THE MECHANISMS OF MELT STABILISATION OF POLYOLEFINS

by

ROUHALLAH BAGHERI

Submitted for the degree of Doctor of Philosophy

of

The University of Aston in Birmingham

NOVEMBER 1981

The University of Aston in Birmingham

THE MECHANISMS OF MELT STABILISATION OF POLYOLEFINS

A thesis submitted for the degree of Doctor of Philosophy
by ROUHALLAH BAGHERI
November 1981

SUMMARY

The effects of melt stabilisers on the oxidative degradation of polyolefins (polypropylene, low density polyethylene) have been studied under a variety of processing conditions. The changes in the both chemical and physical properties of unstabilised polymers occurring during processing were found to be strongly dependent on the amount of oxygen present in the mixer.

2,6,3',5'-tetra-tert-butyl-4'-phenoxy-4-methylene-2,5-cyclohexadiene-1-one (galvinoxyl), iodine, nitroxyl radicals and cupric stearate were found to be very efficient melt stabilisers particularly when processed in a restricted amount of air. The mechanisms of their melt stabilising action have been investigated and a common cyclical regenerative mechanism involving both chain-breaking electron acceptor (CB-A) and chain-breaking electron donor (CB-D) antioxidant activity was found to be involved in each case.

2,6,3',5'-tetra-tert-butyl-4'-hydroxy phenyl-4-methylene-2,5-cyclohexadiene-1-one (hydrogalvinoxyl), 4-hydroxy, 2,2,6,6-tetra methyl-N-hydroxy piperidine and hydrogen iodide were formed together with olefinic unsaturation in the substrates during the melt processing of the polymers containing galvinoxyl, 4-hydroxy, 2,2,6,6-tetra methyl piperidine oxyl and iodine respectively.

No bonding of the melt stabilisers to the polymers was found to occur. Cupric stearate was found to undergo a similar redox reaction during its action as a melt stabiliser with the formation of unsaturation in the polymer. Evidence for the above processes is presented.

The behaviours of melt stabilisers in the subsequent thermal and photo-oxidation of polyolefins have also been studied.

Galvinoxyl which is very effective under both mild and severe processing conditions has been found to be an effective antioxidant during thermal oxidation (oven ageing) and it is also moderately good as a photo-stabiliser. Iodine and cupric stearate acted efficiently during melt stabilisation of polymers, however they were both ineffective as thermo-oxidative antioxidants and UV stabilisers. Although the melt stabilisation effectiveness of stable nitroxyl radicals (e.g. 4-hydroxy, 2,2,6,6-tetra methyl piperidineoxyl and Bis-(2,2,6,6-tetra methyl-4-piperidinyl-N-oxyl) sebacate) is not as high as that of galvinoxyl during processing particularly in excess of air, they have been found to be much more efficient as UV stabilisers for polyolefins. The reasons for this are discussed.

KEY WORDS: Polyolefins, Melt Degradation, Melt Stabilisation, Photo-stabilisation, Regenerative Antioxidants

ACKNOWLEDGMENTS

I would like to express my gratitude to Dr K B Chakraborty and Professor G Scott for their encouragement and advice throughout the course of this study.

I am grateful to the Ministry of Science in Iran for partial support financially and also to the technical staff of the Chemistry Department of Aston University for their co-operation.

Thanks to my wife for enduring discomfort during the course of the work.

CONTENTS

CHAPTER FIVE PHOTO-OXIDATION OF POLYOLEFINS 197

REFERENCES

SUPPORTING PUBLICATIONS

1. R Bagheri, K B Chakraborty and G Scott, Chem and Ind, 865 (1980)
2. R Bagheri, K B Chakraborty and G Scott, Poly Degr and Stability, in press.

LIST OF TABLES

CHAPTER ONE

INTRODUCTION

1.1 Autoxidation of Polyolefins

1.1.1 General Degradation Processes

All polymers are susceptible to oxidative degradation by elemental oxygen on exposure to environmental condition. Scott(1) points out that the most important accelerating environmental influences apart from oxygen which are deleterious to polymer stability are heat, light, contamination by metal ions, ozone and mechanical deformation.

Degradation of polymers is generally considered to occur in two principal stages(2), the first is manifested during processing operations characterised by high temperature thermal treatment and mechanical shear (mechano-oxidation), the other occurs during the service life of the fabricated articles subjected to relatively mild or intermittent oxidative attack.

As a result of autoxidation undesirable changes occur in the physical, mechanical and electrical properties of polymers. The nature of the degradation reactions varies in rate and extent depending on the chemical (3) and physical (4) structure of the polymers, the presence of impurities (5,6) and the environment (1) to which they are exposed. The presence of a 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 impurities such as transition metal ions from polymerisation and the hydroperoxide/ carbonyl group formed during processing treatments.

Autoxidation is undesirable in the majority of cases because of the deterioration in properties of the polymeric materials. It is therefore necessary to stabilise materials like, oils and polymers against atmospheric oxidation (7) and this is achieved by the use of additives known as antioxidants.

1.1.2 Mechanism of Oxidative Degradation of Polymers

All oxidative degradation processes (both thermal and photo) take place via the same radical chain autoxidation mechanism originally proposed by Bolland and his co-workers (8-10).

A reaction scheme to explain the kinetic features of this reaction (autoxidation) applicable to saturated hydrocarbons and polymers(7) can be summarised as follows:

Initiation:

$$RH + O_2 \longrightarrow R^{\bullet} + {}^{\bullet}OOH$$

$$ROOH \longrightarrow RO^{\bullet} + {}^{\bullet}OH$$

$$\text{or } 2\ ROOH \longrightarrow RO_2^{\bullet} + H_2O + RO^{\bullet}$$

Many papers have been published by Scott and co-workers(11-20) to prove that polymeric hydroperoxides are the main initiators for the process of oxidative degradation of polymers both during thermal oxidative degradation and UV initiated degradation. The evidence provided by other workers, Carlsson and Wiles(21-25), Shelton(26) support the hydroperoxide theory. Therefore the initial products of autoxidation are hydroperoxides and derived carbonyl compounds and the initial rates of both thermal and photo-oxidation are primarily dependent on the concentration of the former(27,28).

Propagation:

$$R^{\bullet} + O_2 \xrightarrow{(a)} RO_2^{\bullet}$$

$$RO_2^{\bullet} + RH \xrightarrow{(b)} RO_2H + R^{\bullet}$$

Termination:

$$2RO_2^{\bullet} \xrightarrow{(2a)} \text{Inert Products}$$

$$2R^{\bullet} \xrightarrow{(c)} \text{Inactive Products}$$

$$ROO^{\bullet} + R^{\bullet} \xrightarrow{(d)} \text{Inactive Products}$$

At normal oxygen pressure the rate of reaction (a) is so fast that the concentration of the alkyl peroxy radicals, $RO_2^{\bullet}$, is very much higher than the alkyl radicals, $R^{\bullet}$(29) and hence the reaction (b) is the rate determining step. Under these circumstances the reaction rate depends on the structure of the hydrocarbon (RH).

The easier it is for hydrogen to be abstracted from RH, the higher will be the rate of oxidation. The ease of hydrogen abstraction from different types of hydrocarbons has been shown by Bolland(30) to increase in the following order

prim C-H $<$ sec $<$ tert $<$ allylic $<$ H-C aromatic

A practical consequence of high concentration of alkylperoxy radicals is that termination occurs predominantly by reaction of alkylperoxy radical species (2a).

There are however, some exceptions to this generalisation:

1) When oxygen is deficient in the system⁽²⁹⁾ as in the barrel of a screw extruder.

2) When the rate of initiation is high compared with the rate of diffusion of oxygen into the polymers as in UV initiated oxidation or in mechano-chemical oxidation e.g. during flexing of rubbers⁽³¹⁾ In all cases the alkyl radical concentration will be higher than in normal oxidation and the termination steps (c) and (d) will assume greater importance.

1.1.3 Mechano-Degradation of Polymers During Processing

Shear, heat and oxygen act together during the processing operations and the determination of the individual role of these factors is rather complex. If we consider a shearing force in a bulk polymer on a portion of the molecular chain, then the internal stresses set up during deformation will be redistributed between the principal chemical-valency bonds in the chains and secondary intermolecular bonds associated between the chains⁽³²⁾. The dissipation of this energy will depend on the relative energies of the chemical principal valency bonds in the chains and of the intermolecular interactions. If the cumulative strength of the intermolecular interactions is greater than that of the chemical principal valency bonds then scission of these bonds will be energetically favoured.

In polypropylene the relative large crystallites are bound together in such a way that large stress concentrations inevitably develop during the processing leading to destruction of the crystalline regions resulting in a progressive change in structure when it is molten(33). In mechano-degradation the following structural changes occur in polymers:

1) Reduction in molecular weight.
2) Alteration in solubility and plasticity.
3) Variation in molecular distribution and polymer configuration and strength.

Mechano-oxidation of rubber to produce a product of lower viscosity has been practiced by the rubber industry as part of the polymer fabrication processes. Without such a treatment it would be impossible to incorporate compounding ingredients which are essential to the final performance of the fabricated products(34). Ceresa and Watson extended these studies to plastics(35). They were able to show that most polymers undergo a rapid reduction in molecular weight on cold mastication. The polymer molecules (R-R) undergo shear induced fracture to produce macroalkyl radicals(36,37,35), $R^{\cdot}$, under most commercial processing conditions ($R - R \xrightarrow{\text{shear}} 2R^{\cdot}$) which react rapidly with oxygen to yield alkylperoxy radicals ($R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}$). In the presence of oxygen two types of free radicals have been shown to be formed in milled polymers by e.s.r technique (38). Since both radicals are unstable and their spectra fade rapidly with time, they can be studied only at low temperatures under vacuum (40). Continuous processing leads to a build up of polymeric hydroperoxides (34) and that they are responsible for a subsequent decrease in stability (UV, thermal) of the fabricated polymer. Scott and co-workers (41-43) have shown that during the processing of PVC the initial degradation is induced by the mechano-chemically formed macroradicals and oxygen reacts rapidly with alkyl radicals with the formation of alkylperoxy radicals which subsequently lead to the formation of hydroperoxides. It has been shown (44) that the formation of hydroperoxides during the processing of PVC is primarily responsible for its subsequent behaviour during photo-oxidation. The results emphasise that (42) under processing and oxidative technological conditions the main causes of PVC degradation are largely to be sought in mechano-chemically induced chemical modifications rather than in structural defects arising during the course of polymerisation.

1.2 Stabilisation Mechanisms of Polyolefins

Susceptibility of polymers to oxidative degradation could be resolved in one of the following ways:

(1) by the removal of sensitising impurities within the polymers that are known to initiate and accelerate polymer degradation e.g. hydroperoxides(28), carbonyl groups and transition metal ions.

(2) by the incorporation of chemical additives(45,46) that would inhibit the degradation processes; this method is widely adopted in commercial practice in the stabilisation of polymers.

(3) by modification of polymer structure or changing to polymers that are more resistant to degradation(47).

To evaluate antioxidant effectiveness the following factors need to be considered(48):

(1) The intrinsic activity (inherent behaviour) of the antioxidants, which is structural dependent.

(2) Compatibility or solubility of the antioxidants in the polymers.

(3) Volatility and solubility of the antioxidants in H_2O or other solvents with which the polymer comes into contact during service (or rate of loss).

At high temperatures or under reduced pressures antioxidants may be lost by volatilisation. The use of high molecular weight antioxidants reduces both volatility and solubility.

To determine antioxidant distribution in polypropylene as a measure of compatibility, Billingham and co-workers(49) in their studies on a nickel-containing additive using a UV microscopy technique, showed that additive resides predominantly in the amorphous region. It was suggested that this behaviour should generally be applicable to other additives in a crystalline polymer. 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. The accumulation of antioxidants in the amorphous phase of the polymer matrix appears to be advantageous since Hawkins(50,51) has demonstrated that the major oxidation reactions occur primarily in the less ordered regions.

There are two ways in which an antioxidant functions, the first is by a radical chain-breaking mechanism in which alkylperoxy and alkyl free radicals (the two main species in propagation step) are trapped. The second is called the preventive mechanism since it prevents the initiation of the free radical chain mechanism.

1.2.1 Chain Breaking Antioxidants

The removal of alkyl and alkylperoxy radicals are potential chain breaking processes(52). The former involves an electron acceptor (oxidising agent) and the latter an electron donor(53) (reducing agent).

chain-breaking (acceptor mechanism) (CB-A)

chain-breaking (donor mechanism) (CB-D)

a) Chain-breaking Donor Mechanism (CB-D)

Hindered phenols and secondary amines are widely used as chain-breaking donor antioxidants in polymers and other organic compounds(7,54,55). The antioxidant activity of phenols and amines is associated with their ability to donate electrons to alkylperoxy radicals(7), resulting in consumption of the inhibitor (InH).

$$RO_2^{\bullet} + InH \longrightarrow ROOH + In^{\bullet}$$

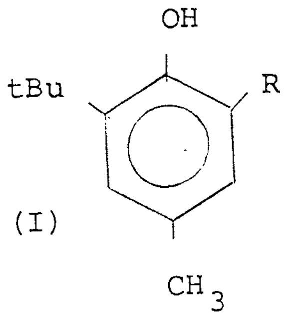
Inhibitor radicals may recombine or react with other peroxy radicals; consequently the stoichiometric coefficient (f) of the inhibitor is normally 1 or 2.

$$I^{\bullet}n + I^{\bullet}n \longrightarrow In - In \qquad f = 1$$

$$I^{\bullet}n + RO_2^{\bullet} \longrightarrow ROOIn \qquad f = 2$$

(Scheme I)

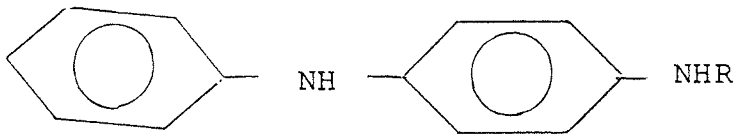
The following hindered phenols (I) and aromatic amines (II) are the two best known classes of commercial antioxidants that exhibit the CB-D mechanism$^{(45)}$.



(I)

R = CH_3(TBX)

R = tBu(TBC)



(II) R = isopr (IPPD)

R = ph (DPPD)

IPPD = isopropylphenylenediamine

DPPD = diphenylphenyldiamine

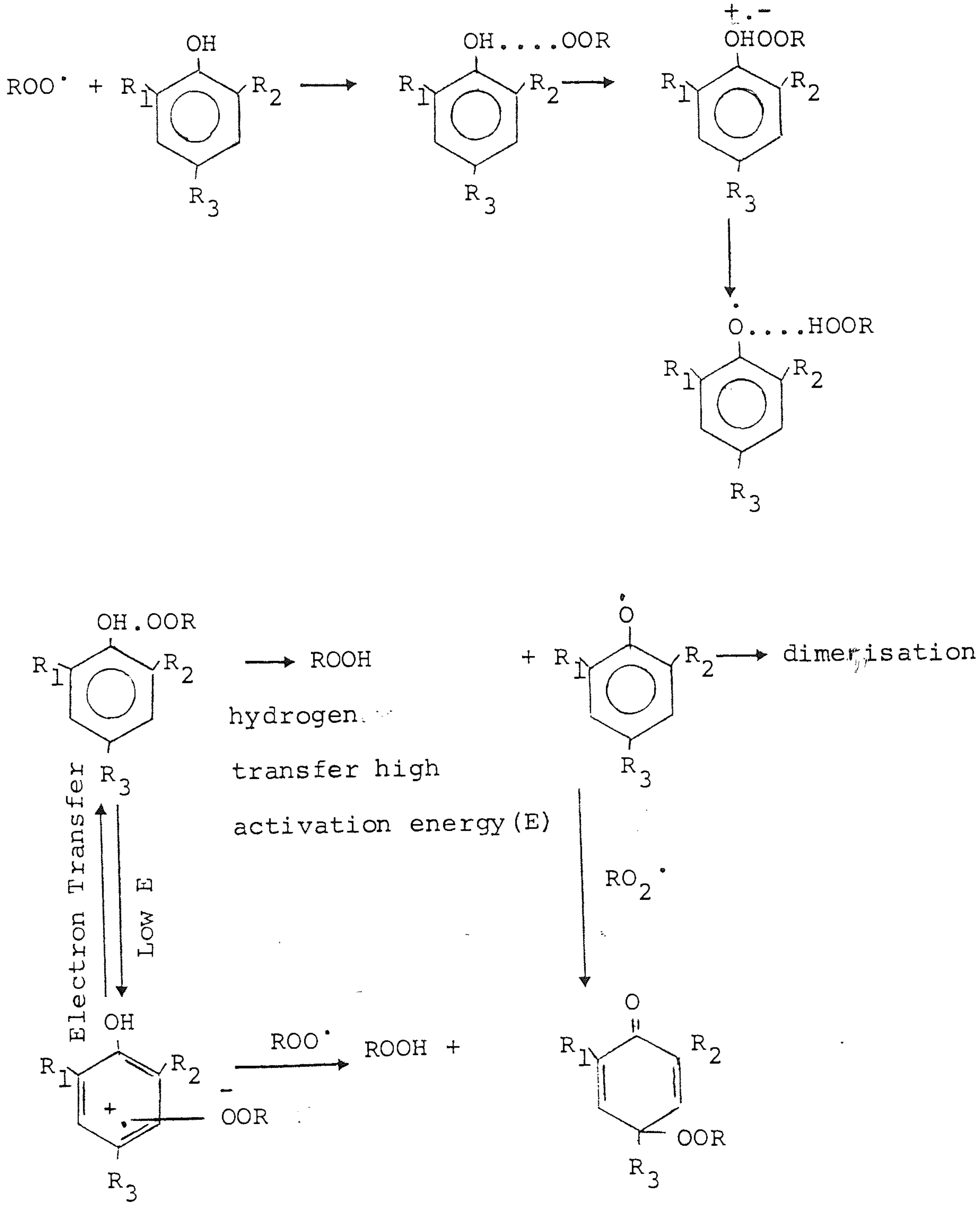
Both phenol and amine antioxidants interfere with the process of autoxidation by transferring either a hydrogen atom or an electron to the alkylperoxy radicals(7). The presence of a reactive (N-H) or (O-H) functional group in these materials, suggests that they compete with the polymer substrate for the peroxy radicals, $RO_2^{\cdot}$, and thus terminate the propagation reaction by transfer of hydrogen to form RO_2H and a stabilised $Ph_2N^{\cdot}$ or PhO. radical.

If the inhibiton mechanism involves hydrogen abstraction as a rate determining step, then replacement of the reactive phenolic or aromatic hydrogen by deuterium ought to lead to a difference in antioxidant efficiency(56). This is detectable in the case of weak antioxidants in which the activation energy of the hydrogen transfer is appreciable(56). In the case of phenol and aniline the isotope effect is appreciable(56). In accordance with the hydrogen abstraction theory, there is a decrease in isotope effect with increasing inhibitor efficiency.

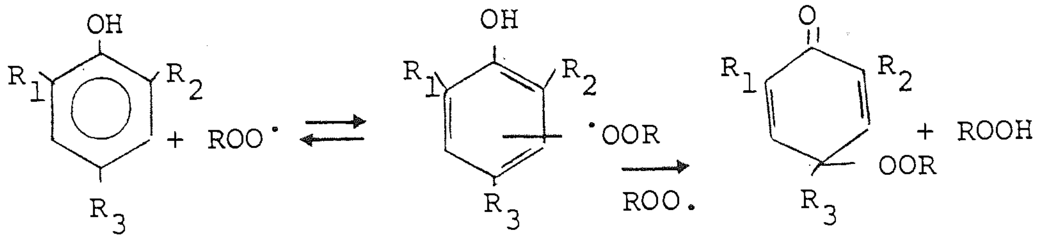
Oxidation of hydrocarbons involves a transition state(56)

$$ROO. + H{-}R \longrightarrow ROO^{\cdot}H{-}R \longleftrightarrow RO\overset{-}{O}H{-}\overset{+}{R}^{\cdot} \longleftrightarrow ROOH^{\cdot}R$$

By analogy it seems likely that a similar transition state must be involved in the formation of a phenoxy radical by any electron abstracting agent (56) (scheme II).



Overall mechanism of inhibited oxidation:



(Scheme II)

The evidence for radical complex formation is stronger for arylamine antioxidants than it is for phenols(56). It has been shown that(54,58) the mechanism of chain-stopping action by amine and phenolic antioxidants in the inhibited autoxidation of polymers is now clearly established on the basis of the deuterium isotope effects in the initial stage of retarded autoxidation of purified Cis-1,4-polyisoprene.(57) There is, therefore no need to postulate a reversible complexing of $RO_2^{\cdot}$ with the antioxidant. If such complexing occurs, it would be an additional but not essential feature, which may occur prior to the rate-controlling hydrogen transfer reaction.

In the relation between the activity of phenolic antioxidants and their structure it has been shown that(52);

1) electron releasing groups (such as alkyl,alkoxy, etc.) in the ortho and para positions markedly increase the antioxidant activity (this is also

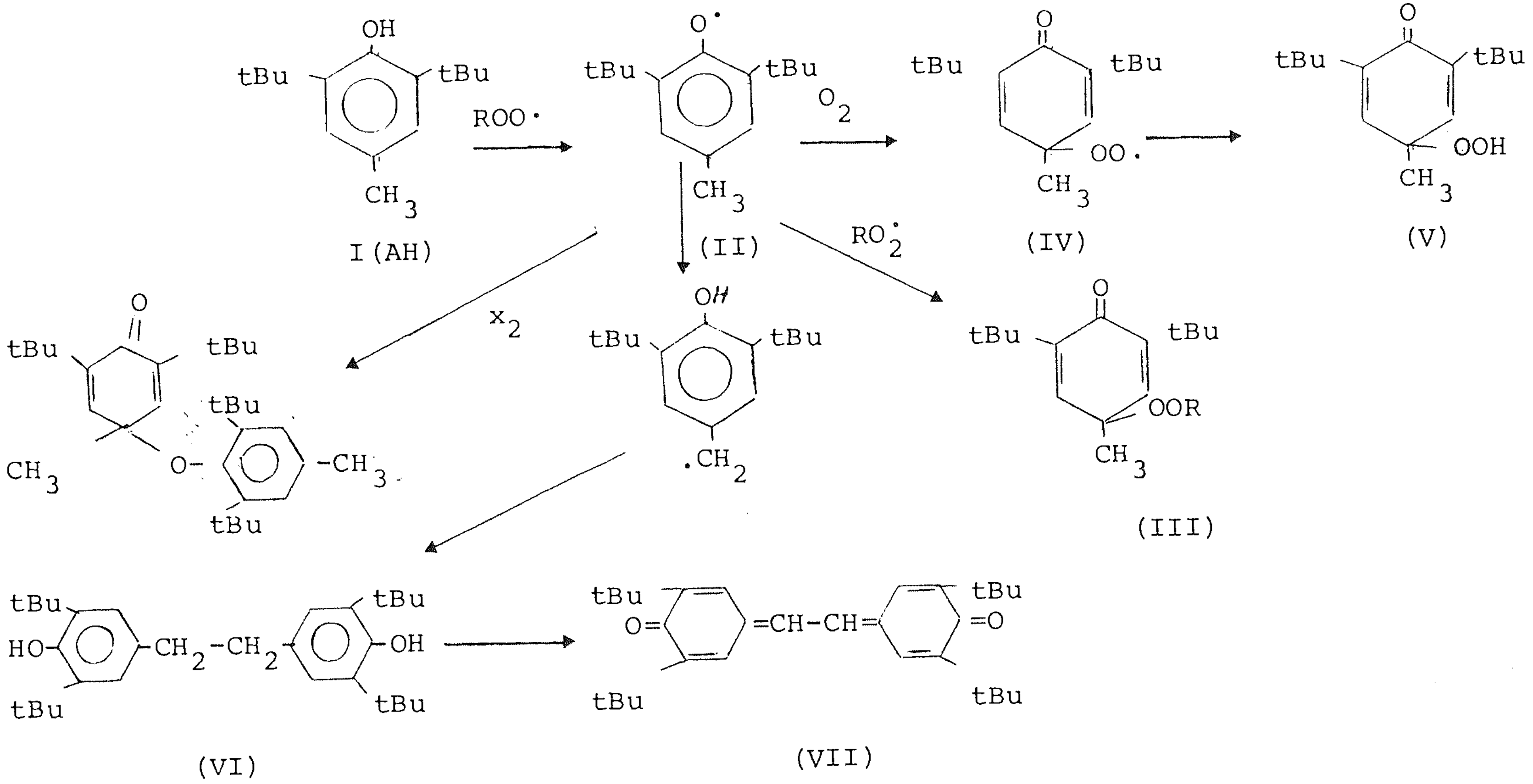
true of substituents in the meta positions although much less so than in ortho and para).

2) electron attracting groups (e.g. nitro, carboxyl, halogen, etc.) decrease activity,

3) α- branched ortho alkyl groups considerably increase antioxidant activity whereas such groups in para decrease it. In amine antioxidants N-aryl and N-alkyl substituents and electron releasing groups in the para position of the benzene ring increase antioxidant activity.

The products formed by further reaction of the initially formed phenoxy radicals are complex, (scheme III) and they may exhibit some positive activity in autoxidation (59).

The ethylene bisphenol (VI) is as effective an antioxidant as the starting phenol and the stilbene quinone (VII) is effective in oxygen deficient atmospheres. On the other hand, the peroxydieneones (III) and (V) are potential pro-oxidation products, particularly at high temperatures, because of the lability of the peroxidic bond.



Scheme (III)

Aromatic primary and secondary amines inhibit the autoxidation in the same way as phenols (7). Secondary oxidation products from aromatic amines are nitroxyl radicals (60-67) which are believed to be formed by the following reactions (scheme IV)

$$\mathrm{ROO.} + \mathrm{Ph_2NH} \longrightarrow \mathrm{ROOH} + \mathrm{Ph_2N^{\bullet}}$$ Iminoxyl radical

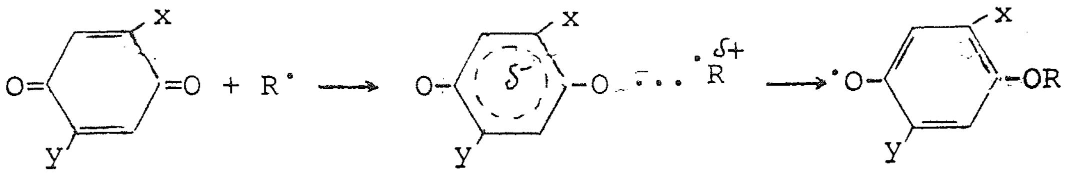
$$\mathrm{Ph_2N.} + \mathrm{ROO.} \longrightarrow \mathrm{RO.} + \mathrm{Ph_2NO^{\bullet}}$$

Scheme (IV)

Nitroxyl radicals are not formed from primary and tertiary amines but only from secondary amines.

b) Chain-breaking Acceptor Mechanism (CB-A)

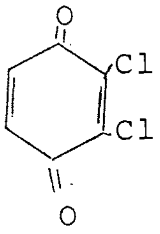
Polymer alkyl radicals are not powerful oxidising agents but they are themselves readily oxidised, so a variety of oxidising agents are capable of removing alkyl radicals from an autoxidising system (45). They include quinones, nitro compounds, and a variety of stable radicals of which phenoxyls and nitroxyls are the most important. A consideration of the transition state in the reaction of an alkyl radical with a quinone reveals the molecular requirements for an effective CB-A antioxidant.

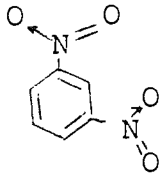


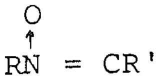
Since the transition state involves partial transfer of an electron to the aromatic π bond, electron attracting and delocalising substituents (x,y) both increase antioxidant activity. Similar principles apply to other well-known classes of CB-A antioxidants.

Typical CB-A antioxidants are:

(1) oxidising agents as alkyl traps

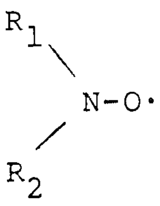




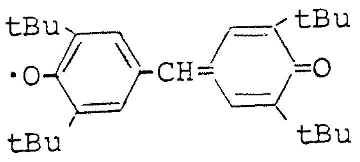


$$R\overset{\overset{O}{\uparrow}}{N} = CR'$$

(2) stable radicals as alkyl traps



nitroxyl



galvinoxyl (G$^{\cdot}$)

$R\text{-}S\text{-}\dot{O}$

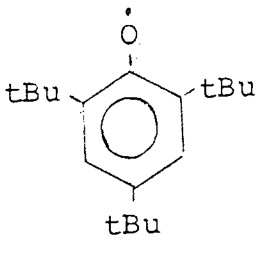
sulphoxyl

Stable Free Radicals as Alkyl Traps

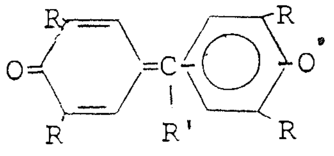
a) Stable Phenoxy Radicals

For the production of stable phenoxy radicals, it is necessary that the reactive ortho- and para-positions be blocked by suitable groups which give increased resonance stabilisation or steric protection. Some of these free aryloxy mono and diradicals, listed below, (I)$^{(68,69)}$, (II)$^{(70-72)}$ and (III)$^{(73)}$ are coloured and stable both in solution and in the solid$^{(74)}$.

