di-tertiarybutyl-4-methylphenol supplied by Imperial Chemical Industries Limited under the trade name of Topanol OC. Both were recrystallised from ether with their melting points being 51 and 72°C respectively.

(c) Ultra-violet stabiliser - The most widely used commercial uv stabiliser, 2-hydroxy-4-octyloxy benzophenone was taken for the present study. It was supplied by American Cyanamid under the name UV531.

(d) 2,6-di-tertiarybutylphenol - This was obtained from Aldrich Chemical Company Limited at 99 + % purity and was used without further purification in the syntheses of antioxidants.

(e) 2,4-dihydroxybenzophenone - A 99 + % purity grade was obtained from Koch Light Limited and was used direct in the syntheses of uv stabilisers.

(f) Alkyl bromide - The following were used as supplied by Koch Light Limited:

n-Butyl bromide, bpt 100-104°C; n-Octyl bromide, bpt 201°C; n-Dodecyl bromide, mpt -10 - -9°C, bpt 134-135°C/6 mm; n-Octadecyl bromide, mpt 26-28°C.

(h) Thioglycollic acid - This was used as supplied by Aldrich Chemical Company Limited, mpt -16°C, bpt 96°C/5 mm.

(i) Paraformaldehyde - This was used as obtained from Koch Light Limited.

(j) Azobisisobutyronitrile (AZBN) (ex Koch Light Limited) was recrystallised from ether, mpt 105°C (106°C(195)).

(k) Hexane was used for the solubility measurements of antioxidants. The technical grade was fractionally distilled at 69°C before use (ex Aldrich Chemicals).

(l) Chlorobenzene - The general purpose grade (ex BDH Limited) was fractionally distilled from phosphorus pentoxide and the fraction boiling at 132°C was collected (132°C/760 mm(195)).

(m) Dichloromethane - Standard laboratory reagent grade (ex Fisons) was distilled and the fraction boiling at 40°C was collected (40°C/760 mm[(196)]).

(n) 36% Hydrochloric acid - This was obtained from BDH Limited.

(o) Decalin - Technical grade decalin (ex BDH Limited) was distilled and the distillate was washed with successive solutions of 10% sulphuric acid until no further darkening occurred. It was then washed with water, sodium hydroxide and again with water and dried over calcium sulphate. The product was distilled in vacuo at 1 mm with a slow nitrogen purge (bpt 40°C). The centre cut was collected and stored in nitrogen at -15°C.

(p) Tertiarybutyl hydroperoxide (ex Koch Light Limited) - This was purified according to the method of Kharasch et al(197). To a cooled (0°C) solution of 200 g of technical grade tertiarybutyl hydroperoxide in 200 ml hexane, 160 ml of a cooled 25% aqueous solution of soidum hydroxide was added. The sodium salt which separated was washed with 100 ml of the sodium hydroxide solution followed by hexane. The salt was then suspended in hexane and the tertiarybutyl hydroperoxide was liberated by a treatment with acetic acid. The hexane layer was thoroughly washed with water and was then fractionally distilled. The fraction boiling at 60°C/ 12 mm was collected.

(q) N-bromosuccinimide (NBS) - This was used as supplied by BDH Chemicals Limited, mpt 181-182°C.

2.1.2 Incorporation of Additives and Processing of Polymers

The additives were tumble mixed with the powdered polymer, either dry or, where necessary, dissolved in the minimum quantity of an extremely volatile solvent, normally dichloromethane which was removed by rotary evaporation under reduced pressure.

Processing conditions were simulated by the use of the prototype RAPRA torque rheometer(198). This is essentially a small mixing chamber, containing mixing screws contra-rotating at different speeds. It has good temperature control, and a continuous readout is provided of both melt temperature and the torque required for mixing. The chamber may be operated either open to the atmosphere or sealed by a pneumatic ram. A full charge was 35 g of polypropylene and when this charge was used the chamber was sealed and processed for varying periods. When it was desired to process in the presence of oxygen, a charge of 20 g was employed and the chamber left open to the atmosphere. A minimum processing time of 5 mins was required to ensure complete fusion of the polymer.

On completion of processing, the polymer sample was rapidly removed and quenched in cold water to prevent further thermal oxidation.

2.1.3 Determination of Torque -vs- Time Curve

An idealised torque -vs- processing time curve(199) is depicted in Fig 2.1. Initially there is a sharp rise in the torque when the polymer is introduced into the processing chamber of the RAPRA torque rheometer (point a). As the polymer gradually melts, the torque decreases and reaches a minimum (point b). This is then followed by a slight increase in torque due to the transition from the rubbery to the melt phases (point c). The time to reach point c is called fusion or flux time. The fusion

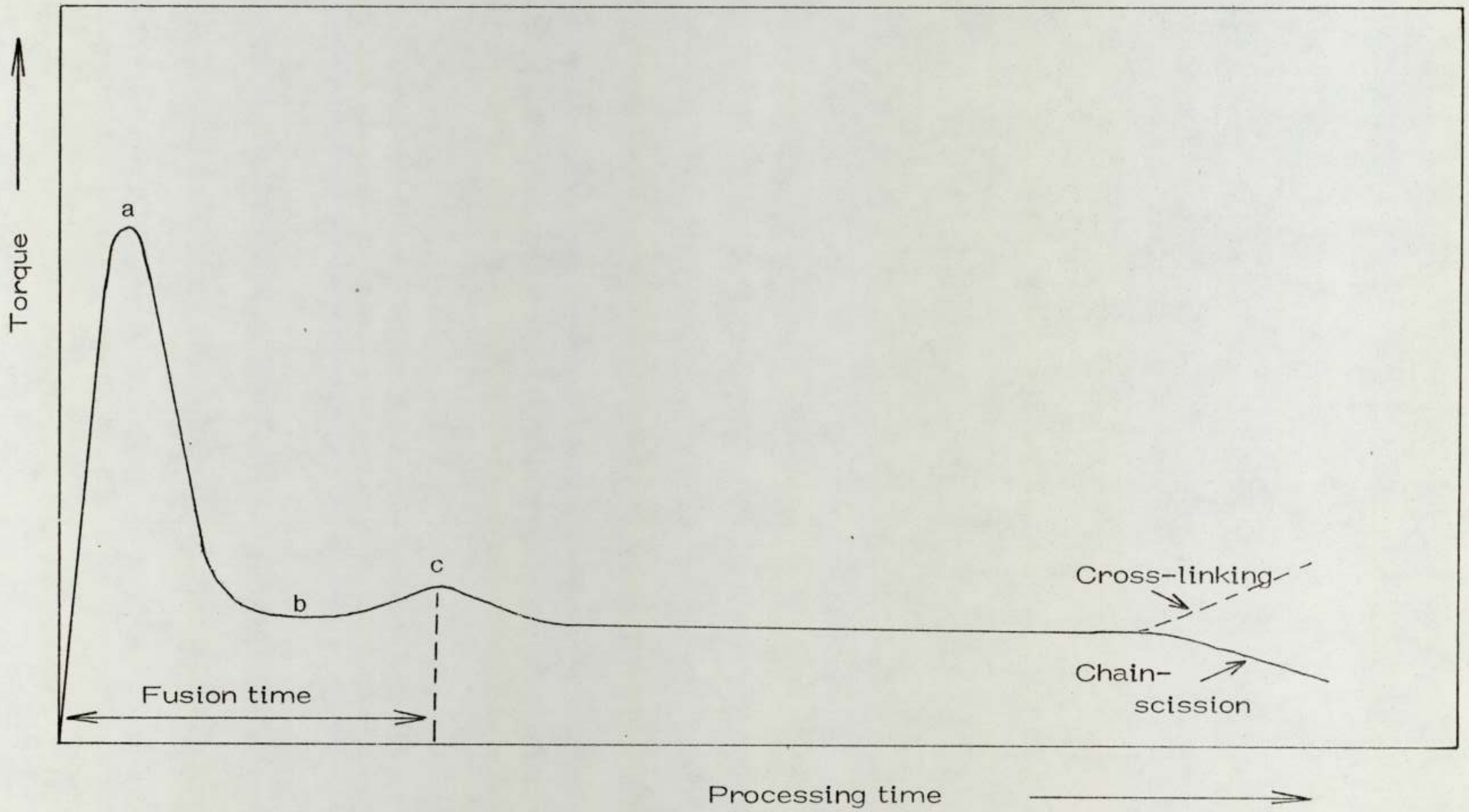


Fig 2.1 An idealised torque -vs- processing time curve

time of a particular polymer shows a strong dependence on mechanical stress, temperature and the presence of additives. Irreversible changes due to thermal oxidative degradation (eg cross-linking or chain-scission) during further processing of the polymer may be reflected by the subsequent increase or decrease of torque.

2.1.4 Preparation of Polymer Films

The films were obtained by compression moulding of processed polypropylene using stainless steel glazing plates. The plates were thoroughly cleaned before use to ensure smooth surfaces and a special grade of cellophane paper was used to prevent the film sticking to the plates. Control of film thickness was achieved by using a standard quantity of polymer ; about 6.5 g of polypropylene was found to produce film of approximately 1.8×10^{-2} cm (0.007"). The weighed amount of the polymer was placed between the glazing plates and inserted into an electric press whose platens were maintained at 180±2°C. After an initial pre-heating of 0.5 min and subsequently subjecting the sample to a pressure of 85 kg/cm^2 (60 tons on a 12-in diameter ram) for a further 2 mins, the platens were cooled to about 40°C by running cold water while maintaining the full pressure. The plates were then removed from the press and the films obtained were stored in the dark. Portions of uniform thickness and dimensions were cut for testing.

2.1.5 Oxygen Absorption Measurement

Numerous types of apparatus for measuring gas absorption have appeared in the literature, the most common type consisting of a simple manometer(200) or a more elaborate version of it(201,202). The present work employed the latter technique in preference to the former. Absorption of oxygen by the sample was followed continuously and automatically by means of a strain gauge type pressure transducer (Pye Ether Limited, Model UP3, 5 psi range). This was connected to an absorption vessel containing the sample and a ballast vessel of corresponding dimensions. The vessels were placed side by side in a thermostatted oil bath (140± 0.5°C) as shown in Figs 2.2 and 2.3.

As oxygen was absorbed by the sample, a pressure difference developed between the two vessels, proporortional to the output voltage of the transducer. The latter was monitored using a Perkin Elmer Model 165 recorder. The system was calibrated by syringing out known volumes of oxygen.

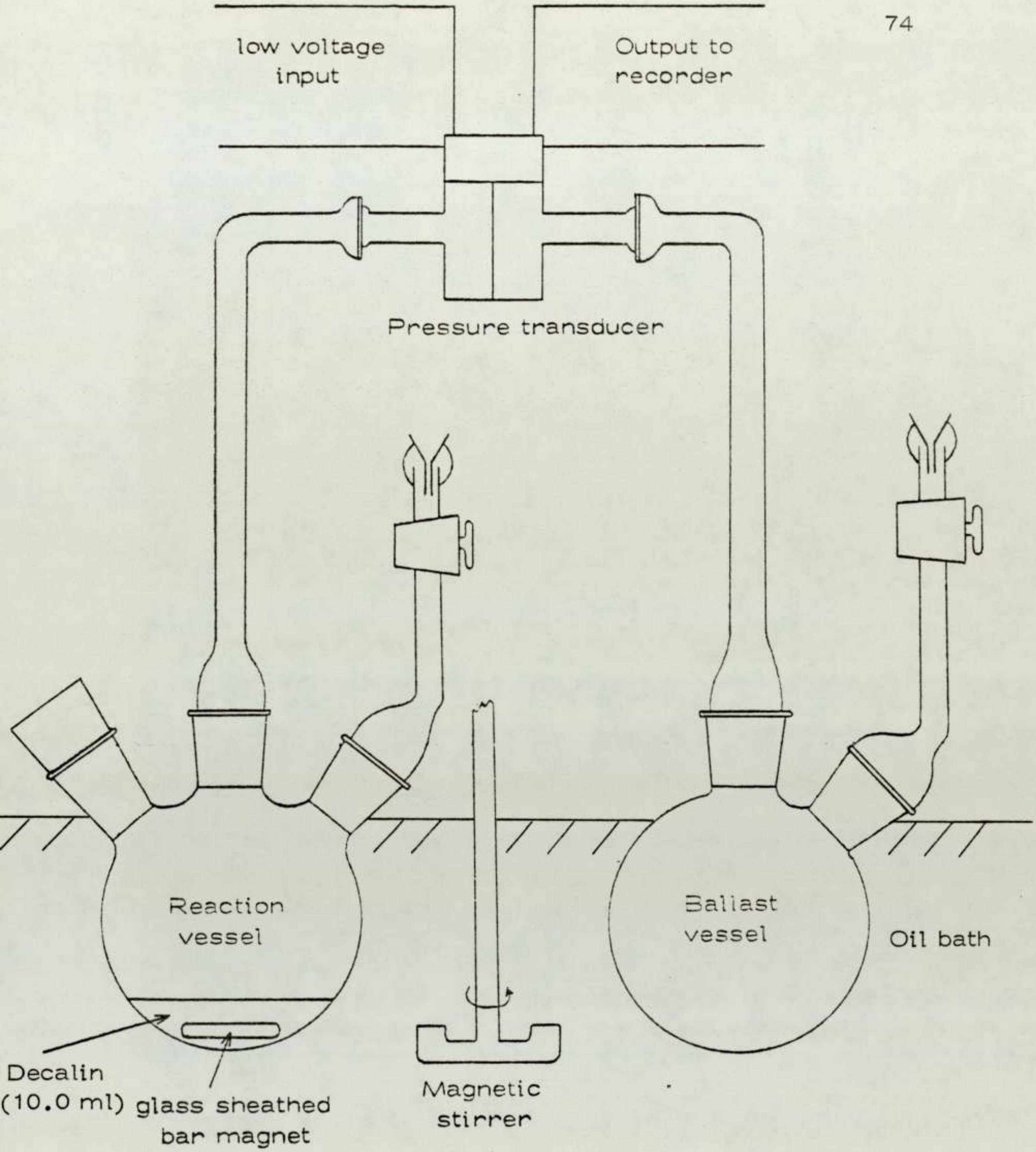


Fig 2.2 Oxygen absorption studies of liquid substrate (decalin) at 140°C

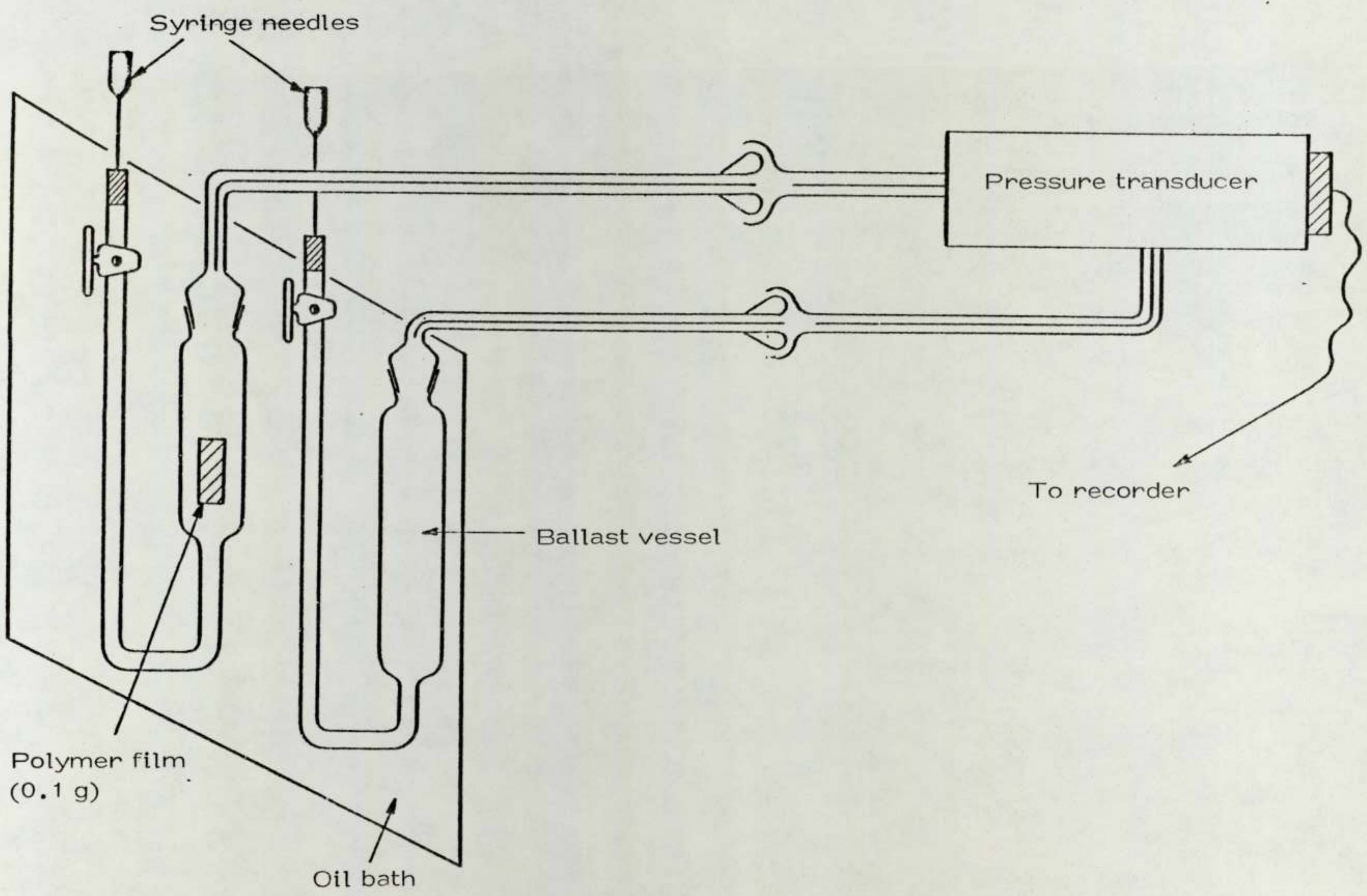


Fig 2.3 Oxygen absorption studies of polypropylene film at 140°C

2.1.6 Thermal Ageing of Polymer Films

The accelerated thermal oxidations of processed polymer films were carried out in a Wallace oven at 140°C in the presence of air. Each sample was contained and suspended in a separate cell to prevent the cross-contamination of the additives by volatilisation and was subjected to an air flow of 3.0 cu ft/hr (85 litres/hr).

2.1.7 Ultra-violet Irradiation of Polypropylene Films

All the film samples were irradiated in an ultra-violet light ageing cabinet (supplied by Ciba-Geigy Limited), cylindrical in shape and composed of 1:3 combination of fluorescent sun lamps and black lamps each of 20 watts power and mounted alternately around the periphery of the metallic cylindrical board which was mounted vertically on the circumference of a rotating drum fixed inside the cabinet. In this manner, the light beam fell perpendicularly and isotropically on the surface of the film. The distance of the sample from the light source was 10 cm and the temperature recorded inside the cabinet with the light on was $30 \pm 1^{\circ}C$.

Fig 2.4 compares(203) the radiation from the 1:3 combination of sunlamps/black lamps with that from the sun.

2.1.8 Measurement of Brittle Fracture Time of Polymer Films

This is essentially a destructive test method. Films of identical size (3 cm x 4 cm) and of uniform thickness (1.8×10^{-2} cm) containing various additives along with the control were uv irradiated or thermally aged at 140°C. They were periodically checked for embrittlement times. The time to embrittlement was determined by a manual bending of the film onto itself, ie to an angle of 180°C. Each polymer sample was carried out in triplicate. The reproducibility of the results was found to be good and variation from the mean value was of the order ± 2.5%.

2.1.9 Solvent Extraction of Polymer Films

Non-bound free antioxidants and other derived soluble materials were removed from polypropylene films by a cold acetone extraction process. This involves subjecting the films (0.007 in thickness) to continuous contact with a regulated stream of acetone which was replenished by an adjoining distillation

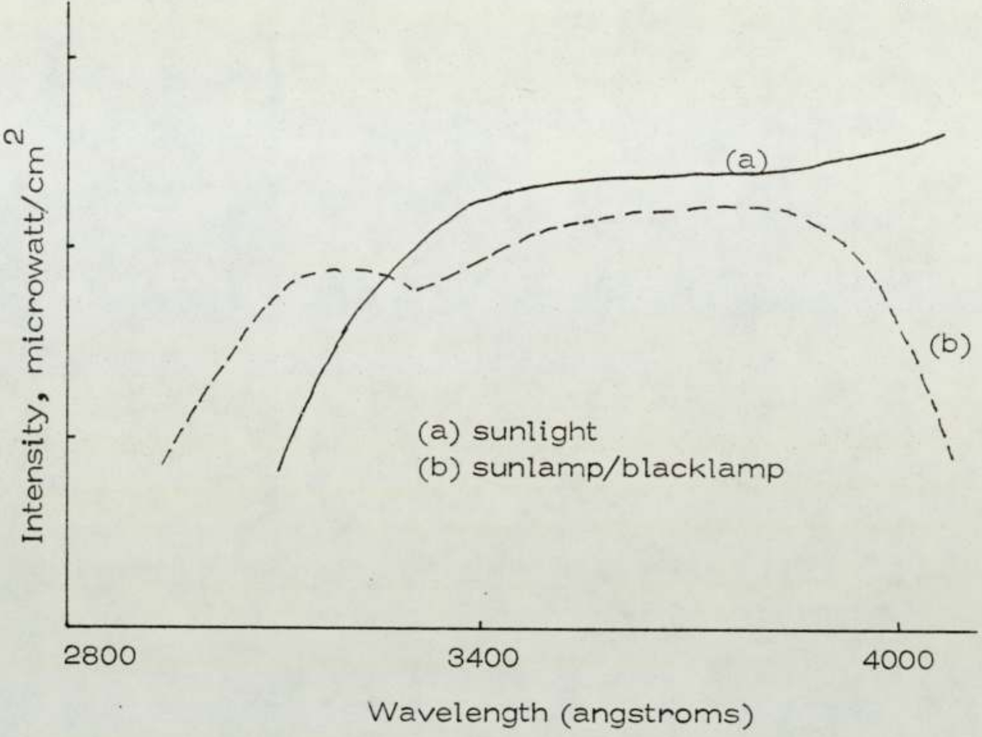


Fig 2.4 Comparison of radiations of ordinary sunlight and sunlamp/blacklamp(203)

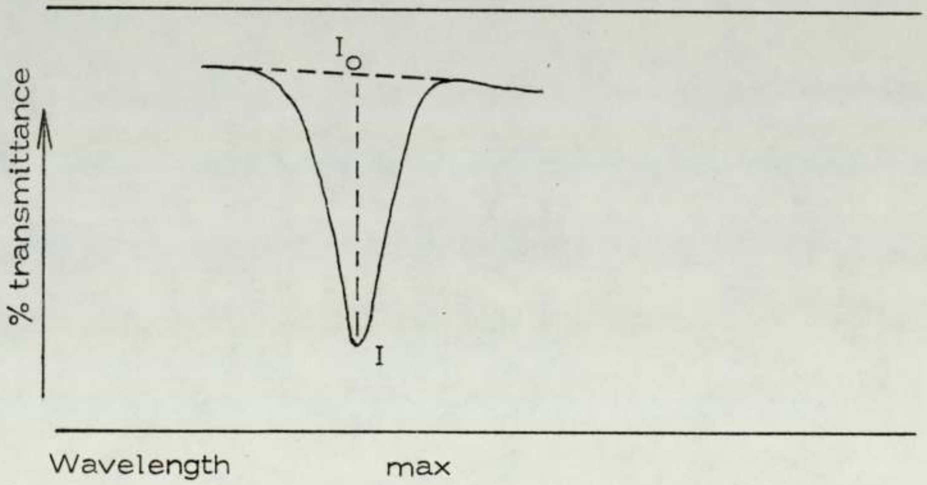


Fig 2.6 Baseline technique of functional group measurement

set-up. It was found that a 100-hr period of extraction was sufficient to completely remove all the soluble materials in the films. The cold extraction was preferred to the normal hot Soxhlet extraction in order to minimise the oxidation of the polymer films.

2.1.10 Chemical Measurement of Polymeric Hydroperoxides

The method used by Manasek et al(48) and Geddes(204) was modified as follows: 0.5–1.0 g of polymer film (in small pieces) was introduced into 20 ml of chloroform and purged with nitrogen for half an hour. The polymer was then allowed to swell for 18 hrs. 3.3 ml of glacial acetic acid was added and the solution was purged with nitrogen for 3–5 mins before and after addition of freshly prepared deaerated 5% solution of sodium iodide in methanol. After storage for 4 hr in the dark for complete reaction, the liberated iodine was titrated using 0.01 N sodium thiosulphate.

2.1.11 Functional Group Index Determination

Infra-red absorption spectra were used for the determination of the functional group index. The spectra were recorded using the Perkin Elmer ir spectrophotometer Model 457. The evaluation of the thermal as well as the photodegradation of polypropylene films by ir methods was done by following an increase in carbonyl absorbance peak at 1715 cm^{-1} at intervals and before ageing. A peak at 2710 cm^{-1} characteristic of the polypropylene itself (ie due to C-H stretching vibration) was used as a reference band or internal standard to minimise errors due to variation in sample thickness. This band whose intensity was directly proportional to film thicness (Fig 2.5) was found to remain unchanged during irradiation. Evaluation of bound phenolic antioxidant was also found by measuring the absorbance at 3620 cm^{-1} due to O-H stretching of non-hydrogen bonded phenolic hydroxyl group.

The base line technique(205) was used to calculate the optical density or absorbance due to the various functional groups. This was done as illustrated in Fig 2.6 by drawing a vertical line through the analytical wavelength until it intersects the base line which has been drawn tangential to the adjacent absorption maxima or shoulders. This was similarly repeated for the reference peak. Before the commencement of any spectral measurement, the spectrophotometer was adjusted to read 100% transmittance at 2800 cm^{-1} and this was known as the background

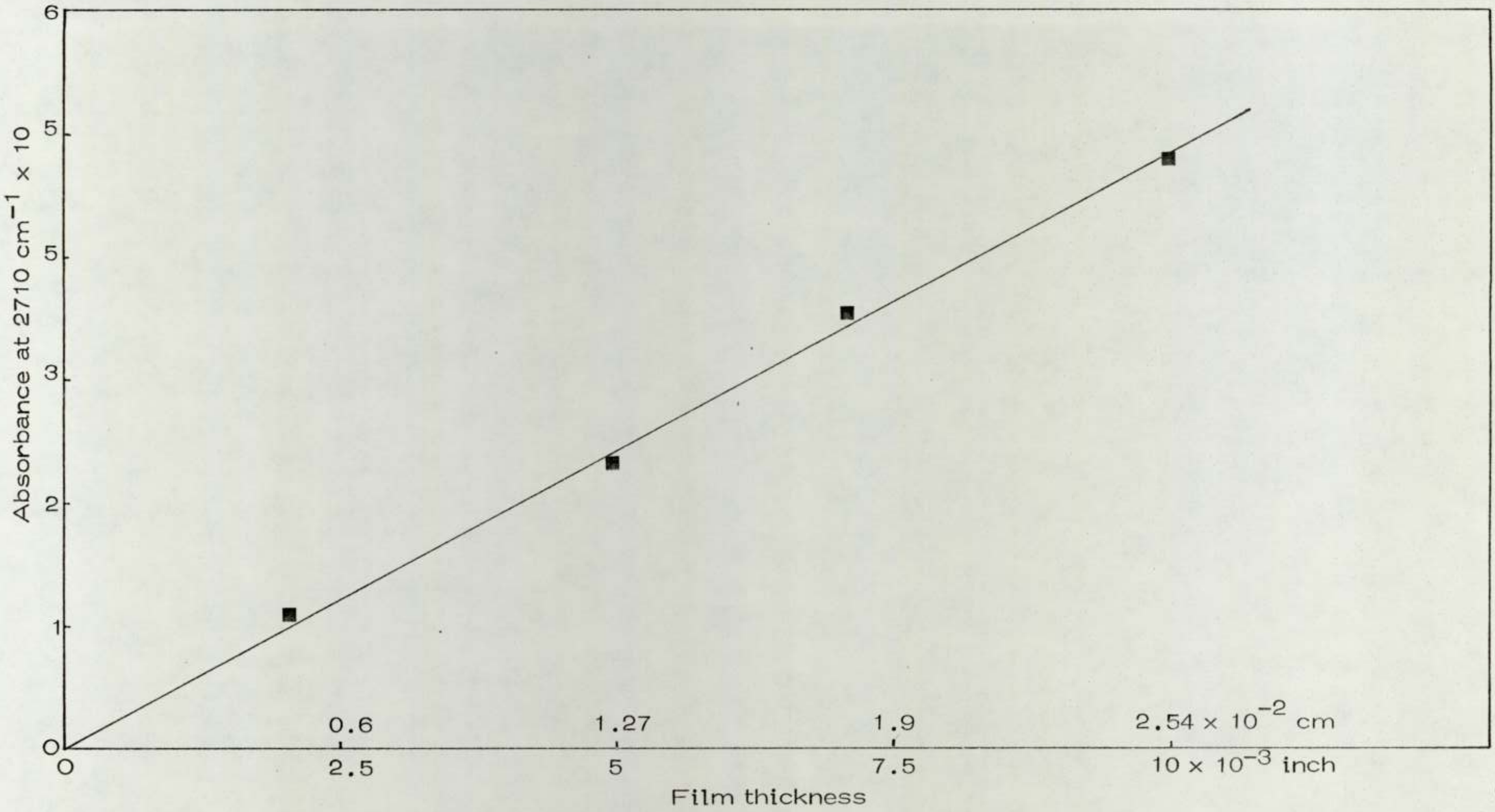


Fig 2.5 Relationship between absorbance at 2710 cm^{-1} and thickness of polypropylene films

line.

In all quantitative analyses, the following combined form of Beer–Lambert equation was used(206):

$$A = \log_{10} {}^{I_o}/_{I} = Ecl$$

where: A = Absorbance or optical density

I_o = Intensity of radiation effectively entering the sample

I = Itensity of radiation emerging from the sample

E = Extinction coefficient expressed in litres mole^{-1} cm^{-1}

c = Concentration of absorbing group present in sample, moles/litre

l = Path length of the radiation within the sample in cm

Hence: $\text{carbonyl index} = \dfrac{A(1715\ \text{cm}^{-1})}{A(2710\ \text{cm}^{-1})}$

and $\text{hydroxyl index} = \dfrac{A(3620\ \text{cm}^{-1})}{A(2710\ \text{cm}^{-1})}$

2.1.12 Ultra-violet Spectroscopy Studies

The uv spectroscopy studies of the additive-containing polymer films and model solutions were carried out using the Perkin Elmer uv/visible spectrophotometer Model 137. For the former, an unprocessed additive-free polymer film of identical thickness was used (as a compensator) in the reference beam. In the case of the model solutions, the spectra were recorded using quartz cells of 10.0 mm path length with the pure solvent being used in the reference beam. Uv absorption maxima of the additives in the films were always compared with those of the solutions. They were found to correspond closely to one another. A typical example is shown in Fig 2.7.

2.1.13 Determination of Melt Flow Index

The apparatus used was as described in the British Standard method for determination of melt flow index of polyethylene(207). Determinations were made at a temperature of 230°C and using a load of 2.16 kg. The operational procedure was essentially that described in the manufacturer's handbook(208) except that the die of the internal diameter 0.0465 in was used throughout the work. The polymer was allowed to extrude for one minute

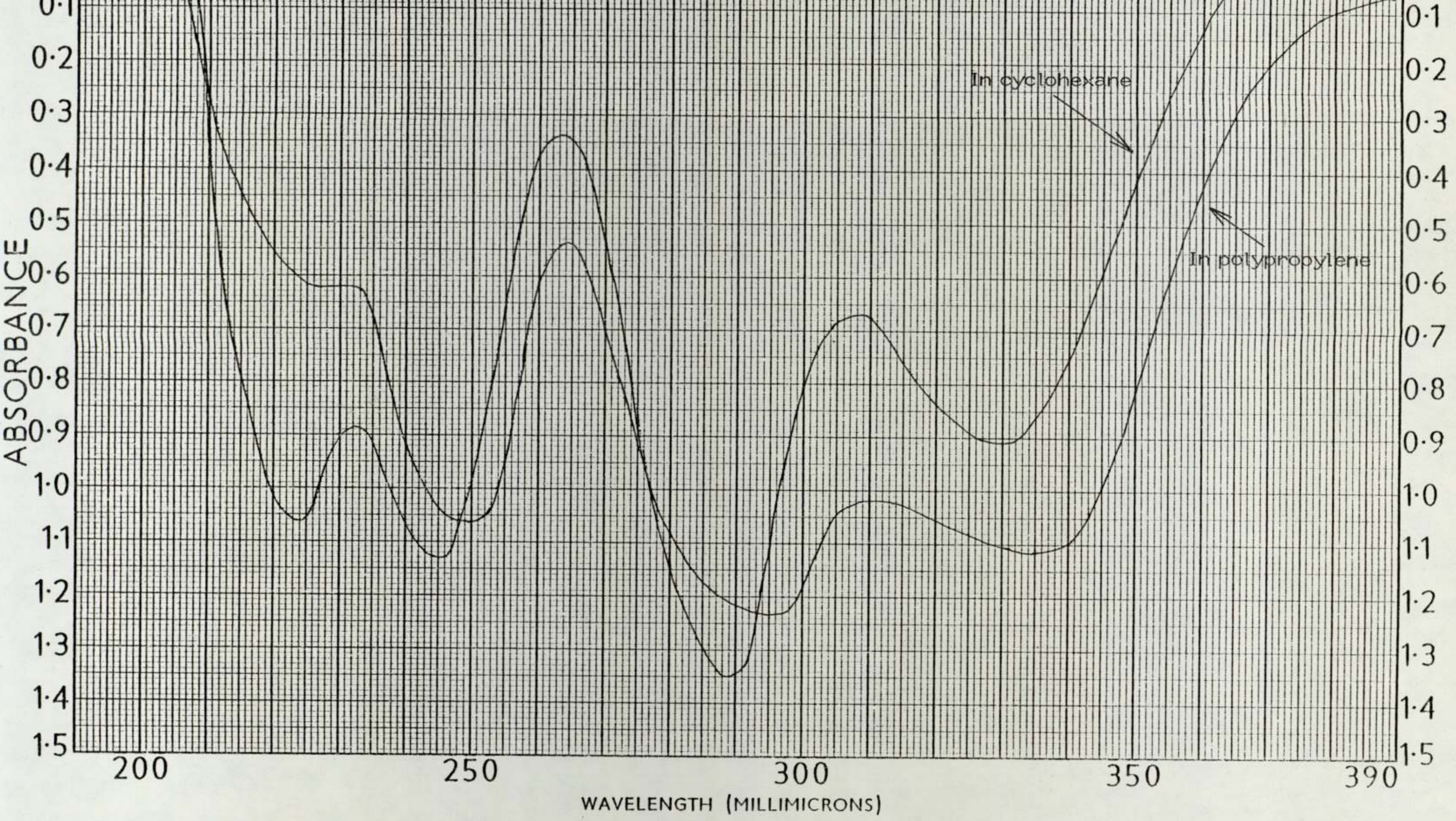


Fig 2.7 Comparison of the uv spectra of 2-hydroxy-4-oxyoctylbenzophenone (HOBP) in cyclohexane (1.5×10^{-4} M) and in polypropylene (10^{-3} mole/100 g)

before sampling commenced. Sample 'cut-offs' were taken every 30 seconds. The average weight of five consecutive samples was determined and melt flow index was expressed as weight of polymer (in grams) extruded in 10 mins.

2.1.14 Solubility Determination of Additives in a Hydrocarbon Solvent

A saturated solution of each additive in hexane was prepared by maintaining an excess of additive under a small quantity of the solvent at 25 ± 1°C in a sealed phial. Equilibration was allowed to take place over two days whereby the solutions were shaken occasionally. A portion of the supernatant saturated solution was removed from the bulk with a warm syringe (30°C), and placed on an aluminium dish and immediately weighed.

The solvent was then allowed to evaporate under slightly reduced pressure at 25°C until no weight change was noted at 24 hr intervals. Duplicate measurements were carried out in each case.

2.1.15 Volatility Evaluation of Neat Additives

The volatility cell is illustrated in Fig 2.8. Approximately

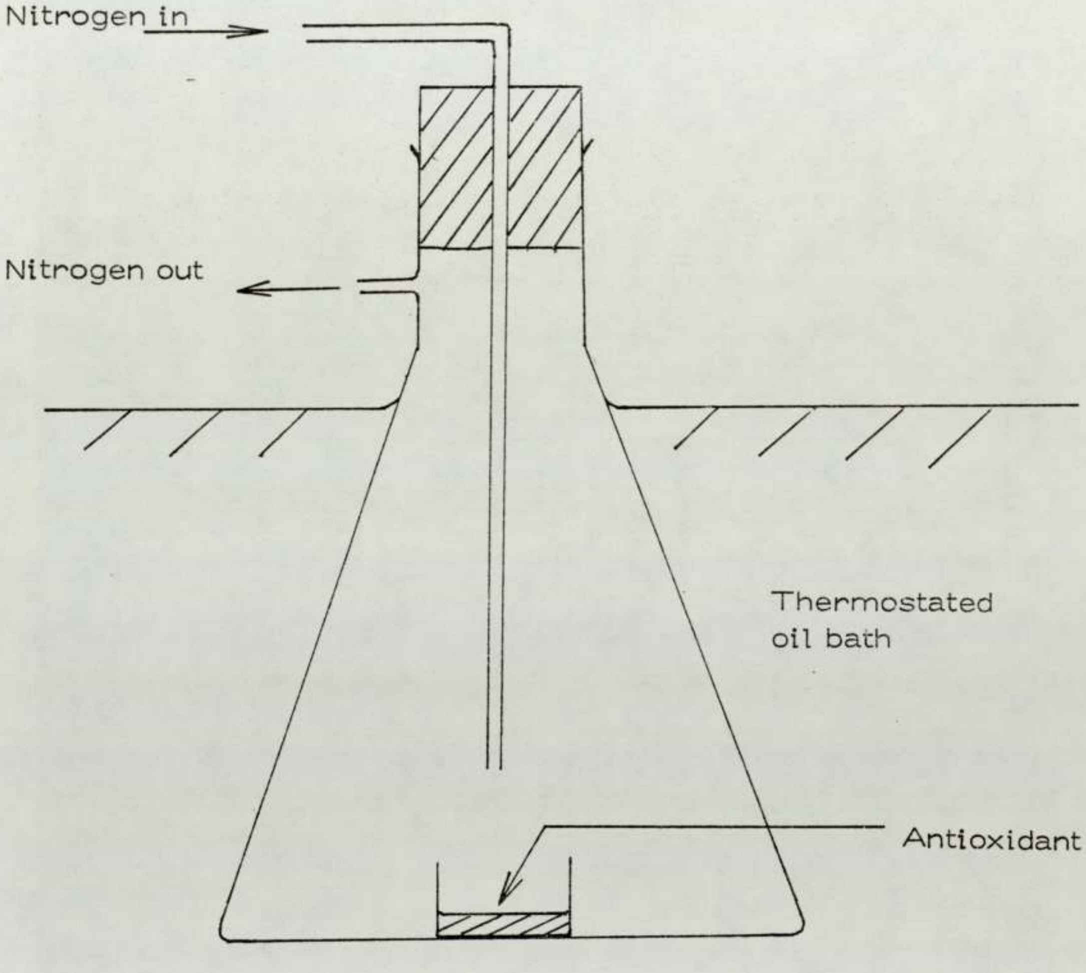


Fig 2.8 Volatility determination of neat antioxidant in nitrogen atmosphere

1 g of antioxidant was placed in a low form beaker of internal diameter 2.0 cm. The open surface area of internal diameter was therefore 3.14 cm^2.

The beaker was placed in the chamber of the volatility cell which was immersed in an oil bath set at the required temperature. The cell was quickly and momentarily purged with oxygen-free nitrogen through a 1.5 mm bore capillary tube and the passage of nitrogen was subsequently continued at the rate of 10.0 cu in/min. The beaker was periodically taken out and weighed to determine the amount of additive which had volatilised. Three volatilisation temperatures were used, viz: 120, 140 and 160°C.

2.1.16 Colour Change Measurement

Colour change of polypropylene films subjected to uv exposure was followed using the MEECO Colourmaster Colourimeter Model V. The colour change before and at intervals of uv irradiation was determined using the unprocessed film without additive as the reference. Since the samples were relatively transparent, the transmittance measurement procedure was adopted as described in the instruction manual(209a). The readings were obtained using red, green and blue filters. The total colour difference was calculated using the following formula:

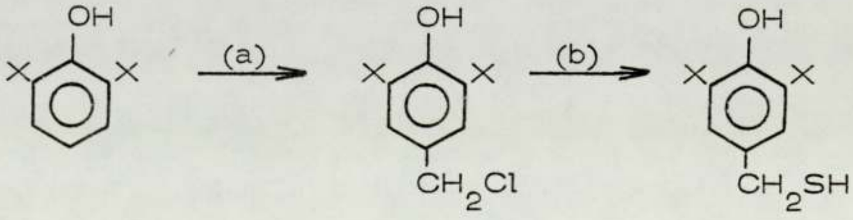
$$\text{Total colour difference} = \sqrt{\Delta R^2 + \Delta G^2 + \Delta B^2}$$

where: ΔR, ΔG and ΔB = difference between instrument readings for the red, green and blue filters respectively and that of the reference beam.

2.2 Syntheses and Characterisations of Antioxidants

2.2.1 Synthesis of 3,5-di-tertiarybutyl-4-hydroxybenzyl mercaptan

This was prepared according to the following scheme:



(a) Preparation of 3,5-ditertiary-butyl-4-hydroxybenzyl chloride

A mixture of 206.0 g of 2,6-ditertiarybutyl phenol, 120 g of paraformaldehyde and 500 ml of 36% hydrchloric acid was vigorously stirred in a one-litre three-necked flask by means of a fast electric motor. Simultaneously, dry hydrogen chloride gas was passed into the stirred mixture for 7 h after which the mixture was allowed to stand for 20 h. The stirring and passage of the HCl gas recommenced for a further period of 2 h. On standing an orange-coloured oily layer was formed above an aqueous layer. The oily layer was separated and repeatedly washed with distilled water. Ether was then added to it and any HCl present was repeatedly washed with a 2% sodium bicarbonate solution.

The ether phase was dried over anhydrous magnesium sulphate, filtered and the filtrate was rotary evaporated under reduced pressure to remove the solvent. The residue, a viscous reddish liquid, was distilled under reduced pressure to collect the fraction that boiled at 128-132^{o}C (0.5 mm Hg).

(b) Reaction of 3,5-ditertiarybutyl-4-hydroxybenzyl chloride and hydrogen sulphide (209b)

5.8 g of magnesium hydroxide powder was poured into a 500 ml round-bottom flask and 200 ml of N,N-dimethyl formamide was added to it. The mixture was stirred and H_2S gas was passed into it for 30 mins. A deep blue colour developed.

A solution of 22.5 g of 3,5-ditertiarybutyl-4-hydroxybenzyl chloride in 50 ml of hexane was added to the mixture over a period of 15 mins. The addition was controlled so that the white colour remained throughout the period (and not yellow).

The mixture was then added to ice-cooled water. The organic layer that was formed was extracted with ether and dried over anhydrous magnesium sulphate. This was left overnight after which it was solvent evaporated. The residue was vacuum distilled and the fraction that boiled at 128°C (1.0-1.5 mm) was collected. The infra-red spectrum of the neat compound on sodium chloride disc is shown in Fig 2.9.

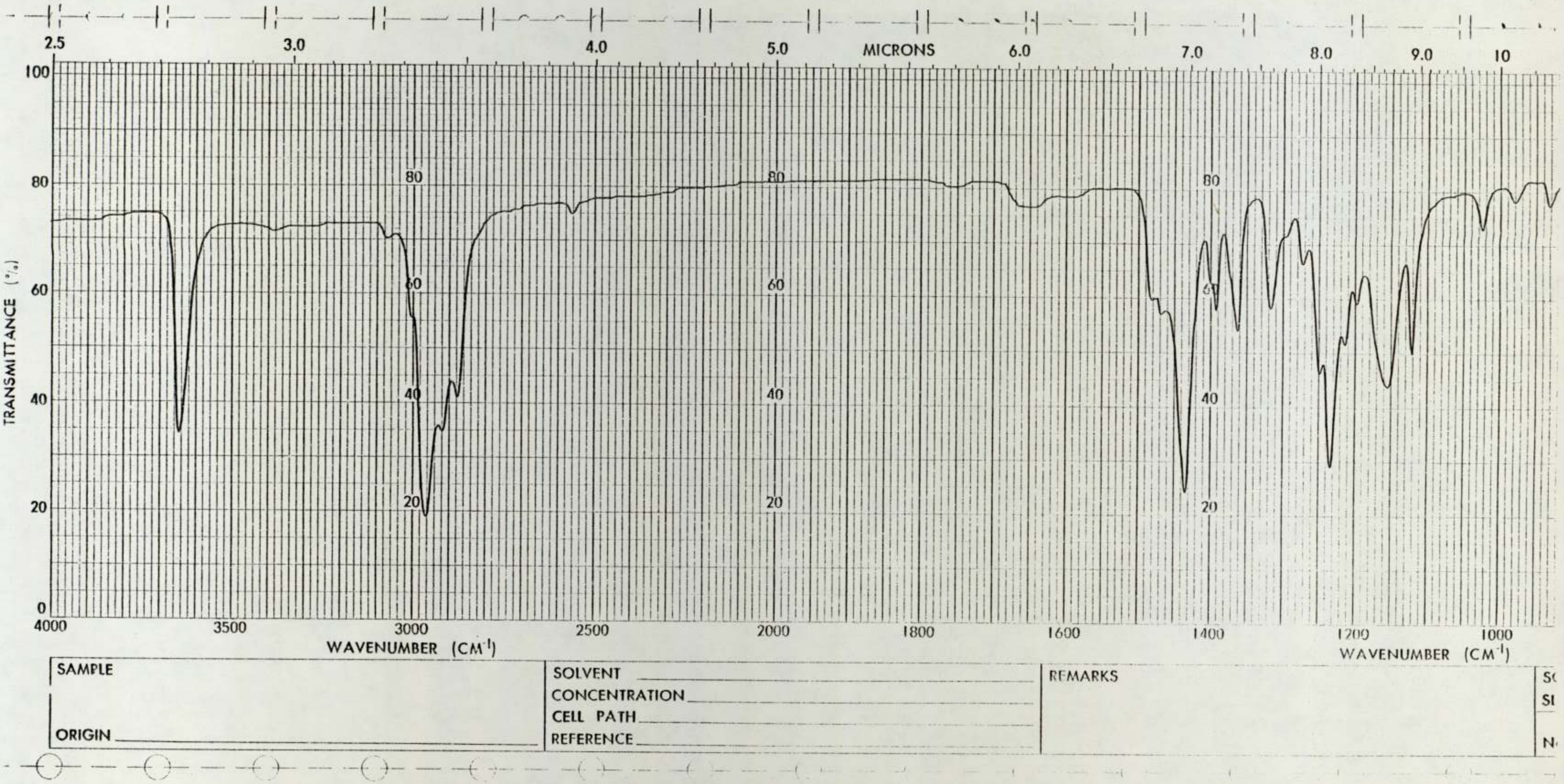


Fig 2.9 Infra-red spectrum of neat 3,5-di-tert-butyl-4-hydroxybenzyl mercaptan (BHBM) on sodium chloride disc

IR Data:

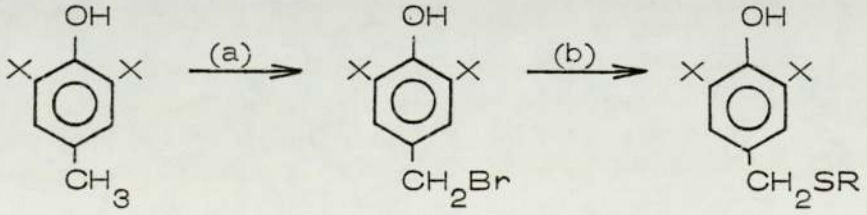
Free phenolic -OH	3640 cm^{-1}
Tertiary butyl group	1393 cm^{-1}
Mercaptan group -SH	2560 cm^{-1}

NMR Data:

Aromatic protons	2.96 τ (singlet)
Hydroxyl protons	4.98 τ (singlet)
Methylene protons	6.3 τ (doublet)
Tertiary butyl protons	8.54 τ (singlet)

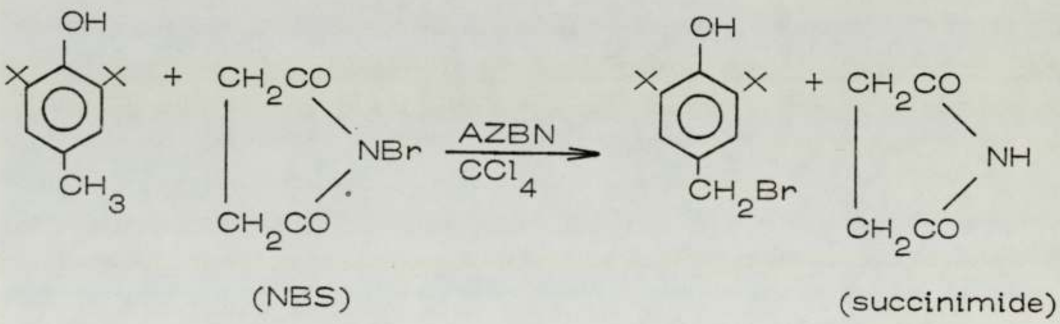
2.2 2 Synthesis and Characterisation of 3,5-ditertiarybutyl-4-hydroxybenzyl alkyl monosulphide

This was prepared according to the following scheme:



(a) Preparation of 3,5-ditertiarybutyl-4-hydroxybenzyl bromide(211)

To a 0.1 mole (22.0 g) of 2,6-ditertiarybutyl-p-cresol dissolved in 200 ml of carbon tetrachloride, 0.1 mole (17.8 g) of N-bromosuccinimide (NBS) was added. 0.005 mole (0.82 g) of azobisisobutyronitrile (AZBN) was also added as initiator. The mixture was warmed to 35°C and continously stirred by means of a teflon-coated magnetic follower until the resultant succinimide was seen floating on the top, (ca 1.0 h). This was filtered off and the remaining solution was rotary evaporated to remove the solvent. The benzyl bromide was left as a reddish-brown viscous liquid.



(b) Reaction of 3,5-ditertiarybutyl benzyl bromide with alkyl mercaptans

Equimolar quantities (0.1 mole) of the benzyl bromide and alkyl mercaptan were dissolved in 150 ml of ethanol contained in a

250-ml round-bottom flask. Slow stirring of the solution was effected by a magnetic follower and the temperature of the solution was raised to 30°C. Tiny bubbles of HBr were seen escaping from the solution. Completion of the reaction was noted by the stoppage of the HBr evolution and the concomittant formation of an upper layer of the monosulphide. This was separated and washed several times with water and dried over calcium sulphate. It was vacuum distilled and only the middle fraction was collected.

The following alkyl mercaptans were used to produce the corresponding monosulphides:

(1) ethyl mercaptan,
(2) pentyl mercaptan,
(3) octyl mercaptan,
(4) dodecyl mercaptan, and
(5) octadecyl mercaptan.

A typical infra-red spectrum of the antioxidant series is represented by the dodecyl homologue shown in Fig 2.10 and the data of the elemental analyses of the series is listed in Table 2.1.

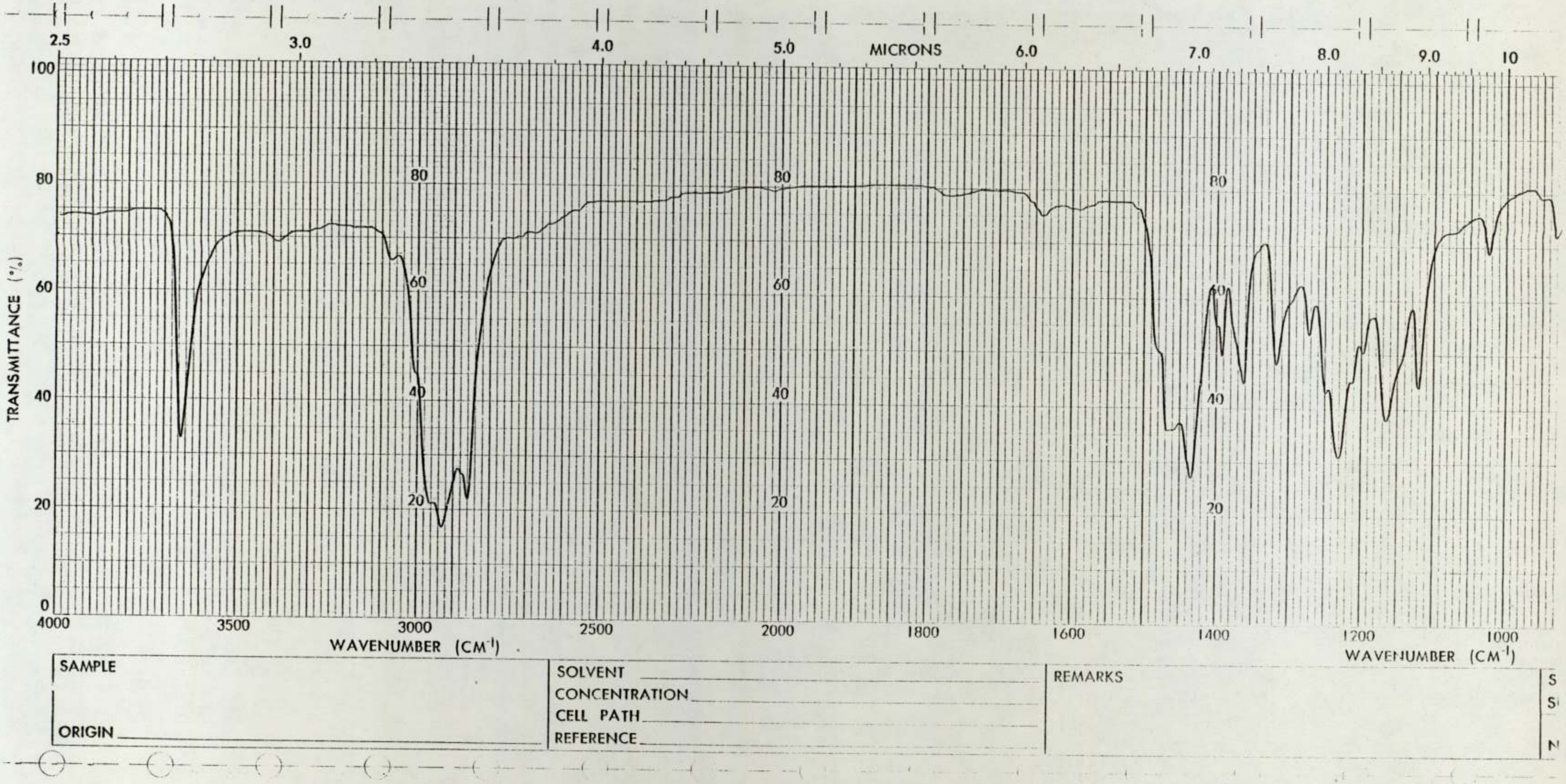
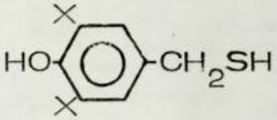
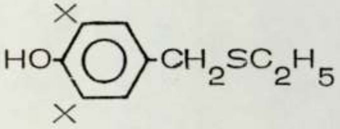
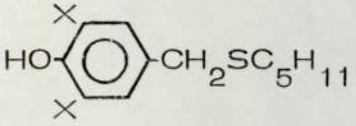
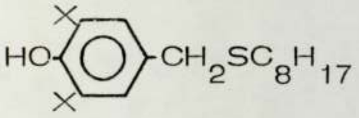
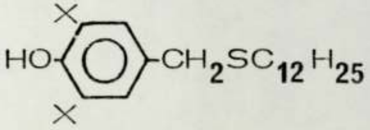
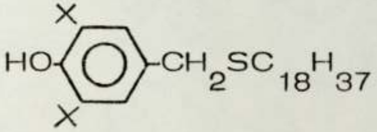


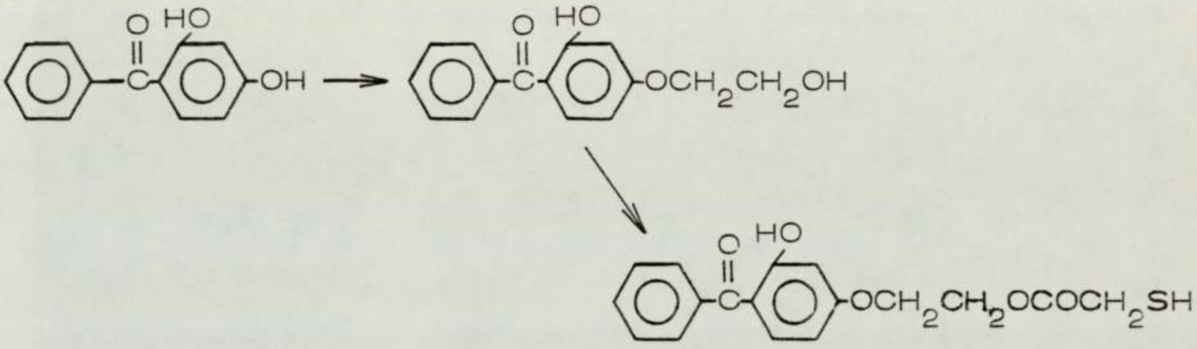
Fig 2.10 Infra-red spectrum of neat 3,5-di-tert-butyl-4-hydroxybenzyl dodecyl sulphide (AOS-C12) on sodium chloride disc

Table 2.1 Elemental analyses of the synthesised antioxidant series

Synthesised additives	Carbon (%)		Hydrogen (%)		Sulphur (%)		Oxygen (%)	
	Theoret	Expt	Theoret	Expt	Theoret	Expt	Theoret	Expt
1 	71.4	71.0	9.5	9.2	12.7	12.3	6.4	6.8
2 	72.8	73.1	10.0	10.2	11.4	11.7	5.8	6.2
3 	74.5	74.9	10.6	10.9	9.9	10.4	5.0	4.8
4 	75.8	75.3	11.0	11.2	8.8	8.7	4.4	4.3
5 	77.1	76.6	11.4	11.8	7.6	7.5	3.9	4.2
6 	79.0	79.6	11.9	12.3	6.4	6.8	2.7	3.0

2.2.3 Synthesis of 4-benzoyl-3-hydroxyphenyl ethoxy thioglycollate

The following two-stage reactions were carried out in the synthesis of the compound(210):



Preparation of 2-hydroxy-4-(β-hydroxy ethoxy)benzophenone

21.4 g (0.1 m) of 2,4-dihydroxybenzophenone and 4.0 g (0.1 m) of sodium hydroxide were dissolved in 125 ml of distilled water. 8.1 g (0.1 m) of ethylene chlorohydrin was then added to the solution and was left to stir for 4 h at 90°C. A tacky solid separated on cooling to room temperature. Solidifcation of the product was enhanced on standing the mixture overnight. The solid was filtered and repeatedly washed with distilled water. The yield was found to be 60% (mp 92°C).

Infra-red Data:

Phenolic hydroxyl and alcoholic hydroxyl	3500-3100 cm^{-1}
Benzophenone carbonyl	1630 cm^{-1}
Aliphatic CH_2	2920 cm^{-1}

NMR Data:

Aromatic protons	2.3-2.5 τ (multiplet)
Phenolic protons	2.2 τ (singlet)
Alcoholic hydroxyl proton	4.0 τ
Methylenic protons	6.5-6.7 τ (multiplet)

Reaction of 2-hydroxy-4(β-hydroxy ethoxy)benzophenone with thioglycollic acid

25.8 (0.1 m) of 2-hydroxy-4(β-hydroxy ethoxy)benzophenone and 10.0 g (0.109 m) of thioglycollic acid were dissolved in 200 ml of dry toluene contained in a flask fitted with a Dean and Stark apparatus and a condenser. The solution was refluxed until no further water was collected in the apparatus (5-6 h). The solution was washed neutral with sodium bicarbonate solution, distilled water and dried with anhydrous $MgSO_4$. The toluene was removed by rotary evaporation under reduced to give a brownish viscous liquid. The infra-red spectrum of the neat compound on sodium chloride disc is shown in Fig 2.11.

Infra-red Data:

Hydrogen-bonded phenolic -OH	3400-3200 cm^{-1}
Ester carbonyl group	1740 cm^{-1}
Mercaptan group -SH	2560 cm^{-1}

NMR Data:

Aromatic proton	2.3-2.6 τ
Methylenic protons	6.2-6.5 τ
Phenolic proton	2.2 τ
Thiol proton	7.2 τ

2.2.4 Synthesis and Characterisation of 4-benzoyl-3-hydroxyl phenyl ethoxy alkyl glycollate

This was prepared according to the following reaction(210):

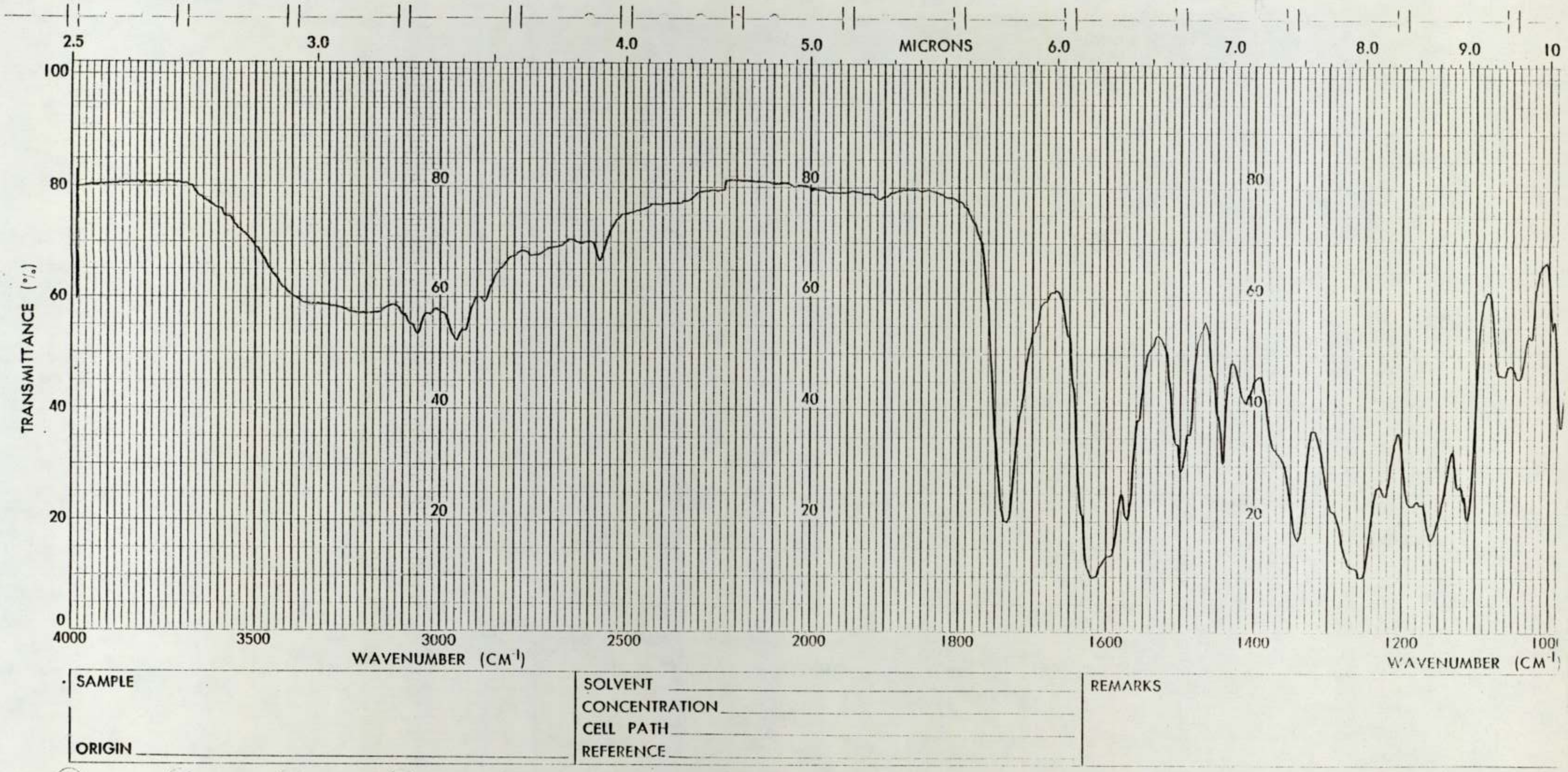
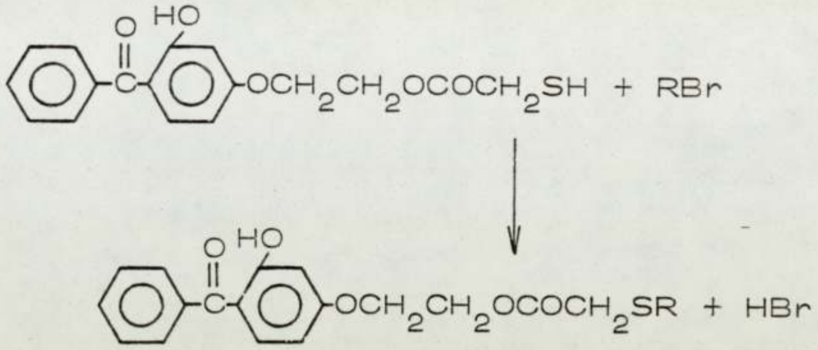


Fig 2.11 Infra-red spectrum of neat 4-benzoyl-3-hydroxyphenyl ethoxy thioglycollate (UVS-H) on sodium chloride disc



0.1 mole of 4-benzoyl-3-hydroxy phenyl ethoxy thioglycollate and 0.1 mole of alkyl bromide were dissolved in 200 ml of toluene. The solution was gently stirred and the temperature gradually increased to 35°C. Tiny bubbles of HBr escaped from the solution. The reaction was stopped until no gas was evolved. The solution was poured into ice-cooled water and the organic phase was extracted with ether. This was dried over calcium sulphate for 24 h after which the solvent was evaporated to give the required product. Absence of extraneous band in the infrared spectrum showed the compound to be satisfactorily pure and no further purification was made.

The following alkyl bromides were used to produce the compound of increasing molecular weights:

(1) butyl bromide,

(2) octyl bromide,

(3) dodecyl bromide, and

(4) octadecyl bromide.

A typical infra-red spectrum of the uv stabiliser series is represented by the octadecyl homologue shown in Fig 2.12 and the data of the elemental analyses of the series is listed in Table 2.2.

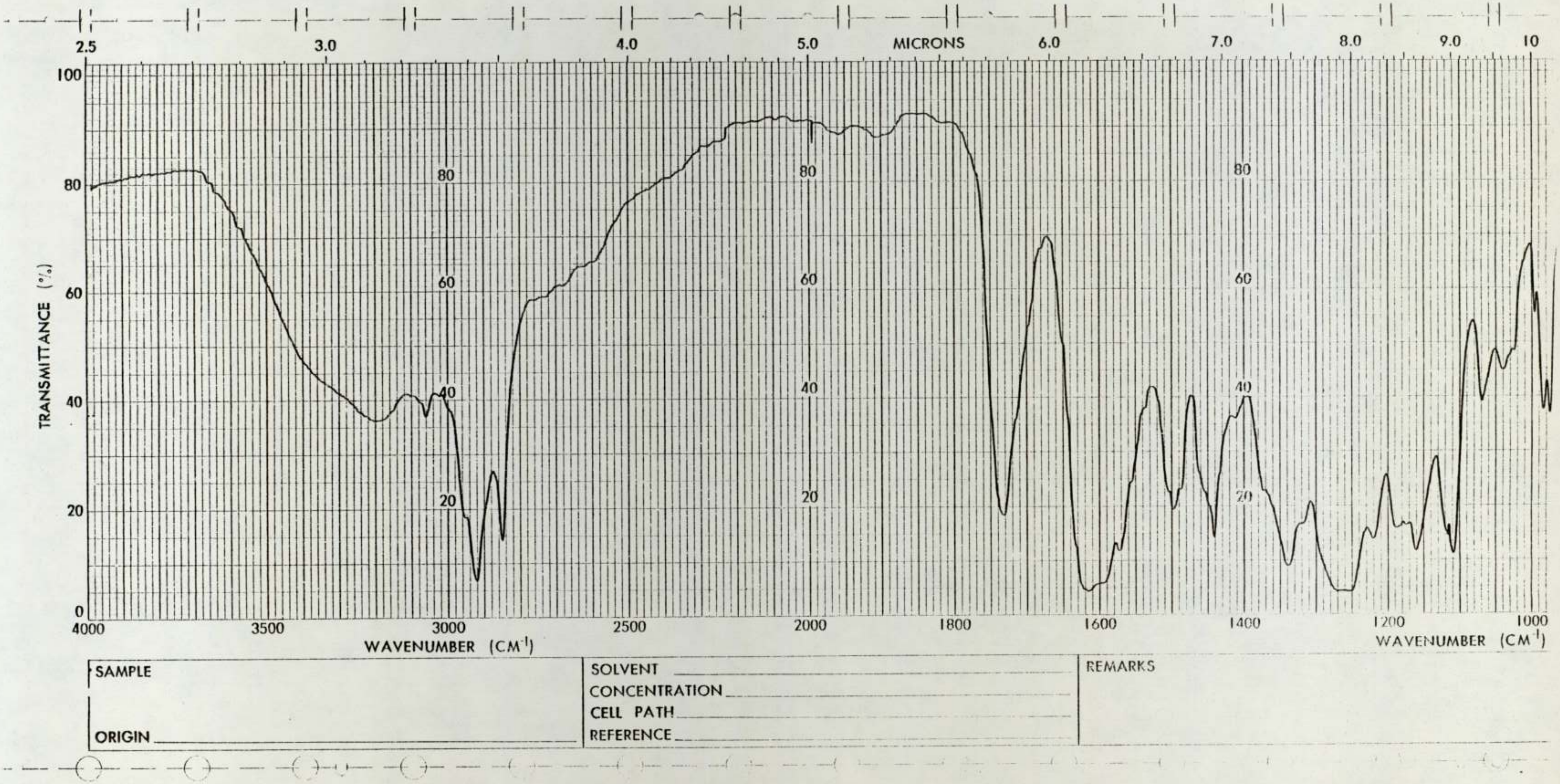
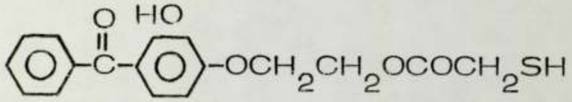
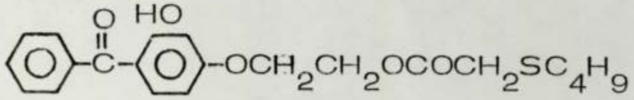
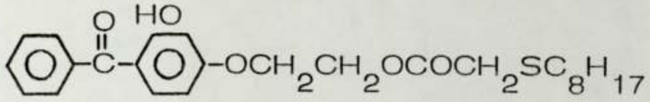
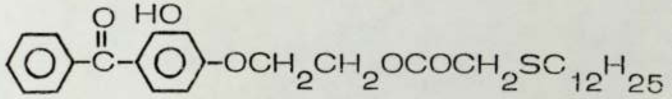
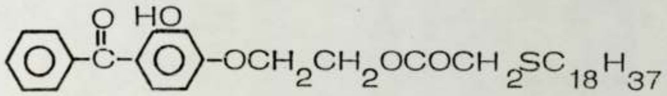


Fig 2.12 Infra-red spectrum of neat 4-benzoyl-3-hydroxyphenyl ethoxy octadecyl glycollate (UVS-C18) on sodium chloride disc

Table 2.2 Elemental analyses of the synthesised uv stabiliser series

Synthesised additives	Carbon (%)		Hydrogen (%)		Sulphur (%)		Oxygen (%)	
	Theor	Expt	Theor	Expt	Theor	Expt	Theor	Expt
1 	61.4	61.7	4.8	4.9	9.6	9.9	24.2	23.9
2 	64.9	65.3	6.2	6.0	8.2	8.0	20.7	20.3
3 	67.6	67.2	7.2	7.7	7.2	7.5	18.0	18.3
4 	69.6	70.0	8.0	8.3	6.4	6.8	16.0	15.7
5 	71.9	71.6	8.9	9.2	5.4	5.6	13.8	13.5

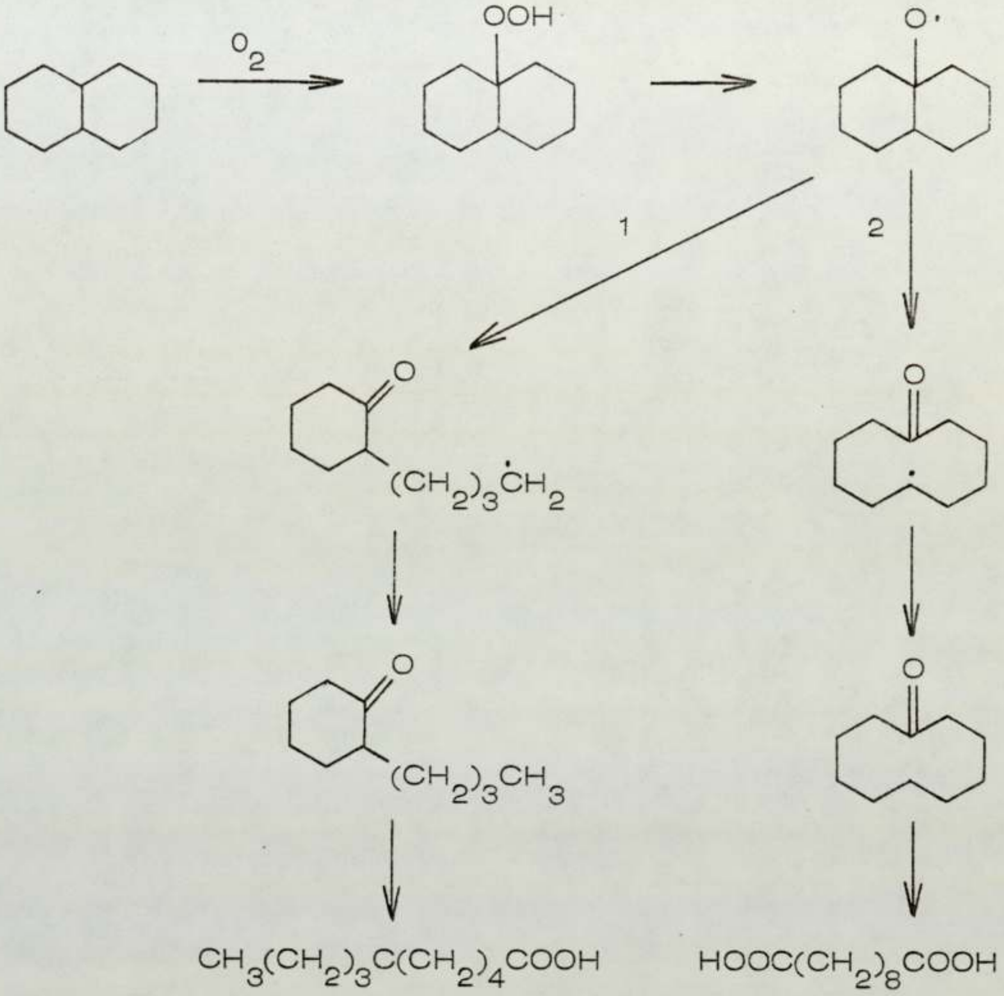
CHAPTER THREE

BEHAVIOUR OF SYNTHESISED ANTIOXIDANT SERIES IN MODEL SYSTEM AND IN POLYPROPYLENE

3.1 Intrinsic Antioxidant Activity in a Liquid Substrate

Decalin was chosen as the liquid hydrocarbon substrate. The structure of decalin, although not a direct model of polypropylene, does contain the tertiary hydrogen functionality associated with the polymer. In addition, the aliphatic structure of decalin has advantages over other common model compounds such as cumene or tetralin in that no phenolic products could form during autoxidation. Thus the confusion caused by adventitious synergism which might arise during the studies of sulphur antioxidants activity was avoided.

Holmquist and co-workers(212) suggested that at 120-130°C, the oxidation of decalin could follow two possible routes as shown:



They showed that route 1 appeared to be favoured since 2-n-butylcyclohexone and 6-oxodecanoic acid were found together with the further oxidation products of adipic and butyric acids.

Decalin exists in cis and trans isomeric forms and Jaffe et al(213) demonstrated that the oxidation of decalin is stereo-dependent, the cis isomer oxidising about four times as fast as the trans isomer. Because of the problems that any variation in the cis/

trans decalin content would produce in the evaluations of antioxidant effectiveness, it was considered of major importance that all work was carried out on one batch of the purified hydrocarbon substrate.

The liquid oxidation studies were made using the experimental set-up described in section 2.1.5. Preliminary experiments showed that reproducible oxidation characteristics could not be obtained with new apparatus in particular with new oxidation flasks. Successive oxidations carried out in new flasks tended to exhibit a generally declining rate of oxidation. After several experiments, the oxidation behaviour tended to settle down. It was suspected that there was some involvement of active sites on the glass surface of the oxidation vessels which appeared to initiate or catalyse the oxidative reactions but were removed or destroyed during the initial oxidations. Irreproducible behaviour of this type in studies of liquid phase oxidation had been noted by several workers(214-216). In subsequent work, all flasks were 'aged' by oxidising decalin in them for a period of 24 hrs and repeating the process thrice with the usual interim acetone wash.

Two other factors were suspected of causing irreproducibility:

the rate of stirring and the ingress of light. It was found that if the stirring rate was fast enough to produce a deep vortex in the oxidising decalin and thereby break the surface into bubbles, the oxidation characteristics were not controlled by the diffusion of oxygen into the sample of the hydrocarbon. A plot of oxidation rate -vs- stirring rate as illustrated by Fig 3.1 shows a dependence of the parameters up to a limiting stirring rate of 150 rpm when oxidation rate was constant and non-diffusion controlled.

Any possible extraneous catalysis of oxidation by light was eliminated by completely enclosing the oxidation vessels in aluminium foil.

Fig 3.2 shows the oxygen absorption curves of decalin containing BHBM, AOS-C12, 1076 and TBC at a concentration of 6×10^{-4} mole/100 ml decalin. Considering the commercial antioxidants first, it was apparent that TBC showed a better stabilising activity relative to that of 1076. Since these liquid oxidation studies precluded the influence of physical constraints on the antioxidant performance, the reasons for the difference must be primarily attributed to chemical phenomena.

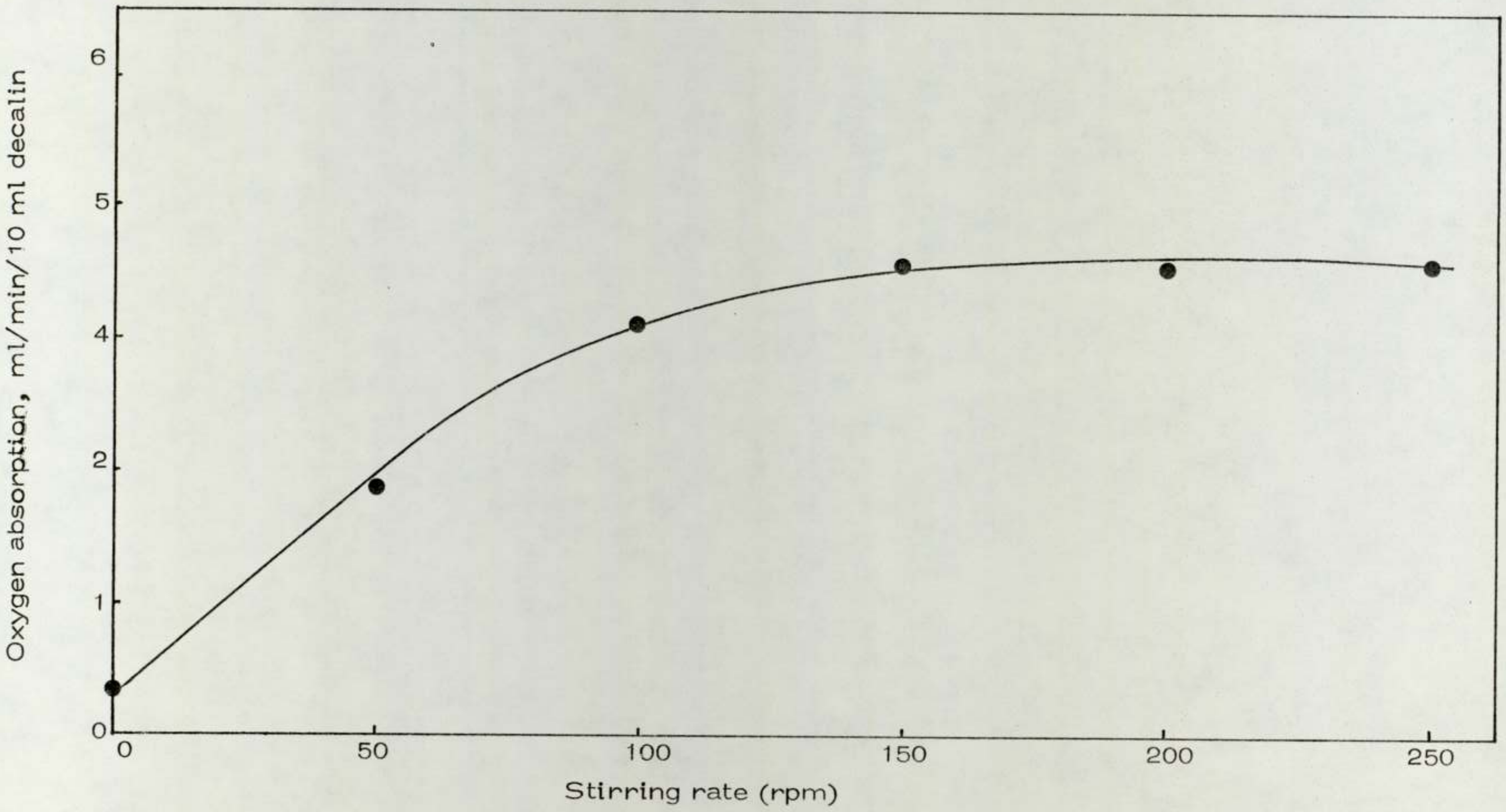


Fig 3.1 Variation of oxidation rate of decalin (at 140°C) with stirring rate

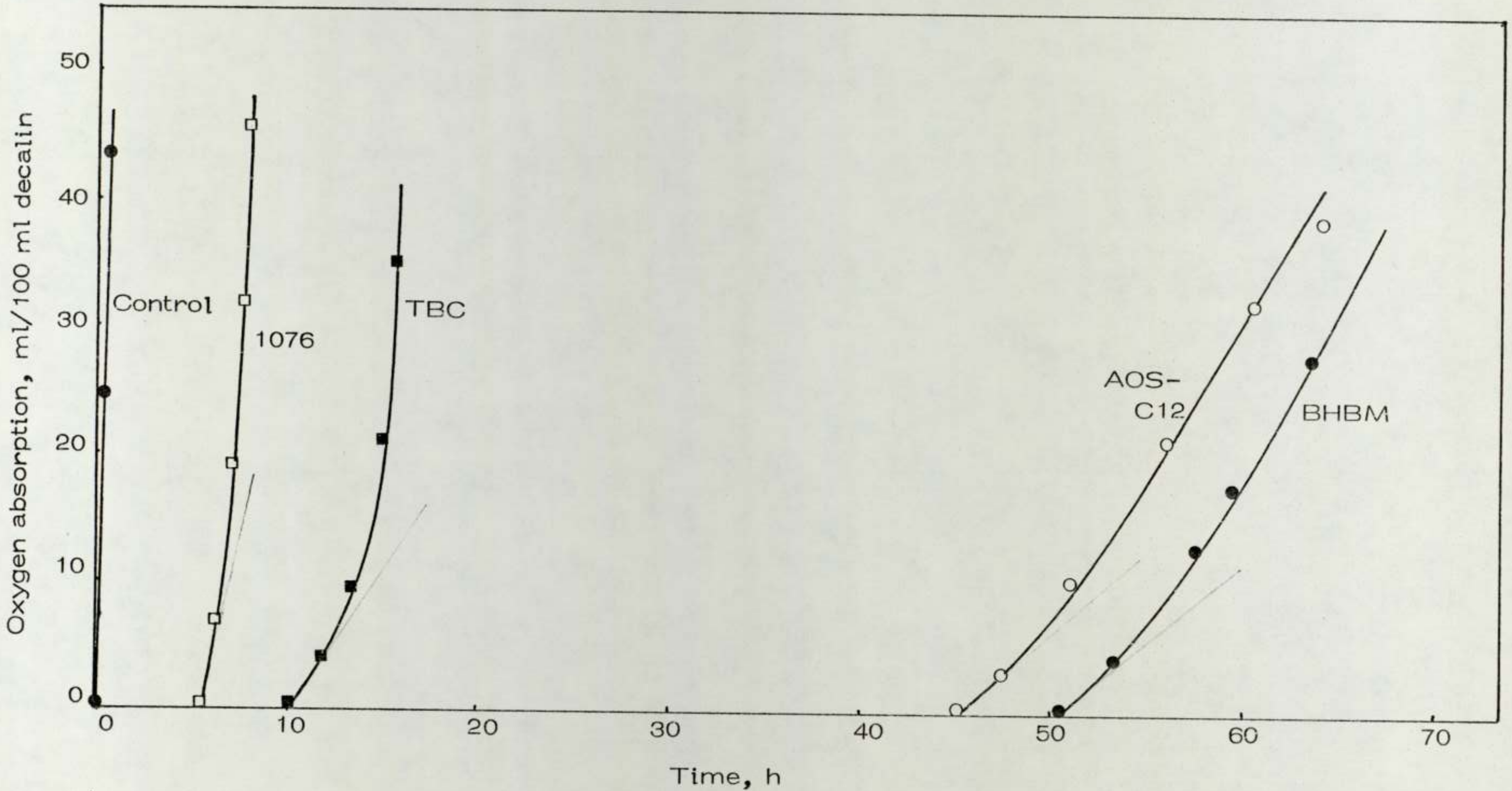
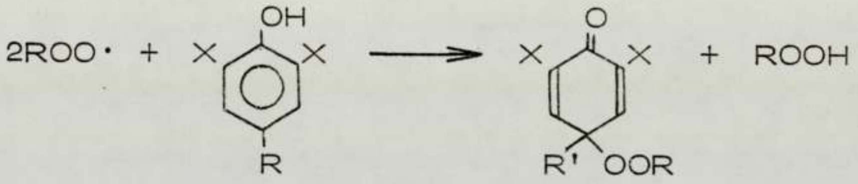


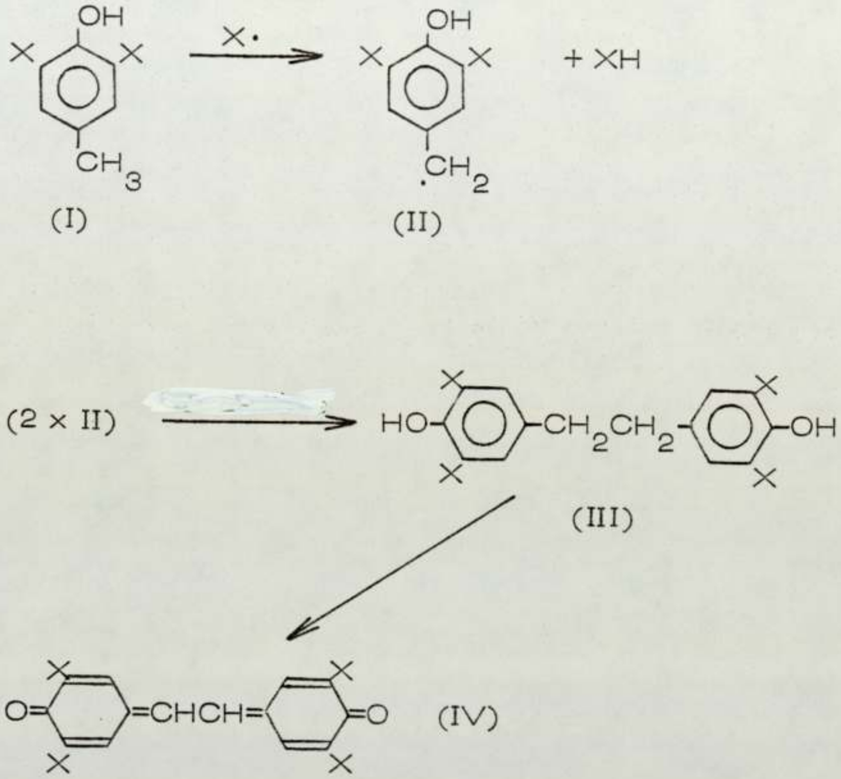
Fig 3.2 Oxidation of decalin (at 140^{o}C) in the presence of various antioxidants. Concentration of additives = 6×10^{-4} mole/100 ml decalin

The principal reason for the significant difference in behaviour of TBC and 1076 must be associated with the nature of the substituent para to the phenolic OH group. It is generally known that phenolic antioxidants like TBC and 1076 could terminate more than one oxidative kinetic chain: one is by the conventional termination of the peroxy radical by the phenolic hydroxyl and the other by the 4-position of the phenolic ring. The former involves the normal hydrogen donation to the peroxy radical while the latter calls for the addition of the peroxy radical to the ring, ie:



While hydrogen donation might show comparable facility for the two antioxidants, addition of the peroxy radical to the 4-position could be substantially different. The high steric hindrance at the para position of 1076 imposed by the n-octadecyl propionate group presumably contributes to its inferior antioxidant performance.

Furthermore, TBC is known(217) to undergo dimerisation reactions at the 4-methylene group which produced mild thermal antioxidant species such as stilbenequinone, IV:

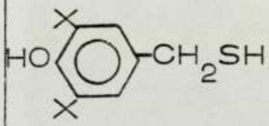
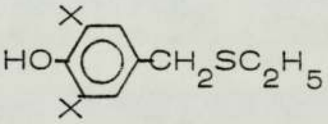
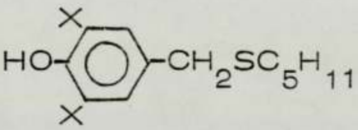
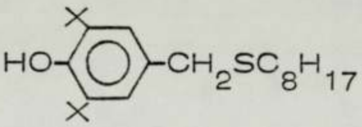
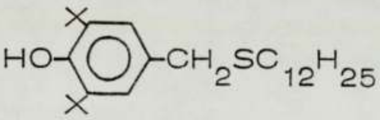
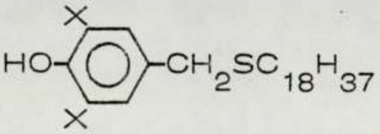
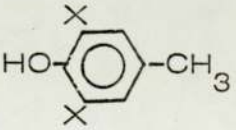
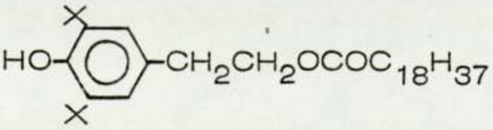


The bis-benzyl phenol (III) is a powerful antioxidant but is relatively unstable and is readily converted to the more stable stilbenequinone. This type of reaction however is not expected to proceed as readily in 1076 so that further antioxidant species are not being produced like those with TBC. In addition it has been suggested(217) that TBC is more effective because the hyperconjugation phenomena related to the methyl group is greater than that of the propionate in 1076.

The behaviour of BHBM and AOS-C12 in decalin showed a much superior performance as evidenced by the prolonged induction period. The presence of the sulphur moiety in BHBM, for instance, increased the induction period 5-fold (10 hrs for TBC, 51 hrs for BHBM). The marked activity exhibited by BHBM may be rationalised in terms of the operation of autosynergism. Fernando(188b), in the oxidation studies on tetralin, also reported similar behaviour of BHBM. Recently Farzaliev, Fernando and Scott(218) showed the powerful autosynergistic activity of BHBM in relation to simple bis-benzyl sulphide compounds. The comparable performance shown by AOS-C12 is thought to be an extension of this principle.

The stabilising acitivities of the other members of the antioxidant series were also examined in decalin and their induction periods are shown in Table 3.1 and Fig 3.3. It is apparent that all the antioxidants exhbitied similar activities although there appeared to be a slight decrease even though marginal in effectiveness as the length of the pendant chain increased. Presurnably this is associated with the bulkiness of the molecules in performing their activities. Plant(219) also reported similar trends in his studies of phenolic antioxidants of increasing pendant chain length.

Table 3.1 Chemical activity of the antioxidant series in decalin at 140°C by the O_2 absorption technique (Conc of antioxidants = 6×10^{-4} moles/100 ml decalin)

Additives	Induction period, $h \pm 0.5h$
Control	–
	51.0
	47.5
	47.0
	46.5
	45.0
	44.5
	10.0
	5.0

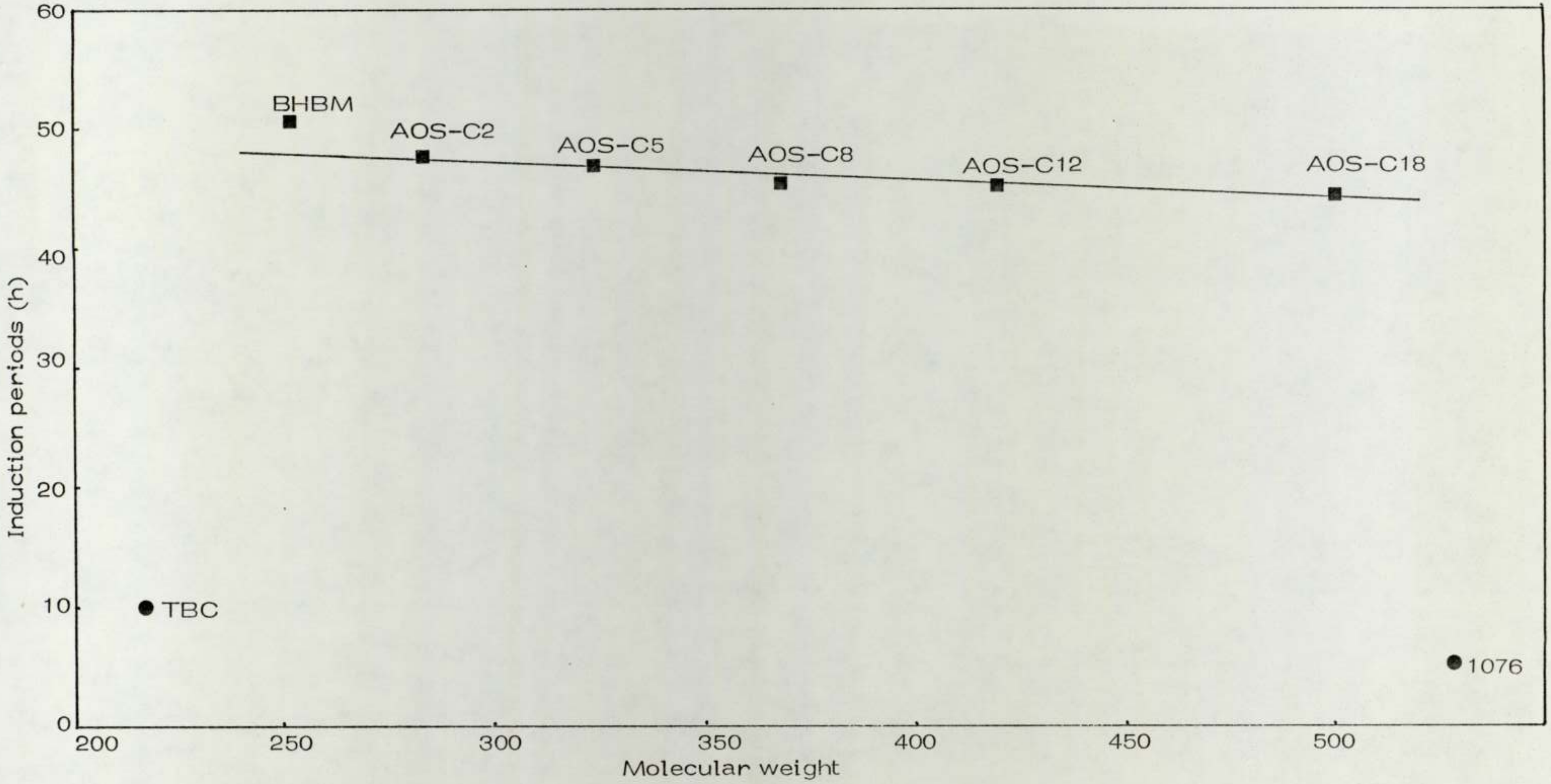
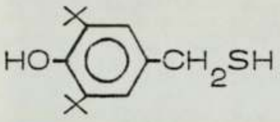
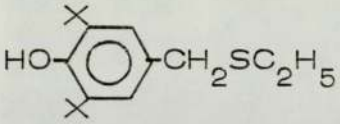
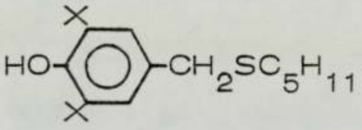
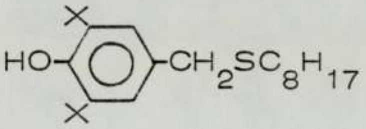
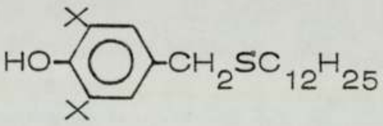
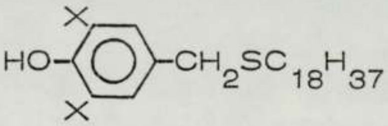
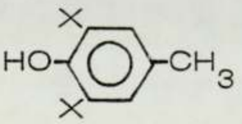
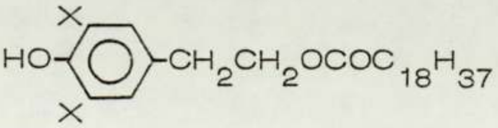


Fig 3.3 Variation of induction periods of decalin oxidation with the additives' molecular weight. Concentration of additives = 6×10^{-4} mole/100 ml decalin

The rate of oxidation of decalin following the end of the induction period requires comment. Two types of oxidation rates were identified (see Fig 3.2) and are shown in Table 3.2: the initial oxidation rate which is the rate immediately after the induction period, obtained by drawing a slope tangential to the oxidation curves at the point on the X-axis; and the other is the linear oxidation rate equivalent to the general slope of the curves.

The control decalin showed no induction period and an immediate oxygen absorption was observed after the equilibration period of five mins. It showed a constant and linear absorption rate of 180 ml/h/100 ml decalin. TBC and 1076 exhibited similar magnitude for the linear oxidation rate signifying the complete depletion of antioxidant activities. However, the much reduced initial oxidation rates of the two antioxidants bring to surface the supporting evidence that the oxidation by-products of these antioxidants were themselves providing some stabilising activities. TBC gave an initial oxidation rate of 2.2 ml/h/100 ml in comparison to that of 1076 which was 9.0 ml/h/100 ml. This difference is in accord with earlier proposition that TBC provided greater facility for reactions in the 4-position than 1076 thereby producing a higher concentration of derived antioxidant species.

Table 3.2 Oxidation rates of the antioxidant series in decalin at 140°C by O_2 absorption technique (conc of antioxidant = 6×10^{-4} mole /100 ml decalin)

Additive	Initial oxidation rate, ml/hr/100 ml	Linear oxidation rate, ml/hr/100 ml
Control	180	180
	1.2	2.4
	1.4	2.5
	1.4	2.5
	1.4	2.4
	1.5	2.5
	1.4	2.4
	2.2	175
	9.0	180

The synthesised antioxidant series showed an even more marked reduction in the oxidation rates. Table 3.2 shows that their linear oxidation rates were of the order of 2.4 ml/h/100 ml in contrast to 175 ml/h/100 ml for TBC. This emphasises the superiority of sulphur-containing antioxidants whose activities are associated with the catalytic decomposition of hydroperoxides (to be further discussed in section 3.6). Similar reduction of the initial oxidation rates were also observed and their values were of the order of 1.4 ml/h/100 ml. This again brings to focus the essentially similar fundamental chemical behaviour of the antioxidant series in decalin.

Hence the general conclusion that could be reached from these studies is that in the absence of the effects of volatility and compatibility phenomena, the synthesised antioxidants exhibit similar stabilising effectiveness and increasing the molecular weight does not give any significant difference in the inherent chemistry of the inhibited autoxidative reactions.

3.2 Antioxidant Performance in Polypropylene in a Closed Environment

The studies of antioxidant activities in the liquid phase which were described in the preceding section were designed to compare the intrinsic stabilising effectiveness of the antioxidants.

The following evaluations were carried out in polypropylene and the determinations of antioxidant effectiveness were made in a closed apparatus in order to eliminate the effects of antioxidant volatility. However, in the highly viscous polymeric medium, other physical factors such as compatibility might be expected to affect their behaviour. The measurement of the induction period to the onset of the oxidation was again used as the parameter of antioxidant activities.

Fig 3.4 demonstrates the varying activities of BHBM, AOS-C12, TBC and 1076 in polypropylene films under conditions of closed environment. Again considering the two commercial antioxidants first, it is seen that 1076 had a greater stabilising effect in the polymer films relative to that of TBC. Since this investigation attempted to severely curtail the influence of volatility on the antioxidant performance, the results obtained may be rationalised in terms of the antioxidants' chemical activity and compatibility phenomena. But the previous chemical activity studies in decalin unequivocally showed TBC to perform better than 1076. The fact that the reverse holds true in the present studies pointed to

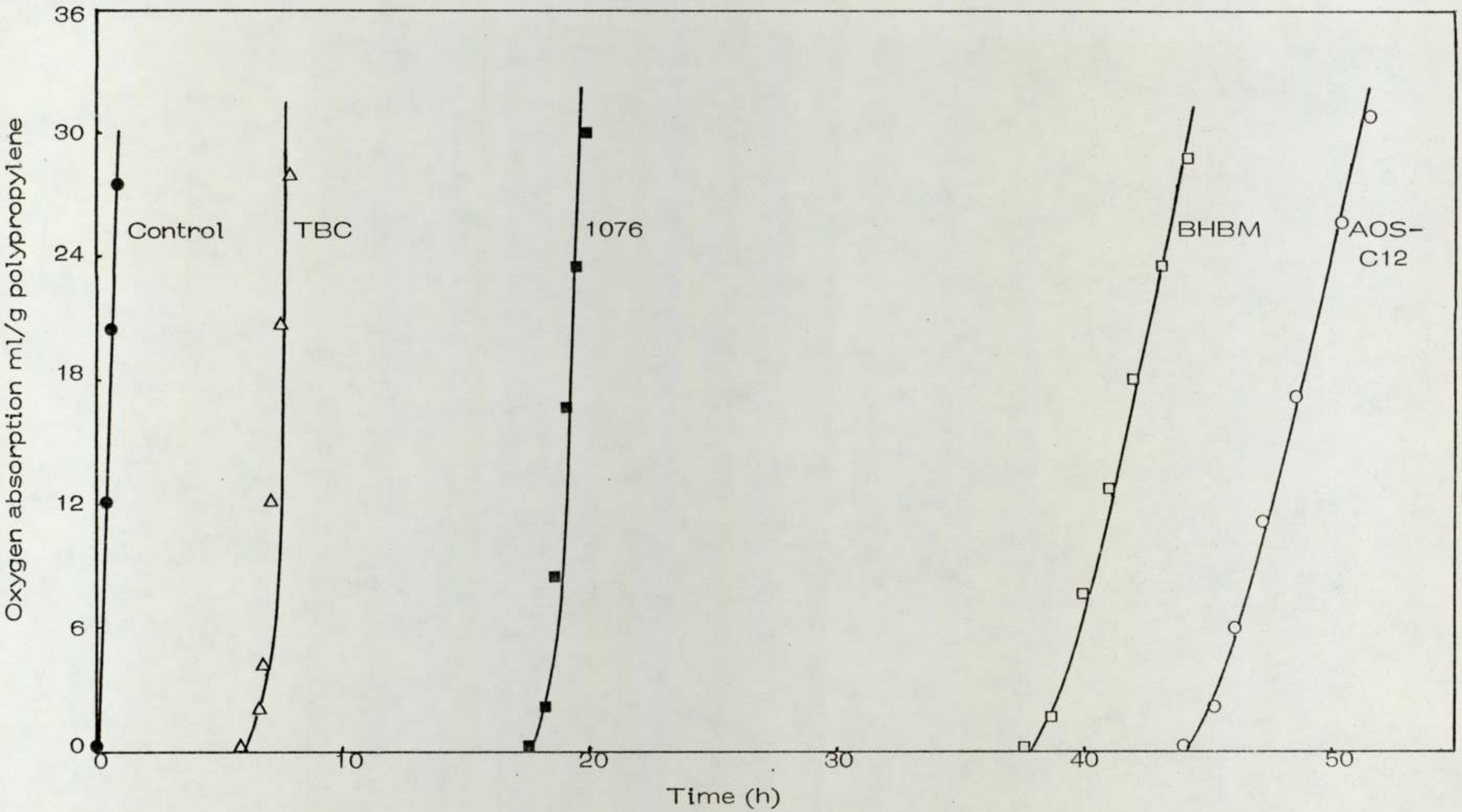


Fig 3.4 Thermal oxidation of polypropylene films (at 140°C) in a closed atmosphere. Concentration of antioxidants = 6×10^{-4} mole/100 g polymer

the probability that compatibility is exerting a dominating influence. Fig 3.4 suggests that the magnitude and extent of the compatibility of 1076 outweighs its inherent inferior chemical activity.

A similar inversion was observed by BHBM and AOS-C12 in that while they exhibited comparable intrinsic chemical activities, the latter was superior to the former in enclosed atmospheric studies, presumably for reasons of greater compatibility.

Fig 3.5 depicts the performance of the series of synthesised antioxidants in polypropylene in the enclosed oxygen-rich conditions. Again the findings appear to highlight the inevitably strong dependence of stabilising performance on compatibility as shown by the differing induction periods. There was a general increase in antioxidant activities from AOS-C2 to AOS-C12 followed by a sharp drop in the stabilising performance of AOS-C18 as shown in Table 3.3. This trend was exemplified in Fig 3.6 which seems to indicate that there was the initial positive contribution of compatibility as the pendant chain length increased from C2 to C12 but the effect was nullified and even showed adverse consequences for the C18. However, further discussion will be deferred to section 3.9.

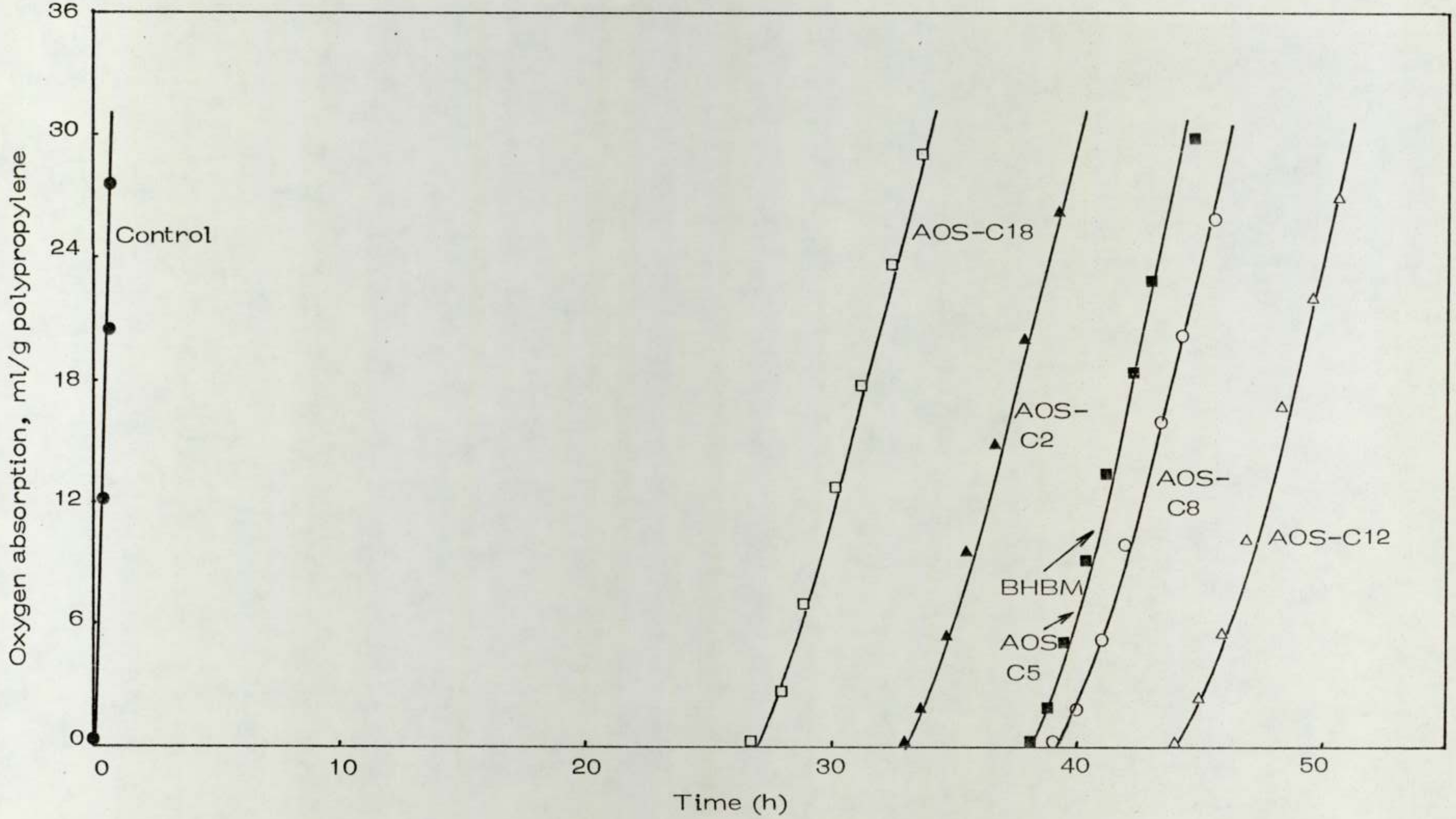
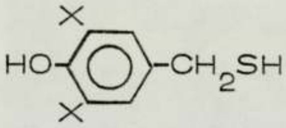
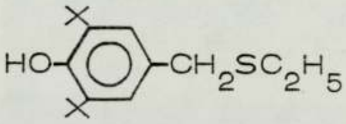
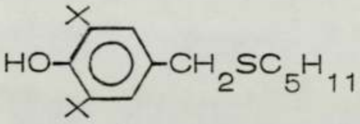
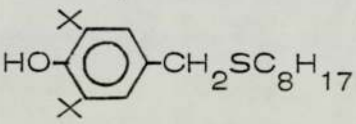
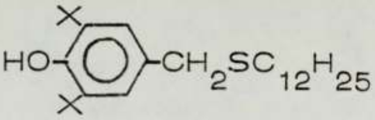
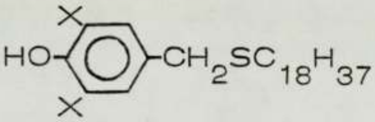
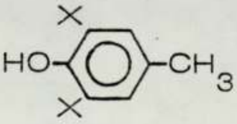
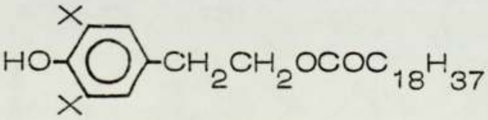


Fig 3.5 Thermal oxidation of polypropylene (at 140°C) in a closed atmosphere. Concentration of antioxidants = 6×10^{-4} mole/100 g

Table 3.3 Induction periods of polypropylene films thermally aged in a restricted O_2-rich atmosphere at 140°C (conc of antioxidants = 6×10^{-4} mole/100 g)

Additives	Induction period, h±0.5h
Control (no additives)	-
	38.5
	33.0
	38.0
	39.5
	44.5
	27.0
	6.0
	18.0

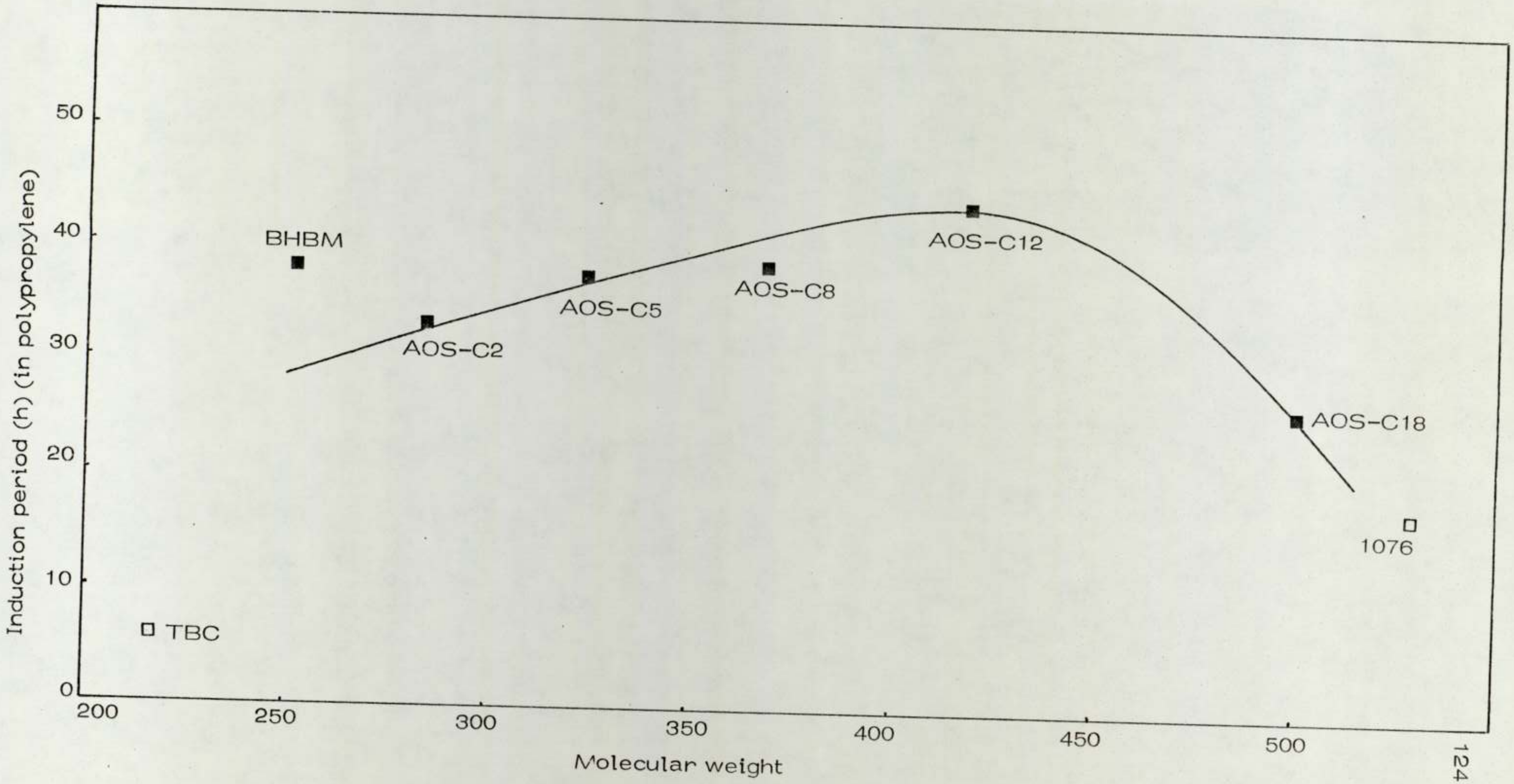


Fig 3.6 Variation of the antioxidants' activity (in polypropylene) with their molecular weights in enclosed atmosphere at 140°C

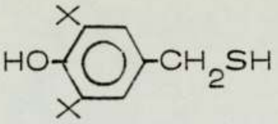
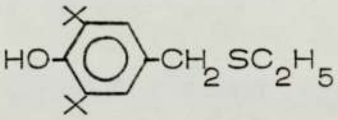
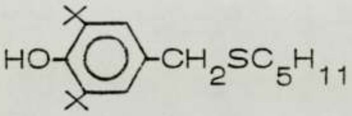
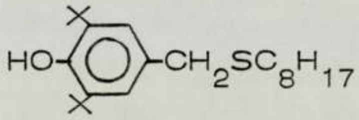
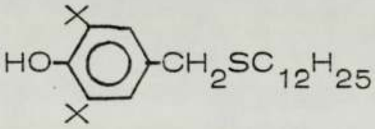
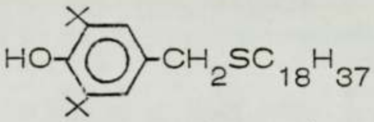
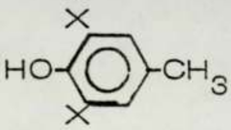
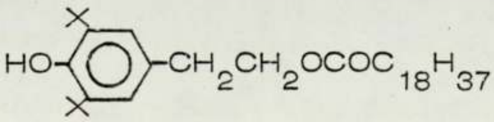
Another feature evident in Figs 3.4 and 3.5 concerns the linear oxidation rates subsequent to the induction period. While 1076 and TBC showed a similar rate to that of the control, the synthesised antioxidants showed a significantly less pronounced gradient. This is presumably indicative of the fact that the oxidative by-products of the sulphur antioxidants induce mild inhibitory reactions in the polymer. Table 3.4 which quantifies the linear oxidation rates of the antioxidants, supports the above proposition. The antioxidant series showed a constant (within limits of experimental error) linear oxidation rate of 5.0 ml/h/g while that of the control gave value of 28.0 ml/h/g. This is remarkable in that the sulphur antioxidants had reduced the oxidation rate approximately 6-fold.

3.3 Antioxidant Performance in Polypropylene in a Flowing Atmosphere

The previous studies of antioxidant activity in a restricted and static atmosphere eliminate the confusing influence of volatility. The present evaluation attempted to assess the importance of volatility upon antioxidant effectiveness.

Fig 3.7 delineates the behaviour of the synthesised antioxidants

Table 3.4 Linear oxidation rate of polypropylene films in an O_2-rich enclosed atmosphere (conc of antioxidants = 6×10^{-4} mole/100 g; Temp 140°C)

Additives	Linear oxidation rate, ml O_2/h/g
Control (no additives)	28.0
	5.0
	5.4
	5.0
	5.0
	5.0
	5.5
	21.0
	25.0

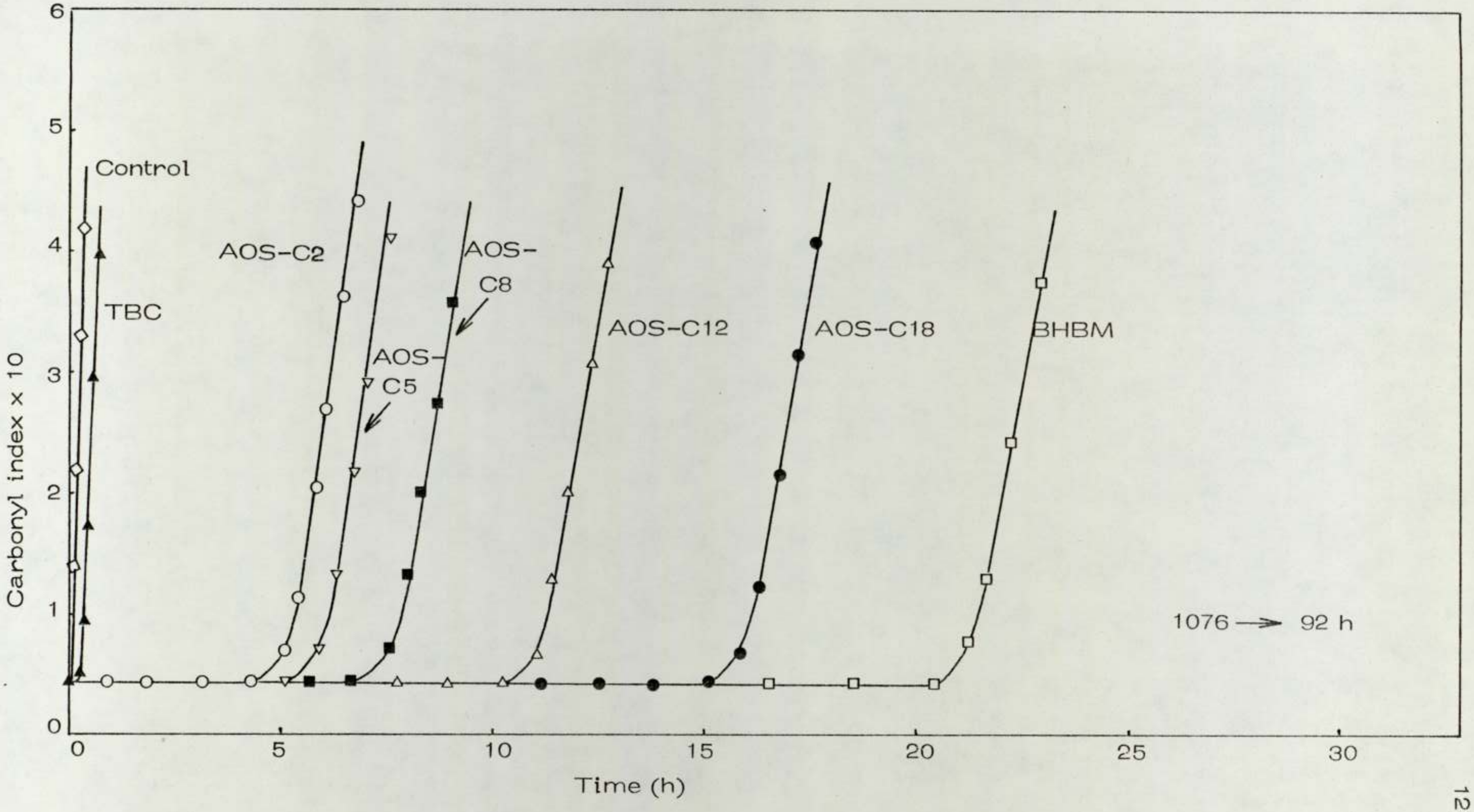


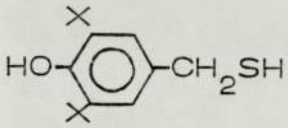
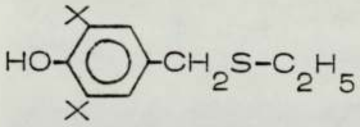
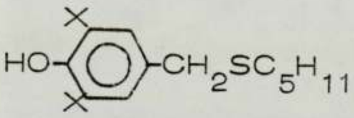
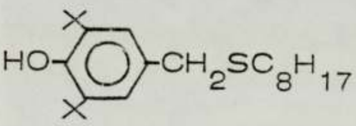
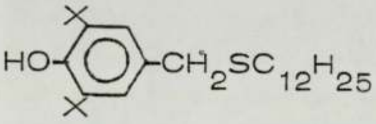
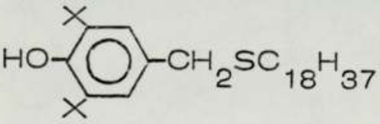
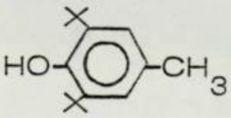
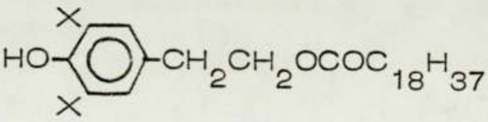
Fig 3.7 Thermal oxidation of polypropylene films (at 140°C) in a flowing atmosphere (3.0 cu ft/h). Concentration of antioxidants = 6×10^{-4} mole/100 g)

and the two commercial antioxidants in polypropylene films subjected to thermal oxidation in a flowing atmosphere (air at 3.0 cu ft/h). The higher molecular weight homologues (with the exception of BHBM) showed greater stabilising activities in comparison to their lower molecular weight counterparts. These effects were probably due, in large measures, to the differing contribution made by the physical loss of antioxidants by volatilisation. It is also seen that TBC, despite its high chemical activity relative to 1076 as shown in the decalin studies, was rendered ineffective in a flowing atmosphere. Table 3.5 shows the differing induction periods given by the antioxidants and Fig 3.8 succinctly illustrates the dependence of the stabilising activity on the antioxidants' molecular weight.

It also appeared that BHBM showed anamolous behaviour in that its comparative antioxidant effectiveness did not fall in line with the other members of the antioxidant series. Possibly binding reactions of BHBM to the polymer backbone and/or the formation of higher molecular weight antioxidants might provide an explanation to the anomaly (to be discussed in Chapter 6).

In order to further collate the contributions and influences made by the physical characteristics of antioxidants to their stabilising

Table 3.5 Induction periods of polypropylene films containing various antioxidants subjected to thermal oxidation in a flowing (air) atmosphere (conc of antioxidants = 6×10^{-4} mole/100 g; Temp = 140°C)

Additives	Induction period, h
Control (no additives)	0.2
	21.0
	5.0
	6.0
	7.5
	11.0
	15.0
	0.4
	92.0

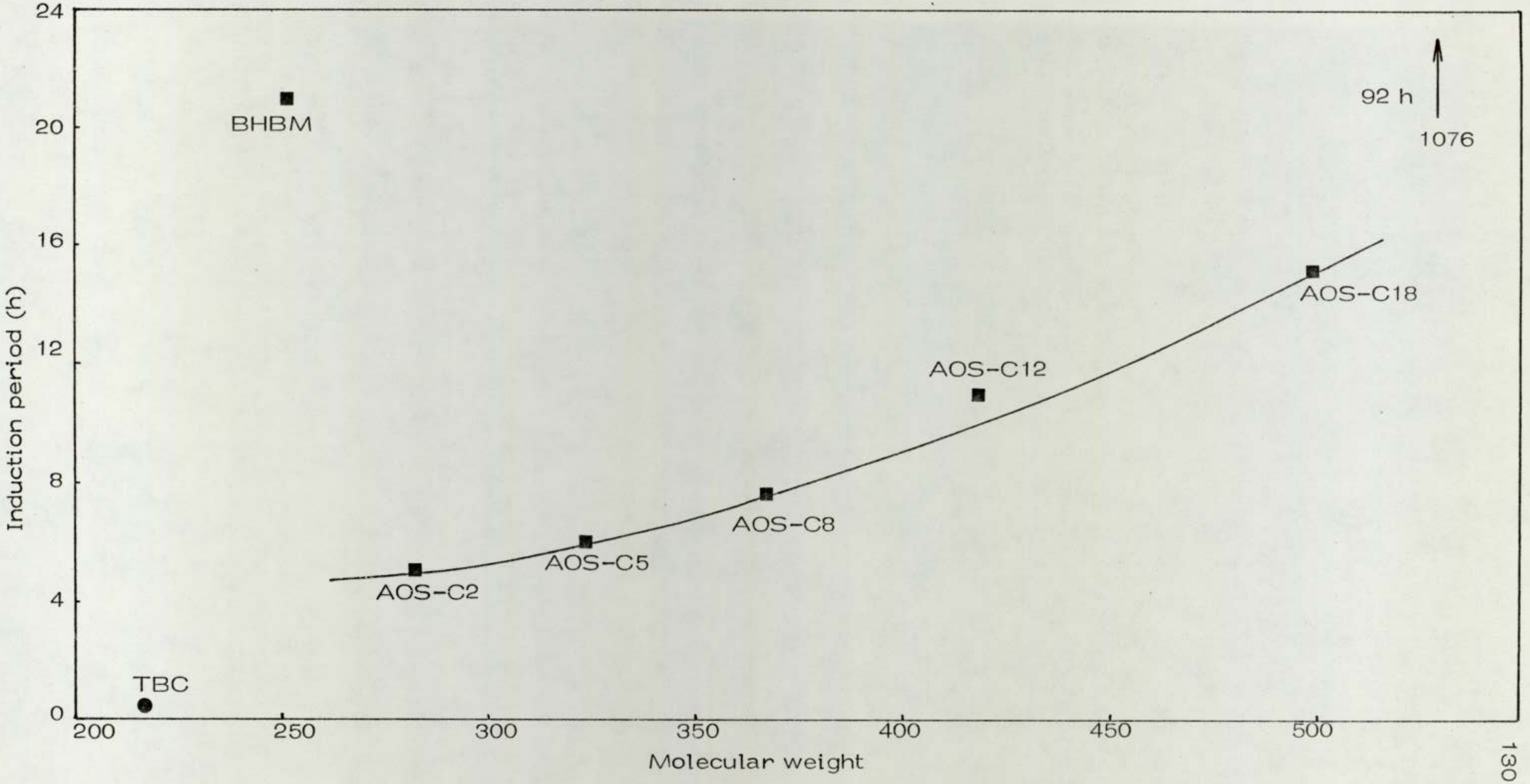


Fig 3.8 Dependence of stabilising activity (in polypropylene) on the antioxidants' molecular weight in a flowing atmosphere (3.0 cu ft/h) at 140°C

effectiveness, a study of volatility characteristics of the neat antioxidants was undertaken.

3.4 Antioxidant Volatility in Nitrogen Atmosphere

The method of determination of volatility of neat antioxidants was as described in section 2.1.15. The differences in the volatilities of the antioxidants were found to be large and in order to obtain conveniently measurable weight losses on all the antioxidants studied, temperatures of 120, 140 and 160°C were used.

The procedure for the determination of volatility was found to be very reproducible. The typical weight loss measurements at 140°C are shown in Fig 3.9 for the synthesised antioxidants and Fig 3.10 for the comparison of TBC, 1076, BHBM and AOS-C12. It is seen that the plot of the weight loss by volatilisation against time is a straight line. The strict linearity of the plot confirms that the antioxidants were probably not undergoing reaction at the test temperature. Table 3.6 shows the rate of weight loss of the antioxidants at varying temperatures depicting the trend that increasing the pendant chain lengths reduced the volatility behaviour of the additives.

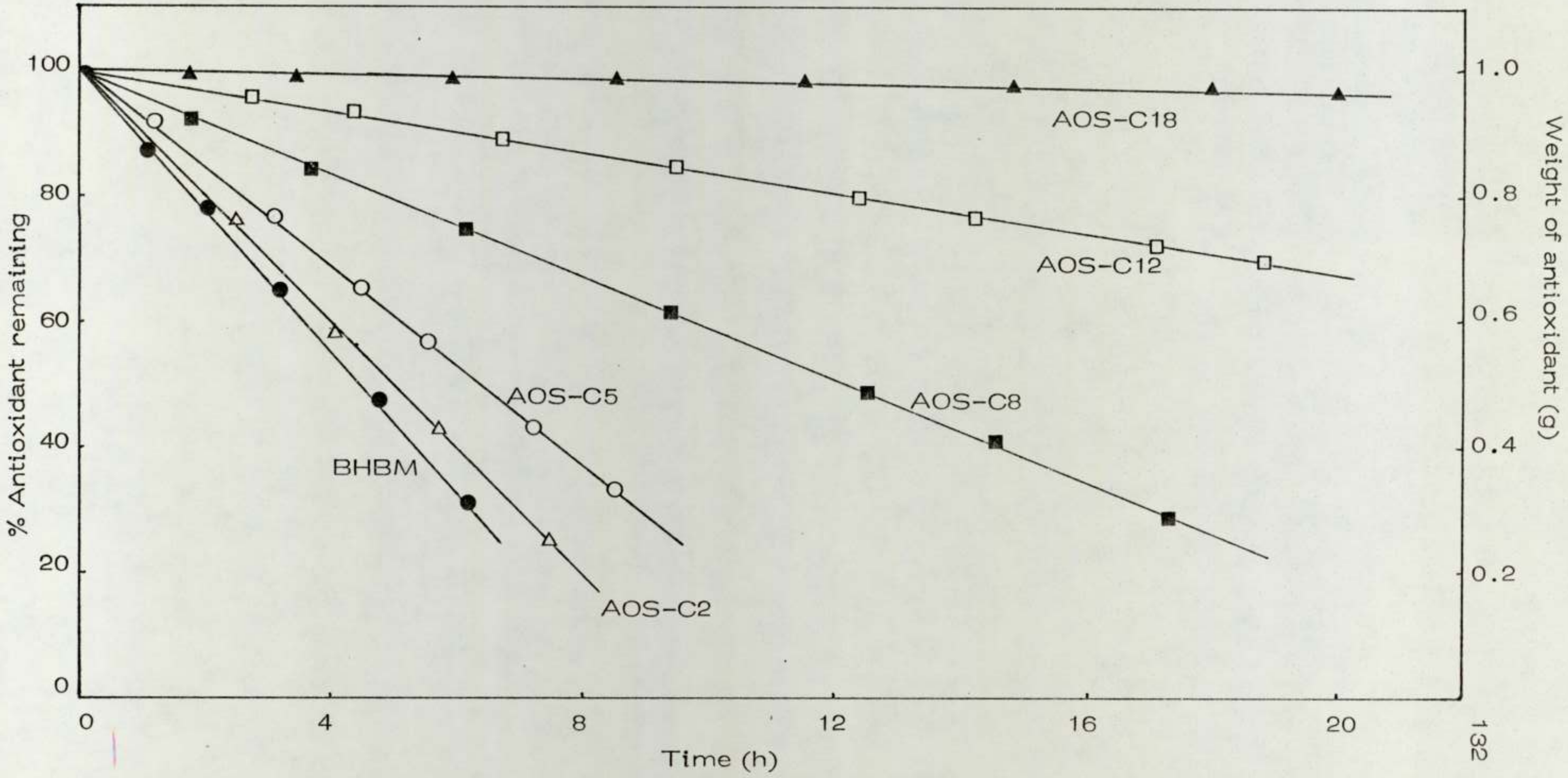


Fig 3.9 Volatilities of the neat antioxidant series in nitrogen atmosphere at 140°C

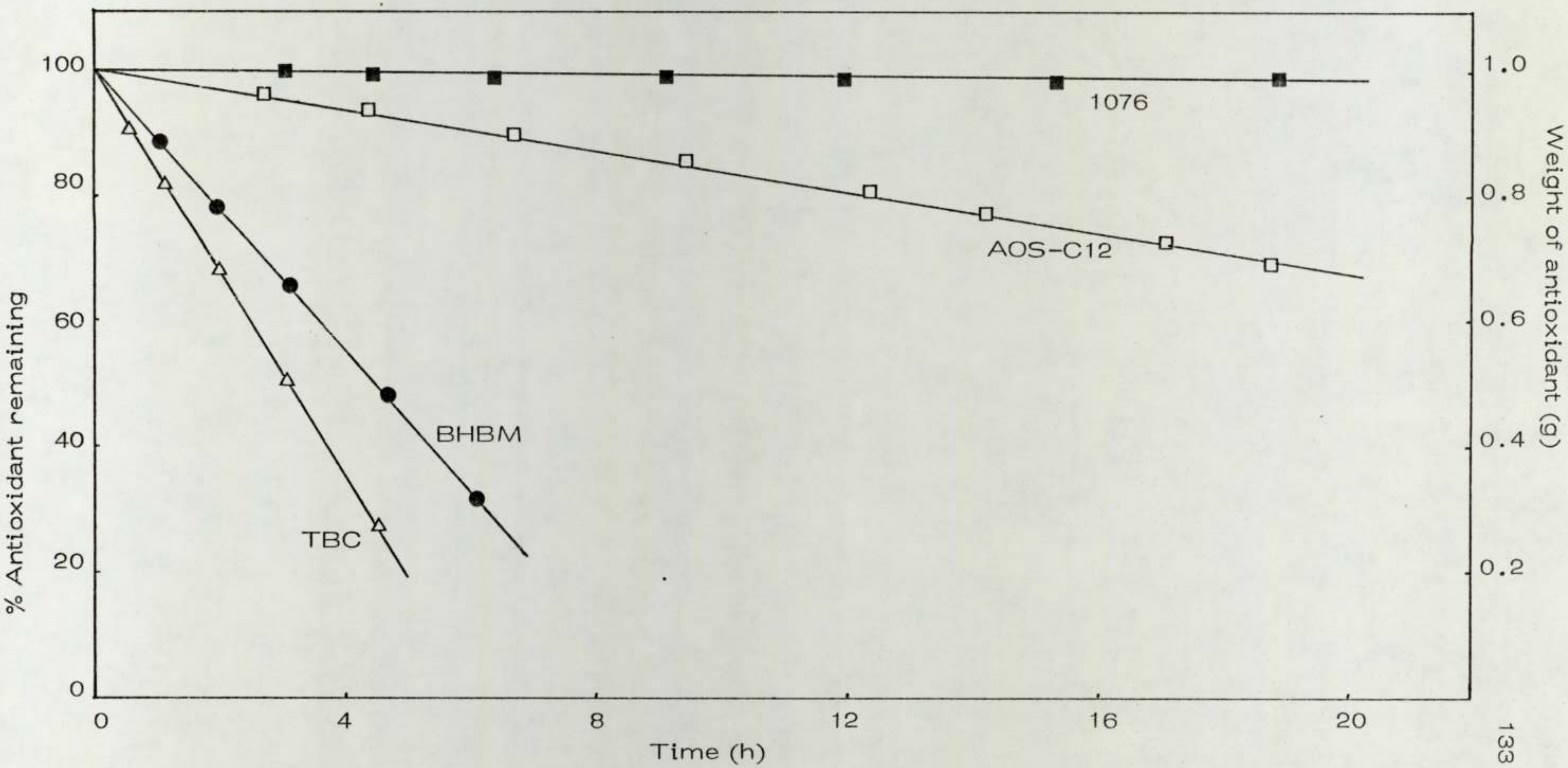
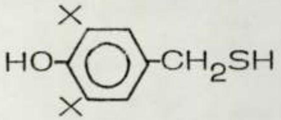
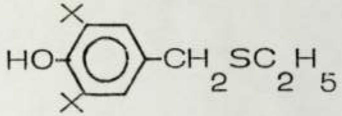
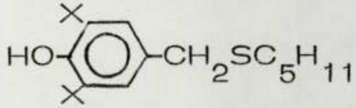
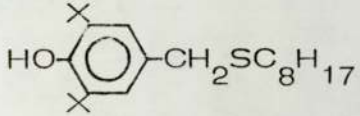
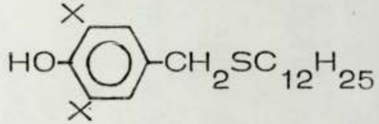
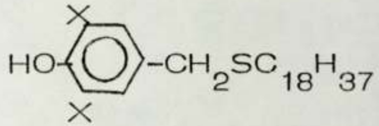
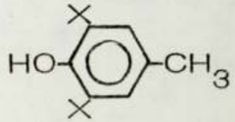
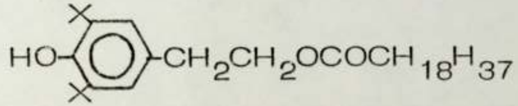


Fig 3.10 Comparison of the volatilities of commercial antioxidants and the synthesised antioxidants in nitrogen atmosphere at 140^{o}C

Table 3.6 Weight loss of antioxidants at different temperatures of 120, 140 and 160^oC

Additives	Weight loss, g/h × 10^3		
	120^oC	140oC	160^oC
	26.9	110.0	475.0
	26.4	100.0	460.0
	18.7	77.5	350.0
	10.1	41.3	220.0
	3.3	15.0	80.0
	0.45	2.0	10.1
	34.2	157.5	600.0
	–	0.7	3.2

Semi-log plots of volatility loss -vs- temperature (Fig 3.11) exhibits a straight line relationship. This is in accord with those found by Spacht et al(149) and Plant and Scott(145) in that the semi-log plot of volatility loss -vs- temperature showed a linear relationship. A semi-log plot of volatility loss against the antioxidants' molecular weight was also carried out and this is shown in Fig 3.12 which conclusively shows the strong influence of molecular weight on the volatility of the antioxidants.

3.5 Antioxidant Solubility in a Hydrocarbon Solvent

The hydrocarbon solvent chosen as a model for polypropylene in evaluating antioxidant solubility was n-hexane. The solubilities of the antioxidants in the solvent are shown in Table 3.7. Within the antioxidant series, BHBM appeared to be highly soluble having a solubility of 96 g/100 g hexane. In contrast, AOS-C2 was least soluble (43.0 g/100 g hexane). AOS-C5 and AOS-C8 were both fully miscible followed by a declining solubility depicted by AOS-C12 (94 g/100 g) and AOS-C18 (57 g/100 g). TBC and 1076 both possessed solubilities of 98.0 g/100 g and 64 g/100 g respectively. The implications of these data for antioxidant effectiveness in polypropylene will be made in section 3.9.

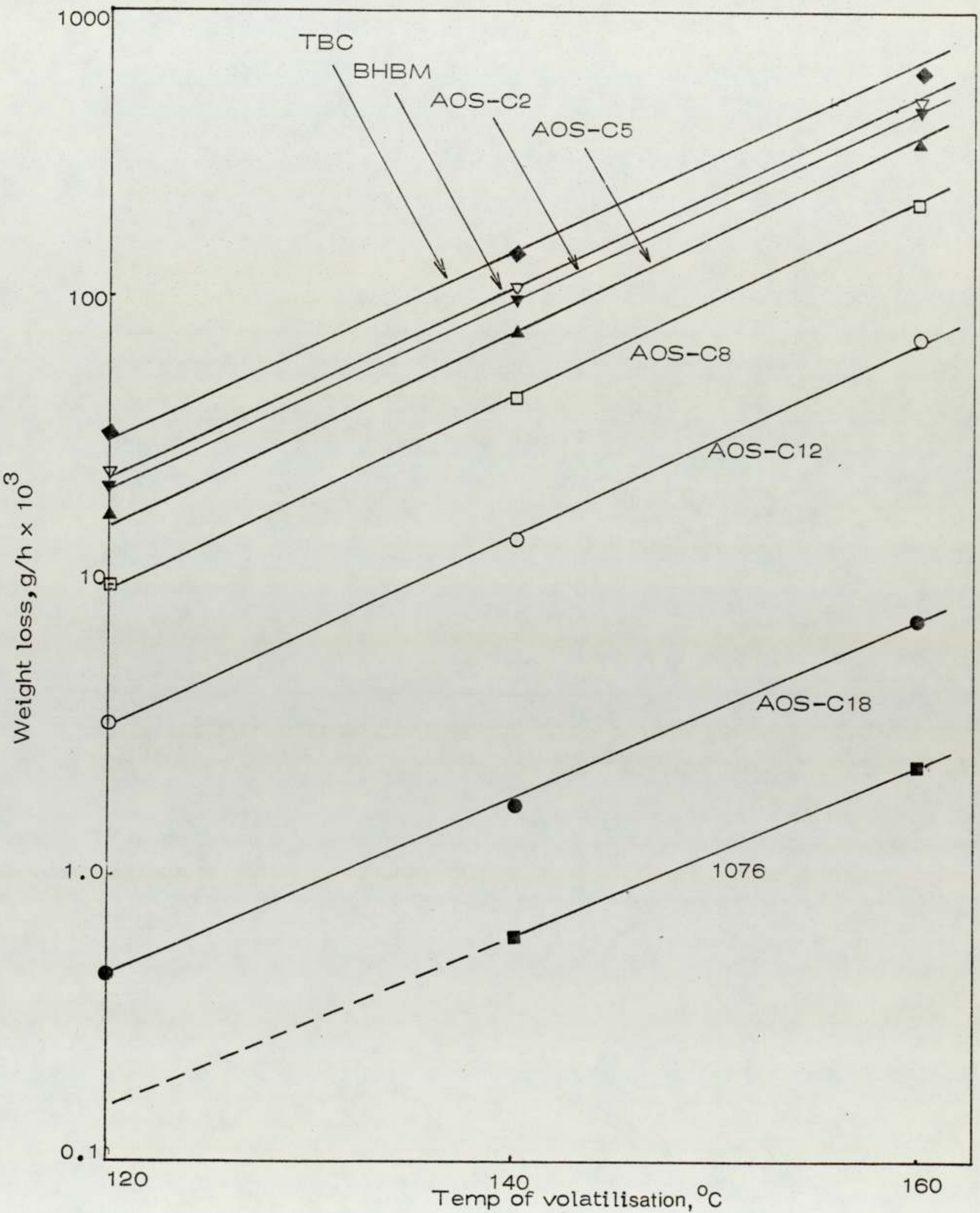


Fig 3.11 Semi-log plot of volatilities -vs- temperature

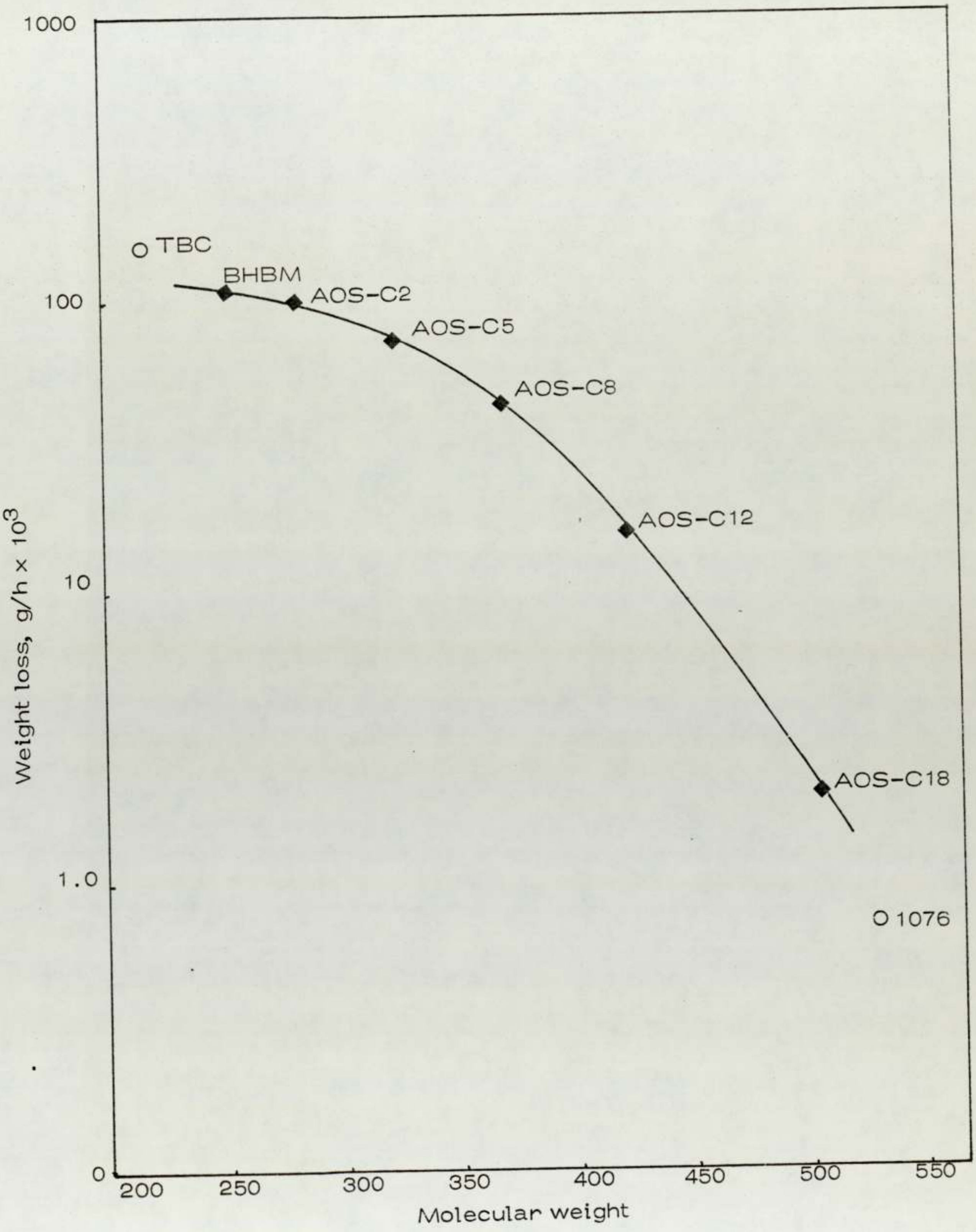
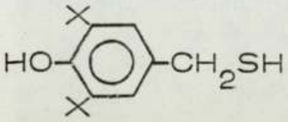
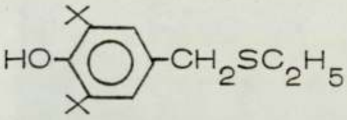
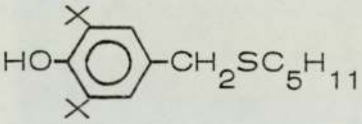
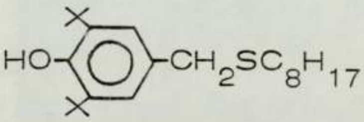
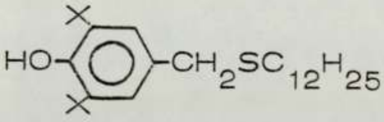
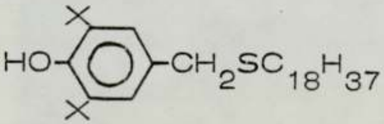
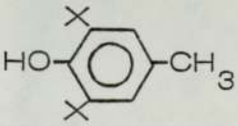
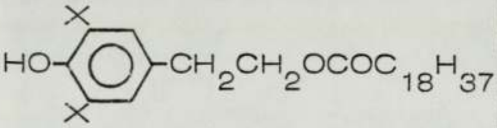


Fig 3.12 Semi-log plot of volatility -vs- molecular weight of the additives at 140°C

Table 3.7 Solubility of Additives in n-hexane at 25°C

Additives	g additives/100 g n-hexane
	96
	43
	Fully miscible
	Fully miscible
	94
	57
	98
	64

3.6 Peroxide-decomposing Activity of the Synthesised Antioxidant Series

Even though it is now known that BHBM, for instance, shows dual functionality of a chain-breaking-cum-peroxide decomposer, the present studies attempted to examine the series of antioxidants as catalysts for the destruction of tertiarybutyl hydroperoxide (TBHP). The same equimolar concentration (5.8×10^{-2} mole/l) in chlorobenzene was used in all cases.

All showed an induction period followed by a rapid pseudo first-order catalytic destruction of the hydroperoxide shown typically for BHBM and AOS-C12 in Fig 3.13. The molar ratio of TBHP to the antioxidant was $\simeq$10:1. The rate of decomposition of TBHP at the same temperature but in the absence of the catalyst was very low by comparison. Fig 3.13 also shows the effect of adding more hydroperoxide when the concentration of the initially added hydroperoxides had been reduced to a very low concentration. In each case, the reaction recommenced at the same first-order rate within the limits of experimental error but without the induction period.

The first order rate constants of the first and second stages of

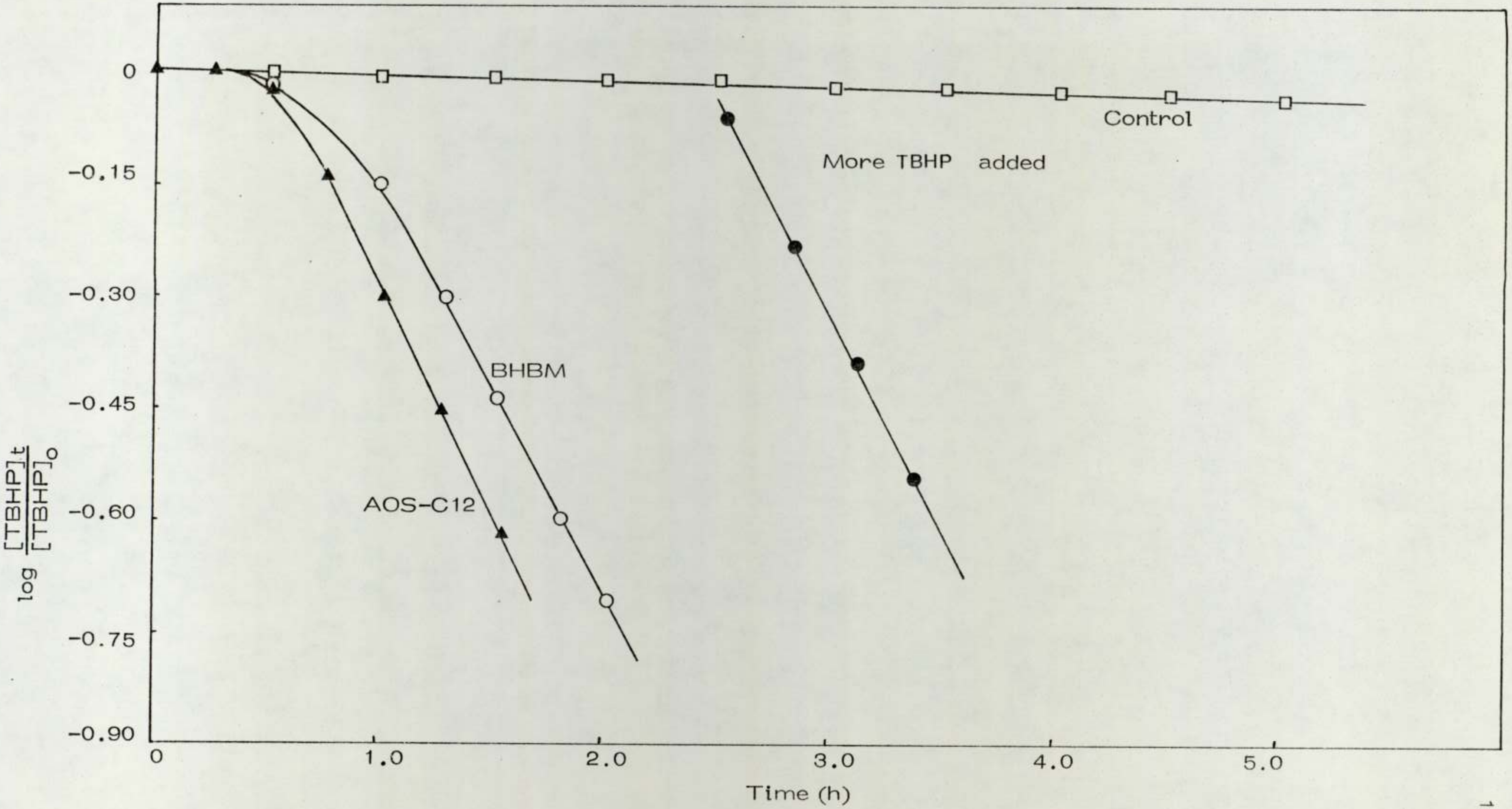


Fig 3.13 Catalytic decomposition of TBHP by BHBM and AOS-C12 at 65°C. $[TBHP]_o = 2.6 \times 10^{-1}$ M, $[Additive]_o = 5.8 \times 10^{-2}$ M in chlorobenzene. (Method of TBHP evaluation was by monitoring ir peak at 3538 cm^{-1})

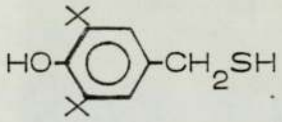
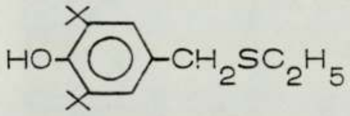
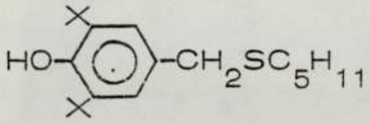
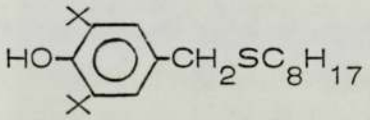
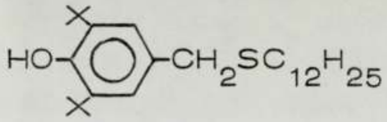
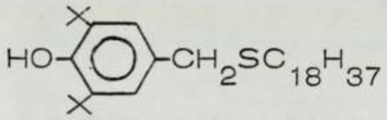
the reactions together with their average values are listed in Table 3.8 which shows rather good reproducibility. The induction periods measured for each additive showed a relatively insignificant departure from the value of 30 mins. Hence the studies demonstrated the antioxidant series to be powerful peroxide decomposers and increasing the molecular weight did not give any positive or deleterious effect.

3.7 Uv Ageing Behaviour of Polypropylene Films Containing the Antioxidant Series

The results of the preceding section demonstrated the synthesised antioxidants to be powerful peroxide decomposers. It was therefore thought desirable to evaluate the contribution of this facile reaction in the photo-stabilisation of polypropylene films. In addition to the peroxide decomposing activity, the presence of the phenolic OH within the molecule should further enhance the protective ability imparted by the additives.

Fig 3.14 shows the photo-stability afforded by the antioxidants at a concentration of 2×10^{-4} mole/100 g. BHBM was found to be least effective. However, increasing the pendant chain from C2 to C12 gave a marginal but positive effect. Whilst TBC,

Table 3.8 Induction periods and pseudo first-order rate constants for the destruction of TBHP by the sulphur antioxidants at 65°C (TBHP conc = 2.6×10^{-1} M; additive conc = 5.8×10^{-2} M)

Additives	Induction period, m	Rate constants, $k10^3s^{-1}$		
		1st stage	2nd stage	Av
	30	1.7	1.4	1.6
	35	1.6	2.0	1.8
	30	1.7	1.9	1.8
	30	2.2	1.8	2.0
	35	2.0	2.0	2.0
	35	1.6	2.0	1.8

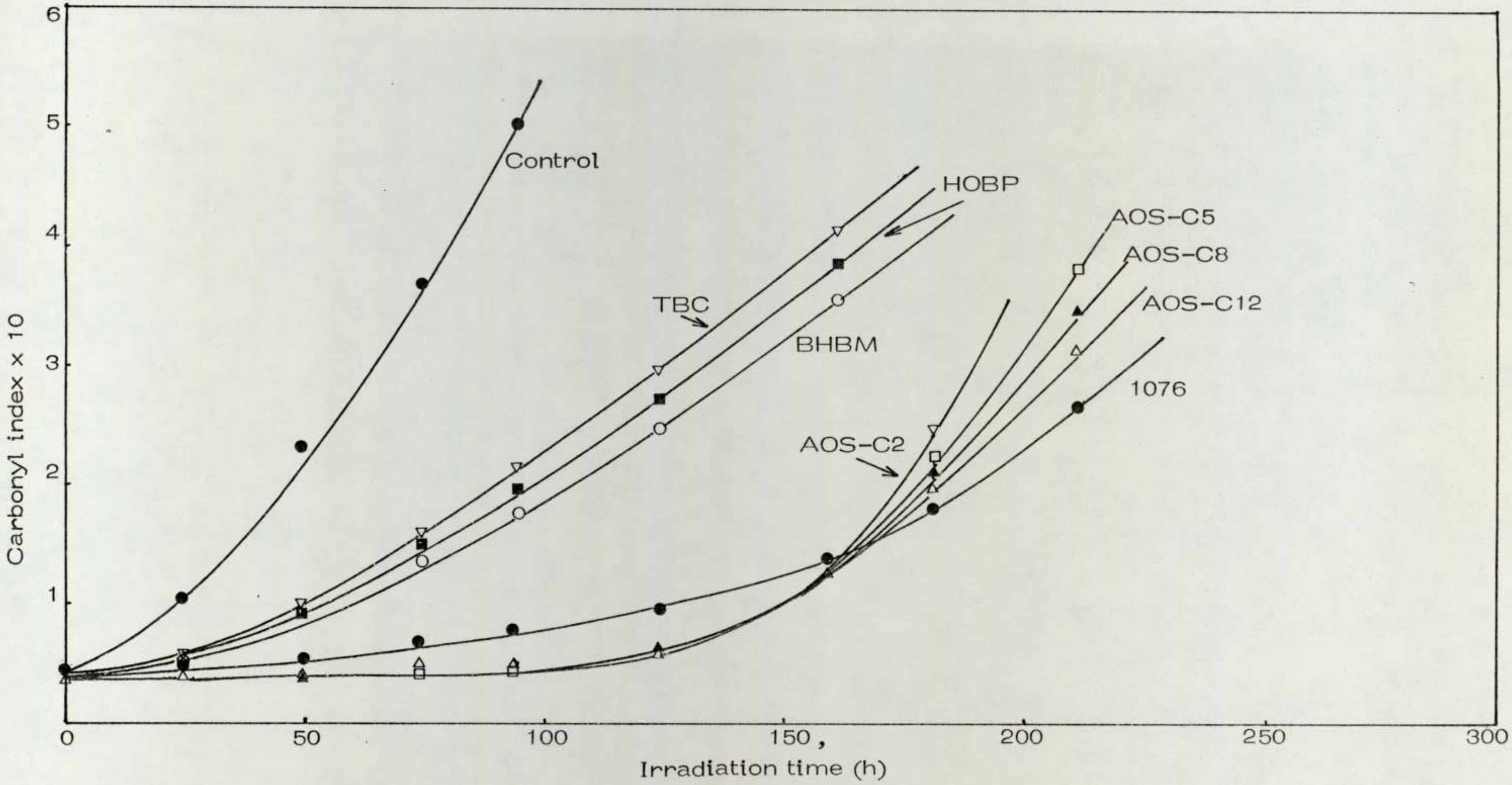


Fig 3.14 Uv exposure of polypropylene films containing antioxidants at 2×10^{-4} mole/100 g polymer

BHBM, HOBP and 1076 showed auto-accelerating characteristics, those of the antioxidant series exhibited a truer induction period as mirrored by the insignificant increase in carbonyl index within 125 h of uv exposure. This is presumably indicative of the operation of the catalytic peroxide-annihilating activities of the additives. It is not clear why BHBM showed anomalous behaviour at this particular concentration. Probably this could be accounted for by the losses due to volatilisation during the film-making stage.

However, increasing the antioxidant concentration to 6×10^{-4} mole/100 g as illustrated in Fig 3.15 brought BHBM into congruity with the other members of the antioxidant series and with the added bonus of offering the best photoprotection amongst the sulphur antioxidants. The change-over from being the least effective to the most effective antioxidant probably suggests the presence of a critical concentration above which its inhibitory performance becomes potent. Closely allied to this is the proposition that the binding reaction of BHBM to the polymer backbone has taken place (to be discussed further in Chapter 6).