Aryloxy radicals with a heteroatoms, as illustrated by examples of the nitrogen - containing radicals (IV)$^{(75)}$ and (V)$^{(76)}$, which are very stable to oxygen and exist in the solid state, and those containing phosphorus (VI)$^{(77)}$ and sulphur (VII)$^{(78)}$, which have been generated in solution.



(I) Solid and Solution, blue

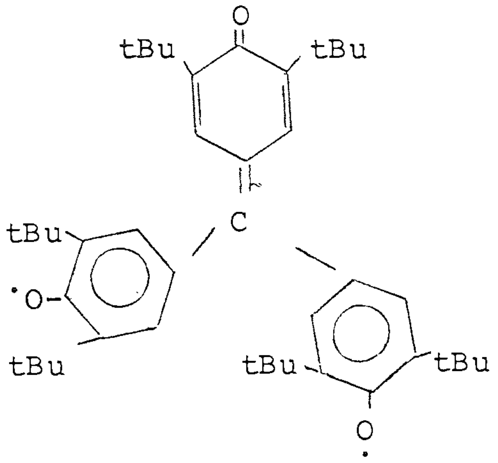


(II) Solid and Solution, coloured

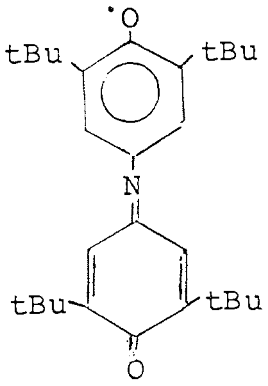
(a) R=t-Bu, R'=H

(b) R=t-Bu, R'=Ph

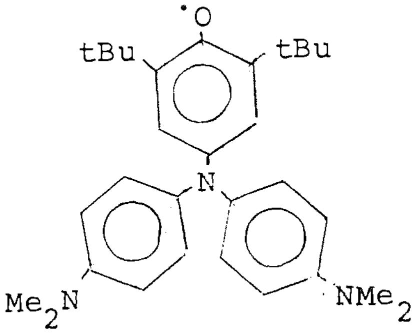
(c) R=OMe, R'=H



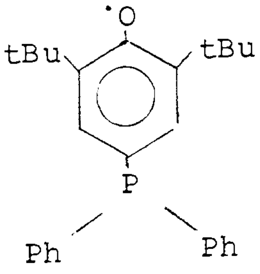
(III) Solid and Solution, deep purple



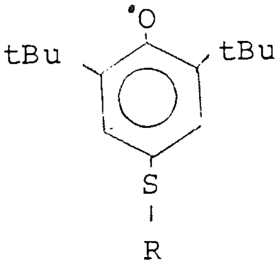
(IV)



(V)



(VI)



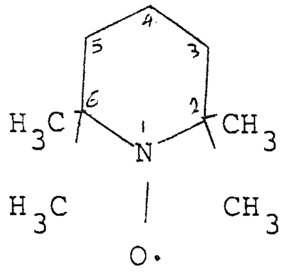
(VII)

R=Me, t-Bu, Ph

Stable phenoxy radicals are prepared by oxidising the corresponding phenols using oxidising agents capable of one-electron abstraction (79,80a), such as lead dioxide (80b), silver oxide, manganese dioxide, ferric ions, alkaline potassium ferricyanide (81). Phenoxy radicals are paramagnetic and usually show in their infra red spectra a broad strong band in the 1560 - 1600 cm^{-1} region (74) (which probably arises from the contribution of the quinonoid resonance structures). The electronic spectra of phenoxy radicals are quite different from those of the parent phenols and show several maxima in the ultra violet and visible regions (74). These bands and the characteristic colours of most phenoxy radicals represent further evidence for the contribution of quinonoid and dipolar resonance structures.

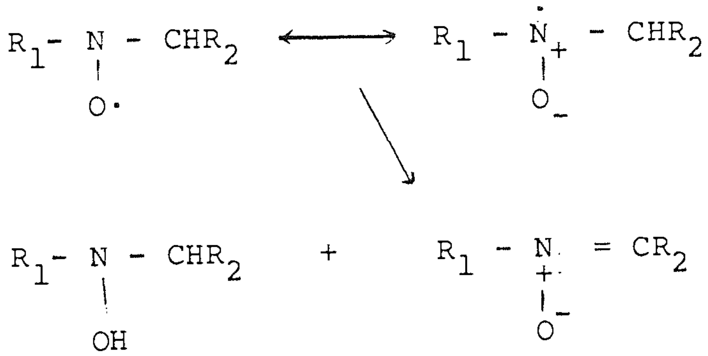
b) Nitroxyl Radicals

It has been shown (82,83) that free nitroxyls having no α-hydrogen atoms are stable free radicals. For example, piperidine-1-oxyl is unstable, but the compound completely alkylated in positions 2 and 6 of the ring is stable.



(I)

The substituents are not for stability reason; what is important for the nitroxyl to be stable is that it should not be capable of valence tautomeric transformations which are the conditions of subsequent disproportionation leading to hydroxylamine and nitrone formation in the following way(84,85)



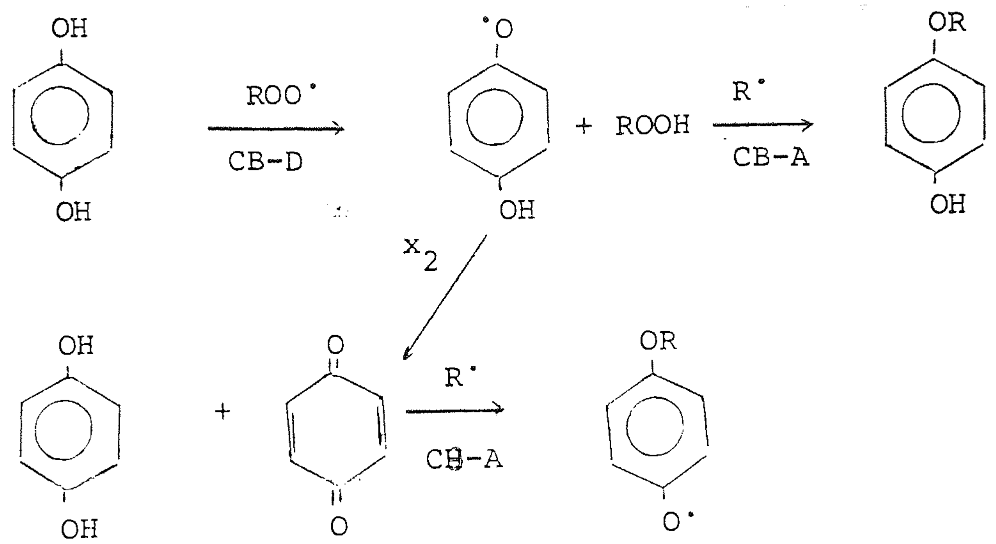
The e.s.r. spectrum of the radical (I) dissolved in benzene, chloroform, heptane, and tetrahydrofuran showed a symmetrical triplet with equidistant components of equal intensities with a hyperfine splitting constant of about 15.6 Gauss(86).

Dialkyl nitroxyl radicals do not react with alkyl peroxy radicals but do react rapidly with alkyl radicals(85,87-90).

The characteristic N-O frequency of nitroxyls lies near 1350 cm^{-1}, the exact position varying from one structure to another. Di-t-alkyl nitroxyl radicals have two main bands in their UV absorption, spectra; an intense band about 230 nm and a weak one in the region of 410-450 nm(91).

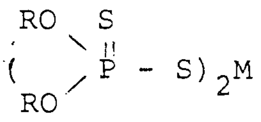
c) Complementary Mechanism Involving Both CB-A and CB-D Antioxidants

CB-D antioxidants are most effective when alkyl peroxy radicals are the major propagating species present (oxygen excess) in an autoxidising system while CB-A type operates best in an alkyl radical predominance (in oxygen deficient systems). Antioxidants involving both kinds of activity are expected to be superior to those acting by a single mechanism since in many antioxidant processes both species (alkyl, alkyl peroxy) are present to some degree. For example, hydroquinones are converted to the corresponding benzo quinone by the CB-D mechanism, the latter scavenges alkyl radicals by the CB-A mechanism as illustrated below:

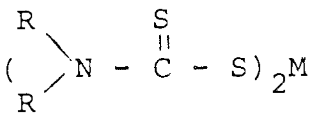


1.2.2 Preventive Antioxidants

Phenolic antioxidants are comparatively ineffective at high temperatures and in UV initiated oxidation (section 1.2.1). Hydroperoxides are known to initiate autoxidation readily under the influence of heat(92), light(93) and metal catalysis(94). Thus, any agent that removes hydroperoxides in a process which does not involve free radical formation or which protects hydroperoxides from decomposition should effectively inhibit oxidation of substrate(53). They are known as preventive antioxidants and include mainly metal ion deactivators, peroxide-decomposers, U.V absorber and quenchers. Sulphur containing antioxidants of which the most important are dialkylmono and disulphides, metal dialkyldithiophosphates and the metal dithiocarbamates (e.g. I, II, III, IV, V) have been shown(95-100) to act by decomposing hydroperoxides in a process which does not involve the formation of free radicals.



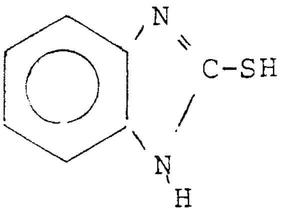
(I)



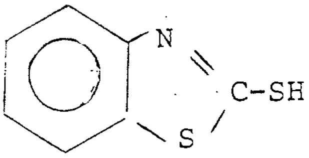
(II)

$(ROCOCH_2CH_2)_2S$

(III)



(IV)



(V)

Zinc dithiophosphate(101) (I M=zn) and dithiocarbamate(100,102) (II) are widely used in lubricating oils.

The dialkyl thio dipropionates (III) are used in foodstuffs(103) and polyolefins(104,105). Mercaptobenzimidazole (IV) and mercaptobenzothiazole (V) are used in rubbers(106).

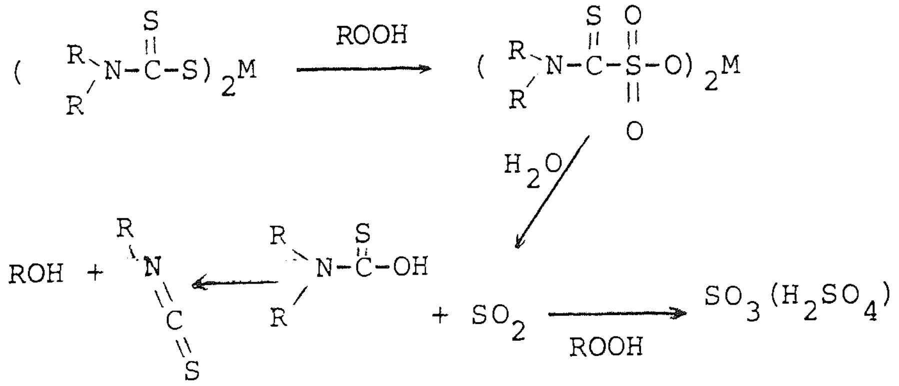
Barnard et al(107) on studying the effect of mono and disulphides on the oxidation of squalene, found that di-t-butyl sulphide and di-n-butyl disulphide both strongly retarded the autoxidation after a small amount of oxygen had been absorbed, therefore the active species was suggested to be the respective oxidation products.

Oxidation of polypropylene in the presence of dibenzyl-monosulphide showed, also, an initial rapid autoxidation (pro-oxidant effect) followed by autoretardation and a long induction period(108). The pro-oxidant effect of dilauryl thiodipropionate (as an antioxidant) has been shown to depend on the hydroperoxide: antioxidant ratio and pro-oxidant effects occur at low hydroperoxide concentrations. An investigation of its effect on the melt stability of polypropylene has shown(109) that in the early stages of oxidation the stabilising effect of dilaurylthiopropionate (DLTP) is reduced with increase in its concentration, the overall antioxidant effect was increased, however.

Previous studies(94) have indicated that the antioxidant activity of sulphides is related to production of the sulphoxide by oxidation with hydroperoxide. The lack of activity in technological media may be related to the rapid destruction of the sulphoxide at the processing temperature(110,111).

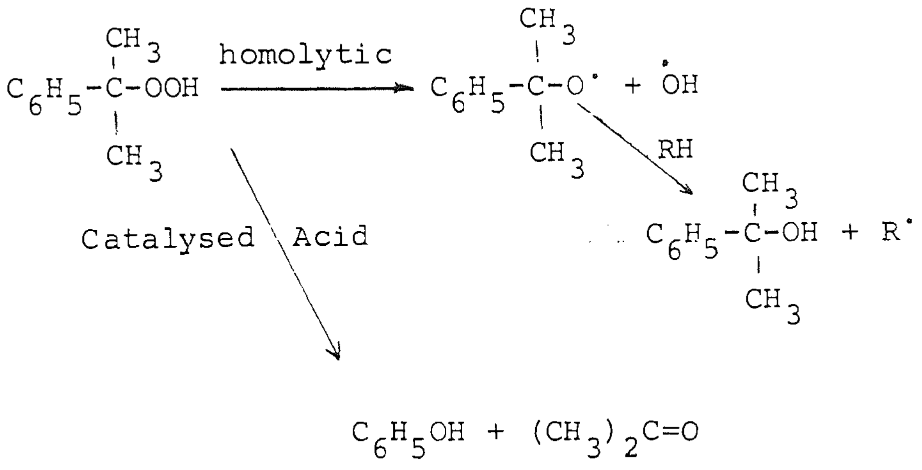
The thermal decomposition of sulphoxides has been investigated by some workers (112-114). This is important because of the relationship which has been shown between antioxidant activity and thermal stability (95,115).

Scott and co-workers have published several papers (11, 17,116-123) on the mechanism of sulphur containing antioxidants. The breakdown products of metal dithiocarbamates (11,110) and mercaptobenzthiazole (117) has indicated the formation of isothiocyanate, sulphurdioxide and benzthiazole, 2-hydroxybenzthiazole, sulphurdioxide respectively. The following mechanism was proposed to account for this (in the case of dithiocarbamate)



Sulphurdioxide has been shown (11,95,124-127) to be a very powerful Lewis acid catalyst for the decomposition of hydroperoxide. Lewis acid species such as sulphurdioxide and sulphurtrioxide have been shown to be primarily responsible for catalytic peroxidolysis with one mole of sulphur compound destroying more than 3 x 10^5 mole of hydroperoxides$^{(128,129)}$.

The products formed from cumene hydroperoxide with metal dithiocarbamates (on thermal UV oxidation) are phenol and acetone which are formed by an ionic decomposition$^{(11)}$.



$$C_6H_5\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}OOH \xrightarrow{\text{homolytic}} C_6H_5\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}O^{\bullet} + {}^{\bullet}OH \xrightarrow{RH} C_6H_5\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}OH + R^{\bullet}$$

$$C_6H_5\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}OOH \xrightarrow{\text{Catalysed Acid}} C_6H_5OH + (CH_3)_2C{=}O$$

It has also been shown$^{(130-133)}$ that the sulphur-containing phenols (sulphides and sulphoxides) form active catalytic species (sulphuroxides) in hydroperoxide decomposition.

Cyclic phosphite esters (such as, ethylene and propylene isopropylene phosphite, o-catecholphosphite) have been shown$^{(134)}$ to decompose hydroperoxide stoichiometrically and their transformation products (cyclic phosphate esters) are powerful antioxidants$^{(135)}$ in auto-oxidation catalysed by hydroperoxides and the products formed from cumene hydroperoxie and cyclicphoshate esters are mainly phenol and acetone which are known to be typical products of a Lewis acid catalysed process.

Scott(136) has classified the function of peroxide decomposers (PD) into (a) PD antioxidants as melt stabilisers (b) PD antioxidants as heat stabilisers (c) PD antioxidants as light stabilisers.

Antioxidants which destroy peroxides either stoichiometrically(134), (PD-S) or catalytically (PD-C)(11,110) effectively inhibit hydroperoxide and carbonyl formation during processing(134) and oxidative thermal ageing of polyolefines. In this respect their effect is similar to that of an effective hindered phenol CB-D antioxidant (Inganox 1076) whereas a conventional UV stabiliser (HOBP) is ineffective and a hindered piperidine (Tin 770) is a pro-oxidant(138) in terms of peroxide and carbonyl formation.

All the metal thiolate antioxidants show two distinct phases of antioxidant activity(136).

(1) Initially they show CB-D activity which varies, depending on the type of metal complex.

(2) PD activity appears during the latter stages of

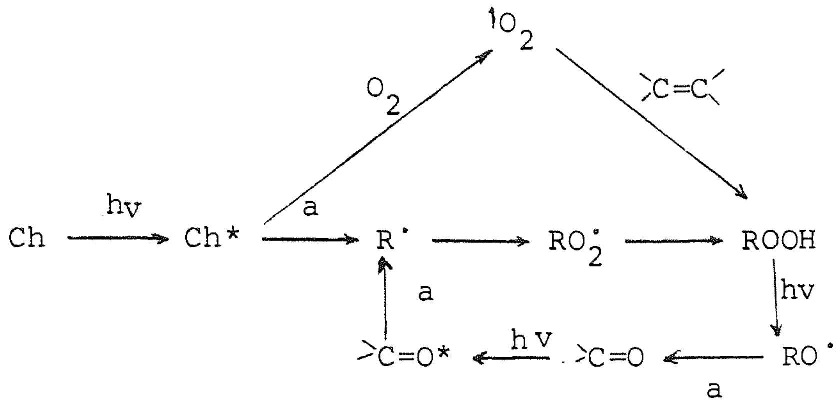
the oxidation and particularly at high peroxide to sulphur complex ratios.

Since metal contamination in polymers initiates auto-oxidation, metal ion deactivators (preventive anti-oxidants) are an important class of antioxidants (45).
The deactivation process may be achieved by complexing the metal ion to its maximum co-ordination numbers using various ligands, or stabilising one valency state at the expense of the other, or forming an insoluble product, e.g. FeS.

1.2.3 Photo-oxidation and Photo Stabilisation of Polyolefins

A) Photo-oxidation

It is now generally accepted that photo-oxidation of polymers involves the same free radical mechanism as the thermal oxidative degradation (139-142). The main difference lies in the nature and rate of the initiating step which is much faster in photo-oxidation. The key processes in photo-oxidation can be illustrated as follows:

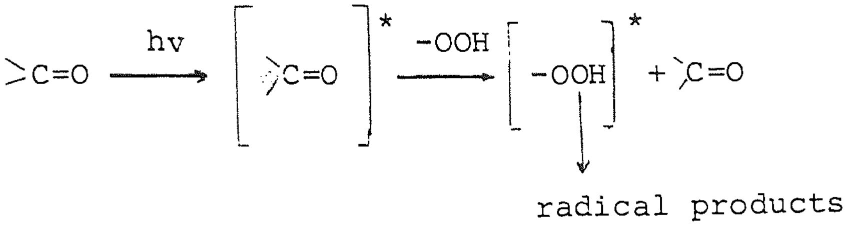


(a) indicates processes which can cause backbone scission

Two important chromophores for polymer degradation are the carbonyl and the hydroperoxide groups.

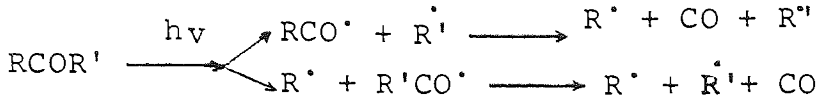
Carlsson and Wiles (21,143) have shown that photolysis of hydroperoxides formed in polymers as a result of thermal oxidation during processing etc., are significant chromophores (main initiators) in the photodegradation of polyolefins (24,144) Wiles (145) has suggested that excited carbonyl species can transfer their energy to -OOH groups (reaction (1)) (146,147). This increases the amount of absorbed UV energy which is available for -OOH cleavage. In addition several other UV absorbing species which are known impurities in polyolefins can also transfer energy to -OOH groups by a reaction analogous to reaction (1) (147).

(1)

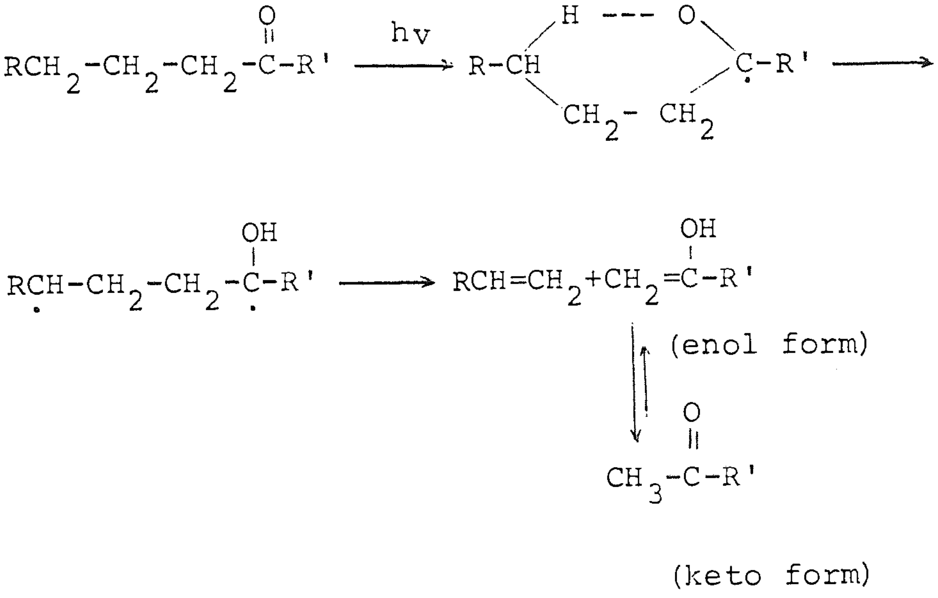


Scott and co-workers(7,15,122,17,148,149) have demonstrated that the hydroperoxide formed during processing are the main photoinitiators in the early stages of photo-oxidation of polyolefins, and hydroperoxides are the precursors to carbonyl formation. When carbonyl compounds are formed they take part in the later stages of photo-oxidation.

In the case of carbonyl groups either excited singlet or triplet intermediate states are involved. For chemical purposes the excited triplet state (formed by intersystem crossing from singlet) is more important than the singlet, since the former has a longer lifetime. $(>C{=}O) \xrightarrow{h\nu} {}^{1}(>C{=}O)^{*} \longrightarrow {}^{3}(>C{=}O)^{*}$ Norrish type I and Norrish type II reactions are principally involved during the photolysis of aliphatic ketones(150,151). In the Norrish type I reaction the bond between carbonyl group and adjacent α-carbon is homolytically cleaved producing two radicals.



A non-radical intramolecular process which occurs with the formation of a six membered cyclic intermediate is involved in Norrish type II reactions.



Norrish type I and II reactions are important in the photo-oxidation mechanism of polymers since they both lead to scission of bonds in the main polymer chain.

If carbonyl groups act as sensitisers for the photo-oxidation of polyolefins, one would expect that the reaction rate would rise with increased carbonyl concentration, but it has been shown (152) that this rate is independent of bulk carbonyl concentration in the polymer.

It has also been suggested(153,154) that the possibility of peroxide formation by the attack of singlet oxygen on the vinyl groups produced by Norrish type II process

$$\text{ketone} \xrightarrow{h\nu} 3(>C=O)^{*} \xrightarrow{3O_2} >C=O + 1O_2$$

$$RCH_2CH=CH_2 + 1O_2 \longrightarrow RCH=CHCH_2OOH \longrightarrow$$

further reaction.

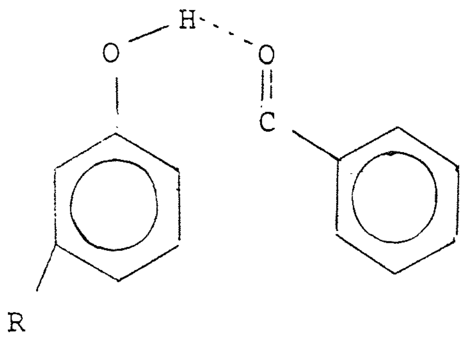
On the basis of theoretical calculations Carlsson and co-workers have shown(22) that the low hydroperoxide level detectable in a commercial unstabilised polypropylene sample is alone adequate to account for the photoinitiation processes. Initiation by O_2-polymer charge transfer complexes(154a) and polynuclear aromatic compounds(154b) have also been suggested. However the role of above initiators have been found to be insignificant compared to photo-initiation by hydroperoxides.

B) Photo-stabilisation:

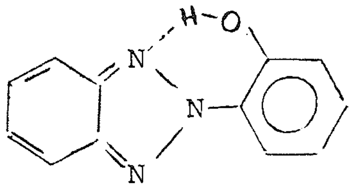
Five established mechanisms are known to be involved in UV stabilisation: CB-D (e.g. Irganox 1076, UV531), PD-S (e.g. phosphite esters), PD-C (E.g. NIDEC, nickeldiethyldithiocarbamate, ZNDEC, zincdiethyldithiocarbamate, CB-A (e.g. TinUVin 770) and UV screening (e.g. UV531, NIDEC) but whichever mechanism is involved, an over-riding factor is the UV stability of the additives.

Compounds such as orthohydroxybenzophenones (I), orthohydroxybenzotriazoles (II) and salicylates (III) have been known(25,155) as UV absorbers. All of them have a common structural feature, the intramolecular hydrogen bond (permits energy transfer; energy dissipation mechanism).

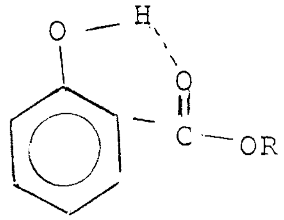
The protective efficiency of orthohydroxybenzophenones has been shown(25,156-158) to be in excess of its screening effect. This suggests that the 2-hydroxybenzophenones function also by other mechanisms in addition to UV screening and their activity during photo-oxidation appears at least in part to be the removal of photo-generated initiating radical species(159,156,160). UV531 (4-octyloxy-2-hydroxybenzophenone) has been shown to be involved in removal of radicals from a photo-oxidising medium(156,160) CB-D) and is highly susceptible to destruction under photo-oxidative conditions by hydroperoxides preformed during processing(160).



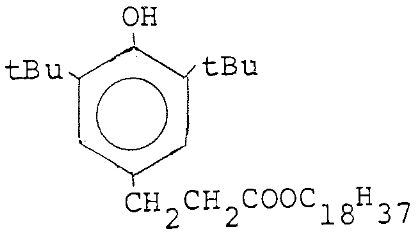
(I)



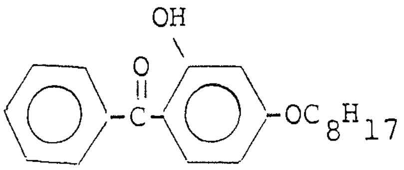
(II)



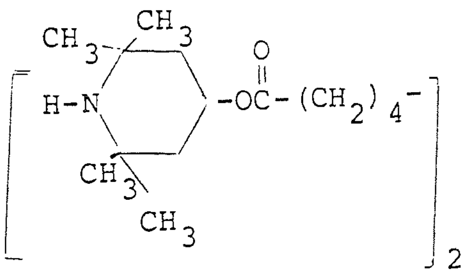
(III)



Irganox(1076)



UV531, (HOBP)



TinUVin 770

Dialkyldithiocarbamate complexes of various transition metals can photoprotect polyolefins although their concentration falls steadily during irradiation and they are the most extensively studied of PD-C classes(14,25,137,156,159,161-165).

A comparison between UV stabilising activity of a typical chain breaking antioxidant (Irganox 1076), UV absorber (HOBP), and peroxide decomposers (NIDEC, ZnDEC) has been recently carried out(166) and the order of activity is: (on the basis of same molar concentration)

NIDEC > HOBP > 1076 > ZnDEC

The first two show a strong concentration dependence whereas the last two do not.

The difference in behaviour of ZnDEC and NIDEC in photo-oxidation is not a reflection of a difference in PD-C activity since under thermal-oxidative conditions they have very similar antioxidant activity and this appears to relate to the UV stability of the antioxidant, thus HOBP and NIDEC are both much more UV stable than Irganox 1076 and ZnDEC(167).