A new feature is observed in Fig 3.15 in which the sulphur antioxidantsshow a distinct initial pro-oxidant effect. This

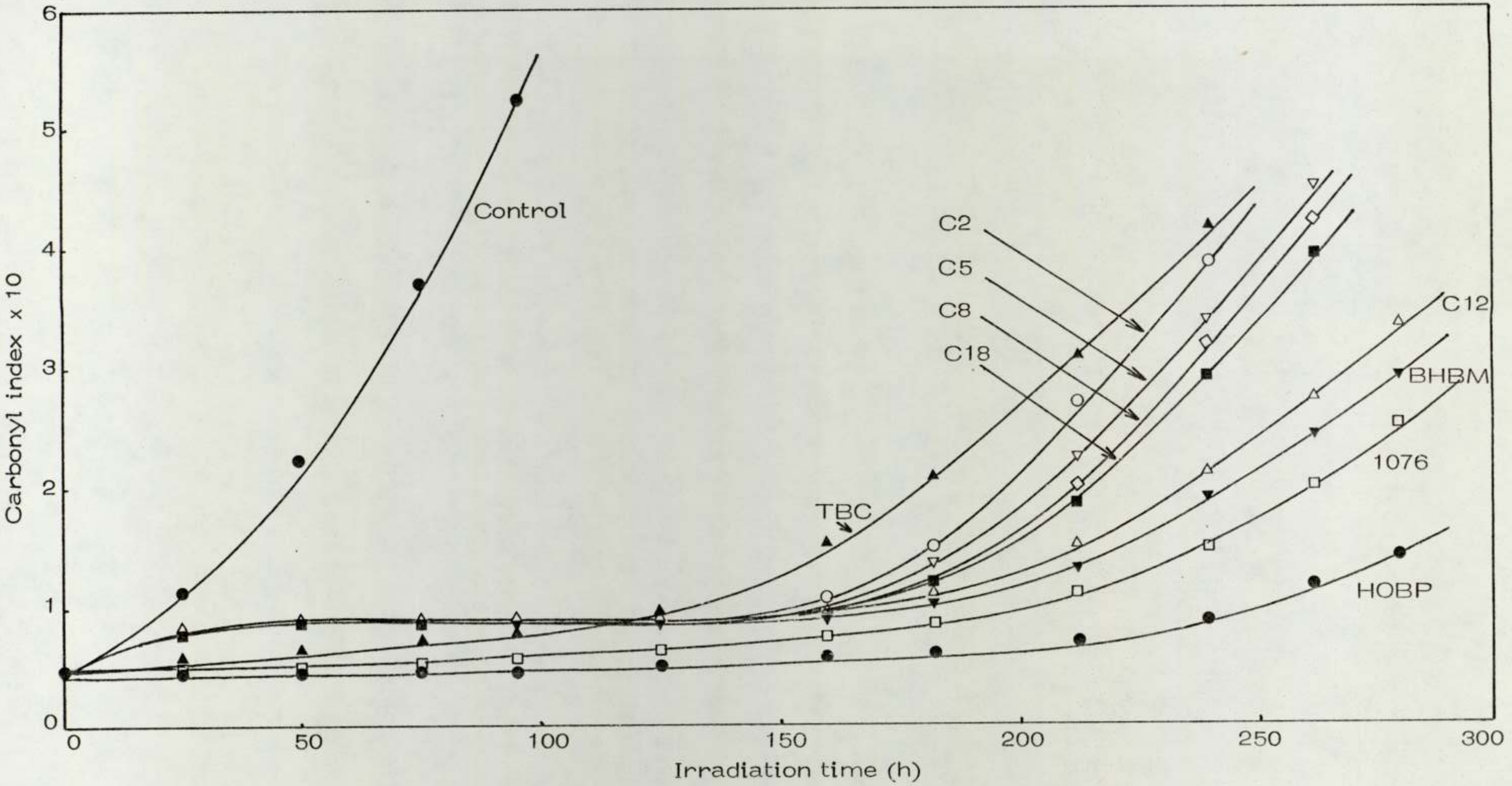


Fig 3.15 Uv exposure of polypropylene films containing antioxidant at 6 x 10^{-4} mole/100 g

occurrence however is in line with the known photo-chemistry of sulphur compounds in that on uv irradiation they initially generate free radicals in their transformation to active stabilising species, as mentioned in Chapter 1. The pro-oxidant behaviour was then followed by a period of effective stabilisation for about 180 h after which carbonyl content within the polymer began to increase. TBC, 1076 and HOBP did not give a true induction period and again showed auto-accelerating characteristics.

It is also observed from Figs 3.14 and 3.15 that increasing the pendant chain from C2 to C12 provided a positive even though marginal increase in stabilisation up to C12 followed by reduced performance of AOS-C18. The inferior performance of AOS-C18 was probably indicative of its lower compatibility with the polymer as reported in section 3.2. Under conditions where volatilisation was not important, the influence of antioxidant-polymer compatibility may play a determining and major role in the stabilisation process.

The marginal increase in photoprotection shown in the antioxidant series again appears to be in accord with the known photochemistry of sulphur compounds in that their peroxide decomposing ability occurs at the expense of the severance of the sulphur bonds to other lower molecular weight products, thereby rendering the synthesised antioxidants ineffective with increasing molecular weight.

A similar trend is shown at the still higher concentration of 10^{-3} mole/100 g as shown by Fig 3.16. The initial pro-oxidant effect was even more marked followed by effective stabilisation behaviour. BHBM now out-performed the other antioxidants (with the exception of HOBP) suggesting that binding of BHBM had taken place and/or the formation of other molecular species such as the bis-monosulphide or disulphide.

Embrittlement times of the exposed polymer films are shown in Table 3.9 indicating comparable stabilisation afforded by the antioxidant series to that of the simple phenolic antioxidants such as 1076. This fact suggests that ~~despite the peroxide-decomposing behaviour of the antioxidants, the initial pro-oxidant acitivity that generates free radicals and stabilising species could not redeem greater photo-stability to the polymer as to significantly out-weigh that given by the phenolic antioxidant. In other words,~~ the damage incurred to the polymer during the pro-oxidant stage was just off-set by the stabilisation endowed by the oxidation products.

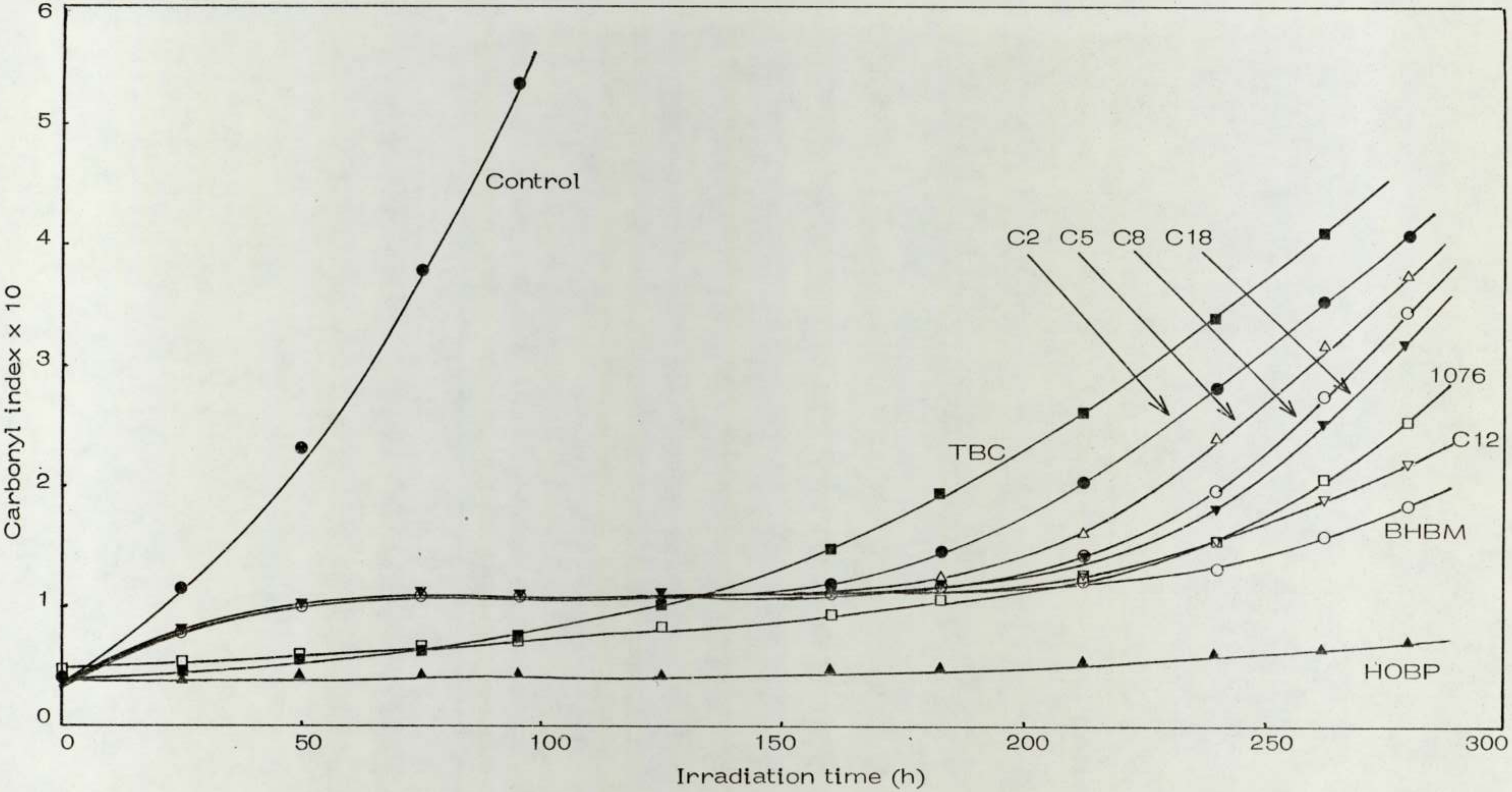


Fig 3.16 Uv exposure of polypropylene films containing antioxidants at 10×10^{-4} mole/100 g

Table 3.9 Embrittlement times of polypropylene films containing varying concentrations of antioxidants subjected to uv exposure

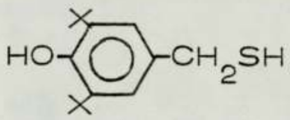
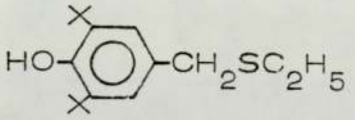
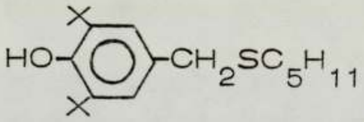
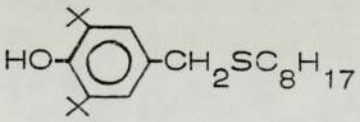
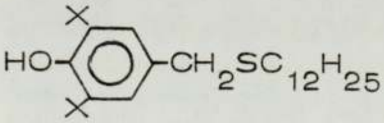
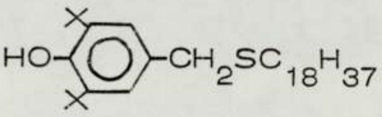
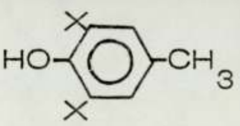
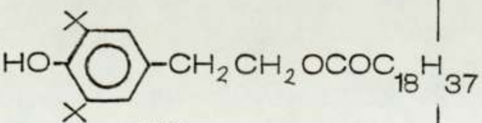
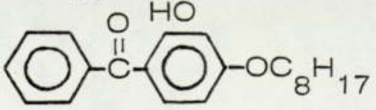
Antioxidants	Embrittlement times, $h \pm 2.5\%$		
	2×10^{-4} mole/100 g	6×10^{-4} mole/100 g	10×10^{-4} mole/100 g
Control		75	
	125	225	270
	160	180	210
	165	180	220
	165	195	245
	165	210	260
	160	190	235
	120	155	190
	180	215	260
	140	460	750

Fig 3.17 clearly shows the relatively low concentration-dependence of the photo-stabilising performance of the antioxidant series as typified by AOS-C12. 1076 showed similar behaviour. HOBP on the other hand demonstrated strong concentration dependence of photo-stabilising activity lending testimony to the findings of Chakraborty and Scott(137) where similar trends of HOBP and 1076 behaviour were shown.

3.8 Processing Behaviour of Polypropylene Melt Containing the Antioxidant Series

When unstabilised polypropylene was processed in the chamber of the torque rheometer exposed to air at 180°C, the polymer underwent a rapid and catastrophic reduction in viscosity which resulted in a sticky unprocessable material. This is shown in Fig 3.18 indicating the changes in melt flow index (MFI) with processing time that accompanied this breakdown. The incorporation of 6×10^{-4} mole/100 g of the synthesised antioxidants prior to the melt processing dramatically delayed the rapid breakdown process. In fact, one of them (BHBM) showed no sign of any polymer breakdown within the 20 mins processing operation. However, for the antioxidant series from AOS-C2 to AOS-C12 the MFI values showed an inverse relationship with molecular

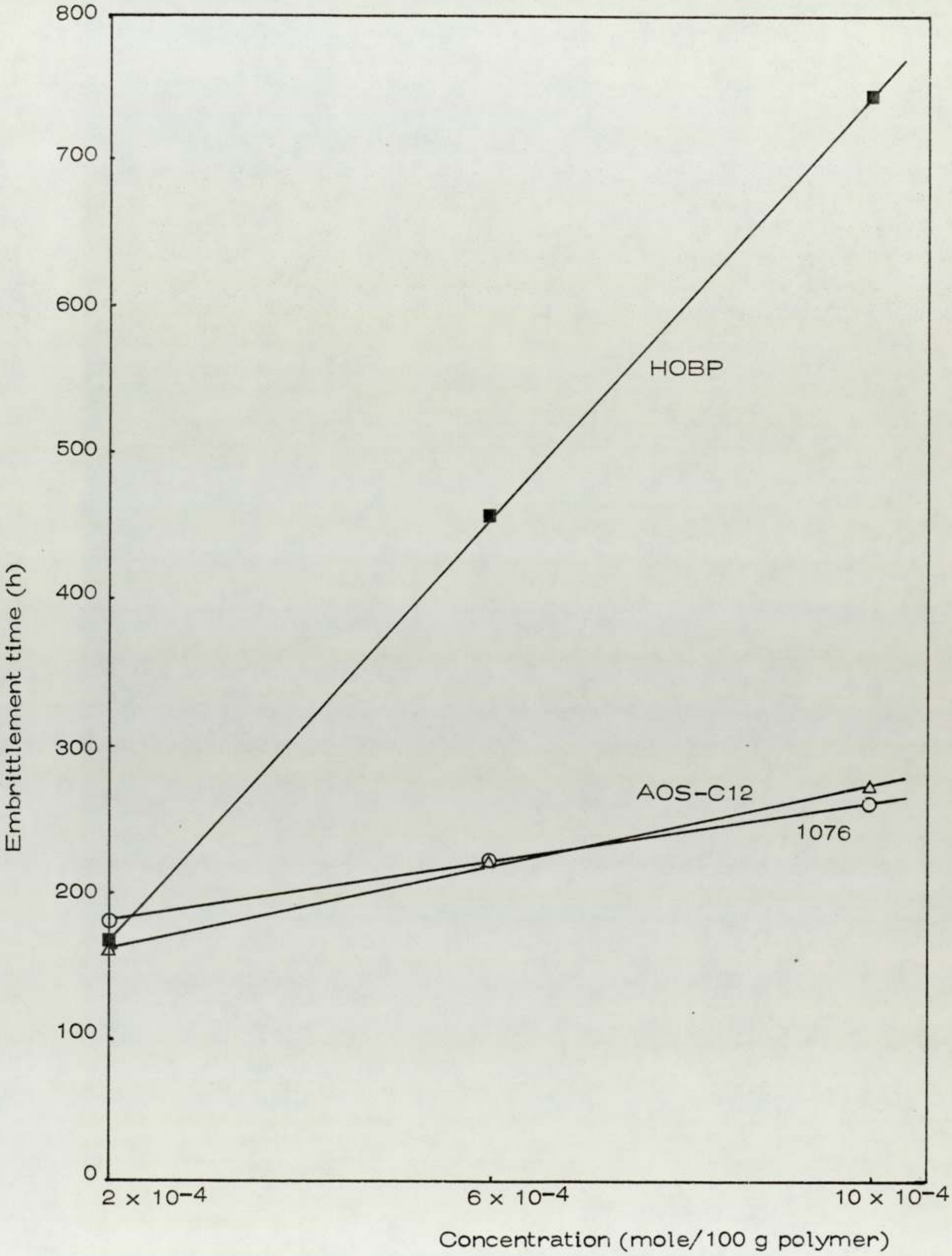


Fig 3.17 Effect of varying the antioxidant concentrations to uv embrittlement times

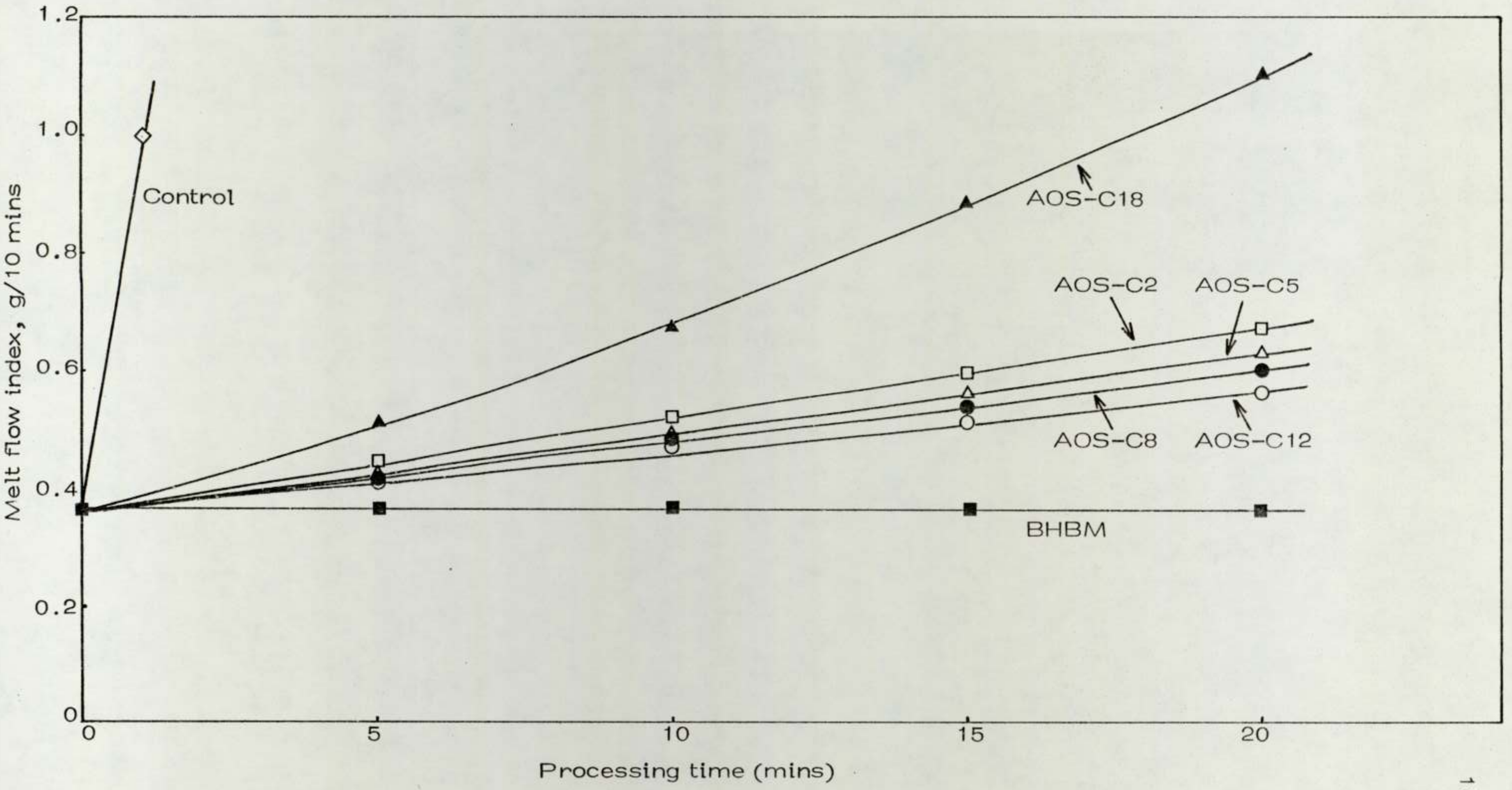


Fig 3.18 Variation of MFI with processing time in open chamber processing at 180°C (Concentration of additives = 6×10^{-4} mole/100 g)

weight suggesting that possibly volatility as well as compatibility phenomena were positively operating. An incongruous behaviour was however shown by AOS-C18. Even though its volatility was minimal, it did appear that the adverse influence of its relative incompatibility with the polymer was exerting a more prominent role. The lower solubility of this antioxidant in the n-hexane further substantiated this contention.

It appeared paradoxical that BHBM, being the most volatile additive within the series showed outstanding melt stabilisation properties when processed in open chamber. Obviously then, other factors were exerting a more dominant influence. There are at least two possibilities. One is the formation of the bis-monosulphides and disulphides which are themselves effective antioxidants and less volatile and secondly, the binding reaction of BHBM to the polymer thereby giving its high retention and permanence within the polymer. In fact these two possibilities are real as will be shown in Chapter 6.

Similar studies were made on the two commercial antioxidants as illustrated in Fig 3.19. 1076 and TBC were both effective melt stabilisers showing no appreciable increase in MFI with increasing processing time. It is hardly surprising that 1076 imparted

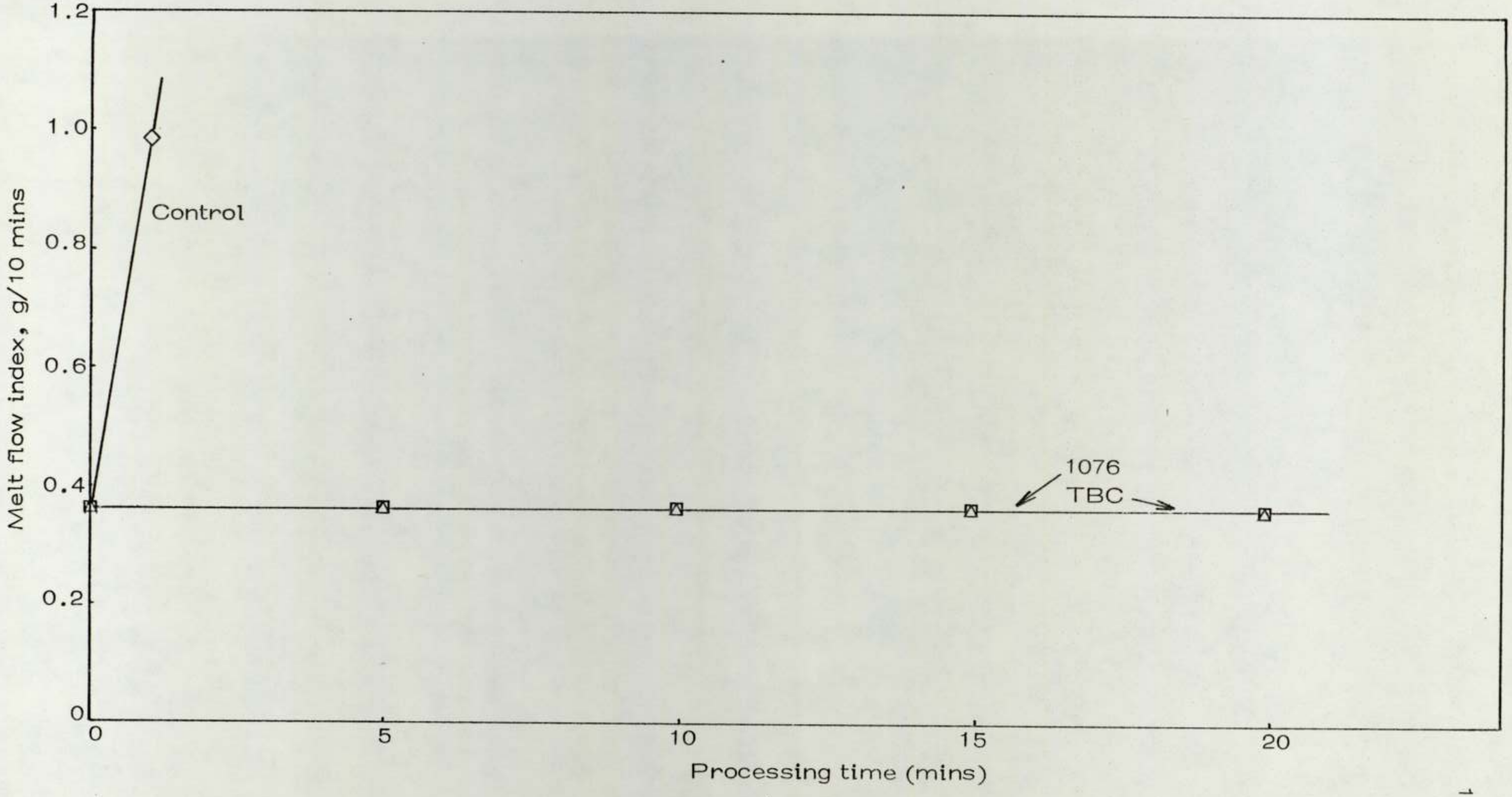


Fig 3.19 Variation of MFI with processing time in open chamber processing at 180^{o}C (Concentration of additives = 6 × 10^{-4} mole/100 g)

melt stability since it is a well-known thermal stabiliser and in addition the least volatile additive. Yet TBC, even though the most volatile antioxidant, still showed excellent melt stabilisation under aggressive melt processing operation. Inspection of the processed samples showed increasing intensity of yellowish discolouration with prolonged processing suggesting that TBC had been transformed to coloured products which were themselves melt stabilisers.

Pressing the samples to form films and taking their total colour difference (as described in section 2.1.16) gave the results depicted in Fig 3.20. BHBM also showed similar increase in colour intensity but to a lesser extent while 1076 gave minimal discolouration approaching that of the control samples. AOS-C12 which is inherently a light yellow antioxidant imparted its colour to the polymer. However the colour intensity decreased with prolonged processing times, indicative possibly of the destruction and/or volatilisation of the additives.

Data of torque -vs- processing times further substantiated the melt stabilisation provided by BHBM, 1076 and TBC as illustrated by Figs 3.21 and 3.22. The control sample showed a gradual decrease in torque with processing time when, after 20 mins, the

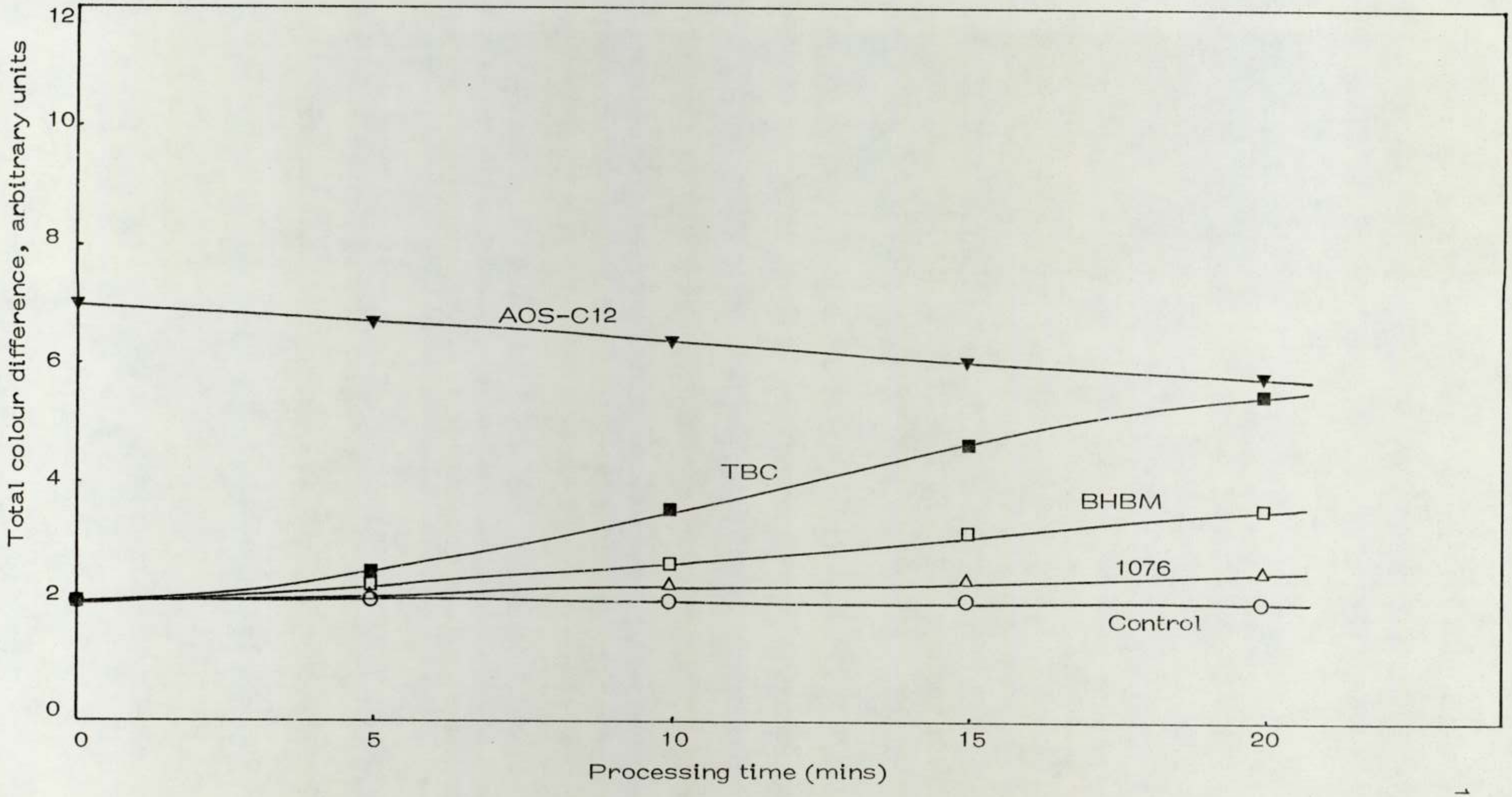


Fig 3.20 Variation of colour intensity with open chamber processing time at 180°C

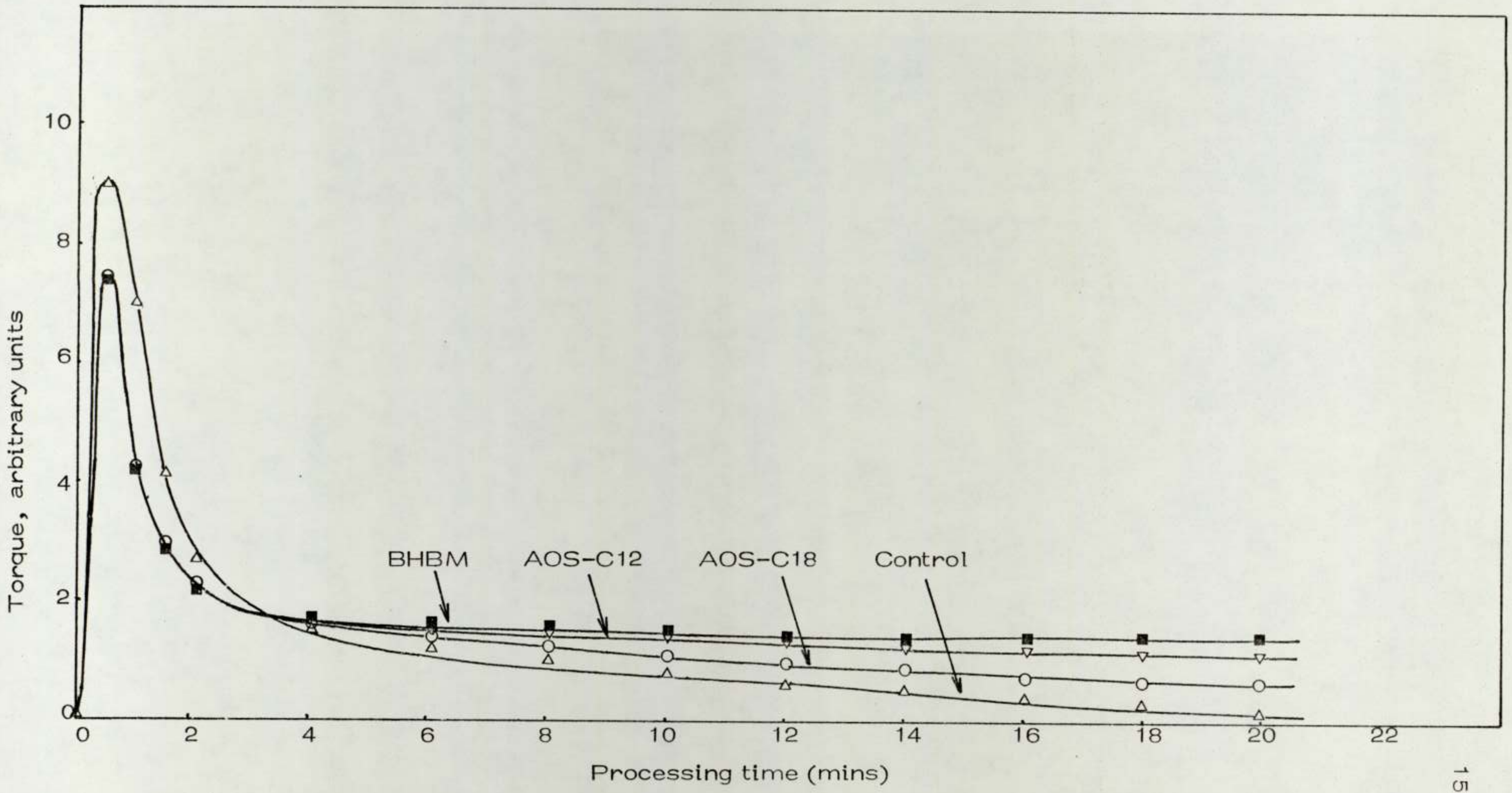


Fig 3.21 Dependence of torque of polymer melt on the (open chamber) processing time at 180°C
(Concentration of additives = 6×10^{-4} mole/100 g)

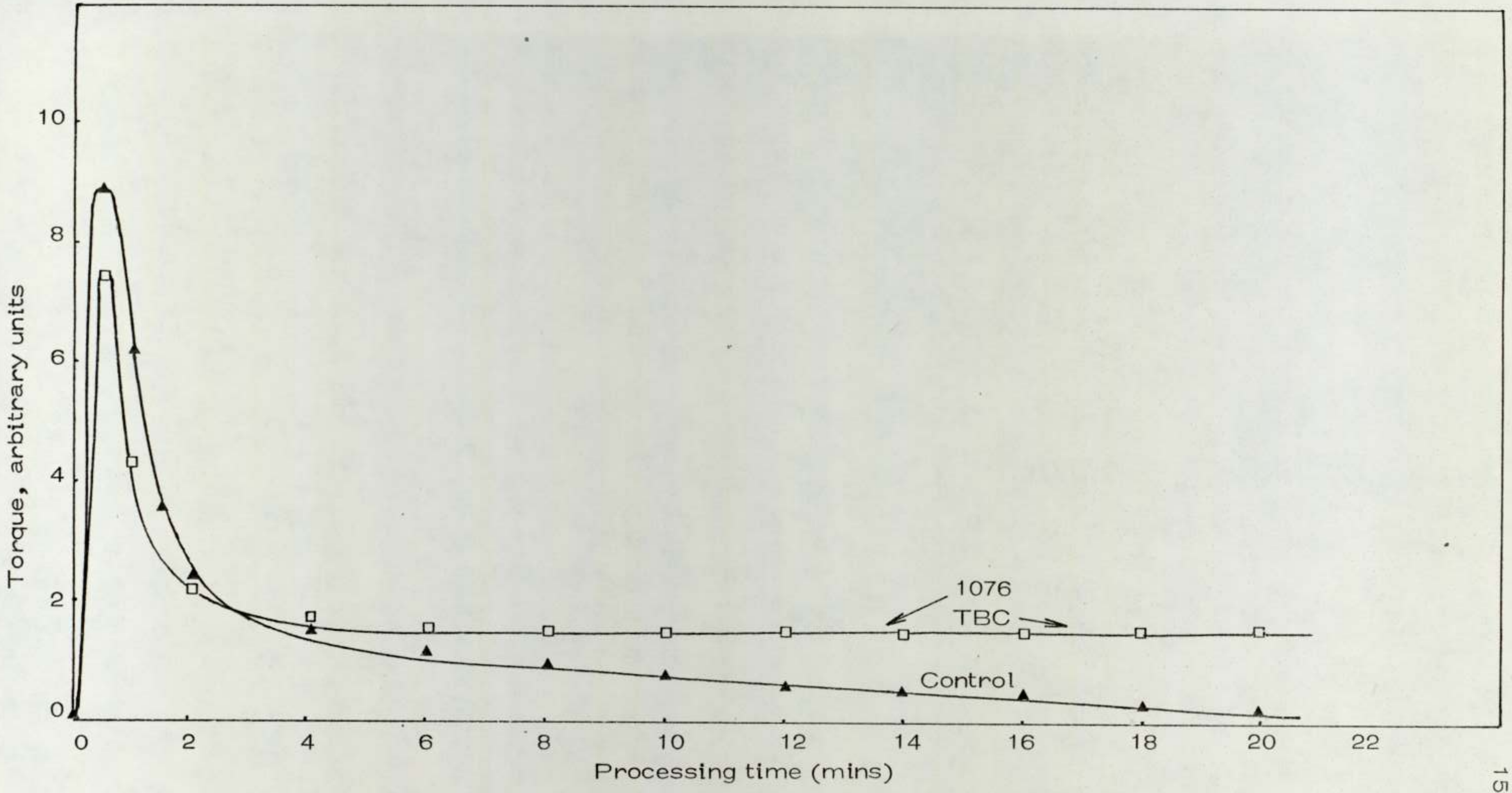


Fig 3.22 Dependence of torque of polymer melt on the (open chamber) processing time at 180°C
(Concentration of additives = 6×10^{-4} mole/100 g)

torque was virtually zero and the polymer was liquid-like in behaviour and appearance. In contrast, BHBM, 1076 and TBC showed constant torque between **5** and 20 mins of processing times reflecting the melt stabilisation imparted by the antioxidants. The antioxidant series which proved to be the lesser effective melt stabilisers demonstrated slight decrease in torque with processing time as typified by AOS-C12. The incongruous behaviour of AOS-C18 was also shown to be still less effective as reflected in the reduced torque values.

In order to restrict the influences of volatility and oxygen on the melt processing characteristics given by the antioxidants, processing operations were also carried out in the closed chamber of the torque rheometer. Fig 3.23 illustrates that while BHBM showed similar behaviour both in open and closed chamber processing, AOS-C12 demonstrated a relative reduction in the MFI values. AOS-C18 showed even greater reduction. It was not clear why this was so, but presumably the limited availability of oxygen destroyed the less compatible AOS-C18 to a much reduced extent so that comparatively more of the antioxidant was available to effect stabilisation to the polymer melt.

Fig 3.23 also shows the control sample to exhibit vastly differing

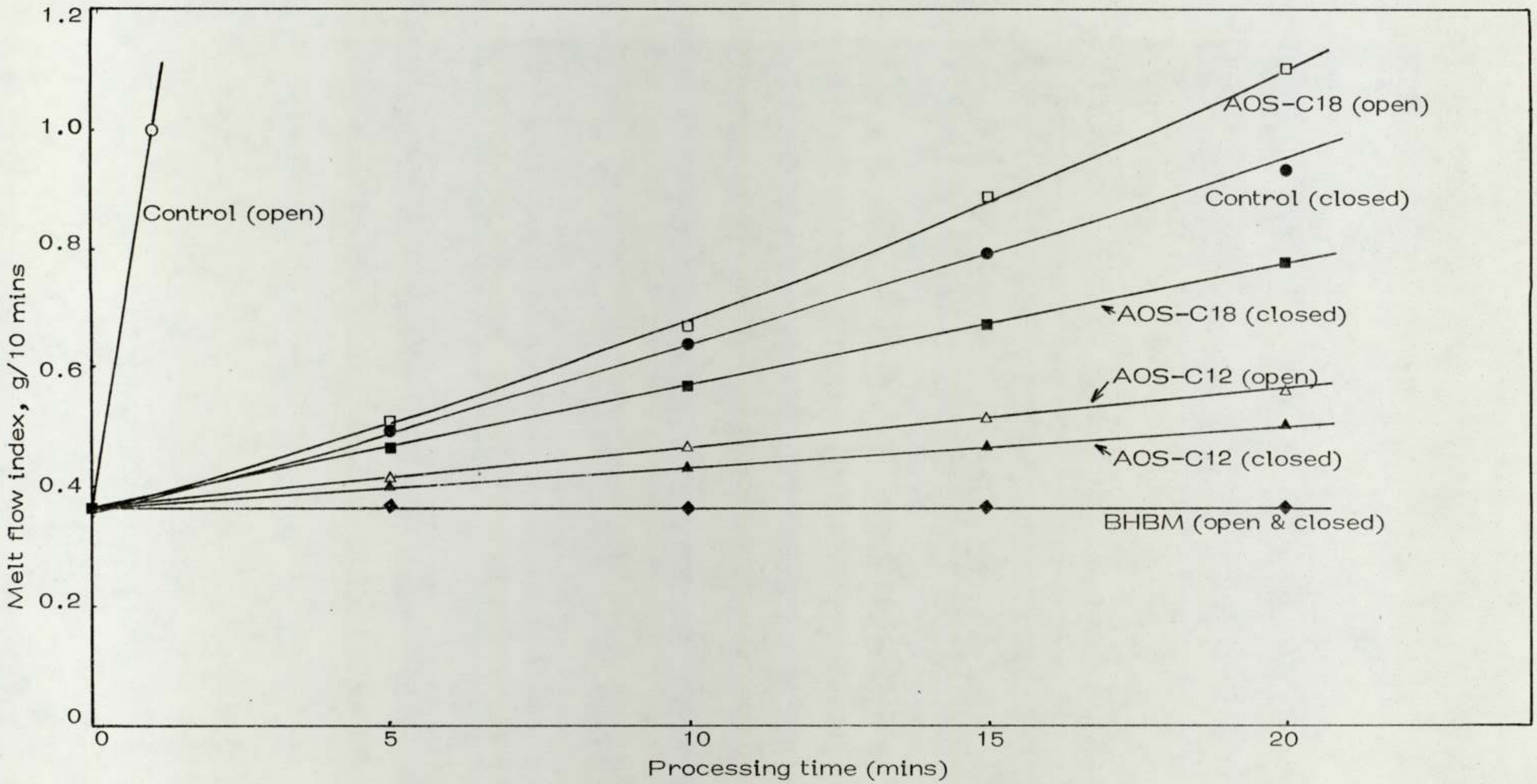


Fig 3.23 Variation of MFI with processing time processed in open and closed chambers at 180°C
(Concentration of additives = 6×10^{-4} mole/100 g)

melt flow behaviour when processed in the open and closed chamber providing testimony to the destructive role played by oxygen in the stability of polymers. The commercial antioxidants 1076 and TBC both showed similar behaviour in the two processing conditions as illustrated in Fig 3.24.

Fig 3.25 brings into focus the effect of increasing the additives' molecular weight to melt stabilisation. Increasing the pendant chain from C2 to C12 gave a significant reduction in MFI but then culminated in the inferior performance of AOS-C18. As mentioned earlier, the latter's incongruity was suggestive of the incompatibility phenomena of the antioxidant-polymer system.

Evaluation of the initial carbonyl content of the processed polymers should provide substantiative evidence regarding the melt stabilisation process. Fig 3.26 depicts the comparative carbonyl content of the control polymer samples processed under both aggressive and mild processing operations. It is seen that greater rate of carbonyl formation was observed in the open chamber processing relative to that in the closed chamber.

The trend shown by the antioxidant series (Fig 3.27) was similar to that reflected by the MFI data. The commercial

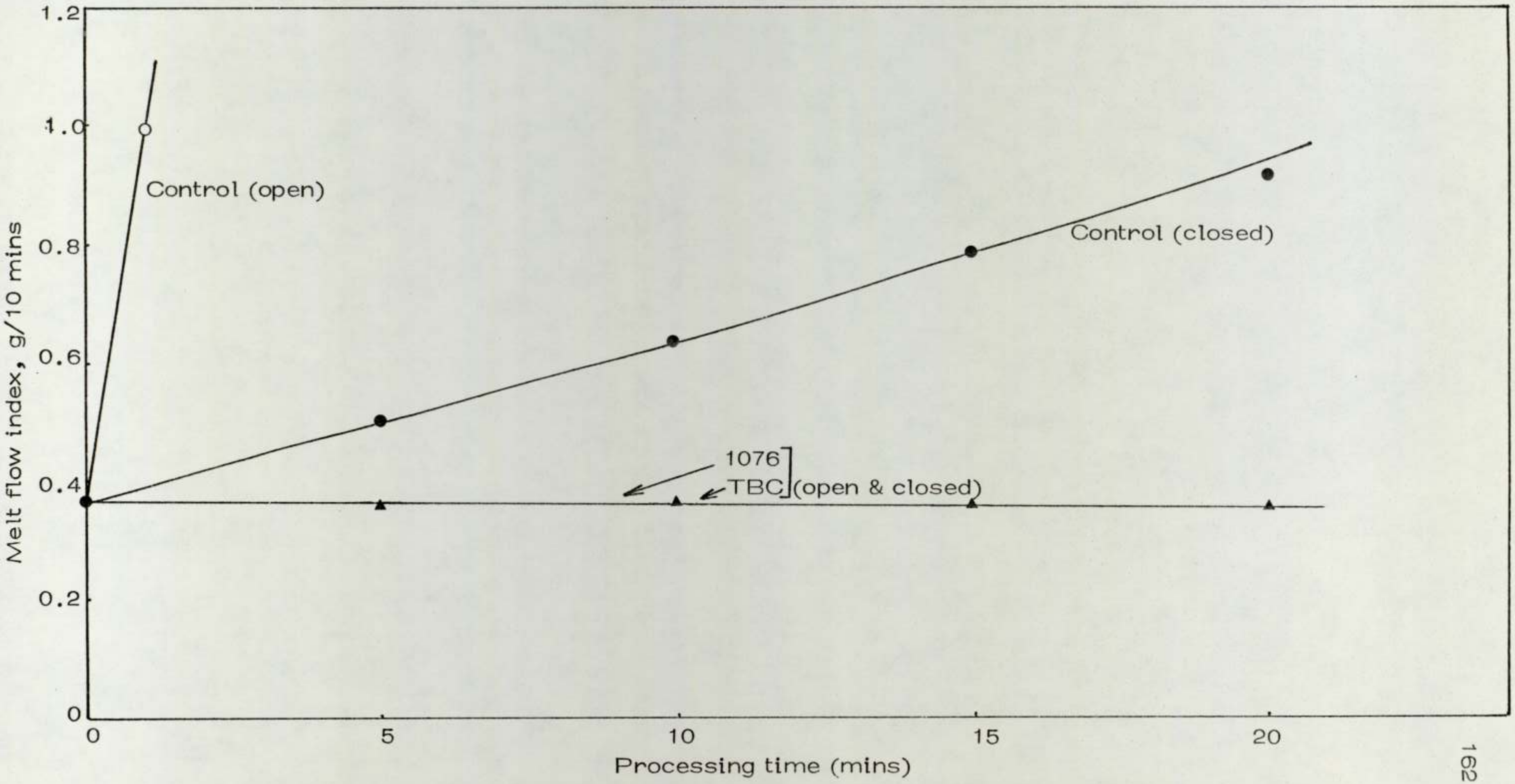


Fig 3.24 Variation of MFI with processing time processed in open and closed chambers at 180°C (concentration of additives = 6 × 10–4 mole/100 g)

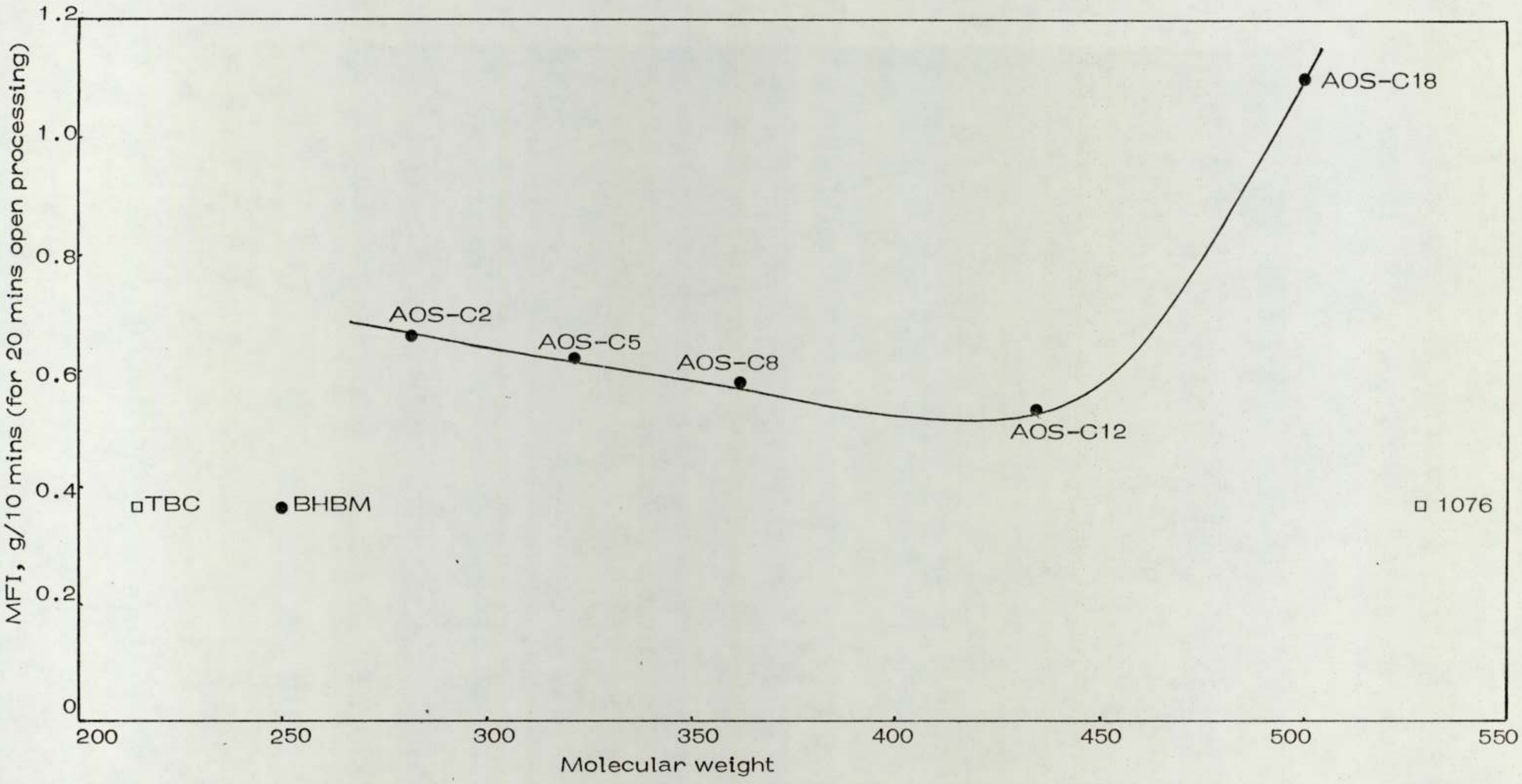


Fig 3.25 Variation of MFI (for 20 mins open chamber processing) with the molecular weight of antioxidants

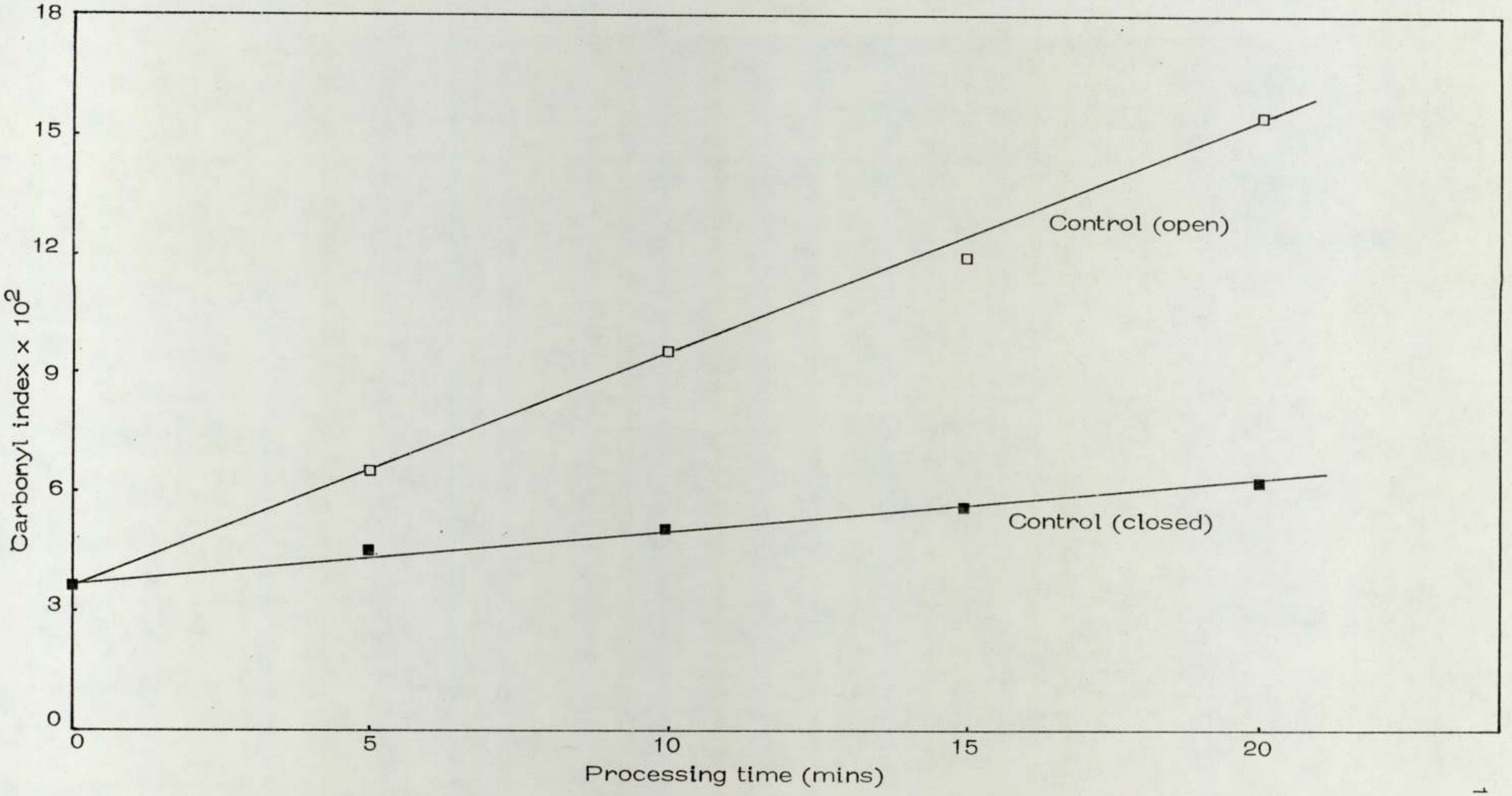


Fig 3.26 Effect of processing (at 180°C) on the carbonyl content in polypropylene

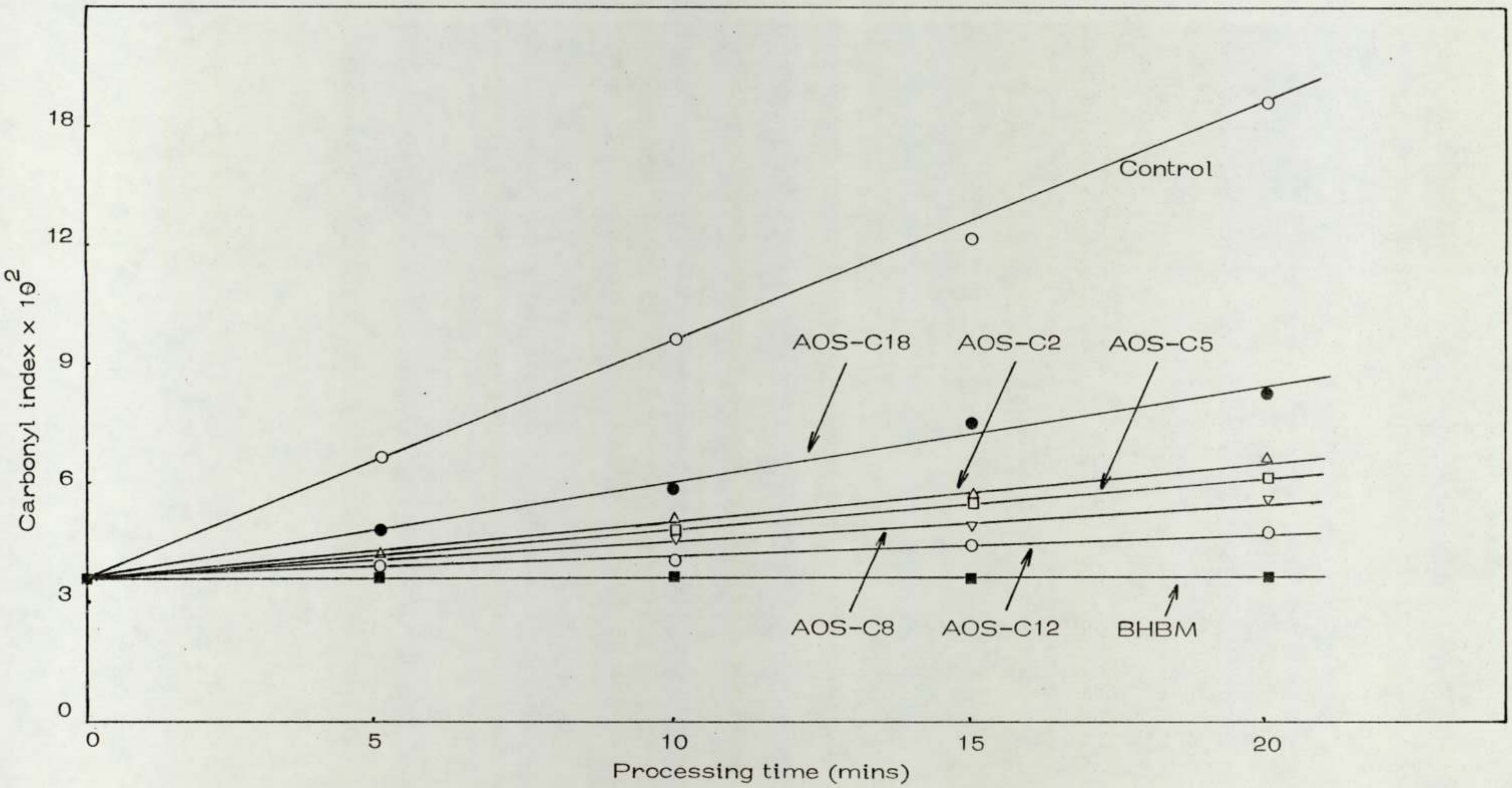


Fig 3.27 Effect of open chamber processing at 180°C on the carbonyl content of polypropylene (concentration of additives = 6×10^{-4} mole/100 g)

antioxidants (Fig 3.28) showed invariable carbonyl content with processing time providing further evidence of the outstanding melt stabilisation given by the antioxidants. The apparent higher initial carbonyl content of 1076 as shown in Fig 3.28 was due to the depression of the 1715 cm^{-1} peak attributed to the ester content of the antioxidant.

3.9 An Overview and Discussion

Fig 3.29 reveals a comparative and an integrated delineation of the antioxidant performance studied at 140°C in decalin and in polypropylene under both restricted and open atmospheric conditions.

Although the synthesised antioxidants exhibited very similar activities in the liquid hydrocarbon, a markedly different pattern of behaviour was apparent in the polymer system either in closed or flowing atmospheric environments. In the restricted atmosphere, the activities of the antioxidants were enhanced with the increase in pendant chain from C2 to C12 but then were reduced when the chain length was further increased to C18. As the volatilisation of these antioxidants would be markedly curtailed in the enclosed vessel, it would appear that these

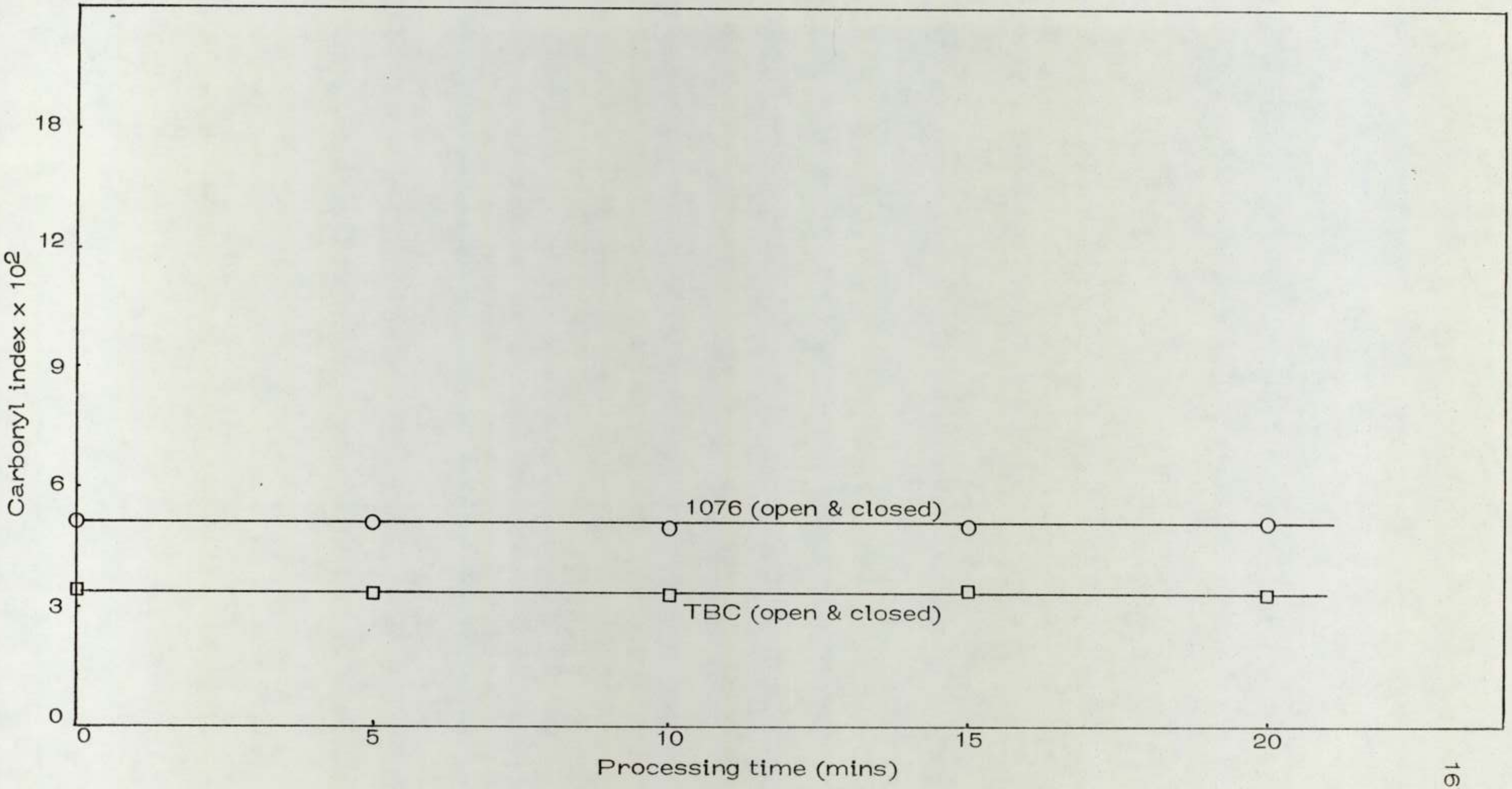


Fig 3.28 Effect of processing (at 180°C) on the carbonyl content in polypropylene (concentration of additives = 6 × 10^{-4} mole/100 g)

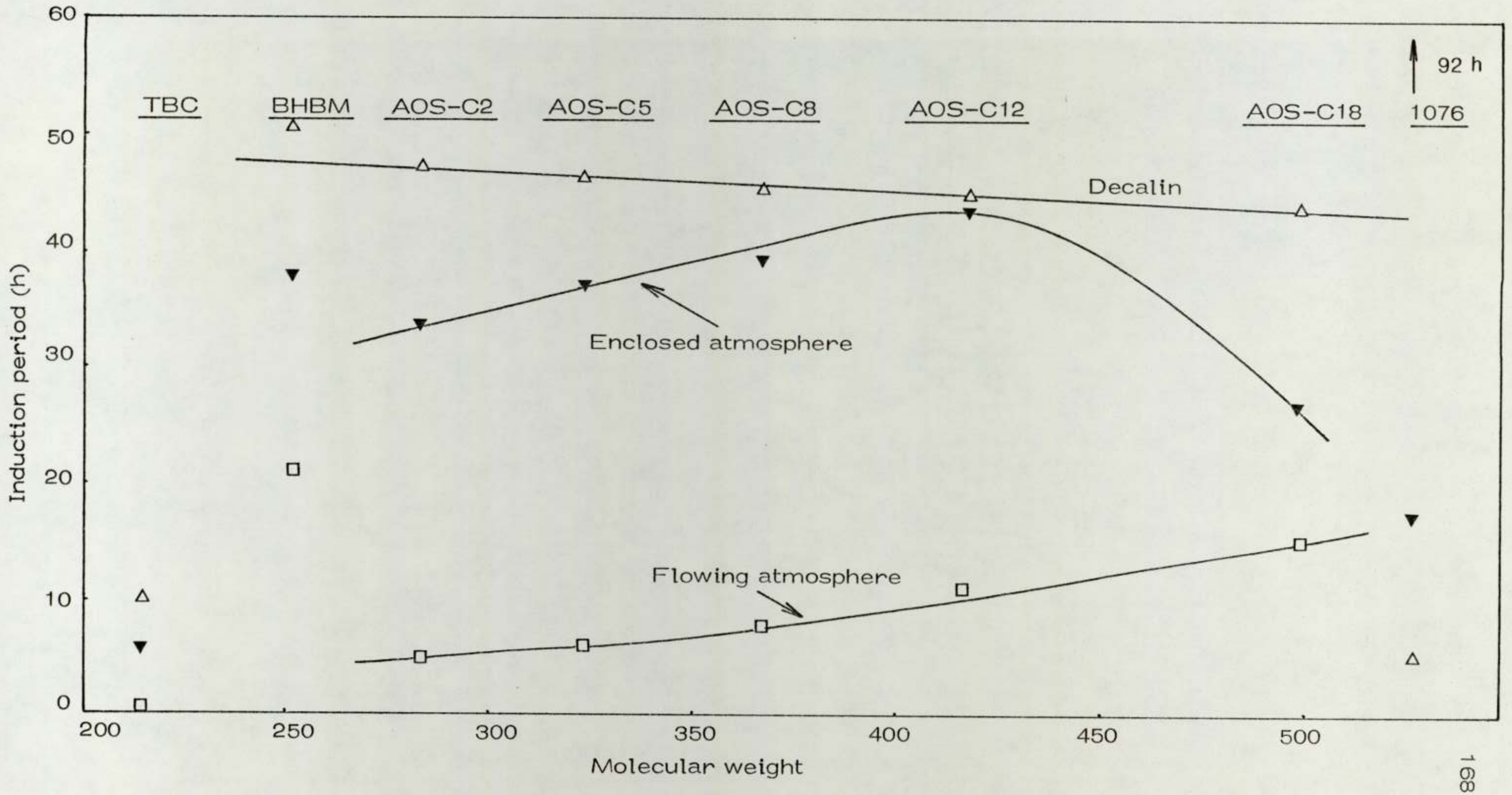


Fig 3.29 Comparative stabilising behaviour of the antioxidants under different environments at 140°C

effects were linked with compatibility phenomenon. For the commercial antioxidants, ie TBC and 1076, the inferior performance of the latter in decalin was, to a significant extent, due to the non-facile formation of quinonemethide (A) or its derived stilbenequinone from the parent compound since Pospisil et al(220) in model studies of 1076 with tertiarybutyl hydroperoxide found this to be the case.

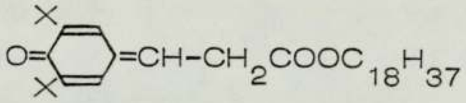

(A)

Fig 3.30 compares the activities of the antioxidant in closed environment with their melting points and solubilities in n-hexane. There appeared to be a relationship between low melting point, high solubility in hexane and high antioxidant activity. Low melting point and high hexane solubility could possibly be associated with low intermolecular polar bonding and high affinity for hydrocarbon substrates. Although the use of data on solubility in hydrocarbon solvent to assess compatibility phenomenon in polymers was tentative and may be criticised, it did appear that in the present work solubility information had produced correlation with the stabilising activities of the additives. Even though this relationship might be fortuitous, related work done by Plant(219) on phenolic antioxidants

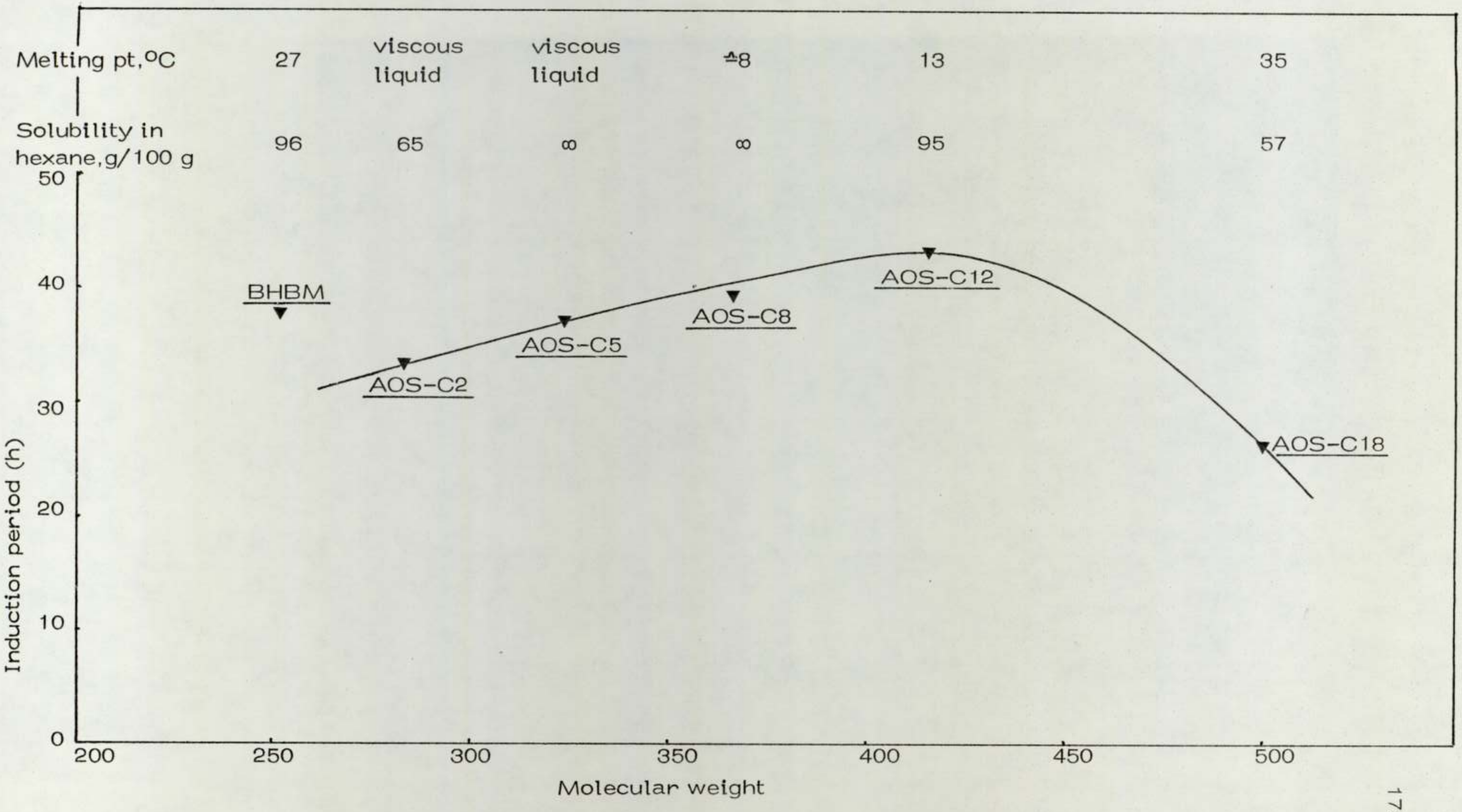


Fig 3.30 Comparison of the additives' stabilising performance in the enclosed atmosphere with their melting points and solubilities in hexane

of increasing pendant chain length revealed a similar trend.

Although the antioxidant series from AOS-C2 to AOS-C12 imparted greater thermal stability to the polymers under conditions where their volatilisation was severely reduced, their effectiveness in flowing atmospheric test was diminished to a low level as illustrated in Fig 3.29. The performance of AOS-C18 however tended to approach its effectiveness where volatilisation was negligible. This seemed to suggest that when antioxidant volatility was minimal, the aggressive influence of volatilisation played little part in reducing the antioxidant performance in polymers.

The examination of the effects of the volatilisation of the antioxidants on their effectiveness was taken further in Fig 3.31 which forceably demonstrates the very marked increase in the activity of the antioxidants in the flowing atmosphere test as antioxidant volatility decreased. The induction period of 15.0 h provided by AOS-C18 would have been greater but for the negative influence of incompatibility and the consequent poor melt stabilisation performance. However, the mere fact that the antioxidant still showed a strong inverse function with its volatility served to demonstrate the overwhelming influence of

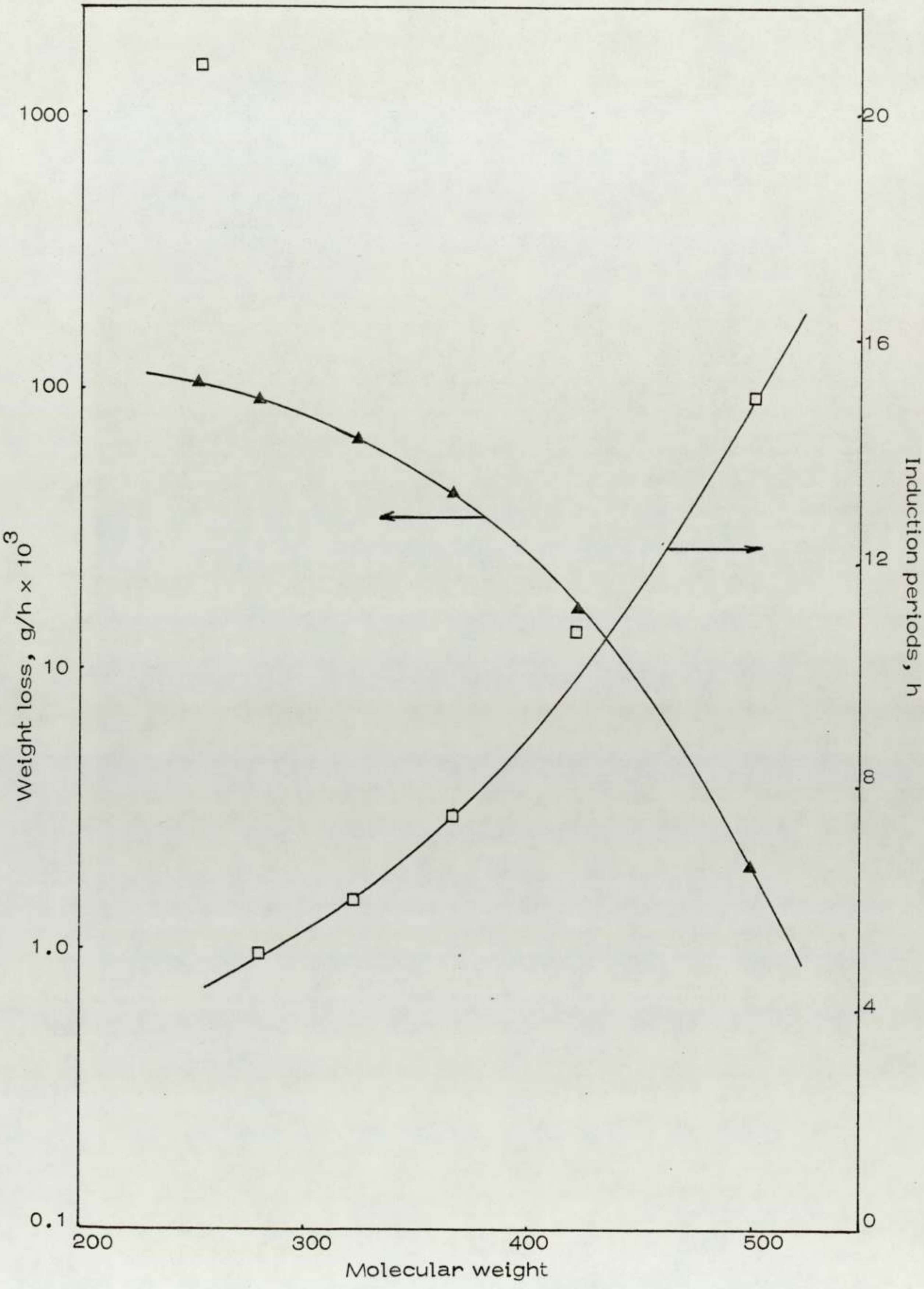


Fig 3.31 Comparison of antioxidant volatility and antioxidant effectiveness in a flowing atmosphere at 140°C

the additives' volatility over compatibility under flowing atmospheric conditions.

On the other hand where volatilisation was not facilitated as during uv exposure and open chamber processing, the contribution of antioxidant compatibility appeared to be an over-riding factor in determining antioxidant effectiveness. This manifested itself by the poor performance shown by AOS-C18 in relation to the other members of the series. Figs 3.32 and 3.33 illustrate the inferior stabilising property of AOS-C18 on uv exposure and melt processing which was in accord with its poorer compatibility characteristics. In fact Fig 3.33 depicts a striking mirror image of the induction period (in restricted atmosphere) curve to that of the MFI's. The decrease in MFI and the increasing induction period from AOS-C2 to AOS-C12 was indicative of increasing compatibility and to a lesser extent of decreasing antioxidant volatility. However, the sharp increase in MFI and the drop in induction period for AOS-C18 reflects the poor compatibility of the antioxidant in the polymer. BHBM did not fall into the pattern of behaviour and as already discussed the high reactivity of the paraphenolic substituent was primarily responsible for the anomaly. Fig 3.32 also supports the contention of inferior compatibility of AOS-C18 as mirrored

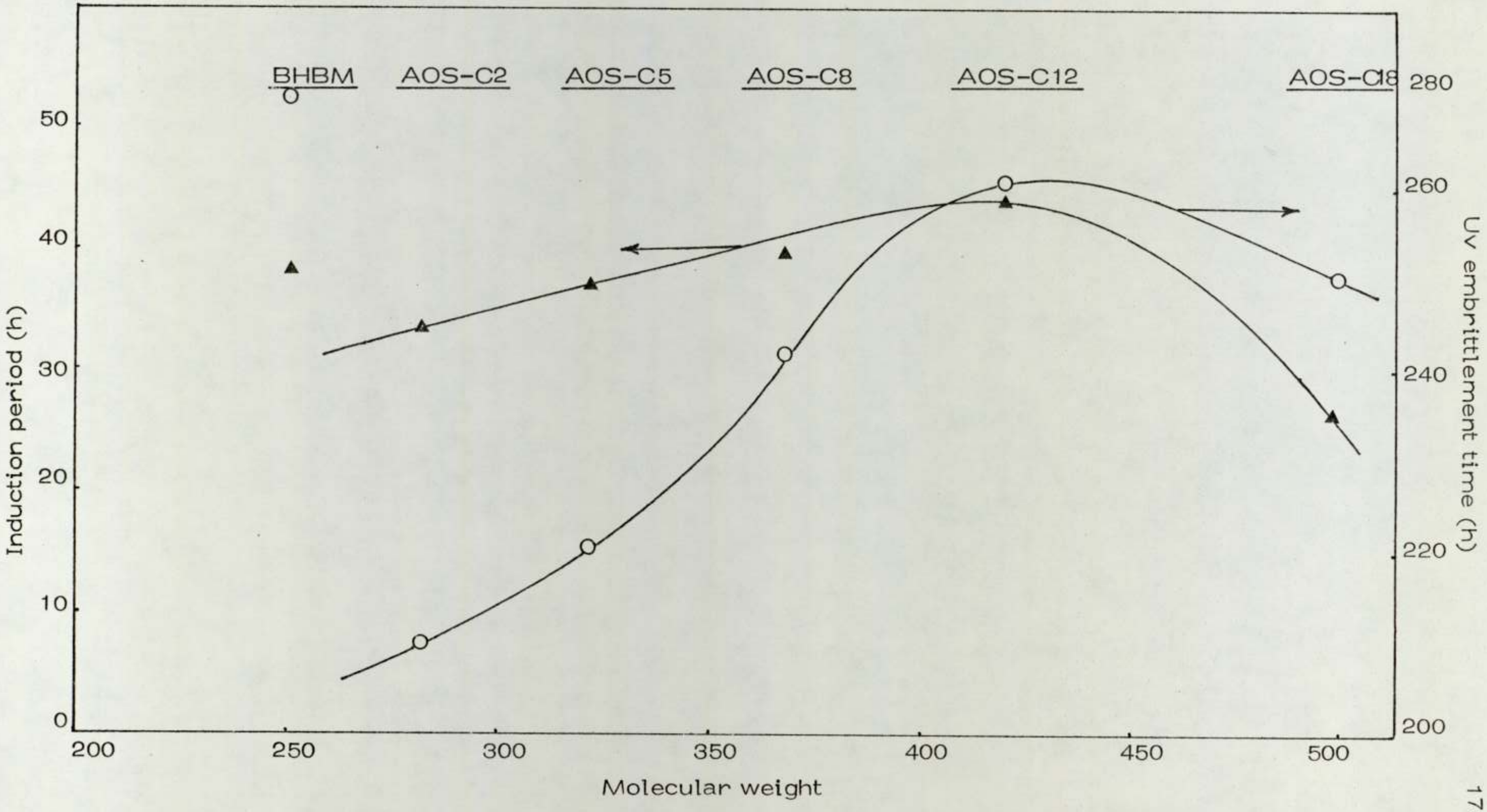


Fig 3.32 Comparison of antioxidants' effectiveness in the enclosed atmosphere with their photo-protective activity

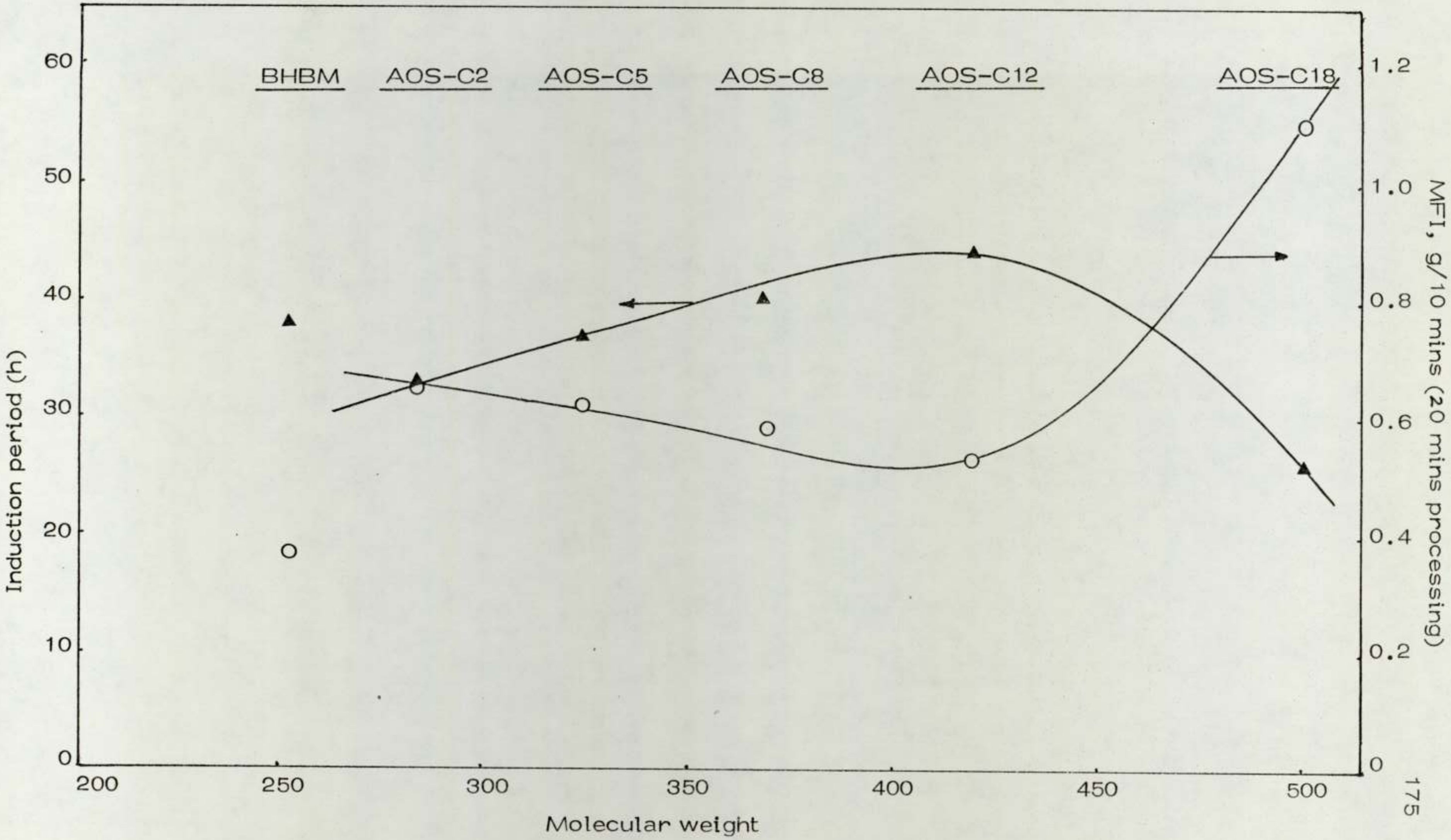


Fig 3.33 Comparison of the antioxidants' effectiveness in the enclosed atmosphere (at 140°C) with their melt stabilising performance

by the reduction in embrittlement time for AOS-C18 in comparison to the stabilisation shown by the other members of the series.

It was seen in Chapter 1 that the peroxide decomposing activity of the sulphur antioxidants occurred at the expense of the breakdown of the antioxidants to more volatile species. Thus it appeared that volatilisation effects associated with these antioxidants were a combination of the volatilisation of the parent compounds and their oxidative breakdown products. At high temperatures, the volatility of the lower molecular weight homologues is probably so dominant that the oxidation of the parent compounds to more volatile species makes little contribution to the overall loss of these stabilisers. This presumably explains the relatively poor activities of AOS-C2, AOS-C5 and AOS-C8 in the flowing atmosphere showing induction periods of 5, 6 and 7.5 h respectively while AOS-C12 and AOS-C18 imparted significantly greater induction periods of 11.0 and 15 h respectively.

CHAPTER FOUR

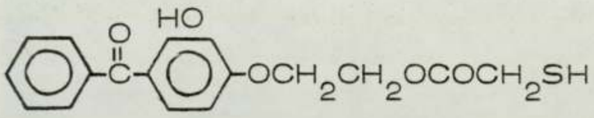
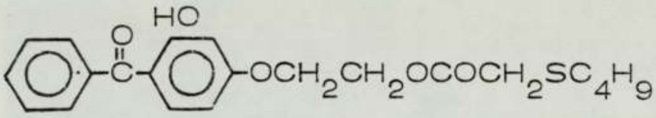
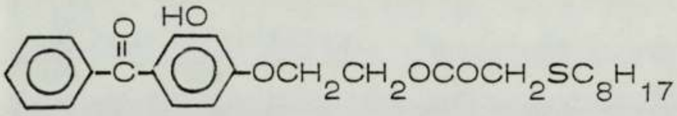
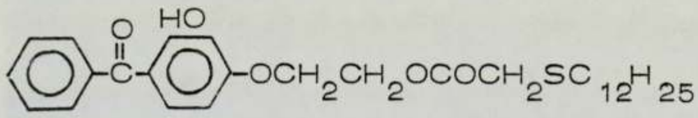
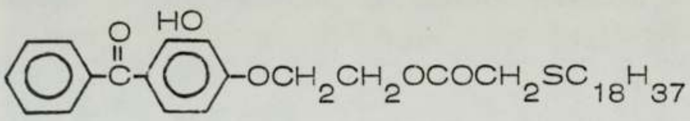
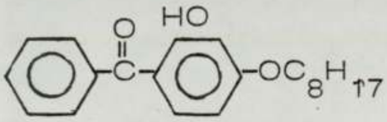
BEHAVIOUR OF SYNTHESISED UV ABSORBER SERIES IN MODEL SYSTEM AND IN POLYPROPYLENE

4.1 Intrinsic Screening Activity of the uv-absorber Series

Since uv absorbers function primarily by screening the uv light, it was thought to be essential to study their inherent screening activities in an environment devoid of physical constraints. Chlorobenzene was found to be a suitable medium for the study and with the aid of the uv spectrophotometer described in section 2.1.12, the absorbance at 330 nm of the synthesised uv absorbers and HOBP were determined at equimolar concentration of 1.5×10^{-4} M. Molar extinction coefficient of the compounds are listed in Table 4.1. Fig 4.1 shows the uv spectrum of UVS-C18 and typifies the uv spectra of the synthesised stabilisers. Fig 4.2 illustrates that of a well-known uv absorber, HOBP. It is apparent that they exhibited comparable absorbance at 330 nm .

A plot of absorbance -vs- molecular weight of the uv absorber series as shown by Fig 4.3 demonstrates the similar nature of

Table 4.1 Molar extinction coefficient of the additives in chlorobenzene at λ_{max} = 330 mμ

Additives	Molar extinction coefficient $\times 10^{-3}$, M^{-1} cm^{-1}
	6.5
	6.4
	6.5
	6.5
	6,7
	5.9

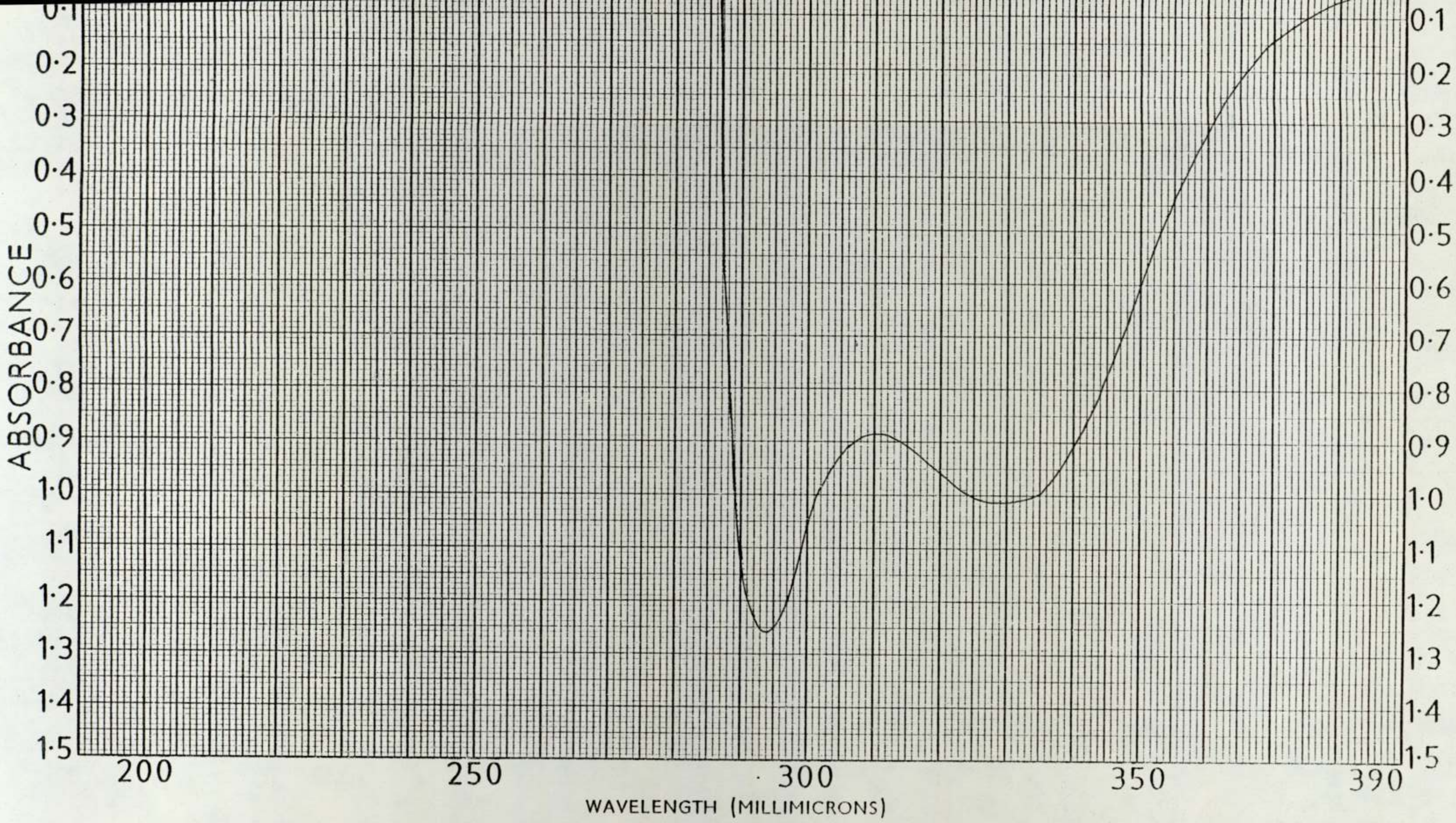


Fig 4.1 Uv spectrum of UVS-C18 in chlorobenzene, 1.5 × 10^{-4} M

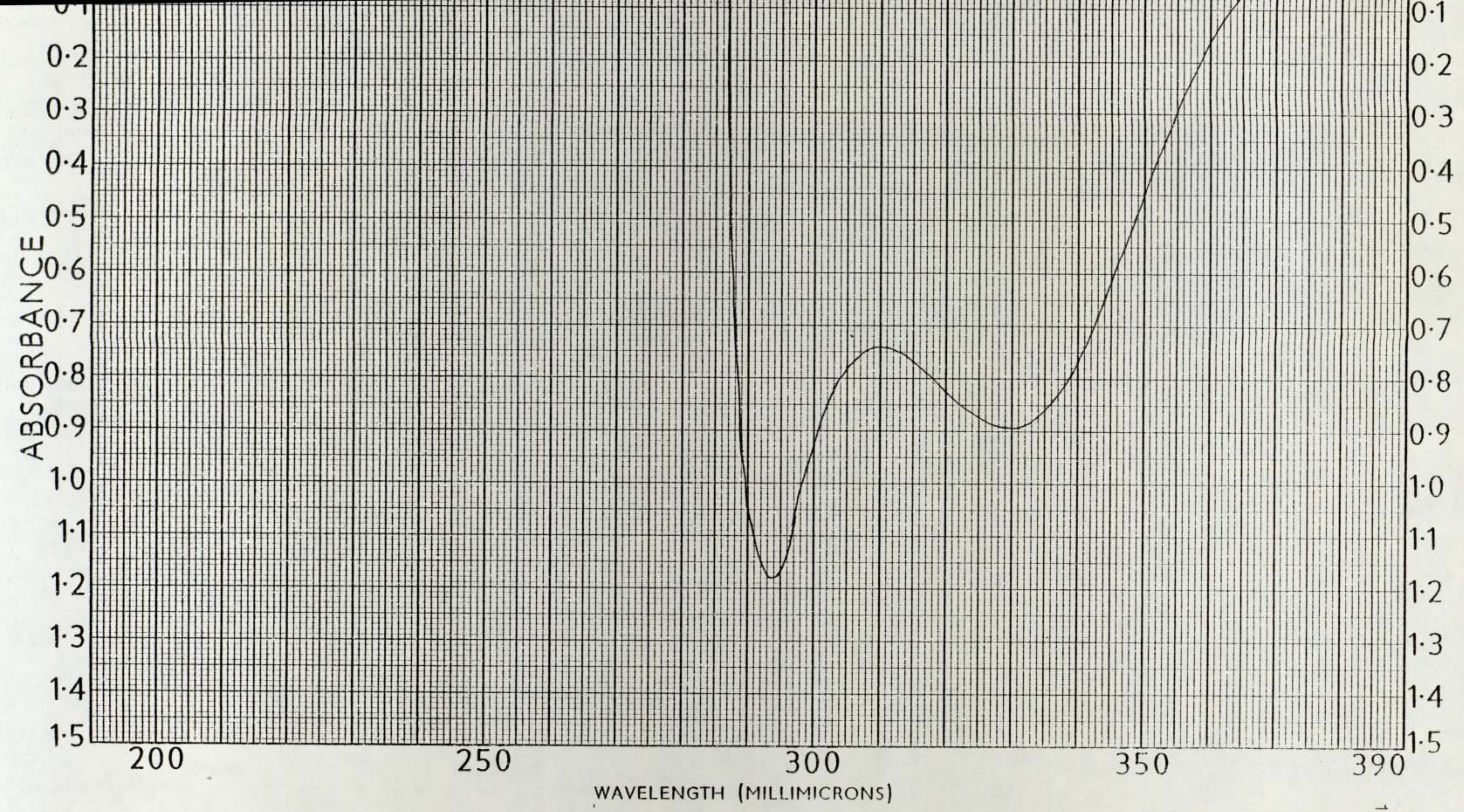


Fig 4.2 Uv spectrum of HOBP in chlorobenzene, 1.5 × 10^{-4} M

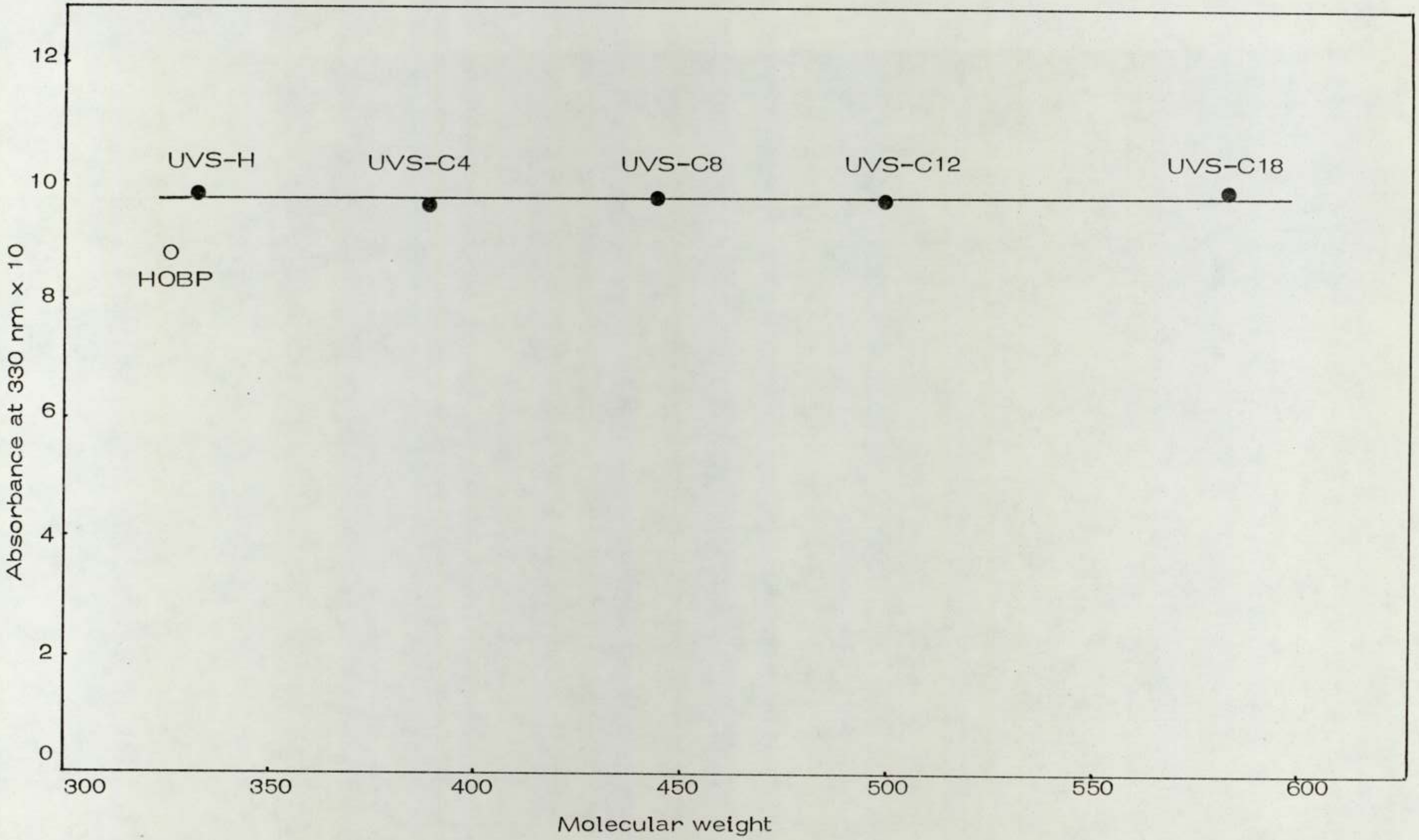


Fig 4.3 Absorbance at 330 nm of the uv stabiliser series in chlorobenzene at a concentration of 1.5×10^{-4}M

the uv screening capacity of the additives. This suggests that increasing the pendant chain at the 4-position did not bring about any variation in the screening performance of the stabilisers.

4.2 Uv Absorbance Characteristics of the Synthesised Stabilisers in Polypropylene Films

As a qualitative measure of compatibility of the uv absorbers in polypropylene, it was attempted to measure the uv absorbance maximum (330 nm) of the additives within the polymer matrix using the method of uv spectroscopy. This is based on the tenet that lower compatibility of the stabiliser with the polymer would be reflected by poorer screening effectiveness since it has been shown earlier that inherent uv absorbance capacity of the stabiliser was of the same order of magnitude. HOBP would be used as a standard of reference.

Fig 4.4 shows the differing absorbance characteristics exhibited by UVSH, UVS-C18 and HOBP for varying concentrations of the stabilisers. The striking difference in the absorbance activity shown by UVSH and UVS-C18 compared with HOBP appeared to indicate the problem of incompatibility of the synthesised stabilisers with the polymer. The absorbances for the other

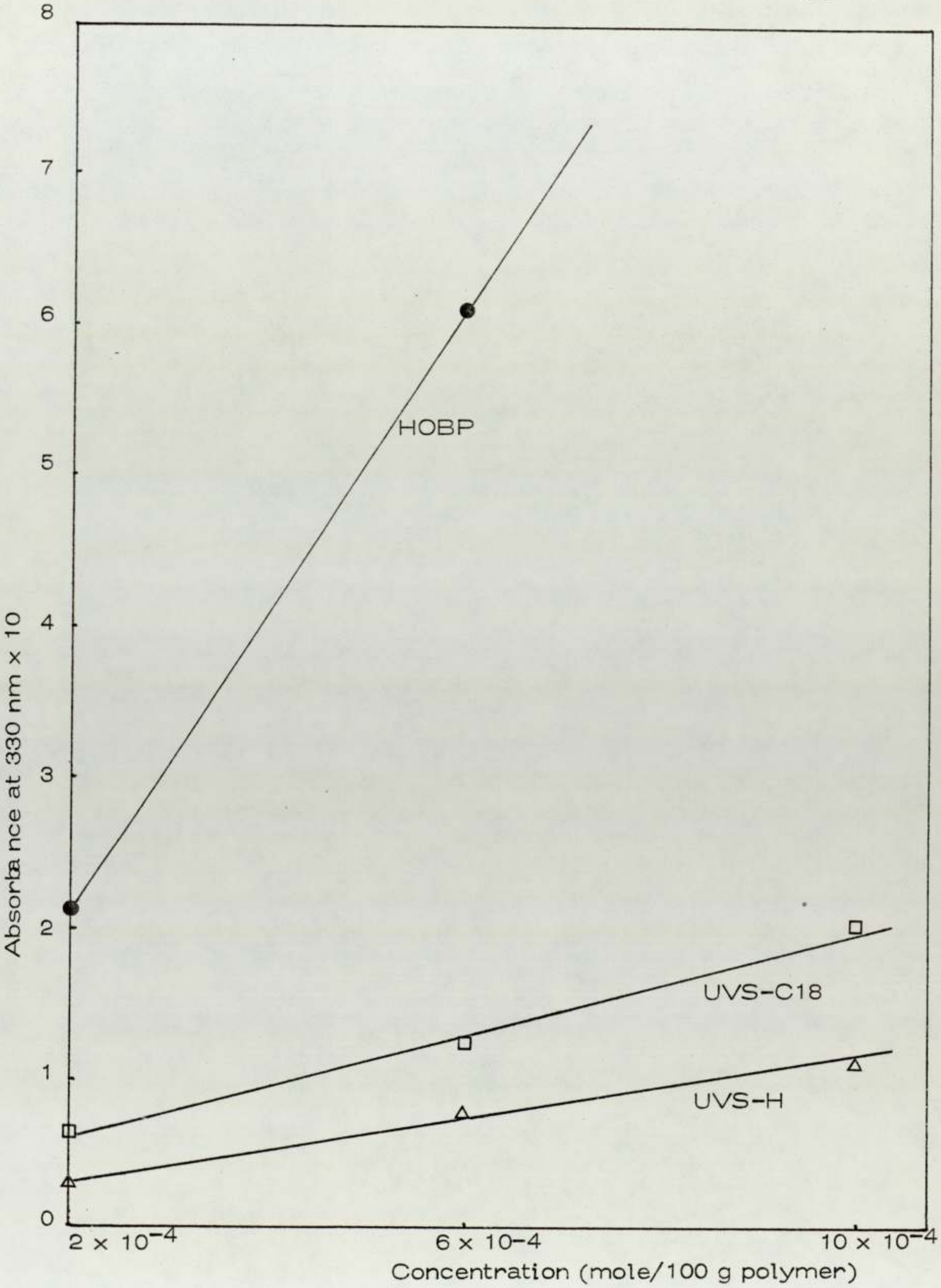


Fig 4.4 Screening performance in polypropylene films of the uv stabilisers containing varying concentration levels

members of the series were within the UVS-C18 and UVSH curves.

Data from infra-red spectral investigation of the polymer films containing the stabilisers (conc 10^{-3} mole/100 g) showed the esteric carbonyl peak (1740 cm^{-1}) of the additives to be virtually absent while similar studies in chlorobenzene showed a distinct carbonyl peak at 1740 cm^{-1}. This confirms that the stabilisers are particularly incompatible and possibly even completely insoluble in polypropylene. Further discussion on the compatibility factor will be deferred until a subsequent section.

4.3 Uv Ageing Behaviour of Polypropylene Films Containing the uv-absorber Series

Figs 4.5, 4.6 and 4.7 illustrate the uv ageing behaviour of polypropylene films containing the uv absorber series at three concentrations of 2×10^{-4}, 6×10^{-4} and 10×10^{-4} mole/100 g respectively.

Fig 4.5 shows the uv ageing behaviour of polymer films with the lowest stabiliser concentration of 2×10^{-4} mole/100 g to exhibit only a marginal stabilisation effect and increasing the pendant chain length appeared to give a positive contribution to polymer

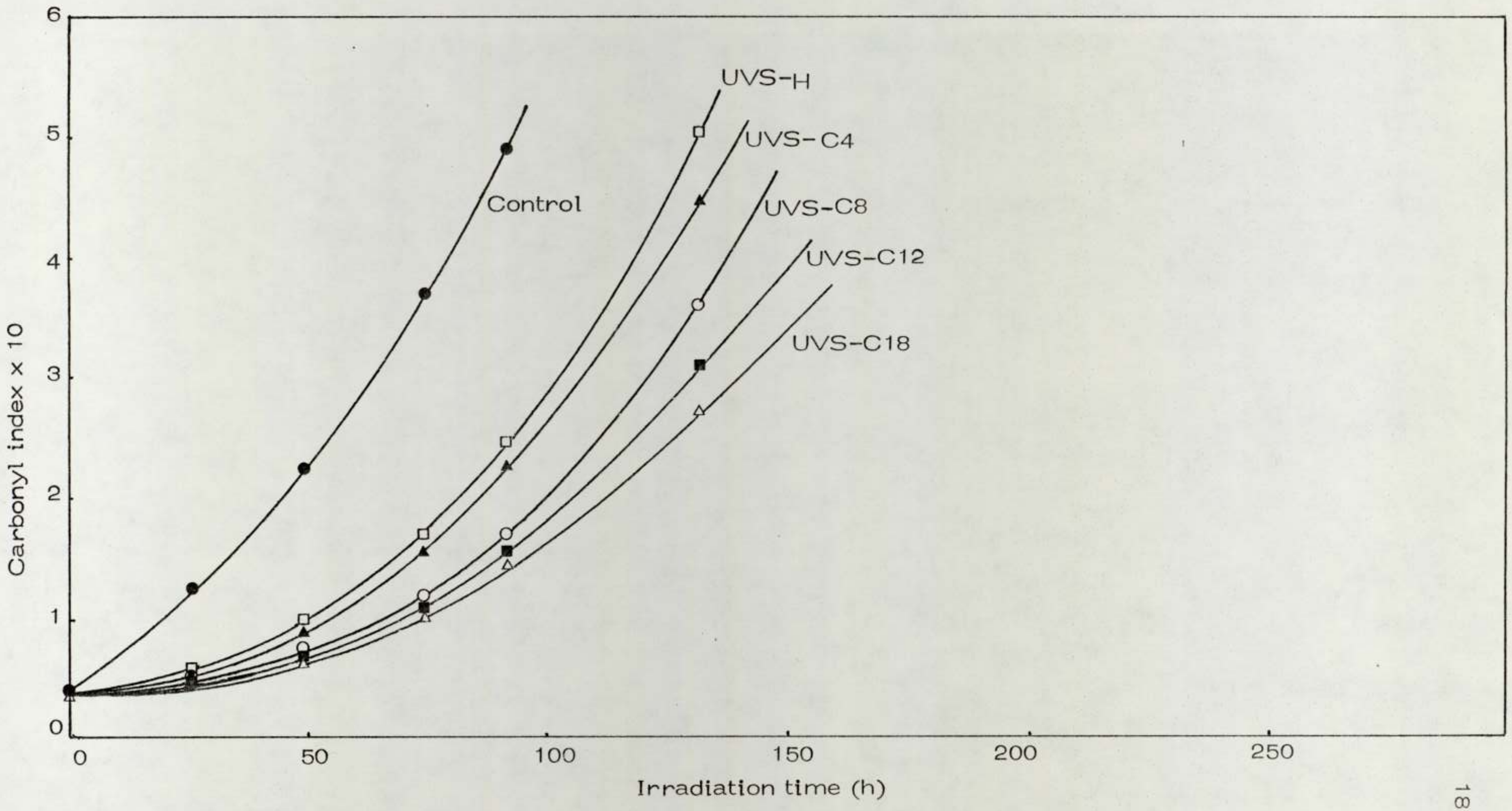


Fig 4.5 Photo-stability of polypropylene films containing the uv stabiliser series at a concentration of 2×10^{-4} mole/100 g polymer

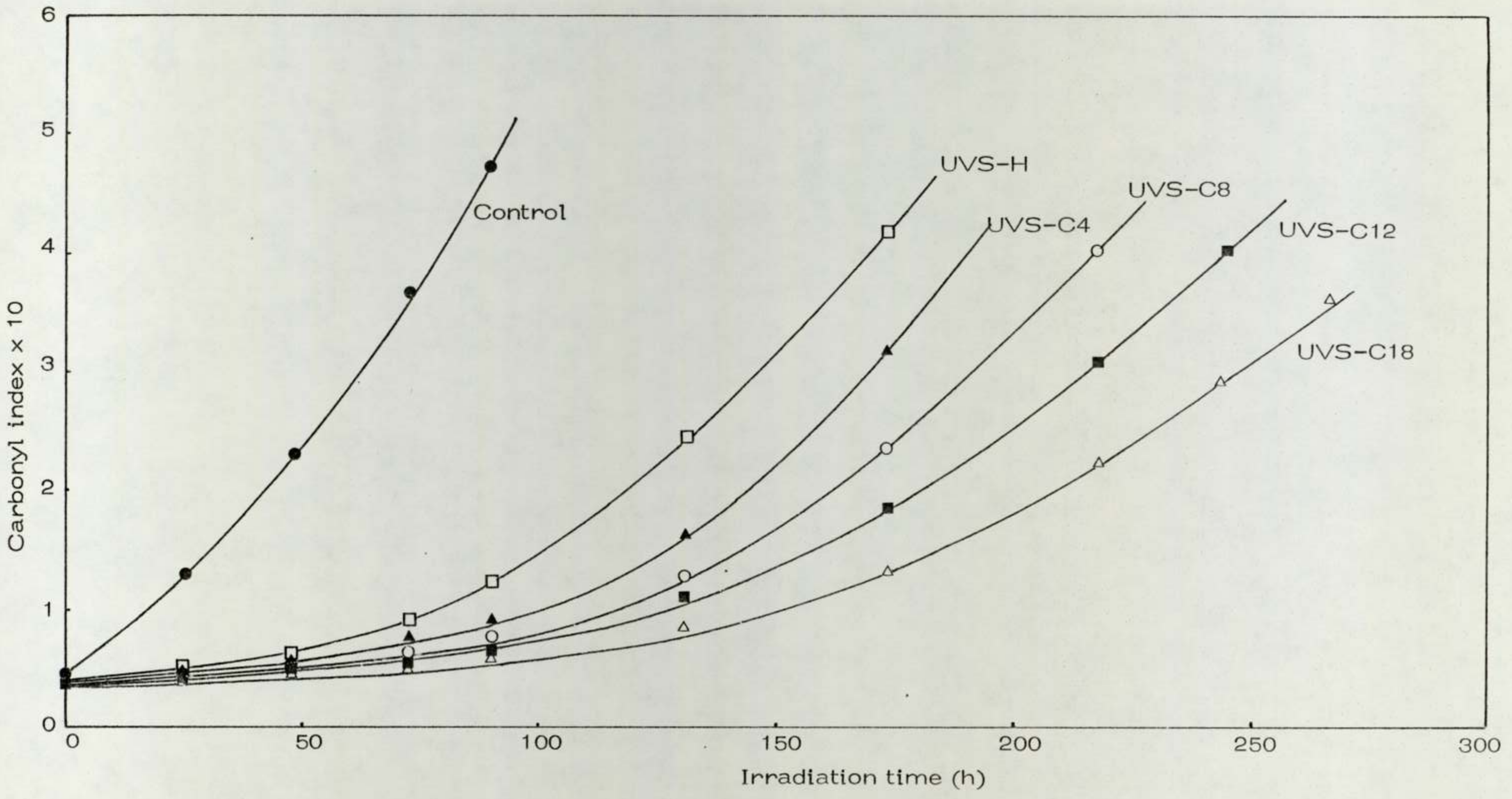


Fig 4.6 Photo-stability of polypropylene films containing the uv stabiliser series at a concentration of 6×10^{-4} mole/100 g polymer

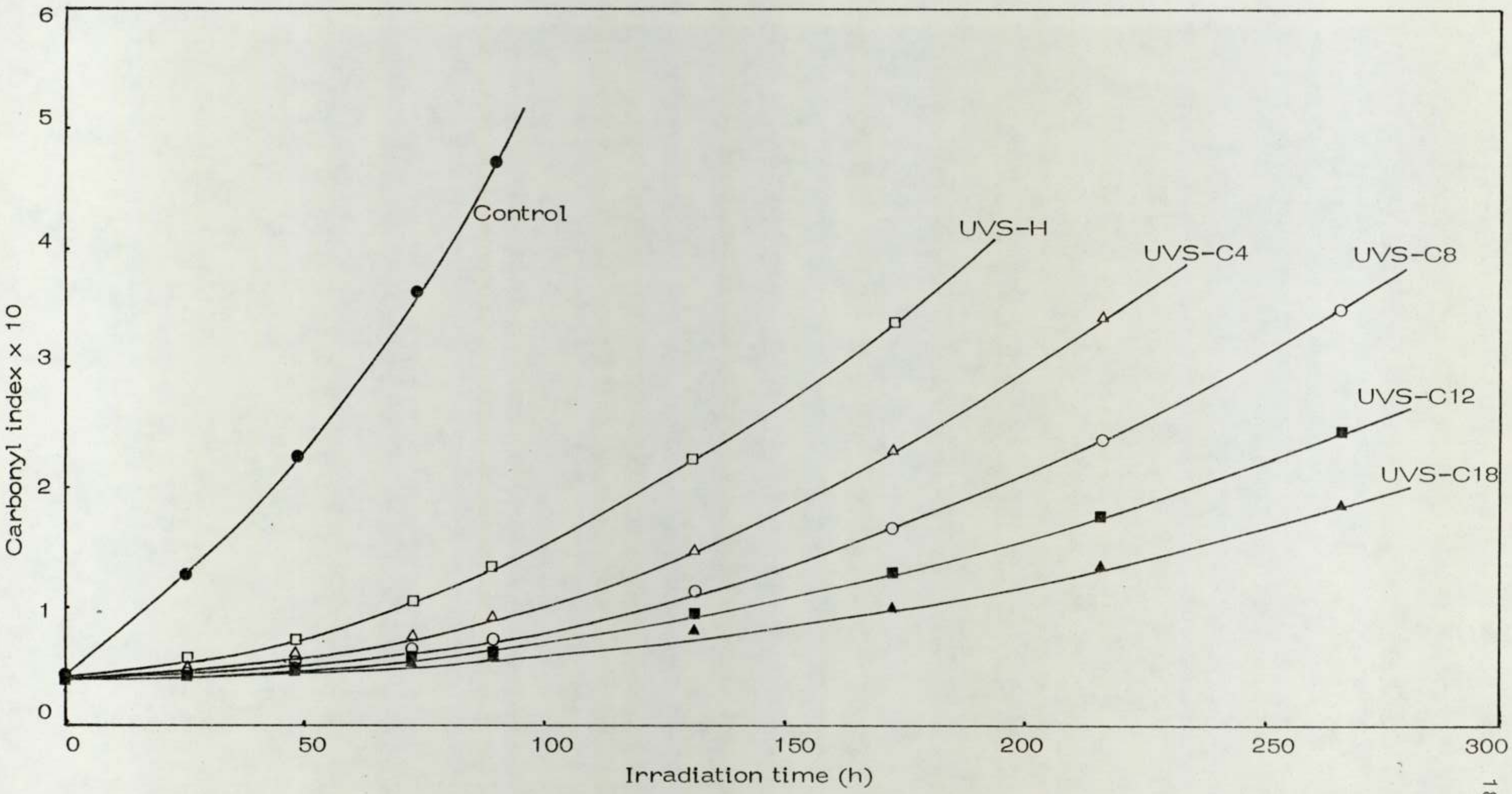


Fig 4.7 Photo-stability of polypropylene films containing the uv stabiliser series at a concentration of 10×10^{-4} mole/100 g polymer

stability. A similar trend was displayed by a 3 and 5-fold increase in stabiliser concentrations with further uv stabilisation imparted to the polymer (Figs 4.6 and 4.7).

It is also apparent that no pro-oxidant effect was observed during the initial uv irradiation even though it was suspected that the sulphur moiety of the stabiliser had been destroyed. Further discussion was deferred until section 4.9.

Despite the uv stabilising property shown by the uv absorber series, comparison of their behaviour with that of HOBP showed obvious inferior performances of the former. Figs 4.8 and 4.9 typify this behaviour where UVSH and UVS-C18 were compared with HOBP at corresponding molar concentrations.

Their deficiencies are further brought into focus by Table 4.2 and Fig 4.10 which illustrate the variation of embrittlement times with molecular weight and stabiliser concentration. Even though Fig 4.10 appears to show that increasing the molecular weight of the stabiliser gave marginally greater photo-protection to the polymer, comparison to the stabilising activity provided by HOBP highlighted the relative ineffectiveness of the synthesised stabilisers. Fig 4.11 depicts clearly the superior

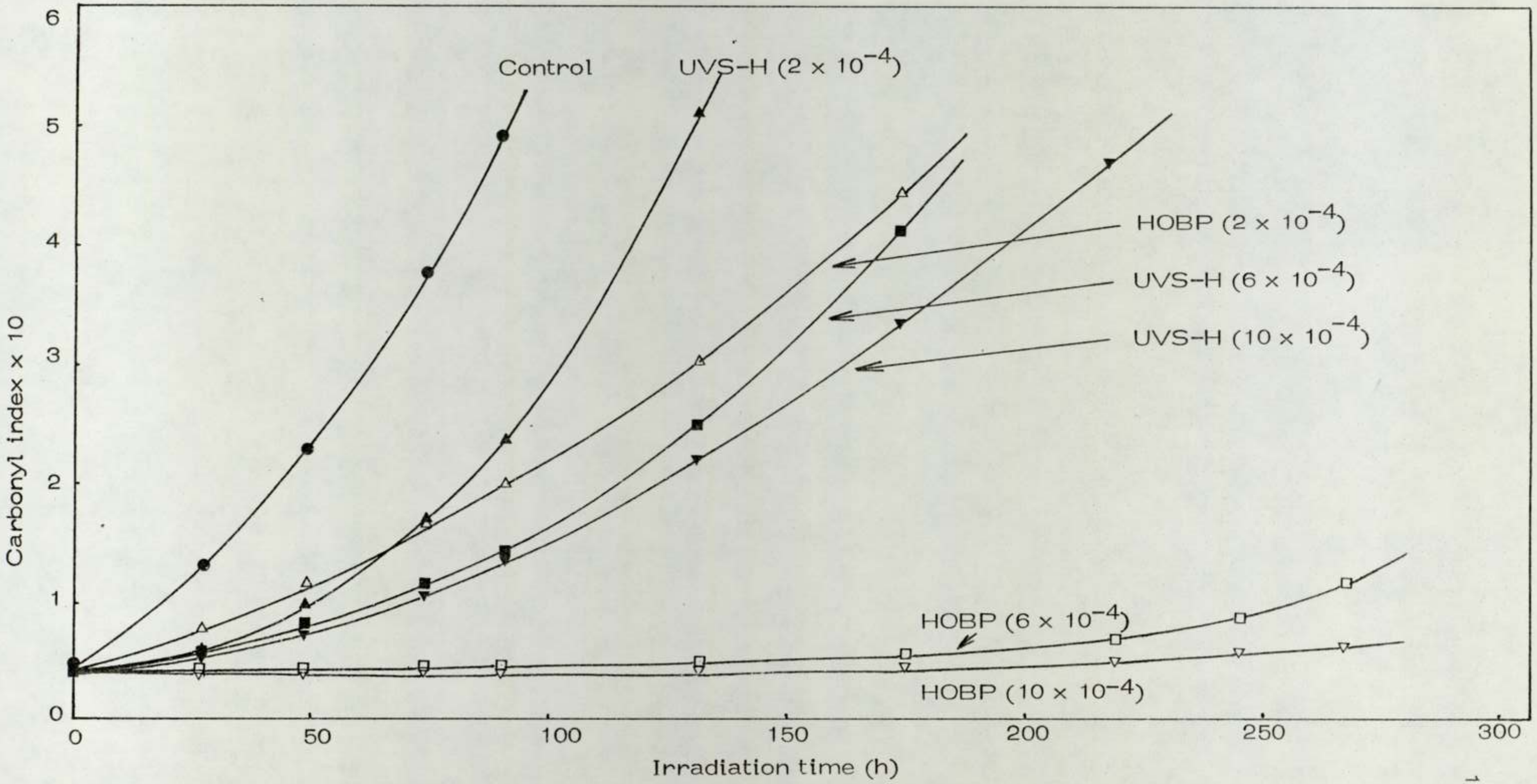


Fig 4.8 Comparison of photo-protection provided by UVS-H and HOBP at three concentration levels (mole/100 g polymer)

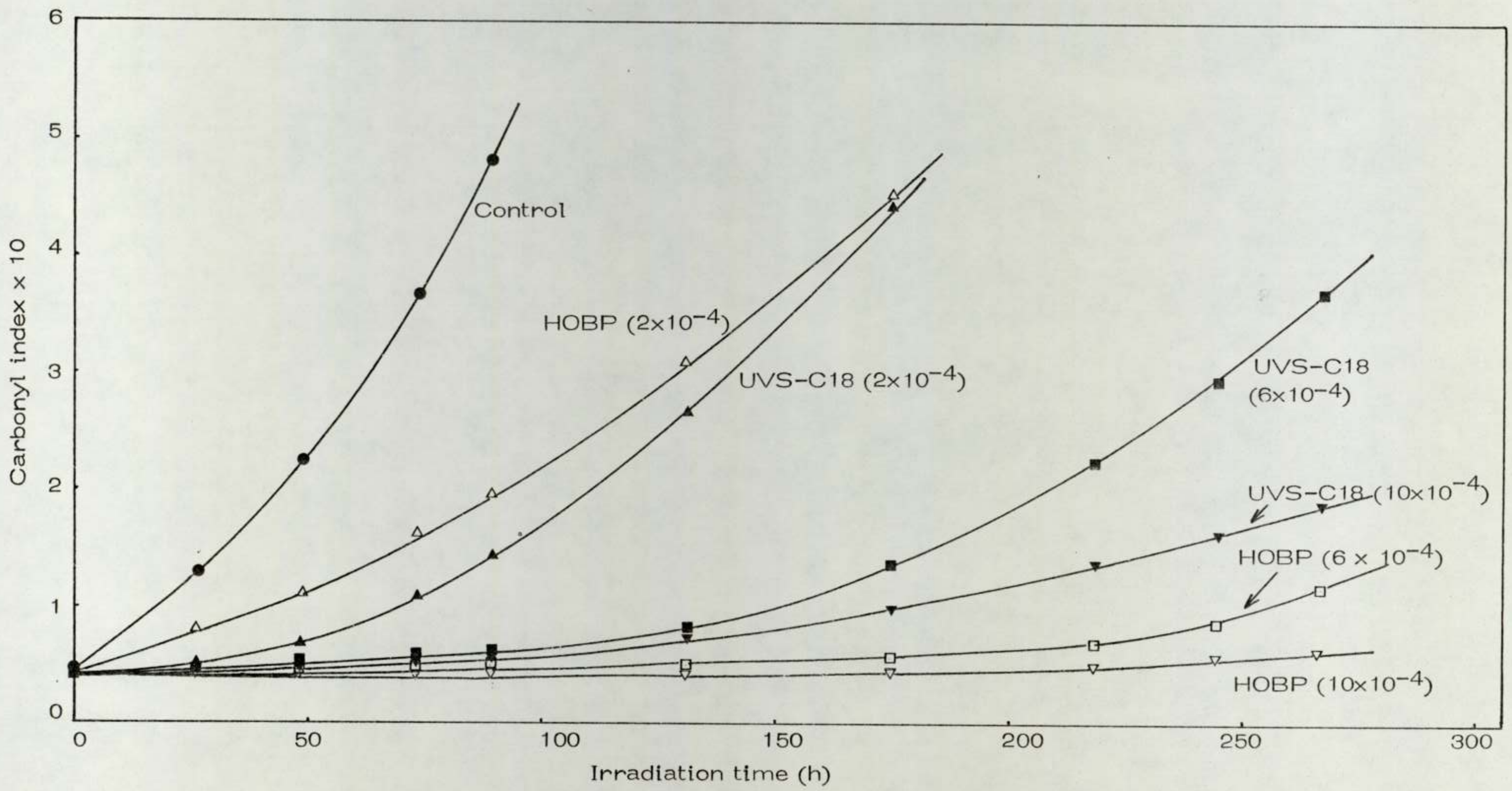
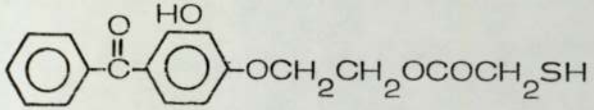
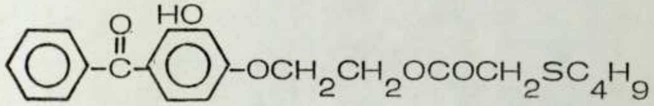
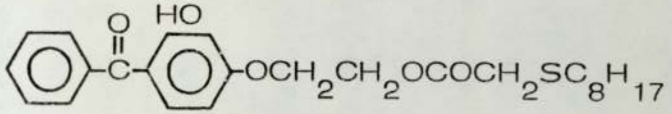
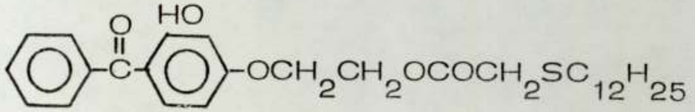
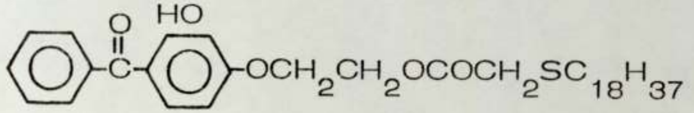
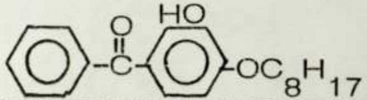


Fig 4.9 Comparison of photo-protection provided by UVS-C18 and HOBP at three concentrations (mole/100 g polymer)

Table 4.2 Variation of embrittlement times with concentrationsof the uv absorber series and HOBP

Additives	Embrittlement time, h$\pm$2.5%		
	2×10^{-4} mole/100g	6×10^{-4} mole/100g	10×10^{-4} mole/100g
Control		75	
	90	115	130
	95	140	160
	95	150	225
	100	180	250
	115	230	295
 (HOBP)	170	460	750

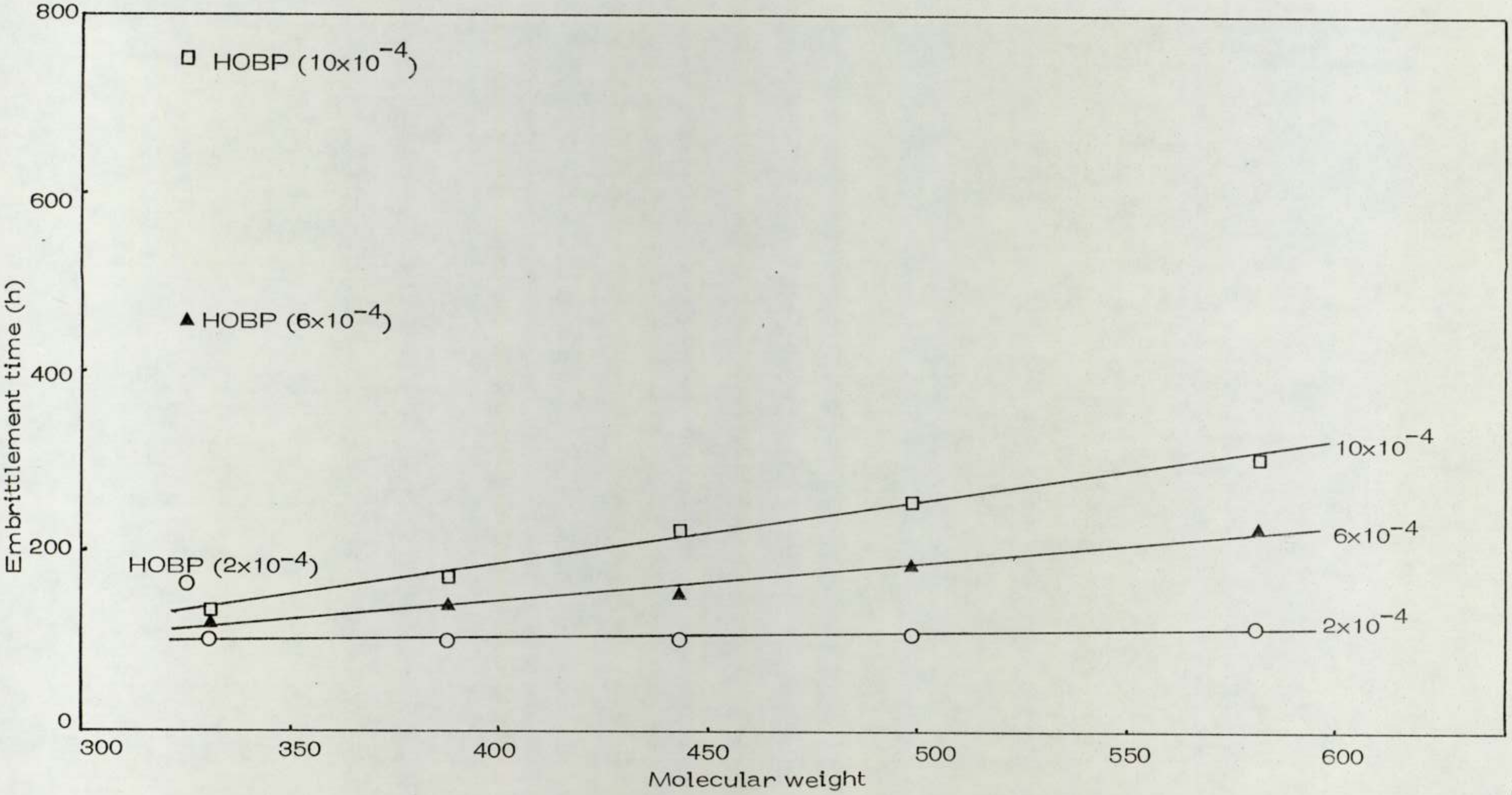


Fig 4.10 Variation of polypropylene photo-stability with the uv stabilisers' molecular weight and concentrations (mole/100 gpolymer)

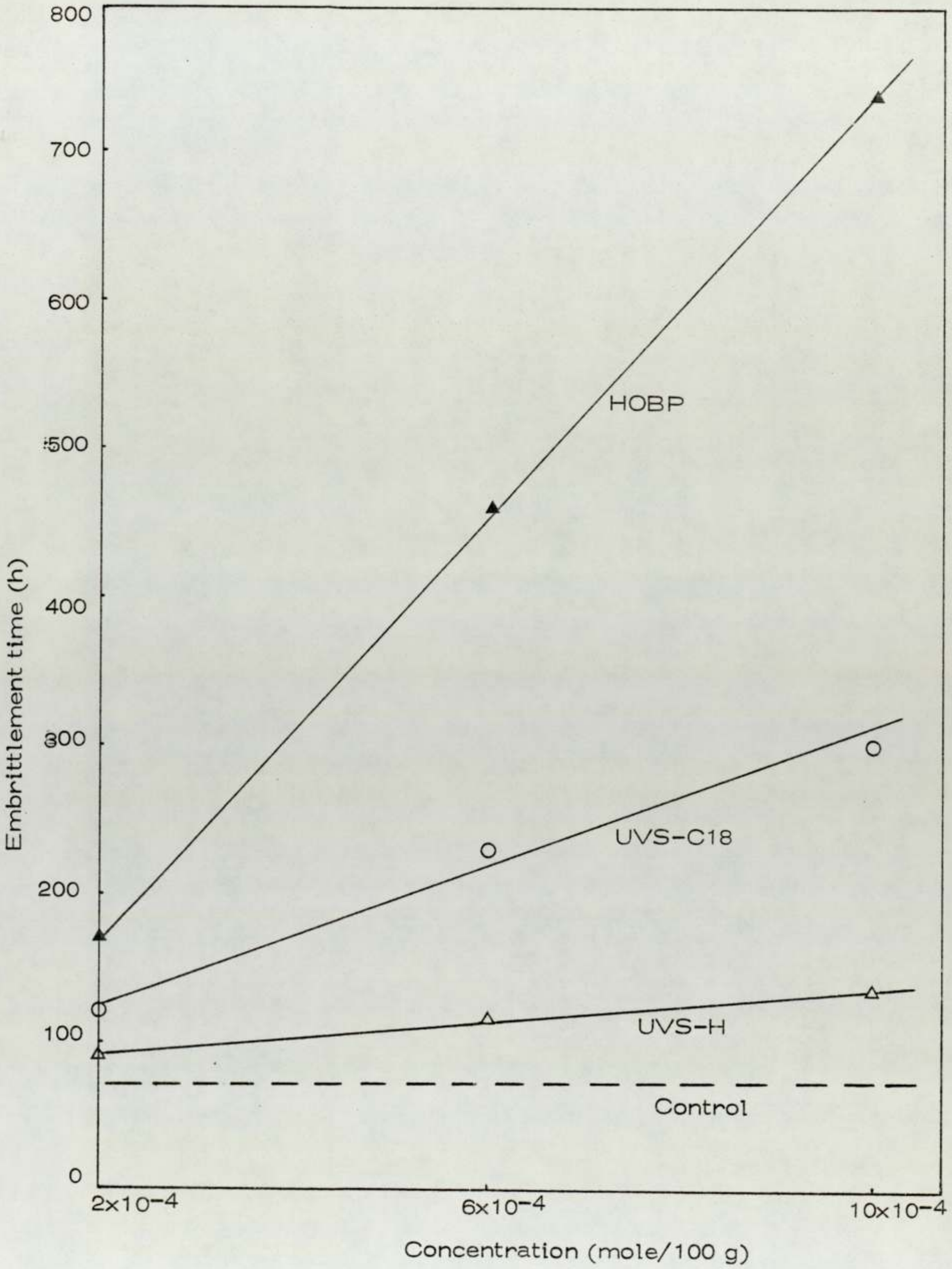


Fig 4.11 Photo-protective performance of UVS-H, UVS-C18 and HOBP at varying concentrations in polypropylene films

photo-protective behaviour of HOBP to UVS-C18 and UVSH. The curves of Fig 4.11 are almost replicas of those shown in Fig 4.4 which attempted to show the degree of stabiliser-polymer compatibility phenomenon and hence screening effectiveness. The relatively close agreement in the nature of the curves in the two figures suggests that the photo-protective activity of the uv absorbers series is due to their screening activity and possibly also by the peroxidolytic activity of the sulphur moiety. To test the latter hypothesis, a plot of embrittlement times -vs- uv absorbance (at 330 nm) of HOBP and UVS-C18 was made as illustrated in Fig 4.12. It shows the existence of two separate lines which implicates that the peroxidolytic activity of UVS-C18, presumably manifested both during melt processing and the uv exposure, is significantly contributing to the photo-stability of the polymer since at equivalent absorbance, UVS-C18 gave greater embrittlement times in comparison to that of HOBP.

4.4 Thermal Stabilising Activity of the Synthesised Stabiliser Series

Recognising that the synthesised stabilisers contained a sulphur moiety that should impart thermal stabilising activity, it was therefore proposed to study the thermal behaviour of the polypropylene films containing the additives.

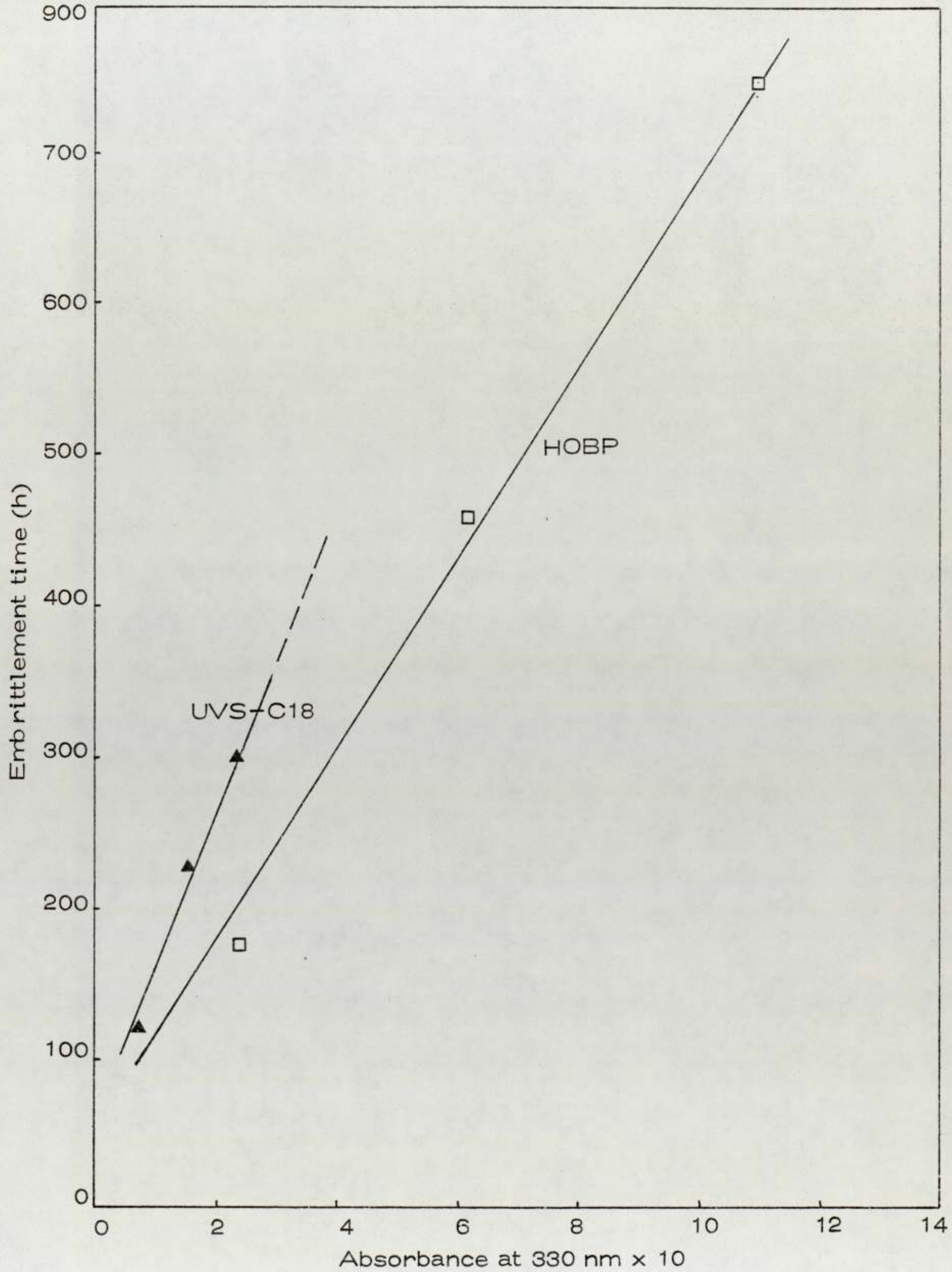


Fig 4.12 Dependence of photo-stability of polypropylene films on the initial uv absorbance at 330 nm

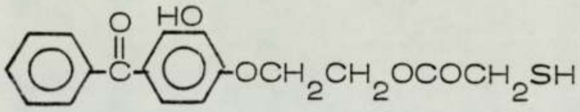
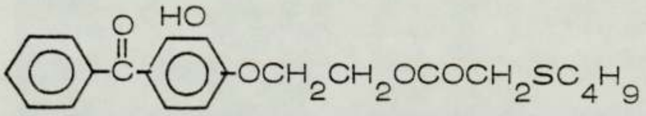
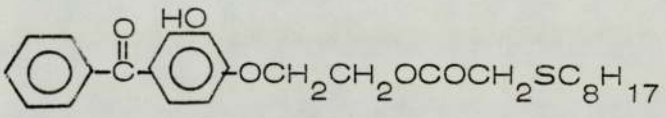
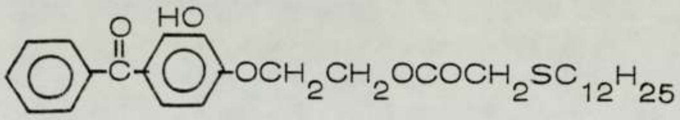
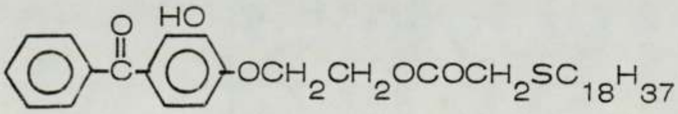
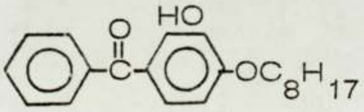
Dilaurylthiodipropionate (DLTP) was used for comparison.

Table 4.3 shows the embrittlement times given by the additives to the polymer films subjected to oven ageing at a temperature of 120°C. The lower temperature was used in order to reduce the severity of the ageing process that would give measureable embrittlement times.

Despite the apparent absence of the sulphur moiety in the polymer as evidenced from infra-red spectral data, the polymer films appeared to show slightly improved thermal stability compared with the control. The mild stabilising properties were probably attributable to the partially solubilising additives or of their oxidation products and also possibly due to very low hydroperoxide concentration.

One or both of the above possibilities appeared more plausible when comparison of embrittlement times was made with that of HOBP. While the stabiliser series provided embrittlement times within the range 1.7 - 2.5 h, that of HOBP showed a significantly low value of 0.9 h and was only marginally more effective than that of the control. DLTP gave the highest embrittlement time

Table 4.3 Oven ageing of polypropylene films containing the synthesised uv stabiliser series at 120°C (conc of additives = 10^{-3} mole/100 g)

Additives	Embrittlement time, h
Control (no additives)	0.8
	1.7
	2.0
	2.0
	2.3
	2.5
$CH_{25}OCOCH_2CH_2-S-CH_2CH_2COOC_{12}H_{25}$ (DLTP)	3.7
	0.9

of 3.7 h. The possible reasons for this were at least two-fold: presence of minimal hydroperoxide concentration and the greater compatibility and higher solubility of the additive in the polymer that would provide a higher reservoir of stabilising activity.

4.5 Volatility of Neat uv-stabilisers

Fig 4.13 shows the loss of the stabilisers with time through volatilisation at 140°C in a nitrogen atmosphere. Like the antioxidant series described in the preceding chapter, they showed distinctly decreasing volatility with increasing pendant chain lengths.

The rate of weight loss of the stabilisers is illustrated in Table 4.4 and a semi-log plot of rate loss against molecular weight (Fig 4.14) shows a similar pattern to that of the antioxidant series.

Hence increasing the molecular weight of the uv stabiliser brought about a reduction in the volatility characteristics of the additives.

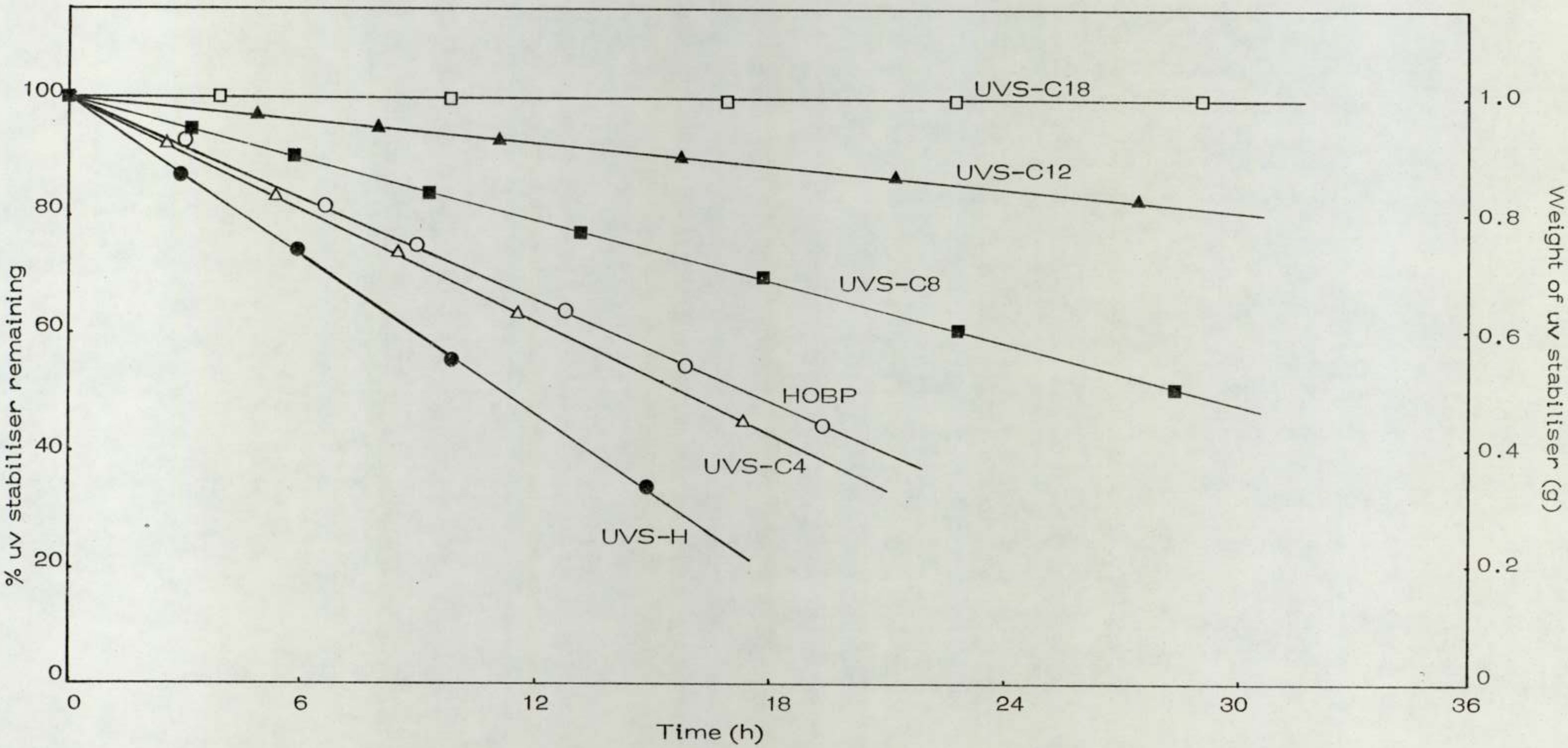
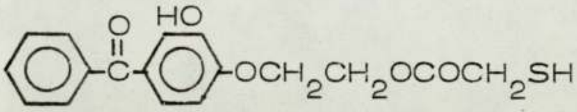
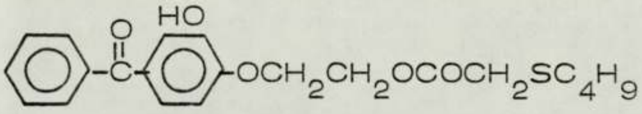
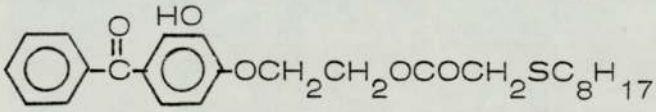
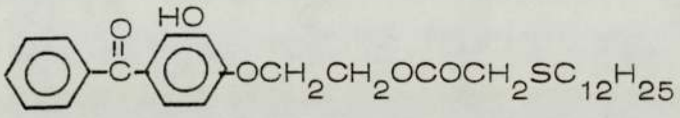
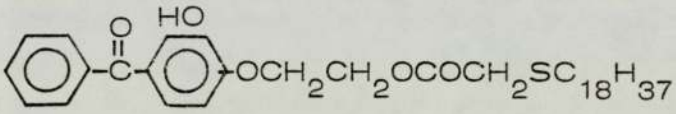
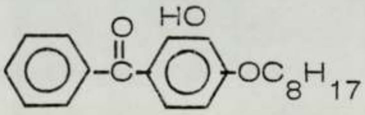


Fig 4.13 Volatilities of neat uv stabilisers in a nitrogen atmosphere at 140°C

Table 4.4 Volatility of Neat uv stabilisers at 140°C

Additives	Weight loss, g/h × 10^3
	45.0
	32.0
	17.0
	6.2
	0.6
	30.0
$C_{12}H_{25}OCOCH_2CH_2SCH_2CH_2COOC_{12}H_{25}$ (DLTP)	0.5

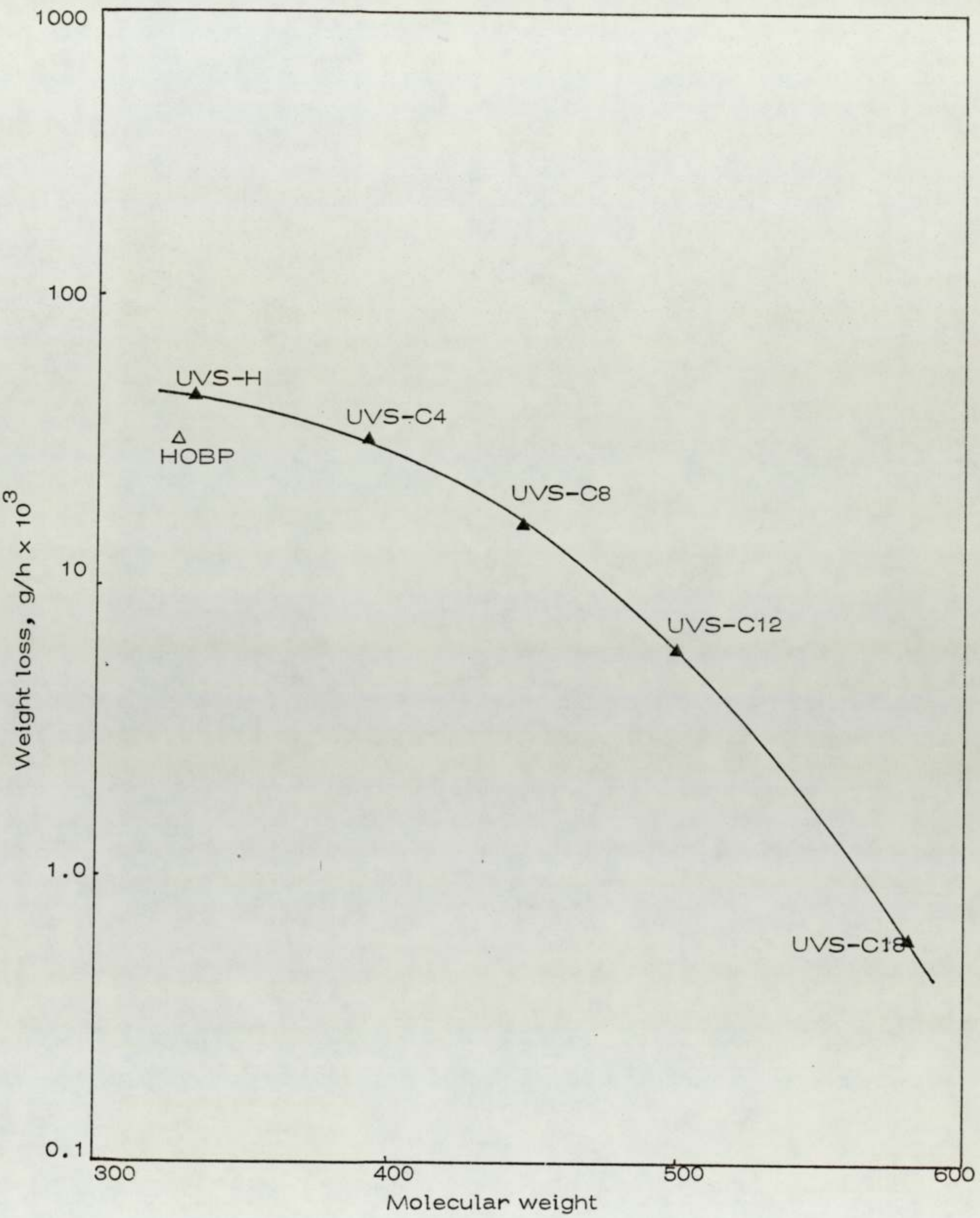


Fig 4.14 Semi-log plot of rate loss -vs- molecular weight of the uv stabiliser series

4.6 Solubility of the uv stabilisers in a Hydrocarbon Solvent

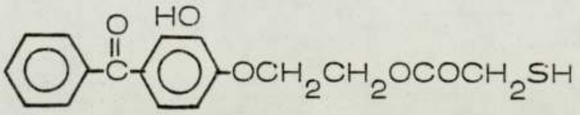
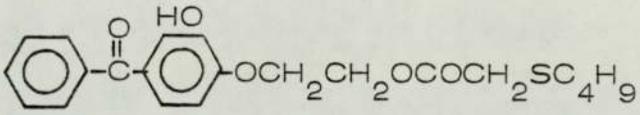
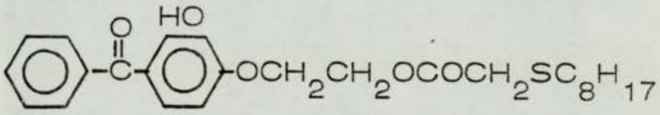
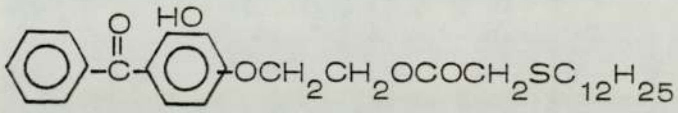
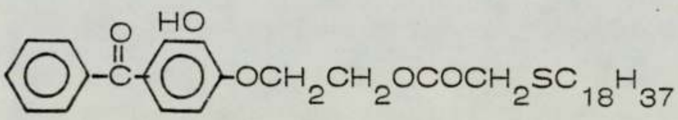
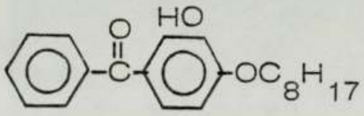
The solubilities of the uv stabiliser series, HOBP and DLTP in n-hexane at 25°C are shown in Table 4.5 which succinctly illustrates the very different solubility behaviour of the synthesised stabilisers and HOBP. While the uv absorber homologues exhibited relative insolubility in hexane, HOBP showed a finite solubility of 41.0 g/100 g hexane.

This presumably contributed to a major extent to the relatively poor screening effectiveness of the stabiliser series in polypropylene with the consequent inferior uv stabilising performance. DLTP showed relatively high solubility in hexane which, again in part, explained its greater thermal stabilising property relative to the synthesised stabilisers.

4.7 Peroxide Decomposing Activity of the Synthesised Stabilisers

Apart from screening ability, the synthesised uv stabilisers were also expected to exhibit peroxide decomposing behaviour due to the presence of the sulphur moiety. Studies similar to those described for the antioxidant series (section 3.6) were carried out. Fig 4.15 shows a typical plot of peroxide decomposition -vs-

Table 4.5 Solubility of additives in n-hexane at 25°C

Additives	Solubility, g/100g hexane
	immeasurably low
	"
	"
	"
	"
	41.0
$C_{12}H_{25}OCOCH_2CH_2S\text{-}CH_2CH_2COOCH_{12}H_{25}$ (DLTP)	101.0

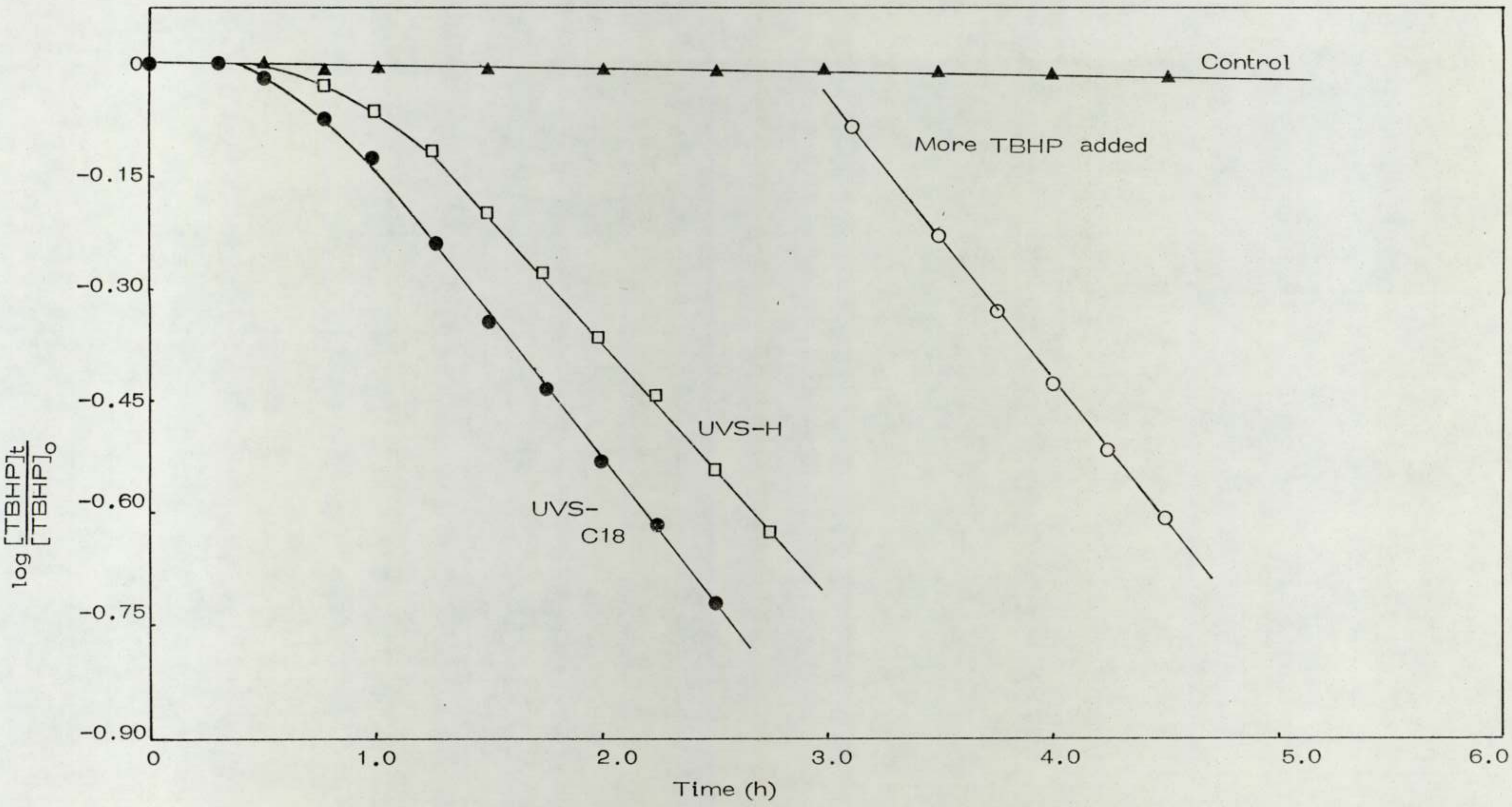


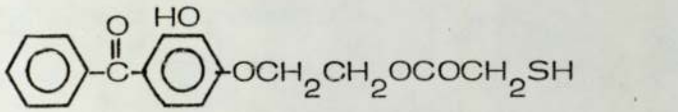
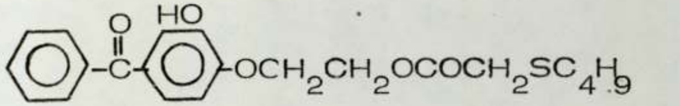
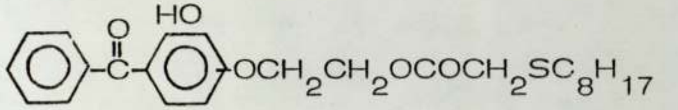
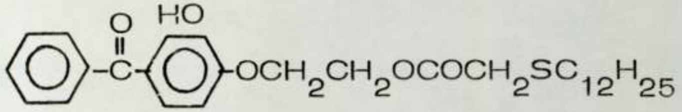
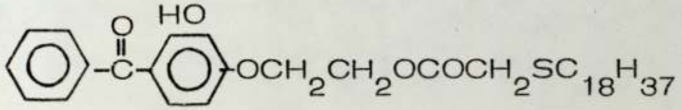
Fig 4.15 Catalytic decomposition of TBHP by UVS-H and UVS-C18 at 65°C ($[TBHP]_o = 2.6 \times 10^{-1}$M, $[Additive]_o = 5.8 \times 10^{-2}$ M in chlorobenzene (method of TBHP evaluation was by monitoring ir peak at 3538 cm^{-1}))

time at 65°C for UVSH and UVS-C18 which saliently demonstrates the catalytic potency of the stabilisers. All showed an induction period followed by a rapid pseudo first-order catalytic destruction of the hydroperoxide. The molar ratio of TBHP to the stabiliser was ≙10:1. Fig 4.15 also shows the effect of adding more hydroperoxide when the concentration of the initially added hydroperoxide had been reduced to a very low measurable value. In each case, the reaction recommenced at the same first order rate, within the limits of experimental error, but without the induction period.

The first order rate constants of the first and second stages of the reactions together with their average values are listed in Table 4.6 which shows rather good reproducibility. The induction periods measured for each additive showed a range from 30 mins to 40 mins.

Hence the results, like the antioxidant series, served to demonstrate the facile peroxide-annihilating reactions of the synthesised stabiliser series.