Free Radical Scavenging in Photo-stabilisation:

The photo oxidising systems contain radicals such as alkyl, alkoxy, peroxy, hydroxy. One or more of these reactive species are involved in the photodegradation process, and hence stabilisation of polyolefins can be achieved by reducing the number and activity of these radicals(24,168).

Since hindered phenols have shown little value as light stabilisers due to their destruction under UV irradiation(137,169), the radical scavenging role of these compounds in photo-oxidation has been ignored for some years.

If additive loss by volatilisation is prevented, hindered phenols provide photostabilisation of polyolefins(168). Scott has shown(170) that hindered phenols become effective polypropylene stabilisers when grafted to the polymer through acrylic groups and also 2-hydroxy-4-octyloxybenzophenone acts as radical scavenger to retard oxidation under processing conditions(171).

Evidence for radical scavenging by 2-hydroxybenzophenone and zincbis(dibutyldithiocarbamate)(macroalkyl) during UV irradiation has also been obtained(172).

It has been(159) found that Ni(II)bis(2-hydroxyacetophenoneoxime) did not act as a simple UV absorber in the oxidation of cumene initiated by cumene hydroperoxide photolysis. This chelate did not decompose hydroperoxides, but retarded thermally initiated oxidation, presumably by $RO_2^{\bullet}$, $RO^{\bullet}$ or $R^{\bullet}$ scavenging.

Work at Sankyo company (Japan), Ciba - Geigy A. - G. (Switzerland), and in Russia has shown that the piperidines are very effective in the UV stabilisation of polypropylene. Temchin et al(173) have reported that 2,2,6,6-tetramethylpiperidines are better UV stabilisers than Ni(II)bis(dialkyldithiocarbamates) or 2-hydroxybenzophenones. Other workers also have shown that hindered piperidines effectively stabilise polyolefins against photo-oxidation(174-177).

A lot of effort has been directed to identifying the mechanism by which hindered amines provide such effective stabilisation(174). It is generally agreed(24, 178-182) that the starting structure of the additive is converted to the corresponding nitroxyl (I) during processing(177) and in the initial UV irradiation stages.

$$>NH \xrightarrow{\text{oxidation}} >NO^{\bullet} \quad (I)$$

Nitroxyl radicals are effective alkyl radical scavengers to give a substituted hydroxylamine (II)(183-185).

$$>NO^{\cdot} + R^{\cdot} \longrightarrow >NOR \quad (II)$$

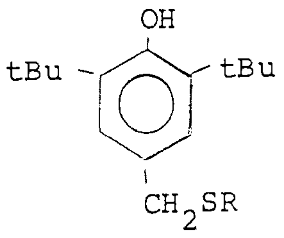
Nitroxyl radical regeneration has been suggested to(178,181,186-188) explain the ability of nitroxyl radicals to scavenge many times their stoichiometric equivalent (f) of radicals ($f \approx 10$). The mechanism of antioxidant action of nitroxyl radicals during processing and on UV exposure of polypropylene will be discussed in detail in the subsequent chapters.

A substantial improvement in UV stabilising efficiency of polyolefins has been achieved by the use of mixtures of CB (chainbreaking) and PD (peroxide decomposition) antioxidants (heterosynergism)(160) and this has been attributed to mutual additive protection.

A UV absorber (HOBP) and its analogues synergises effectively with both CB (1076) and PD (NiDEC, ZnDEC) antioxidants (protecting each other from destruction) in polypropylene(166,136) and polyethylene(137) under UV exposure.

Synergism between HOBP and autosynergistic antioxidants in polypropylene during photo-oxidation has recently been reported(189) indicating that hindered phenols containing benzylic sulphur (III) are more effective than conventional hindered phenols (1076) (at the same molar concentration).

Their synergistic effect with UV absorbers increases when they are molecularly dispersed by reaction with the polymer backbone(190,191). They have also been shown(192) to be among the most effective thermal antioxidants so far discovered, due in part to their ability to destroy hydroperoxides in a non-radical process(129,192).



(III)

Some PD-C antioxidants are so unstable to light that they cannot be used alone as UV stabilisers. The thiodipropionate esters are widely used as synergistic thermal stabilisers in combination with phenolic antioxidants in polyolefins but they have no utility as UV stabilisers.

The design and selection of stabilisers for use in polymers is complicated by the conflicting antioxidant requirements during processing and service due to variable oxygen availability in the system and changes in the mechanism of initiation$^{(53)}$.

1.2.4 Scope and Object of the Present Work:

Depending on oxygen availability and the nature of initiation, the antioxidant mechanisms in the polymer melt may differ very considerably from those in fabricated products during service.

Since all thermoplastic polymers are subjected to powerful shearing forces during processing, mechanochemical scission of polymer chains is a major source of initiating radicals$^{(40)}$ and has significant influence on the subsequent ageing behaviour$^{(42)}$. It is therefore very important to prevent polymer breakdown during processing and to design an effective melt stabiliser.

An effective melt stabiliser should be a material that acts in several ways, preferably deactivating alkyl radicals before they react with oxygen.

The object of the present work was to investigate the melt stability of polyolefins. Polypropylene (PP) and low density polyethylene (LDPE) under different processing conditions using various melt stabilisers.

Hindered nitroxyl radicals which are effective UV stabilisers of polyolefins (174-177) also show powerful activity as melt stabilisers in polypropylene (194a). The effectiveness of the above compounds as UV stabilisers has been suggested to be due to the regeneration of nitroxyl radicals in the UV oxidation stage (168-188). It is therefore, of both theoretical and practical interest to investigate in detail the behaviour and mechanism of melt stabilisation action of hindered nitroxyl radicals during processing of polyolefins under various conditions.

The effect of other radical scavenging agents viz Galvinoxyl and Iodine will also be investigated in polypropylene and low density polyethylene in a greater detail as melt stabilisers and an attempt will be made to explain the mechanisms of melt stabilisation action of the above compounds on the basis of qualitative and quantitative products analysis and model compound studies.

The effect of cupric stearate as melt stabiliser in polyolefins has also been studied and the results were compared with other known commercial melt stabilisers.

Finally, the behaviour of all the melt stabilisers examined will also be studied in polyolefins under the conditions of UV exposure and thermal oxidation.

CHAPTER TWO

Preparation and Characterisation of Compounds and General Experimental Techniques

2.1 Preparations

2.1.1 2,6-Ditert-butyl 1,4 Benzoquinone(193)

3,5 di-t-butyl 4-hydroxyl benzaldehyde (5 g) was dissolved in 5% sodium hydroxide solution (106 ml) and 15 ml of 6% H_2O_2 solution was added dropwise over 15 mins. The temperature was maintained at 50-60°C and throughout the addition, air was bubbled through the mixture. A deep yellow crystalline solid was precipitated. This was filtered, dried and recrystallised from methanol (m.p 66°C (Lit 67°C)(193). The structure of the compound was confirmed by I.R, UV and NMR spectroscopy.

Infra-red data:	Conjugated carbonyl	1660 cm^{-1}
Chlorobenzene used	C-H aromatic	3010 cm^{-1}
as solvent	C-H aliphatic	2900 cm^{-1}
UV absorption	(λ_{max} 254 nm, methanol as solvent)	

NMR data:	tertiary butyl protons	8.55τ(singlet)
CCl_4 used as solvent	aromatic protons	3.4 τ(singlet)

2.1.2 Hydrogalvinoxyl (HG) (2,6,3',5'-tetra-tert-butyl-4'-hydroxyphenyl-4-methylene-2,5-cyclohexadiene-1-one)

Hydrogalvinoxyl was prepared by a modified procedure of Greene's method(194).

Galvinoxyl (0.421 g, 1 m-mole) and 4,4'-dihydroxy-3,5,3',5'-tetra-tert-butyl diphenyl methane (0.212 g, 0.5 m-mole) were added to a small round flask (50 cc). To the mixture was added 30 ml of freshly distilled and degassed ether. The solution was degassed and the flask was sealed under vacuum. The flask was left in the dark for a few days and complete change of colour from violet to yellow was observed after 4 days. Then the flask was opened and the ether was removed under reduced pressure in a rotary evaporator.

Two crystallisations of the compound from aqueous ethanol gave a bright yellow product which melted at 158-159°C (Lit 158°C(212). The structure of the compound was confirmed by I.R and UV spectroscopy studies. The O-H stretching absorption band at

3620 cm^{-1} was characteristic of the compound (solution, chlorobenzene as solvent).

UV spectra of the diluted solution (hexane as solvent) showed a strong absorption at 380 nm due to conjugated structure of hydrogalvinoxyl.

2.1.3 Bis-(2,2,6,6-tetramethyl-4-piperidinyl-N-oxyl) sebacate)(195)

To a solution of 4.8 g (0.01 mole) TinUVin 770 in 200 ml ether, 8.1 g (0.04 mole) m-chloro-perbenzoic acid was added in powder form with stirring over 1 hr (at room temperature). The solution was magnetically stirred for a further 23 hours at room temperature. At the end of the reaction period, the reaction mixture was washed 3 times with 5%. Sodium carbonate solution, dried over anhydrous $MgSO_4$ and evaporated to dryness on the rotary evaporator. The orange/red residue was recrystallised from petroleum ether, mp 100-101°C (Lit 101°C)(195a).

The nitroxyl radical formation was confirmed by e.s.r. (g-value = 2.00067, a_H (splitting factor)= 15.4 Gauss, benzene as solvent).

2.1.4 Cupric Stearate

Metathesis (precipitation method) was used for preparation of cupric stearate(195b).

A solution of sodium stearate (3 g) in water was treated with an aqueous solution of cupric sulphate (7.52 g, anhydrous).

Cupric sulphate solution was added slowly to the solution of sodium stearate while the latter was stirring vigorously and cupric stearate was precipitated.

The product was filtered and washed thoroughly with hot water several times and then dried.

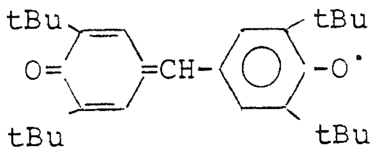
The product in the form of uniform powder was obtained.

$$2\ C_{17}H_{35}Na + CuSO_4 \longrightarrow (C_{17}H_{35})_2Cu + Na_2SO_4$$

Several crystallisation of the compound from benzene gave a product which was melted at 122-124°C (Lit ÷ 125°C)(195b).

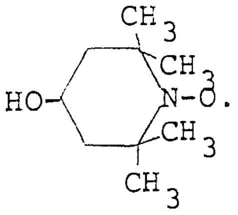
The following commercially available additives were used as stabilisers in polypropylene and low density polyethylene.

a) Galvinoxyl(G˙),2,6,3',5'-tetra-tert-butyl-4'-phenoxy-4-methylene-2,5-cyclohexadiene-1-one radical, supplied by Aldrich Chemical Co.Ltd. mp 158-159°C.

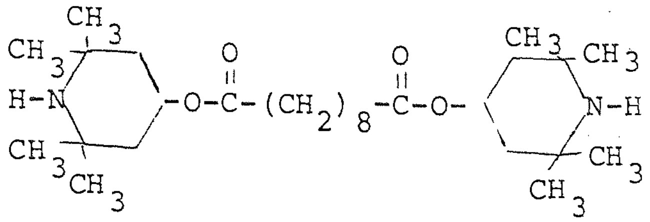


(Galvinoxyl) G˙

b) A stable N-oxy radical, 4-hydroxy2,2,2,6,6-tetramethyl piperidinoxyl was purchased from Aldrich Chemical Co.Ltd. (mp 68-71°C) and the corresponding hydroxylamine was prepared by the method of Rozantsev (mp 156°C (Lit 156°C)(195c).



c) A substituted piperidine compound, Bis (2,2,6,6-tetra-methyl-4-piperidininy) sebacate (Trade name, TinUVin 770), supplied by Ciba-Geigy Ltd., mp 100-101°C (Lit.101°C)(196).



d) Iodine, obtained from Aldrich Chemical Co.Ltd.

e) A phenolic antioxidant, n-octadecyl-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate (Trade name, Irganox 1076) supplied by Ciba-Geigy.

f) A nickel complex, nickeldibutyldithiocarbamate (NIDBC).

2.2 Purification of Solvents

a) Chlorobenzene - The general purpose grade (ex. Fisons) was fractionated from phosphorus pentoxide and the fraction boiling at 132°C was collected.

b) Chloroform - Technical grade was distilled and the fraction boiling at 76°C was collected.

c) Dichloromethane - Standard laboratory reagent grade was used.

d) Decalin - Technical grade decalin (ex. BDH and

Fison) was distilled and the distillate was washed with portions of 10% sulphuric acid until no further darkening occurred. It was then washed with water, sodium hydroxide and again with water and dried over $CaSO_4$.

e) Carbontetrachloride, hexane, methylcyclohexane, benzene were all of spectroscopic grade and used without further purification.

2.3 General Experimental Techniques

General methods and materials are described here, which were used throughout the present work. Other specific experimental methods are described in the relevant chapters.

2.3.1 Materials

The polymers used were:

1) Polypropylene (PP)

Unstabilised polypropylene in powder form identified as 'Propathene" HF-18, supplied by Imperial Chemical Industries (ICI), Plastics Division Limited.

2) Low density polyethylene (LDPE)

Low density polyethylene in granular (bead) form containing no antioxidant and identified as "alkathene" polyethylene supplied by Imperial Chemical Industries (ICI) Limited. The polymer had a density of 0.918 g/cm^3 and melt flow index 2.45.

2.3.2 Processing of Polyolefins, Film Preparation and Extraction

2.3.2.1 Processing of Polyolefins in the RAPRA Torque-Rheometer

Polymers (both polypropylene and low density polyethylene) were processed using the prototype RAPRA torque-rheometer(197), which is essentially a small mixing chamber, containing mixing screws contra-rotating at different speeds(198).

Two rotor speeds are available (high and low). All the processings were done using high speed which corresponded to 60 rev/min. It has a good temperature control and a continous read out is provided of both melt temperature and the torque required for the mixing. The chamber may be operated either open to the atmosphere or sealed by a pneumatic ram. A full charge was calculated out for each polymer according to its density, and when this charge was used the chamber was sealed. When it was desired to process in the presence of air, a charge of about 20 g was employed, and the chamber was left open to the atmosphere.

The additives were mixed with the polymers at room temperature by tumble mixing before introducing into the torque-rheometer chamber. The hot polymer melt was chilled in water on removal from the rheometer to avoid uncontrolled thermal oxidation.

2.3.2.2 Film Preparation

Polymer films for spectroscopy examination were prepared by compression moulding using an electric press. The appropriate weight of processed polymer was compression moulded using glaze steel plates with steel backing plates and a special grade of cellophane as a mould releasing agent between two plates. Control of films thickness was achieved by using a definite amount of processed polymer, (about 6-7 g of material was found to produce film of desired thickness, 1.8×10^{-2} cm). The weighed amount of polymer was placed between the glazing plates in two cellophane sheets and inserted into the press. The temperature of the hydraulic press was set at 150°C and 190°C for low density polyethylene and polypropylene respectively. The platen was closed and 0.5 - 1 minute preheating was allowed for the polymer to soften. The pressure was then slowly raised to the maximum (28 tons/6" ram) and left at full pressure for 1.5 - 2 minutes. The mould was then water cooled and the films were removed when the platen temperature dropped to 40°C and stored in a refrigerator. Strips of uniform thickness (1.8 x 10^{-2} cm or ft) were selected for tests.

2.3.2.3 Extraction

In order to remove low molecular weight materials and unreacted additives from the samples (films, powders), a continuous hot extraction in a soxhlet apparatus with a solvent (acetone, dichloromethane) was carried out under a steady stream of nitrogen for about 48 hrs. After the extraction the samples were dried under vacuum at 35 - 30°C for 24 hrs. The solutions of the extracted products were collected in a small flask, and the solvent was completely removed on a rotary evaporator. Extracted products were dissolved in a suitable solvent (hexane, chlorobenzene) for spectroscopic examination.

2.3.3 Evaluation of Torque Versus Time (Ideal)

Materials have characteristically shaped torque-time curves and it is therefore essential that the rheometer curve be interpreted correctly to derive the maximum information from the results(198).

Variations in torque are caused by changes in the consistency of the material and since the materials may be in solid, granule or liquid form, the torque variation may be used to indicate changes such as melting, solidification or any other process which may occur when a material is heated and sheared. It is therefore possible to record changes in the consistency of a polymer material due to fusion, degradation, gelation, cross-linking etc.(197)

An idealised torque - VS processing time curve(199) is depicted in Figure 2.1. When the polymer is introduced into the torque rheometer the torque rises sharply. The polymer is heated and when it reaches its glass transition temperature (Tg) it becomes rubbery. The torque then decreases and reaches a minimum (b,Fig. 2.1). This stage is followed by the gelation of the material (crosslinking occurs). The polymer starts to melt causing the torque to increase. When the melting (or gelation) is completed the torque decreases again giving rise to a peak "C". The time to reach the peak "C" is called fusion time. The fusion time for a particular polymer depends mainly on mechanical stress, temperature and the presence of additives. Crosslinking or chain scission of polymers is also reflected in the torque vs processing time curve at a later stage.

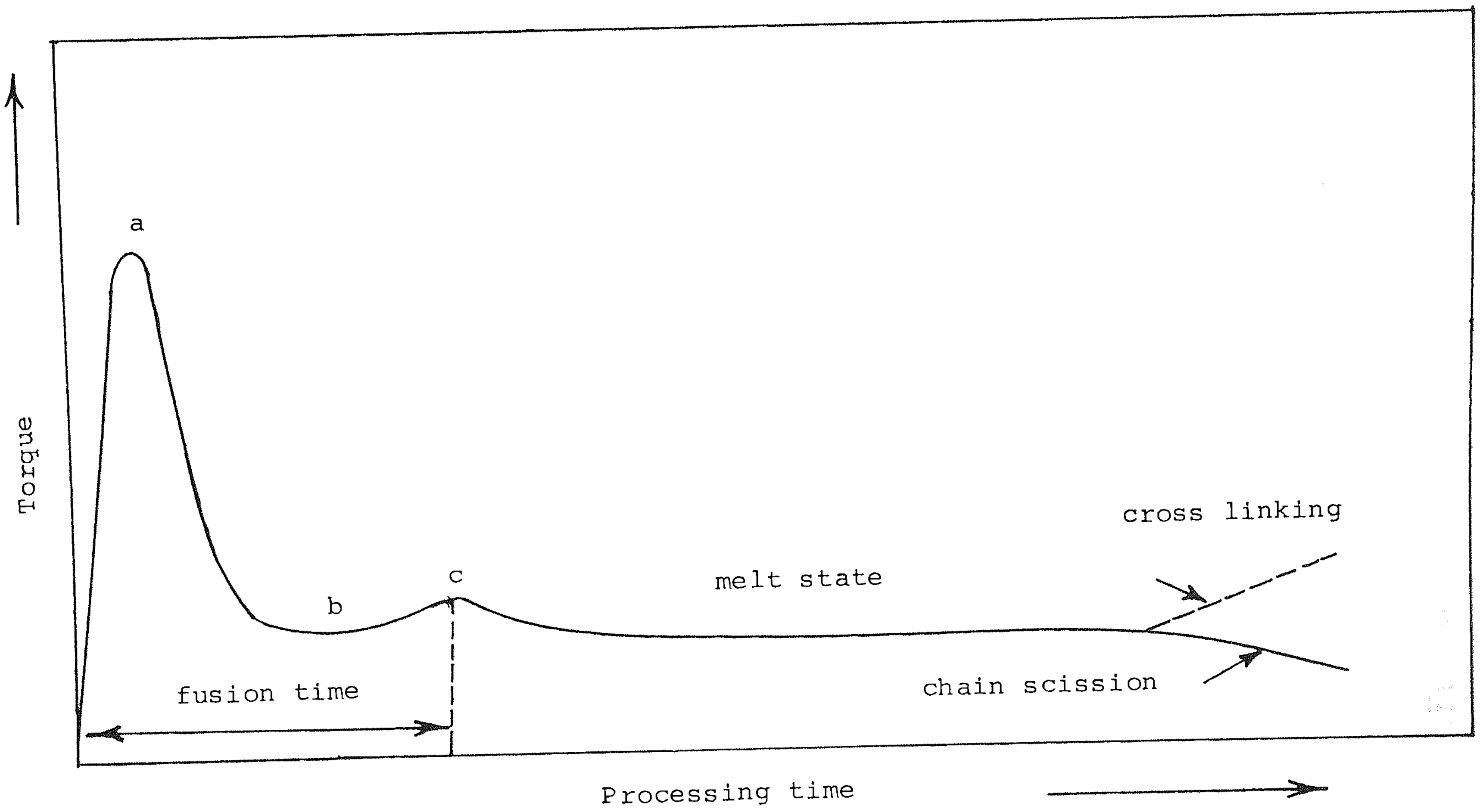


Fig. 2.1 Changes in torque with time during processing of polyolefins (a typical curve)

2.3.4 Measurement of Melt Flow Index (MFI)

The melt flow index (MFI) is defined as the amount of polymer in grammes extruded through a standard die in a given time (e. g. 10 minutes). It is an inverse measure of melt viscosity of the polymer which is inversely related to the molecular weight. The apparatus used was described in the British Standard method for determination of melt flow index of polyethylene MFI (200).

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 manufacture's hand book except that the die of the internal diameter (0.0465" bore) was used throughout the work. The polymer was allowed to extrude for one minute before sampling commenced.

Samples (cut-offs) were taken every one minute or 30 second. The average weight of each six (cut offs) was taken.

2.3.5 Gel Permeation Chromatography (GPC)

To determine the molecular weight changes during thermal processing of polypropylene due to chain scission or crosslinking and the effect of stabilisers on these changes gel permeation chromatography (GPC) was used. A chain scission process shifts the molecular distribution (MWD) to lower molecular weight. An increase in molecular weight (crosslinking) will lead to a molecular enlargement. Molecular weight and molecular weight distribution for the processed polypropylene (various processing time) samples were obtained using GPC and were kindly carried out by the Polymer Supply and Characterisation Centre of RAPRA. Experimental conditions used were as follows:
Styragel columns, connected in series:

1×10^6 Å , 1×10^4 Å , 1×500 Å
flow rate - 1 ml/min.
solvent - O-dichlorobenzene stabilised with 2,6-di-tert-butyl-P-cresol
temperature - 145°C

Polystyrene standards were used for calibration and Mark-Houwink constants ($[\eta] = KM^{\alpha}$) used for conversion via universal calibration:

Polystyrene K $= 1.38 \times 10^{-4}$, $\alpha = 0.7$

Polypropylene K $= 1.3 \times 10^{-4}$, $\alpha = 0.78$

Molecular weight distribution curves were obtained by the plot of $dw/d_{\log}M$ versus log M.

This technique has been incorporated into an automatic machine which when properly calibrated for the polymer samples could determine all necessary information. A digital computer has been used to convert this information into a complete molecular weight distribution curve data with calculation of any desired molecular weight averages, dispersivity ratios (dw/dM), etc.

2.3.6 Gel Content Measurement of the Processed Low Density Polyethylene (LDPE)

Gel content in the processed low density polyethylene samples were determined in p-xylene at 90°C. After heating the solution (in an oil bath) for 30 minutes at 90°C the solution was filtered hot. (Solubility of unprocessed LDPE in p-xylene at 90°C = 3.85g/100ml). Gel was collected and vacuum dried to constant weight.

2.3.7 Measurement of Unsaturation in Processed Polymers

The following procedure(201) was used to determine unsaturation formation in polypropylene containing additives.

The processed polypropylene samples were filed to very small pieces (powder) and extracted by a solvent (such as acetone, dichloromethane, benzene, etc.) to remove the additive for about 50 hours under nitrogen, dried under vacuum at 30°C for 24 hours. 0.5g of each sample was swollen in 75 ml of chloroform ($CHCl_3$) in a conical flask for about 48 hours (3 hours in an oil bath at 60°C), 5 ml of 20% (20g/100cc) trichloroacetic acid in $CHCl_3$ was added followed by 25 ml 0.1 N iodine (1.269g/100cc $CHCl_3$). 25 ml of 5% mercuric acetate (5g/100cc) in glacial acetic acid was added, the contents were swirled gently and stored in the dark for 2.5 hrs. After addition of 75 ml 7.5% potassium iodide solution, the excess iodine was titrated with 0.1 $Na_2S_2O_3$ employing the customary starch end point (the starch end point noted in the aqueous phase).

2.3.8 Identification of Chemical Products Formed from the Additives during Processing with Polymers.

Formation of hydroxylamine during the processing of polypropylene with a nitroxyl radical (2,2,6,6-tetramethyl4-hydroxy piperidineoxy), hydrogen iodide (processed with iodine), and hydrogalvinoxyl (processed with galvinoxyl) were carried out respectively using the following chemical tests.

A - Hydroxylamine detection$^{(202)}$

1 ml of test solution (extracted product dissolved in CH_2Cl_2), just acidified with dilute HCl, was treated with 1 ml of 1% (w/v solution of oxine (8-hydroxy quinoline) in ethyl alcohol, followed by 1 ml of 2N sodium carbonate solution. The whole was well shaken and the green colouration which developed immediately (indo-oxine formation) indicated the presence of hydroxylamine.

B - Hydrogen iodide detection:

A fresh sample of processed polypropylene with iodine was filed, a few grammes of it was hot extracted with water (250cc water) to extract any trapped hydrogen iodide in the polymer for 24 hrs. The aqueous solution was filtered and its PH was determined by a PH meter. It was found to be quite acidic (PH=3.5). In a small test tube a few ml of extracted solution was poured and a few drops of each of the following ingredients were added to it in a dilute NaOH, concentrated H_2SO_4, benzene fresh starch solution and tert-butylhydroperoxide.

Test tube was well shaken and a blue colour (indication of iodine formation) appeared in the aqueous phase. The coloured test tube, was then put in a hot water bath, the blue colour disappeared turning the benzene layer purple. This test (oxidation-reduction) confirmed hydrogen iodide formation during the processing of polypropylene with iodine.

C-Hydrogalvinoxyl formation

To a few ml of an extracted product in hexane, two or three drops of 1% (w/v) ferric chloride solution in ether were added. The production of a light blue colouration was typical of The presence of O-H groups in phenol(202a).

2.3.9 Peroxide Measurement in Processed Polymers

A) Chemical methods: 1) Iodometric method

The method used by Manasek et al(203) and Geddes(204) was modified as follows:
0.5g of cold extracted processed polypropylene films was placed in a small flask (in small pieces). 30 ml

of deaerated chloroform ($CHCl_3$) was poured in the flask and nitrogen was passed into the solution for about 20 minutes. The flask was sealed and allowed to stand for 48 hrs for complete swelling of polymer films. Then 3 ml glacial acetic acid was added followed by 2 ml of deaerated 5% solution of sodium iodide in methanol while the solution was purged with nitrogen. The flask was again sealed using rubber seals. After storage in dark for two hours, the expected liberated iodine was tested using UV spectroscopy.

$$ROOH + 2\overset{-}{I} + 2\overset{+}{H} \longrightarrow ROH + H_2O + I_2$$

The absorption band at 360 nm was followed.

2) Ferrous ion oxidation technique (used in the presence of cupric additive which interferes with iodide).

The following experimental procedure was adapted from BOCEK[(205)]. 0.5g of processed powdered polypropylene was swollen in 75 ml of deaerated chloroform for 48 hrs. One ml of deaerated 0.004M phosphoric acid was added, followed by 2 ml of a deaerated solution of 0.005M ferrous ammonium sulphate in methanol. Both reagents were added using a syringe to prevent contamination by oxygen. After standing in the dark for 2 hrs, 1 ml of a 0.5% solution of 1-10phenanthroline in deaerated benzene was added. The reaction mixture was allowed to stand for 15 minutes after swirling. Five ml of the reaction mixture free of polymer was carefully withdrawn and its absorption in the visible region (510 nm) was examined against the blank reference in a Pye Unicam SP800 model spectrophotometer.

B) I.R method

Thermally oxidised low density polyethylene film gives a sharp band in the IR spectra at 3555 cm^{-1} which is due to O-H stretching of free hydroperoxide$^{(206,207)}$. This band was measured as index (defined as $A_{3555}/A_{1895cm^{-1}}$). A very good co-relation was found between hydroperoxide measured chemically and hydroperoxide measured by the IR method in the case of low density polyethylene$^{(27)}$.

2.3.10 Infra-red Spectroscopy

Structural changes take place during the mechano,-thermo and photo-oxidation of polymers resulting in the buildup of different oxidation products or functional groups in the backbone of the polymer chains such as hydroxyl, carbonyl, carboxyl, vinyl etc. Infra-red spectroscopy has been used to determine the nature of these oxidation products and kinetics of the growth of these functional groups.