Table 4.6 Induction periods and pseudo first-order rate constants for the destruction of TBHP by the uv stabiliser series at 65°C (TBHP conc = 2.6×10^{-1}M; additive conc = 5.8×10^{-2} M)

Additives	Induction period, m	Rate constants, $k10^3\ s^{-1}$		
		1st stage	2nd stage	Average
	40	0.9	1.2	1.1
	35	1.0	1.4	1.2
	37	1.0	1.2	1.1
	35	1.3	1.1	1.2
	30	1.2	1.1	1.2

4.8 Processing Behaviour of the Polymer Melt Containing the uv Stabilisers

In order to further assess the thermal stabilising contribution of the sulphur moiety of the uv stabilisers, a study of the polymer melt processing behaviour was made.

Fig 4.16 illustrates the variation of MFI with increasing processing time for the synthesised homologues, HOBP as well as DLTP, at equimolar concentrations of 6×10^{-4} mole/100 g. The control sample showed a calamitous reduction in viscosity which reflected the remarkably high rate of chain-scission of the polymer molecules. Incorporation of the homologous series of uv stabilisers resulted in a less dramatic oxidative breakdown of the polymer; the magnitude of the rate of degradation processes varying inversely, even though marginal, with increasing molecular weight. This presumably, in part, signified the influence of volatility since the trend showed a weak but direct correlation with the volatility characteristics of the additives. DLTP however showed relatively better stabilisation performance as evidenced by the significant reduction in the slope of the curve. The explanation might well be due to its excellent compatibility and solubilising properties.

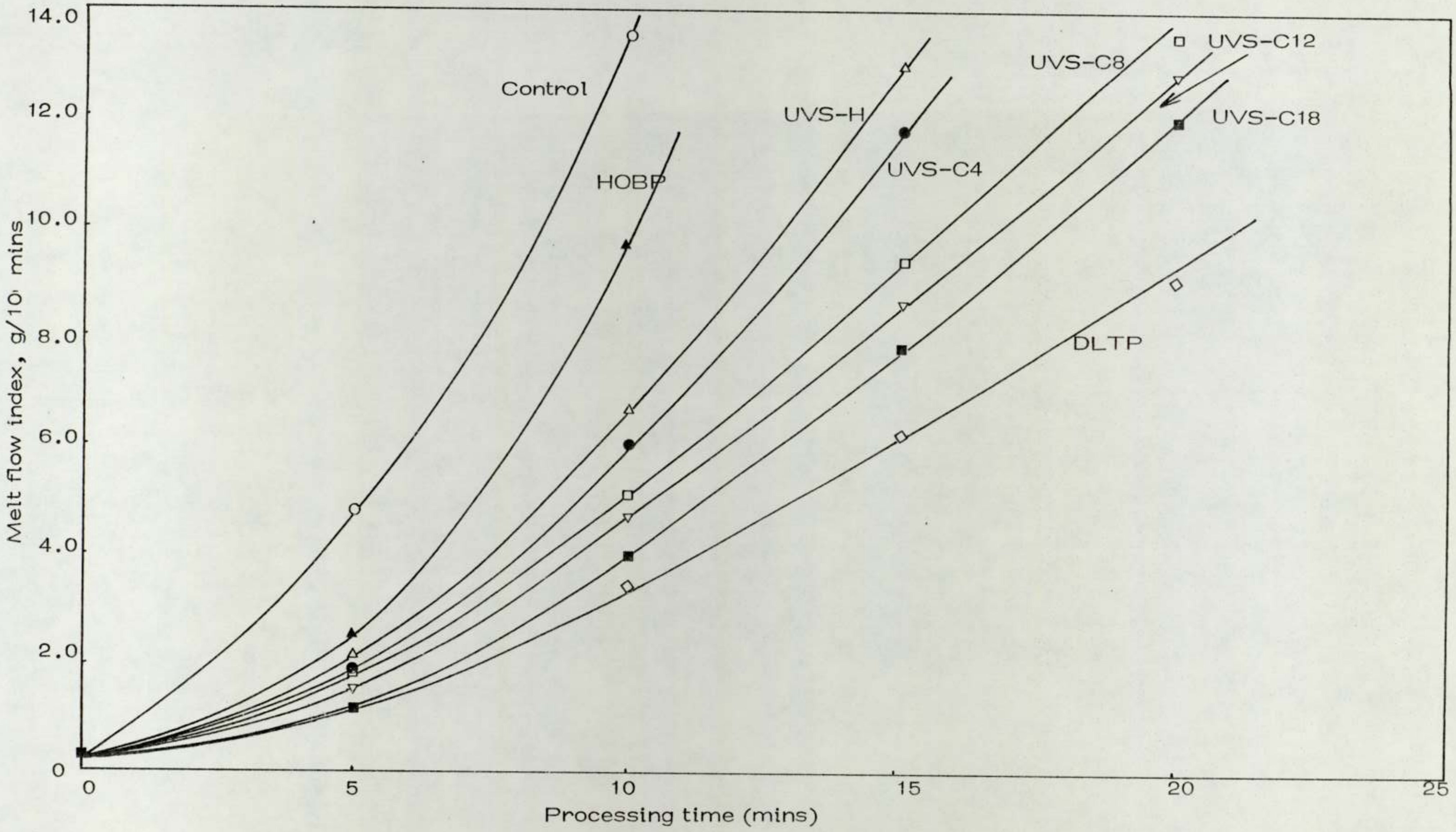


Fig 4.16 Melt processing behaviour of the polypropylene (at 180^{o}C) containing the uv stabilisers (open chamber processing; concentration of additives = 6 x 10^{-4} mole/100 g)

It is not clear why the stabiliser series, despite its low solubility and compatibility in polypropylene showed a significant melt stabilisation property under the aggressive processing operation (ie open chamber processing). A plausible explanation might be that at the processing temperature of 180°C, which is essentially well above the crystalline melting point of the polymer (165°C), compatibility and solubility of the additives were relatively enhanced thereby enabling the additives to perform the stabilising function. When cooled, the crystalline phase of the polymer would again be formed with the inevitable ejection of the additives from the polymer matrix. This rationale is in accord with the conclusions made by Billingham and co-workers(161) in their studies on a nickel-containing antioxidant in polypropylene in that the additive, on cooling, resides predominantly in the non-crystalline region of the polymer where it is needed most in conferring polymer stability.

Another important feature shown in Fig 4.16 is that HOBP, even though destitute of any apparent thermally stabilising moiety within the molecule, still imparted mild melt stabilisation to the processed polypropylene. This behaviour however is in line with the proposition made by Hutson and Scott(125) that at high temperatures the intra-hydrogen bonding characteristic of the additive is comparatively diminished allowing the 2-hydroxy group to function as a simple phenolic antioxidant.

Fig 4.17 further substantiates the relatively poor performance of the uv stabilisers as melt stabilisers as shown by the increasing carbonyl content with prolonged processing time. Since DLTP contains carbonyl groups within its molecule the film was initially solvent extracted before the infra-red spectral studies so that only the polymer carbonyl content was determined. Fig 4.17 shows the carbonyl content of the polymer for DLTP samples to be relatively low, again indicative of the better stabilisation given to the polymer.

Closed chamber processing of the polypropylene samples was also carried out in the presence of additives. Fig 4.18 depicts the slight increase in MFI with processing time suggesting that the presence of a limited amount of oxygen and reduced volatilisation dramatically inhibited the chain-scission reactions. This is also reflected by the marginal increment in the carbonyl content as shown in Fig 4.17.

Recognising that UVSH, for instance, was a relatively poor melt

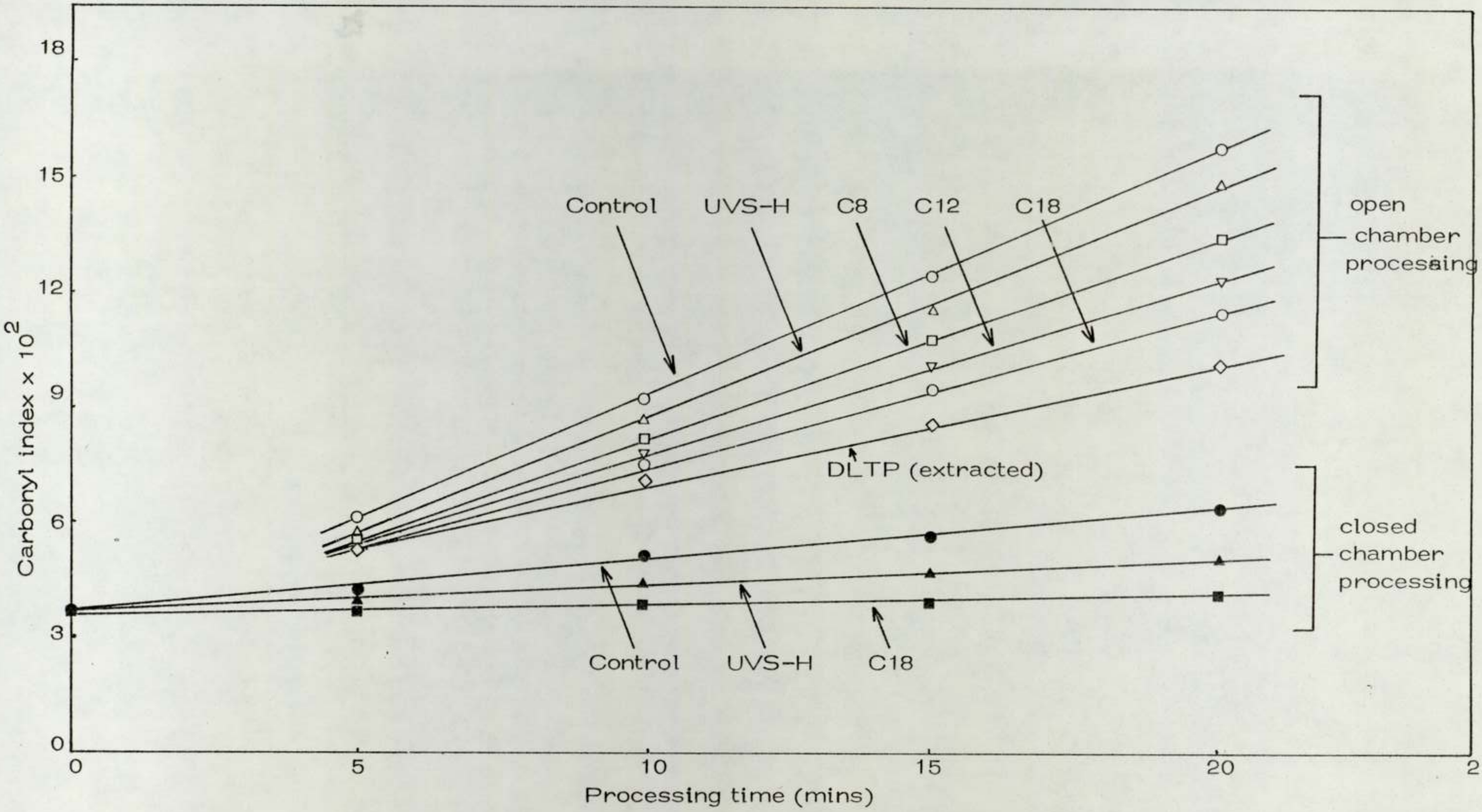


Fig 4.17 Increase of polypropylene carbonyl content with varying processing treatments at 180°C (concentration of uv stabilisers = 6 x 10^{-4} mole/100 g)

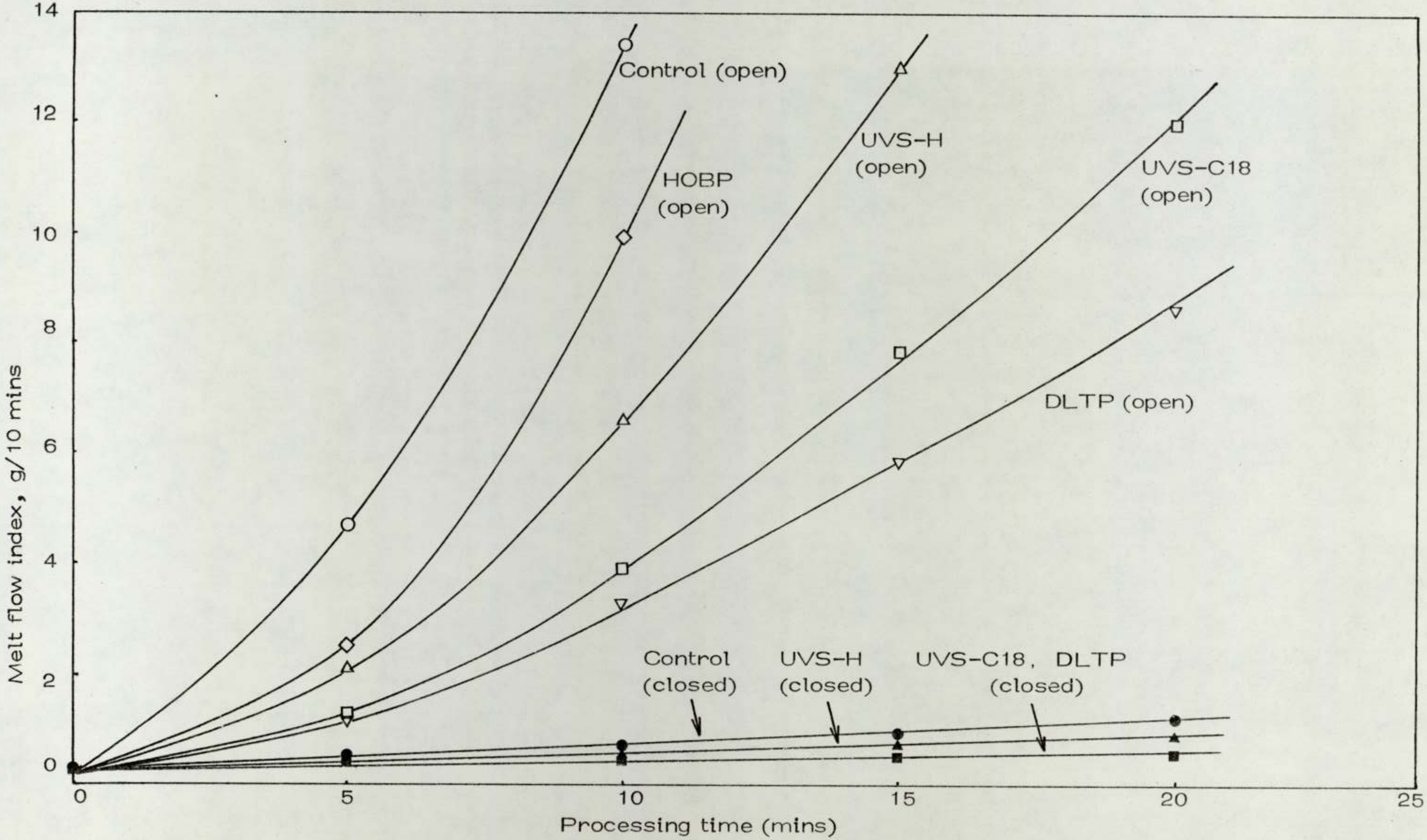


Fig 4.18 Comparison of polypropylene melt stability processed in open and closed chambers operations (concentration of uv stabilisers = 6×10^{-4} mole/100 g)

stabiliser, its effect on the melt stabilising performance of 1076 was investigated. Fig 4.19 shows the small adverse influence of UVSH on the 1076 performance as evidenced by the minor increase in MFI after 15 and 20 mins aggressive processing. This possibly implies that 1076 was not affected or destroyed to any significant extent by UVSH under the processing operation. Similar work with DLTP showed no adverse effect on melt stability as illustrated by the constant MFI, Fig 4.20.

It is only recently that increasing attention has been paid to the effect of processing conditions on the subsequent degradative behaviour. It is now widely recognised that thermal processing history does play a crucial role in determining the service lifetime of polymers(221). The present work attempted to display this contention and Fig 4.21 shows the differing photo-protection endowed by HOBP after being subjected to aggressive and mild processing operations over the time periods of 10 and 20 mins processing.

When processed under limited availability of oxygen similar to that found in commercial operation, prolonged processing time did not appear to appreciably affect the performance of HOBP as seen by the close proximity of the 10-and 20-min curves.

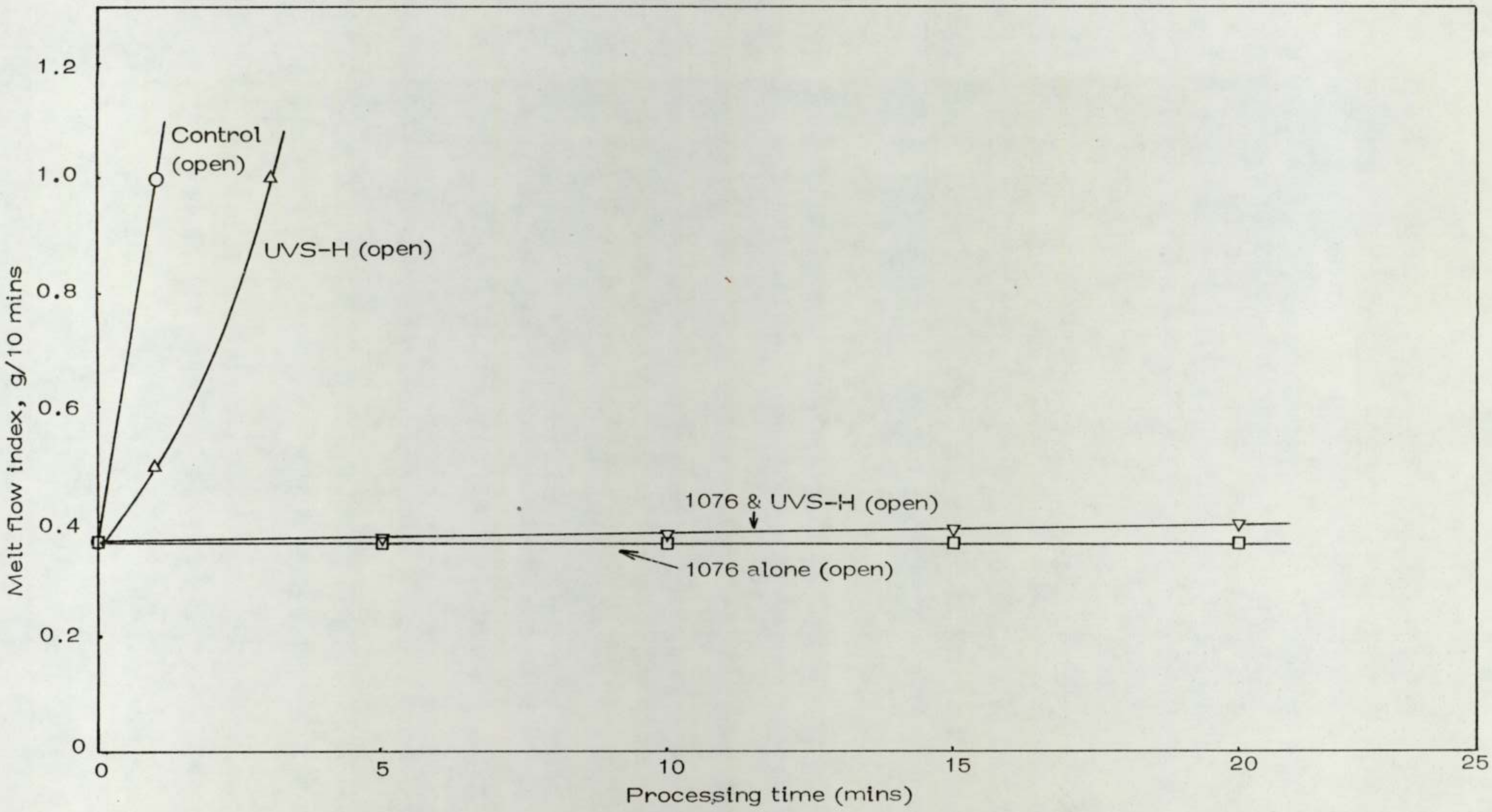


Fig 4.19 Influence of UVS-H on the melt stabilising performance of 1076 (concentration of additives = 6×10^{-4} mole/100 g)

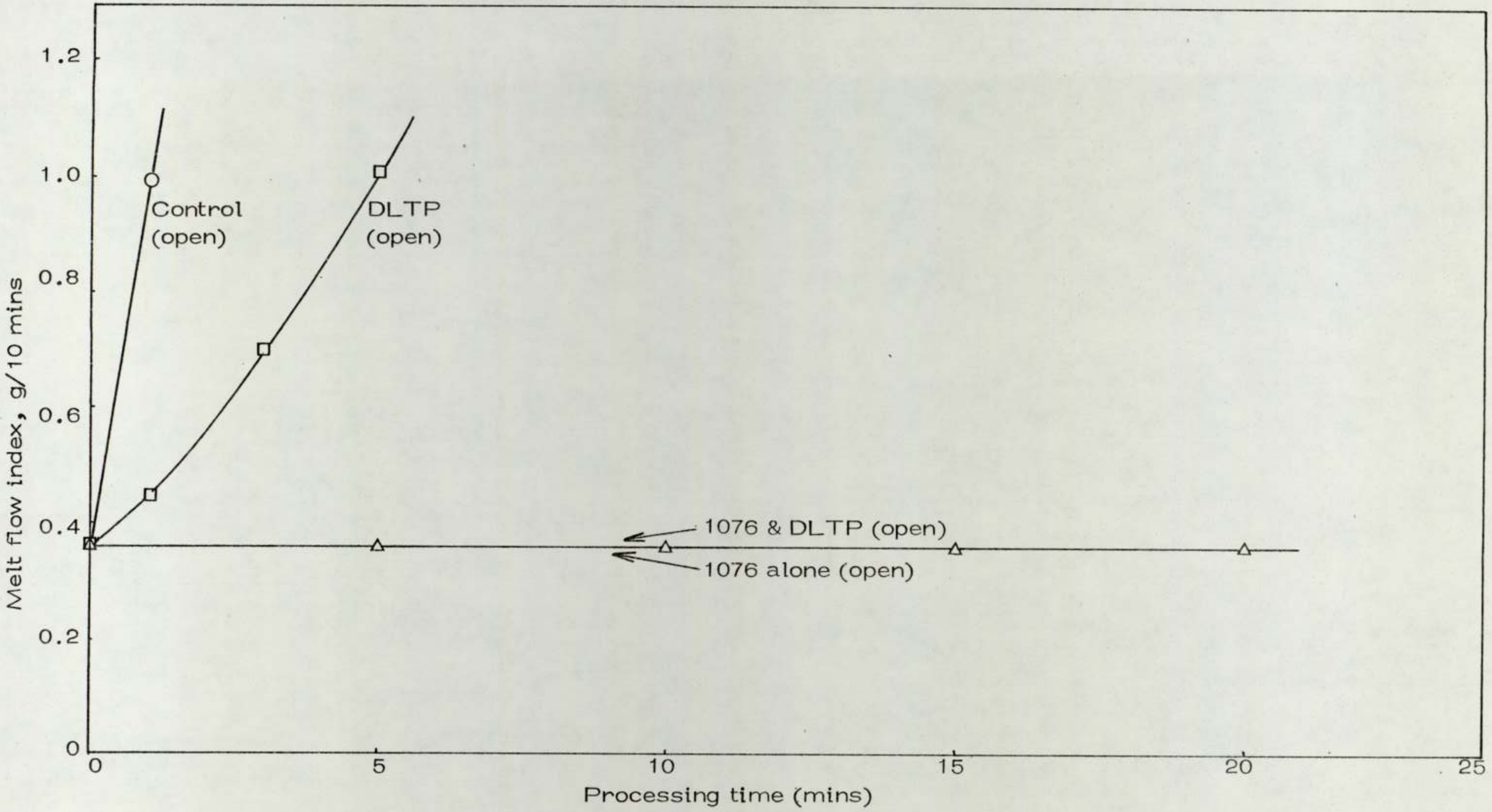


Fig 4.20 Influence of DLTP on the melt stabilising performance of 1076 (concentration of additives = 6×10^{-4} mole/100 g)

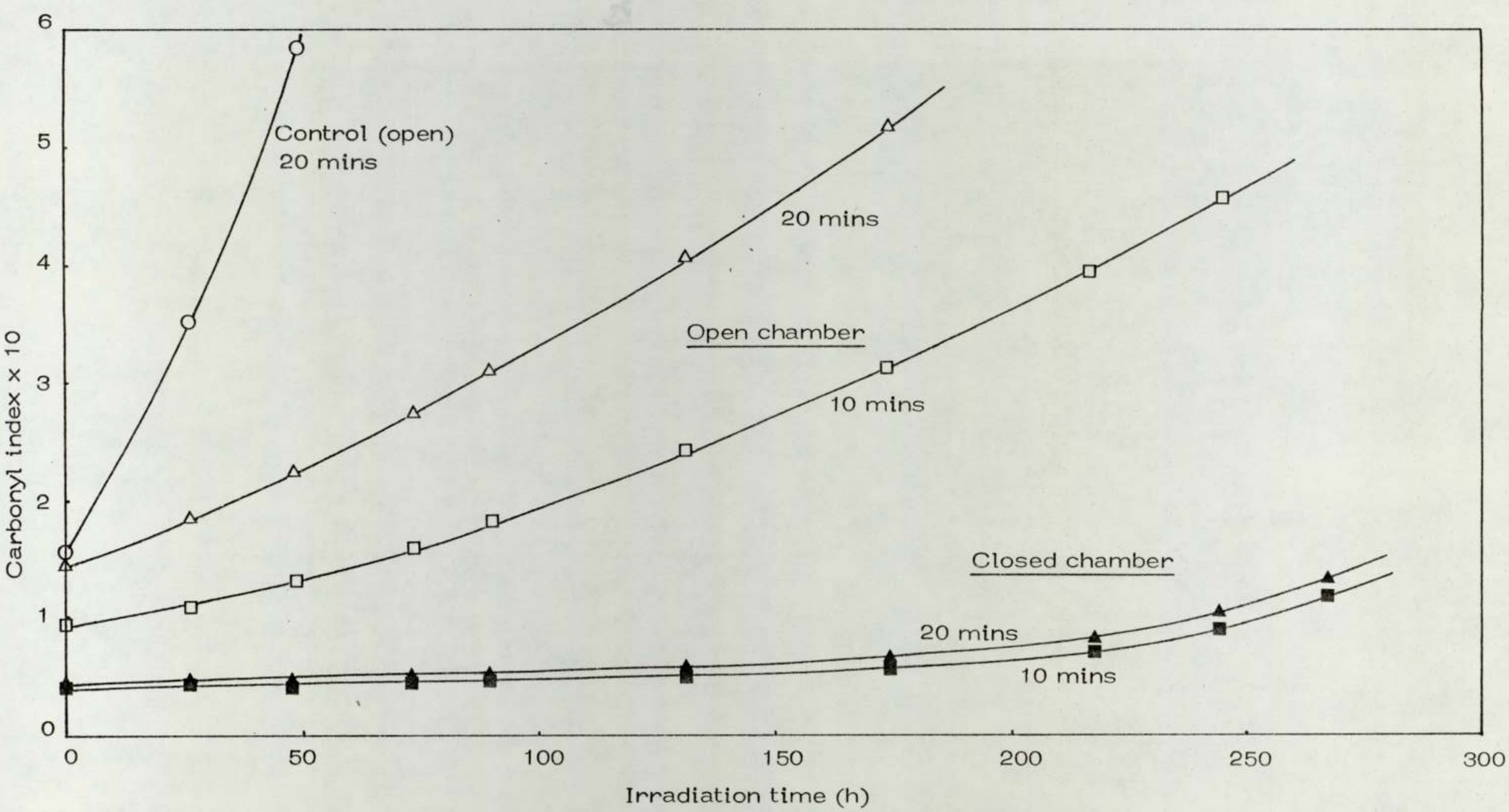


Fig 4.21 Effect of varying processing treatments on the subsequent photo-protective activity of HOBP (concentration of additives = 6×10^{-4} mole/100 g)

However, open chamber processing with an unlimited supply of oxygen brought about severe degradative reactions (as shown earlier from MFI and initial carbonyl content data) and this manifested itself in the subsequent reduced photostabilisation as shown in Fig 4.21. A similar trend was demonstrated by UVSH and UVSC18, Figs 4.22 and 4.23. However, an unusual feature is shown by the latter two figures. Closed chamber processing demonstrated a cross-over of the 10 and 20 mins processing curves with a significant reduction in oxidative rate shown by the 20-min curve despite it being more heavily oxidised as mirrored by the initial higher carbonyl content. It is not known why this be so, but presumably the prolonged processing time produced molecular species derived from UVSH and UVSC18 that were more soluble in the polymer with longer processing time which further inhibited the oxidative chain reactions. This is also reflected in the embrittlement times as shown in Table 4.7 which also provides further substantiative evidence for the dependence of service lifetimes on the polymer melt processing history.

4.9 An Overview and Discussion

Fig 4.24 compares the screening activities of the synthesised

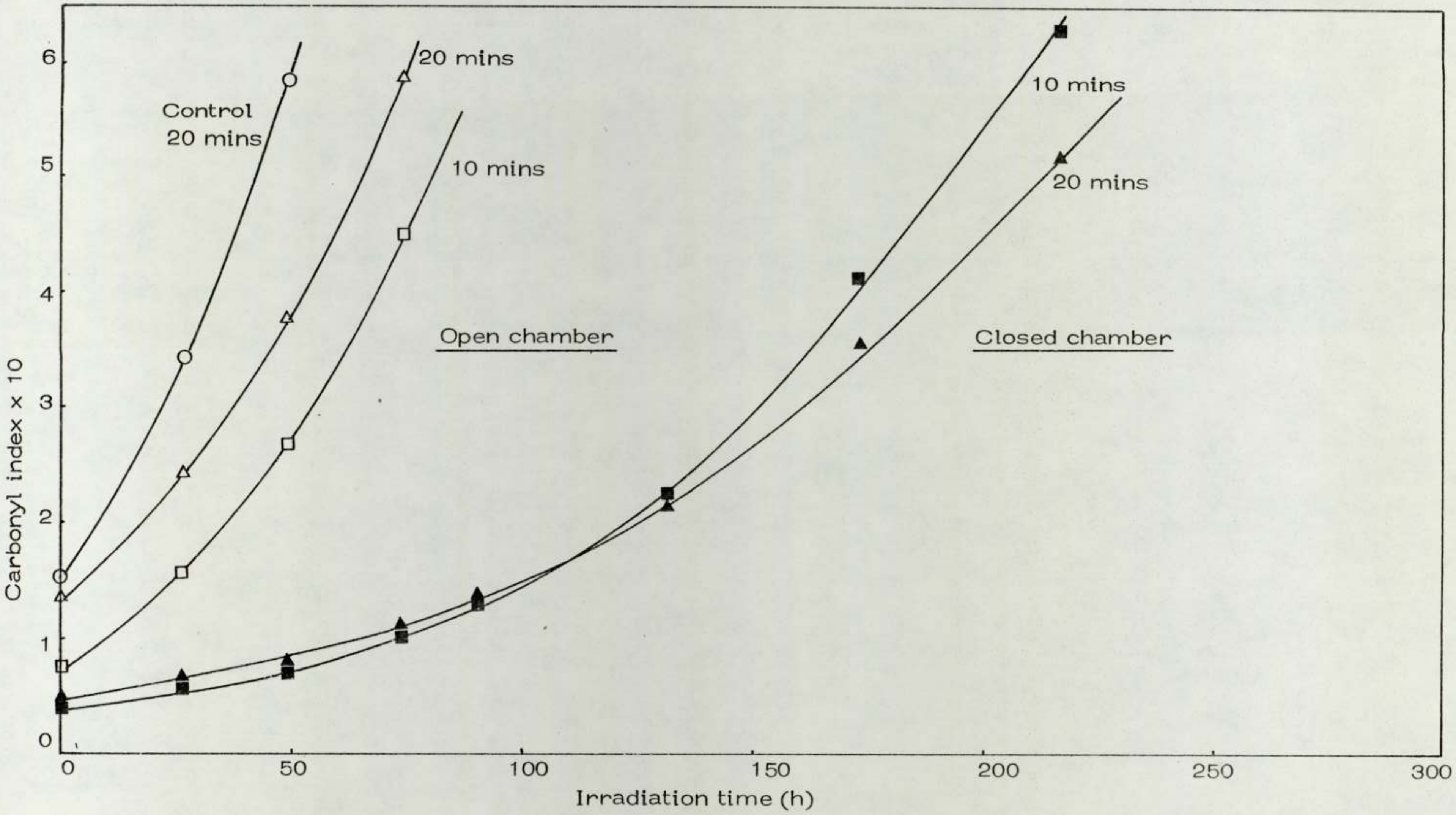


Fig 4.22 Effect of varying processing treatmentson the subsequent photo-protective activity of UVS-H (concentration of additives = 6×10^{-4} mole/100 g)

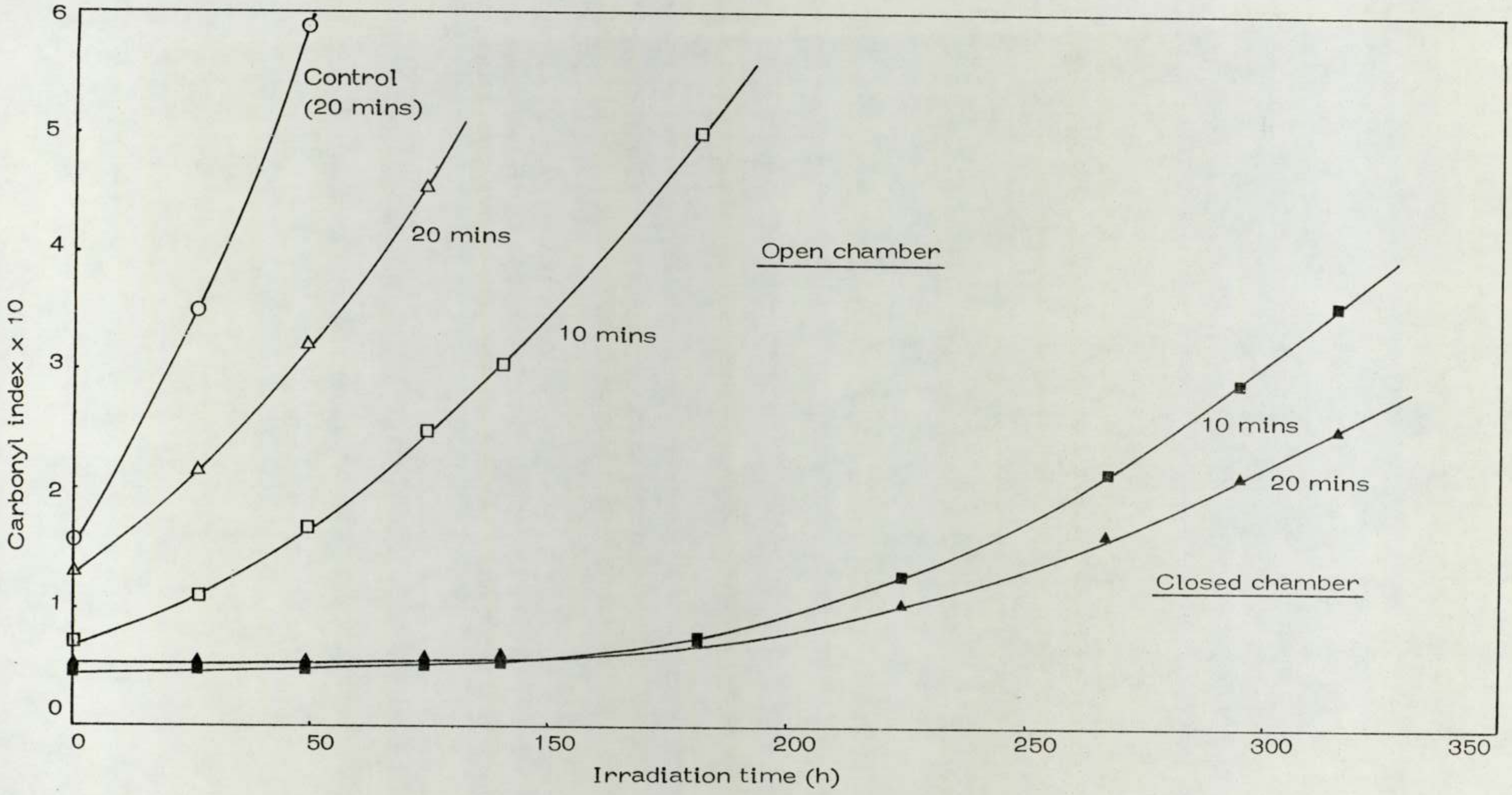
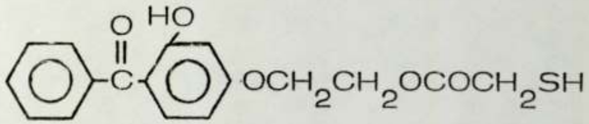
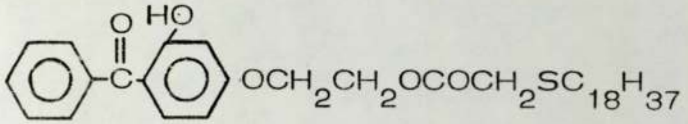
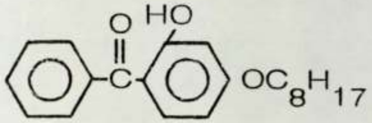


Fig 4.23 Effect of varying processing treatmentson the subsequent photo-protective activity of UVS-C18 (concentration of additives = 6 × 10–4 mole/100 g)

Table 4.7 Influence of processing operations on the subsequent photo-protection of polymer films (Concentration of additives = 6×10^{-4} mole/100 g)

Additives	Embrittlement times (h)			
	10" processing		20" processing	
	Closed	Open	Closed	Open
Control	75	30	64	–
	115	44	123	25
	230	90	250	40
	460	200	420	93

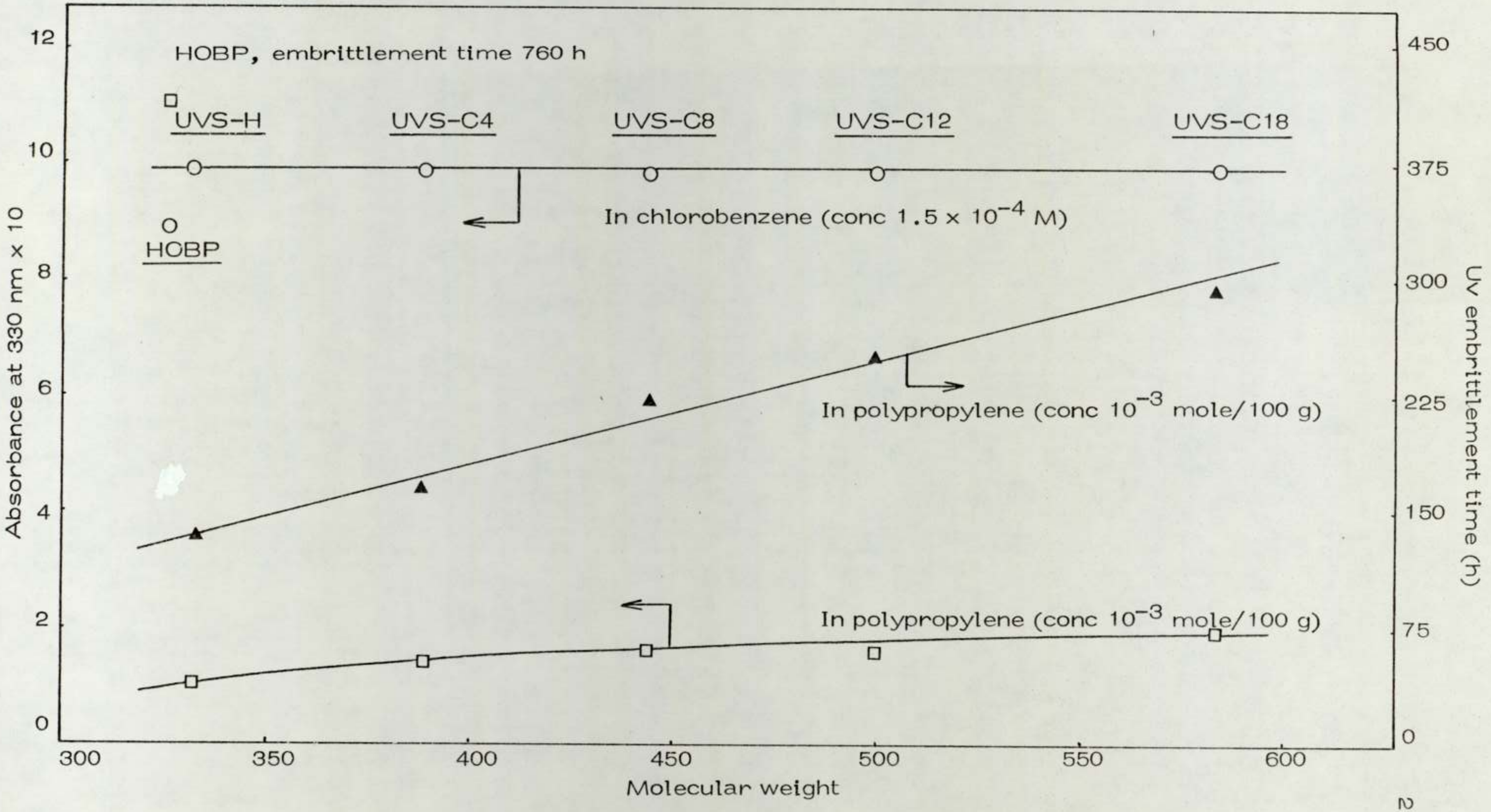


Fig 4.24 Comparative screening activity of the uv stabilisers in chlorobenzene and in polypropylene films and their corresponding photo-stabilisation

uv stabilisers and HOBP in chlorobenzene and in polypropylene films with their corresponding photo-protective behaviour. When dissolved in the solvent where physical constraints were virtually absent, screening activity of the stabilisers was of similar effectiveness indicating that the intrinsic screening performance was independent of increasing molecular weight. However, when incorporated in polypropylene, the synthesised stabilisers showed much reduced absorbance compared with HOBP. While the latter showed an absorbance of 1.1 (at λ_{max} = 330 nm) those of the stabiliser series imparted an absorbance ranging from 0.1 to 0.2 at similar molar concentration of 10^{-3} mole/100g. This was further reflected by the corresponding embrittlement times of 750 h (for HOBP) to those spanning from 130 h (for UVSH) to 295 h (for UVSC18).

Hence despite the excellent inherent screening performance and peroxide decomposing activity, the synthesised additives imparted relatively poor photoprotection to the polymer. The main shortcoming of the stabilisers appeared to be their much inferior compatibility in polypropylene. The evidence of relative insolubility in polypropylene was derived from the poor uv absorbance performance and further substantiated by infra-red spectral investigation and the immiscibility of the additives in n-hexane.

However, the additives exhibited mild melt and thermal stabilising properties as shown by Fig 4.25. This might be due to the well known stabilising activity of most sulphur antioxidants(222). It is also evident from Fig 4.25 that the stabilising performance of the additives followed a direct, even though weak, correlation with increasing molecular weight. It is apparent then that the volatility of the stabilisers played a major role in this respect.

Earlier studies on the antioxidant series described in the preceding chapter showed the octadecyl homologue to be relatively incompatible in relation to that of the dodecycl. A similar trend was however not observed within the uv absorber series. Again this lends weight to the contention that the acute incompatibility of the additives was such that its manifestation was less discriminatory within the stabiliser series so that the volatility behaviour of the stabiliser exerted an over-riding influence. In other words, the solubility of the additives was so low that the influence of additive-polymer compatibility was minimal. From this it follows that the behaviour of the stabilisers could only be rationalised in terms of their chemical

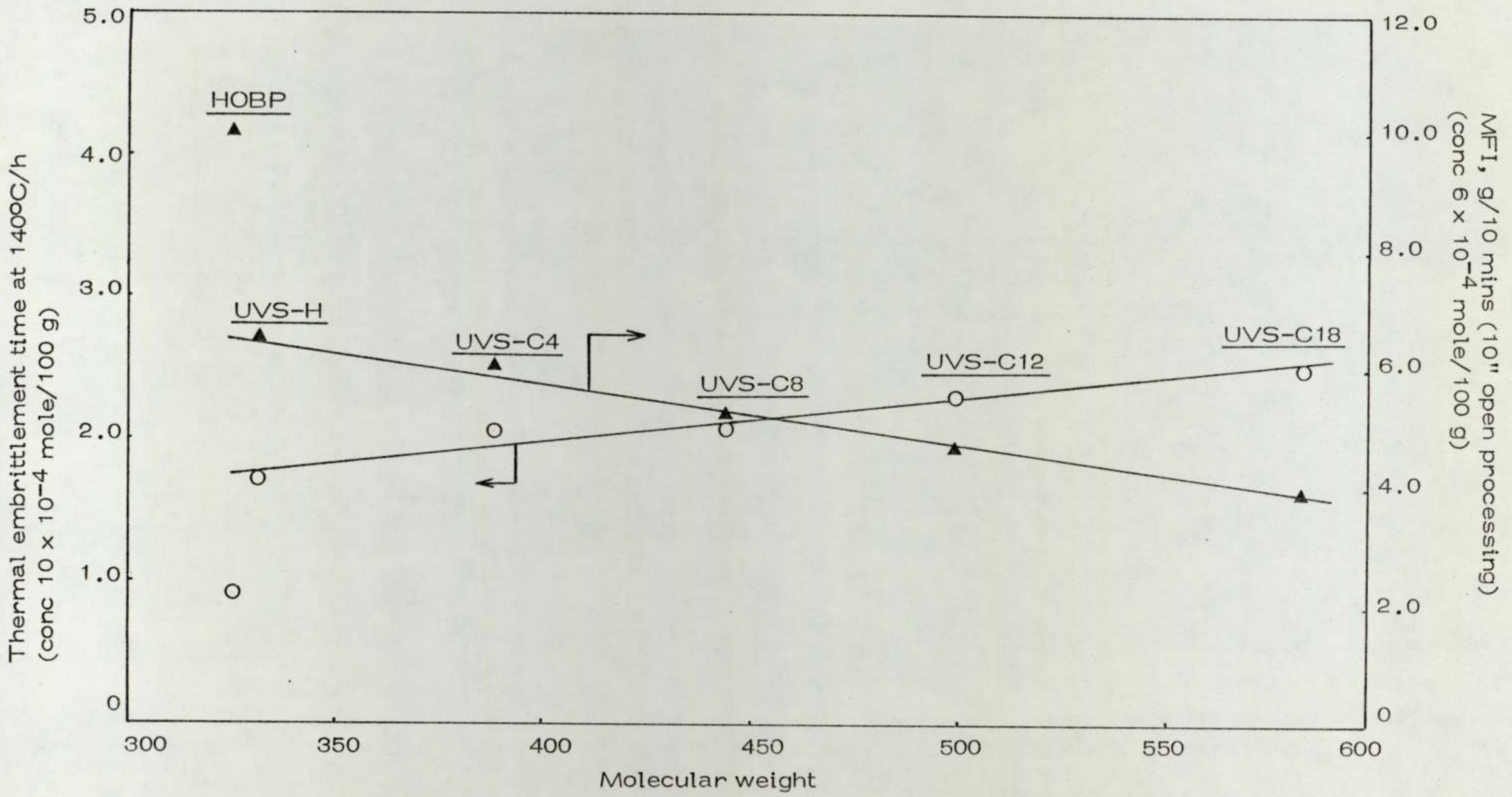
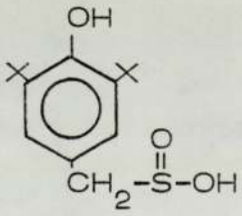


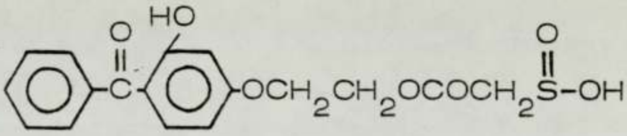
Fig 4.25 Comparison of thermal and melt stabilising performance of the uv stabiliser series in polypropylene

activity-cum-volatility factors.

Comparison of Table 4.6 and Table 3.8 (Chapter 3) shows the antioxidant series to exhibit a generally higher rate of TBHP decomposition (k ca 1.8×10^{-3} $\sec^{-1}$) in relation to those of the uv stabiliser series (k ca 1.0×10^{-3} $\sec^{-1}$). This might well be due to the comparatively facile catalytic activity of the benzylic species of BHBM (I) (sulphinic acid) formed as a consequence of the initial stoichiometric reactions of the parent compound with the hydroperoxide. UVSH on the other hand does not possess such benzylic moiety (II) and possibly accounts for its significantly lower catalytic activity.



(I)



(II)

CHAPTER FIVE

SYNERGISTIC ACTIVITY OF HOBP WITH TBC, 1076, BHBM AND AOS-C12 ON UV IRRADIATION

Studies in the preceding two chapters described the individual performance of HOBP, TBC, 1076 and AOS-C12 in polypropylene films on exposure to ultra-violet light. The present work attempted to evaluate the interaction of HOBP with the phenolic antioxidants in conferring uv stability on the polymer. The principle underlying the investigation was that the mutual protection provided by uv stabilisers and antioxidants enhances their photo-protective performance thereby bringing about hetero-synergistic activity.

In all the synergistic studies that were carried out, a total concentration of 10^{-3} mole additives/100 g polymer was used at the following molar ratios of the two components: 0/100, 20/80, 35/65, 50/50, 65/35, 80/20, 100/0. The percentage synergism imparted by the two-component system was calculated using the following formula:

$$\text{Synergism (\%)}^{(140)} = \frac{(E_s-E_c)-[(E_1-E_c)+(E_2-E_c)]}{(E_1-E_c)+(E_2-E_c)} \times 100$$

where: E_s = embrittlement time of synergist

E_c = embrittlement time of control

E_1 = embrittlement time of antioxidant 1

E_2 = embrittlement time of antioxidant 2

5.1 Synergistic Activity of HOBP and TBC

Fig 5.1 shows the varying performance of polypropylene films containing differing ratio of HOBP and TBC on exposure to uv light. It was evident that the film containing HOBP alone produced an auto-accelerating behaviour as recognised by the absence of the induction period and the nature of the slope of the curve. The behaviour is in line with the well-recognised fact that HOBP functions predominantly as a uv-screener. However, incorporation of 50, 35 and 20 mole % of TBC produced a decreasing initial rate followed by a rapid auto-oxidative reaction. The pronounced reduction of the auto-accelerating mode was presumably indicative of the positive influence of TBC on the photo-protective action of HOBP. Too high a proportion of TBC as shown by the 20/80 and 35/65 curves appeared to give a deleterious effect relative to that containing

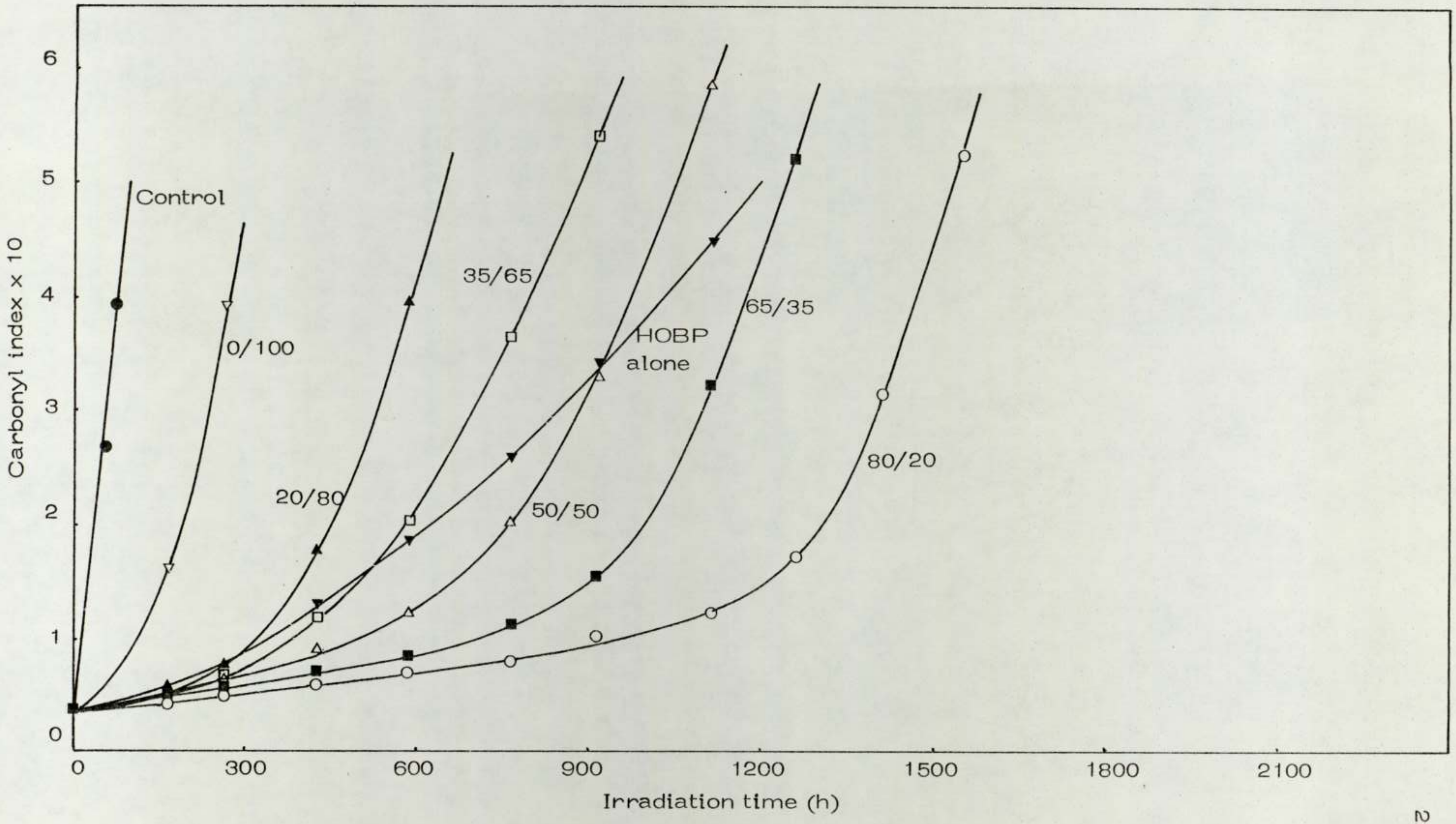


Fig 5.1 Effect of varying the molar ratio of HOBP and TBC on the uv stabilisation of polypropylene films (total concentration 10^{-3} mole/100 g) Numbers on curves refer to mole% ratio of HOBP and TBC

HOBP alone. The reasons might be at least two-fold which might be operating together; lower screening performance due to the decreased HOBP concentration and the production of increasing amounts of photo-active molecular species(8) such as stilbene-quinones. Comparison with the behaviour of the other phenolic antioxidants to be made in section 5.5 will attempt to throw further light on this.

Table 5.1 lists the embrittlement times of the exposed polymer films which further substantiates the above-mentioned trend. A plot of embrittlement times against the mole-fraction of TBC is shown in Fig 5.2 and demonstrates the higher uv stabilising activity with the lower mole-fractions of TBC.

Using the percentage synergism formula, the synergistic activity to uv light of the varying proportions of HOBP and TBC in the polypropylene films was evaluated. The varying embrittlement times of the one-component system containing differing concentrations was calculated from the calibration curves of Fig 5.3 (ie for the evaluations of E_1 and E_2 for the formula). Table 5.2 shows that the 80/20 mole % ratio of HOBP to TBC gave synergistic activity of 123%. However, increasing the TBC concentration with the concomittant reduction in that of HOBP brought about

Table 5.1 Embrittlement times of polypropylene films containing varying compositions of HOBP and TBC on exposure to uv light

Total concentration 10^{-3} mole/100 g		Weight of additives/100 g polymer		Embrittlement times (h)
Mole % HOBP	Mole % TBC	HOBP (g)	TBC (g)	
100	0	0.32	0	750
80	20	0.26	0.04	1420
65	35	0.21	0.08	1170
50	50	0.16	0.1	910
35	65	0.11	0.14	680
20	80	0.06	0.17	500
0	100	–	0.22	230

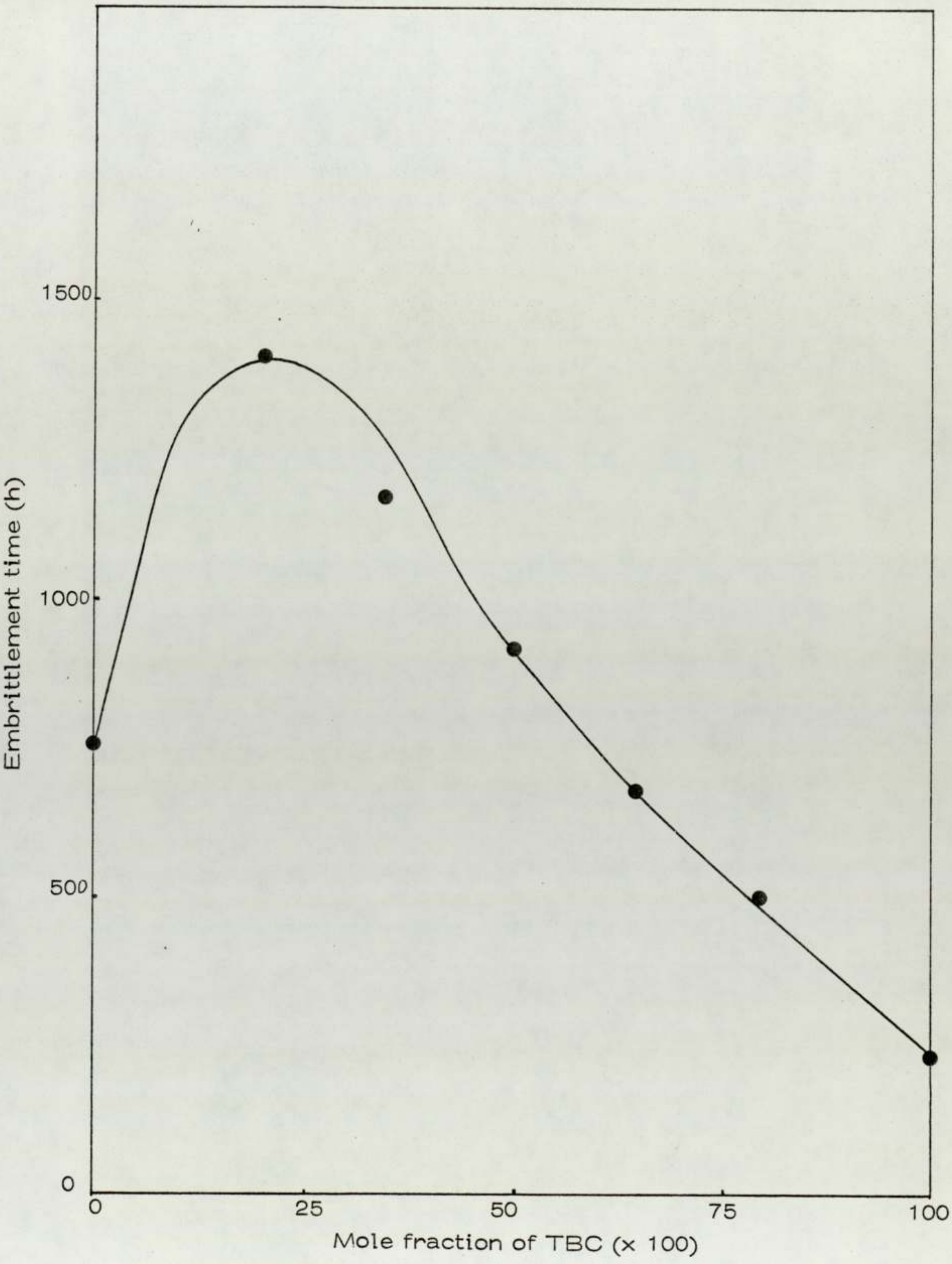


Fig 5.2 Synergism between HOBP and TBC in the photo-stabilisation of polypropylene films (total concentration 10^{-3} mole/100 g)

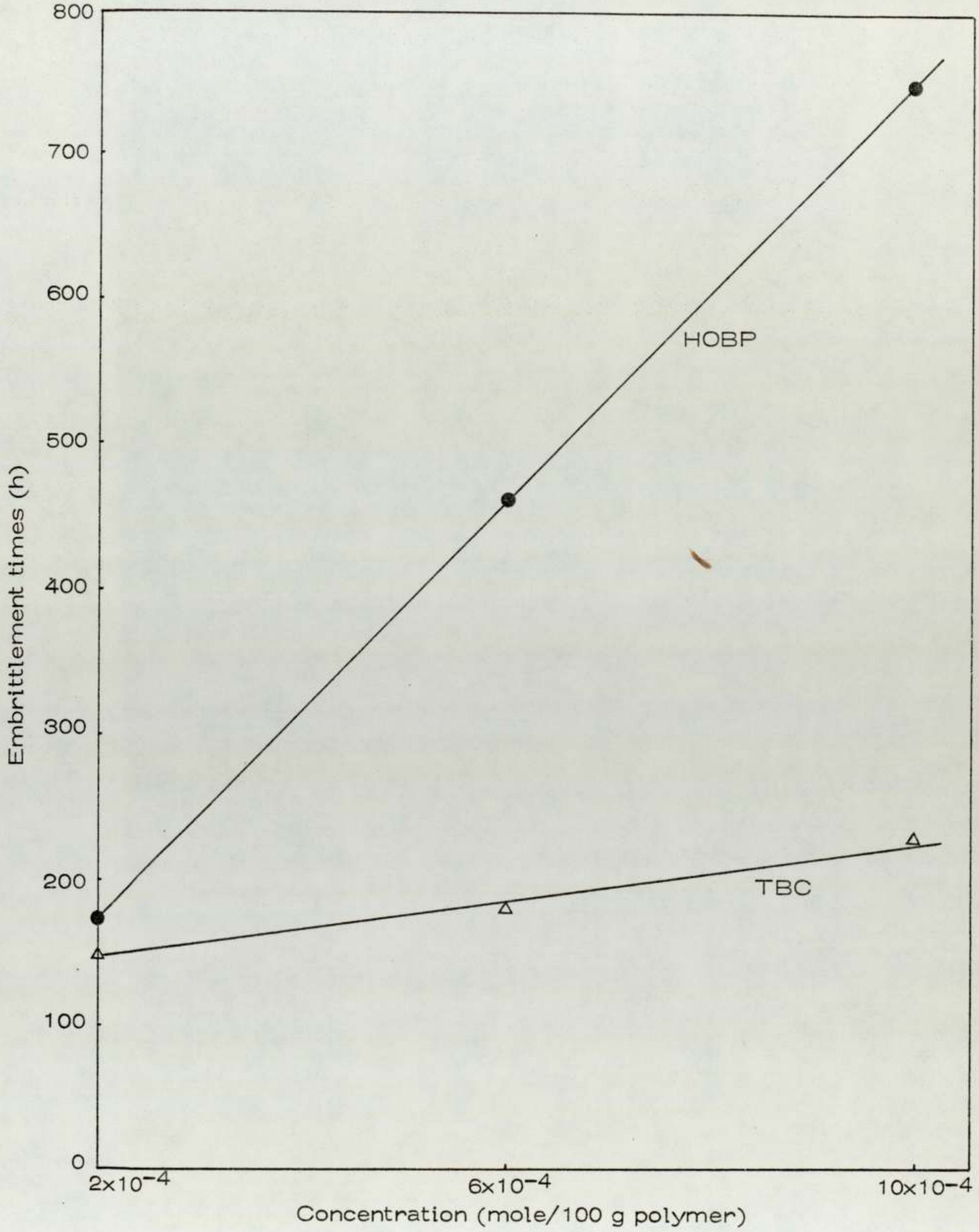


Fig 5.3 Calibration curves of embrittlement times against concentrations for HOBP and TBC

Table 5.2 Synergistic activity of HOBP and TBC at varying compositions in polypropylene films exposed to uv light

Total concentration 10^{-3} mole/100 g		Time to embrittlement of individual component (h)	Time to embrittlement of the two-component system (h)	Calculated effect of synergist (h)	Percent synergism
Mole % HOBP	Mole % TBC				
100	0	750	–	–	–
80	20	604/150	1420	604	123
65	35	500/160	1170	510	115
50	50	388/176	910	414	102
35	65	276/192	680	318	90
20	80	180/208	500	238	78
0	100	230	–	–	–
None (control)		75	–	–	–

a diminished synergism of 78% for the 20/80 HOBP to TBC molar ratio.

The decay of the uv absorbance peak at 330 nm which was indicative of the decreasing HOBP concentration in polypropylene films was also monitored with uv irradiation. The absorbance at 330 nm before exposure to uv light and containing varying ratio of HOBP and TBC showed a linear relationship as illustrated by Fig 5.4 verifying the increased intensity of the absorbance peak with increased HOBP concentration. Irradiation of the films to uv light produced differing rates of HOBP destruction as demonstrated in Fig 5.5. The film containing HOBP alone appeared to show a gradual decay of the 330 nm peak up to about 400 h irradiation followed by a much rapid destruction of HOBP. The other films containing differing amounts of TBC showed similar patter of behaviour in so far as the initial decay was concerned.

A first-order plot of the decrease of the 330 nm peak with irradiation time was also attempted and Fig 5.6 clearly depicts the less pronounced destruction of HOBP when 50, 35 and 20 mole % of TBC were present in relation to that of HOBP alone. Increasing the TBC concentrations to 65 and 80 mole % brought about a

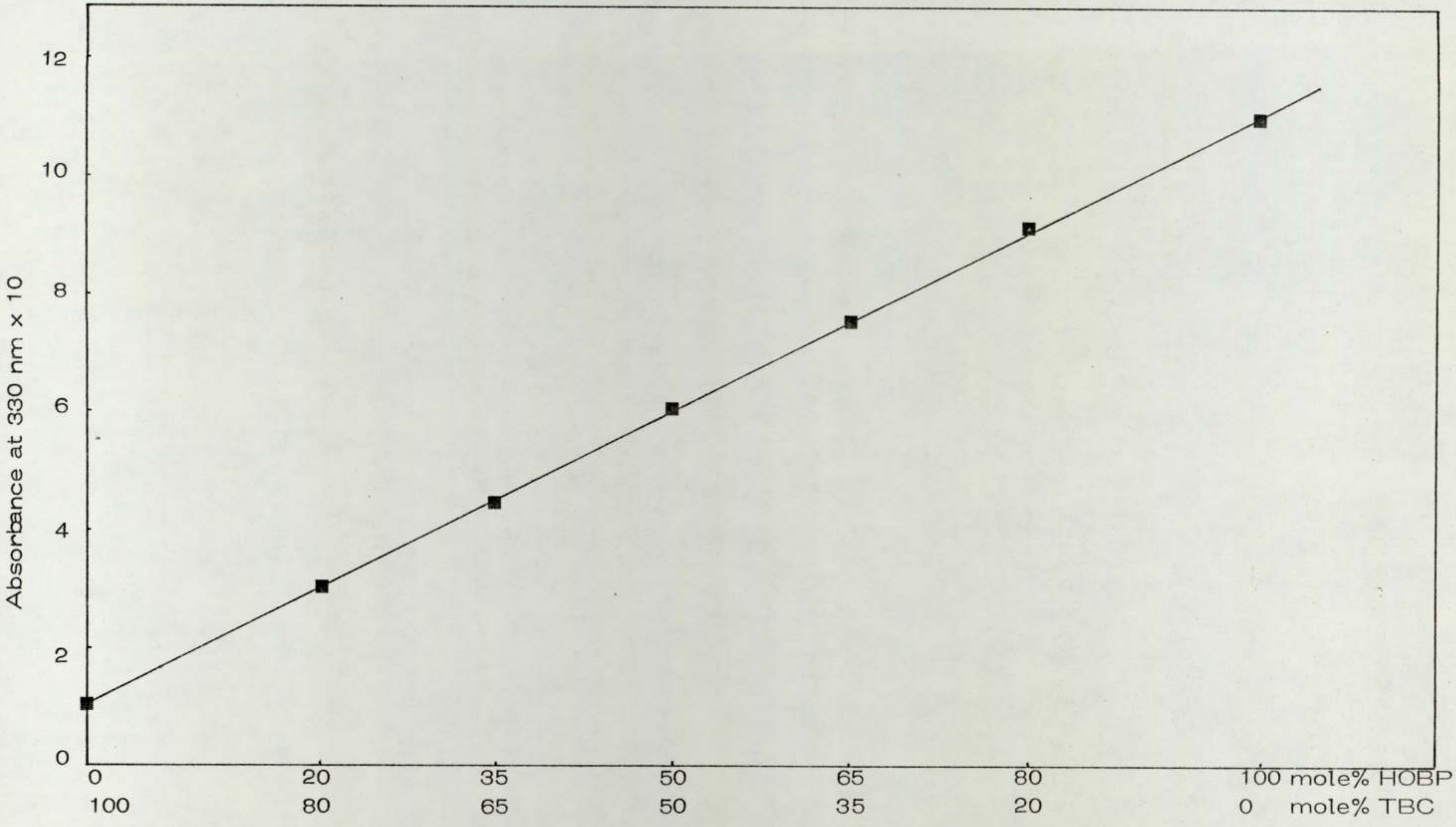


Fig 5.4 Increasing intensity of 330 nm absorbance with increasing HOBP concentrations in polypropylene films (total concentration 10^{-3} mole/100 g)

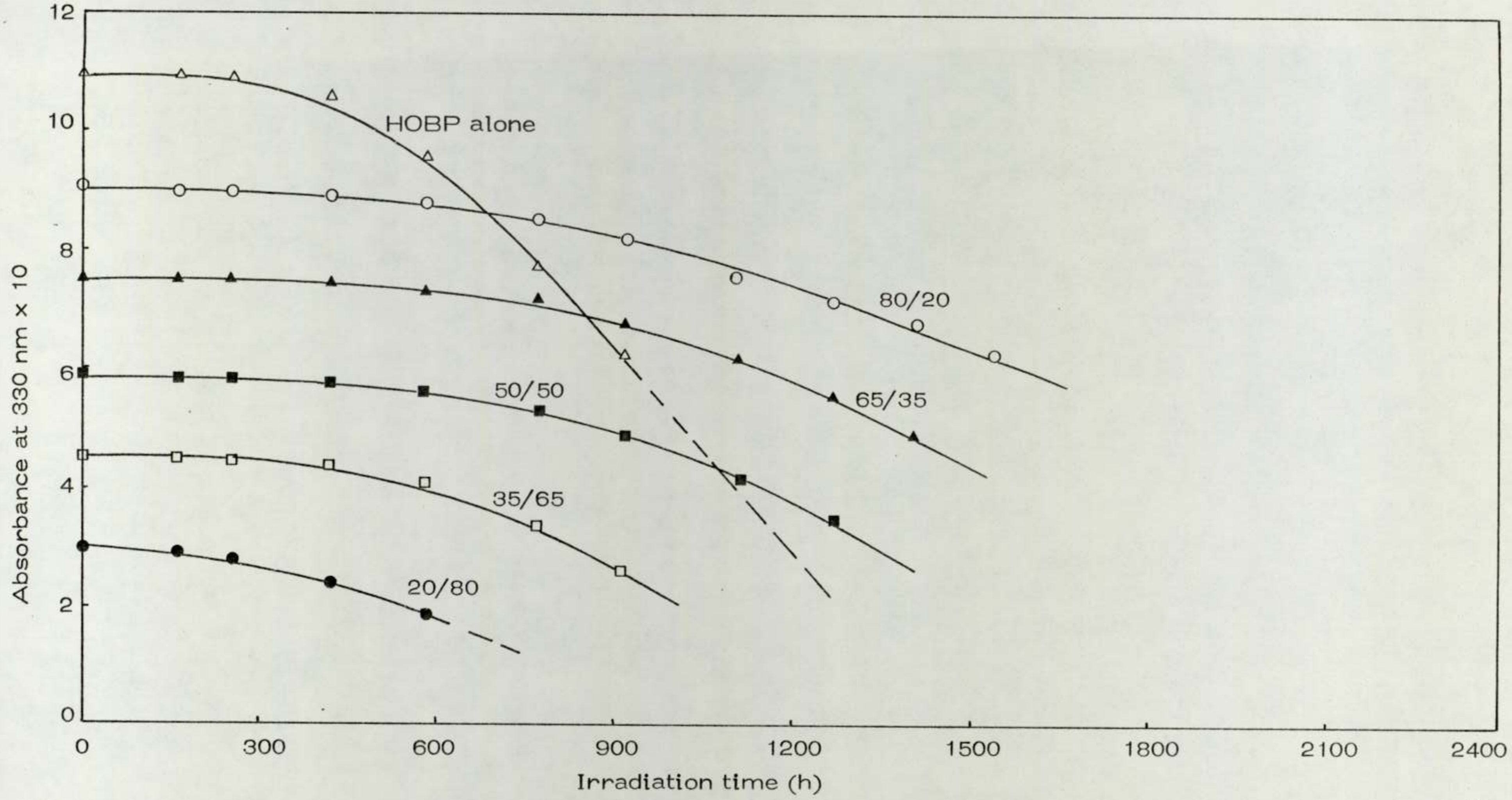


Fig 5.5 Decay of 330 nm peak with uv irradiation of the polymer films containing varying compositions of HOBP and TBC (total concentration 10^{-3} mole/100 g) Numbers on curves refer to mole % ratio of HOBP and TBC

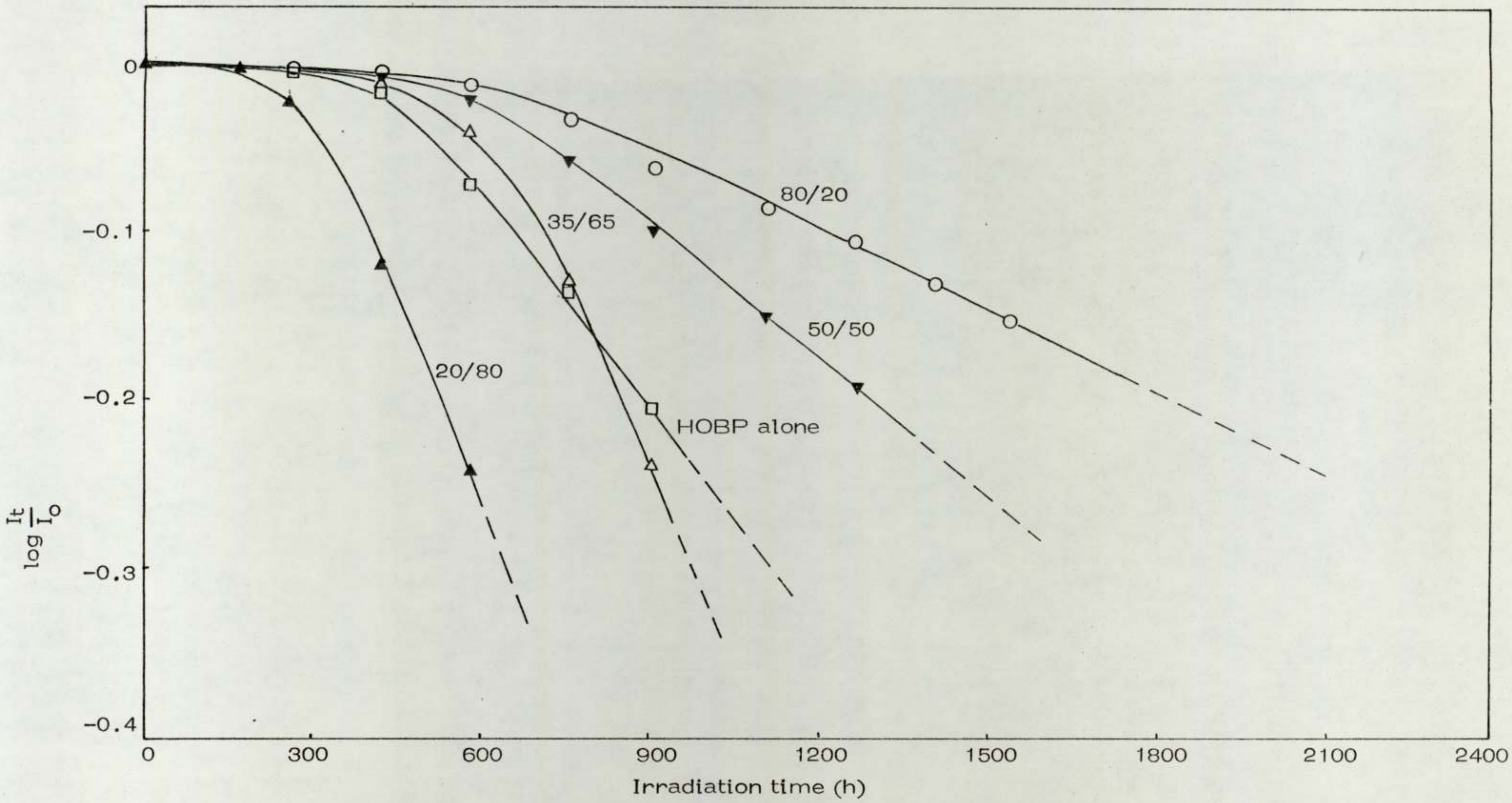


Fig 5.6 First order plot of HOBP decay during uv irradiation of polypropylene films containing varying compositions of HOBP and TBC (Numbers on curves refer to mole % ratio of HOBP and TBC) 65/36 curve was omitted for clarity

much faster destruction of HOBP. The rate constants for the HOBP decay in the polypropylene films are listed in Table 5.3. While HOBP alone gave a rate constant of $3.8 \times 10^{-4}\ h^{-1}$ those of 80/20 and 50/50 HOBP to TBC mole % ratio showed much reduced values of $1.3 \times 10^{-4}\ h^{-1}$ and $2.3 \times 10^{-4}\ h^{-1}$ respectively. Higher TBC concentrations of 65 and 80 mole % gave greater rate constants of HOBP destruction of $7.1 \times 10^{-4}\ h^{-1}$ and $8.3 \times 10^{-4}\ h^{-1}$ respectively.

5.2 Synergistic Activity of HOBP and 1076

Similar studies as described for the HOBP-TBC system were also carried out on the HOBP-1076 synergistic combinations.

Fig 5.7 illustrates the varying uv stabilisation provided by the HOBP-1076 system of differing mole % compositions. Like the HOBP-TBC studies, the presence of 50, 35 and 20 mole % of 1076 produced positive effect in comparison to that containing HOBP alone. Higher molar ratios of 1076 (ie 65 and 80) however showed an adverse influence. Even though a similar pattern of behaviour to that of the HOBP-TBC system was observed, the present synergistic combination showed longer embrittlement times as listed in Table 5.4. This might be suggestive, in part,

Table 5.3 First-order rate constants of HOBP during uv irradiation of polypropylene films containing varying compositions of HOBP and TBC

Total concentration, 10^{-3} mole/100 g		Weight of additives/100 g polymer		Rate constant $k\ 10^4\ h^{-1}$
Mole % HOBP	Mole % TBC	HOBP (g)	TBC (g)	
100	0	0.32	0	3.8
80	20	0.26	0.04	1.3
65	35	0.21	0.08	1.7
50	50	0.16	0.10	2.3
35	65	0.11	0.14	7.1
20	80	0.06	0.17	8.3
0	100	–	0.22	–

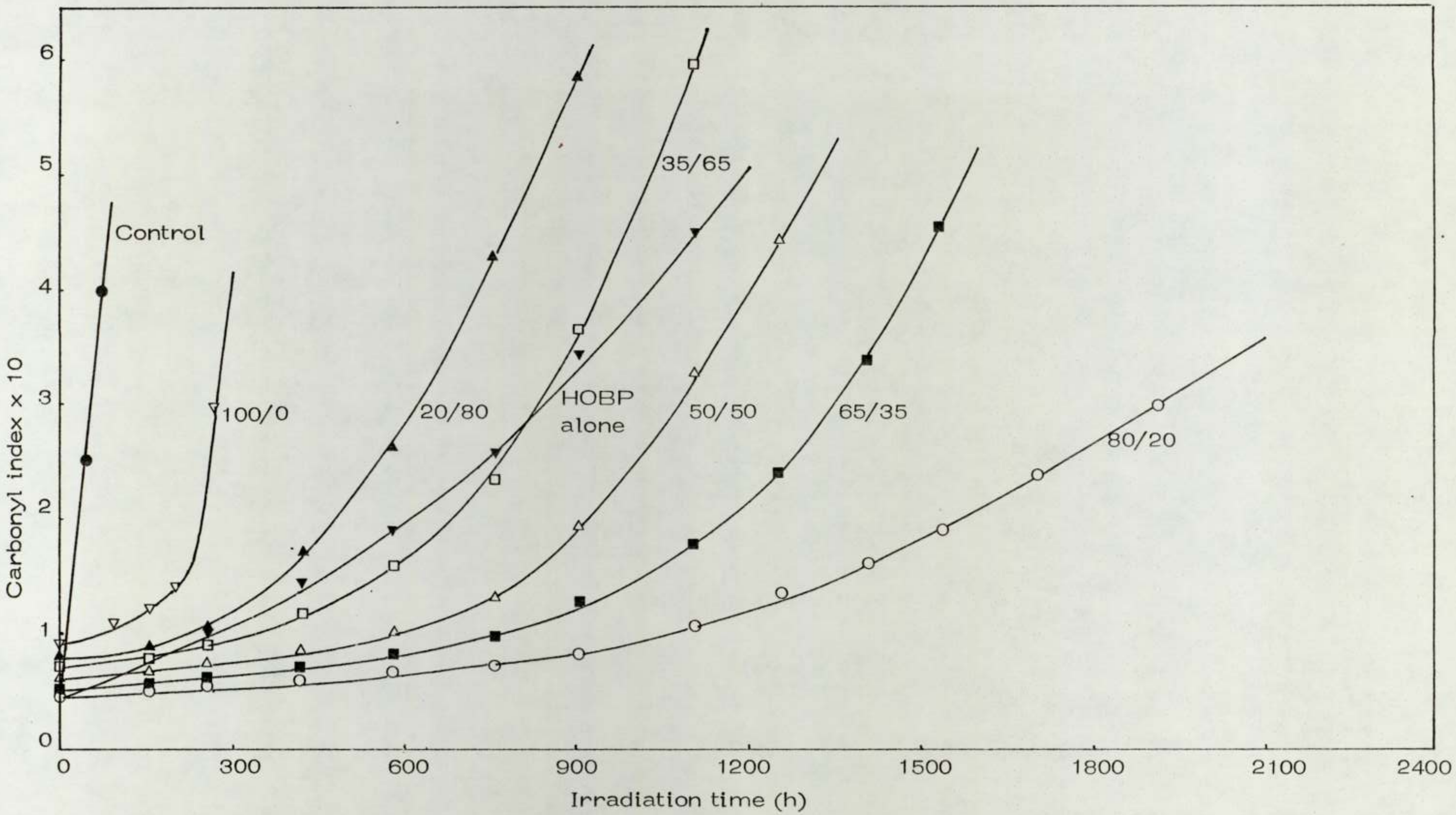


Fig 5.7 Effect of varying the molar ratio of HOBP and 1076 on the uv stabilisation of polypropylene films (total concentration 10^{-3} mole/100 g) Increasing initial carbonyl index was due to increasing carbonyl content from 1076

Table 5.4 Embrittlement times of polypropylene films containing varying compositions of HOBP and 1076 on exposure to uv light

Total concentration, 10^{-3} mole/100 g		Weight of additives/100 g polymer		Embrittlement time (h)
Mole % HOBP	Mole % 1076	HOBP (g)	1076 (g)	
100	0	0.32	0	750
80	20	0.26	0.11	1590
65	35	0.21	0.18	1320
50	50	0.16	0.26	1115
35	65	0.11	0.34	920
20	80	0.06	0.42	705
0	100	-	0.53	260

of the lower concentrations of derived photo-active species within the polymer films. A plot of embrittlement times against the mole fraction of 1076 is shown in Fig 5.8 illustrating again the higher uv stabilising activity with the lower mole fractions.

This was further reflected by the percentage synergism data of Table 5.5 which shows higher synergistic activity to those of the HOBP-TBC at all the corresponding HOBP antioxidant compositions. Fig 5.9 shows the calibration curves that were used in the evaluations of the embrittlement times of the individual component at differing concentrations.

A first order plot of the HOBP decay is shown in Fig 5.10 and clearly demonstrates the reduced rate of HOBP destruction in the presence of the lower mole % of 1076. This was quantified by the values of the rate constants as listed in Table 5.6.

5.3 Synergistic Activity of HOBP and BHBM

The studies described in the preceding two sections focussed on the heterosynergistic activity of a uv stabiliser and a free radical scavenger. The present study incorporated a third functionality namely that of a peroxide decomposer as manifested by BHBM

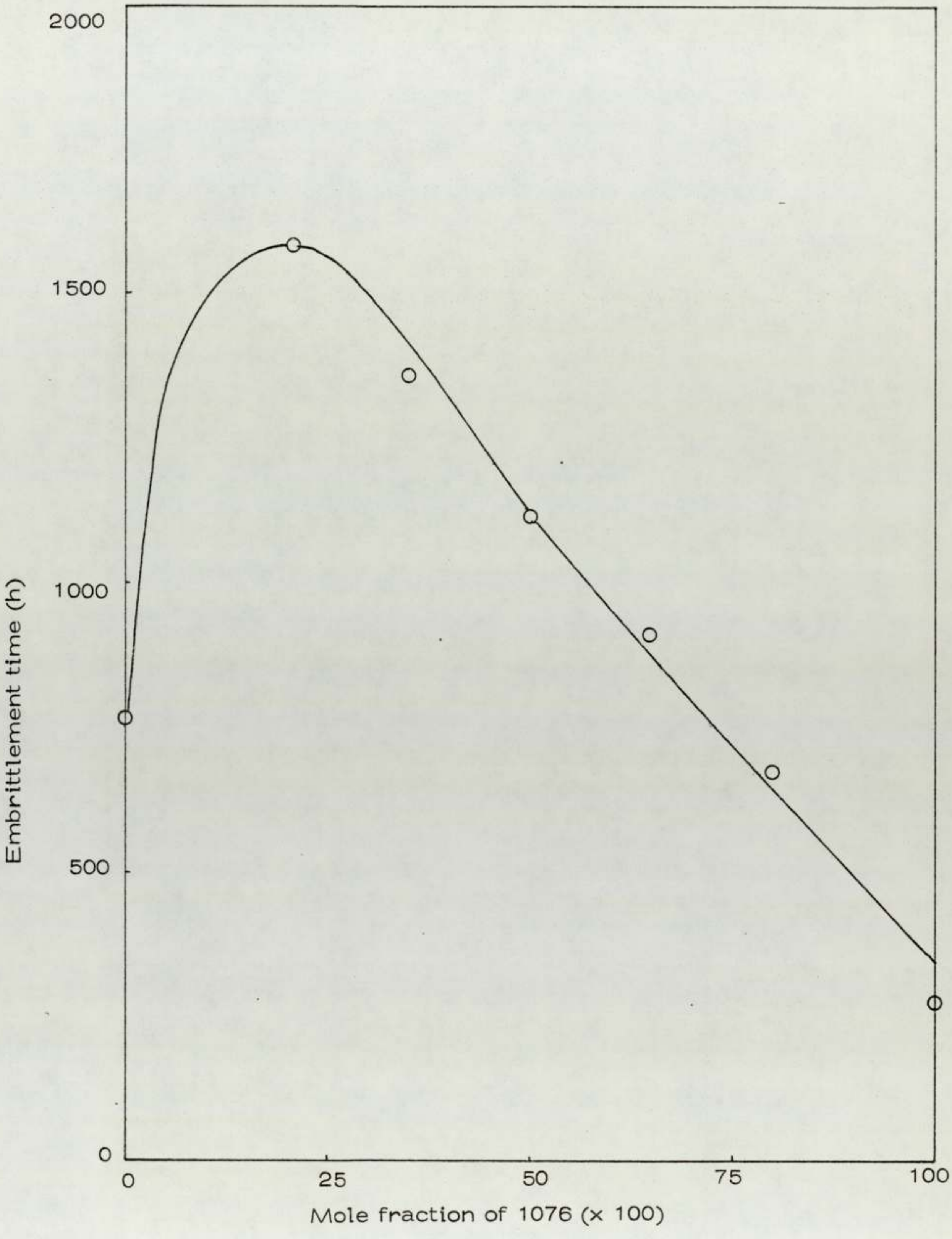


Fig 5.8 Synergism between HOBP and 1076 in the photo-stabilisation of polypropylene films (total concentration 10^{-3} mole/100 g)

Table 5.5 Synergistic activity of HOBP and 1076 at varying compositions in polypropylene films exposed to uv light

Total conc 10^{-3} mole/100 g		Time to embrittlement of individual component (h)	Time to embrittlement of the two-component system (h)	Calculated effect of synergist (h)	Percentage synergism
Mole % HOBP	Mole % 1076				
100	0	750	–	–	–
80	20	604/180	1590	635	139
65	35	500/200	1350	550	132
50	50	388/216	1115	454	129
35	65	276/232	890	358	127
20	80	180/248	705	278	127
0	100	260	–	–	–

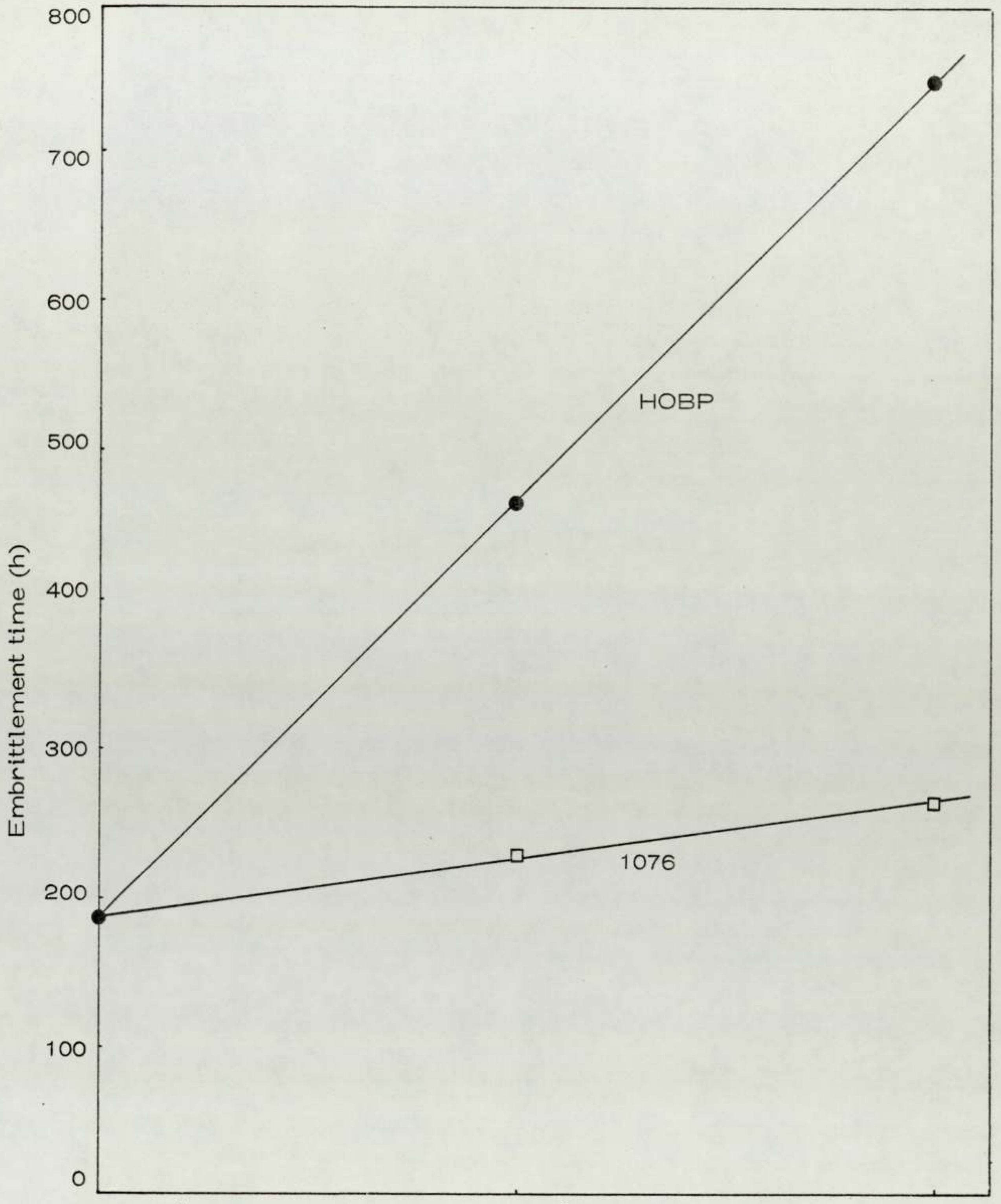


Fig 5.9 Calibration curves of embrittlement times against concentrations for HOBP and 1076

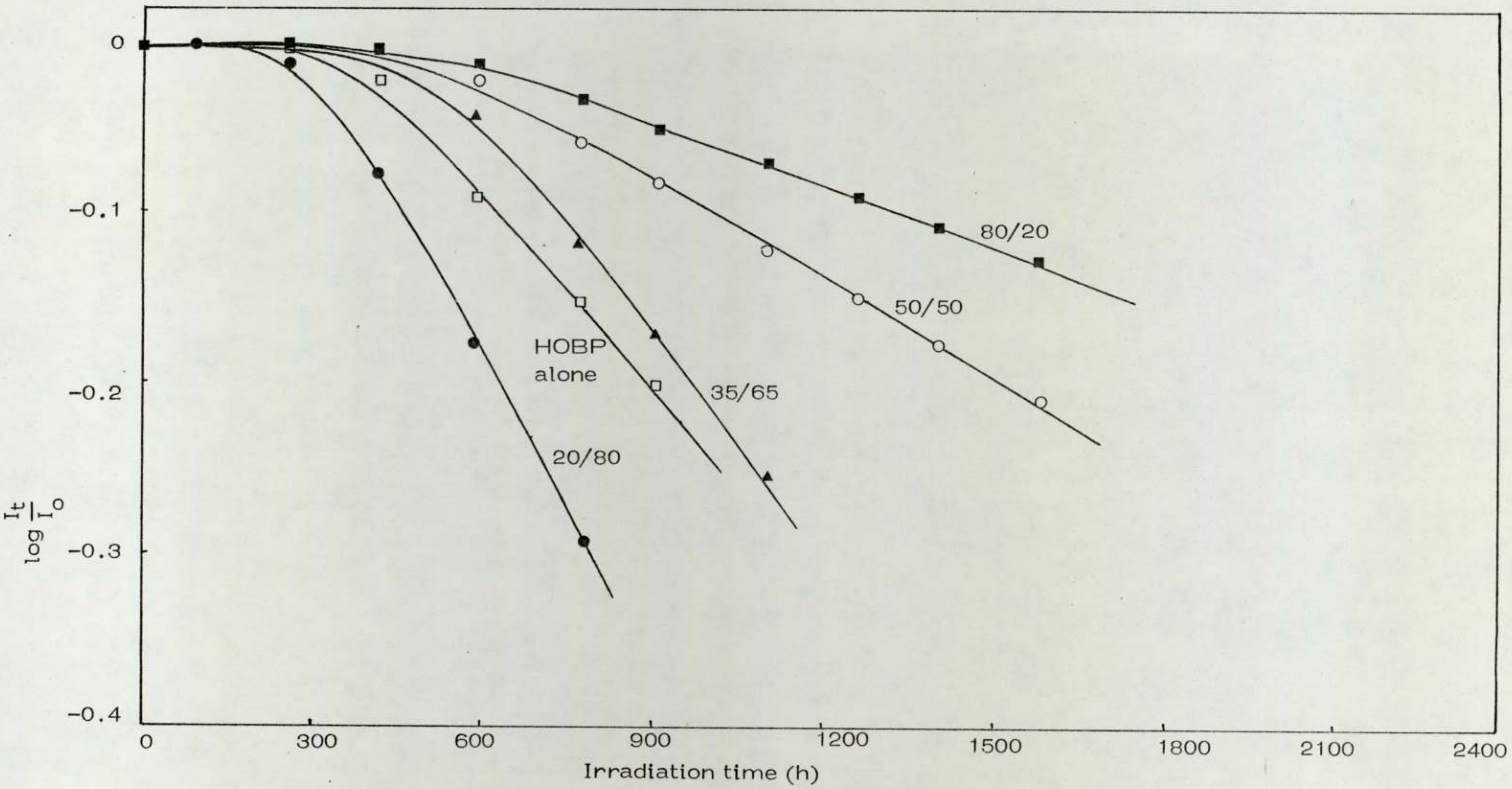


Fig 5.10 First order plot of HOBP decay during uv irradiation of polypropylene films containing varying compositions of HOBP and 1076 (numbers on curves refer to mole % ratio of HOBP and 1076) 65/35 curve was omitted for clarity

Table 5.6 First-order rate constants of HOBP decay during uv irradiation of polypropylene films containing varying compositions of HOBP and 1076

Total concentration 10^{-3} mole/100 g		Weight of additives/100 g polymer		Rate constant k 10^4 h^{-1}
Mole % HOBP	Mole % 1076	HOBP (g)	1076 (g)	
100	0	0.32	0	3.8
80	20	0.26	0.11	1.1
65	35	0.21	0.18	1.4
50	50	0.16	0.26	1.8
35	65	0.11	0.34	4.1
20	80	0.06	0.42	6.0
0	100	–	0.53	–

which, in addition to possessing a phenolic hydroxyl also exerted a powerful peroxidolytic activity due to the sulphur moiety.

Fig 5.11 illustrates the behaviour of the polymer films containing varying mole % of HOBP and BHBM. A new feature is shown by the figure in that an initial pro-oxidant effect was observed whose magnitude and extent increased with increasing concentrations of BHBM. It did appear then that the screening activity of HOBP was insufficient to arrest the pro-oxidant effect due to the sulphur antioxidant even when present at equimolar concentrations (50/50 curve). The presence of the phenolic hydroxyl also did not seem to provide an effective inhibition to the generation of free radicals. Presumably this is in accord with the well-reconised fact that phenolic antioxidants are generally ineffective as photo-stabilisers due to the shorter kinetic chain of the photo-oxidation processes.

However, the period following the initial pro-oxidation saw a true polymer photo-stability as evidenced by the insignificant increment of carbonyl content. Hence the molecular species generated during the pro-oxidant stage appeared to have imparted,together with the HOBP, considerable photo-stabilisation to the polypropylene films. This was further exemplified by Table 5.7 listing the embrittlement times of the polymer films

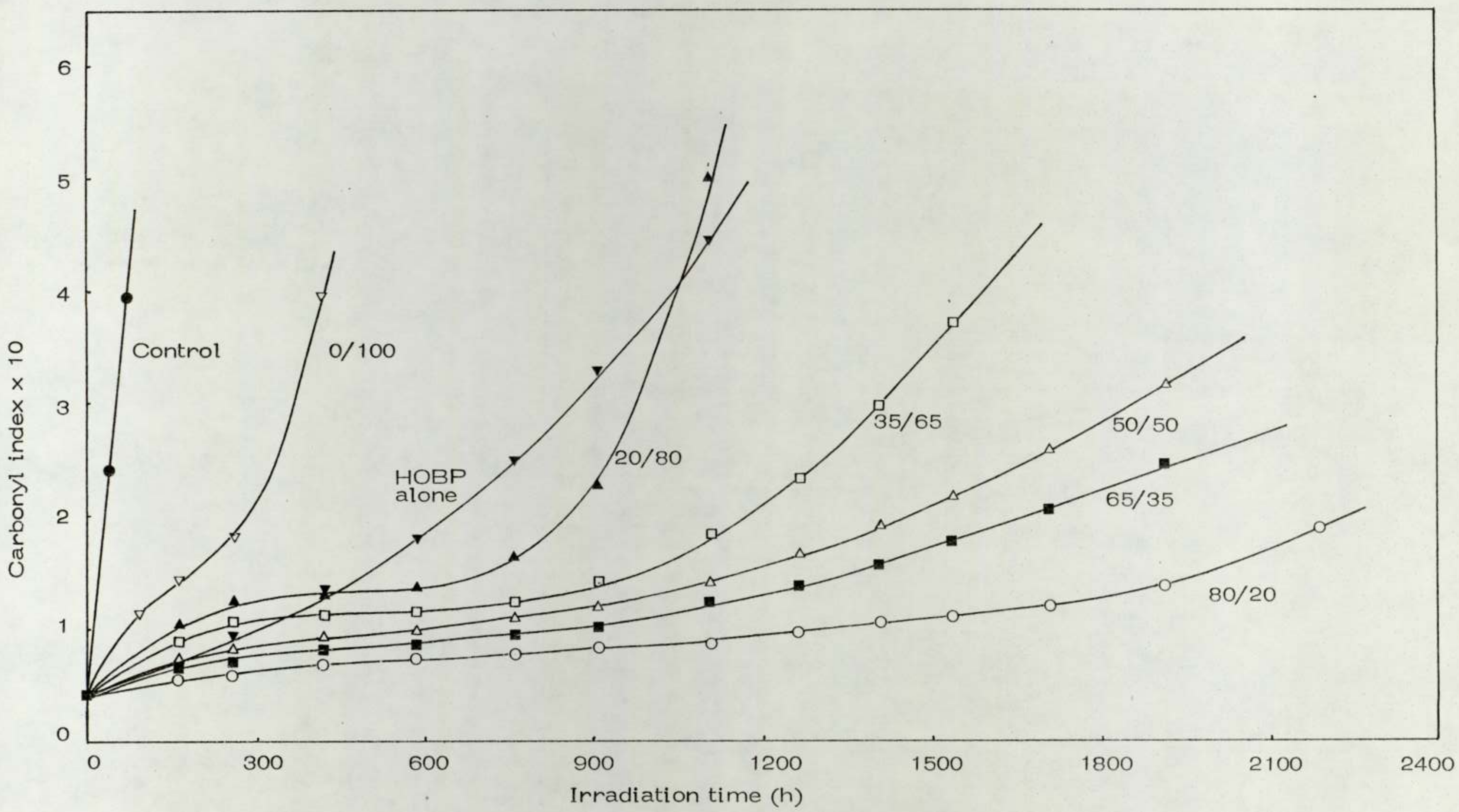


Fig 5.11 Effect of varying the molar ratio of HOBP and BHBM on the uv stabilisation of polypropylene films (total concentration 10^{-3} mole/100 g) Number on curve refers to mole % ratio of HOBP and BHBM

Table 5.7 Embrittlement times of polypropylene films containing varying compositions of HOBP and BHBM on exposure to uv light

Total concentration 10^{-3} mole/100 g		Weight of additives/100 g polymer		Embrittlement time (h)
Mole % HOBP	Mole % BHBM	HOBP (g)	BHBM (g)	
100	0	0.32	0	750
80	20	0.26	0.05	2100
65	35	0.21	0.09	1850
50	50	0.16	0.13	1547
35	65	0.11	0.16	1240
20	80	0.06	0.20	830
0	100	–	0.25	270

containing varying compositions of HOBP and BHBM. A plot of the embrittlement times against the mole fraction of BHBM shown in Fig 5.12 illustrates the outstanding photo-stabilisation with the lower molar ratios of BHBM.

The potency of the peroxidylitc activity of BHBM was further elaborated by the high percentage synergism it exhibited in the presence of HOBP as shown by Table 5.8. The order of synergism was 230%.

A first-order plot of HOBP decay showed a further reduction in the rate of HOBP destruction (Fig 5.14) suggesting that the peroxide-decomposing activity had stabilised HOBP even more than the simple hindered phenol. The rate constant listed in Table 5.9 ranged from 0.8×10^{-4} to 3.7×10^{-4} h^{-1}.

5.4 Synergistic Activity of HOBP and AOS-C12

A similar pattern of activity to that of the HOBP-BHBM system was demonstrated by the HOBP-AOS-C12 synergistic combination which again contained the three functionalities of uv screener, free radical terminator and peroxide decomposer. Fig 5.15 shows the similar trend of the initial pro-oxidation

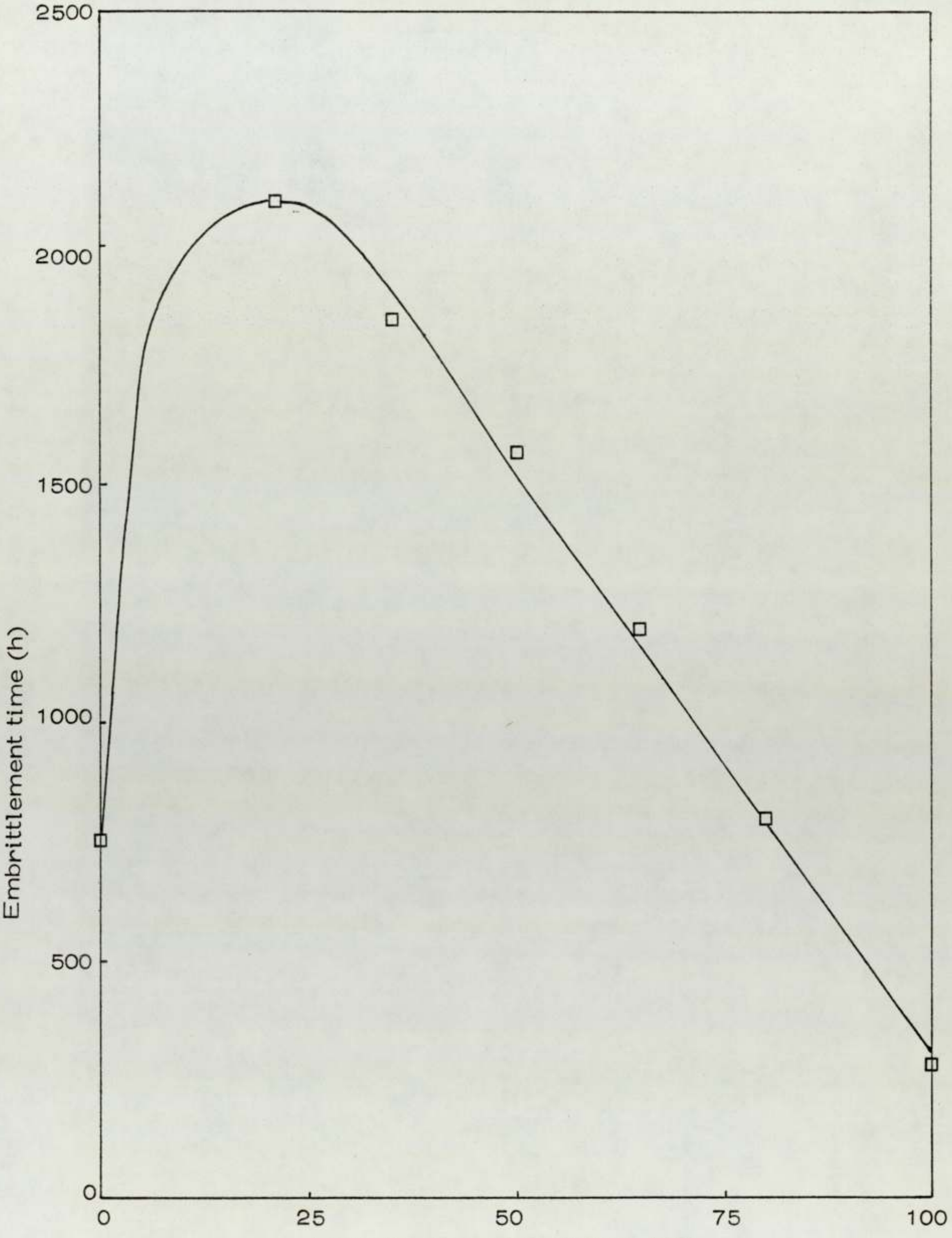


Fig 5.12 Synergism between HOBP and BHBM in the photo-stabilisation of polypropylene films (total concentration 10^{-3} mole/100 g)

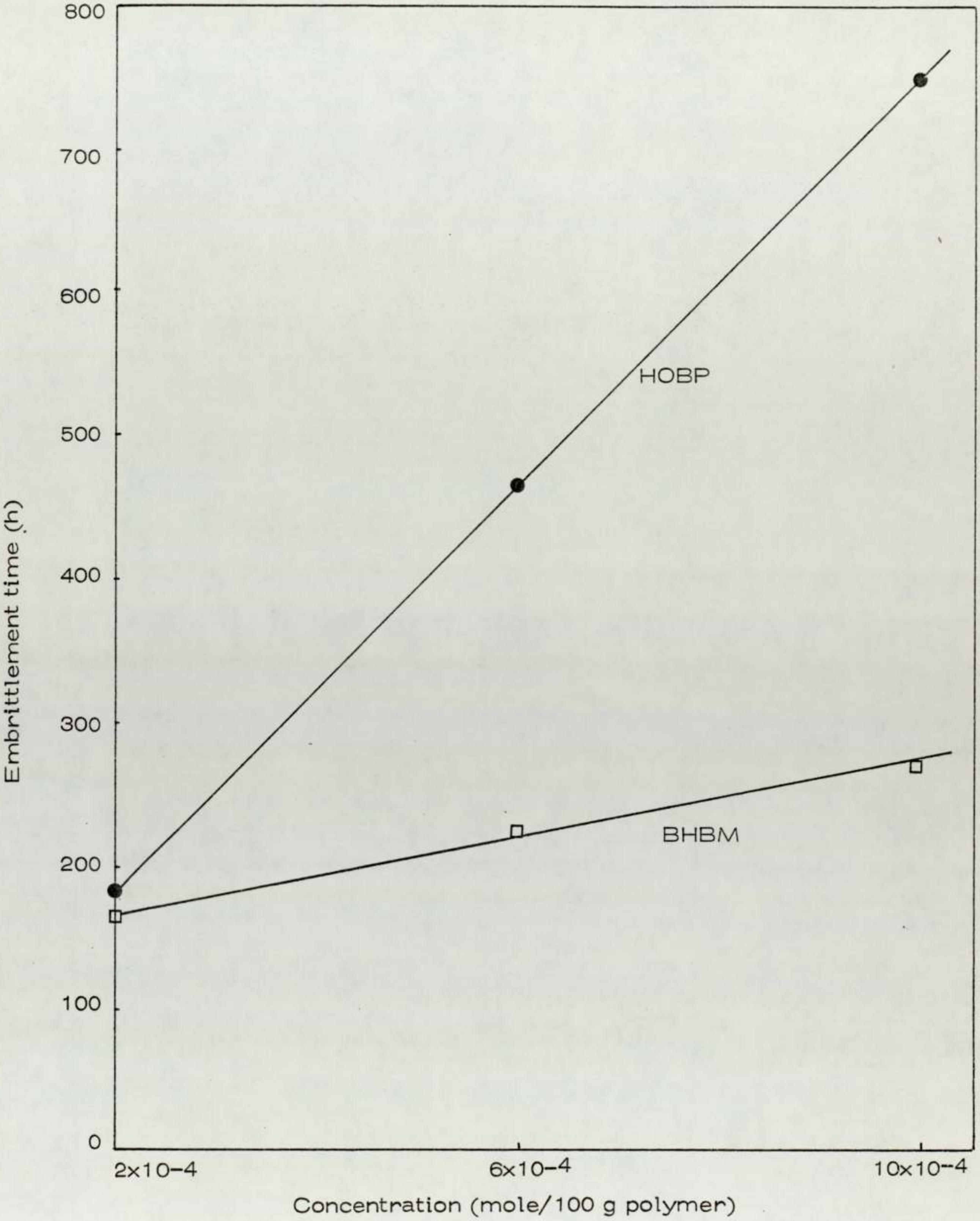


Fig 5.13 Calibration curve of embrittlement times against concentrations of HOBP and BHBM

Table 5.8 Synergistic activity of HOBP and BHBM at varying compositions in polypropylene films exposed to uv light

Total conc 10^{-3} mole/100 g		Time to embrittlement of individual component (h)	Time to embrittlement of the two-component system (h)	Calculated effect of synergist (h)	Percentage synergism
Mole % HOBP	Mole % BHBM				
100	0	750	-	-	-
80	20	604/160	2100	615	230
65	35	500/184	1850	534	232
50	50	388/204	1547	442	233
35	65	276/224	1240	350	232
20	80	180/244	830	274	176
0	100	270	-	-	-
Control		75	-	-	-

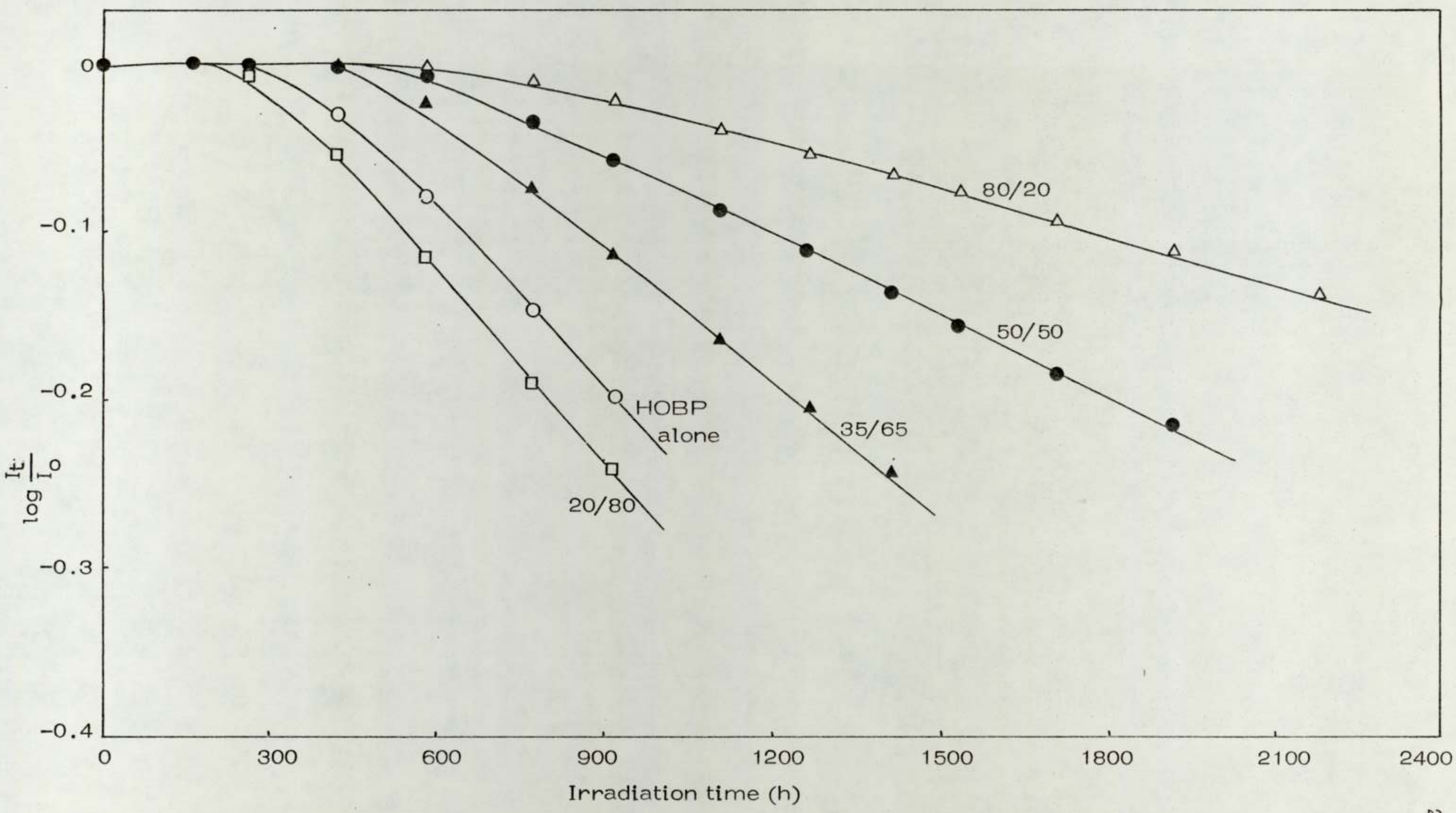


Fig 5.14 First order plot of HOBP decay during uv irradiation of polypropylene films containing varying compositions of HOBP and BHBM (numbers on curves refer to mole % ratio of HOBP and BHBM) **65**/35 curve was omitted for clarity

Table 5.9 First order rate constants of HOBP decay during uv irradiation of polypropylene films containing varying compositions of HOBP and BHBM

Total concentration 10^{-3} mole/100 g		Weight of additives/100 g		Rate constants k 10^4 h^{-1}
Mole % HOBP	Mole % BHBM	HOBP (g)	BHBM (g)	
100	0	0.32	0	3.8
80	20	0.26	0.05	0.8
65	35	0.21	0.09	1.1
50	50	0.16	0.13	1.6
35	65	0.11	0.16	2.9
20	80	0.06	0.20	3.7

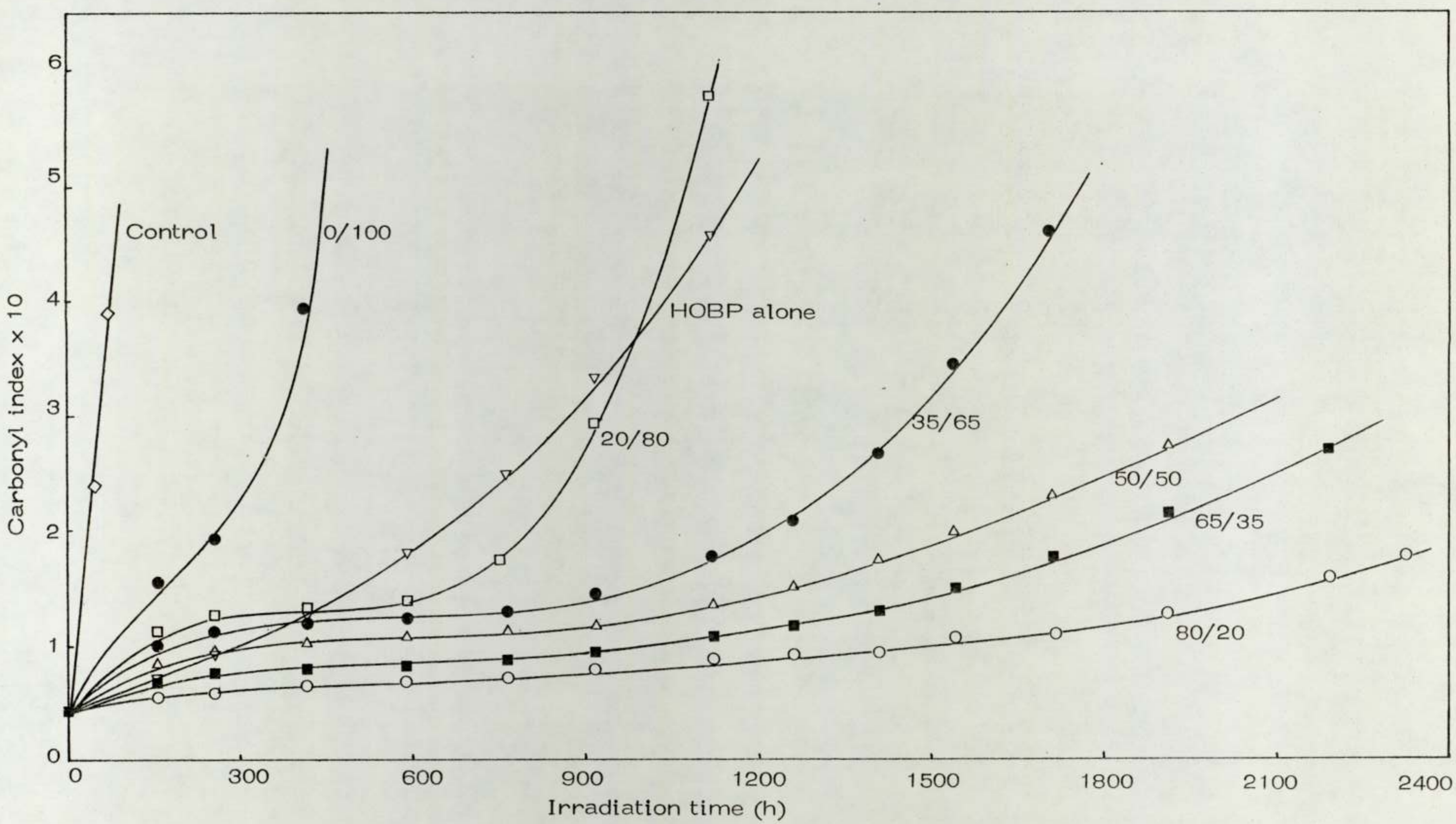


Fig 5.15 Effect of varying the molar ratio of HOBP and AOS-C12 on the uv stabilisation of polypropylene films (total concentration 10^{-3} mole/100 g) Numbers on curves refer to mole % ratio of HOBP and AOS-C12

on uv irradiation whose severity and extent increased with increased AOS-C12 concentrations. The auto-retarding behaviour gives effective photo-stabilisation to the polymer films as evidenced by the subsequent marginal increment of the carbonyl index. Data of embrittlement times as shown in Table 5.10 gave similar levels of photo-stabilisation to the HOBP-BHBM system although the photo-stability was significantly better with the present system. This is probably attributable to the greater compatibility imparted by AOS-C12 relative to that of BHBM since earlier studies described in Chapter 3 showed AOS-C12 to be the more compatible additive in polypropylene. A plot of embrittlement times against mole fractions of AOS-C12 as shown in Fig 5.16 gave a similar shape to that illustrated by the HOBP-BHBM system.

This was further emphasised by the appreciable improvement in the % synergism data exhibited by the present system (Table 5.11) showing synergism of 250% compared with HOBP-BHBM at 230%.

The first order plot of HOBP destruction (Fig 5.18) in the presence of AOS-C12 was in accord with the systems better uv stabilising performance and possessed a rate constant of 0.8×10^{-4} h^{-1}

Table 5.10 Embrittlement times of polypropylene films containing varying compositions of HOBP and AOS-Cl2 on exposure to uv light

Total concentration 10^{-3} mole/100 g		Weight of additives/100 g		Embrittlement time, h
mole% HOBP	mole % AOS-C12	HOBP (g)	AOS-C12 (g)	
100	0	0.32	–	750
80	20	0.26	0.08	2350
65	35	0.21	0.15	1935
50	50	0.16	0.21	1600
35	65	0.11	0.27	1260
20	80	0.06	0.34	840
0	100	–	0.42	

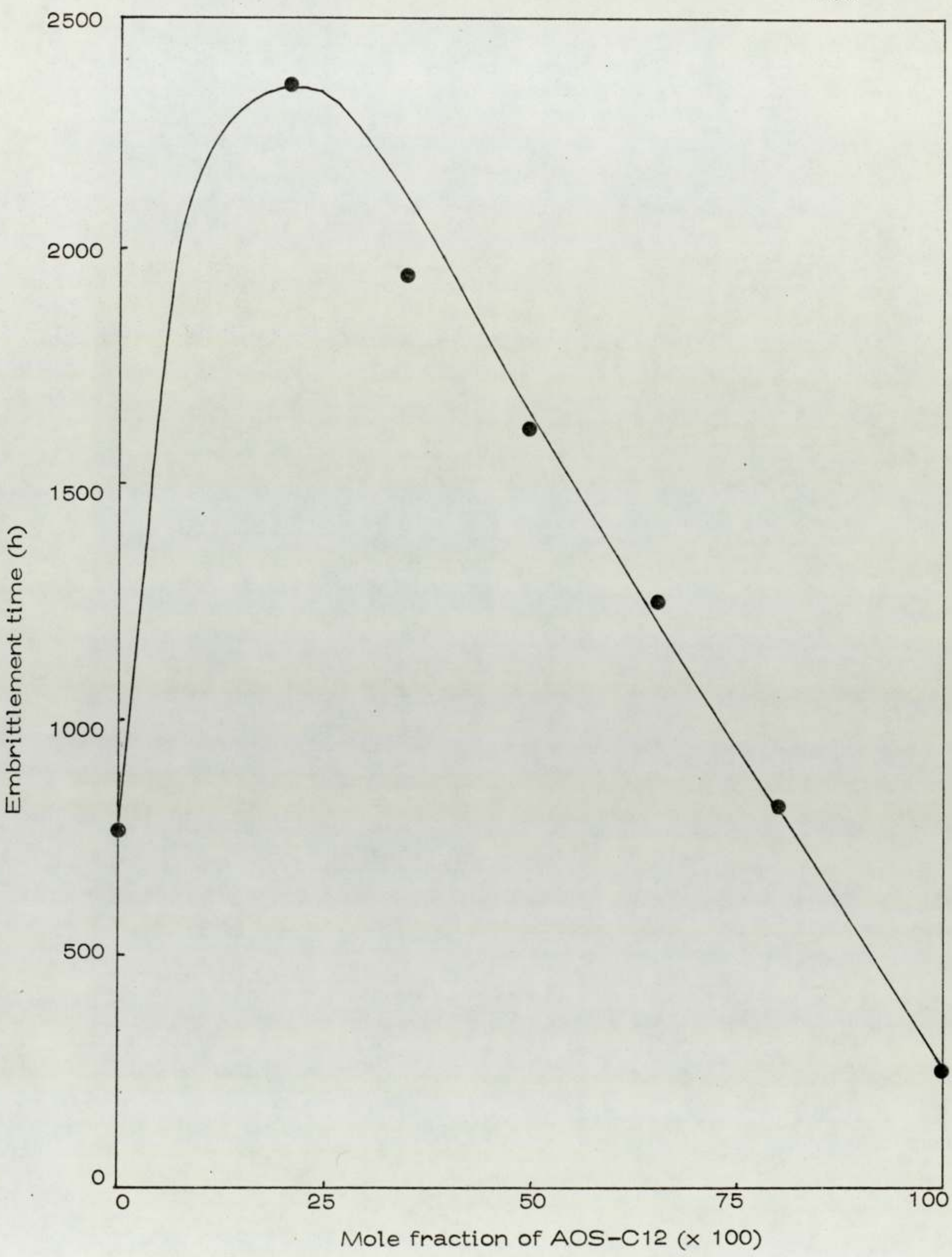


Fig 5.16 Synergism between HOBP and AOS-C12 in the photo-stabilisation of polypropylene films (total concentration 10^{-3} mole/100 g)

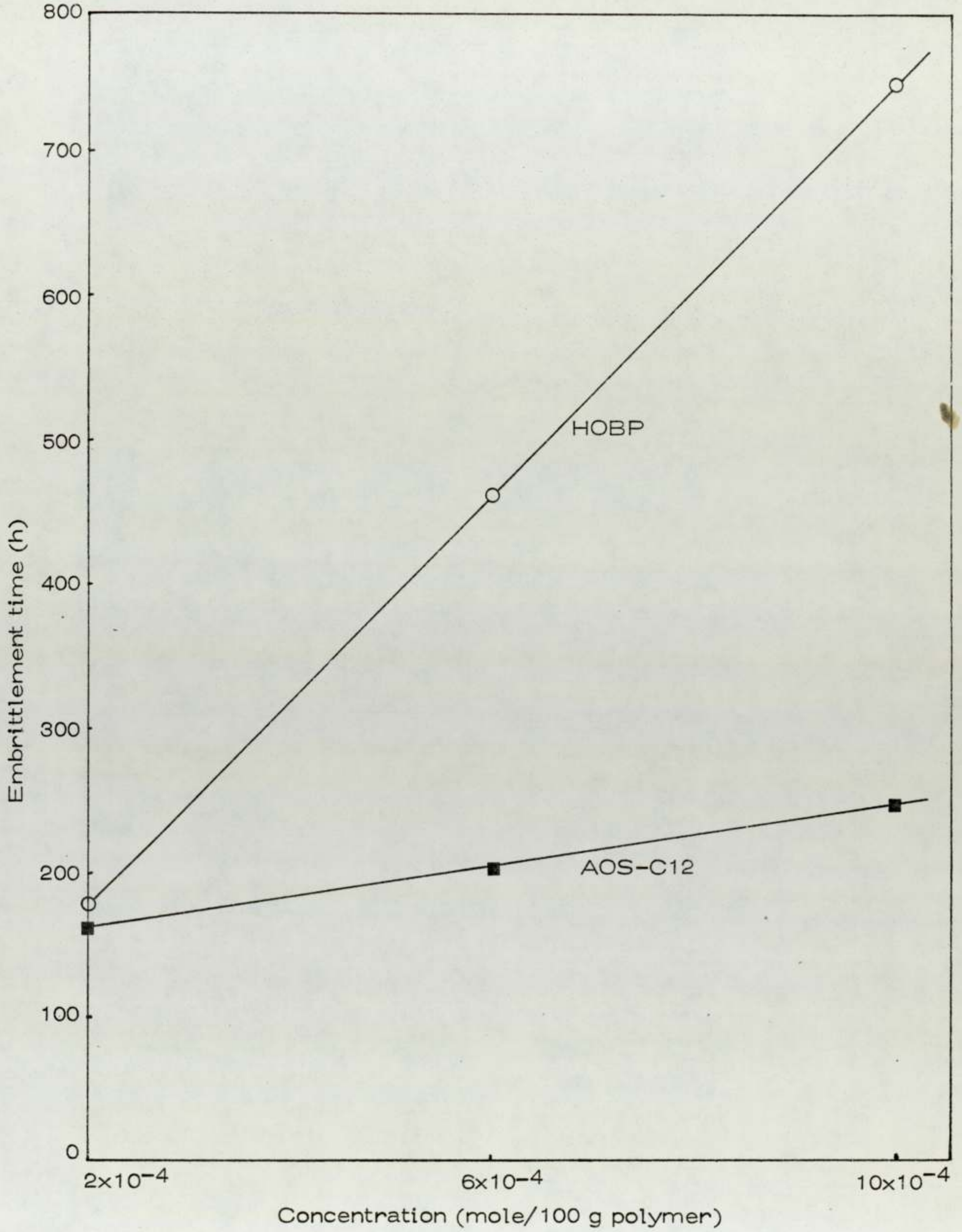


Fig 5.17 Calibration curvesof embrittlement times against concentrations of HOBP and AOS-C12

Table 5.11 Synergistic activity of HOBP and AOS-C12 at varying compositions in polypropylene films exposed to uv light

Total conc 10^{-3} mole/100 g		Time to embrittlement of individual component (h)	Time to embrittlement of the two-component system (h)	Calculated effect of synergism (h)	Percentage synergism
Mole % HOBP	Mole % AOS-C12				
100	0	750	–	–	–
80	20	604/165	2350	254	267
65	35	500/180	1935	338	250
50	50	358/196	1600	434	251
35	65	276/212	1260	530	250
20	80	180/224	840	620	201
0	100	250	–	–	–

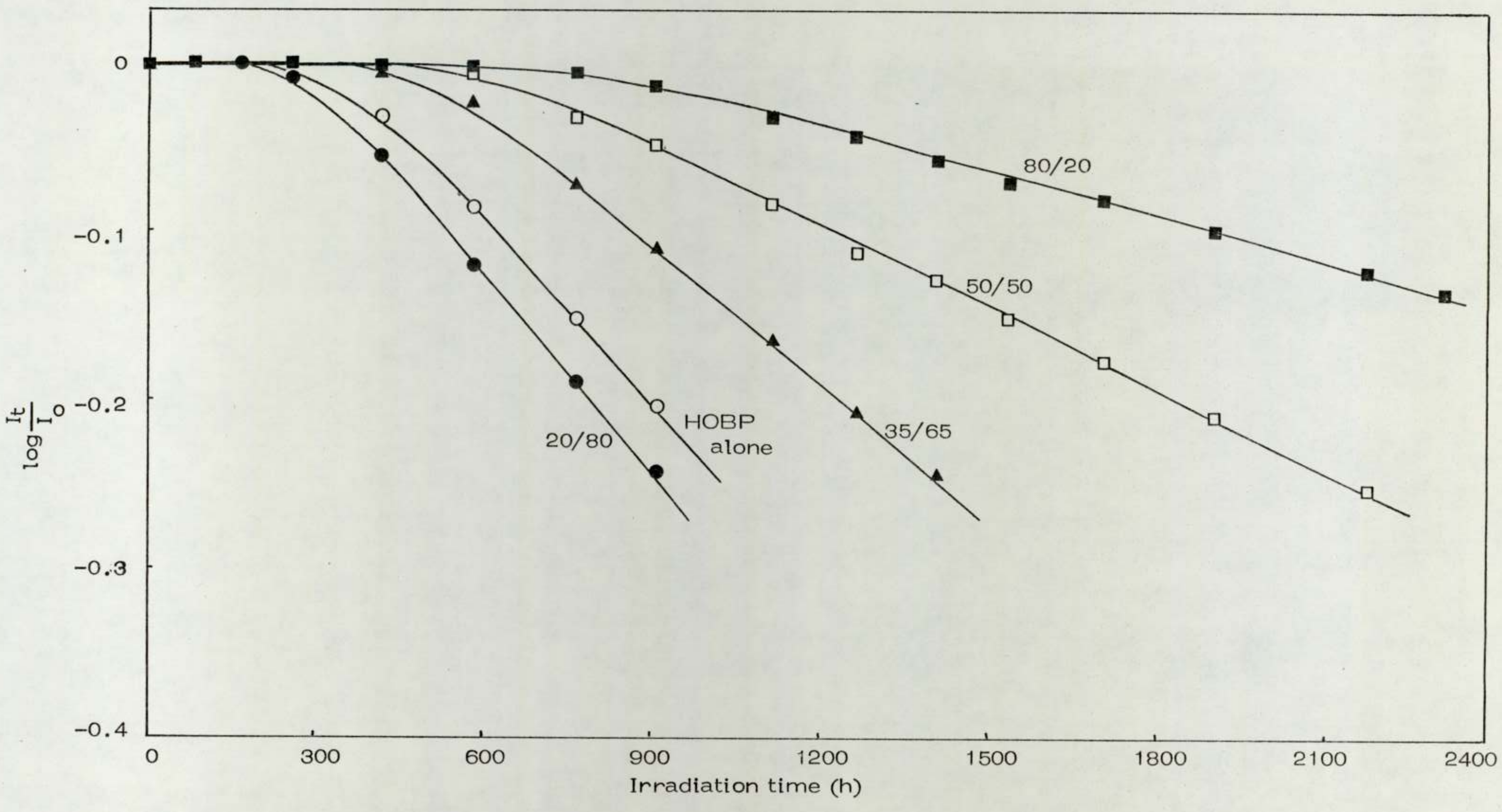


Fig 5.18 First order plot of HOBP decay during uv irradiation of polypropylene films containing varying compositions of HOBP and AOS-C12 (Numbers on curves refer to mole % ratio of HOBP and AOS-C12)

for the 80/20 HOBP to AOS-C12 mole % ratio (Table 5.12).

5.5 An Overview and Discussion

Fig 5.19 shows the comparative performance of the four synergistic systems at 0.2 mole fraction of the antioxidant. It was apparent that in the presence of HOBP, BHBM and AOS-C12 exhibited similar levels of photostabilisation although the latter appeared to be significantly more effective than BHBM. This might be due, in a large measure, to the greater compatibility of AOS-C12 with the polymer and the positive influence of the lower volatility of AOS-C12 could not be ruled out.

The outstanding uv stabilisation observed in the HOBP-BHBM and HOBP-AOS-C12 systems was primarily attributable to the catalytic peroxidolytic activity of the sulphur moiety since comparison with the HOBP-1076 system, for instance, showed the relative ineffectiveness of the non-sulphur antioxidant. The HOBP-TBC system exhibited a much lower photo-stability as evidenced by the greater rate of carbonyl formation after 1200 h uv irradiation. The reason for its diminished photo-stabilisation might be due to the formation of photo-active species within the polymer matrix which resulted in the production of free radicals.

Table 5.12 First-order rate constants of HOBP decay during uv irradiation of polypropylene films containing varying compositions of HOBP and AOS-C12

Total concentration 10^{-3} mole/100 g		Weight of additives/100 g		Rate constants k 10^4 h^{-1}
Mole % HOBP	Mole % AOS-C12	HOBP (g)	AOS-C12 (g)	
100	0	0.32	0	3.8
80	20	0.26	0.08	0.8
65	35	0.21	0.15	1.1
50	50	0.16	0.21	1.5
35	65	0.11	0.27	2.8
20	80	0.06	0.34	3.5

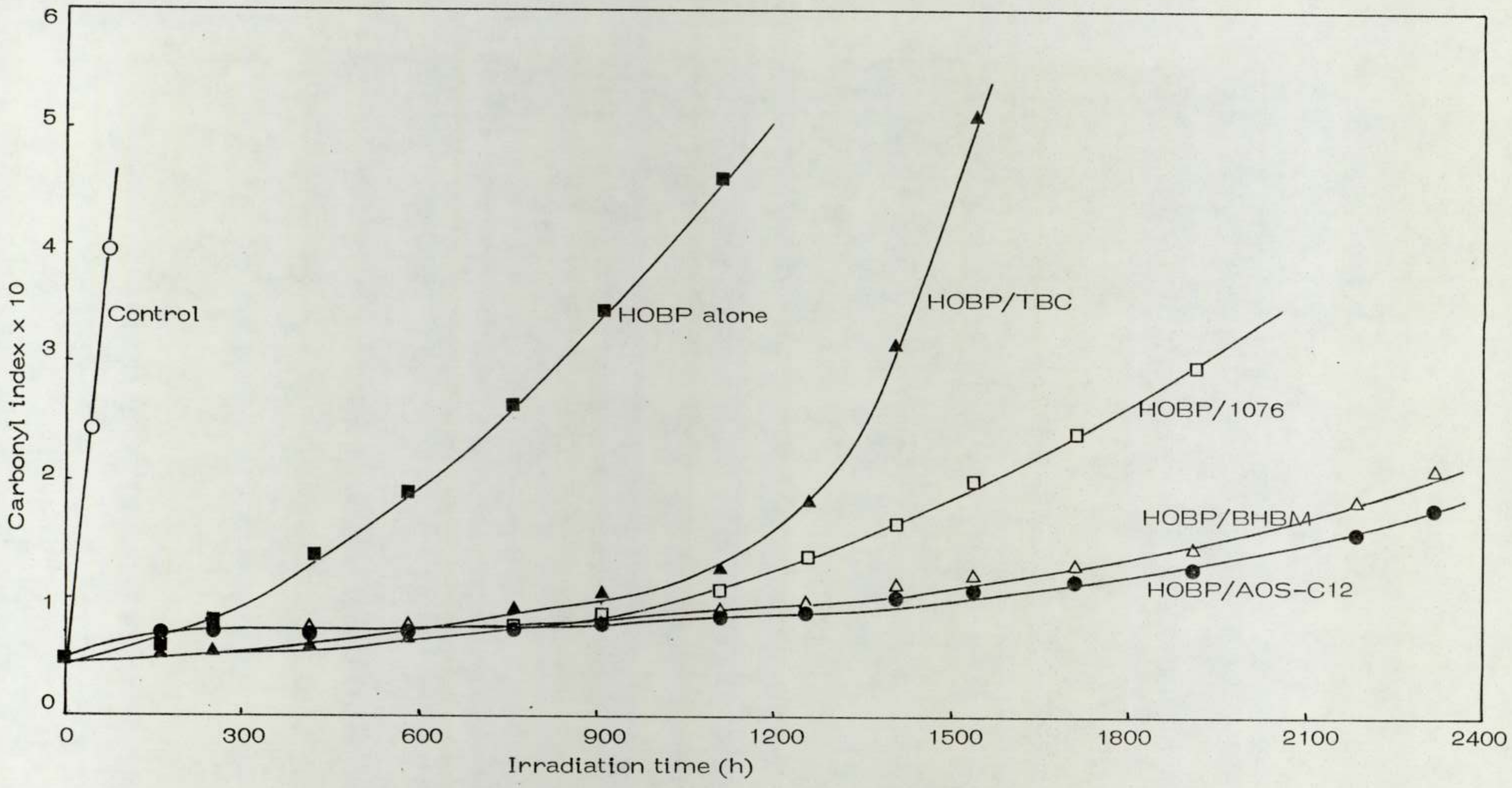
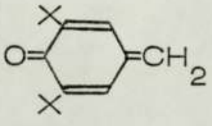
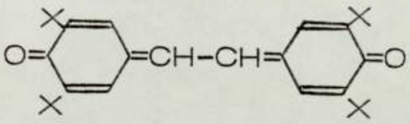


Fig 5.19 Comparative photo-stability of polypropylene films containing 0.2 mole fraction of antioxidants (total concentration 10^{-3} mole/100 g)

It is a well recognised fact(8) that TBC, on uv irradiation, underwent oxidative reactions which brought about the formation of powerful photo-activators such as quinone methide (I) and as its dimeric product, stilbenequinone (II).



(I)



(II)

The formation of the above molecular species was presumably less facile in the case of 1076 due to their lower reactivity at the para position as shown earlier in thermal oxidation studies of decalin (Chapter 3). The influence of antioxidant volatility could not be ruled out even though its role was expected to be insignificant in this instance.

A similar uv stabilisation trend was shown by the other HOBP antioxidant compositions as typified by the 50/50 mole % ratio shown in Fig 5.20.

The summarised tabulation of the uv embrittlement times of the synergistic systems shown in Table 5.13 further emphasises the

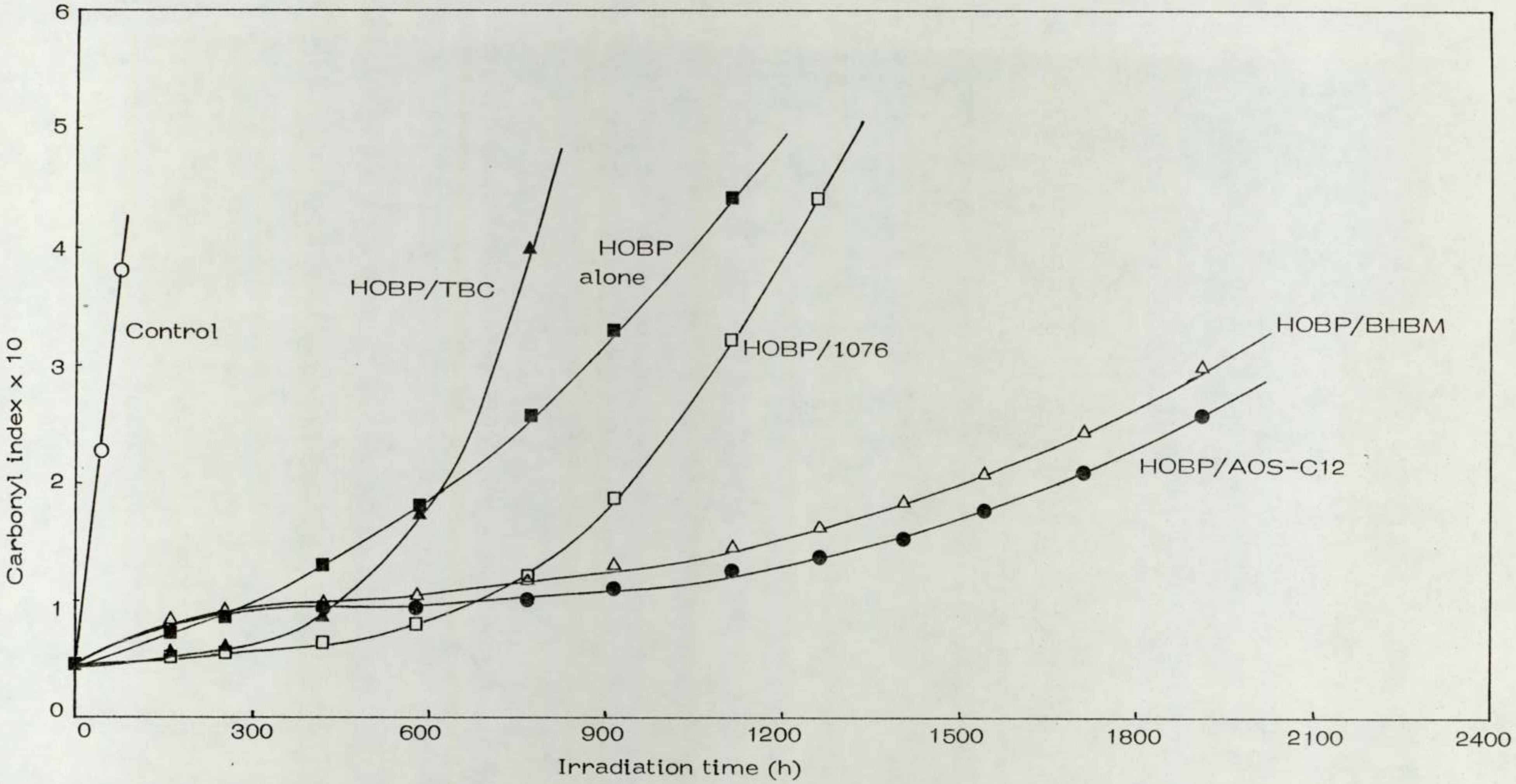


Fig 5.20 Comparative photo-stability of polypropylene films containing 0.5 mole fraction of antioxidants (total concentration 10^{-3} mole/100 g)

Table 5.13 Comparison of uv embrittlement times in hours of polypropylene films containing different synergistic systems at varying compositions (total conc 10^{-3} mole/100 g)

Synergistic system / Mole % ratio of HOBP to antioxidant	HOBP/TBC	HOBP/1076	HOBP/BHBM	HOBP/AOS-C12
80/20	1420	1590	2100	2350
65/35	1170	1350	1850	1935
50/50	910	1115	1547	1600
35/65	680	890	1240	1260
20/80	500	705	830	840

significantly superior performance of AOS-C12 in relation to BHBM and the reduced performance of TBC compared to 1076. This was further elicited by Fig 5.21 whereby plots of embrittlement times against mole fractions of the antioxidant show the above-mentioned trend.

The percentage synergism exhibited by the four synergistic systems was also compared as shown in Table 5.14 indicating the outstanding contribution made by the peroxide decomposing activity in bringing about synergism. A significantly higher synergistic activity was shown by the AOS-C12 system relative to that of the BHBM, which seemed to be attributable to the higher compatibility and lower volatility of the AOS-C12 in the polymer matrix. Varying the compositions of the components in both systems did not appear to appreciably affect the synergistic effect except for the 0.8 mole fraction of antioxidant. It was not known why this was so but it does suggest the operation of a similar non-screening mechanism in all cases.

A similar trend of behaviour but with lower % synergism was also shown by the 1076 which indicated that the peroxide decomposing activity was not alone responsible for the essentially similar % synergism level. The TBC system however

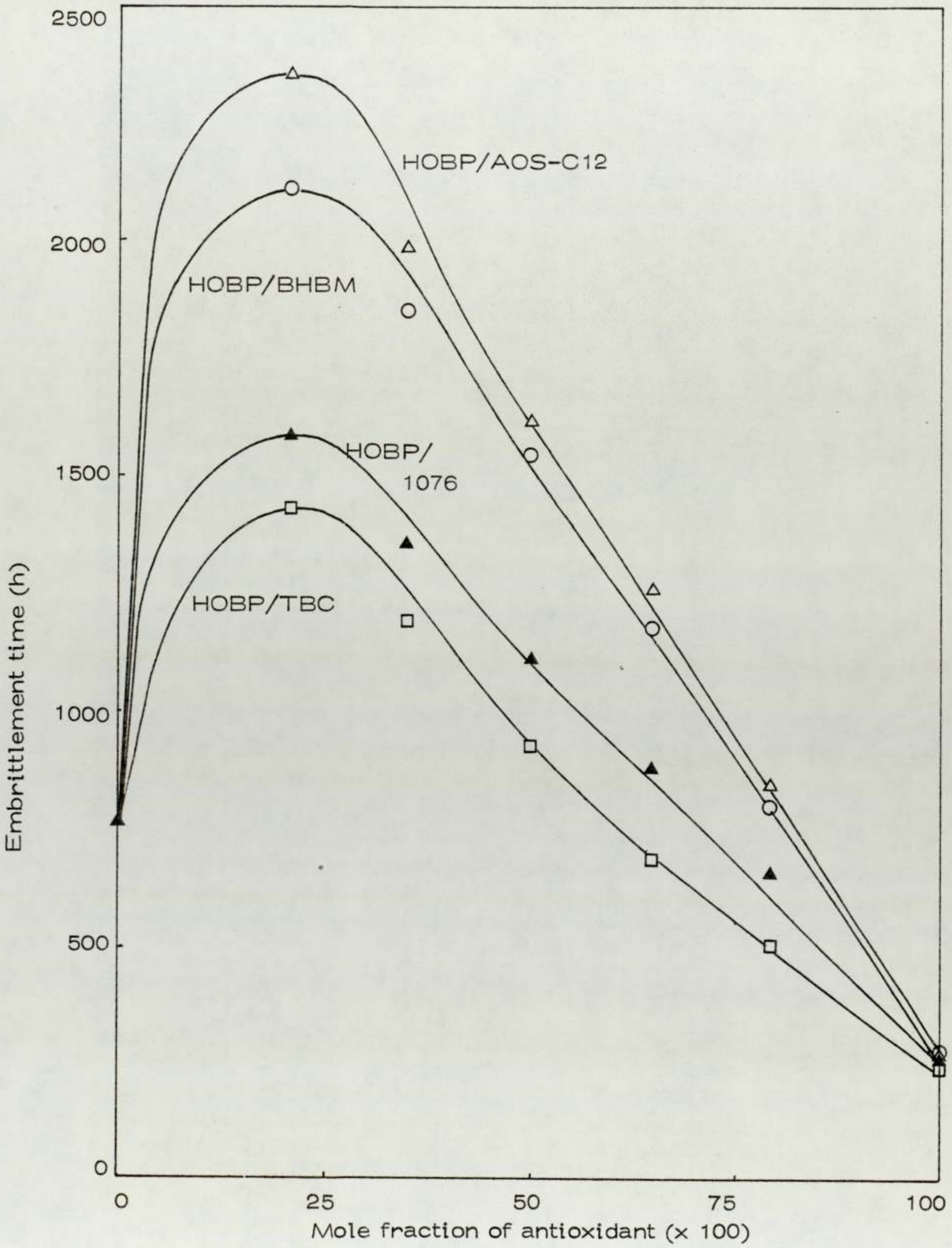


Fig 5.21 Comparison of the synergism between HOBP and the phenolic antioxidants in the photo-stabilisation of polypropylene films (total concentration 10^{-3} mole/100 g)

Table 5.14 Comparison of the synergistic activity of HOBP and the phenolic antioxidants at varying compositions in polypropylene films exposed to uv light (total conc 10^{-3} mole/100 g)

Synergistic system / mole % ratio of HOBP to antioxidant	HOBP/TBC	HOBP/1076	HOBP/BHBM	HOBP/AOS-C12
80/20	123%	139	230	267
65/35	115	132	232	250
50/50	102	129	233	251
35/65	90	127	232	250
20/80	78	127	176	201

showed decreasing % synergism with increasing mole fraction of the antioxidant. It was mentioned earlier that the inferior performance of the TBC system was thought to be due to the generation of powerful photo-activators and that these species could destroy the HOBP and hence the screening activity.

To test this possibility, a comparison of the rate constants of HOBP decay in different synergistic systems on uv irradiation was carried out. Table 5.15 illustrates that lower rates of HOBP destruction were observed in the presence of the peroxide decomposing antioxidants than in the presence of 1076 and TBC. The latter exhibited marked increase in rates with increasing mole fraction of the antioxidant. This might indicate that the increasing concentration of the photo-activators participated in some way in destroying the HOBP possibly through sacrificial quenching.

Chakraborty and Scott(142b) recently concluded that the main limitations of HOBP as a uv stabiliser was not in its intrinsic instability to photolysis but its instability to hydroperoxides and carbonyl compounds under photo-oxidative conditions. The data presented in Table 5.15 appear to be in agreement with the conclusion since BHBM and AOS-C12 diminished the rate

Table 5.15 Comparison of the first-order rate constants of HOBP decay during uv irradiation of polypropylene films containing varying compositions of HOBP and antioxidants (total conc 10^{-3} mole/100 g, rate constants, k 10^4 h^{-1})

Synergistic system / Mole % ratio of HOBP to antioxidant	HOBP/TBC	HOBP/1076	HOBP/BHBM	HOBP/AOS-C12
80/20	1.3	1.1	0.8	0.8
65/35	1.7	1.4	1.1	1.1
50/50	2.3	1.8	1.6	1.5
35/65	7.1	4.1	2.9	2.8
20/80	8.3	6.0	3.7	3.5

Rate constant of HOBP alone, 3.8×10^{-4} h^{-1}

of HOBP destruction due to the peroxide decomposing activity of the additives.

CHAPTER SIX

REACTIONS OF TBC AND BHBM WITH POLYPROPYLENE

The purpose of the present study was to investigate the interactions between selected antioxidants (viz TBC and BHBM) and polypropylene in the melt subjected to differing processing treatments. The motivation of the work was based on the recent findings of Kularatne and Scott(188a, 193) that TBC and BHBM could be bound to natural and synthetic latices (NR and NBR) with the aid of tertiarybutyl hydroperoxide. While TBC binds via the radical-radical coupling mechanism, BHBM undergoes saturation of the rubber double bonds through the thiyl radicals.

Based on these results, it was therefore decided to generate different levels of polymeric hydroperoxide concentrations in polypropylene followed by incorporation of 2% antioxidants, in order to study the consequent effect of the antioxidant-hydroperoxide-polymer interactions in conferring thermal stability to the polymer, both before and after solvent extraction. The primary reason for the solvent extraction was to remove the non-bound antioxidants and their derived products so that the extent of the polymer binding reactions of the antioxidants, if any, could be assessed. The latter part of the chapter will investigate the uv-initiated grafting of BHBM to polypropylene film.

6.1 Interactions of TBC with Polypropylene Melt During Processing Operations

In order to generate varying amounts of hydroperoxide in polypropylene, a method of open-chamber processing in the RAPRA torque rheometer was adopted(7,35). In all cases, 20 g of the unstabilised polymer (Propathene HF 18/CV 70) was used which was processed for varying periods of time at 180°C. A plot of the hydroperoxide concentration against the processing times as illustrated in Fig 6.1 shows the strong dependence of hydroperoxide formation with the (open chamber) processing times notably after 15 mins of the severe processing treatment. The unprocessed sample showed an undetectably low level of hydroperoxide content by the adopted method of determination (as described in Chapter 2) whose lowest threshold measurement was found to be 10^{-5} mol/g polymer.

The interaction of TBC and the polymer melt was studied by

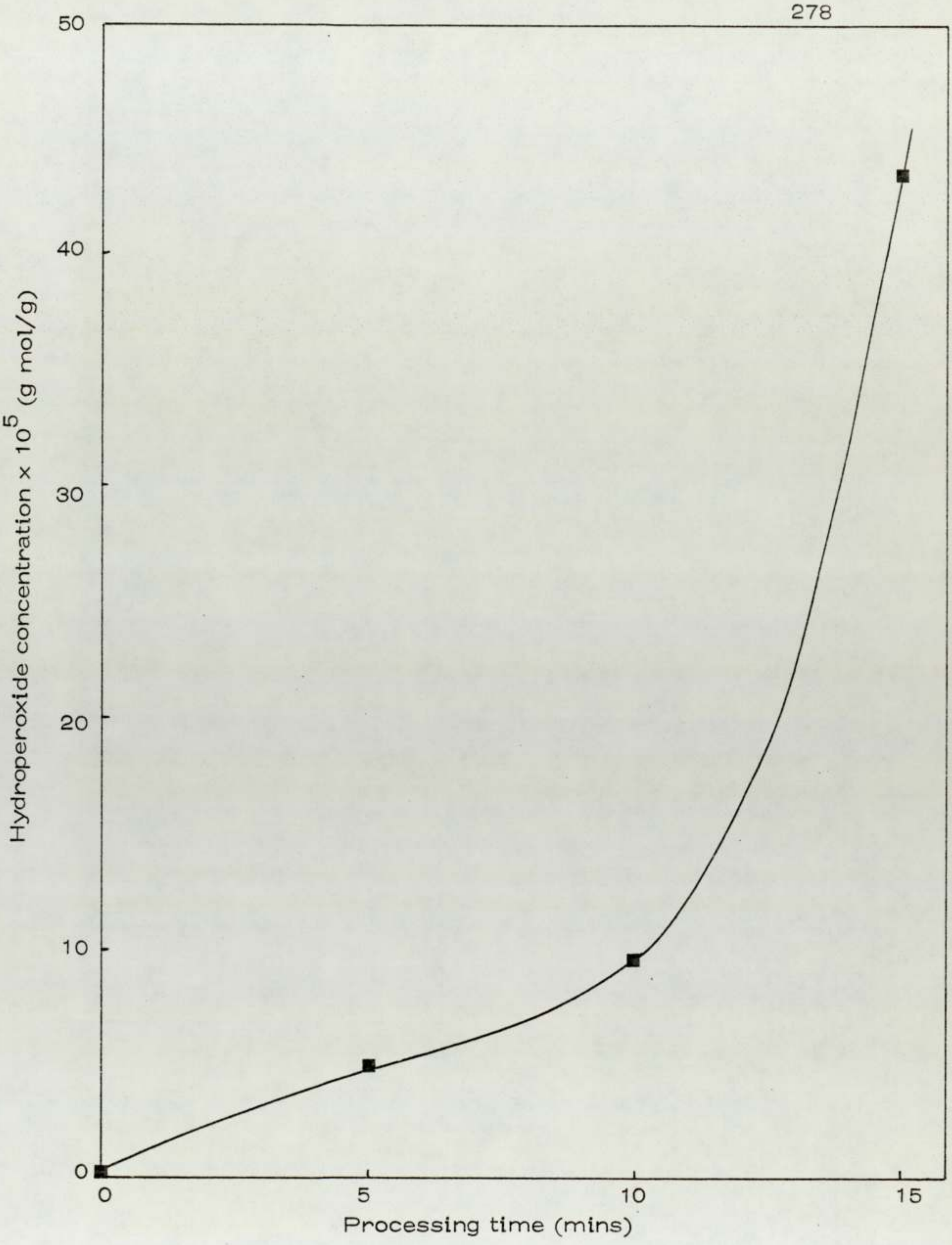


Fig 6.1 Dependence of polymeric hydroperoxide formation on the (open chamber) processing times (temp 180oC)

the incorporation of ca 2% (8 × 10^{-3} mole TBC/100 g) of the additive into the processed pre-oxidised samples (by differing processing periods) and continuing processing them for an additional three mins for the antioxidants to uniformly mix and interact with the polymer melt. The samples were subsequently taken out and quickly chilled in water to arrest further thermal oxidation. The polymer films were then prepared via the normal compression moulding technique.

Fig 6.2 shows the varying thermal stability of the polymer films before extraction after being subjected to differing initial pre-oxidation treatments and subsequent incorporation of 2% TBC. It forceably demonstrates a trend that, despite the extensive polymer oxidation suffered through prolonged pre-oxidation as evidenced by increasing carbonyl content, increasing the pre-oxidation time with the concomittant increase in hydroperoxide concentration, brought about greater thermal stability in the polymer. In addition, it was observed that the intensity of yellowish discolouration (see experimental section 2.1.16) of the processed polymer films containing the antioxidant increased with greater pre-oxidation time as shown in Fig 6.3. It was therefore presumed that the yellow compounds were derived from the antioxidants and might in some way be

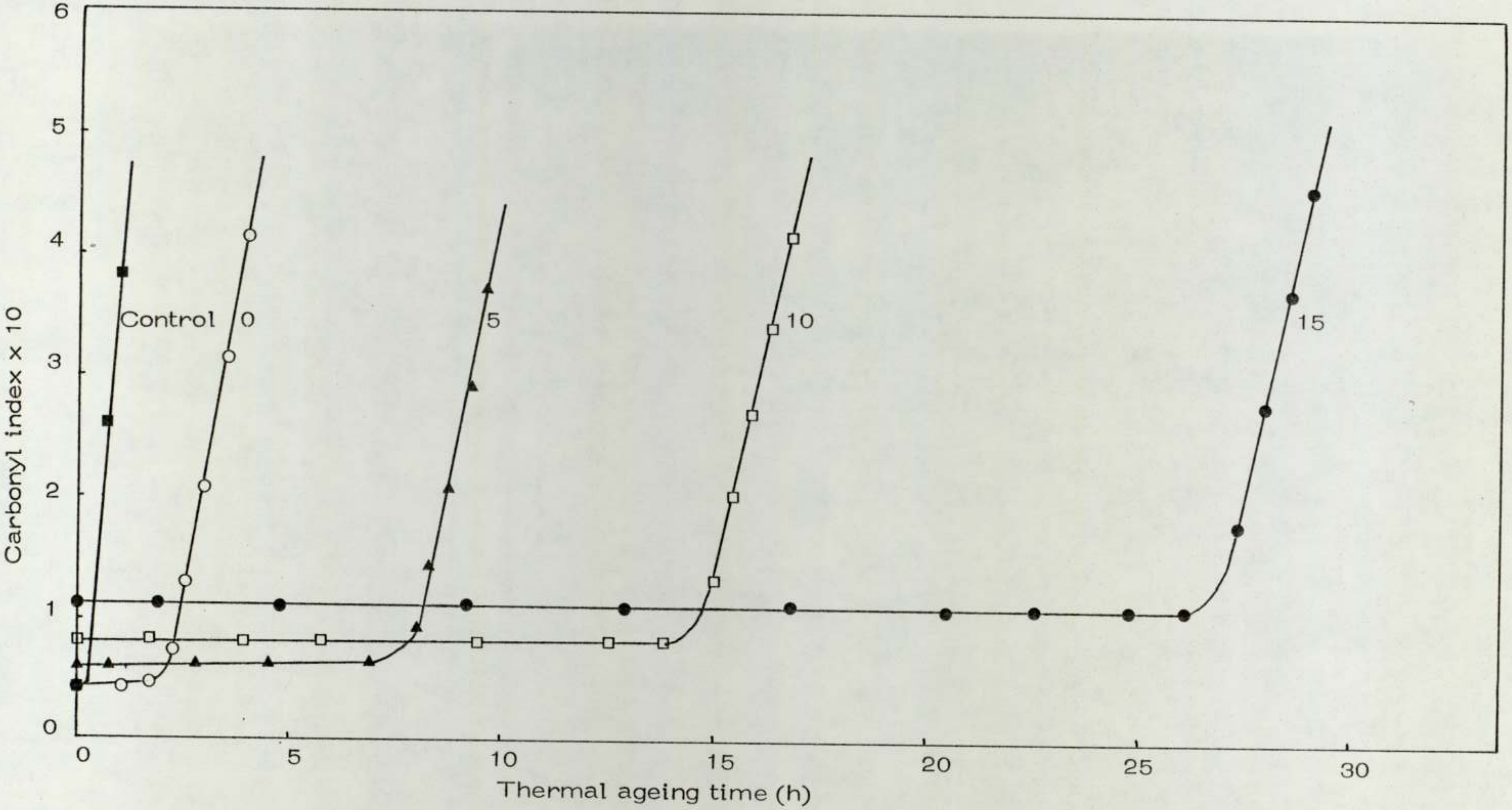


Fig 6.2 Variation in thermal stability of polypropylene films (at 140°C) after subjecting to differing pre-oxidation treatment and subsequent incorporation of ca 2% TBC (numbers on curves refer to pre-oxidation time in mins)

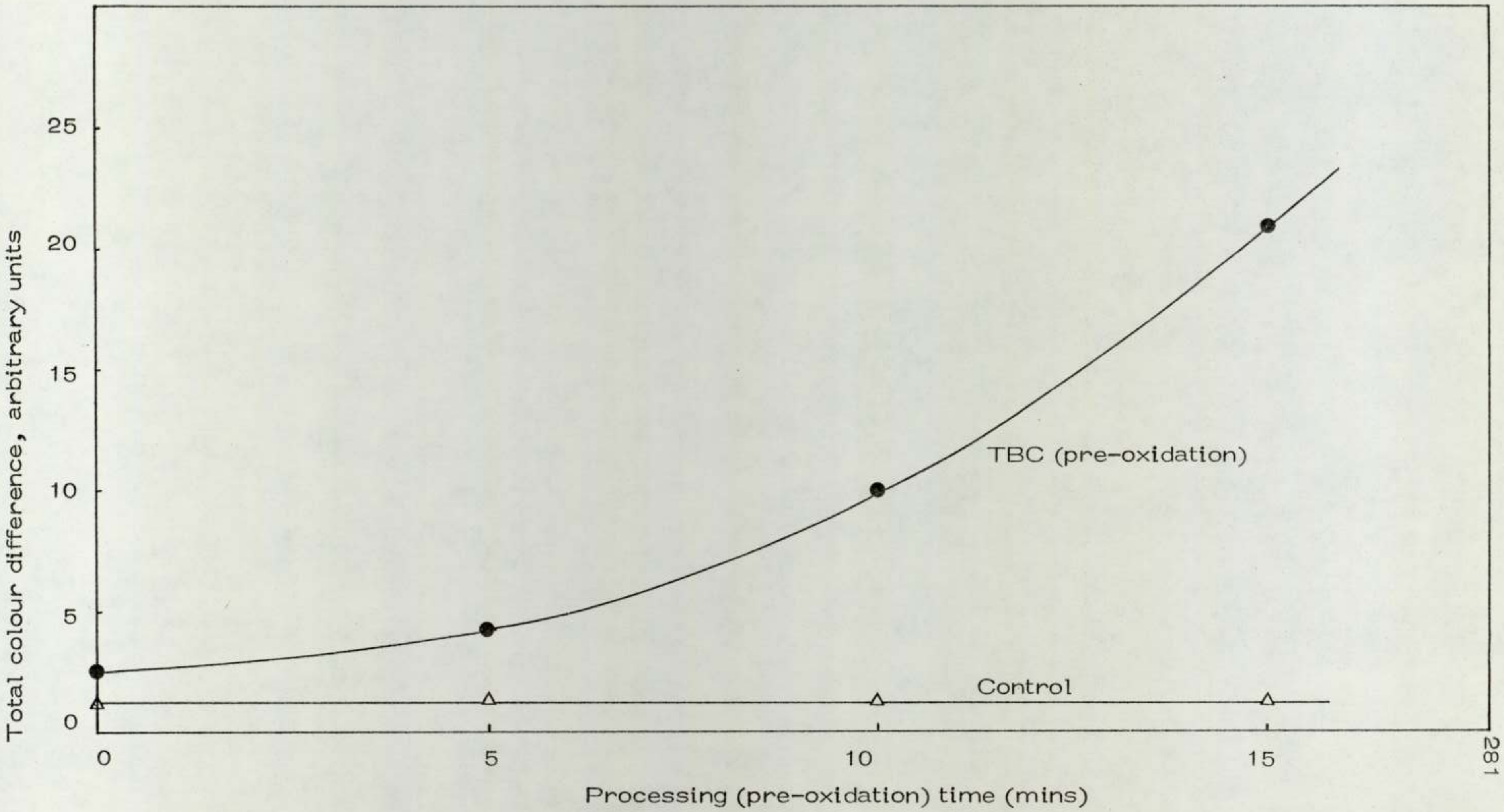


Fig 6.3 Colour formation of polypropylene films containing 2% TBC subjected to varying initial pre-oxidation treatments

responsible for the greater thermal stability of the polymer. It was observed that the end of the induction period coincided with the disappearance of the yellow colour as illustrated in Fig 6.3/ii. To further substantiate this rationale, the films were initially solvent extracted before evaluation of the thermal stability were made. Fig 6.4 compares the behaviour of the unextracted and extracted films on thermal ageing at 140°C as typified by the 15-minute pre-oxidised sample. The vast reduction in thermal stability and the disappearance of the yellow discolouration after the extraction process point to the fact that the yellowish antioxidant derivatives were primarily responsible for the thermal oxidative stability of the polymer. The unprocessed polymer containing 2% TBC showed inferior performance even before extraction suggesting that polymeric hydroperoxides were needed to produce the yellowish antioxidant derivatives.