IR method was used for both qualitative and quantitative analysis. The concentration of carbonyl modification and other functional groups in polyolefins was expressed as indices relative to the polymer reference peak at 2720 cm^{-1} for polypropylene and 1895 cm^{-1} for low density polyethylene. Indices were defined as the ratio of the absorbance of functional group peaks to that of the reference peak. A reference peak is actually selected to minimise errors due to variation in film thickness as well as due to instrument itself and it is a C-H stretching band which remained constant during ageing.

The base line technique(208) was used to calculate the absorbance due to various functional groups (Fig. 2.2).

if S_m = absorbance at standard peak maximum
S_o = absorbance at standard peak baseline
and F_m = absorbance at functional group peak maximum
F_o absorbance at functional group peak baseline

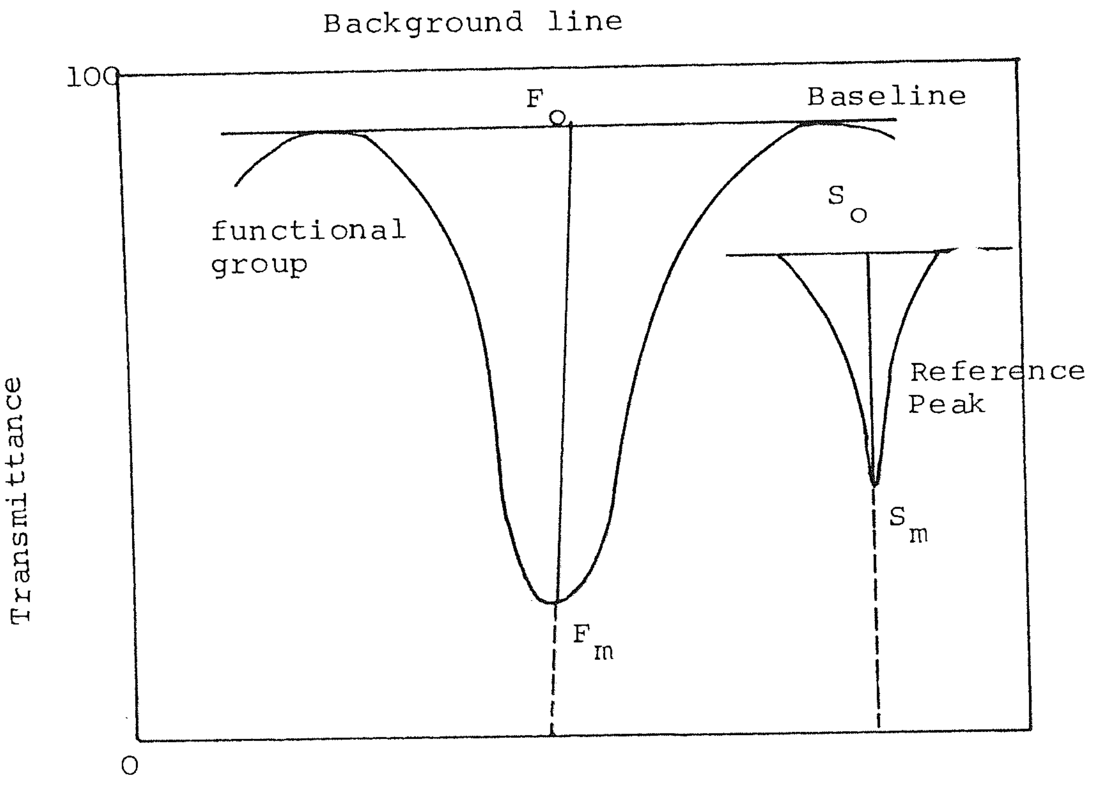


Fig. 2.2 Functional group index measurement (by baseline technique).

Then: Functional group index = $\frac{F_m - F_o}{S_m - S_o}$

A Perkin-Elmer grating infra-red spectrophotometer model 599 was used to record all the infra-red spectra from 4000 cm^{-1} to 250 cm^{-1} at normal scan speed.

Before putting the sample in, the spectrophotometer was adjusted to read 100% transmission and this was known as backgroundline.

2.3.11 UV Spectroscopy

Ultraviolet spectra of polymer films with additives were recorded using PYE UNICAM SP800 UV/visible spectrophotometer.

In order to obtain the specta of the additives in films a film of unprocessed polymer in the form of compression moulded film of identical thickness without additive was used in the reference beam.

In the case of solutions the spectra were recorded using quartz cells 1 cm path length with the pure solvent (e.g. hexane, carbontetrachloride, chlorobenzene etc.) being used in the reference beam.

2.3.12 Gasliquid Chromatography (GlC)

A Pye 104 gas chromatograph with a flame ionisation detector was used. Nitrogen gas used as the mobile phase flowing at a rate of 20 ml/min. The column used was 10-12% polyethylene glycoladipate supported on 80-100 mesh celite. The column was 5 feet long made of glass with an outside diameter 0.6 cm. The column material was packed into the column under vacuum. It was then conditioned by placing it in the column oven at a temperature of 160°C for about 15 hours (max. operating temperature was 180°C and two similar columns, back and front used). After conditioning of the columns sampling was done using a microsyringe. A very small amount of test solution (extracted product in hexane) was injected in the front column (air bubbling to column avoided). Temperature programming technique used as follows:

initial temperature 80°C. Final temperature 160°C, attenuation 2 x 10, chartspeed 20 mm/min, rate of increase in temperature 12°C/min. flow rate 20ml/min.

To identify the observed peaks some reference solutions (such as 3,5 di-t-butyl-4 hydroxylbenzaldhyde,2,6 di-t-butyl 1,4 benzoquinone and hydrogalvinoxyl) were used in the same condition as used in test solution.

2.3.13 Electron Resonance Spectroscopy (e.s.r)

a) A Brief Description of e.s.r Theory(209) and e.s.r Machine

An electron has spin and an associated magnetic moment and can be considered as a small magnet when it is in an external magnetic field (H), its magnetic moment vector has two possible orientations of the spin vector; parallel and antiparallel to the applied magnetic field.

The electron energy (E) in the magnetic field is given by $E = -\mu_e H$, μ_e is the magnetic moment vector for the unbonded electron which is related to the spin vector (S):

$\mu_e = g_e \beta_e S$ erg/gauss, β_e= Bohn magneton and g_e = dimentionless constant called electron freespin g-factor, SO; $E = g_e \beta_e SH$, S in a magnetic field can have one of the two possible value, $+\frac{1}{2}$ and $-\frac{1}{2}$, SO; $E_1 = +\frac{1}{2} g_e \beta_e H$ and $E_2 = -\frac{1}{2} g_e \beta_e H$. The energy difference between the two stages of electron is given by

$$DE = E_1 - E_2 = g_e \beta_e H$$

The measurement of the energy difference (DE) is the basis of electron paramagnetic resonance experiments.

Application of an oscillating radio frequency field perpendicular to magnetic field, whose quanta (hv) have an energy equal to $g_e \beta_e H$, induce transition between the two states of the electron.

$$DE = hv = g_e \beta_e H \text{ (erg)} \quad \text{(I)}$$

h = Planck's constant

only electromagnetic waves with the frequency

$$v = \frac{g_e \beta_e H}{h}$$

contain the right amount of energy to produce transition between the two energy states of the electrons. This coincidence of the energy of the microwave quantum (hv) and the energy difference between the two states of the electron (DE) is called resonance.

The integrated intensity of e.s.r signal represents the total energy absorbed by the sample at resonance conditions. This intensity is expressed by the total area under the resonance curve and it can be used for the determination of the concentration of free radicals in the samples as the number of unpaired spins per

gram or per milliliter (it will be shown later).
The intensity of the e.s.r spectra is influenced by several factors such as:

1) the overall spectrometer gain,
2) the microwave frequency,
3) the modulation amplitude,
4) the concentration of free radicals in the sample
5) the g- factor of the sample,
6) the transition probability,
7) the sample temperature.

Since many factors influence the intensity of e.s.r signal, the absolute determination of free radical concentration involves many corrections. The usual method for measuring the concentration of free radicals is to compare its e.s.r signals with that of a sample containing a known quantity of free radicals (210).

There is a similarity between the theory of electron spin resonance and nuclear magnetic resonance. In an external magnetic field (H) there is interaction between the spin of electron and the spins of other nuclei in the same molecule. This gives an e.s.r spectrum with a number of lines (hyperfine splitting).

The e.s.r method not only makes possible the detection of radicals but also provides a useful tool in the study of their electronic structures and correlations with chemical structure, properties and molecular orbitals[(211)]. It can also be applied to investigations of kinetics including measurement of the rates of radical formation and destruction, lifetimes of radicals and the nature of their subsequent conversions.

A typical e.s.r spectrometer has the following components:

1) The source of microwave radiation is a klystron producing microwave oscillation in a small frequency range, the frequency of monochromatic is determined by the voltage applied to the klystron. Stabilisation of the frequency is made by an automatic frequency control (AFC) system which works on the voltage. The power of the klystrons used in e.s.r spectrometers is usually a few hundred milliwatts. The heat generated by the klystron is removed by circulating water.
2) The magnet is a source of static magnetic field.
3) The cavity system (contains the sample).
4) The modulation system at the commonly used frequency of 100 kHz.
5) The detection and recording system.

b) Preparation of e.s.r Film Samples and Detection of Radicals

All e.s.r samples were prepared by cutting processed polymer films in the same sizes (1.5 x 0.3 x 0.0175 cm) which conveniently fitted in the test tube and before putting the sample in the test tube, it was weighed.

JES-PE electron spin resonance instrument was used and the machine was calibrated using a marker sample made up of MnO powder containing thermally diffused Mn^{+2} ions before the spectrum of the samples were recorded. Test tube containing the sample was inserted in the cavity after adjusting by the insertion length setting device.

The signal then was recorded and the g-value of the recorded signal was determined by utilising the e.s.r marker as follows:

A) Determination of g-value

The line position of an e.s.r spectrum is denoted in terms of 'g-value', in other words the g- factor or 'chemical shift' determines the field at which the centre of the spectrum occurs and it is expressed as a function of microwave frequency and magnetic field at resonance, $g = \frac{hv}{\beta H}$. The position and shape of spectra are dependent on the geometry of their surroundings and direction of the rotation of radical and ease of the rotation.

g-values of radicals were calculated using the MnO marker sample as reference giving six lines with respect to the third and fourth lines of MnO peaks following the instruction in the handbook of the spectrometer.

When the spectrum of the sample and e.s.r marker were obtained simultaneously and by knowing the following data

1) g-value of the fourth line (from marker) counted from the low magnetic field side which is $g_1=1.981$ Gauss.
2) Microwave frequency, 9300 mHz (it is the mean frequency of 9200 mHz and 9400 mHz)
3) DH represents the distance between the measured sample spectrum and the fourth spectra which can easily be obtained by proportional calculation (Fig. 2.3), and using the equation (I) for fourth line spectra of marker (a) and measured sample (b).

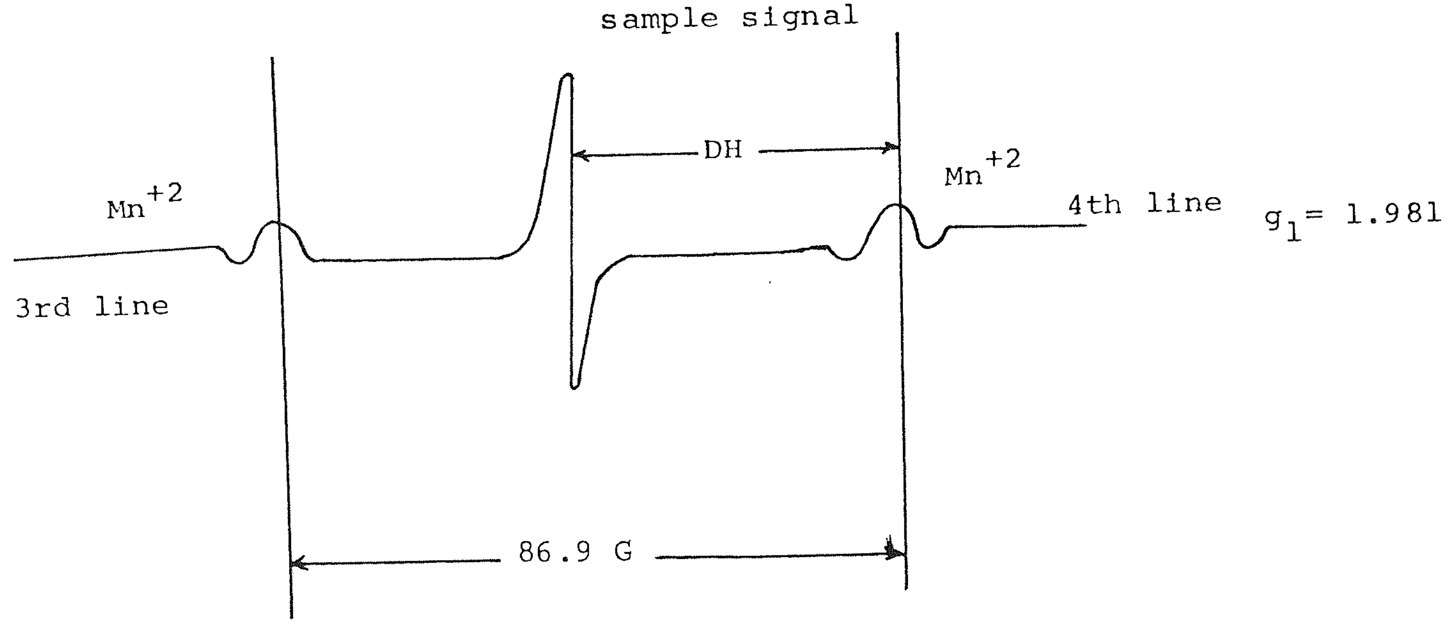


Fig. 2.3

$$hv = g_1 \beta H_o \qquad (a)$$

$$hv = g\beta(H_o - DH) \qquad (b)$$

Therefore: $$g = \frac{hv}{\beta(H_o - DH)} = \frac{\frac{hv}{\beta}}{\frac{hv}{g_1\beta} - DH}$$

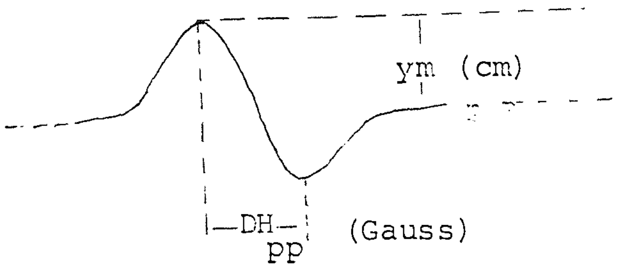
by substituting the amount of v, β and g_1, the following equation is obtained which is used to calculate the g-factor of the samples.

$$g = \frac{6651}{3357 - DH}$$

B) Measurement of radical concentration

To measure the concentration of radicals in polymer samples, a reference was used in the cavity with the polymer sample so that both spectra could be recorded simultaneously$^{(212)}$. For this purpose, a sealed capillary tube containing a known weight of copper sulphate solution was fastened to the outer surface of the glass tube inside which the polymer sample had been placed. The radical concentration was calculated by comparing the ratio $Ym\ (DH_{pp})^2$ for the polymer to $Ym\ (DH_{pp})^2$ for the reference sample.

$$\frac{Ym(DH_{pp})^{2} \text{ sample}}{Ym(DH_{pp})^{2} \text{ reference}} = \frac{\text{concentration of radicals in test sample}}{\text{concentration of radicals in reference}}$$



This method was found to be a close approximation of the summation method(213).

2.3.14 Ultraviolet Accelerated Exposure Cabinet

Polymer films with and without additives were irradiated in an ultraviolet cabinet (Supplied by Ciba-Geigy Limited). UV cabinet was cylindrical in shape and consisted of a circular rotating sample drum whose circumference was 15 cm from the periphery of the metallic cylinder. The radiation source consisted of cylindrical array of 1:3 combination of fluorescent sunlamps and black lamps each of 20 watts power and mounted alternately around the periphery of the metallic cylindrical board.

24 lamps type C (Phillips actinic blue 05) and 8 lamps type Al (Westinghouse sunlamps FS 20) were mounted vertically on the circumference of the rotating drum. The light beam fell perpendicularly and isotropically on the surface of the film (the distance of the sample from the light source was 10cm.

The distribution spectra of both types of lamps has shown(39) that the maximum in the relative intensity of the lamp Al is at 317 nm and of the lamp C 374 nm.

2.3.15 Accelerated Thermal Oxidation of Polyolefins

The accelerated thermal oxidations of processed polymer films were carried out in a Wallace oven at 110°C and 140°C respectively for low density polyethylene and polypropylene.

The samples were placed in a separate cell (the oven has seven separate cells).

Airflow through the cells is controlled by a device on the oven (2.5 cu.ft./hr).

2.3.16 Measurement of the Brittle Fracture of Polymer Samples

All the film samples (identical size and uniform thickness, 1.8×10^{-2} cm) containing various additives along with controls were UV irradiated and they were periodically checked for embrittlement times.

Their embrittlement times were determined by bending of the films onto themselves to an angle of 180°.

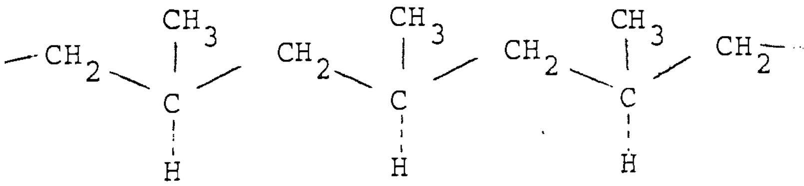
CHAPTER THREE

Melt Stabilisation of Polyolefins

3.A Polypropylene

Polypropylene can be made in isotactic, syndiotactic (crystalline) or atactic (amorphous) forms. Isotactic polypropylene is an essentially linear, highly crystalline polymer with a melting point of 165°C. Its high crystallinity imparts to it high tensile strength, stiffness and hardness.

Isotactic polypropylene has the structure



Mechanical and thermal properties of polypropylene are dependent on the isotacticity, the molecular weight and on other structural factors. It has been shown that(214) an increase in molecular weight (increase in melt viscosity or decrease in MFI) causes a reduction in tensile strength, stiffness, hardness and brittle point but an increase in impact strength. This effect is believed to be due to the fact that high molecular weight polymer does not crystallise so easily as lower molecular weight material and it is the differences in degree of crystallinity which affect the bulk properties. Isotacticity in polypropylene has been studied using IR method by several workers (215-217). By comparison of spectra of crystalline (isotactic) and fully amorphous (atactic) polypropylene it has been found that some of the band intensities drop sharply in the melting region of polymer (temperature sensitive bands, 1330, 1305, 1220, 1105, 1045, 995, 846 and 810 cm^{-1}) which are connected with a degree of crystallinity (218,219). Unsaturation has also been found in isotactic polypropylene (220). Effect of oxidation on polypropylene chain scission, etc. has been discussed in Chapter 1 (see 1.1.2, 1.1.3).

3.A.1 Experimental

Polypropylene with and without tumble-mixed additives was processed in the RAPRA torque-rheometer under three different conditions (a) half full chamber (20g of polymer) and the chamber left open to the atmosphere, (b) full chamber (35g) and the chamber sealed, (c) full chamber, closed after purging with nitrogen. Processing was also carried out at four different temperatures (viz. 170°C, 180°C, 190°C, 200°C) for various lengths of time (5, 10, 15, 20, 30, etc.) using different concentrations of additives. On completion of processing, the polymer samples were rapidly removed and quenched in cold water to prevent further thermal oxidation. The polymer samples were then compression moulded at 190°C for about 2 minutes into sheets of thickness 0.007 inch (1.8×10^{-2} cm) as described in the general experimental chapter (see sections 2.3.2.1, 2.3.2.2).

Melt flow index, molecular weight distribution, hydroperoxide content, unsaturation and carbonyl formation of processed polypropylene and low density polyethylene samples were determined as described in the experimental sections (Chapter 2).

The formation of C-I bonds during processing of polypropylene with iodine was measured by estimating the unsaturation formed in the subsequent reaction of a processed polymer solution in decalin with alcoholic $AgNO_3$. The processed polymer samples were dissolved in decalin at 135°C and titrated with alcoholic $AgNO_3$. Unsaturation thus formed (reaction 1) was estimated as follows:

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-I + AgNO_3(\text{alco}) \longrightarrow AgI + -\overset{|}{C}=\overset{|}{C}- \qquad (I)$$

Polymer was precipitated from decalin using ether which was filtered, washed with ether, water and alcohol and subsequently dried and compression moulded into film. Unsaturation was then determined IR spectroscopically using a calibration graph which was made using dodecene-1 in pure polypropylene (see, Fig. 3.23).

3.A.2 Evaluation of Physical and Chemical Changes Occurring in Polypropylene Under Processing Conditions.

The following studies aim to illustrate the physico-chemical changes occurring on polypropylene during the melt processing under various conditions and an attempt will also be made to study the antioxidant activity of melt stabilisers which prevent the polymer deterioration during processing operations.

Figs. 3.1 and 3.2 show the changes in melt flow index (MFI) of polypropylene processed at various temperatures in the closed chamber and open chamber respectively. Both the figures clearly show the effect of temperature on the degradation of polypropylene in the melt stage. If the processing temperature is increased from 170°C to 200°C, the melt flow index increases at a faster rate with increasing processing time (Figs. 3.1, 3.2, curves, 1, 2 and 3).

Fig. 3.1 Changes in melt flow index (MFI) of polypropylene at various processing temperatures, processed in a closed chamber

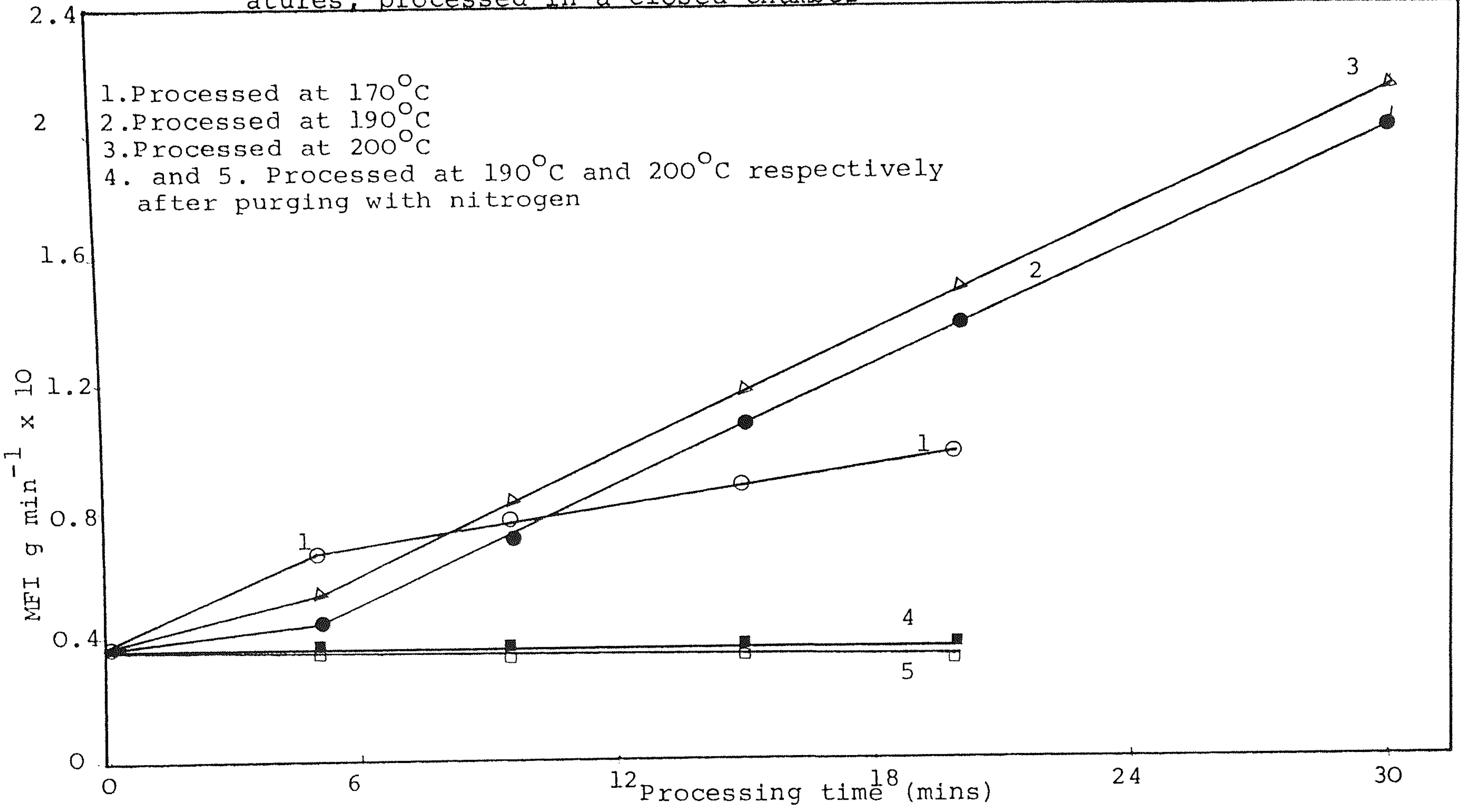
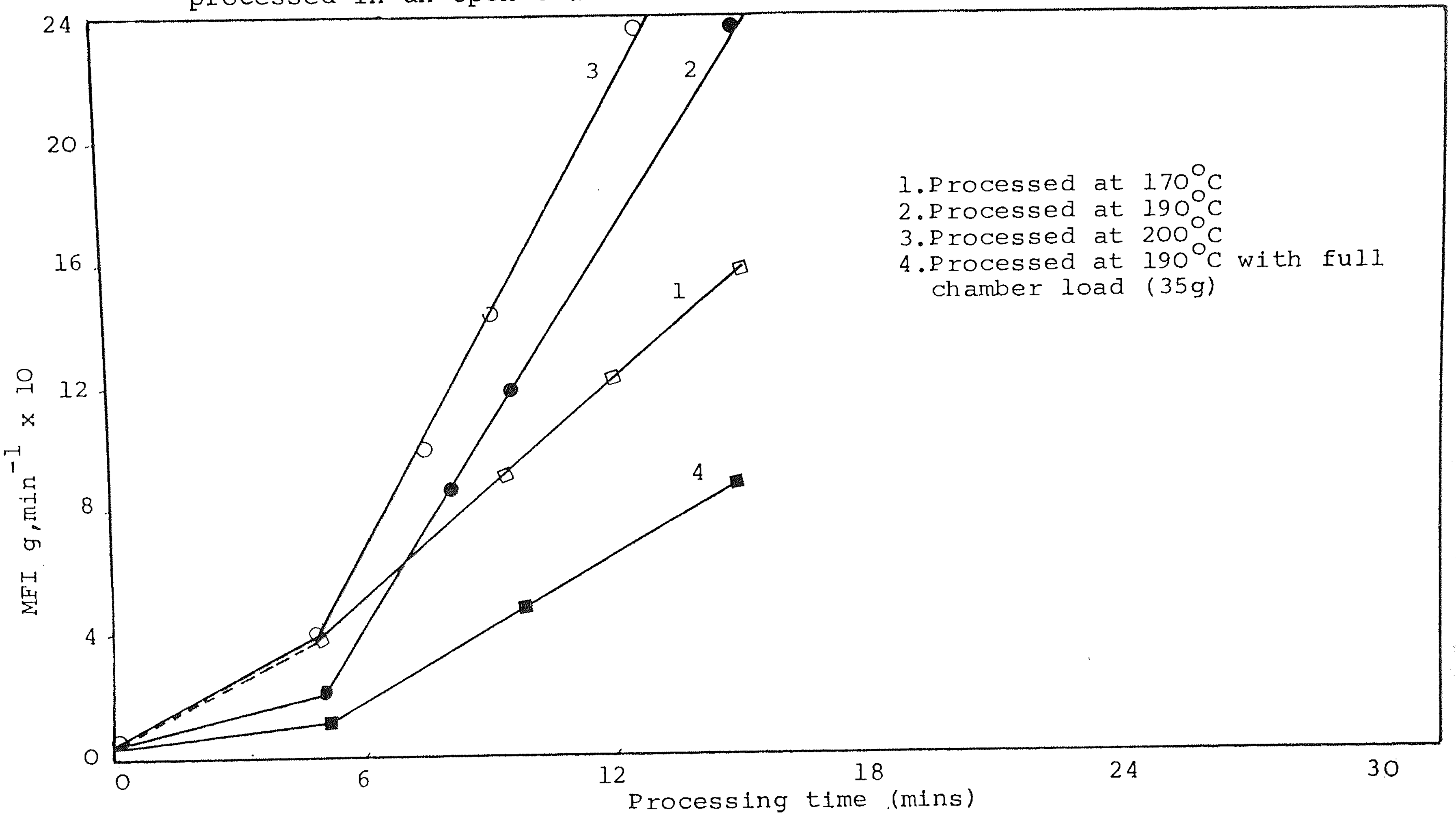


Fig. 3.2 Changes in melt flow index of polypropylene at different processing temperatures, processed in an open chamber



Both the figures also show that melt flow index values is higher in the early stages of processing (Fig. 3.1 curve 1, Fig. 3.2 curve 1) when processed at lower temperature, 170°C compared to the higher processing temperature. This is due to the effect of shear which is higher in early stages of processing at lower temperature (see Fig. 3.3 curve 1).