Fig 6.5 further illustrates the variation in thermal stability of the polymer films with increasing pre-oxidation times, both before and after solvent extraction. The fact that an appreciable stability was observed even after solvent extraction does suggest that part of the 2% TBC became bound to the polymer during the melt processing stage. Moreover, their essentially constant

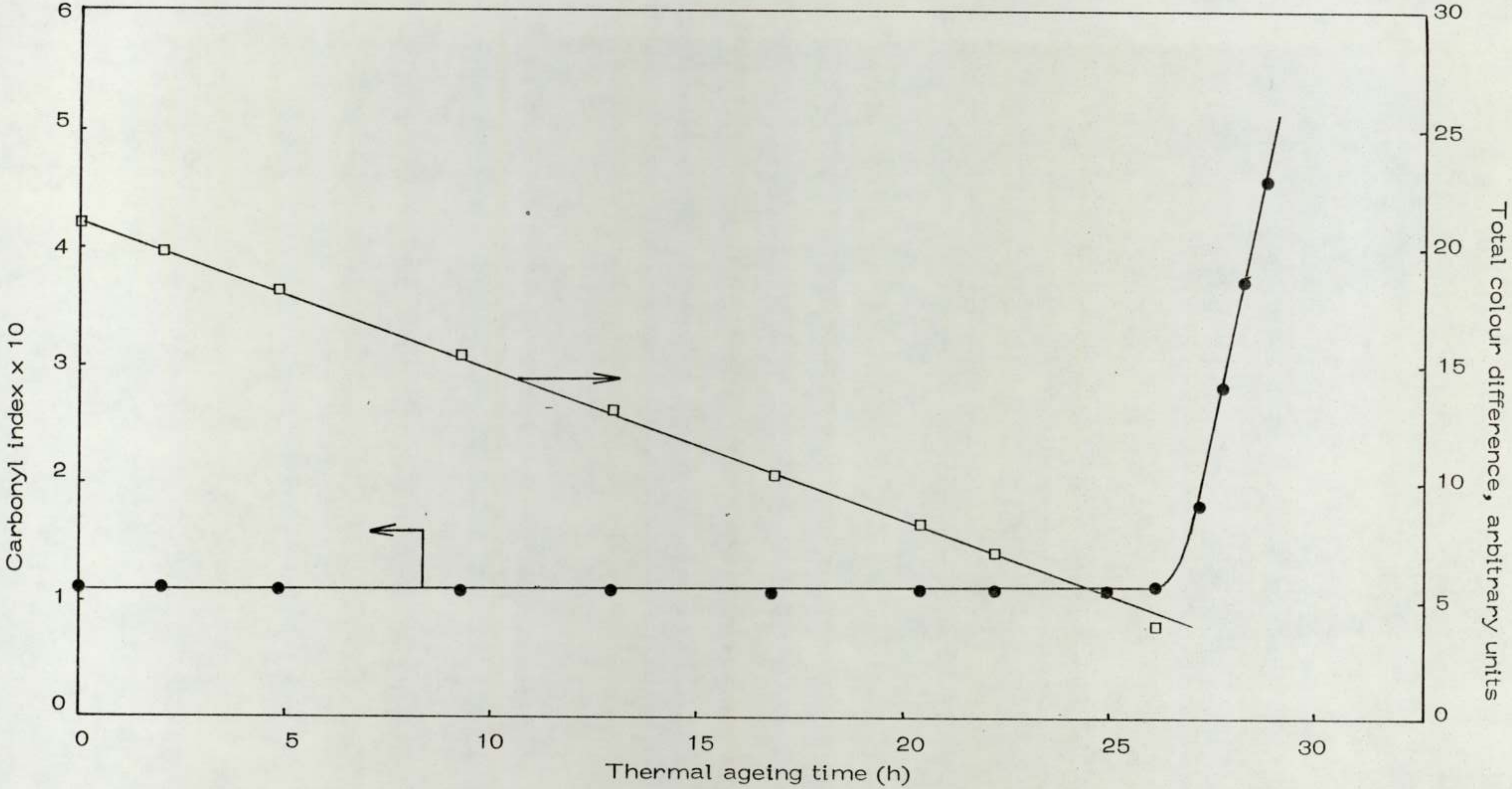


Fig 6.3ii Comparison of decay of colour intensity with thermal stability (at 140^{o}C) of the 15-minute pre-oxidised film

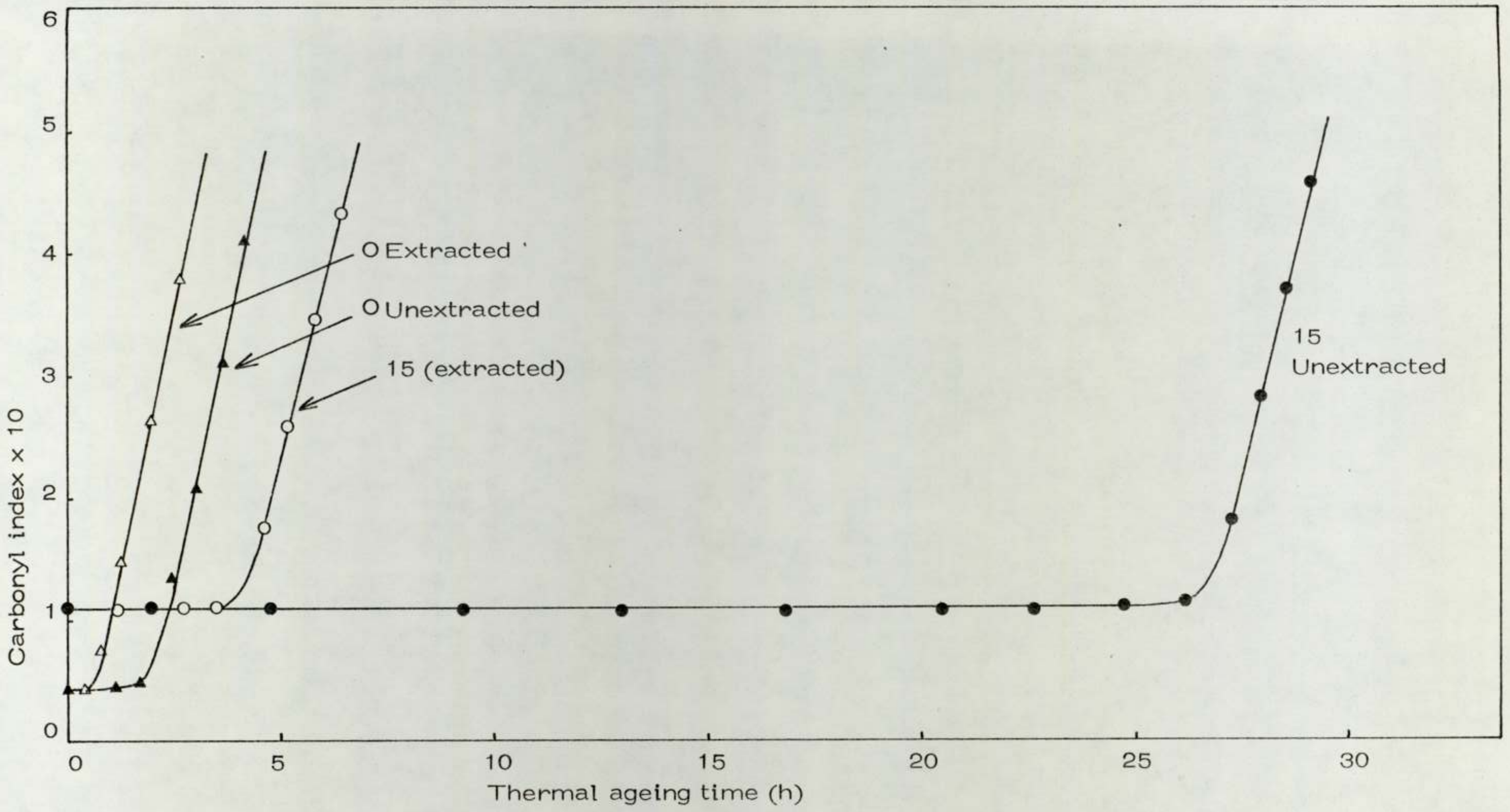


Fig 6.4 Comparison of thermal stability (at 140°C) of extracted and unextracted films containing 2% TBC (numbers on curves refer to pre-oxidation time in mins)

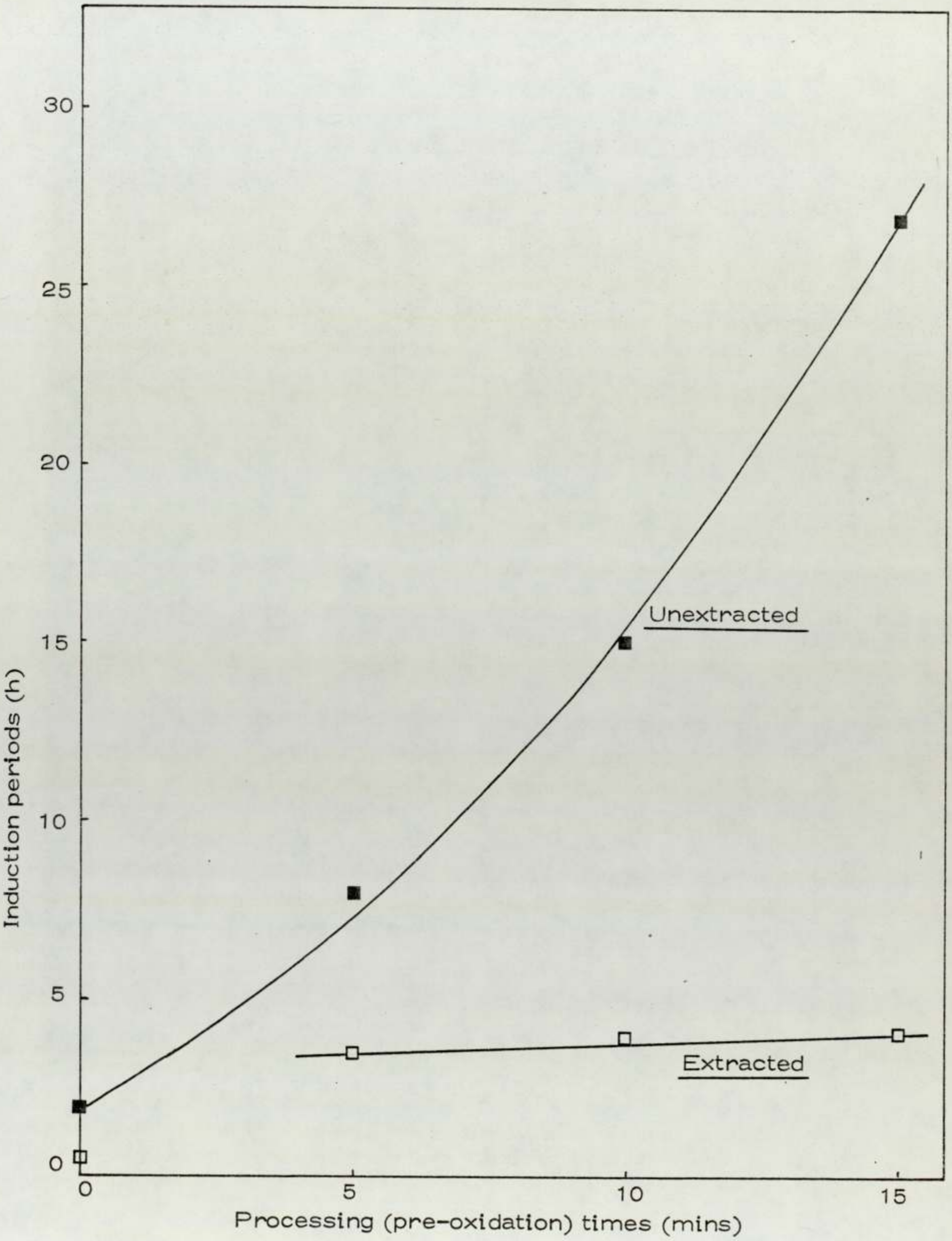


Fig 6.5 Comparison of thermal stability (at 140°C) of extracted and unextracted films containing 2% TBC with differing level of pre-oxidation treatments

induction periods with increasing extent of oxidation also does indicate the greater degree of binding reactions with the higher concentrations of hydroperoxide since the observed stabilisation of the extracted films could be a composite function of reduced stability due to extensive oxidation and increasing level of bound antioxidant. Table 6.1 summarises the thermal stability (at 140°C) of the polymer films subjected to varying levels of pre-oxidative treatments and both before and after solvent extractions.

In an attempt to minimise the influence of hydroperoxides on the antioxidant-polymer interactions, similar studies to the one already carried out were made but without the pre-oxidation treatment. 2% TBC was initially tumble-mixed with the unstabilised polymer powder which then underwent open chamber processing for varying periods of time. This type of processing method would be designated as 'normal processing' in contrast to the initial pre-oxidative treatment. It was expected that the presence of the antioxidant within the polymer melt would arrest the formation of hydroperoxide during the prolonged processing times.

Fig 6.6 again illustrates the superior thermal ageing property

Table 6.1 Thermal induction periods of polypropylene films at 140°C after subjecting to differing pre-oxidation treatments (and containing 2% TBC) both before and after extraction

Pre-oxidation time, mins	Induction periods (h)		
	Control	2% TBC	
		Before extraction	After extraction
0	0.5	2.0	0.5
5	0.3	8.2	3.5
10	0.1	15.0	4.0
15	-	27.0	4.0

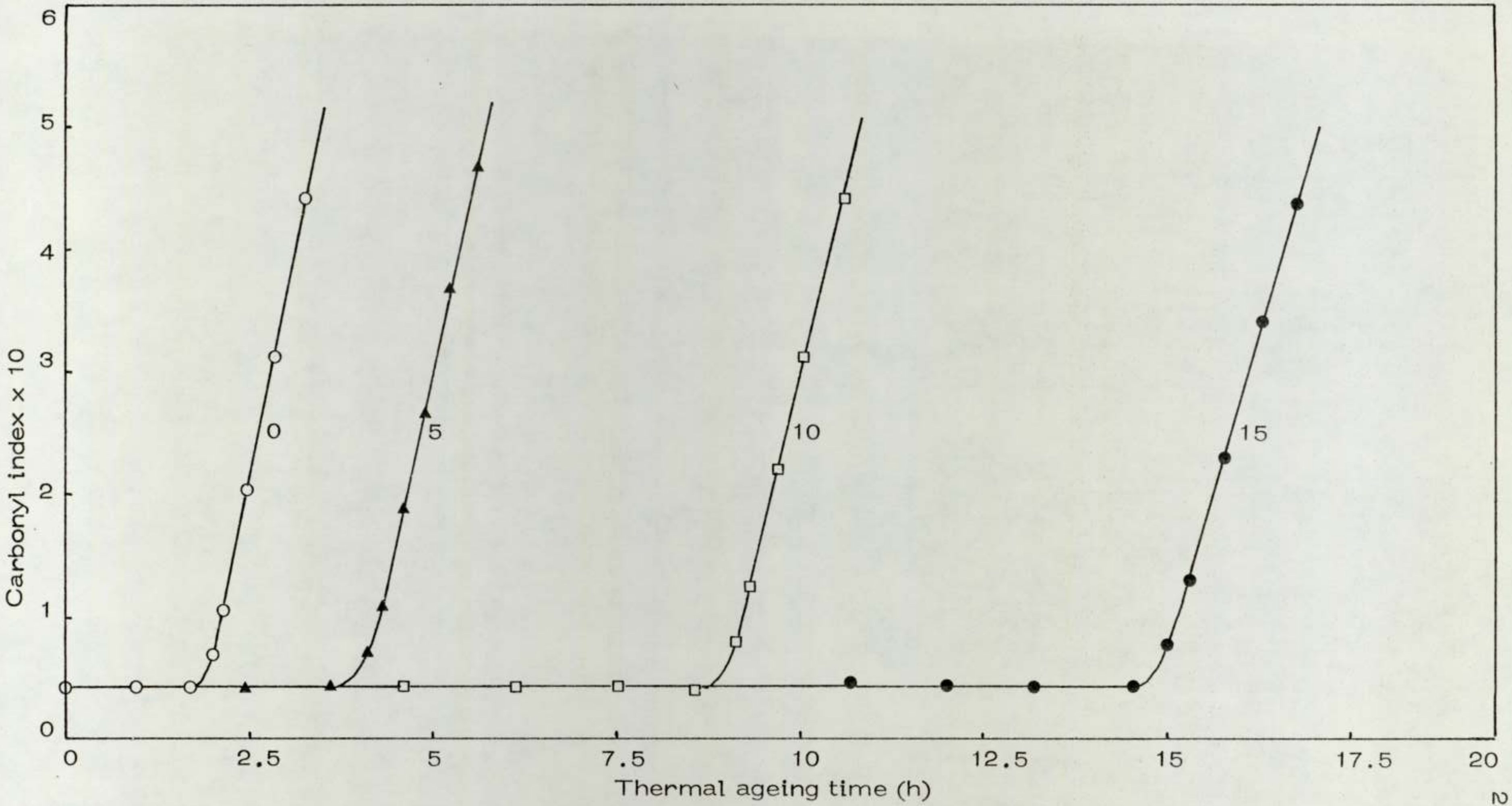


Fig 6.6 Variation in thermal stability (at 140°C) of polypropylene films containing 2% TBC with processing times (numbers on curves refer to processing times in mins)

of the polymer films with prolonged processing time. Moreover the essentially constant carbonyl index with processing time indicates the negligible extent of polymer breakdown. The intensity of the yellow discolouration was less marked in comparison to those which received pre-oxidation treatment. Even though the trend of increased stabilisation with processing time was similar to earlier studies, the absolute level of thermal stability was significantly different. While 15-minute pre-oxidation treatment (and containing 2% TBC) showed an induction period of 27 h, that of normal processing gave a value of 15 h. Hence despite the extensive polymer breakdown suffered by the 15-minute pre-oxidation, it still exhibited superior performance relative to that of 15-minute normal processing. This fact, coupled with the observation of higher colour intensity suggests that in the presence of polymeric hydroperoxides, the formation of the antioxidant derivatives is facilitated and their greater concentrations and presumably higher molecular weight are such as to outweigh the extensive initial oxidation suffered by the polymer. Under the normal processing conditions where the formation of hydroperoxides was curtailed, less of the antioxidant derivatives were formed so that subsequent thermal ageing resulted in most of the volatile TBC being physically lost causing the polymer to exhibit lower thermal stability.

On solvent extraction of the processed films, a marked reduction in thermal stability was observed as typified by the 15-minute processed sample shown in Fig 6.7. Similarly the unprocessed sample showed a decrease in stability. However, the fact that appreciable stabilisation was still evident even after extraction (see Fig 6.8) at all processing times does point to the minor but significant extent of polymer-binding reactions. Table 6.2 summarises and compares the thermal ageing behaviour of the polymer films which were subjected to pre-oxidation and normal processing treatments and after solvent extraction.

It was thought that further evidence of the antioxidant-polymer interaction phenomena might be provided by studying the variation of the antioxidant's phenolic hydroxyl infra-red spectral peak (3620 cm^{-1}) with the differing processing melt treatment. Fig 6.9 shows that while normal processing caused a general decrease of the phenolic OH due presumably to antioxidant loss by volatilisation and by its transformation to other products, that of the pre-oxidation treatment showed a more marked reduction. Therefore in the latter case, even though the antioxidant was subjected to a constant processing period of 3 mins, its greater loss of phenolic OH might be due to its transformation to the yellowish antioxidant derivatives.

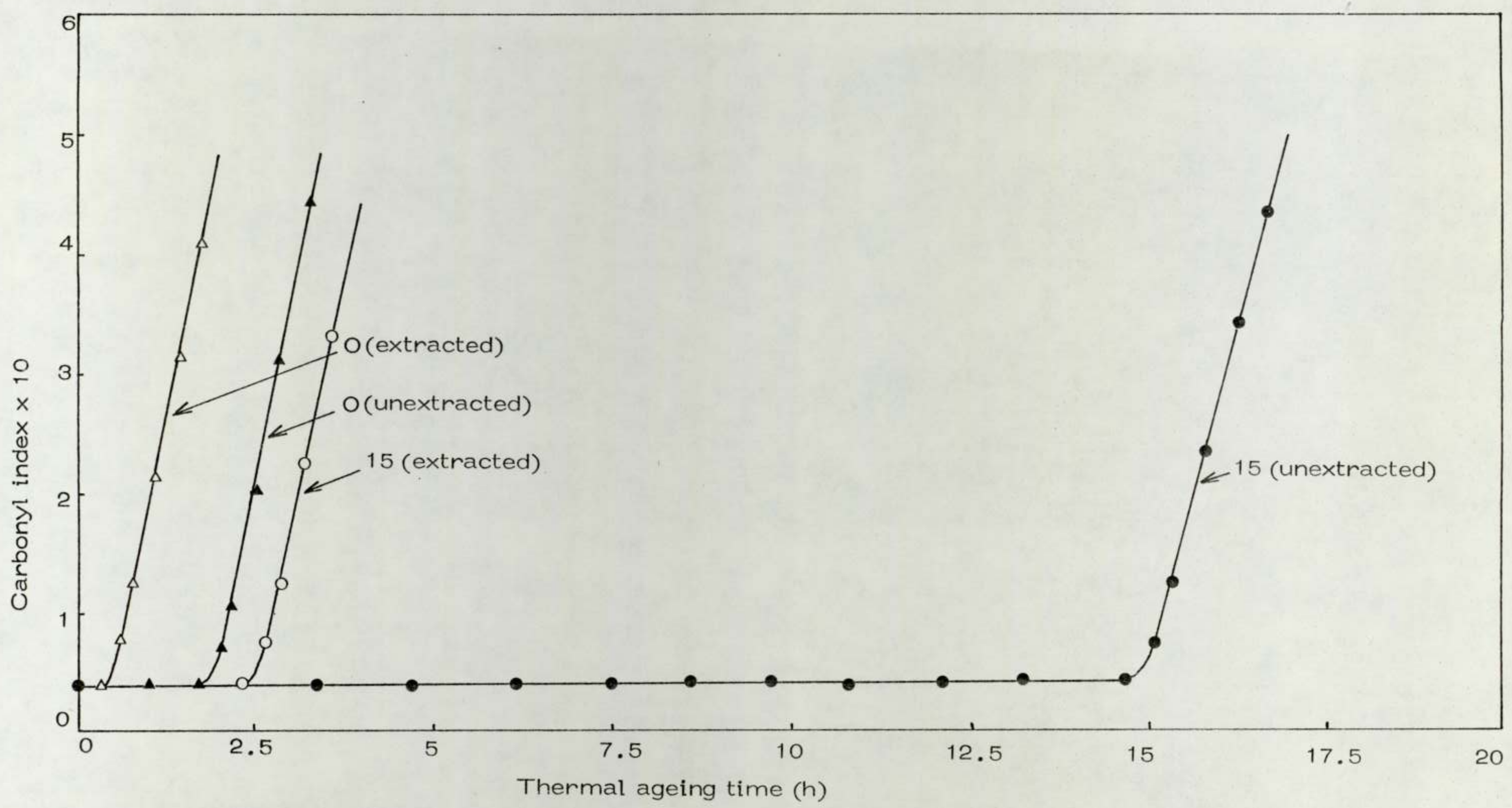


Fig 6.7 Comparison of thermal stability (at 140°C) of extracted and unextracted polypropylene films containing 2% TBC subjected to normal processing (numbers on curves refer to normal processing time in mins)

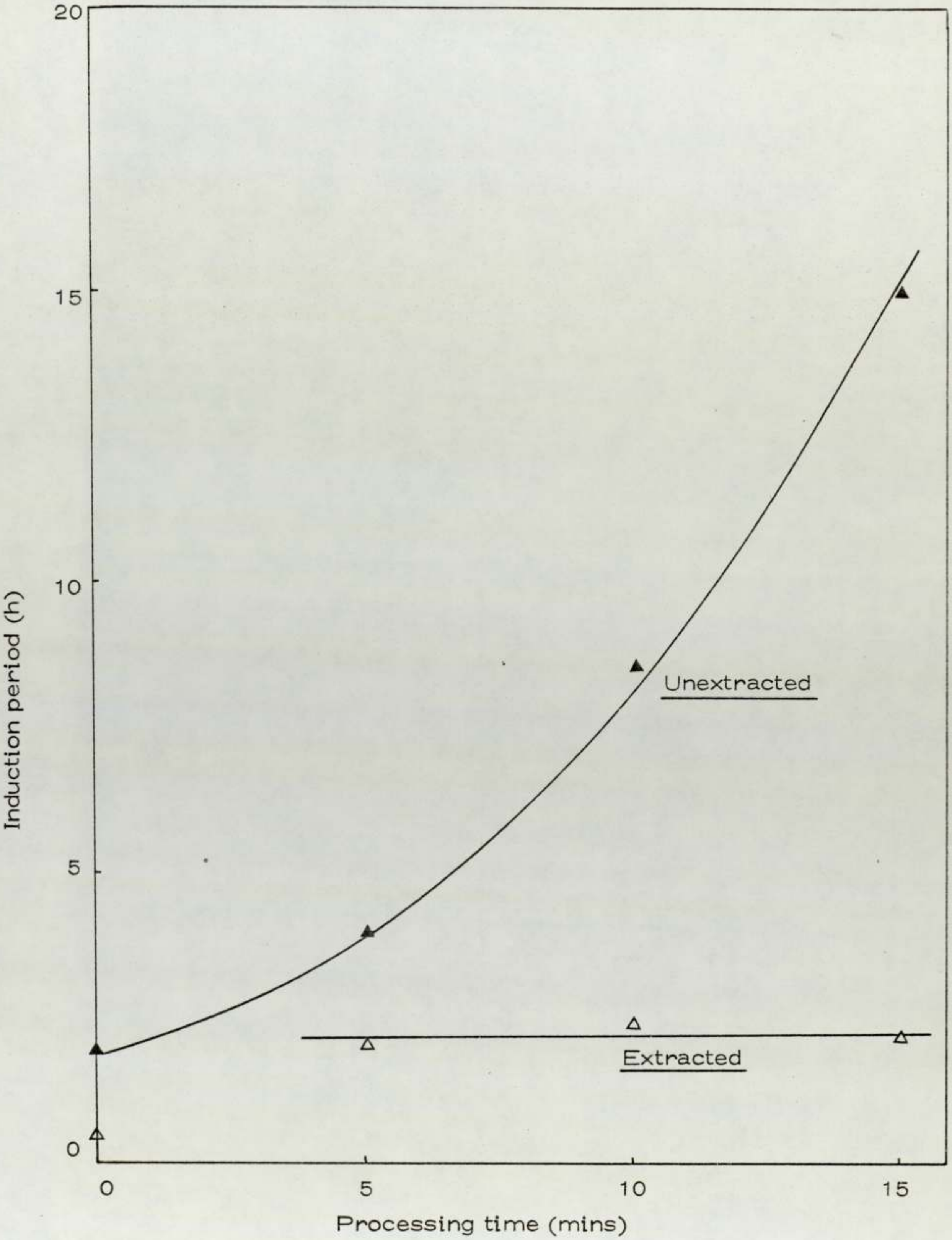


Fig 6.8 Comparison of thermal stability (at 140°C) of extracted and unextracted polypropylene films containing 2% TBC on normal processing time

Table 6.2 Comparisons of the thermal stability (at 140°C) of the polypropylene films containing 2% TBC subjected to differing melt treatments and solvent extractions

Processing time (mins)	Induction periods (h)				
	Control	Pre-oxidation (2% TBC)		Normal processing (2% TBC)	
		Before extraction	After extraction	Before extraction	After extraction
0	0.5	2.0	0.8	2.0	0.8
5	0.3	8.2	3.5	4.0	2.0
10	0.1	15.0	4.0	9.0	2.5
15	-	27.0	4.0	15.0	2.5

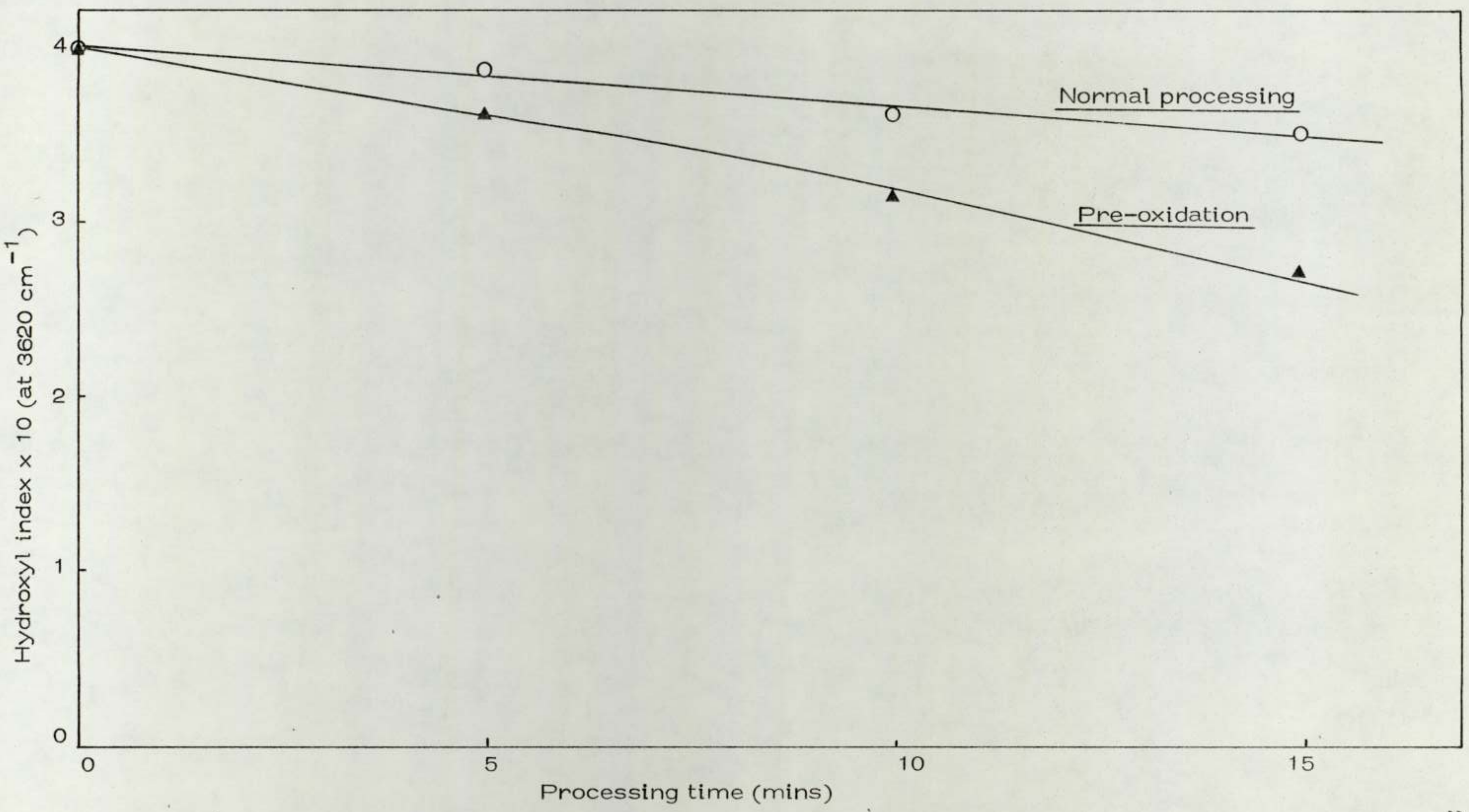


Fig 6.9 Loss of phenolic hydroxyl (at 3620 cm^{-1}) with processing time under pre-oxidation and normal processing treatments

Phenolic OH evaluations were also made when the resultant polymer films were subjected to the thermal ageing in the flowing (air) atmosphere at 140^{o}C. Fig 6.10 demonstrates the marked linear disappearance of the phenolic OH peak on thermal ageing of the polymer films in the flowing (air) atmosphere. For the unprocessed sample, virtually all of the TBC was lost after only six mins of the thermal test. The disappearance of the antioxidant was thought to be mainly due to its loss through the volatilisation process. However, in spite of the apparent absence of the antioxidant within the polymer, the carbonyl index did not increase until 2.0 h of the ageing test as already shown in Fig 6.2. The explanation for the stabilisation could be two fold; that during the compression moulding operation, TBC was transformed, to a significant extent, to higher molecular weight derivatives or that a minute amount of the 2% TBC became bound to the polymer. This will be investigated further in Section 6.3.

Another notable feature shown by Fig 6.10 is the close resemblance of the decay rate of the phenolic OH for the unprocessed, 15-minute pre-oxidised and the 15-minute normal processing samples. The implication of this is that the phenolic species involved must be similar and predominantly

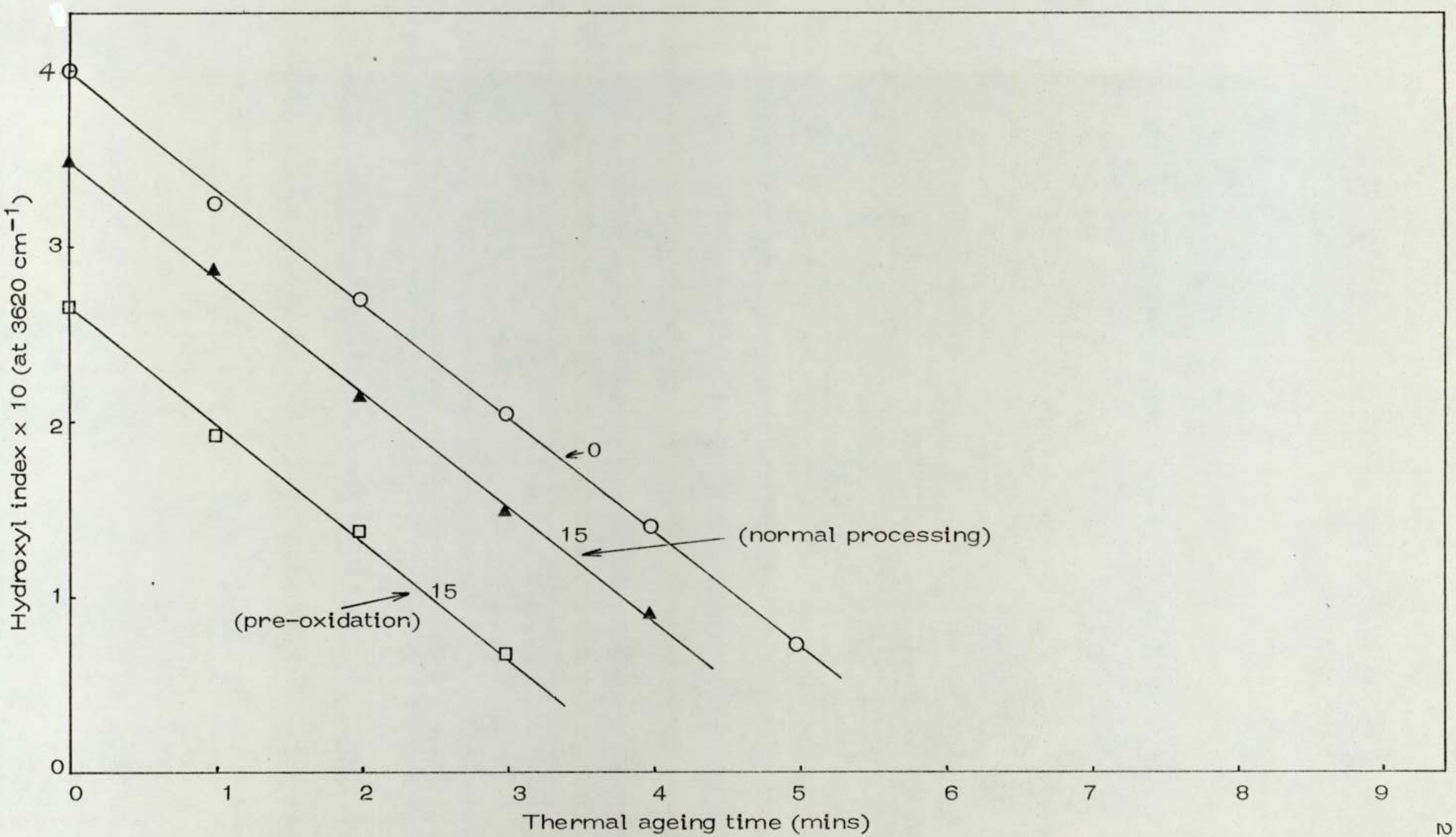


Fig 6.10 Decay of phenolic OH peak (3620 cm^{-1}) on the thermal ageing (at 140°C) of the polypropylene films (numbers on curves refer to processing time in mins)

belong to TBC. Table 6.3 summarises the independence of the rate of phenolic OH disappearance with differing thermal processing history emphasising the acutely high volatility of TBC in polypropylene films.

6.2 Interactions of BHBM with Polypropylene Melt During Processing Operations

Analogous studies to those described for TBC were also made with BHBM. Fig 6.11 illustrates the differing thermal stability of the polypropylene films after being subjected to varying pre-oxidation treatments and the subsequent incorporation of 2% BHBM (8×10^{-3} mole BHBM/100 g). Again BHBM demonstrated a similar trend to that of TBC in that increasing the hydroperoxide concentration with its consequent interaction with the additive within the 3-minute period proved beneficial in so far as thermal stabilisation was concerned. Again, the yellowish colour intensity possessed a positive relationship with pre-oxidation time but was less pronounced compared with TBC. This is succinctly illustrated in Fig 6.12.

As in the TBC system, it was thought that higher molecular weight oxidative by-products of the antioxidant might be

Table 6.3 Independence of the rate of decay of phenolic OH with differing processing history

Processing time (mins)	Rate of disappearance of phenolic OH, $r\ 10^2\ \mathrm{min}^{-1}$	
	Pre-oxidation	Normal processing
0	6.8	
5	6.6	6.6
10	6.4	6.5
15	6.6	6.4

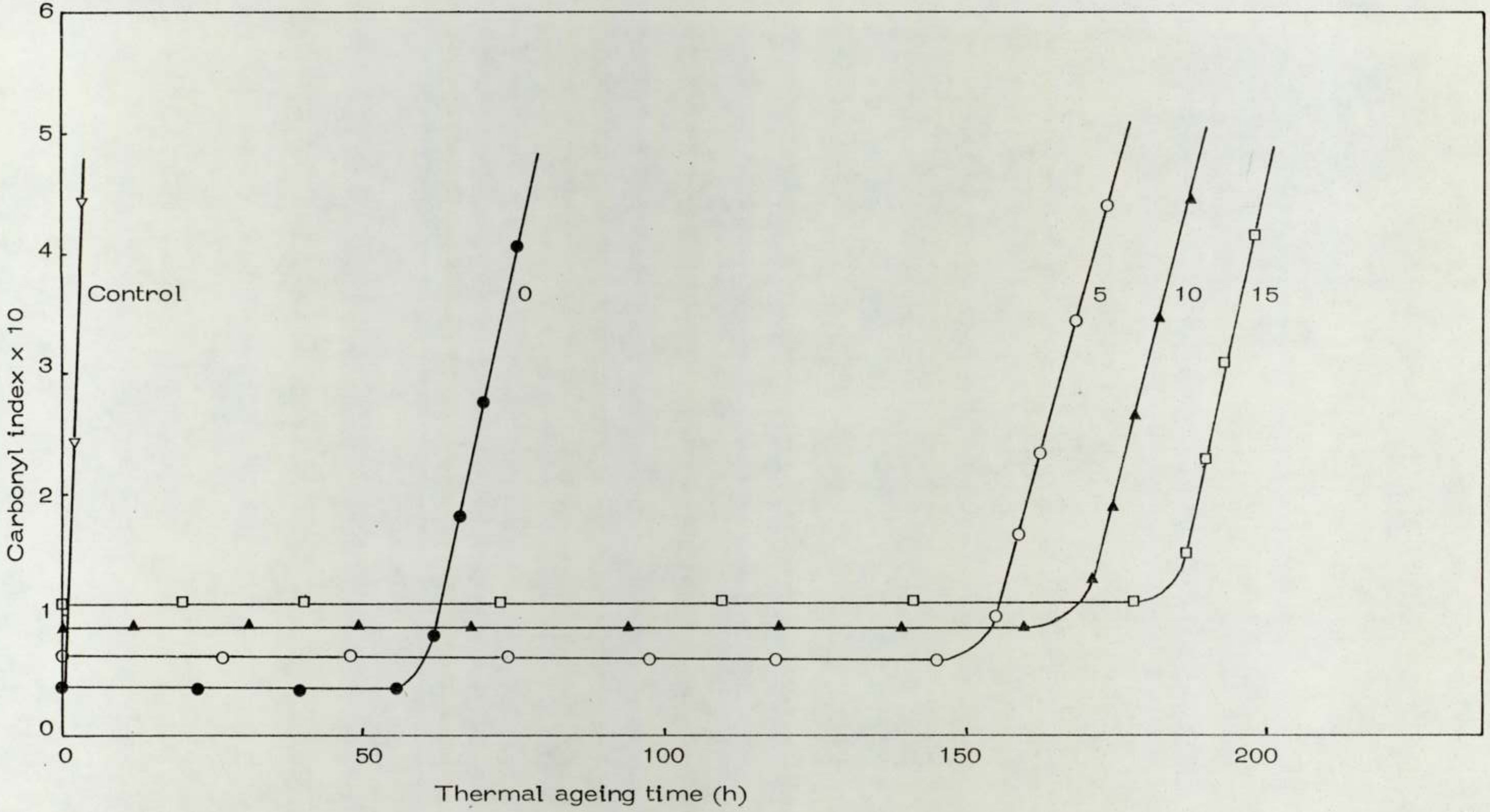


Fig 6.11 Variation in thermal stability (at 140°C) of polypropylene films after subjecting to differing pre-oxidation treatments and subsequent incorporation of 2% BHBM (numbers on curves refer to pre-oxidation time in mins)

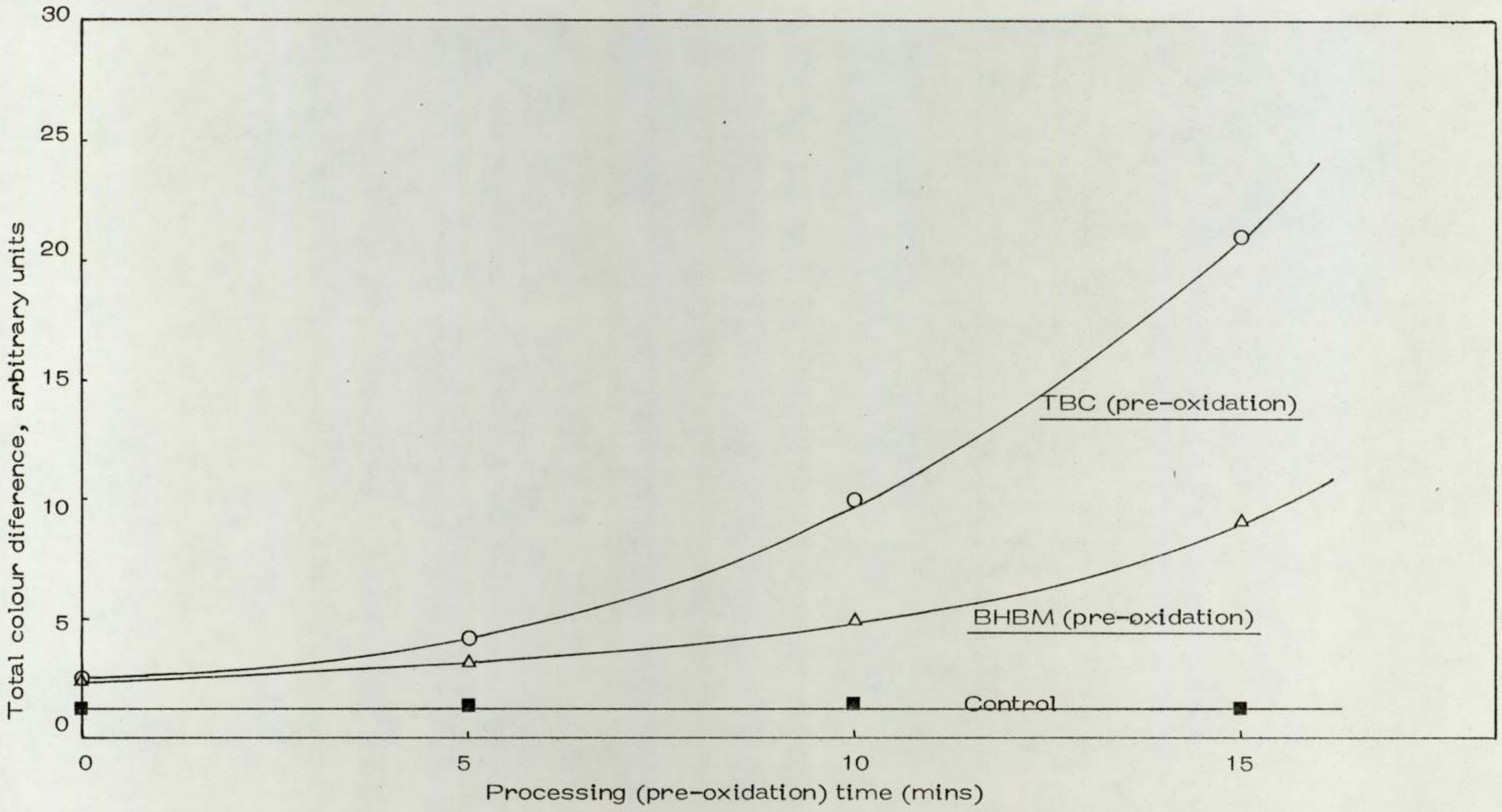


Fig 6.12 Comparison of yellowish discolouration of polypropylene films containing 2% TBC and 2% BHBM with pre-oxidation time

responsible for the observed behaviour. To further confirm this possibility, the processed films were solvent extracted and Fig 6.13 depicts the typical behaviour of the films represented by the 15-minute pre-oxidised and unprocessed samples. Even though the possibility of polymer-binding reactions could not be ruled out due to the appreciable stabilisation still noted after the solvent extraction, Fig 6.13 clearly demonstrates the major contribution of the derived antioxidant products in conferring polymer stability. Fig 6.14 further examines the comparative behaviour of the polymer films before and after solvent extraction which had been subjected to varying periods of pre-oxidation treatment. The non-correlation of the after-extraction curve with pre-oxidation time does imply that the presence of greater concentration of hydroperoxide is advantageous to the polymer-binding reactions since the stabilisation imparted by the higher level of bound antioxidant outweighed the prior extensive polymer breakdown.

Table 6.4 summarises the thermal stability (at 140°C) of the polymer films studied containing 2% level of BHBM. It is noteworthy that while similar trends in stabilisation were shown by the BHBM and TBC systems, the absolute level of stabilisation was vastly different. For the unextracted samples, TBC system

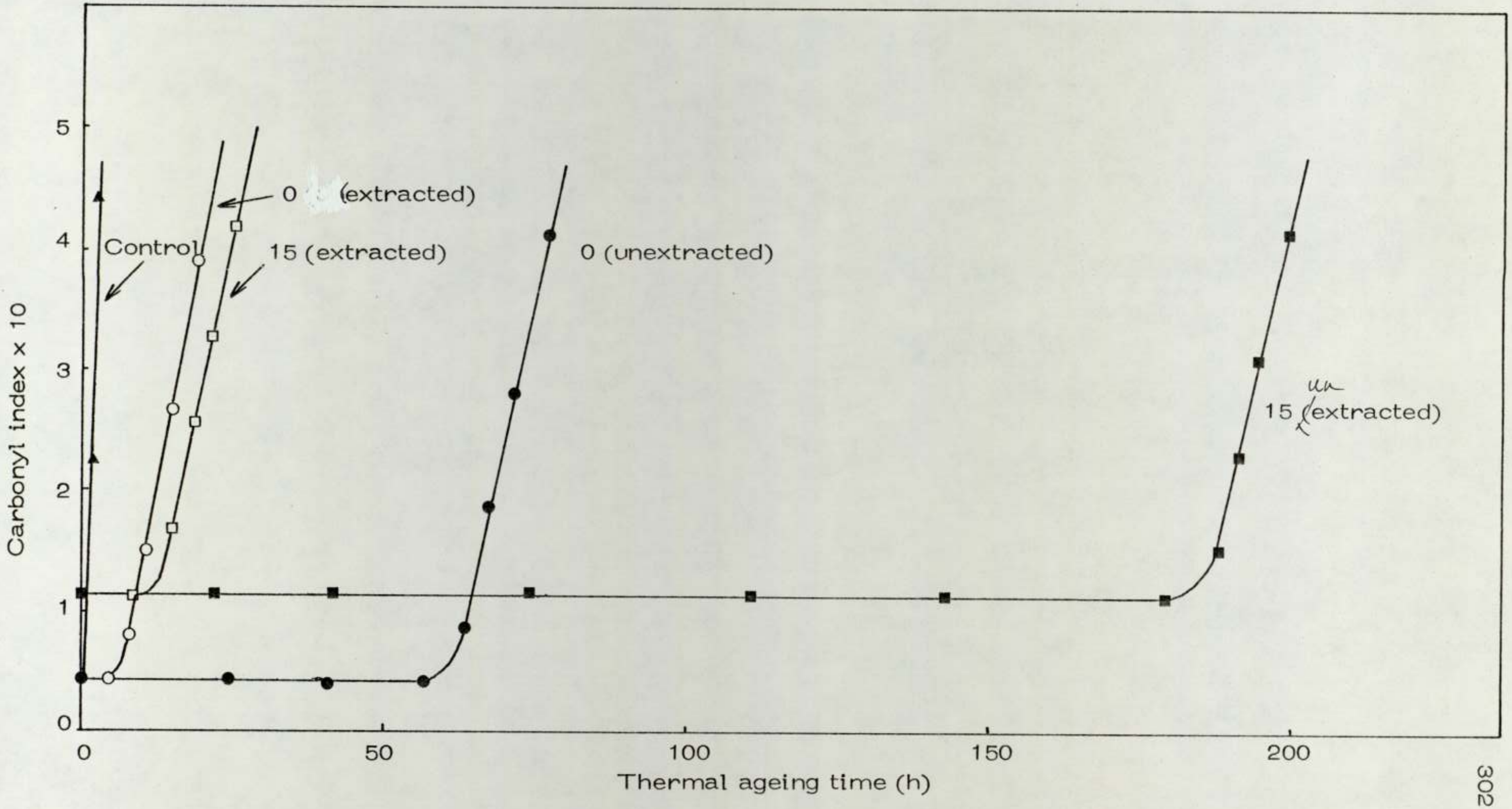


Fig 6.13 Comparison of thermal stability (at 140°C) of extracted and unextracted polypropylene films containing 2% BHBM (numbers on curves refer to pre-oxidation time in mins)

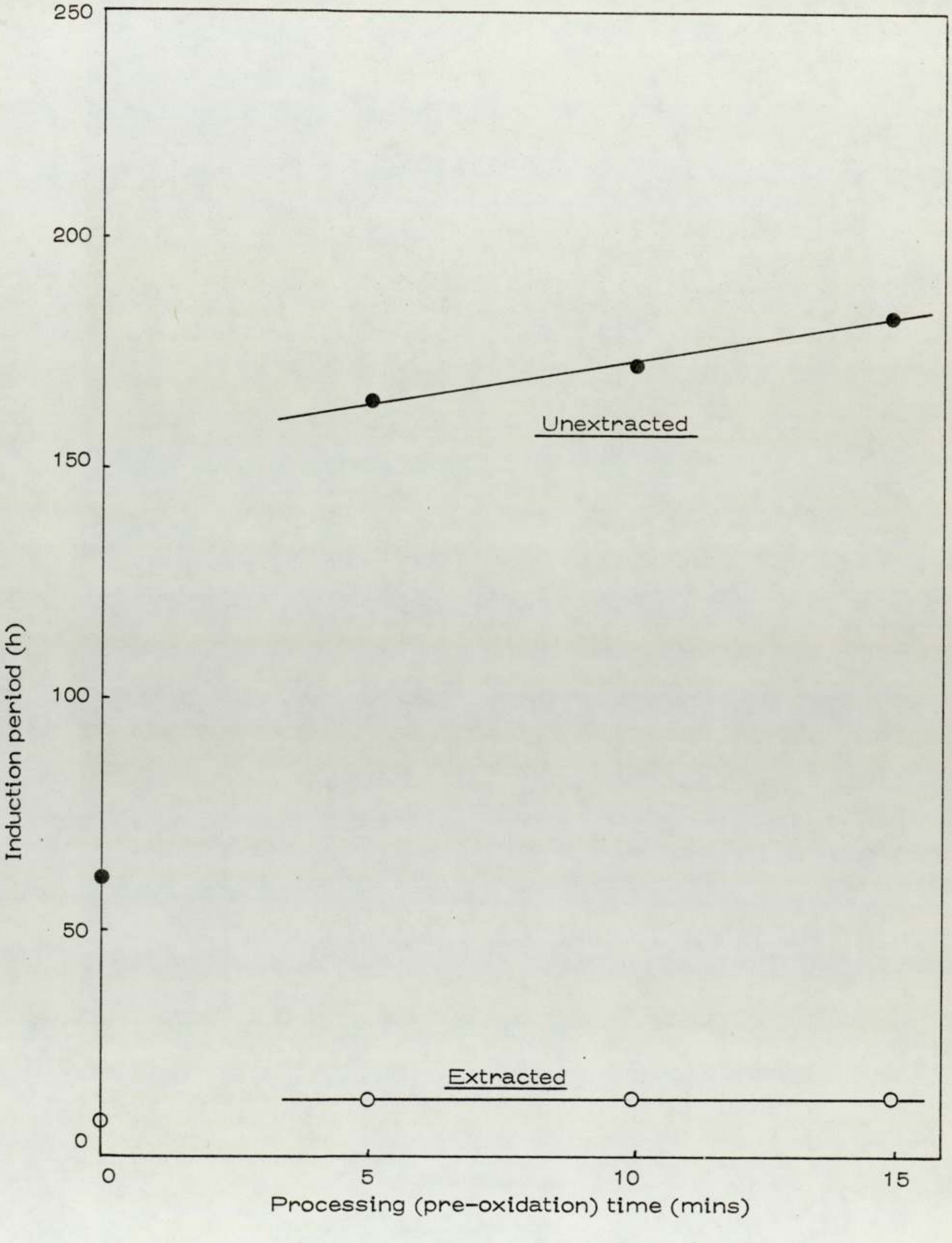


Fig 6.14 Comparison of thermal stability (at 140°C) of extracted and unextracted polypropylene films containing 2% BHBM with different levels of pre-oxidation treatments

<u>Table 6.4</u> Thermal induction periods of polypropylene films (at 140^{o}C) after subjecting to differing pre-oxidation treatments (and containing 2% BHBM) both before and after extractions

Pre-oxidation time (mins)	Induction period (h)		
	Control	2% BHBM	
		Before extraction	After extraction
0	0.5	60	7
5	0.3	155	12
10	0.1	170	12
15	–	181	13

exhibited induction periods ranging from 2–27 h while those for BHBM showed a range of 60–181 h.

To further test whether polymeric hydroperoxides were indispensible to the generation of the higher molecular weight antioxidant derivatives, similar studies to the ones carried out were made but without the pre-oxidation treatment. Fig 6.15 shows the insignificant extent of polymer breakdown with prolonged processing as evidenced by the initially constant carbonyl index. It also demonstrates that increasing the processing time brought about an appreciable improvement in thermal ageing performance. This trend does suggest that prolonged processing resulted in the formation of more antioxidant derivatives of higher molecular weight.

The unprocessed sample showed a markedly inferior performance to those of the processed samples adding testimony to the crucial importance of the processing operations in generating the higher molecular weight derivatives. Solvent extraction of the polymer films reduced their thermal stability to a comparatively low level as typified by the 15-minute processed sample shown in Fig 6.16. This is further elaborated in Fig 6.17 which illustrates the comparative

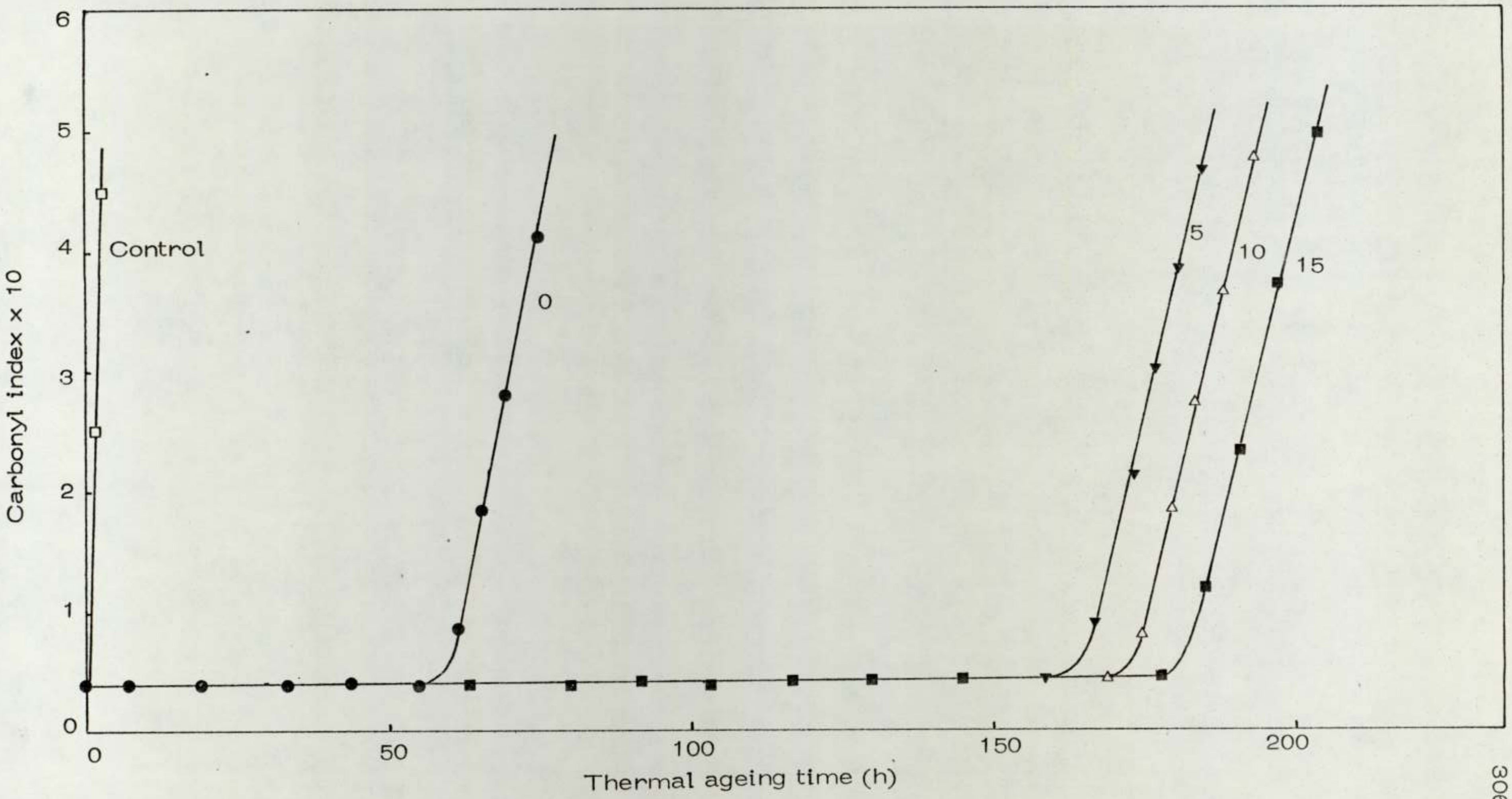


Fig 6.15 Variation in thermal stability (at 140°C) of polypropylene films containing 2% BHBM with processing times (numbers on curves refer to processing time in mins)

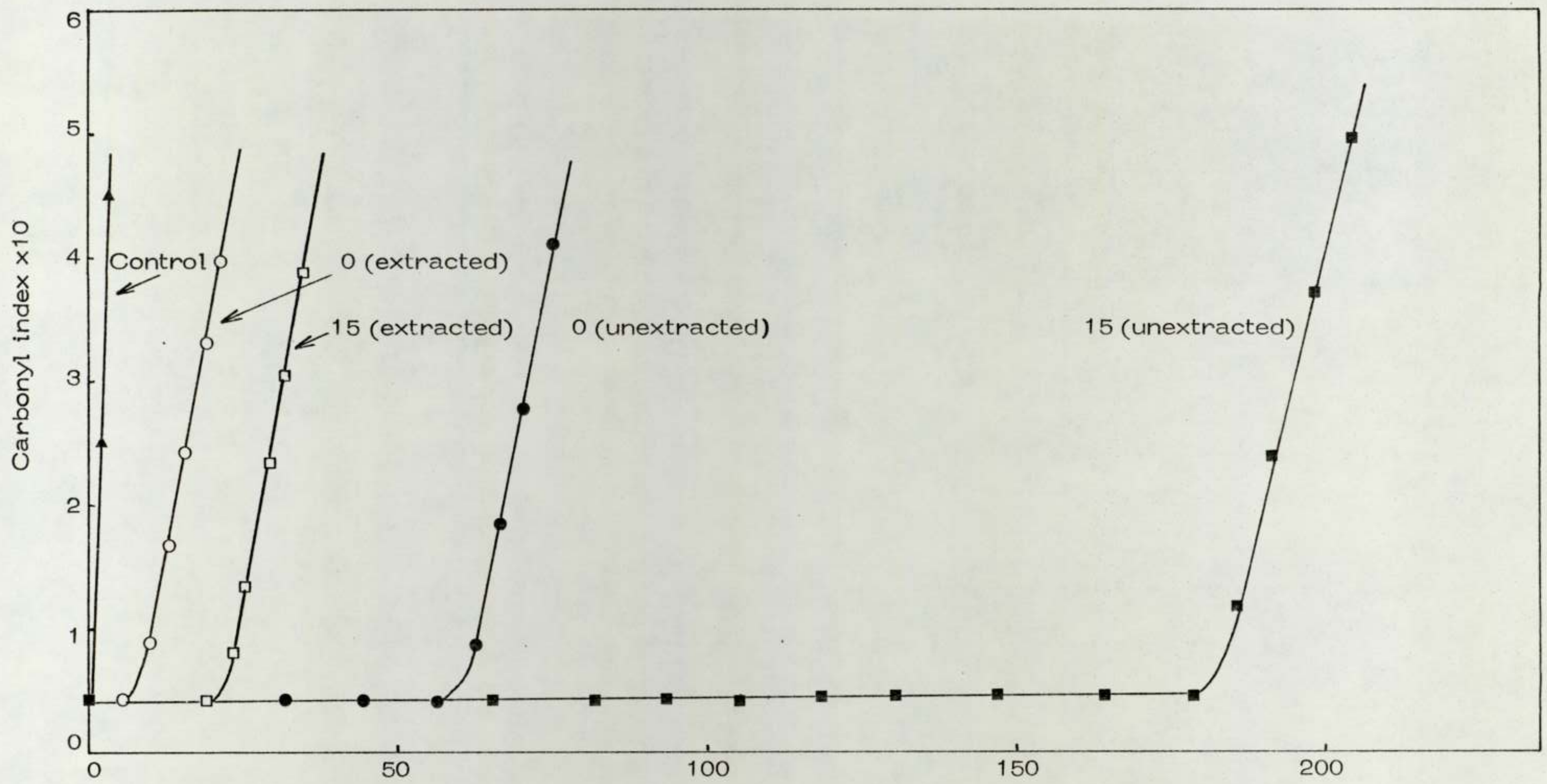


Fig 6.16 Comparison of thermal stability (at 140°C) of extracted and unextracted polypropylene films containing 2% BHBM (numbers on curves refer to processing time in mins)

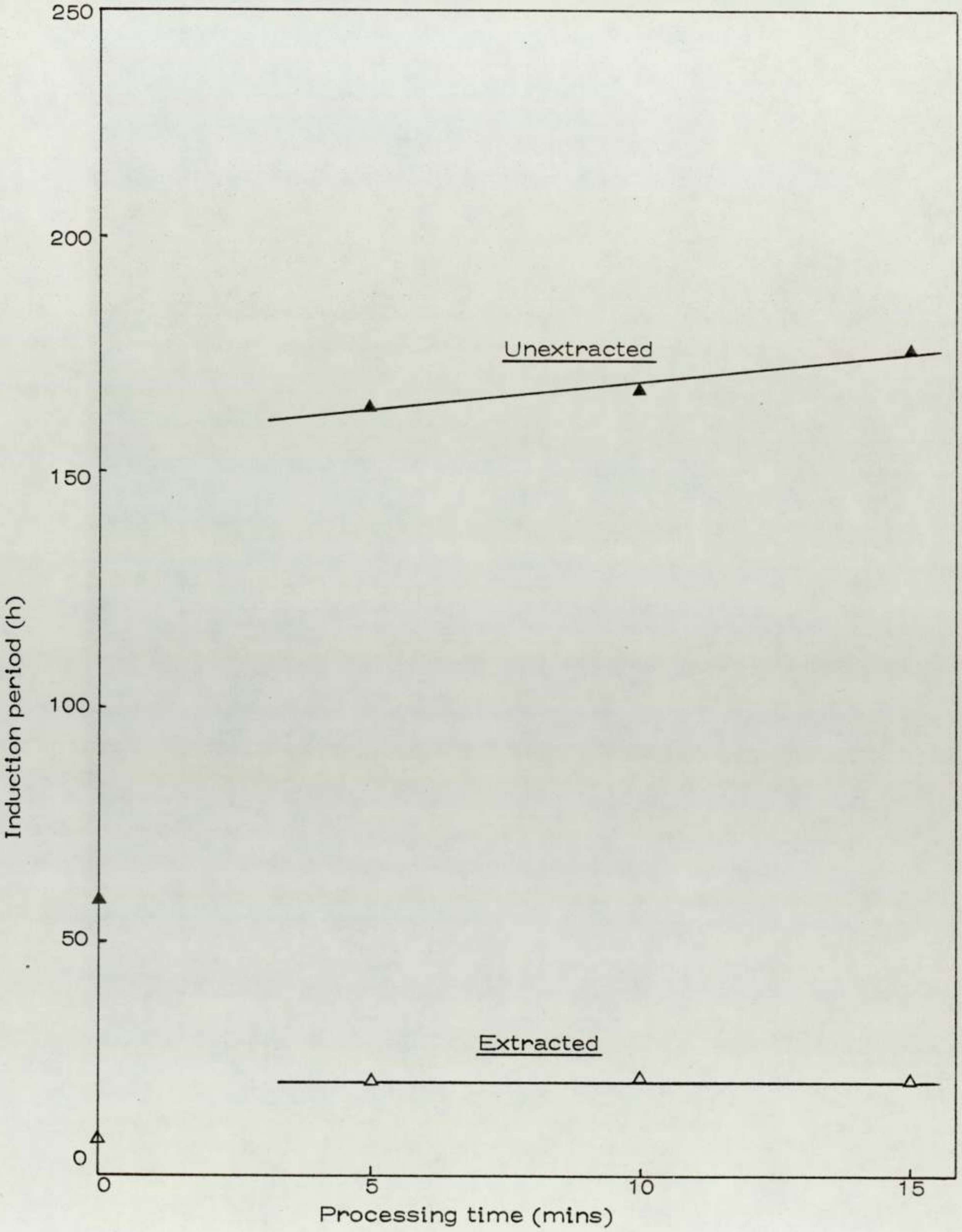


Fig 6.17 Comparison of thermal stability(at 140°C) of extracted and unextracted polypropylene films containing 2% BHBM with processing time

performance of the unextracted and extracted polymer films. Table 6.5 summarises the thermal stability of the pre-oxidised and the normal-processed samples both before and after solvent extractions.

Further supportive work of the antioxidant-polymer interaction phenomena was made by studying the decay of the phenolic OH infra-red spectral peak (at 3620 cm^{-1}) with the processing melt treatment. Fig 6.18 shows that for normal processing, increasing the processing time brought about a linear decrease in phenolic OH due to its physical and chemical losses through volatilisation and transformation to other non-phenolic antioxidant derivatives respectively. The pre-oxidation processes appeared to cause a marginal increase in the rate of the phenolic OH loss despite the constant 3-minute melt processing experienced by the antioxidant. This seems to suggest that the greater concentrations of hydroperoxide significantly transforms the BHBM to non-phenolic antioxidant derivatives (to be further discussed in a succeeding section).

Phenolic OH evaluations were also monitored on subjecting the polymer films to thermal ageing in a flowing (air) atmosphere at 140°C. Fig 6.19 typifies the behaviour of BHBM system

Table 6.5 Comparison of the thermal stability (at 140^{o}C) of the polypropylene films containing 2% BHBM subjected to differing melt treatments and solvent extractions

Processing times (mins)	Induction periods (h)				
	Control	Pre-oxidation (2% BHBM)		Normal processing (2% BHBM)	
		Before extraction	After extraction	Before extraction	After extraction
0	0.5	60	7	60	7
5	0.3	155	12	164	20
10	0.1	170	12	170	20
15	–	181	13	180	22

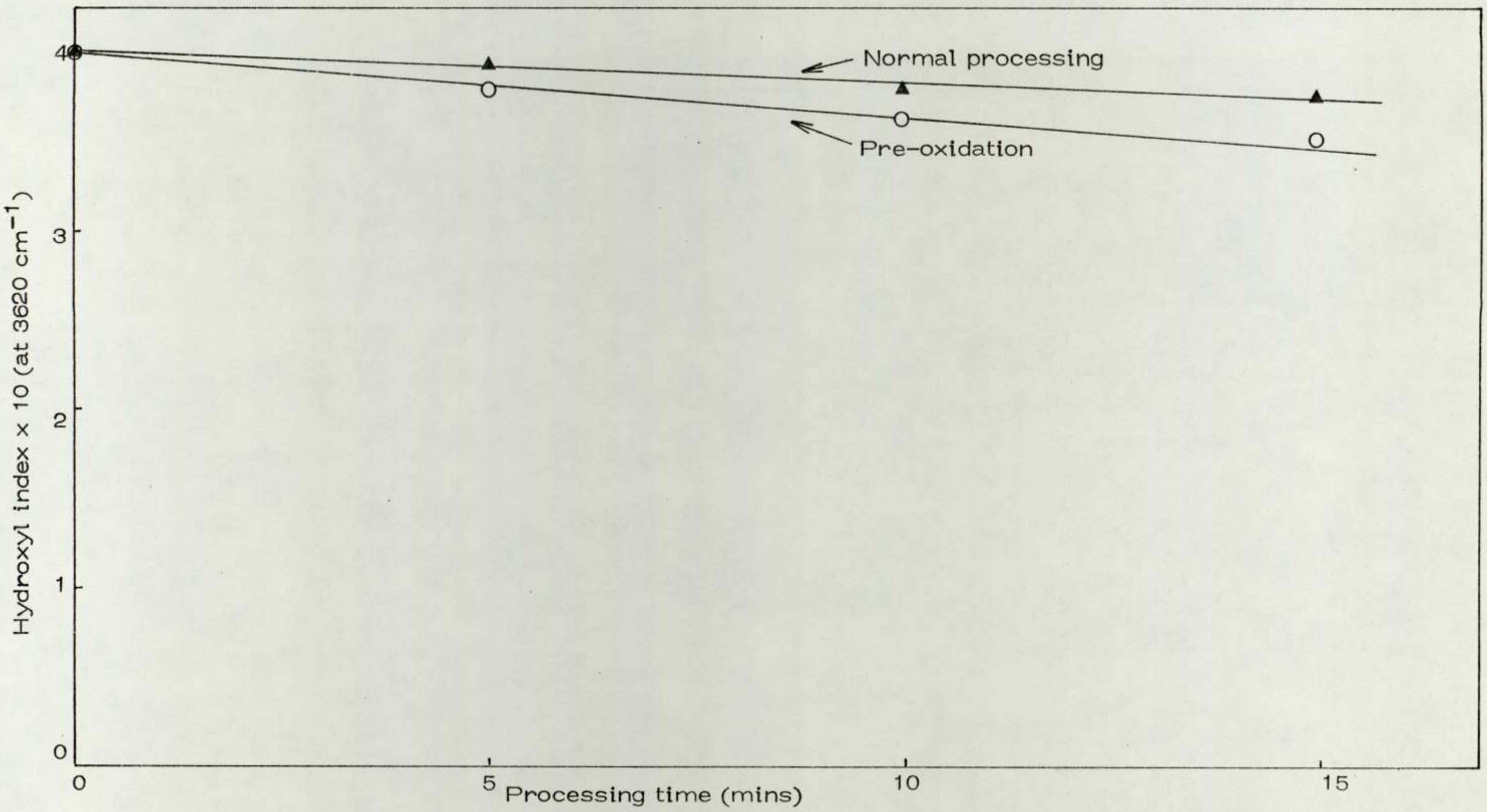


Fig 6.18 Loss of phenolic hydroxyl (3620 cm^{-1}) with processing time under pre-oxidation and normal processing treatments

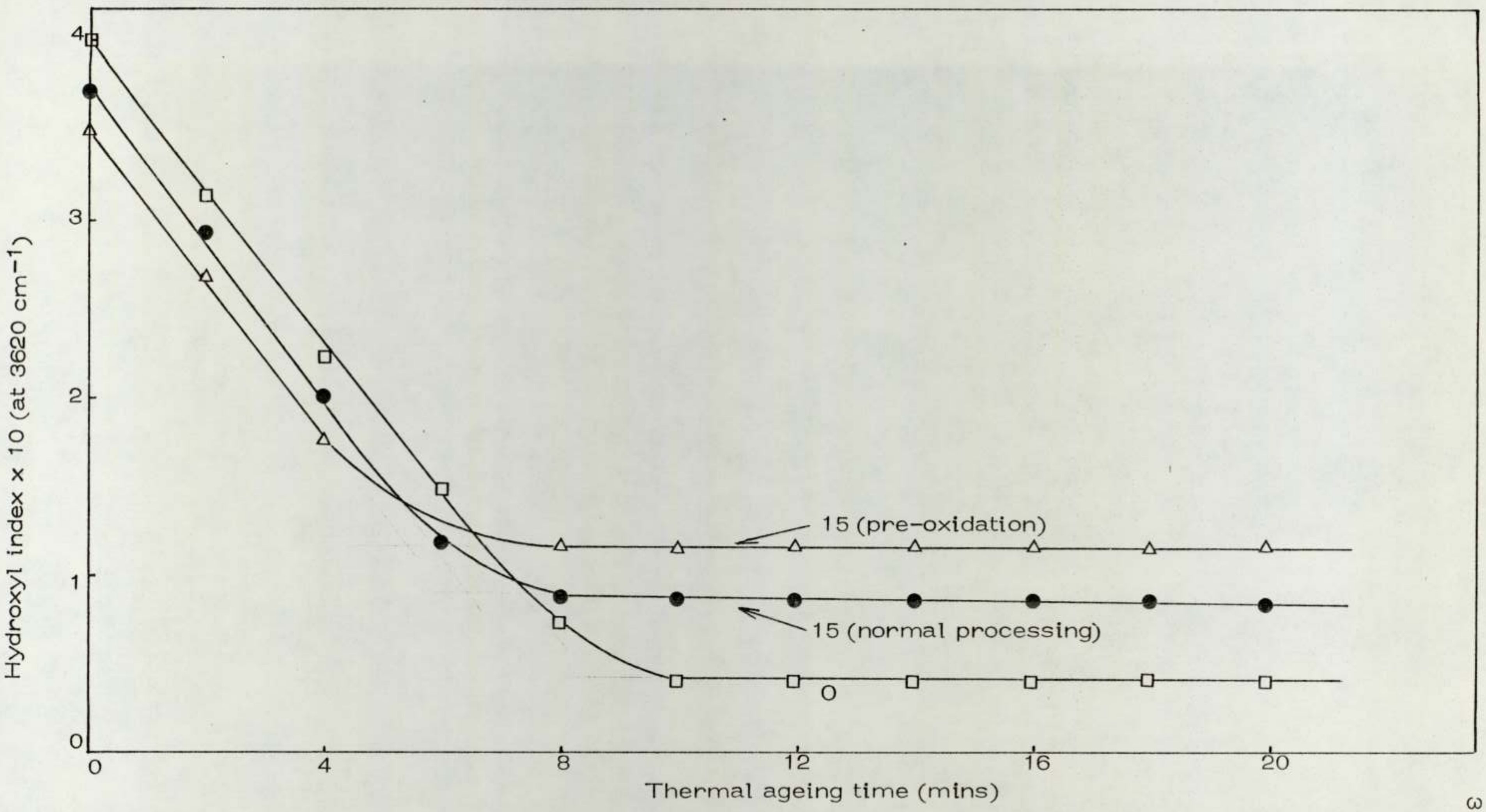


Fig 6.19 Decay of phenolic OH peak (3620 cm^{-1}) on the thermal ageing (at 140°C) of the polypropylene films (numbers on curves refer to processing time in mins)

represented by the unprocessed, the 15-minute pre-oxidised and the 15-minute processed samples. It succinctly illustrates two distinct rates of phenolic OH disappearance; an initial rapid loss followed by a much reduced phenolic OH decay. The implication of the dual nature of the rate loss might well be that two types of phenolic compounds were involved: the initial rapid loss presumably implying the volatilisation of BHBM while the subsequent reduced rate represented the loss of higher molecular weight derivatives of BHBM containing a phenolic moiety. In addition, Fig 6.19 demonstrates the importance of the polymeric hydroperoxides or prolonged processing in bringing about the formation of the higher molecular weight by-products of BHBM whose concentrations were significantly higher than that of the unprocessed sample.