Polypropylene undergoes degradation in the melt stage during processing even in the presence of a limited supply of air (Fig. 3.1 curves 1, 2 and 3). However, when oxygen is completely excluded by purging with nitrogen rheological changes are eliminated (Fig. 3.1 curves 4 and 5) completely. The role of oxygen in the degradation of polypropylene during processing is clearly evident from the Fig. 3.2. The severity of polymer degradation in this case is seen by the higher slope of the melt flow index vs time curves at all processing temperatures compared with Fig. 3.1. The effect of oxygen is again evident by comparison of curves 2 and 4 in Fig. 3.2. In both cases polypropylene is processed at 190°C and the chamber is left open to the atmosphere. The only difference is that chamber is half full (20g of polymer) in the former case and full charge (35g) is used in the latter case. The lower slope of curve 4 indicates a lower rate of polymer breakdown compared with curve 2.

Curves 1, 2 and 3 in Fig. 3.3 show the change of applied torque with time during the processing of polypropylene in the RAPRA torque rheometer at 170°C, 200°C in closed chamber and 200°C in open chamber respectively. The higher amount of torque at lower temperature (170°C) is observed which corresponds to The higher rate of polymer breakdown in the early stages of processing (as it was shown by MFI values, see Figs. 3.1 and 3.2).

The torque decreases with time in all three cases which could be mainly due to the effect of temperature on the viscosity of the polymer, since higher temperature shows higher reduction in the torque with time (compare curves 1 and 2 in Fig. 3.3).

Molecular weight distribution of the processed polymer samples was measured using GPC technique as described in Chapter 2 (see 2.3.5).

Fig. 3.4 which relates molecular weight distribution to the processing time for polypropylene under limited supply of air (closed mixer) shows that there is change in $\bar{M}_w$ from the beginning of the processing. $\frac{dw}{d \log M}$ increases with processing time and $\bar{M}_w$ decreases which corresponds to the increase in the melt flow index (Fig. 3.1 curve 3). No significant broadening of

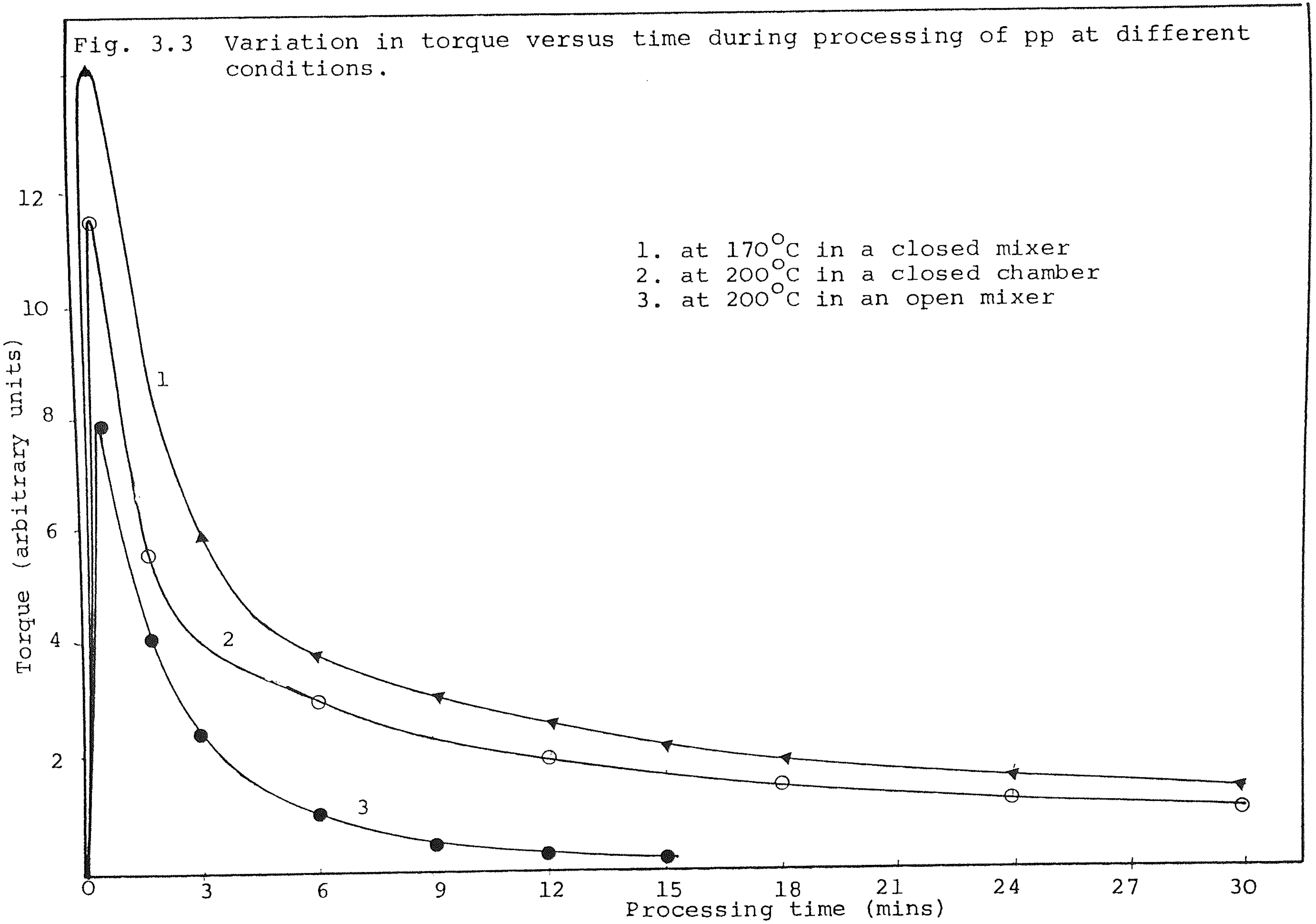
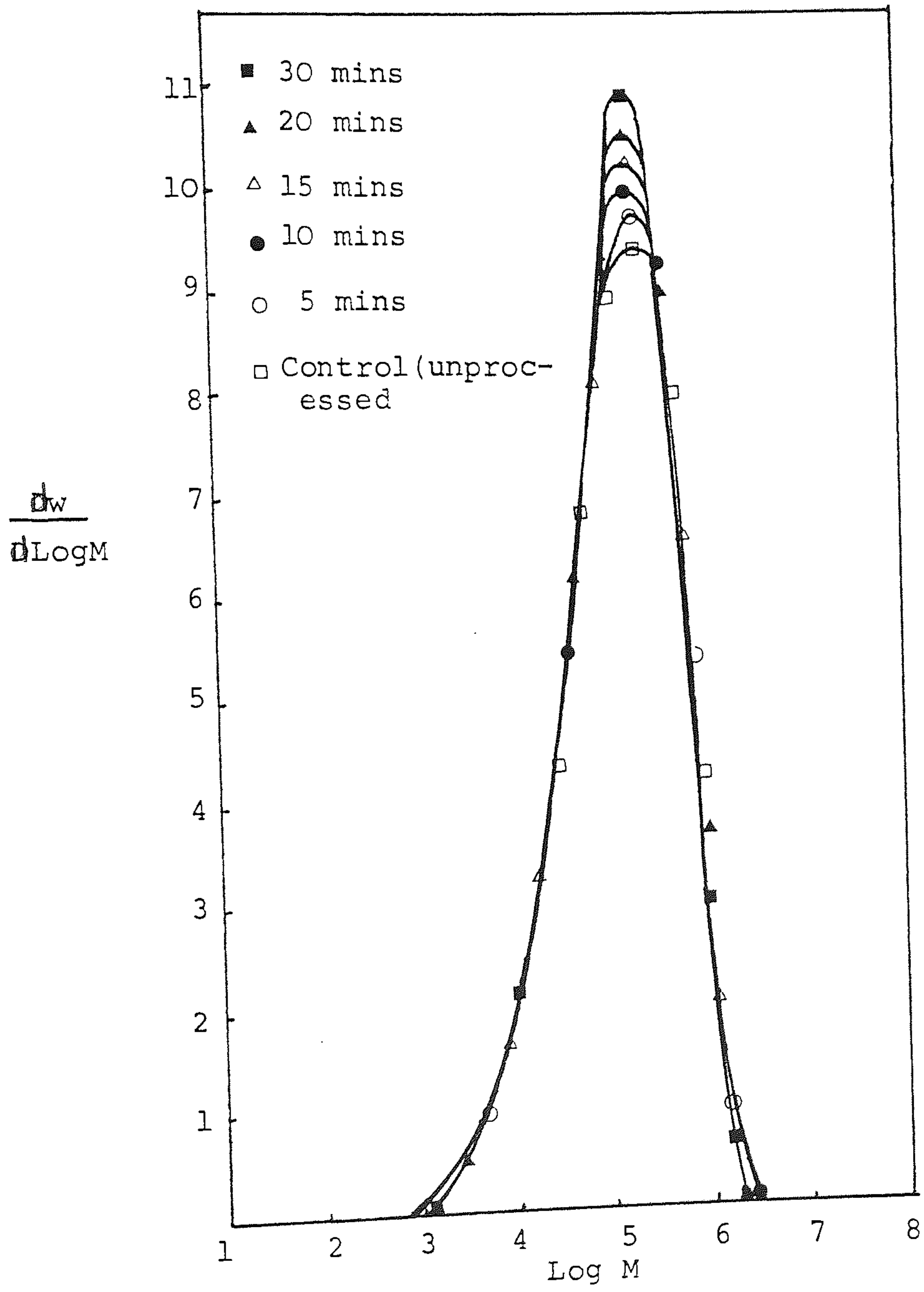


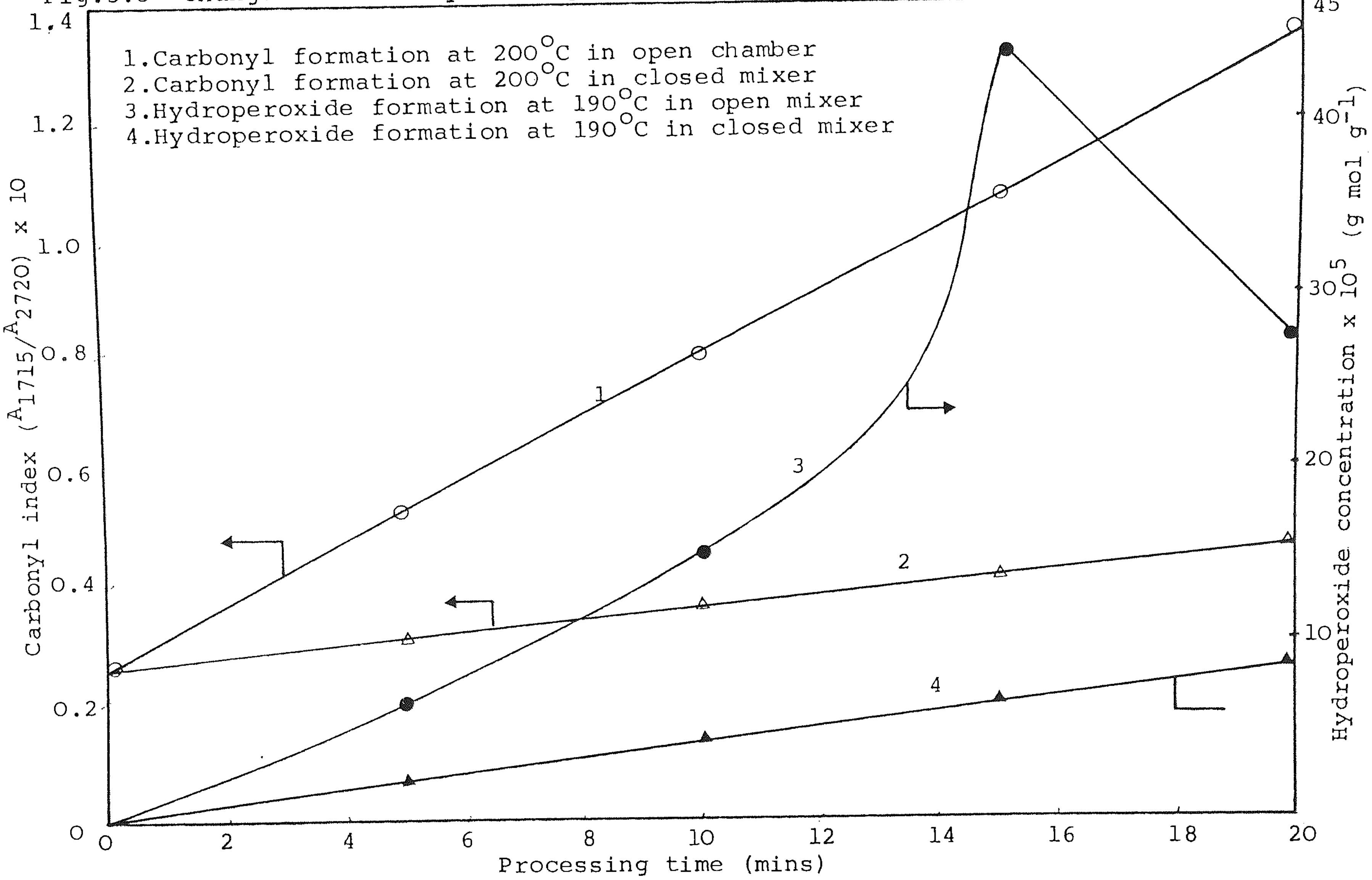
Fig. 3.3 Variation in torque versus time during processing of pp at different conditions.

Fig. 3.4 Effect of processing time on the molecular weight distribution of polypropylene (samples processed in a closed mixer at 200°C)

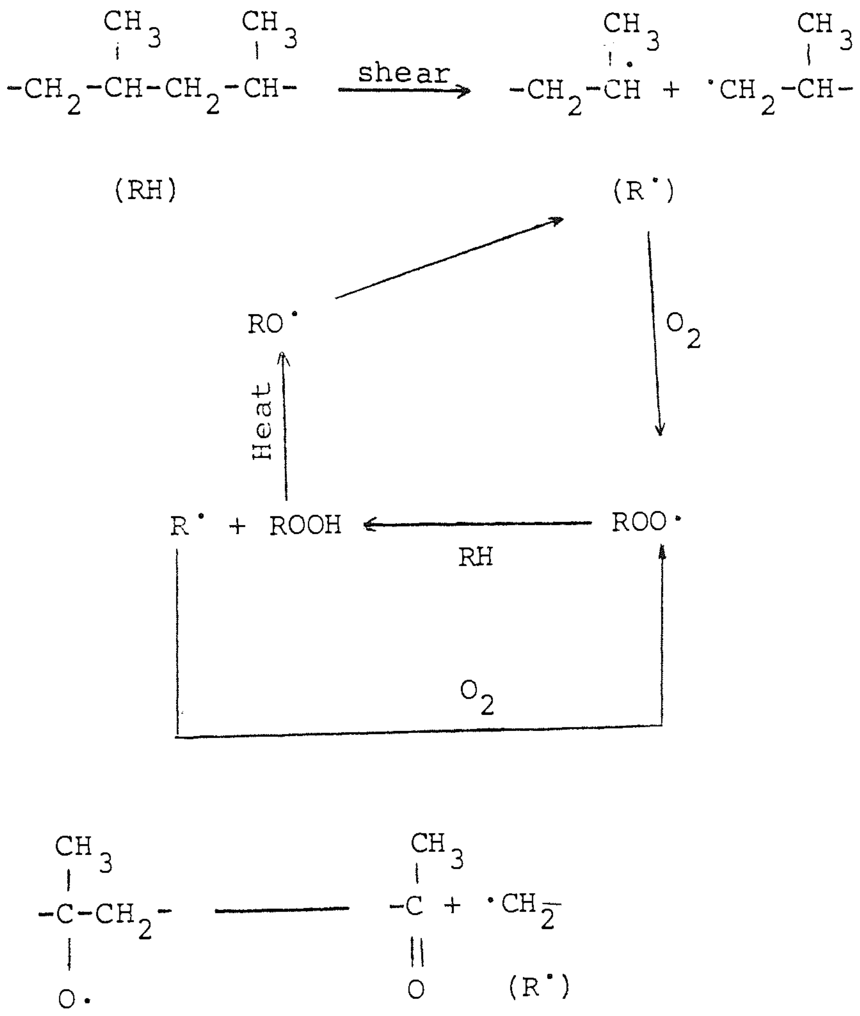


the molecular weight distribution is observed indicating that no cross-linking occurs during the processing operation. A slight narrowing of molecular weight distribution could be explained as being due to chain scission of the polymer molecules during the processing. Fig. 3.5 (curves 1 and 2) relates the formation of carbonyl to processing time under both aggressive and mild processing operations. It can be seen that chemical changes occur even after 5 minutes of processing. As might be expected a greater rate of carbonyl formation is observed in the open chamber processing relative to that in the closed mixer. Fig. 3.5(curves 3 and 4) depicts the formation of hydroperoxides in processed polypropylene at various processing times under both severe and mild processing conditions. The peroxide content (measured chemically, see section 2.3.9A) increased rapidly to a maximum and then declined when processed in the presence of excess of air (Fig. 3.5, curve 3). Fig. 3.5 (curve 4) shows that less peroxides are formed in the closed mixer which contains only a limited amount of air and the rate of peroxide formation is also much lower relative to that in the open chamber processing.

Fig.3.5 Changes in carbonyl and hydroperoxide formation/during processing of polypropylene



The following reaction scheme (2) shows what is happening in chemical terms during thermal processing oxidation.



Tertiary alkoxide scission

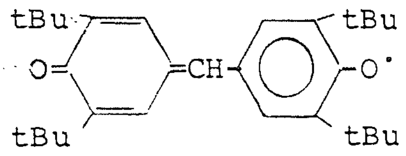
Scheme (2)

3.A.3 Effect of Melt Stabilisers on Processing

The performance of a wide variety of compounds, such as, hindered phenols, quinones, sulphur compounds, phosphoric compounds, stable free radicals, iodo compounds, peroxide decomposers and radical deactivators as melt stabilisers has been empirically evaluated by Henman(194a). He has concluded that the key to an effective melt stabiliser should be a material that can preferably deactivate alkyl radicals before they react with oxygen. In the previous section it is clearly shown that polypropylene undergoes degradation in the melt state even under mild processing conditions. Temperature, shear and oxygen play predominant role in the degradation process. When the polymer is processed in the presence of a limited air supply, a situation found in a commercial processing operation, alkyl radicals are formed in abundance due to the effect of shear in the early stages therefore, shear is primarily responsible for polymer breakdown.

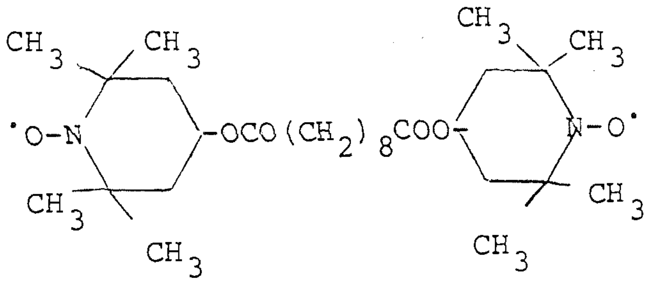
However, in the presence of excess air alkylperoxy radicals predominate in the system. The present study compares the behaviour of effective free radical traps in greater detail during melt stabilisation of polypropylene and the mechanisms of antioxidant action are discussed. The melt stabilisers are listed below with the code name used in this and subsequent chapters.

Additives Code Name



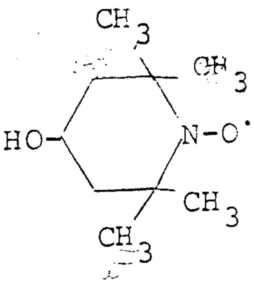
$G^{\bullet}$

2,6 di-tert-butyl-α-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)p-tolyloxy or Galvinoxyl



B(TMPO)S

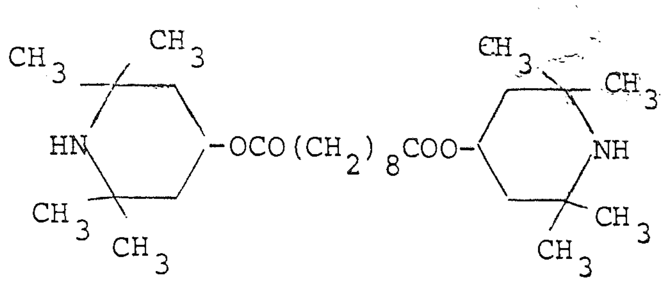
Bis-(2,2,6,6-tetramethyl-4-piperidinyl-N-oxyl)Sebacate



4OHTMPO

4-Hydroxy 2,2,6,6-tetramethyl-piperidineoxyl

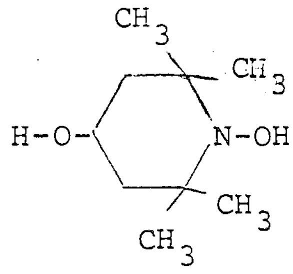
Code Name



B(TM P)S

Bis(2,2,6,6-tetramethyl,4-piperidininy)sebacate

Under the commercial name, Tinuvin 770



4OHTMPOH

4-hydroxy-2,2,6,6-tetramethyl N-hydroxy piperidine

$(C_{17}H_{35}COO)_2Cu$ Cust

Cupric stearate

I_2

Iodine

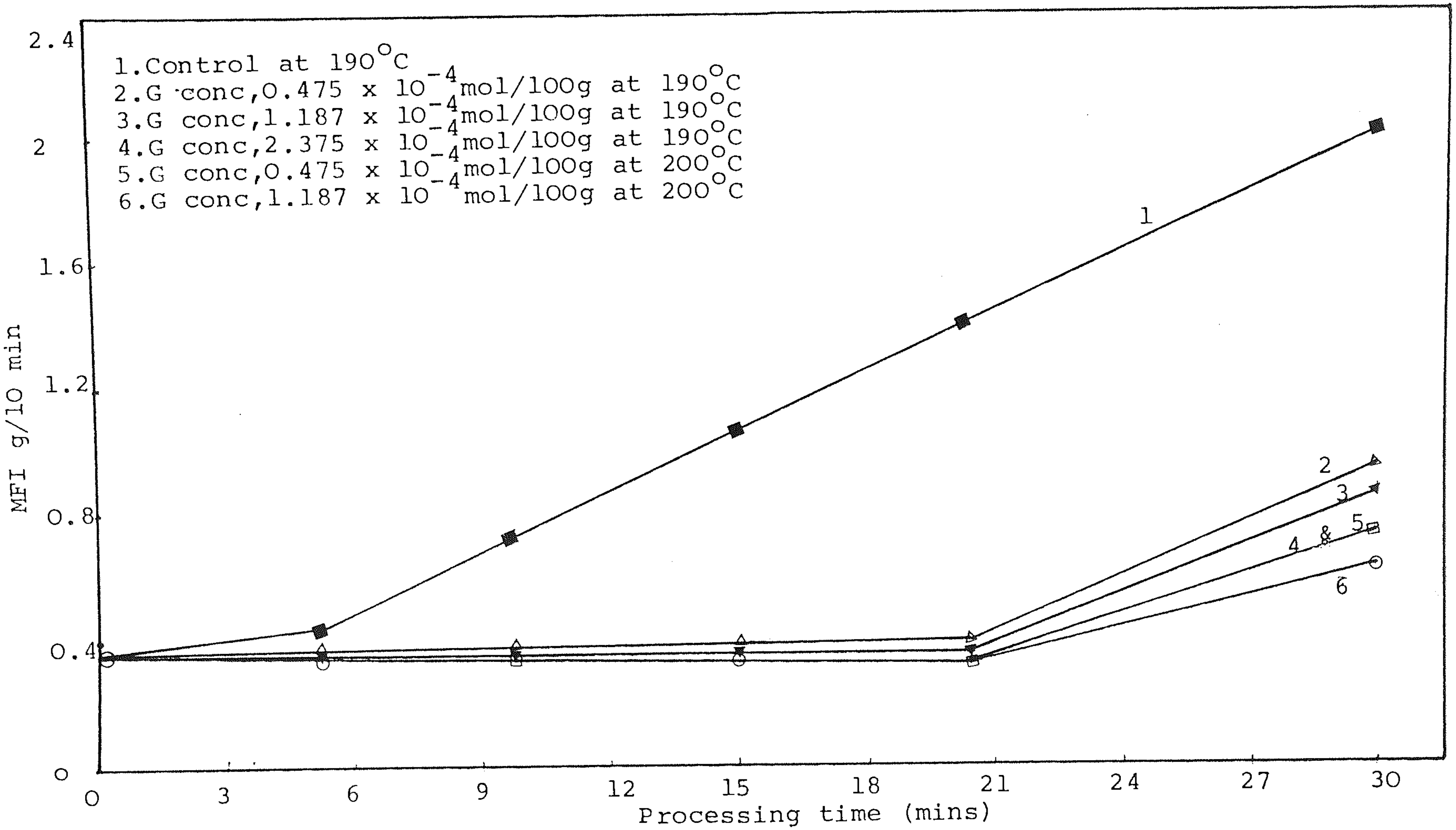
3.A.4 Results

3.A.4.1 Effect of Galvinoxyl on Melt Stability of Polypropylene

Fig. 3.6 shows the effect of Galvinoxyl ($G^{\bullet}$) on the oxidative stability of polypropylene during the processing at 190°C and 200°C in the presence of a limited amount of air for various length of time. This figure also shows the effect of galvinoxyl concentration on the melt stability of polypropylene (curves 2,3 and 4 at 190°C, 5 and 6 at 200°C). It is clearly seen from Fig. 3.6 that galvinoxyl stabilises polypropylene very effectively at all concentrations used under this processing operation up to 20 minutes of processing. After 20 minutes of processing galvinoxyl at higher concentrations shows slightly lower rates of oxidation. Curves 5 and 6 in Fig. 3.6 show the changes in melt flow behaviour of polypropylene containing galvinoxyl at 200°C. An increase in processing temperature does not seem to have a significant effect on the melt stabilisation effectiveness of galvinoxyl and after 20 minutes of processing the rate of polymer degradation at 200°C is relatively lower to that at 190°C, although rate of degradation of the unstabilised polymer is increased with increasing processing temperature.

The effect of galvinoxyl on the oxidative stability of polypropylene during processing in an open chamber (air excess) at 190°C and 200°C is shown in Fig. 3.7. The control samples (curves 1 and 5) show a very fast increase in MFI due to the high rate of chain scission

Fig. 3.6 Effect of galvinoxyl concentrations on the melt flow index of pp processed in a closed mixer at 190°C and 200°C



of the polymer molecules. However, even under severe processing conditions galvinoxyl exerts some melt stabilisation effectiveness in polypropylene at the lowest concentration (1.187×10^{-4} mol/100g, curve 6). Unlike processing in a closed chamber, galvinoxyl does not show a marked concentration effect in the melt stabilisation of polypropylene when processed in the open chamber. As the galvinoxyl concentration is increased the rate of polymer breakdown decreases (Fig. 3.7 curves 2, 3 and 4). Again an increase in processing temperature in excess air does not seem to cause a marked increase in polymer degradation when galvinoxyl is present at the same molar concentration (Fig. 3. 7, curves 2 and 6). No change in melt flow index of polypropylene is observed when polypropylene is processed with galvinoxyl in a closed chamber after purging with nitrogen (Fig. 3.8).

Fig. 3.9 shows the effect of galvinoxyl on molecular weight distribution of polypropylene during the melt processing in the closed chamber at 200°C.

Comparison of the curves with each other reveals that the molecular weight of polypropylene is not changed to any noticeable extent during melt processing which is also reflected in MFI measurements (Fig. 3.6).

Fig. 3.7 Effect of galvinoxyl on the melt flow index of pp, processed at 190°C and 200°C in an open mixer

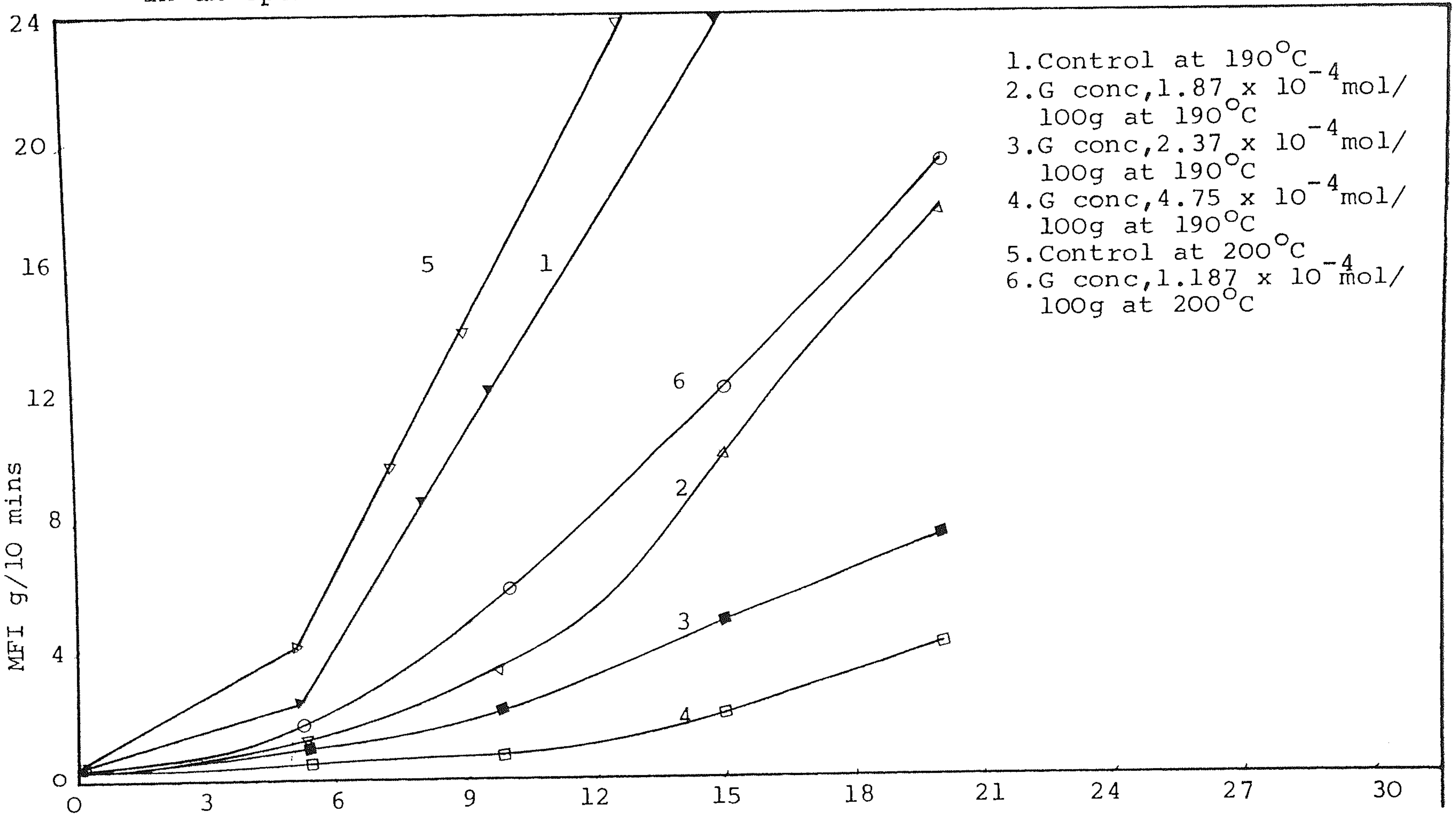
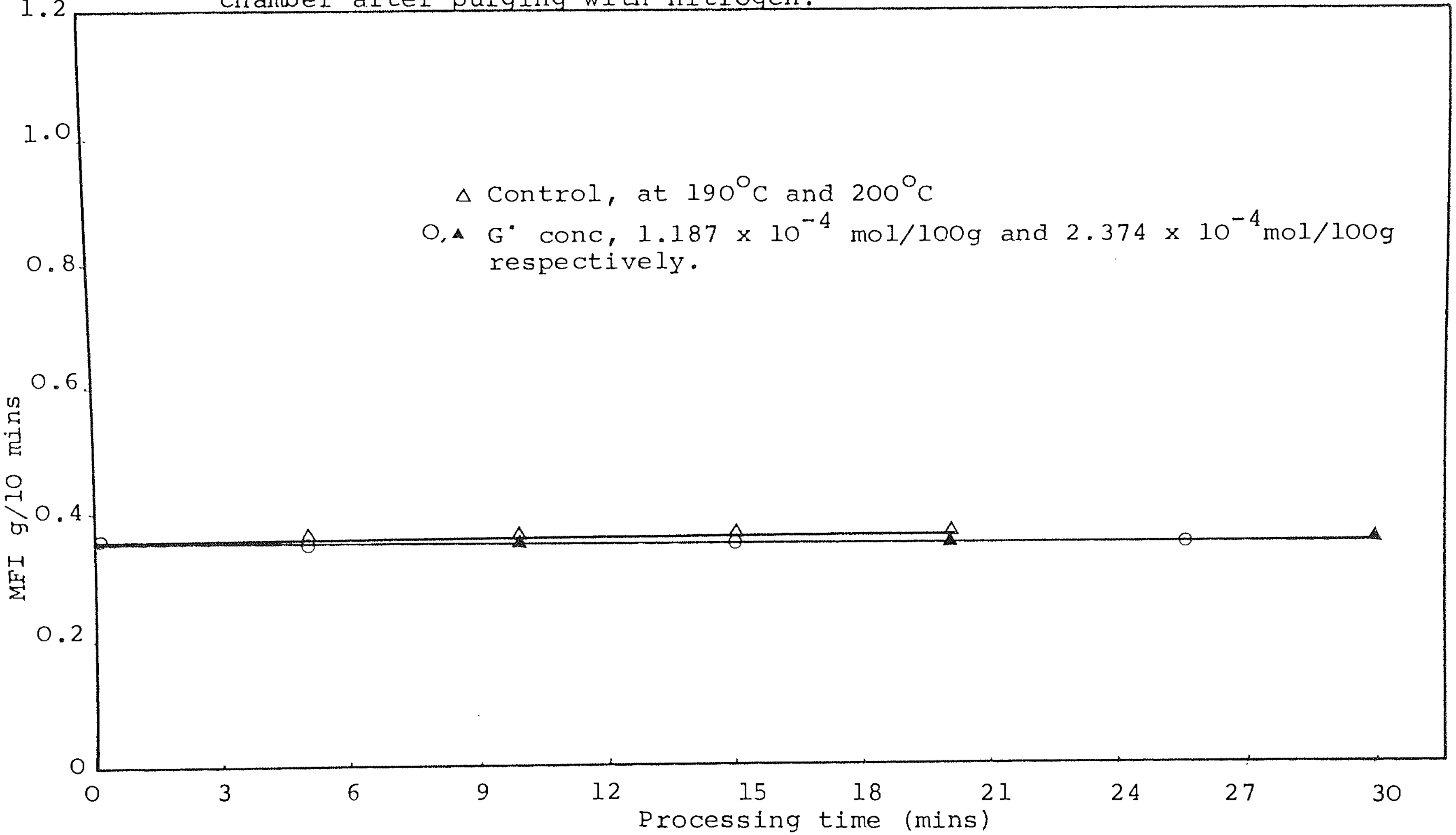


Fig. 3.8 Effect of galvinoxyl on the melt flow index of polypropylene processed in a closed chamber after purging with nitrogen.



At prolonged processing time (30 mins) a decrease in $\bar{M}_w$ occurs which corresponds to the increase in MFI (see Fig. 3.6). No broadening of molecular weight distribution is observed indicating that no cross-linking has occurred.

Fig. 3.10 illustrates the formation of carbonyl in the processed polymer samples containing galvinoxyl under both severe (open chamber) and mild (closed mixer) processing conditions. The physical changes occurring in the polymer during melt processing are directly related to chemical changes produced in the polymer chains. Thus evaluation of the carbonyl content of the processed polymer provides complementary evidence regarding the melt stabilisation process. Comparison of curve 4 with curve 3 in the Fig. 3.10 indicates that galvinoxyl completely inhibits carbonyl formation in polypropylene in a closed mixer which again correlates with the MFI and molecular weight distribution results (see Figs. 3.6 and 3.9).

Carbonyl formation is inhibited by galvinoxyl up to 15 minutes of processing even in air excess whereas in the control film carbonyl formation is autocatalytic from the very beginning of processing operation (Fig. 3.10 curves 1 and 2). Similarly, no hydroperoxide was detected chemically (see section 2.3.9) in the

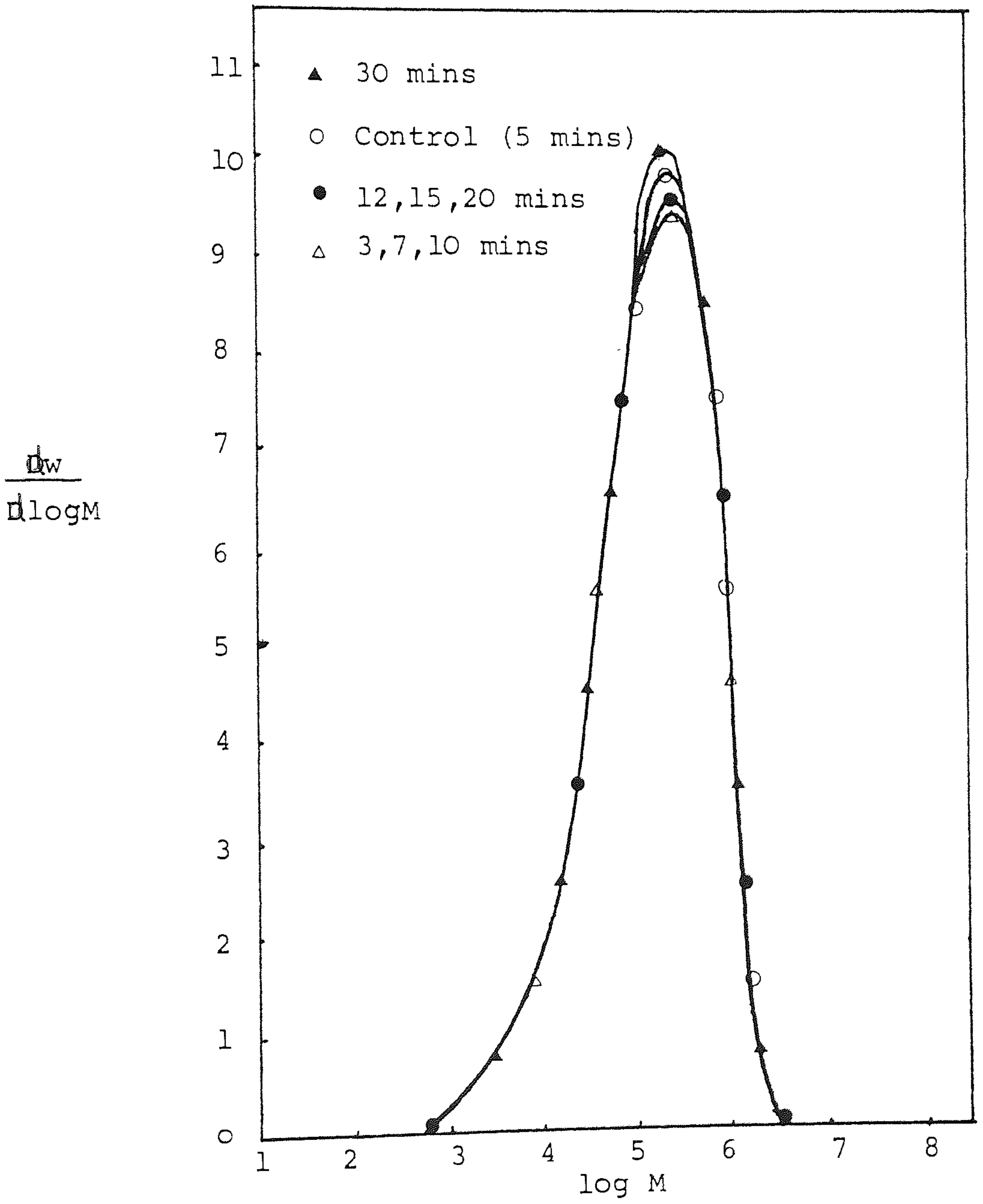


Fig. 3.9 Effect of galvinoxyl on the molecular weight distribution of pp, processed at various times in a closed chamber at 200°C, G·conc=4.75 x 10^{-4} mol/100g

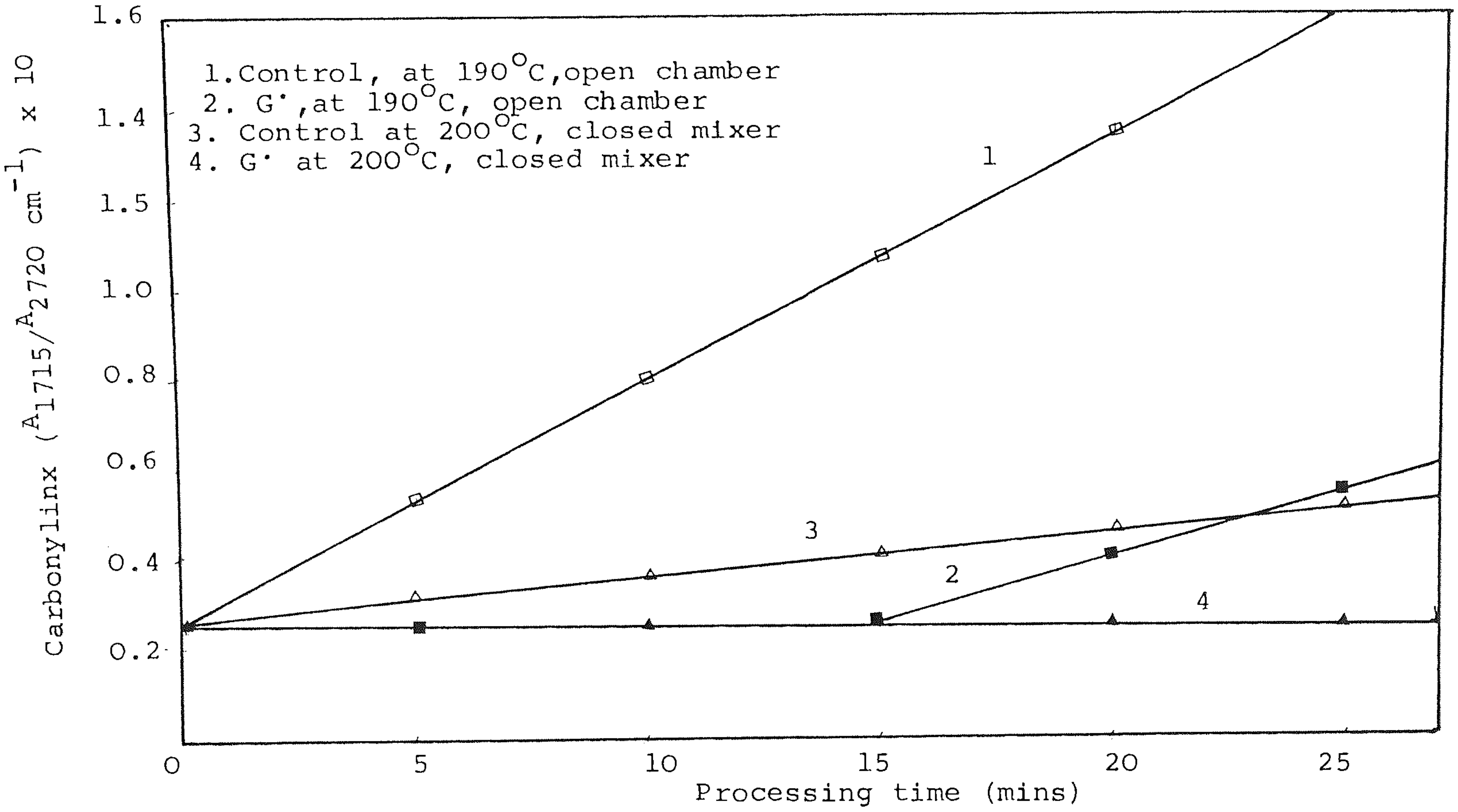


Fig. 3.10 Effect of galvinoxyl on the formation of carbonyl during processing of pp in both closed and open chamber, G˙ conc= 4.75 x 10^{-4} mol/100g

processed polypropylene samples containing galvinoxyl (after cold extraction), although it is present in substantial amounts in control samples (without additive) under the same conditions (Fig. 3.11).

Hydroperoxide formation is not completely inhibited by the presence of galvinoxyl when polypropylene is processed in an open mixer (Fig. 3.11, curve 3). However, it shows an induction period which corresponds to effective initial melt stabilisation (see Fig. 3.7) and then gradually increases (Fig. 3.11, curve 3).

Processed polypropylene samples containing galvinoxyl were compression moulded to films (see, section 2.3.2) and the IR spectra of all unextracted films (identical thickness, 1.8 x 10^{-2} cm) were taken. They showed a hydroxyl absorption at 3640 cm^{-1} and two other small peaks at 1615 cm^{-1} and 1550 cm^{-1} (Fig. 3.12, a typical IR spectra). IR spectra of the extracted films revealed that the above absorptions disappeared, thus galvinoxyl did not become bound to the polymer during the processing operation and these absorptions were due to conversion of galvinoxyl to other products.

Fig. 3.13 depicts the change of hydroxyl absorption with processing time. It shows that on increasing the processing time a fluctuation in hydroxyl

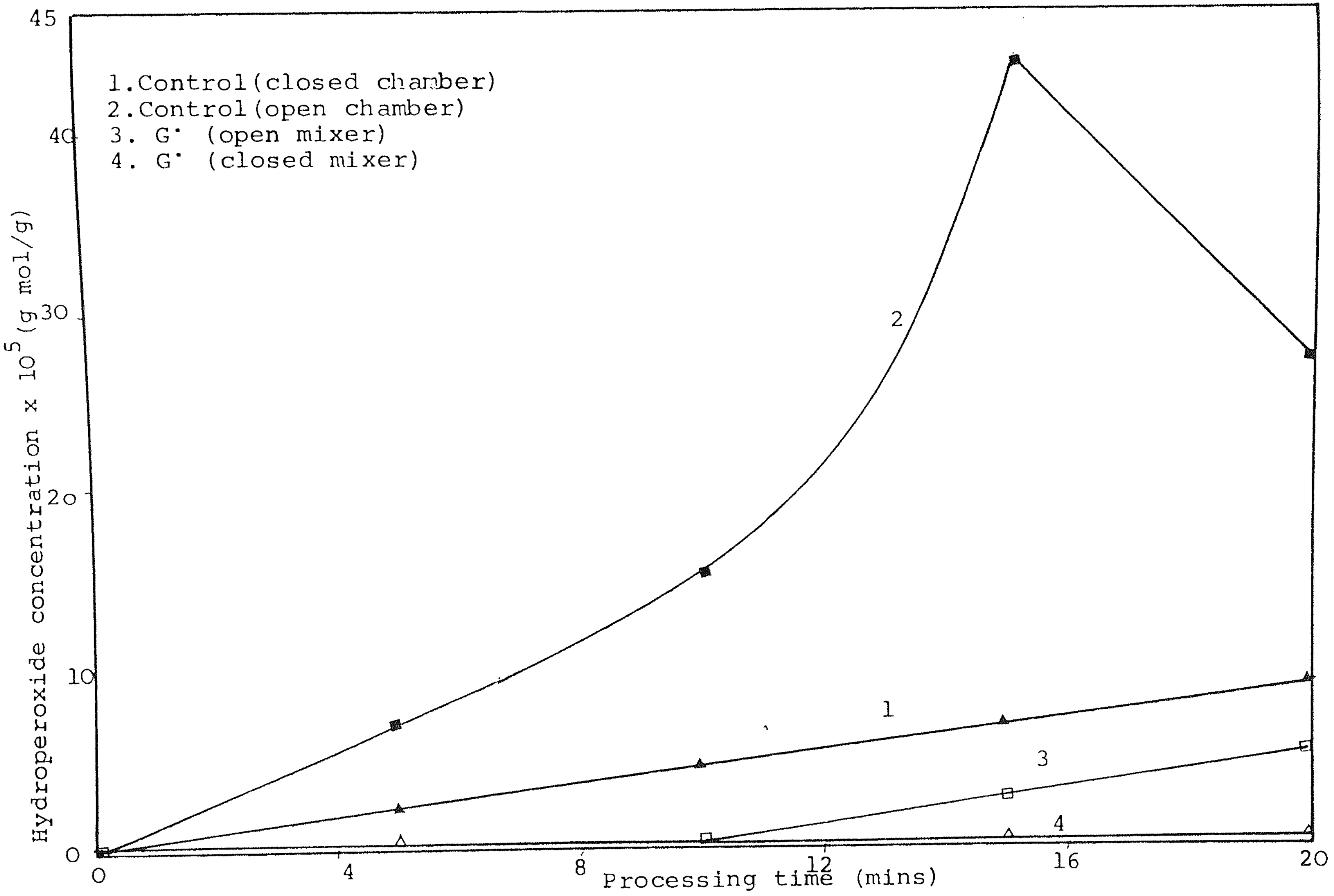


Fig. 3.11 Effect of galvinoxyl on the formation of hydroperoxide during processing of pp in both closed and open chambers, G˙ conc, 4.75 x 10^{-4} mol/100g

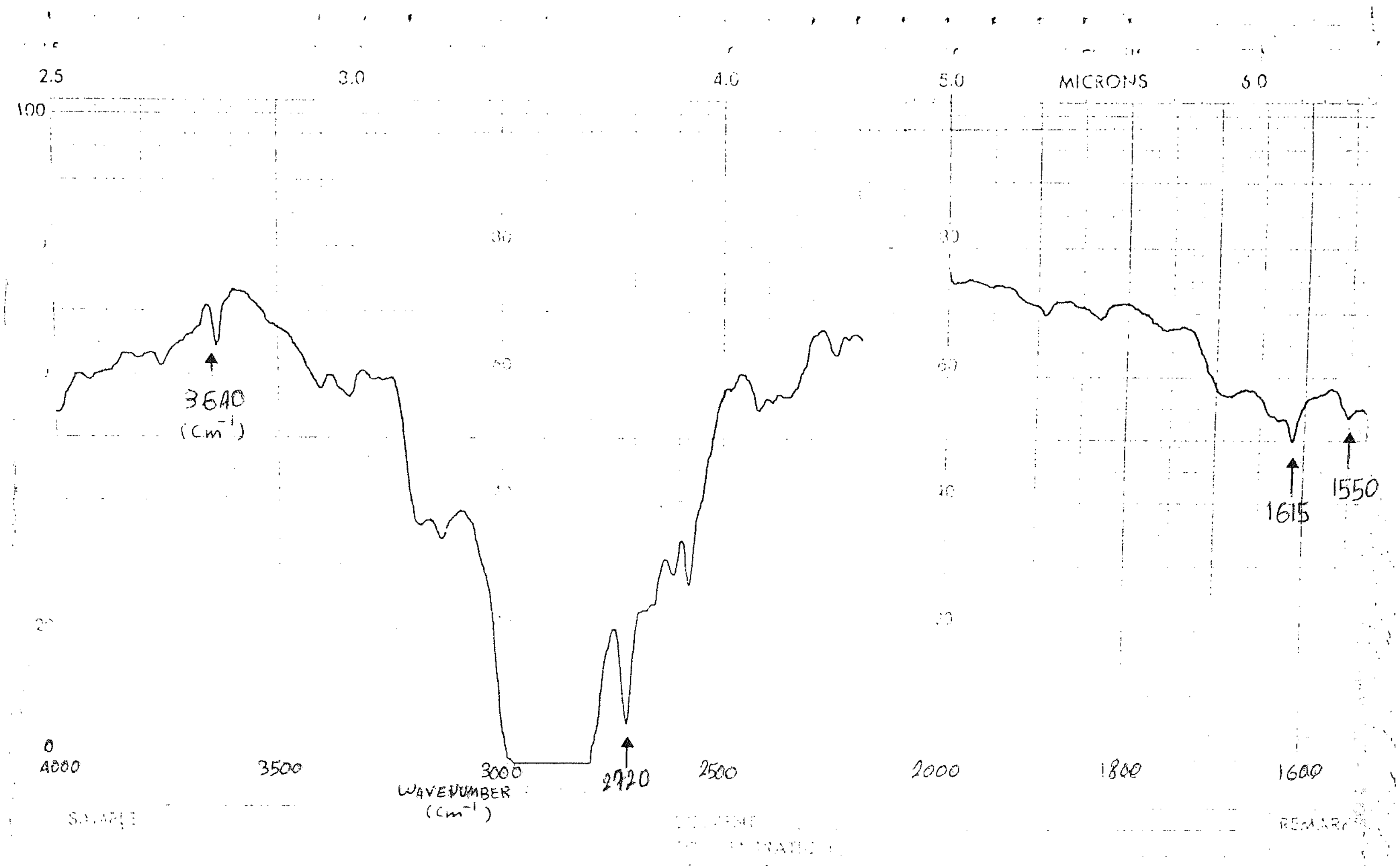


Fig. 3.12 Typical I.R spectra of pp film containing galvinoxyl (processed in a closed mixer at $200^{o}C/10$ mins), G· conc = 9.5×10^{-4}mol/100g

absorptions occurs i.e. the hydroxyl absorption increases at the early stages of processing (3 mins), then decreases to about 8 mins. As the processing operation continues it starts to increase up to about 15 mins. and then again decreases (Fig. 3.13, solid curve).

The UV spectra of all unextracted films were also taken. They showed a strong absorption at 380 nm. Variation of the absorption (λ_{max} = 380 nm) with processing time is observed which corresponds exactly to the variation of phenolic absorption at 3640 cm^{-1} in the infra red. This correlation is shown in Fig. 3.14 in the form of a straight line (linear relationship).

IR and UV spectra of extracted product solution (C_6H_5Cl and hexane used as solvents) showed the phenolic O-H absorbance in the infra red (3620 cm^{-1}) and UV absorption at 380 nm. Investigation of synthesised hydrogalvinoxyl (GH, see section 2.1.2) by IR and UV spectroscopic methods showed that the above absorptions were due to hydrogalvinoxyl formation during the processing operation.