6.3 An Overview and Discussion

Fig 6.20 compares the thermal stability of the polypropylene films containing 2% TBC which had undergone differing melt treatments with the corresponding colour formation. The delineation does imply the strong dependence of the polymer thermal stability on the colour formation. To further confirm this proposition, a plot of induction period -vs- total colour

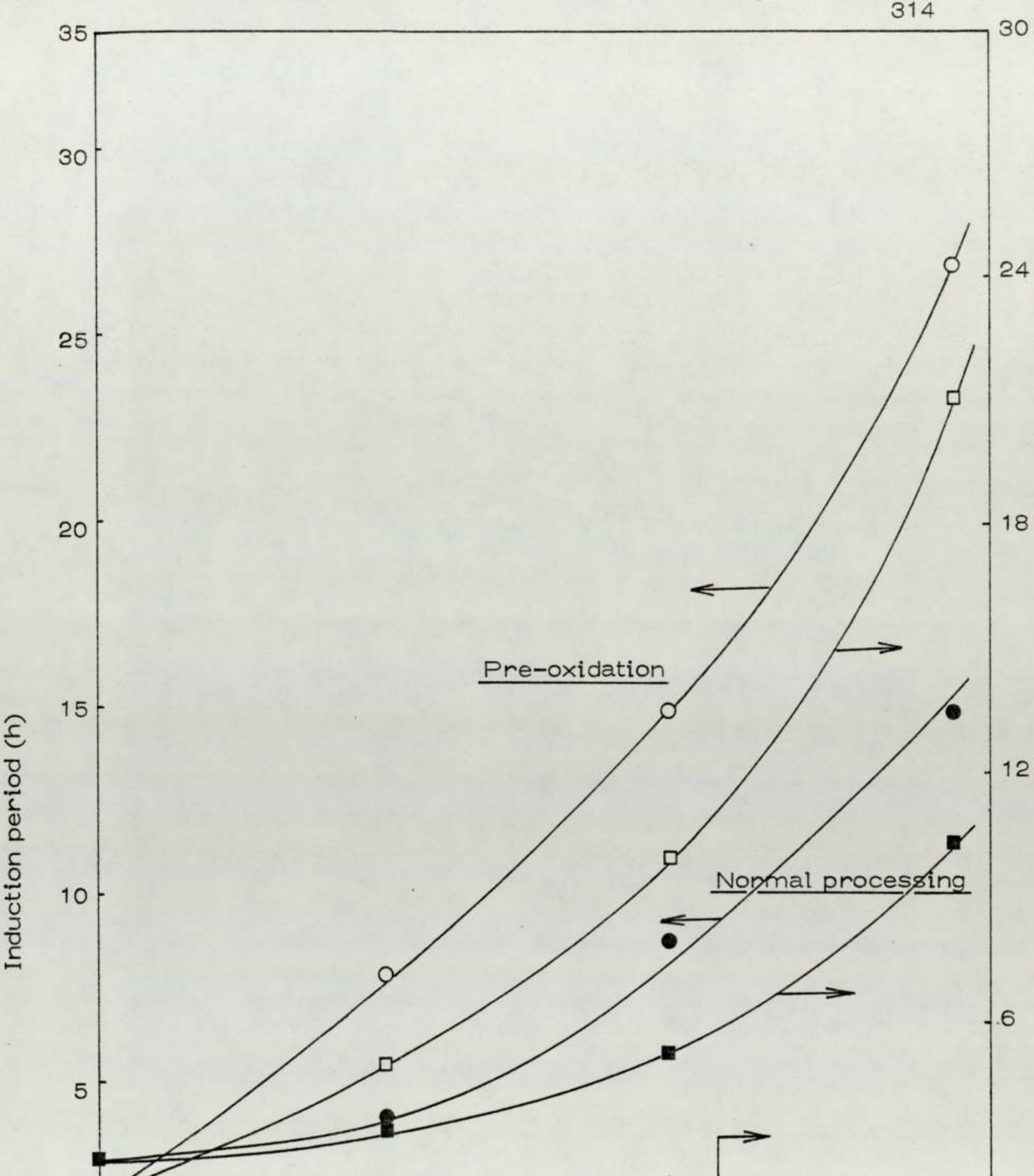
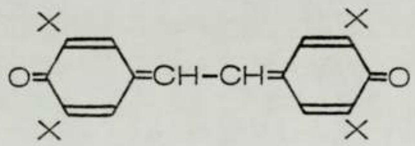


Fig 6.20 Effect of colour formation on the thermal stability (at 140°C) of polypropylene films containing 2% TBC and subjected to varying processing treatments

difference was made and is depicted in Fig 6.21. It clearly shows the strong linear relationship of the two parameters. In addition, the close agreement of the pre-oxidation and the normal processing curves suggests a manifestation of essentially similar mechanism; that the coloured compounds play a major role in the stabilisation processes.

Kularatne and Scott(193) have recently shown that TBC, under appropriate conditions, undergoes facile reactions resulting in the formation of coloured quinonoid compounds, notably stilbene-quinone of type (I) which are known to function as thermal



(I)

3,5,3',5'-tetra-tert-butyl-stilbene-4,4'-quinone

stabilisers. The evidence that greater hydroperoxide concentration or prolonged processing brought about an increase in colour intensity with the concomittant improvement in thermal stabilisation is probably due to the greater abundance of the quinonoid compounds. The reaction mechanism shown in Scheme A is consistent with the findings. Hence the normally

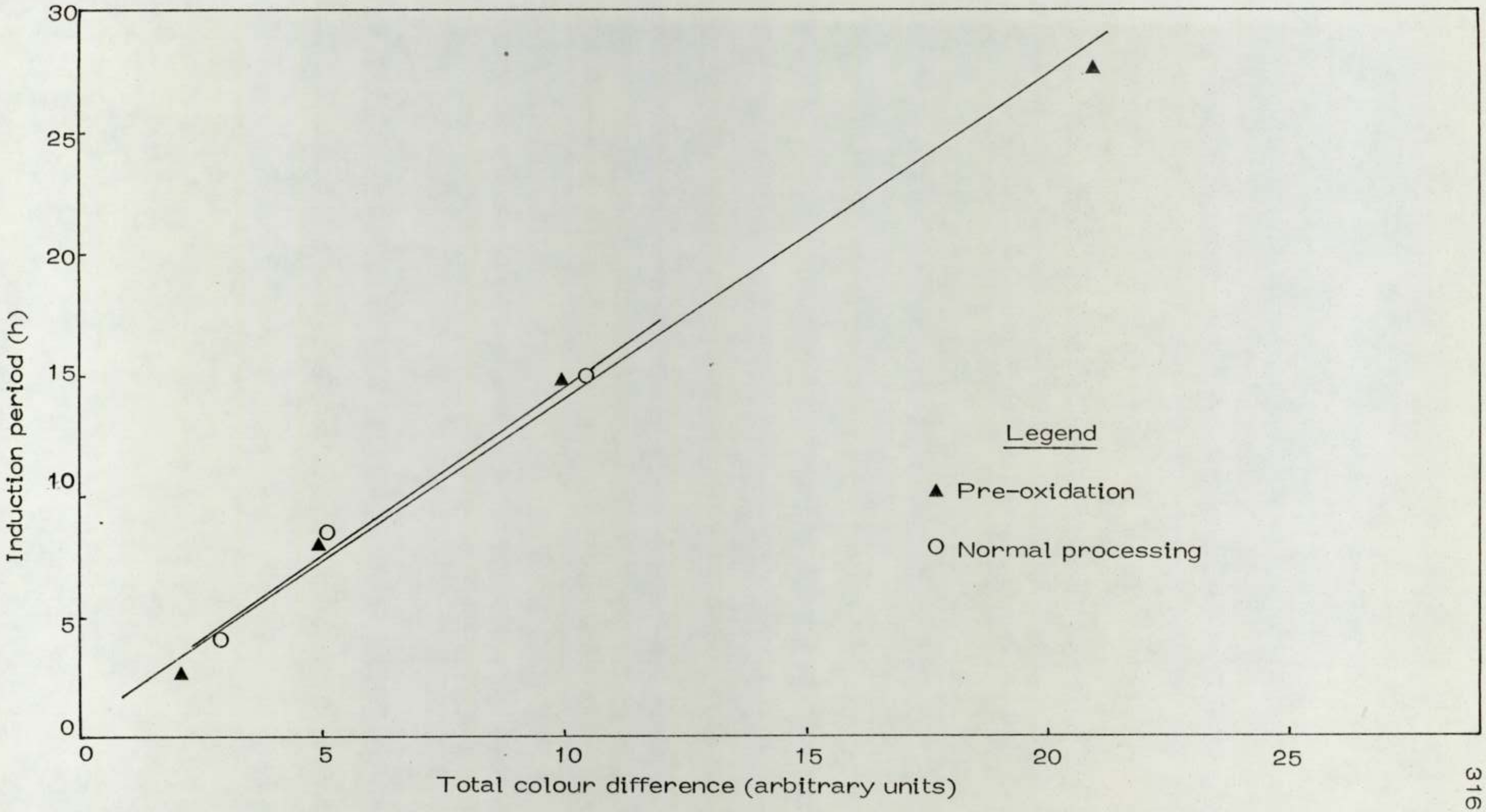
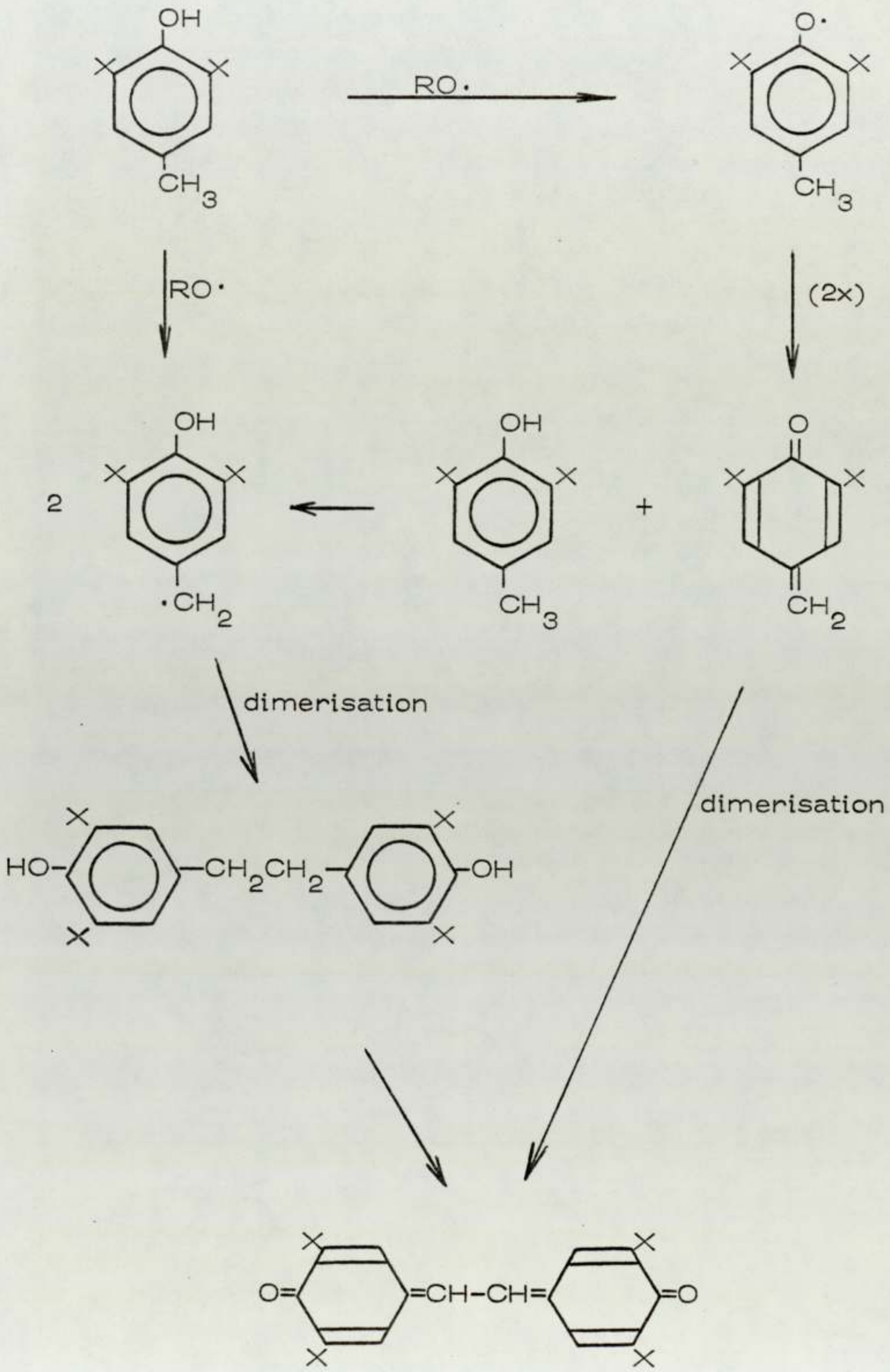


Fig 6.21 Dependence of thermal stability(at 140°C) on colour formation of polypropylene films containing 2% TBC

Reaction Scheme A

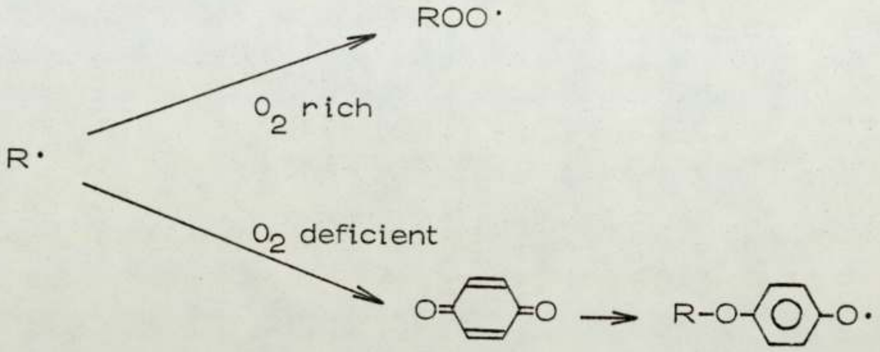


3,5,3',5'-tetra-tertbutylstilbene-4,4'-quinone deleterious influence of hydroperoxides on polymer stability proved advantageous in this particular instance.

The contribution of the stabilising activity of the bis-phenolic compound per se was probably minimal as evidenced by the single rate of phenolic OH decay on thermal ageing, primarily attributable to TBC loss through volatilisation as already shown in Fig 6.10. The evidence from Fig 6.9 also serves to substantiate the greater transformation of TBC to stilbenequinone as illustrated by the lower phenolic OH peak for the 15-minute pre-oxidised sample.

Normal processing operations did limit the hydroperoxide formation but this did not preclude the formation of stilbenequinone during prolonged processing even though its concentration was much less as evidenced from the lower intensity of colour formation and hence reduced polymer stability.

Even though it is widely recognised that quinonoid compounds generally exhibit thermal stabilising property, the mechanistic processes by which they function remain unclear. Presumably an extension of the principle used in vinyl polymerisations could be taken whereby quinone compounds are mainly used as retarders which function in the following manner(8):

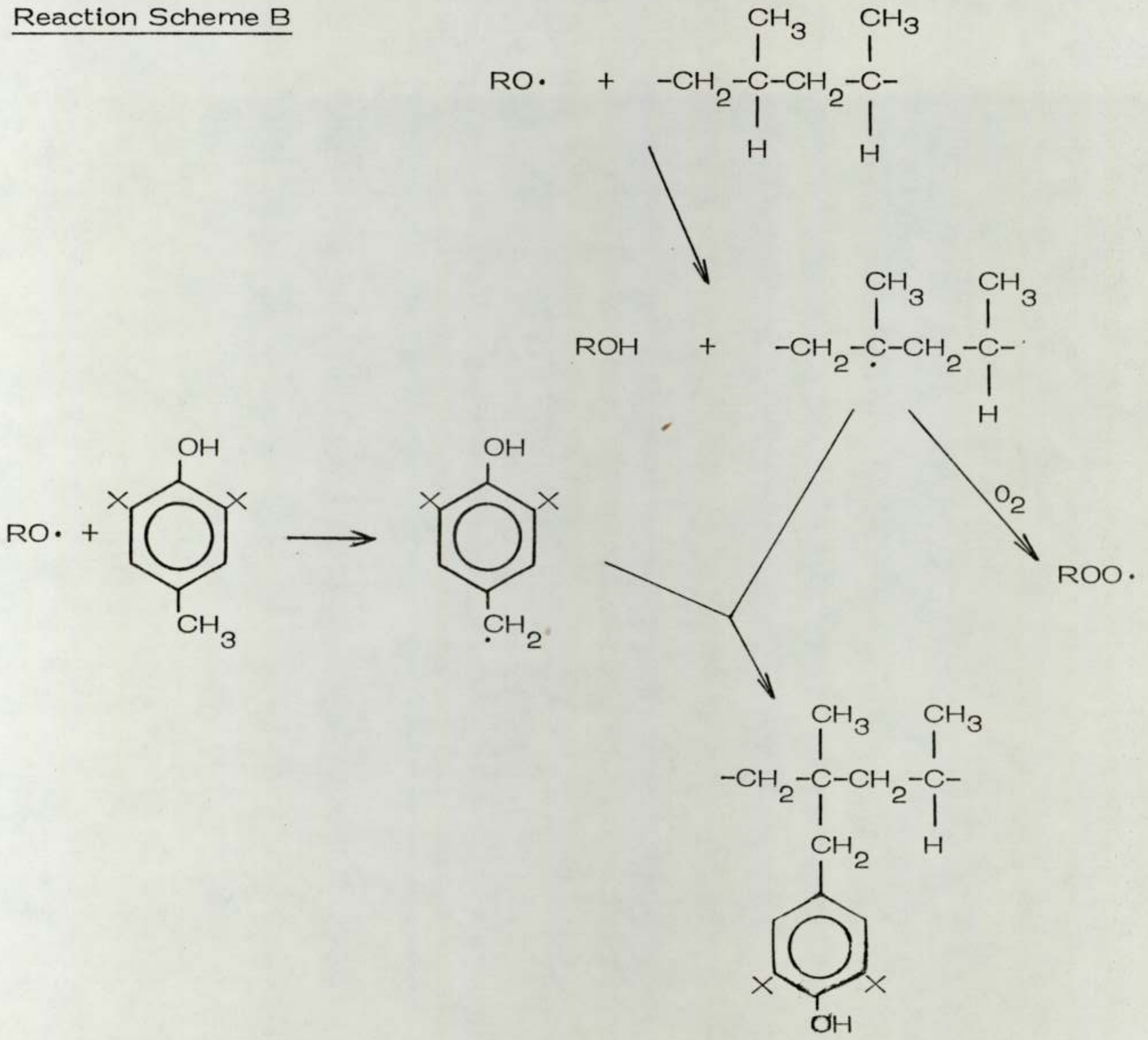


The implication to the present study might possibly be that the quinonoid compounds primarily function by trapping the alkyl radicals in the polymer bulk leading to thermal stability and quinone-adduct formation. However, this remains a possibility.

The minor but significant stability of the polymer after solvent extraction points to the binding reactions presumably via the radical-radical coupling mechanism as shown in reaction Scheme B. The extent of the coupling reaction would be expected to be minimal due to the competing reactions of the tertiary carbon with oxygen which have a very low activation energy.

The behaviour of the BHBM system was similar to that of TBC but the level of stability achieved was greater. This is illustrated in Fig 6.22 for the samples undergoing pre-oxidation treatment.

Reaction Scheme B



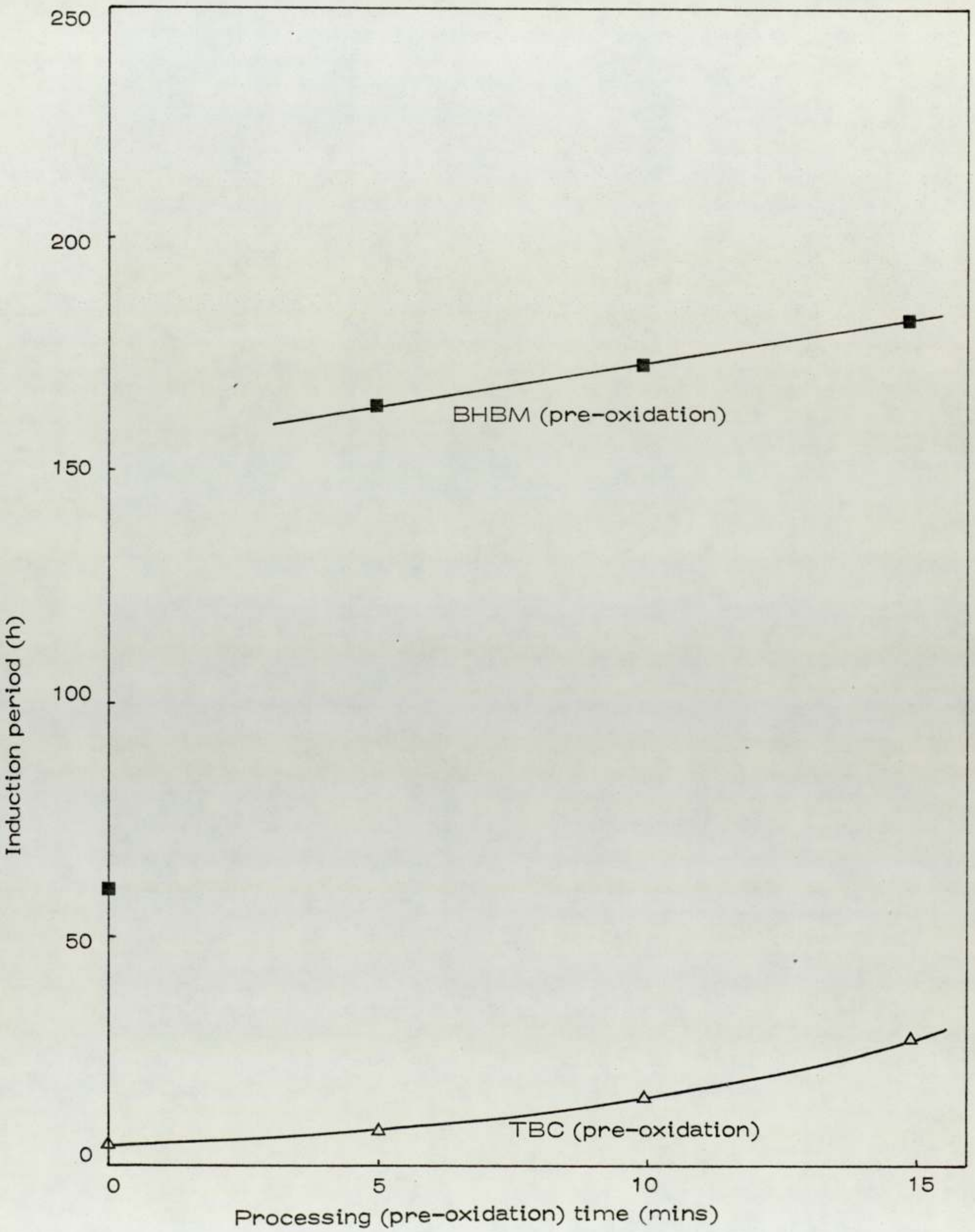


Fig 6.22 Comparison of the thermal stability (at 140°C) of the BHBM and TBC systems

The vastly different stabilities of the two systems could not be rationalised primarily in terms of differing volatilities of the antioxidants nor the formation of stilbenequinone. While the volatilities of the neat antioxidants are essentially similar as already shown in Chapter 3, the formation of stilbenequinone from BHBM was thought to be comparatively less facile as evidenced from the reduced colour intensity as already shown in Fig 6.12.

The contribution of the binding reactions moreover could not account for the outstanding polymer stability since as shown in Fig 6.14, solvent extraction of the film rendered them minimal but significant polymer stability. It was therefore suspected that other higher molecular weight BHBM derivatives, in conjunction with stilbenequinone, might be responsible for the observed behaviour.

This possibility was shown to be real when on monitoring the rate loss of phenolic OH with thermal ageing in the flowing (air) atmosphere, two distinct rates of phenolic OH disappearance were noted as shown in Fig 6.19. The initial rapid disappearance was indicative of BHBM loss through volatilisation while the second stage signified the loss of higher molecular weight

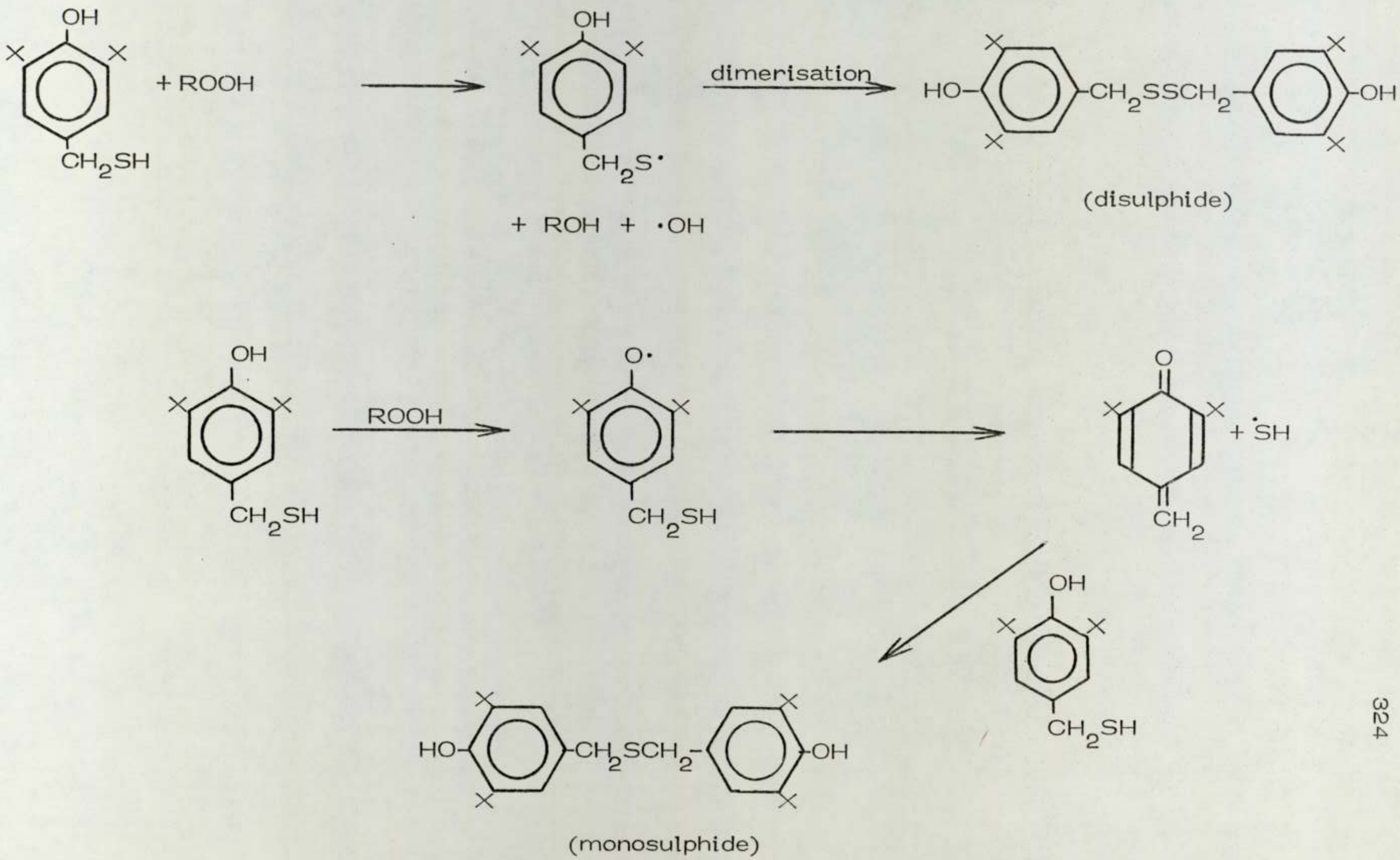
BHBM derivatives containing a phenolic moiety whose formation were encouraged by prolonged processing as evidenced from the increasing hydroxyl index of the second stage. The higher molecular weight derivatives containing the phenolic moiety might be the mono and disulphides of BHBM formed in the presence of hydroperoxides or during prolonged processing via the reaction sequence shown in Scheme C.

6.4 Uv-initiated Grafting of BHBM to Polypropylene Films

Further studies aimed at facilitating the binding reactions between BHBM and polypropylene were made on the basis of the antioxidant-polymer interaction in the presence of uv light. To this end, BHBM was incorporated into the polymer via the mild processing melt treatment in the closed chamber of the torque rheometer for 10 mins at 180°C. Three concentration levels were used: 2, 1 and 0.5%. A plot of hydroxyl index against concentration of BHBM is illustrated in Fig 6.23 and shows a linear relationship of the two parameters suggesting that Beer-Lambert law still applies up to the 2% BHBM level.

The prepared polymer films were uv irradiated under two sets of conditions: one was under normal atmospheric environment

Reaction Scheme C



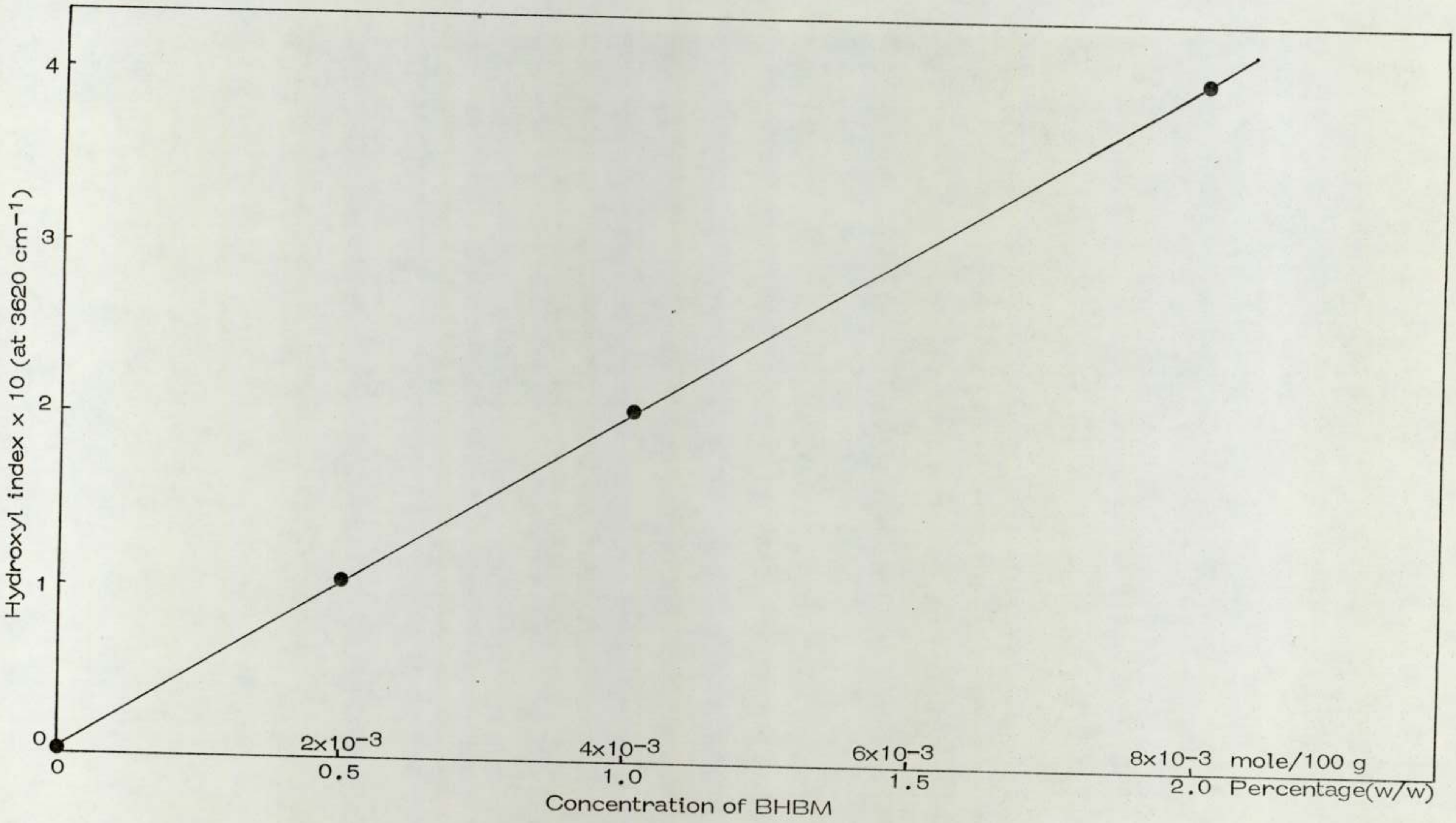


Fig 6.23 Relationship of the phenolic hydroxyl index with the concentration of BHBM in polypropylene

and the other within the tight seal of quartz tubes which were initially flushed with oxygen-free nitrogen, the primary objective being to eliminate the influence of oxygen on the antioxidant-polymer interactions.

Fig 6.24 illustrates the varying hydroxyl index of the polymer films containing 2% BHBM on uv exposure in air both before and after solvent extraction. For the unextracted samples, the decay of the hydroxyl index showed an initial rapid rate followed by a more gradual one after about 25 h of the uv irradiation. This time period might signify the predominance of free-radical reactions that resulted in the higher rate of phenolic OH consumption. At the same time, grafting of BHBM to the polymer appeared prevalent as evidenced by the remaining hydroxyl group after the extraction process. The fact that a maximum level of grafting reactions was observed after 3 h of uv exposure implies the interplay of competing reactions.

Concurrent with the hydroxyl evaluations, total colour difference measurement of the films were also made over the uv exposure time. The relationship between hydroxyl loss and colour formation is illustrated in Fig 6.25 and suggests that

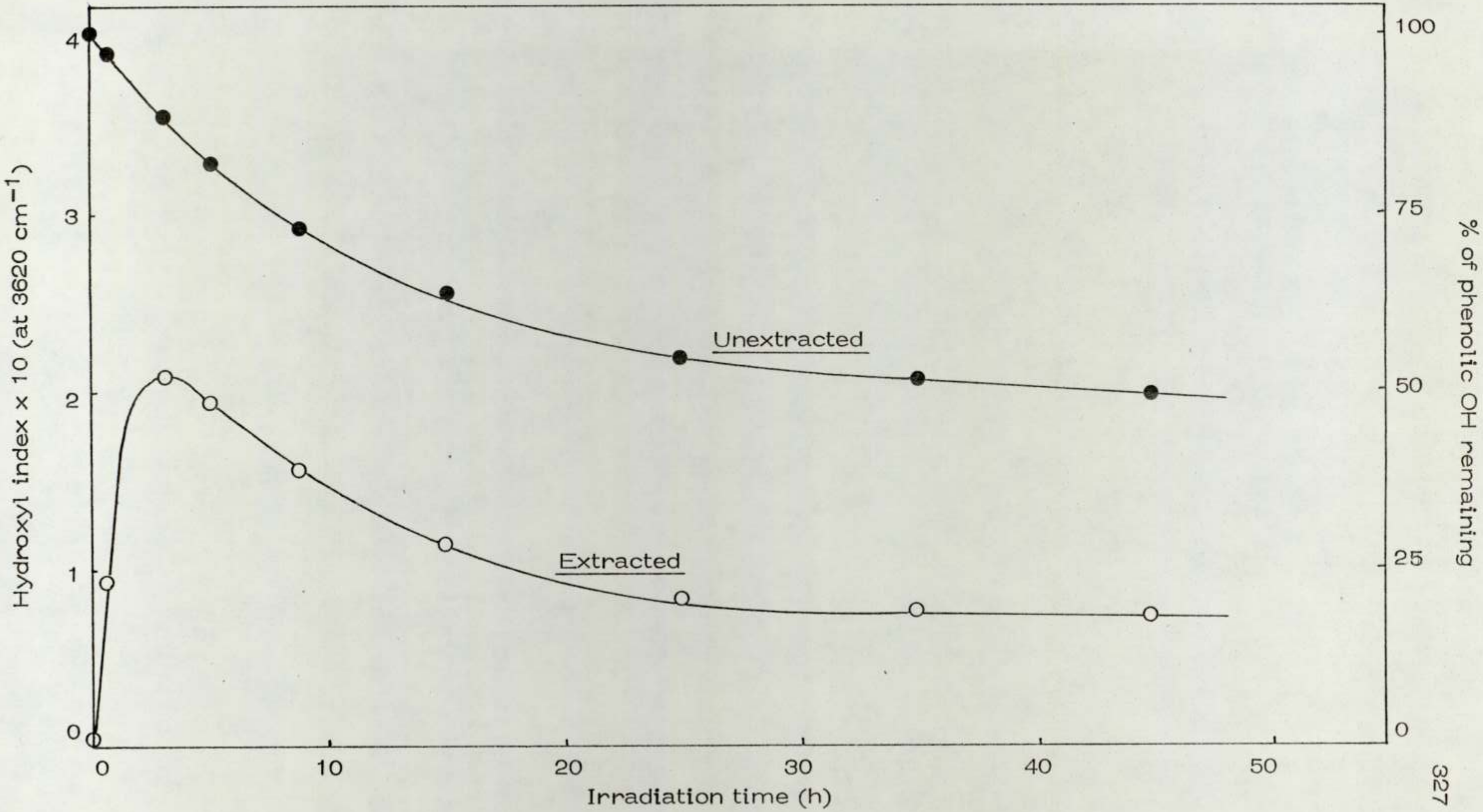


Fig 6.24 Variation of phenolic hydroxyl index with uv exposure (in air) of extracted and unextracted polypropylene films containing initially 2% BHBM

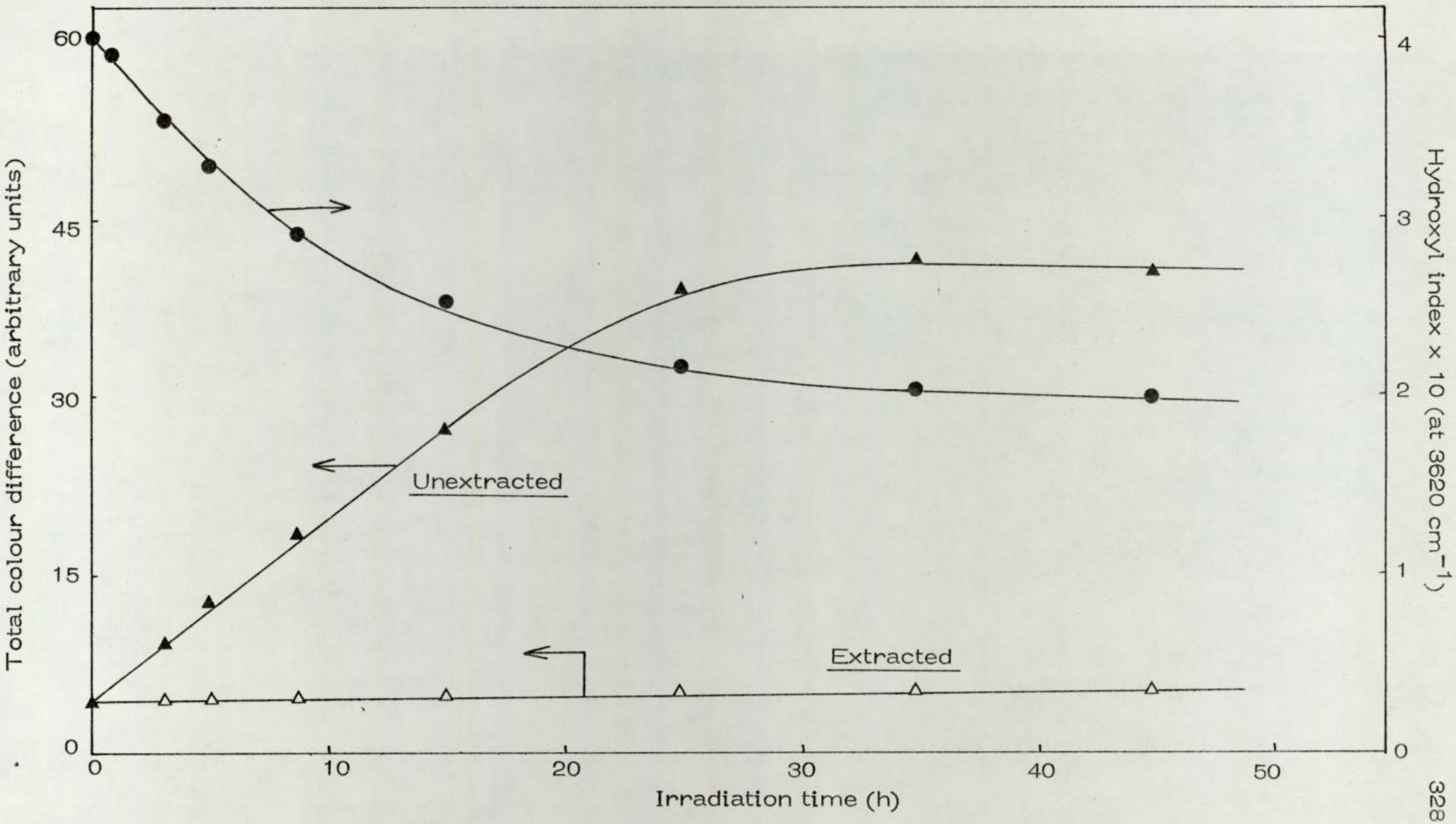


Fig 6.25 Decay of phenolic hydroxyl index with the concomittant development of discolouration on uv exposure of polypropylene films containing 2% BHBM

the latter was exerting a significant and beneficial role in minimising the destruction of BHBM. The protective activity might operate through physical screening mechanism of the yellowish product thereby curtailing the detrimental effect of uv light. On solvent extraction of the irradiated films, the yellow colour virtually disappeared (Fig 6.25) providing evidence to the fact that the coloured compounds were not bound to the polymer.

Further inspection of the infra-red spectrum showed a substantial growth in the 1690 cm^{-1} peak with the initial uv irradiation. The peak is characteristic of the unsaturated carbonyl group(7). A plot of unsaturated carbonyl index against uv exposure time depicted in Fig 6.26 shows the initial dramatic increase in unsaturated carbonyl formation followed by a gradual decay after about 25 h of uv exposure. Solvent extracting the films virtually removed all the carbonyl compounds. Superimposition of the trend of unsaturated carbonyl formation on that of the development of colour with uv exposure time as shown in Fig 6.27 demonstrates similar patterns of behaviour suggesting that the colour formation was due to the conjugated carbonyl compounds.

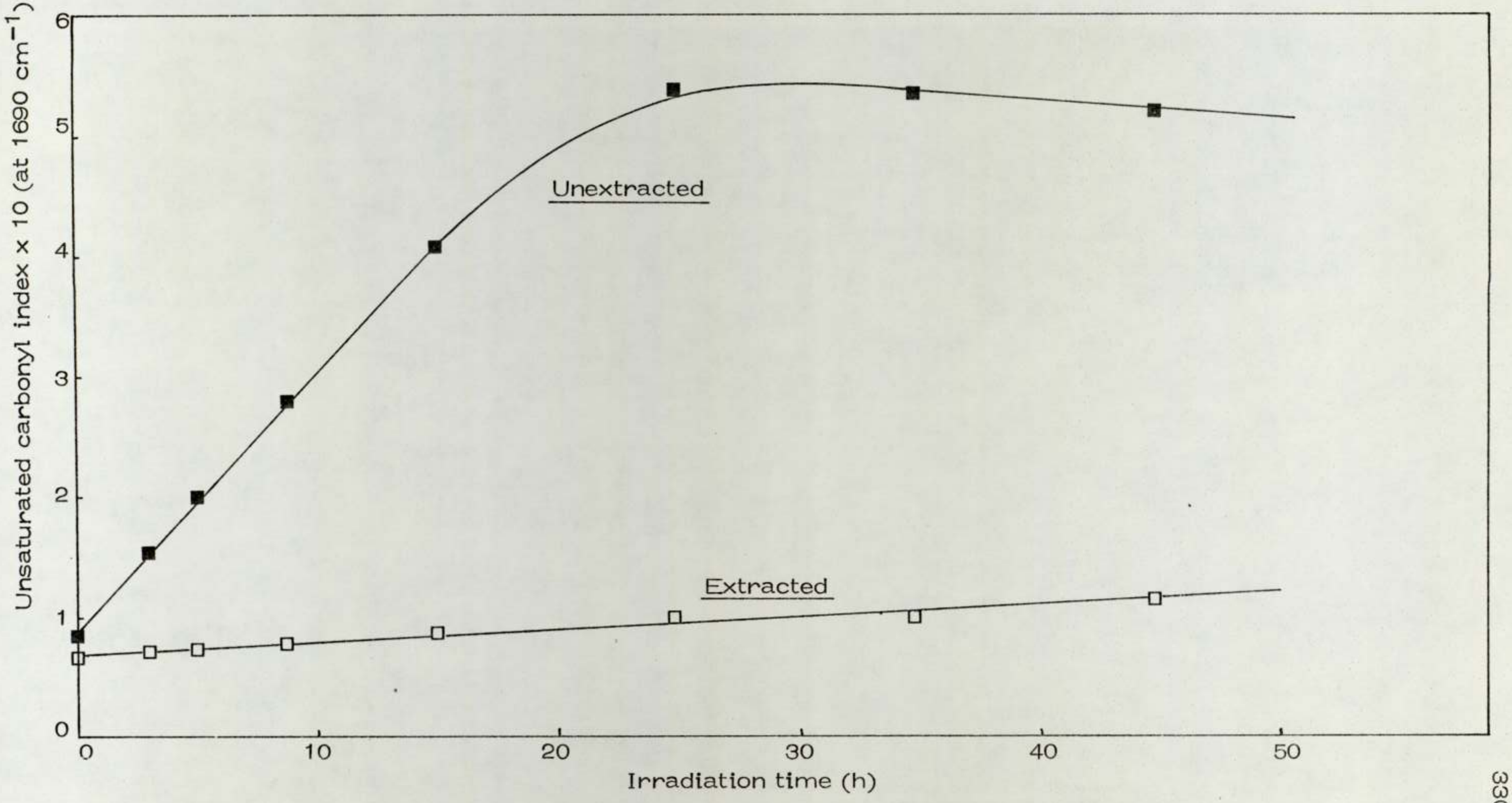


Fig 6.26 Development of unsaturated carbonyl group (1690 cm^{-1}) on the uv exposure of polypropylene films containing 2% BHBM

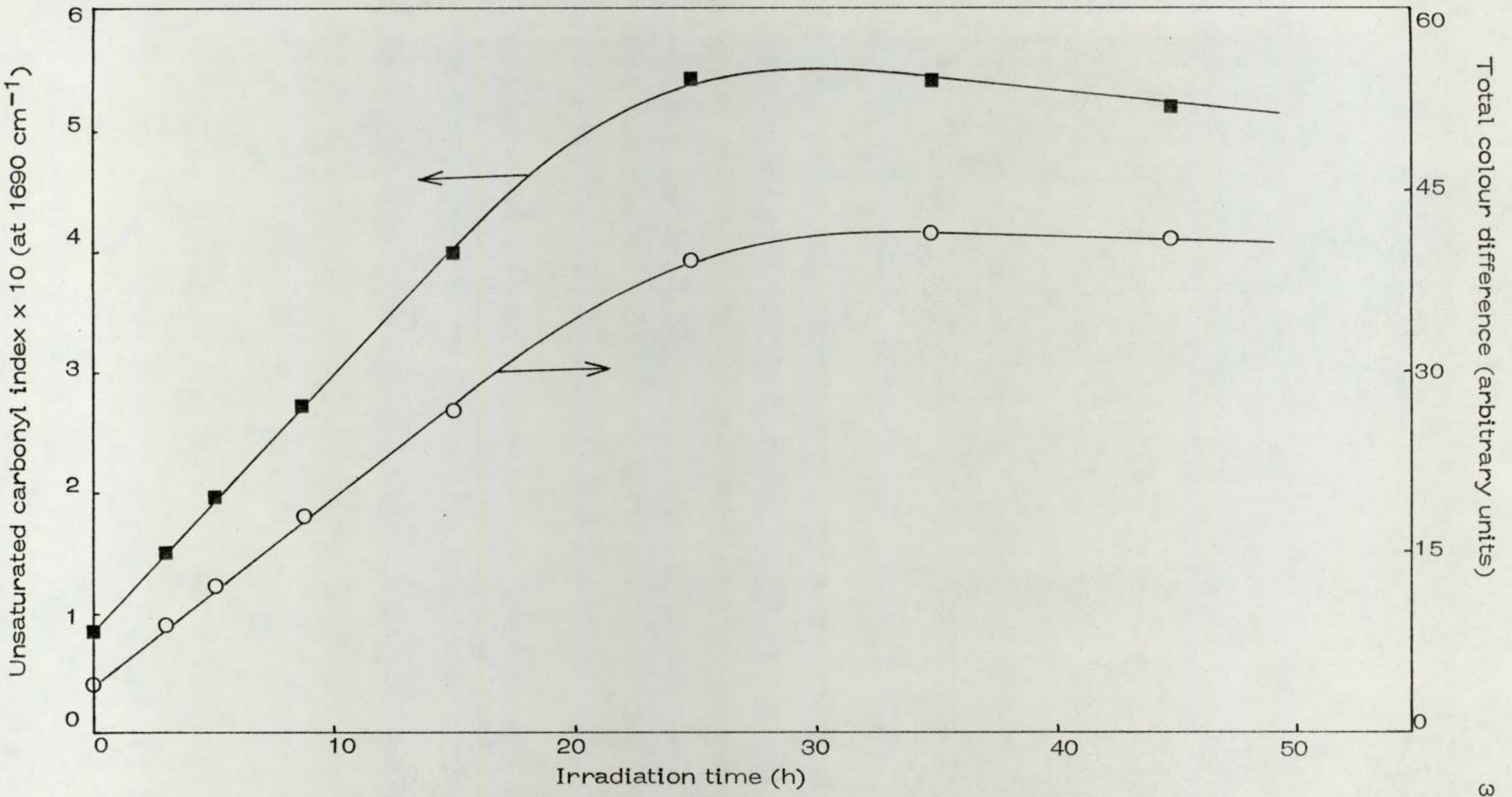
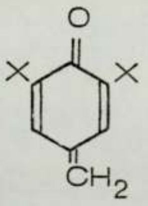


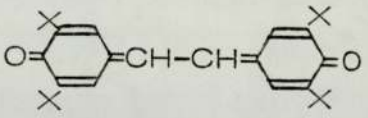
Fig 6.27 Comparison of colour formation and unsaturated carbonyl development (1690 cm^{-1}) on uv exposure of polypropylene films containing 2% BHBM

The evidence thus far gathered shows that the coloured (yellowish) compounds to be, in part, responsible for the screening activity and minimising the BHBM destruction and that not only do they contain unsaturated carbonyl functional groups but they are also not bound to the polymer backbone. These characteristics strongly point to the quinonoid compounds, notably quinonemethide (I) and its dimeric product, stilbenequinone (II).



(I)

2,6-di-tert-butyl quinonemethide



(II)

3,5,3',5'-tetra-tert-butylstilbene-4,4'-quinone

Analogous studies at 1% and 0.5% BHBM showed similar phenomena to those already described implying that no significant deviation of reaction mechanisms occurred within the 2% BHBM level.

In order to negate the influence of oxygen on the BHBM-polypropylene interaction in the presence of uv light, parallel studies were carried out under sealed nitrogen atmosphere in quartz tubes of 2-inch diameter and 5-inch length. Fig 6.28 illustrates the beneficial effect of excluding oxygen in not only reducing the rate of BHBM destruction but also in effecting a higher level of bound antioxidant. Development of unsaturated carbonyl groups (and hence colour formation) was also very much impeded in the nitrogen environment as demonstrated in Fig 6.29.

It does appear then that the inert nitrogen atmosphere augments the binding reactions of BHBM to polypropylene. This is delineated in Fig 6.30 where percentage bound antioxidant (based on 100 g polypropylene) after 3 h of uv irradiation were plotted against the antioxidant concentration initially used.

To realise the technological efficacy of the bound antioxidant, the masterbatch technique of incorporating the polymeric antioxidant into virgin polypropylene was investigated and its thermal stability compared to that of simple BHBM at equimolar concentration. The technical laboratory difficulty of larger scale uv grafting the BHBM to polypropylene under nitrogen atmosphere made it imperative for the uv grafting to be carried out in air where a lower level of binding reaction was observed.

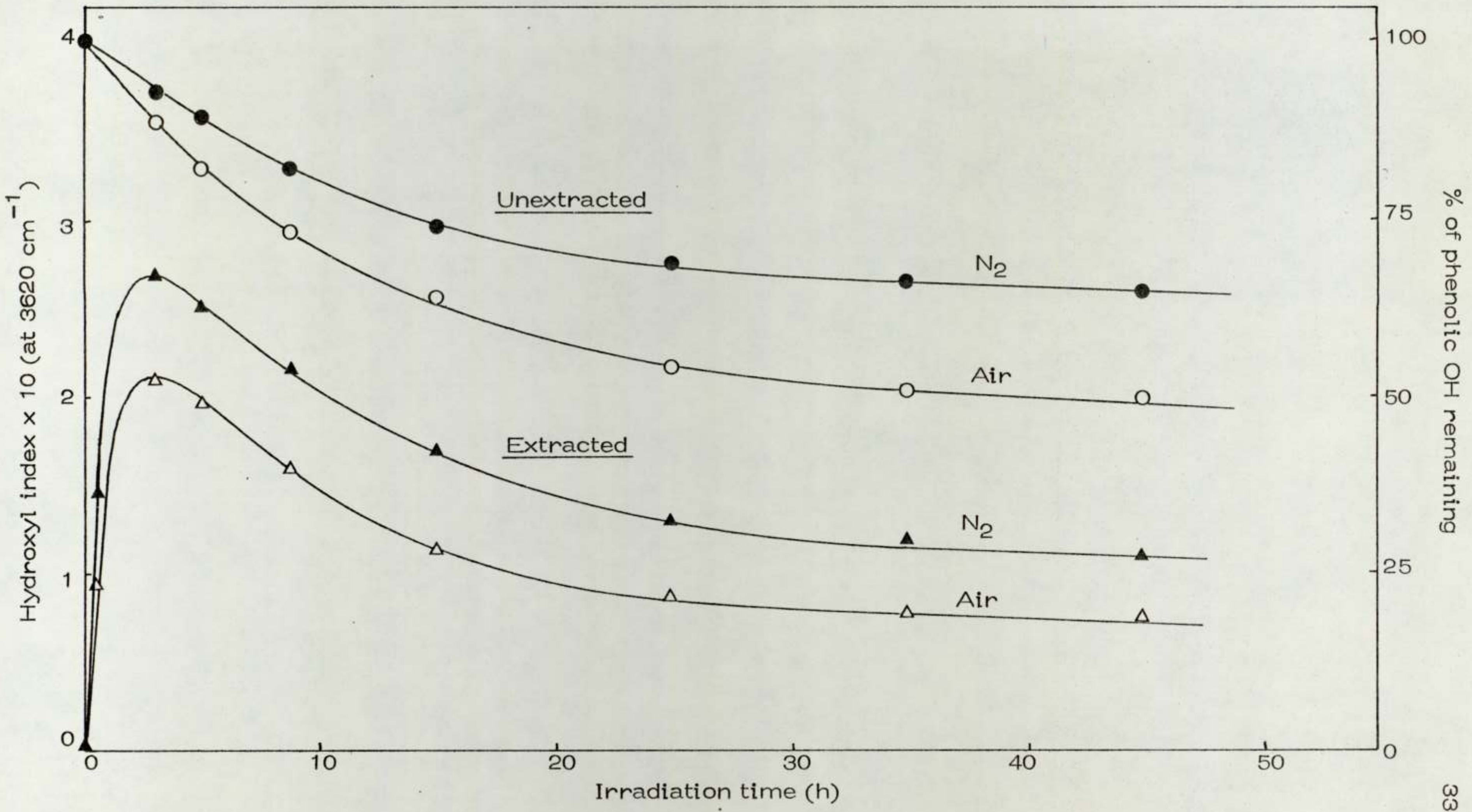


Fig 6.28 Comparison of the variations of phenolic hydroxyl index on uv exposure in nitrogen and air of polypropylene films both before and after extraction (initial conc of BHBM, 2%)

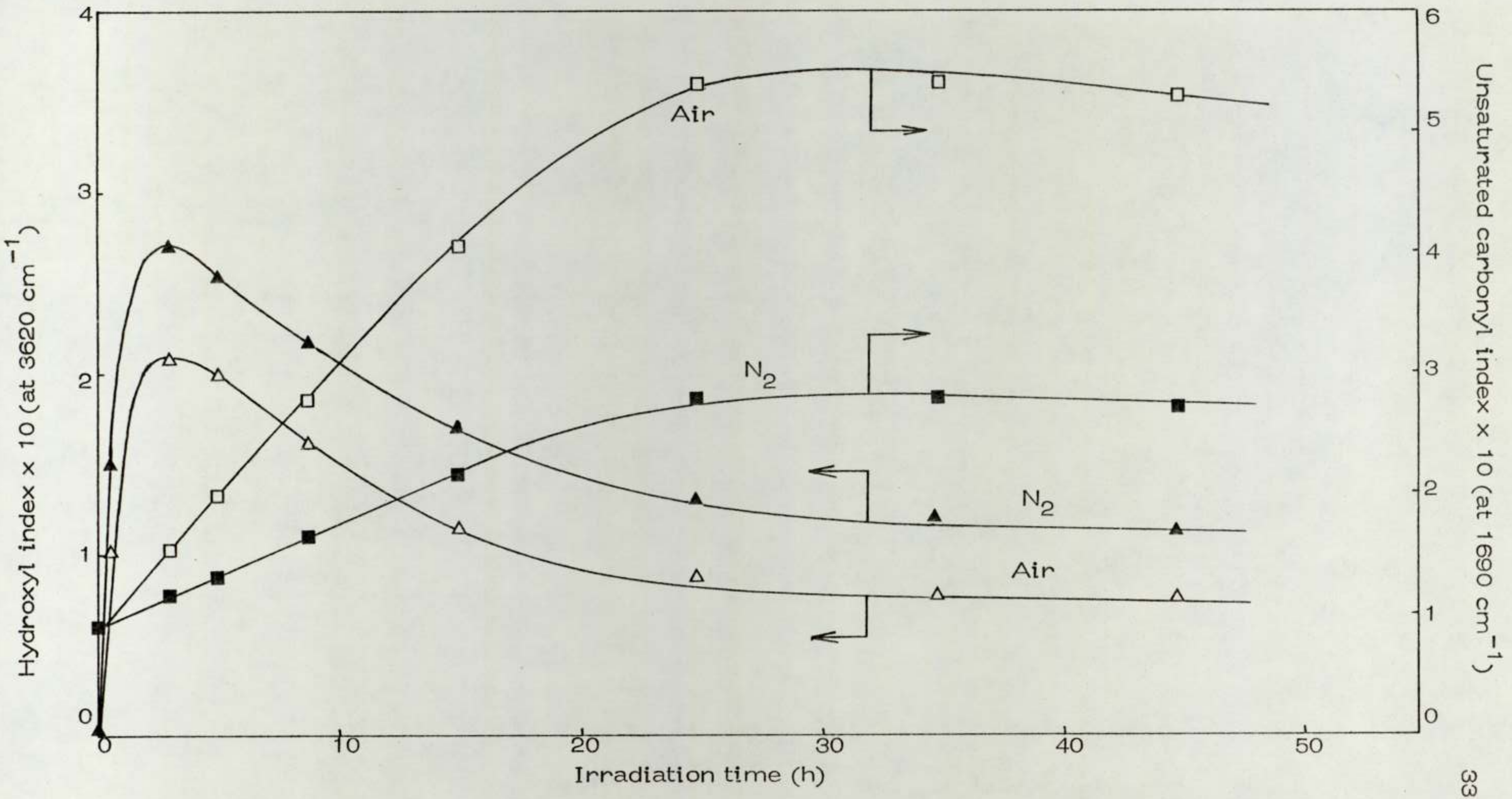


Fig 6.29 Variations of phenolic hydroxyl index and development of unsaturated carbonyl (1690 cm^{-1}) of polypropylene films irradiated in air and nitrogen (conc of BHBM, 2%)

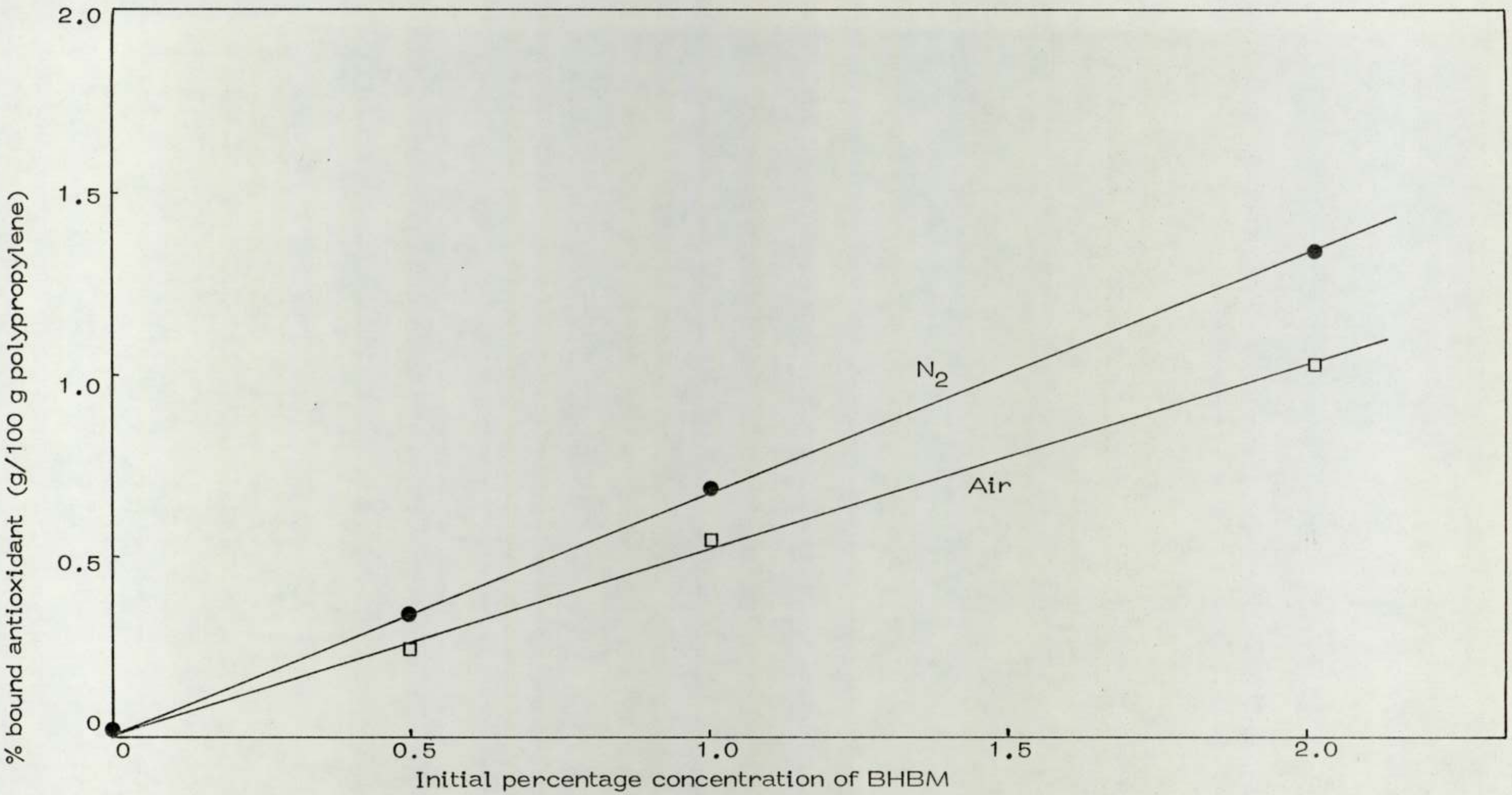


Fig 6.30 Comparison of percentage bound antioxidant in polypropylene films irradiated in air and nitrogen for 3.0 h

Fig 6.30 illustrates that the 2% BHBM sample after extraction contained 1.0 g of bound antioxidant in 100 g of polypropylene. Hence to obtain 0.15 g of bound BHBM (6×10^{-4} mole/100 g), 15 g of the extracted polymer film containing the bound antioxidant would be required. The other 20 g constituted the virgin polypropylene to make up the 35 g for the efficient mixing in the chamber of the torque rheometer at 180°C for 10 mins.

Fig 6.31 compares the thermal ageing performance of polymer films containing BHBM as simple additive and BHBM in bound form subjected to an air flowing environment at 140°C. While the former showed an induction period of 20 h, the latter exhibited a 4-fold improvement of 83 h. Furthermore, Table 6.6 compares the thermal stability (at 140°C) of the polypropylene films containing equimolar concentrations of the commercial antioxidants, the synthesised antioxidant (AOS-C18) and BHBM, both as simple additive and as polymeric form. These unequivocally highlighted the practical utility of the polymeric antioxidant in enhancing the antioxidant substantivity and permanence within the polymer matrix. Of additional significance is the positive contribution shown by the effect of molecular dispersion of the grafted BHBM along the polymer chain in conferring polymer stability in relation to those of the

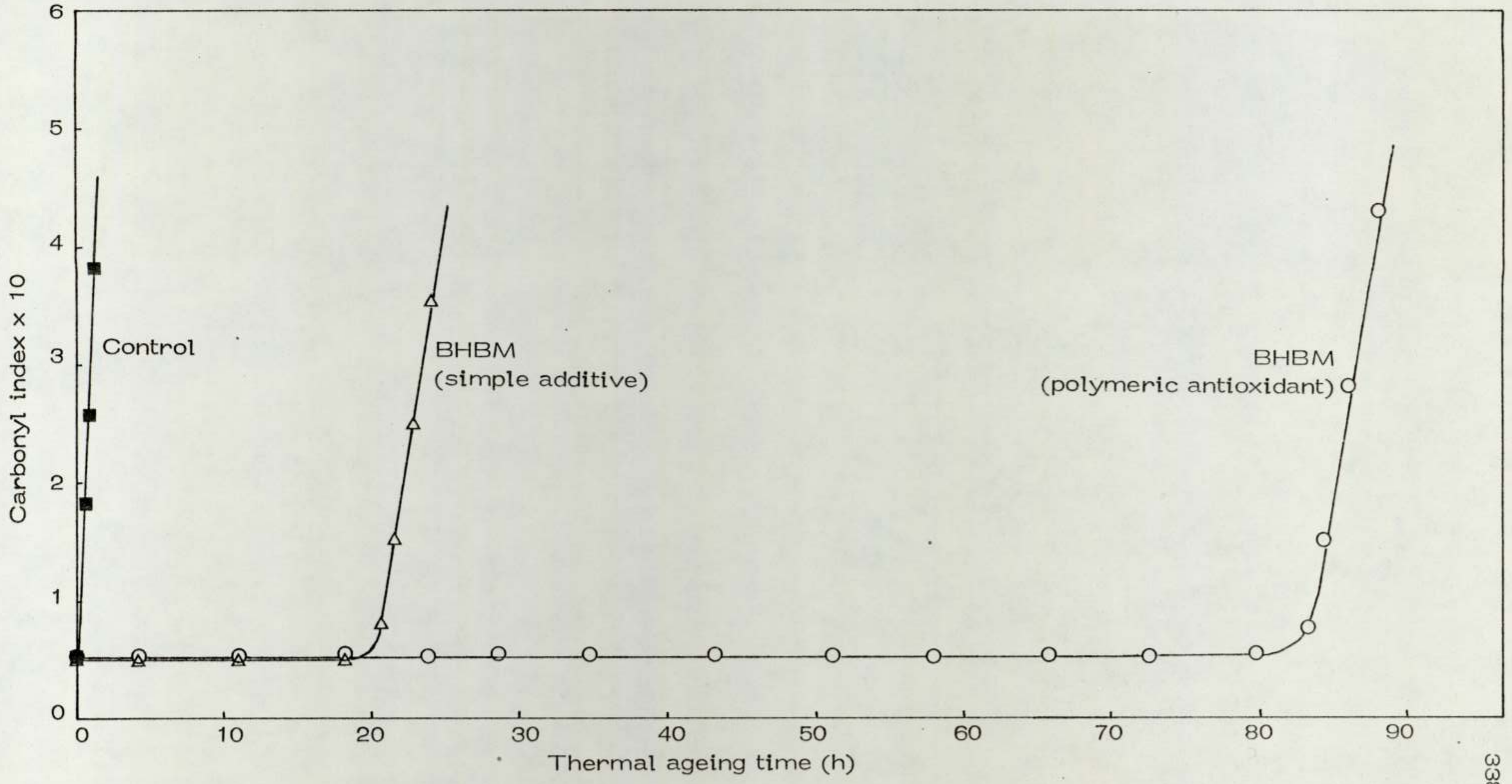


Fig 6.31 Comparison of thermal stability (at 140°C) of polypropylene films containing BHBM as polymeric antioxidant and BHBM as simple additive at equimolar concentration of 6 x 10^{-4} mole/100 g (ca 0.15%)

Table 6.6 Thermal stability of polypropylene films (at 140°C) containing various antioxidants at 6×10^{-4} mole/100 g

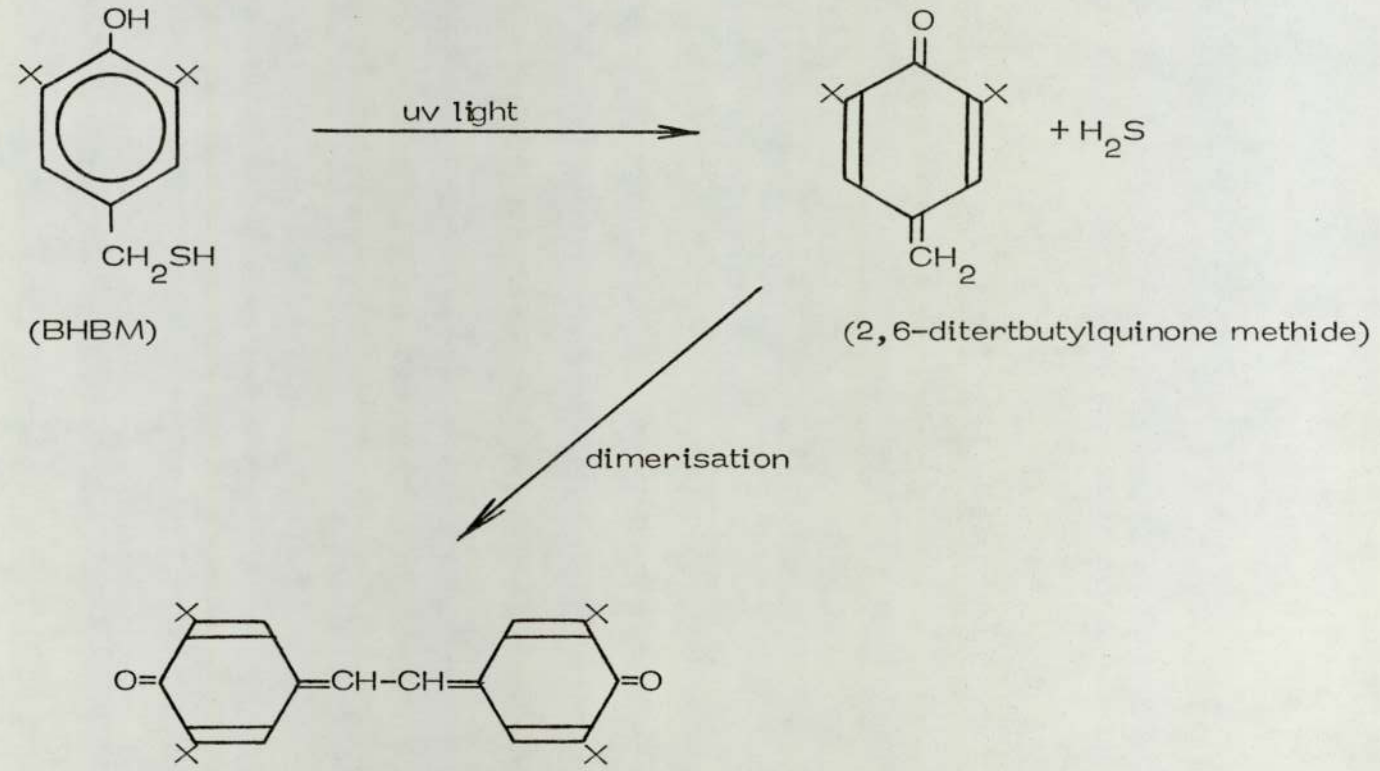
Additive	Induction period, h
None (control)	0.2
TBC	0.4
1076 (before extraction)	92.0
1076 (after extraction)	0.4
AOS-C18	15.0
BHBM (additive)	20.0
BHBM (polymeric)	83.0

simple antioxidant additives.

A model study, carried out on a 2% (w/v) BHBM solution in chlorobenzene initially flushed with oxygen-free nitrogen and exposed to uv light, resulted in the formation of an orange-yellow colouration after only 1 h of irradiation. Unsealing the quartz tube and testing its vapour with lead acetate paper resulted in its blackening, suggestive of the presence of hydrogen sulphide. This is attributable to the probable photolysis of BHBM leading to the 1,6-elimination of hydrogen sulphide and the dimerisation of the quinonemethide as shown in reaction Scheme D.

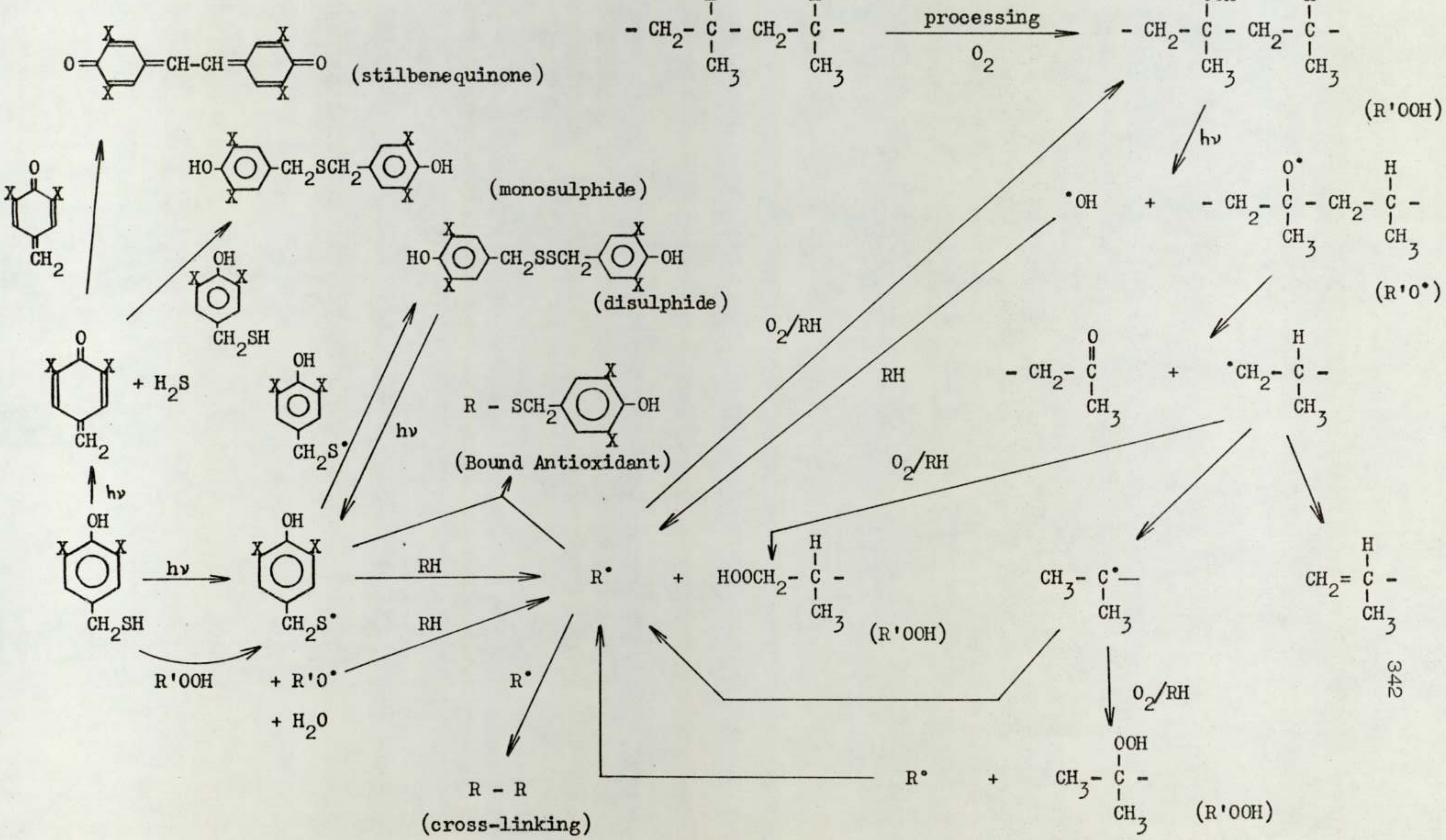
For the uv-initiated grafting of BHBM to the processed polypropylene film, a possible mechanistic route may involve the reactions shown in Scheme E in which thiyl radicals, formed as a consequence of the photolysis of BHBM, underwent radical-radical coupling with the macro-alkyl radicals which were induced and are normally formed during the photo-oxidation process of the polymer. Moreover, thiyl radical formation could also be attributable to the redox reaction of BHBM with hydroperoxide, even though this route is envisaged to provide minimal contribution owing to the expected low level of the

Reaction Scheme D



(3,5,3',5'-tetratert-butylstilbene-4,4'-quinone)
(orange-yellow colour)

Reaction Scheme E



hydroperoxide concentration. The thiyl radicals could undergo competing reactions via dimerisation to form the disulphide as well as abstracting hydrogen from the polymer, giving macroalkyl radicals and itself being regenerated to BHBM.

Preceding studies showed BHBM to photolyse to give 2,6-di-tert-butylquinonemethide and hence the stilbenequinone. Again this type of reaction would be expected to occur in the polymer system and explained the yellowish colour formation and the conjugated carbonyl (1690 cm^{-1}) development. In addition, the quinone methide, apart from dimerising to give the stilbenequinone, would be envisaged to react with BHBM to form the monosulphide.

The uv grafting of BHBM carried out in air showed a lower level of binding reactions in relation to those carried out in nitrogen and the reaction scheme attempts to explain these phenomena in terms of the competing reaction of the macroalkyl radicals for oxygen.

CHAPTER SEVEN

CONCLUSIONS

The studies on the series of synthesised sulphur antioxidants of increasing molecular weight and containing hindered phenolic moiety have shown the insignificant influence of the additives' molecular weight on their thermal stabilising performance, indicating their similar level of intrinsic chemical activity. This only applies where physical interactions between the antioxidant and the oxidising substrate are minimal as manifested in the liquid oxidation studies of decalin.

However, studies in the polymer systems under both enclosed and flowing environments showed markedly differing behaviour, exemplifying the important role played by the antioxidant-polymer physical interactions in bringing about overall polymer stability. Notable factors that exert an overriding importance include the antioxidants' compatibility, solubility and volatility phenomena. In addition, the antioxidants' influence on polymer photostability and processing melt behaviour varied, primarily due to the physical characteristics of the additives.

Analogous studies were also carried out on the second series of sulphur antioxidant of differing molecular weight but containing the 2-hydroxybenzophenone moiety. Despite their outstanding inherent uv absorbance and peroxidolytic activity, their limited solubility in polypropylene proved to be their main shortcoming as polymer stabilisers.

It was also found that the synergistic studies of 3,5-di-tertiary-butyl-4-hydroxybenzyl mercaptan (BHBM) and 3,5-di-tertiary-butyl-4-hydroxylauryl sulphide (AOS-C12) with 2-hydroxy-4-oxyoctylbenzophenone showed superior synergistic activity in relation to those of the commercial phenolic antioxidantsviz 1076 and TBC. This was rationalised on the basis of the known peroxide-decomposing activity of the sulphur antioxidants.

Further improvement of antioxidant substantivity and compatibility was investigated on the basis of the polymer-binding reactions of TBC and BHBM and the simultaneous formation of higher molecular weight antioxidant derivatives during the processing melt treatments. It was found that even though the extent of the binding reactions was low, the formation of the higher molecular weight derivatives offered significantly greater permanence and stabilisation in relation to the parent compounds.

A uv-initiated binding reaction of BHBM to polypropylene films was found to be successful and a maximum level of grafting was noted after 3 h of uv irradiation. It was also found that reactions carried out in inert nitrogen atmosphere appeared to be facilitated. The technological efficacy of the bound antioxidant was demonstrated by the successful application of the masterbatch technique of the polymeric antioxidant to virgin polypropylene whose thermal stability outperformed those containing simple antioxidant additives.

Current trends indicate that the requirements for polymers will continue to get more demanding, calling for higher thermal processing treatment, longer service life and increased use of recycled polymers. These,in their turn, call for more effective and permanent antioxidants. A bright future for high molecular weight and polymer-bound antioxidants seems certain. For as long as there is the need to squeeze every bit of value from the petrochemical supplies as a consequence of the rapidly escalating costs of raw materials for the polymer industry, there will be the demand for these antioxidants.

SUGGESTIONS FOR FURTHER WORK

A retrospective view of the work reveals gaps which appear to justify further work. These include:

(1) Synergistic studies of the phenolic antioxidants with HOBP, as described in Chapter 5, show the 0.2 mole fraction of antioxidant to exhibit the maximum synergistic activity. Further investigation on the 0.1 mole fraction antioxidant would further confirm this finding.

(2) The mechanisms of the binding reactions of TBC and BHBM with polypropylene remain tentative and further model studies would presumably disentangle the chemistry involved. 3-methyl-pentane could be used as a model for polypropylene.

(3) Thin layer chromatography (TLC) studies of the film extracts would identify the molecular species formed and would presumably throw more light on the reaction mechanisms involved. Furthermore, direct incorporation of 3,5,3',5'-tetra-tert-butyl-stilbene-4,4'-quinone into polypropylene and evaluating its thermal stability would substantiate the protective role played by the additive.

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