The effects of other factors such as galvinoxyl concentration, processing temperature and oxygen concentration

(All samples processed in a closed mixer at 200°C for various lengths of times, G˙ conc = 4.75 x 10^{-4}mol/100g

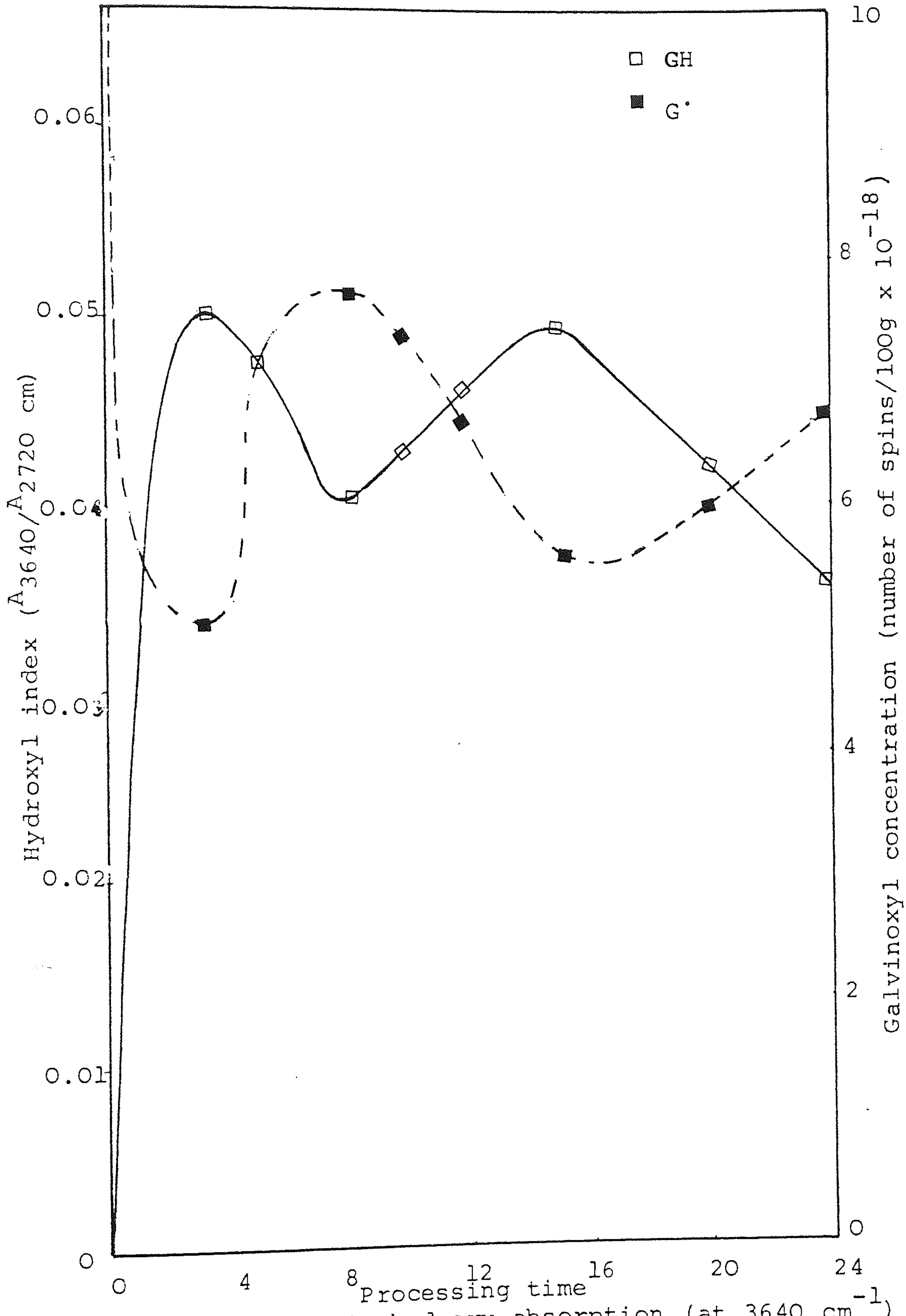


Fig. 3.13 Changes in hydroxy absorption (at 3640 cm^{-1}) and galvinoxyl concentration of pp films containing galvinoxyl with processing time

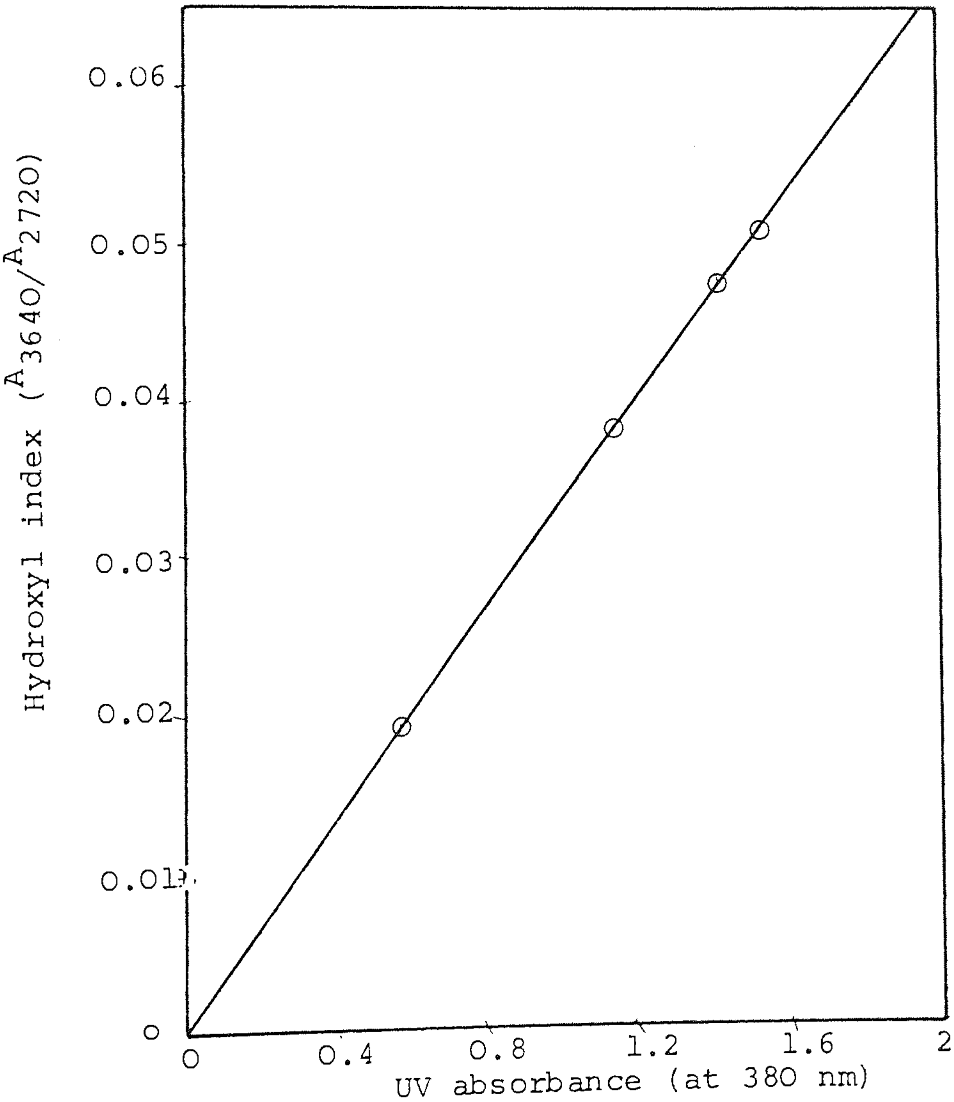


Fig. 3.14 Relation between IR and UV absorbances of GH formed during processing of pp with galvinoxyl (all samples processed in a closed mixer at 200°C for various lengths of times G· conc= 4.75×10^{-4} mol/100g)

on the interaction of galvinoxyl with polypropylene during the melt processing were also studied.

Fig. 3.15 shows the effect of the above factors on the UV absorption at 380 nm (GH).

At half the initial galvinoxyl concentration a much lower concentration of GH was formed (Fig. 3.15, curve d) but when most of the air in the chamber was replaced by nitrogen, GH concentration increased (Fig. 3.15, curve b). An increase in processing temperature from 190°C to 200°C also led to an increase in GH concentration (Fig. 3.15, curve c). The same characteristic fluctuation of GH concentration was observed for all conditions up to 30 mins. of processing.

Examination of all the extracted film samples by IR and UV spectroscopy indicated that galvinoxyl did not become bound to the polymer as shown by the absence of absorptions in the processed polypropylene samples.

Hydrogalvinoxyl concentration was measured from calibration graph (Fig. 3.16). The latter was obtained by compression moulding films containing known amounts of pure hydrogalvinoxyl and measuring the UV absorbance (λ_{max} 380 nm) against concentration.

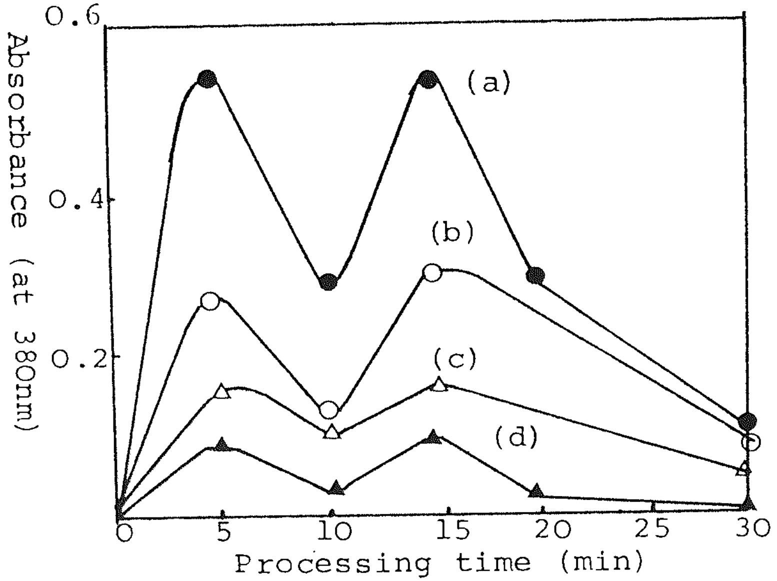


Fig. 3.15 Formation of hydrogalvinoxyl (GH) during the processing of pp containing galvinxoyl (G˙) in a closed mixer.

(a) G˙ conc = 2.374×10^{-4} mol/100g, 190°C, closed mixer
(b) G˙ conc = 1.87×10^{-4} mol/100g, 190°C, closed mixer after purging with N_2
(c) G˙ conc = 1.187×10^{-4} mol/100g, 200°C, closed mixer
(d) G˙ conc = 1.187×10^{-4} mol/100g, 190°C, closed mixer

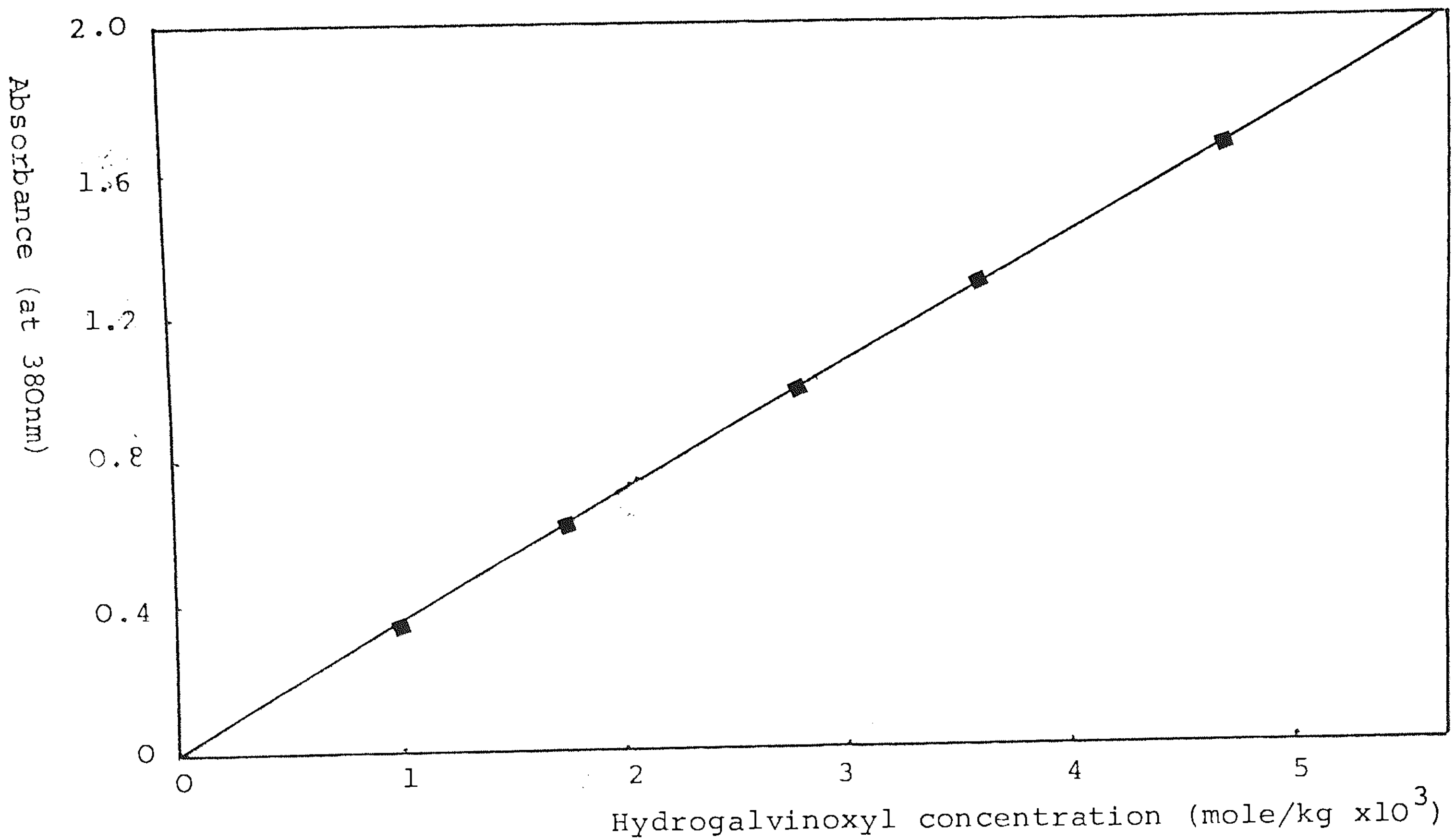


Fig. 3.16 Changes in hydrogalvinoxyl concentrations with UV absorbances (at 380 nm) as a calibration graph

Table 3.1 shows the quantitative results which were obtained from the Fig. 3.15 by measuring the UV absorbance at different conditions and using the calibration graph (Fig. 3.16). A fluctuation of GH concentration is observed in each case (Table 3.1).

Chemical estimation of olefinic unsaturation was carried out on the polymer films after exhaustive acetone extraction (see section 2.3.7). The results, shown in Fig. 3.17 indicate an initial rapid rate of unsaturation formation followed by a lower rate on more prolonged processing.

It was found by glc that 2,6 ditert-butyl,4 benzoquinone was also formed during the processing of polypropylene with galvinoxyl. The amount of the quinone was calculated for 10 mins. processing at 200°C in a closed chamber at 9.5×10^{-4} mole/100g. After extraction with acetone the solution was found to contain only 5.7% of the galvinoxyl originally used.

Examination of unextracted films by e.s.r spectroscopy showed the existence of galvinoxyl in the samples (Fig. 3.18, a typical e.s.r spectra).

The galvinoxyl concentration in the films at various processing times is calculated using cupric sulphate

TABLE 3.1 Concentration of Hydrogalvinoxyl (HG) During Processing of pp at 190°C, 200°C in a closed mixer

Time of Processing (min.)	HG concentration mole/kg x 10^3			
	A	B	C	D
5	0.23	0.41	0.75	1.46
10	0.05	0.3	0.35	0.79
15	0.25	0.425	0.81	1.46
20	0.033	0.35	0.66	0.81
30	0.017	0.135	0.22	0.3

(A) $[G] = 1.187 \times 10^{-4}$ mol/100g, 190°C, closed mixer

(B) $[G] = 1.187 \times 10^{-4}$ mol/100g, 200°C, closed mixer

(C) $[G] = 1.18 \times 10^{-4}$ mol/100g, 190°C after punging mixing chamber with N_2

(D) $[G] = 2.374 \times 10^{-4}$ mol/100g, 190°C, closed mixer

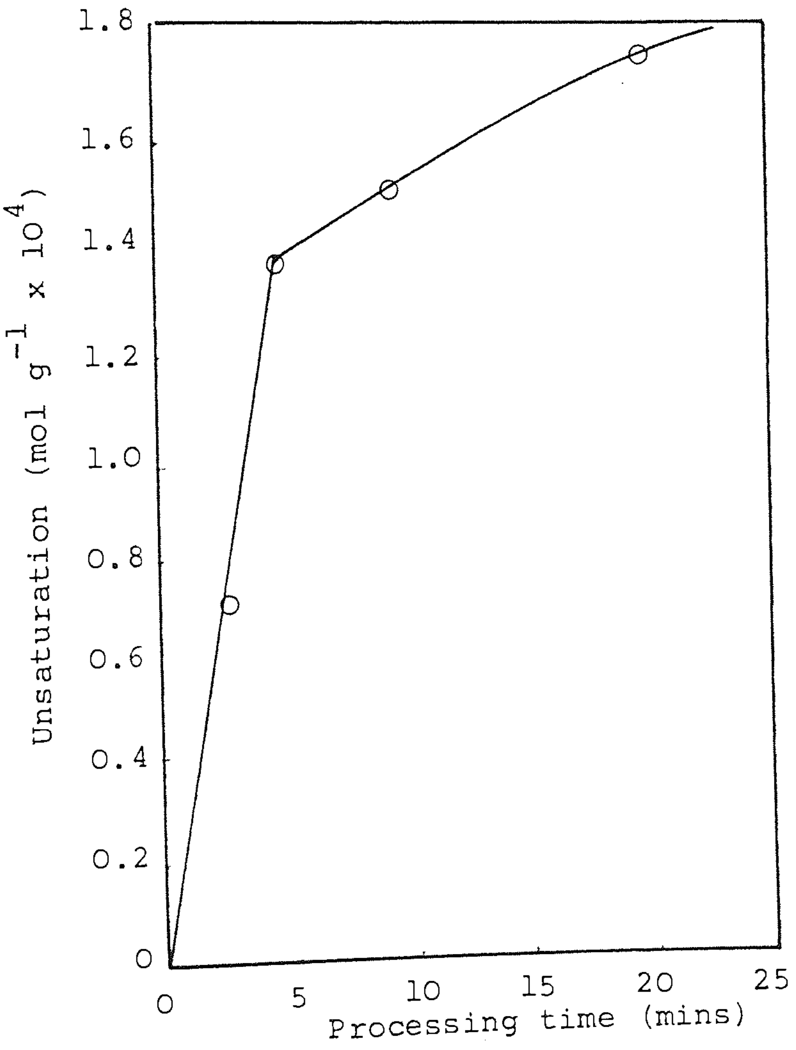
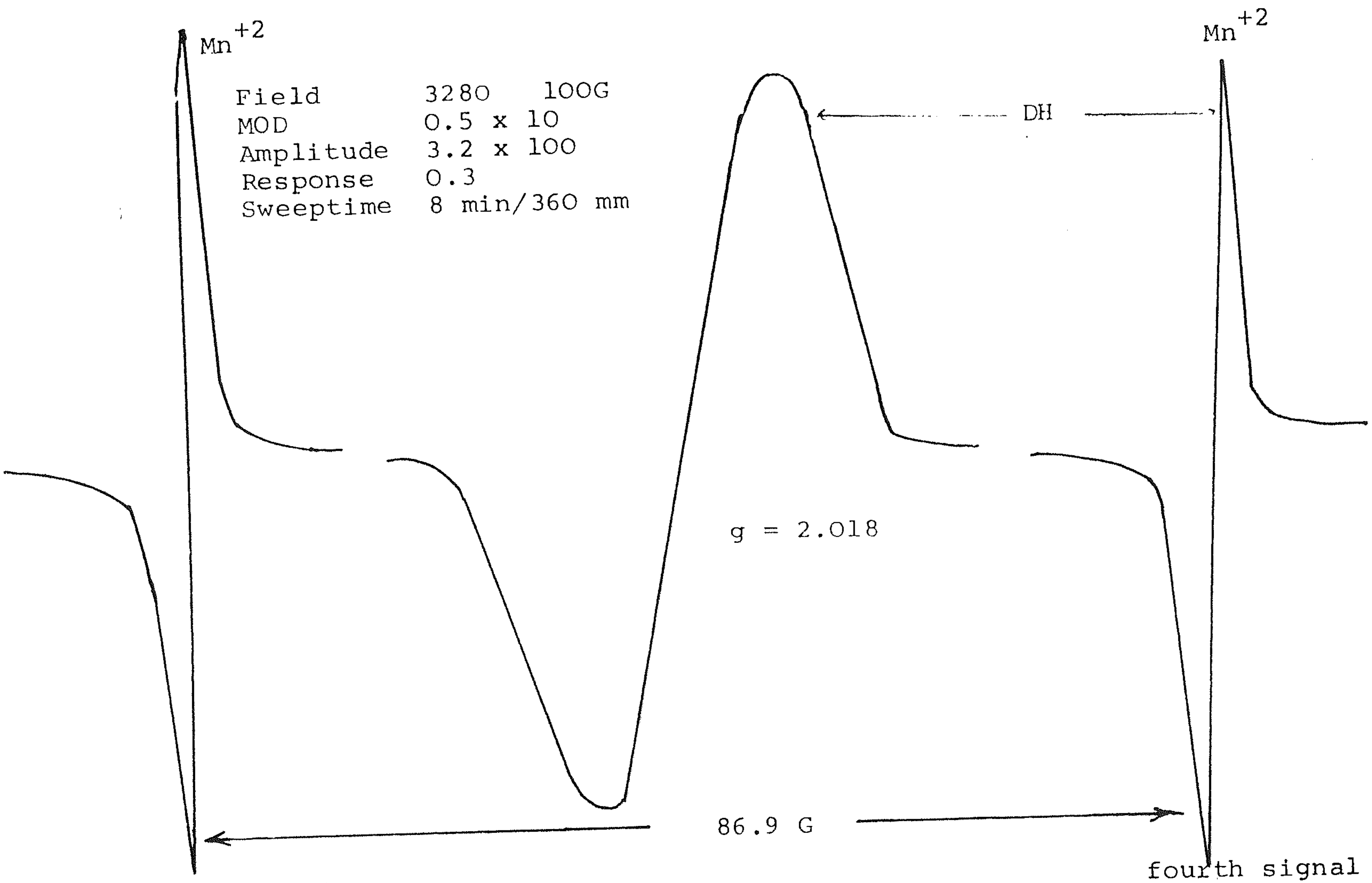


Fig. 3.17 The unsaturation formation during processing of pp at 200°C in the presence of galvinoxyl G· conc = 4.75 x 10^{-4} mol/100g



Field	3280 100G
MOD	0.5 x 10
Amplitude	3.2 x 100
Response	0.3
Sweeptime	8 min/360 mm

Fig. 3.18 Typical E.SR spectra observed in processed pp film containing galvinoxyl (sample processed in a closed mixer at 200°C/10 mins, G· conc 4.75×10^{-4} mol/100g)

solution as a reference (see, section 2.3.13) and the results are shown in Fig. 3.13 (broken curve). A fluctuation of galvinoxyl with processing time is observed.

The e.s.r results and the implications of the above results will be discussed in Chapter 6.

3.A.4.2 Effect of Iodine on Melt Stability of Polypropylene

Fig. 3.19 illustrates the variation of melt flow index of polypropylene with increasing processing time containing iodine at molar concentrations of 1.2×10^{-4}, 3.93×10^{-4}, 7.87×10^{-4} and 1.57×10^{-3} mol/100g processed at 190°C in a closed system. MFI was found to decrease slightly at an early stage of processing and then remained constant. Curves 2 and 3 show that MFI starts to increase after 20 mins. of processing at low iodine concentration and the subsequent rate of increase depends on the iodine concentration. Lower iodine concentrations lead to higher rates of oxidation in the later stages of processing. However, when iodine was used at a higher concentration as a melt stabiliser in polypropylene no change of MFI was observed over 30 minutes of processing (curves 4 and 5).

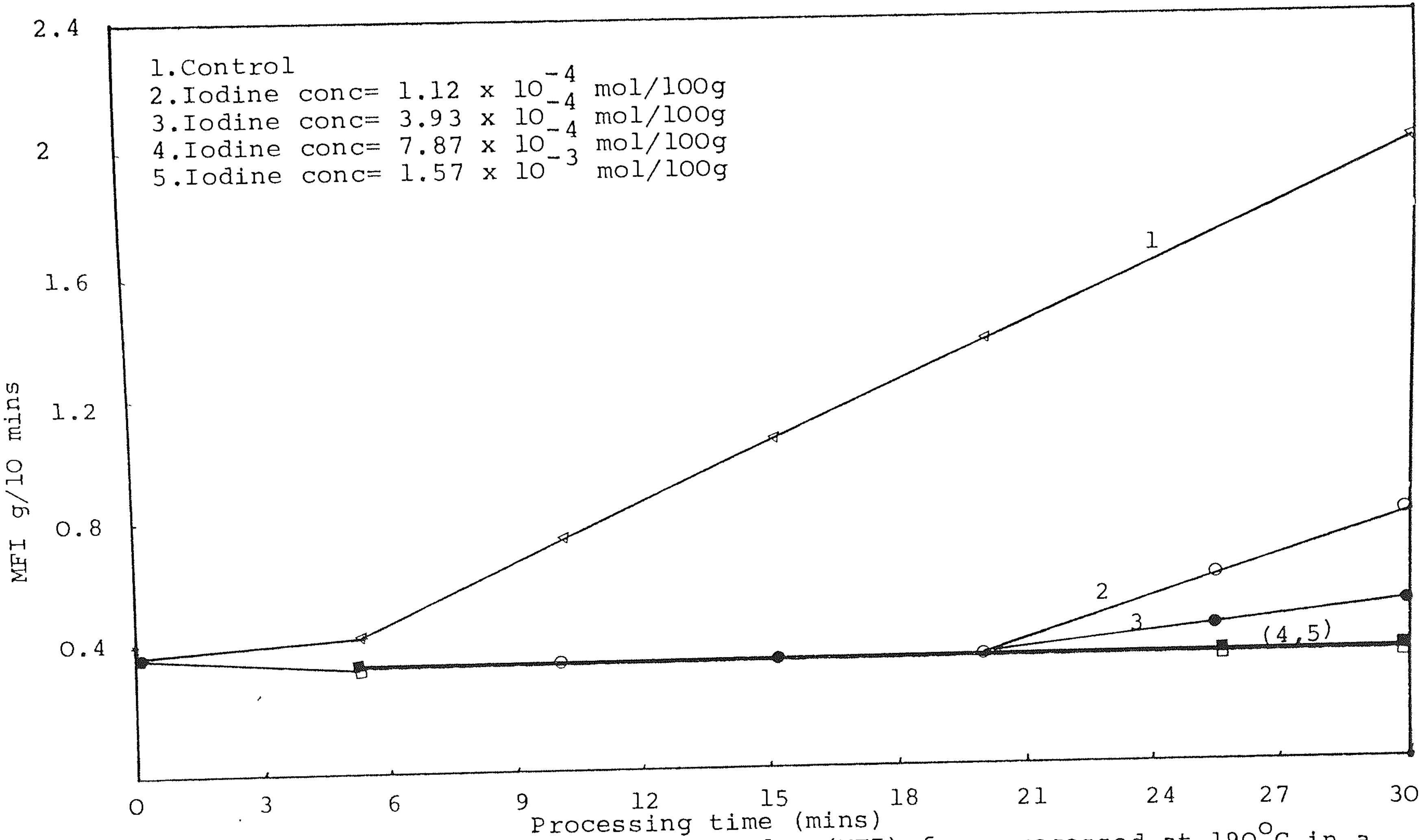


Fig. 3.19 Effect of iodine on the melt flow index (MFI) of pp processed at 190°C in a closed mixer using different concentrations of iodine.

Fig. 3.20 depicts the iodine effect on melt processing of polypropylene at 190°C in excess of oxygen (open chamber). Comparison of curves 2 and 3 with curve 1 (control) reveals that incorporation of iodine led to melt stabilisation even under severe processing conditions.

The addition of 1.57×10^{-3} mol/100g of iodine delayed the onset of chain scission of the polymer molecule for 15 minutes (curve 3). These studies (Figs. 3.19, 3.20) indicate that as long as there is a certain critical concentration of iodine in the system melt stabilisation results. It seems likely that the volatility of iodine under this condition leads to its rapid depleation from the open system.

Fig. 3.21 shows that no significant change in molecular weight distribution of processed polypropylene containing iodine is observed up to 30 mins. processing indicating that no cross-linking has occurred.

Due to interaction of iodine with polypropylene in the melt state hydrogen iodide was formed and was detected using a chemical test described in the experimental section (see, section 2.3.8) and also a PH meter.

Fig. 3.22, curve 1 shows the formation of double bonds

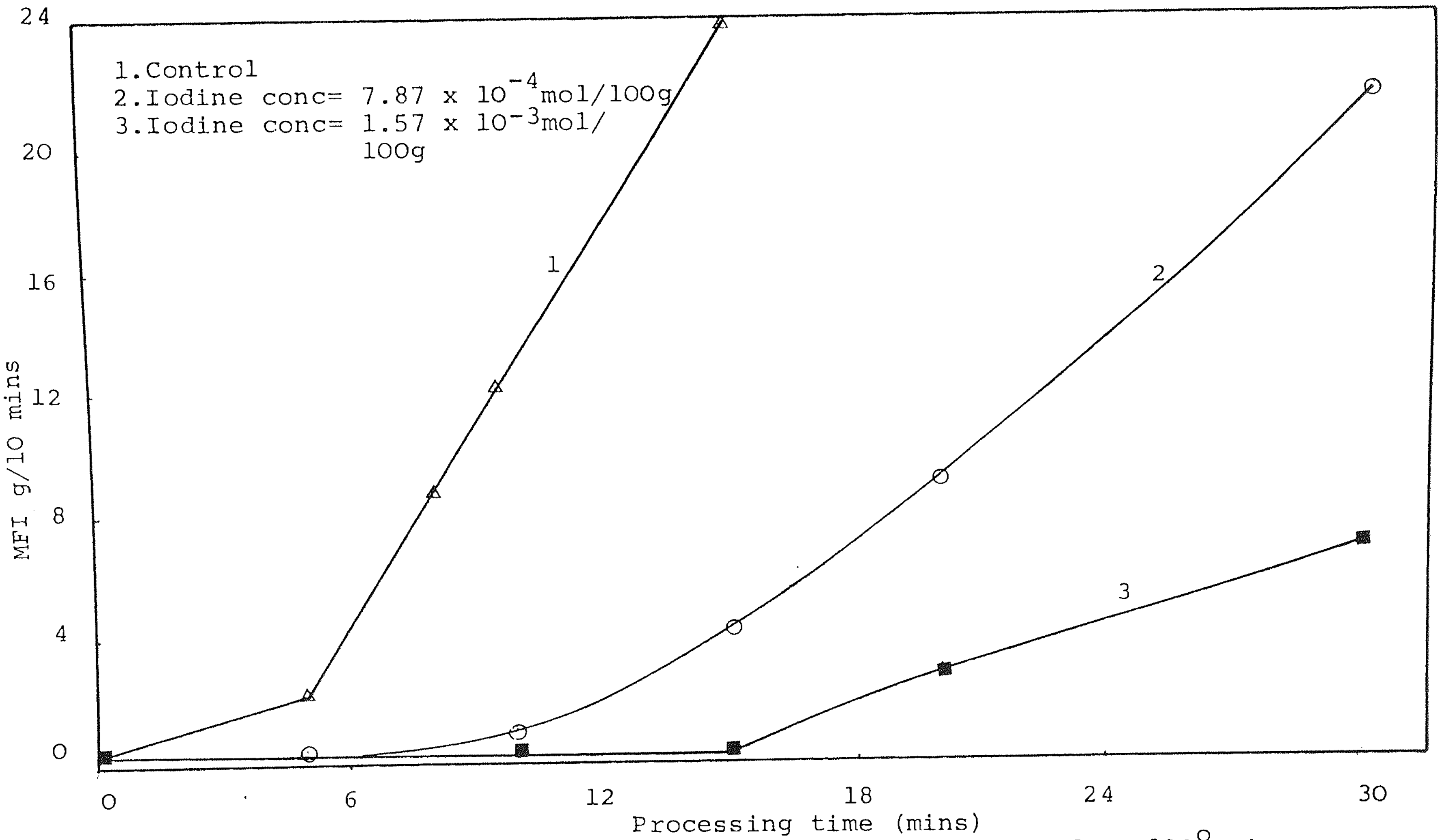


Fig. 3. 20 Effect of iodine on the melt flow index of pp processed at 190°C in an open mixer at two different concentrations.

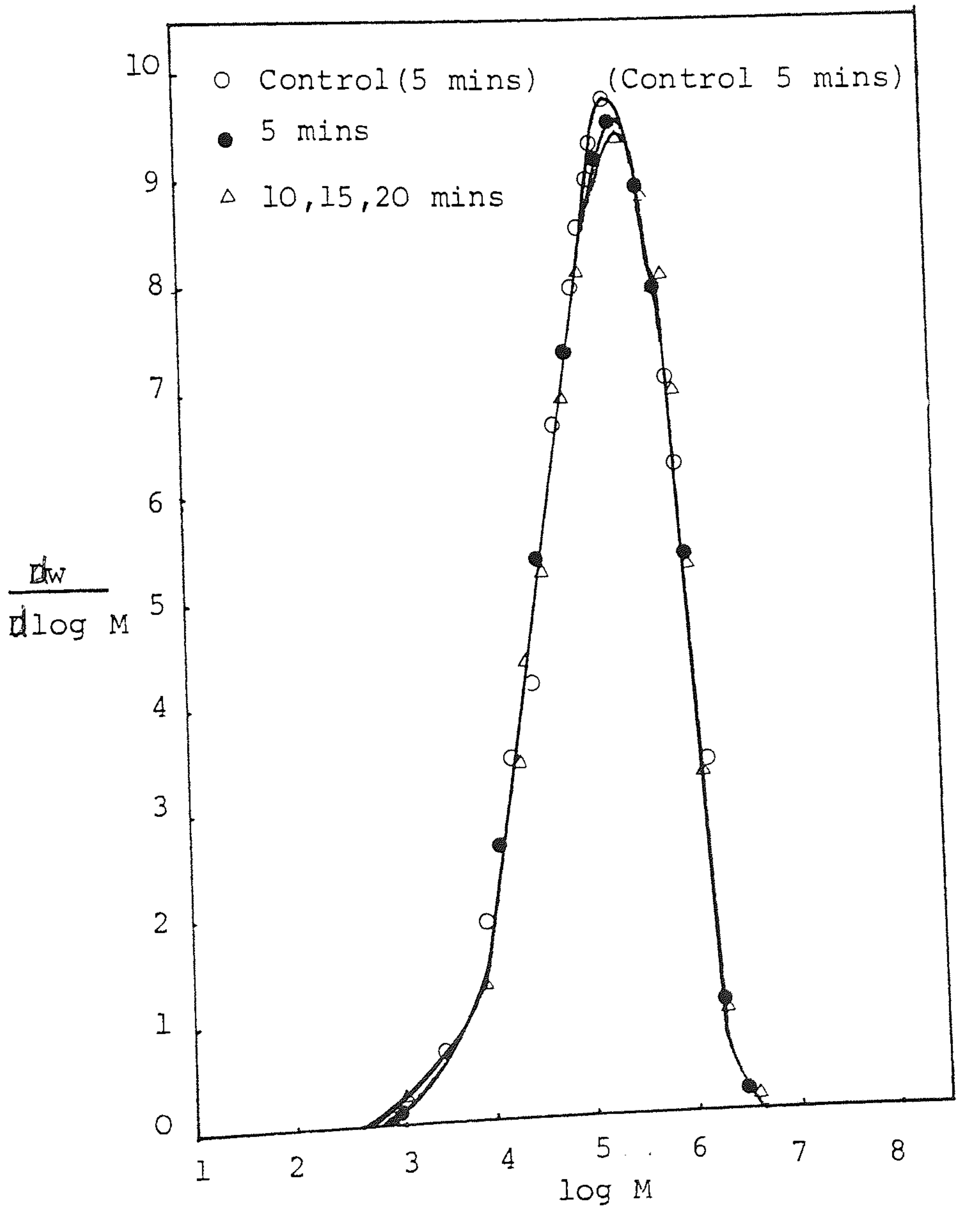


Fig 3.21 Effect of iodine on molecular weight distribution of pp processed at 190°C in a closed mixer at various times, iodine conc = 1.57×10^{-3}mol/100g

due to interaction of iodine with polypropylene during processing at various processing times in the closed chamber by IR method (at 1640 cm^{-1}). It shows a relatively slow linear increase in double bond formation with increasing processing time.

Addition of few ml of $AgNO_3$ (alco) to the solution of extracted processed polypropylene with iodine indecalin (at 135°C) showed a precipitation of silver iodide(221) indicating extraction of iodine from C-I bonds and formation of double bonds in the polymer chains (see Fig. 3.22, curve 3). Curve 3 in Fig. 3.22 indicates the total formation of double bonds, measured by IR method,(a) formed during the processing (b) formed due to reaction of C-I bonds with $AgNO_3$ (alco) which is shown by curve 2 (in Fig. 3.22 double bond index of unstabilised pp is sub-tracted from that of the samples). The unsaturation formation is found to increase linearly with processing time (see Fig. 3.22, curves 2 and 3).

The absolute amount of double bonds forming during the processing of polypropylene containing iodine in the closed chamber and during reaction of processed polypropylene with alcoholic silver nitrate was measured using a calibration graph (Fig. 3.23, see 3.A.1).

1. During processing
2. Due to reaction of C-I bonds with $AgNO_3$ (alco)
3. Total double bond formation.

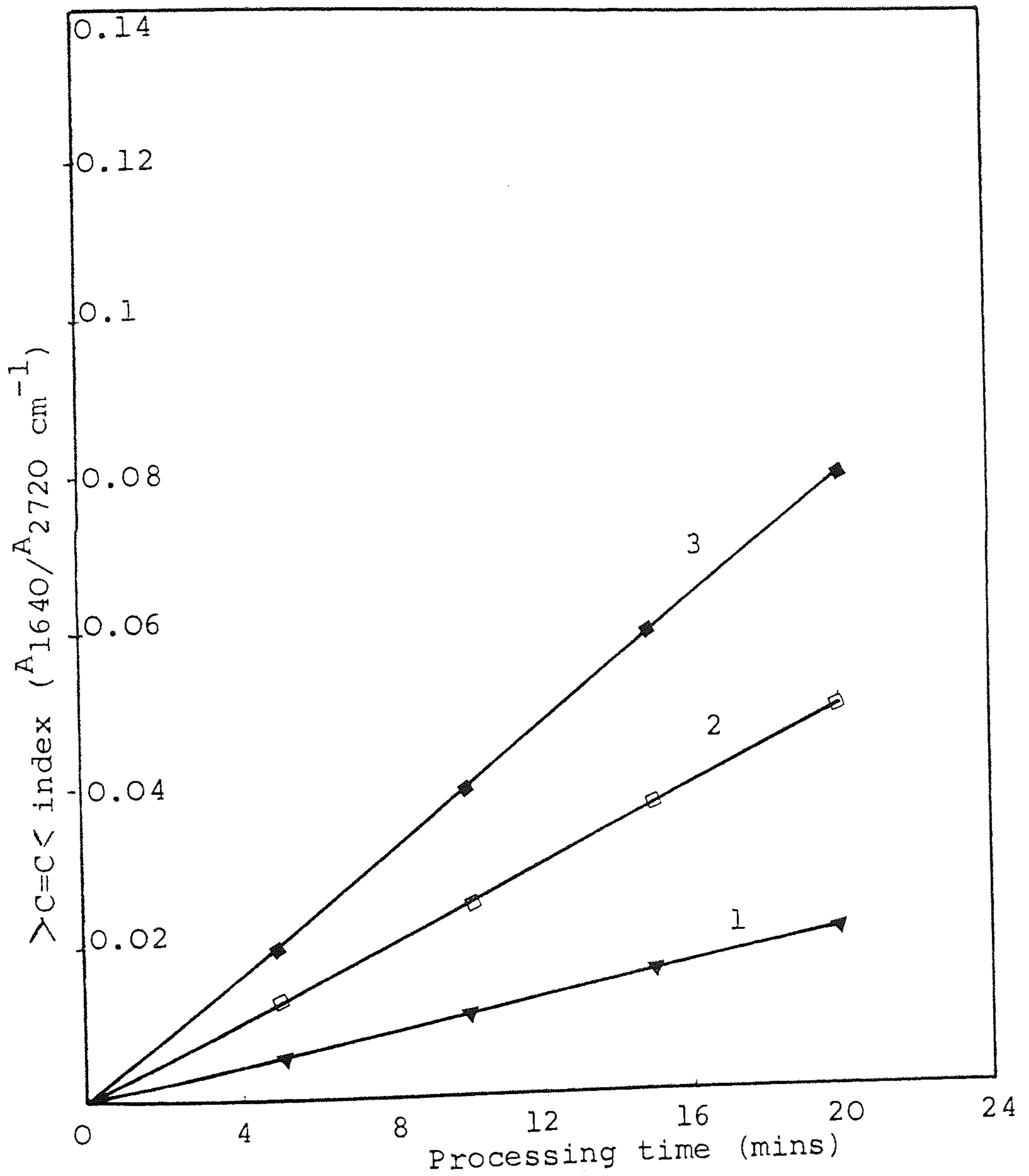


Fig. 3.22 Effect of iodine on the formation of unsaturation ($1640\ cm^{-1}$) during processing of pp at 190°C in a closed mixer at various times, iodine conc = 1.57×10^{-3} mol/100g.

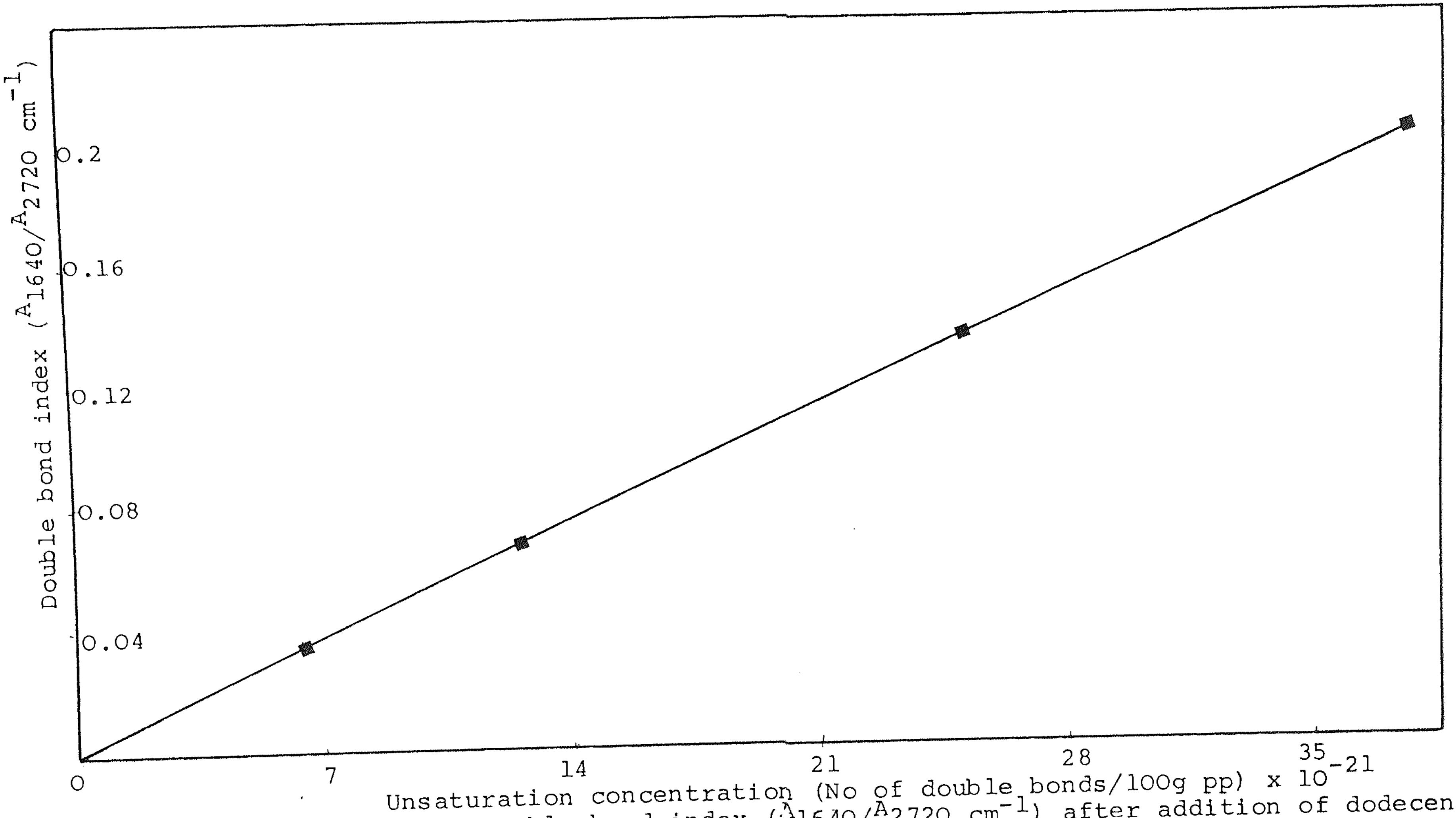


Fig. 3.23 Measurement of double bond index (A_{1640}/A_{2720} cm^{-1}) after addition of dodecene -1 to pp at different concentrations (calibration graph)

The quantitative results are summarised in Table 3.2 indicating that the amount of double bonds increases with increasing processing time (column A) and C-I bonds formed during the processing are increased with processing time up to about 20 mins. processing and then declines (column c).

Stoichiometric coefficient (f) of iodine during the processing which is defined as:

$$\frac{\text{concentration of double bonds}}{\text{initial concentration of iodine}}$$

shows that it is not 2 but quite high suggesting that regeneration of iodine occurs.

Stoichiometric coefficient (f) could be measured using data in Table 3.2 (column B).

For example, it is found to be about 12 and 16 for 15 mins. and 20 mins. processing respectively.

3.A.4.3 Effect of a Hindered Piperidine (TinUVin 770) and Related Oxidation Products on Melt Stability of Polypropylene.

Analogous studies to those described for galvinoxyl

TABLE 3.2 Amount of Double Bond Formation During Processing of pp in a Closed Mixer at 190°C and Reaction of Processed pp with $AgNO_3$ (alc)

$[I_2] = 1.57 \times 10^{-3}$ mol/100g

Time of Processing (mins.)	Number of double bonds/100g pp $\times 10^{-21}$		
	A	B	C
5	1.22	3.325	2.1
10	1.83	6.95	5.12
15	2.8	11.025	8.22
20	3.85	14.875	11.025
30	5.42	7.175	1.755

(A) Processing of pp with iodine

(B) Reaction of processed pp with $AgNO_3$(alco)

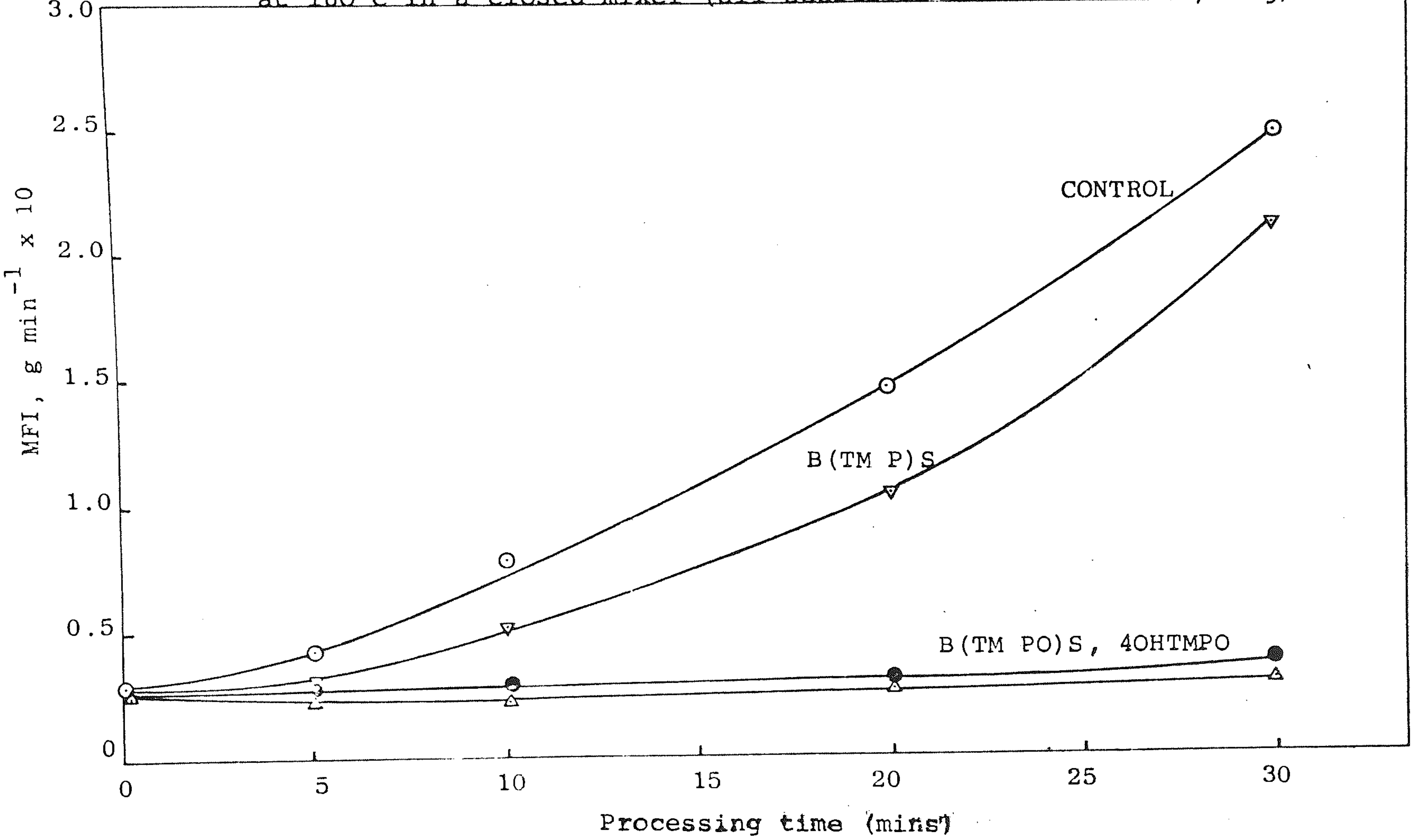
(C) Number of C-I bonds /100g pp

and iodine were also carried out with a commercial hindered piperidine (B(TMP)S, trade name TinUVin 770) and its related nitroxyl radical (B(TMPO)S), 4 hydroxy 2,2,6,6 tetramethyl piperidineoxyl (4OHTMPO) and its related hydroxyl amine (4OHTMPOH).

In Fig. 3.24 the effect of TinUVin 770 on the melt stability of polypropylene processed at 180°C in a closed mixer (restricted air access) is compared with that of related nitroxyl radicals (B(TMPO)S, 4OHTMPO) and hydroxylamine (4OHTMPOH) at the same molar concentration. TinUVin 770 has only a marginal stabilising effect on the polymer under these conditions compared to the nitroxyl and hydroxylamine, which are all powerful antioxidants.

Fig. 3.25 shows that under even more severe processing conditions with air access, this difference is again evident but the hydroxylamine is now more effective than the nitroxyls. Fig. 3.26 depicts the effect of TinUVin 770 on the melt flow behaviour of polypropylene at 200°C in a closed mixer indicating a pro-oxidant effect on the polymer compared with control (at 4.5×10^{-4} mol/100g) while Irganox 1076 (a commercial CB-D antioxidant) and NiDBC (a peroxide decomposer) showing effective melt stabilisation properties under these conditions. Fig. 3.26 also illustrates

Fig. 3.24 Effect of a hindered piperidine, B(TM P)S, and related nitroxyls (B(TM PO)S, 4OHTMPO) and hydroxylamine (4OHTMPOH) on the melt flow index of pp processed at 180°C in a closed mixer (all additives at 3×10^{-4} mol/100g).



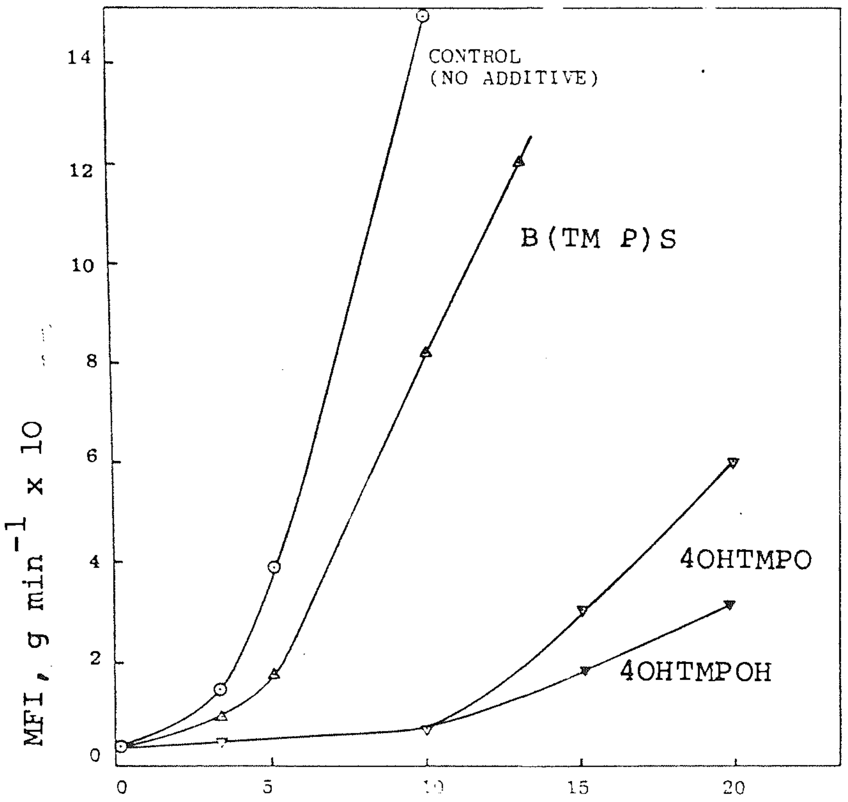
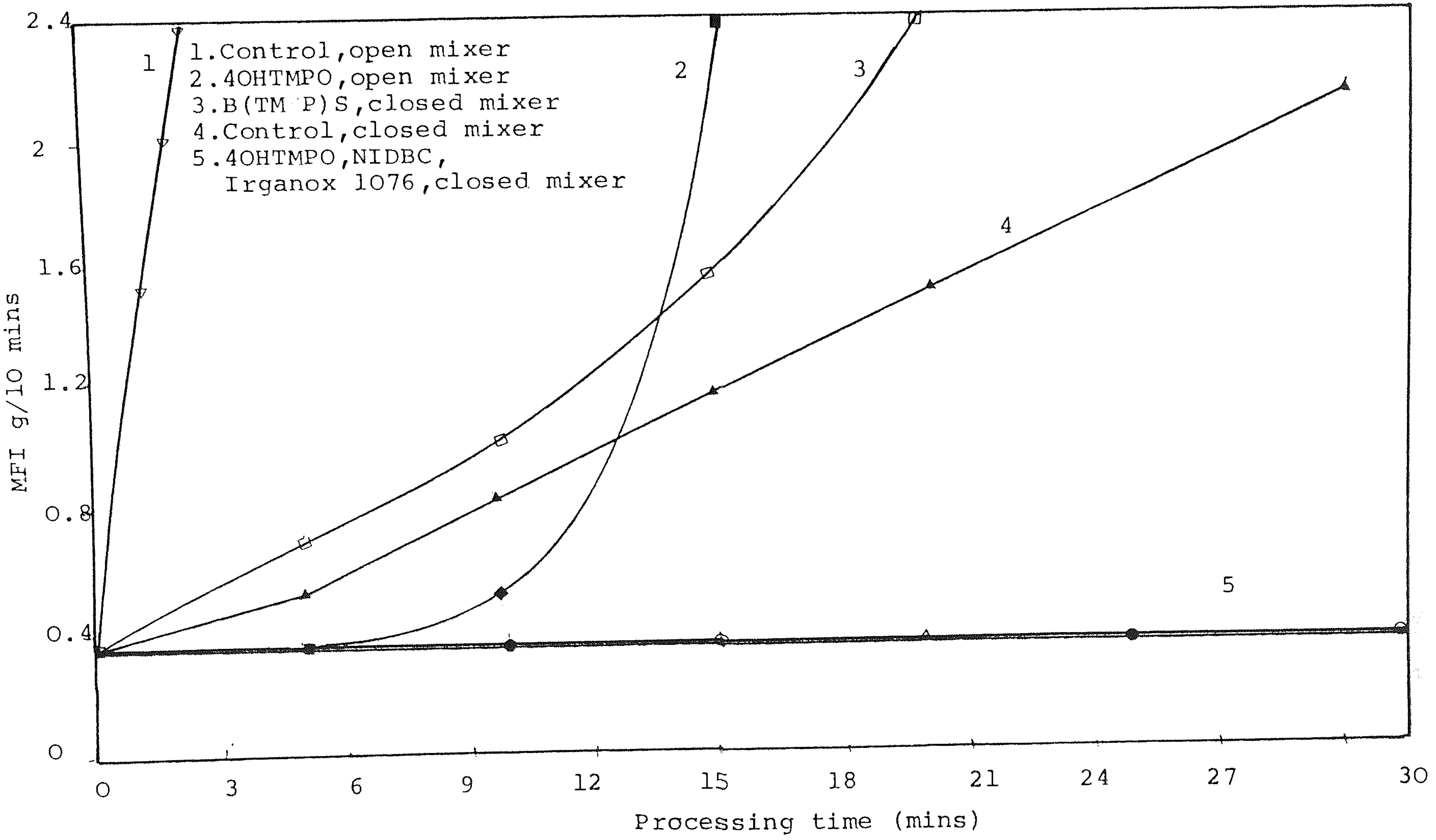


Fig. 3.25 Effect of a hindered piperidine (B(TM4P)S and related nitroxyls (B(TM PO)S, 4OHTMPO) and hydroxylamine (4OHTMPOH) on the MFI of pp processed at 180°C in an open mixer (all additives at 3×10^{-4} mol/100g).

Fig. 3.26 Effect of antioxidants on the melt flow index of pp processed at 200°C in both closed and open mixer (all additives at 4.5x 10^{-4} mol/100g).



the melt flow behaviour of processed polypropylene containing nitroxyl radical (4OHTMPO) at 200°C in both closed and open chamber under conditions corresponding to those (as was shown) in Figs 3.24 and 3.25.

TinUVin is partially converted to the nitroxyl radical during processing (Fig. 3.27) and this occurs more readily in the presence of air. The hydroxylamine (4OHTMPOH) is also converted to the nitroxyl radical (4OHTMPO) during processing (Fig. 3.28). The concentration rises to a maximum at 15 mins., followed by a slow decay.

Examination of all the extracted films containing nitroxyl radicals (4OHTMPO, B(TMPO)$_2$S) by IR and e.s.r methods revealed that no bonding of the nitroxyl radicals to the polymer could be detected during processing. It was found that olefinic unsaturation was formed in the polymer during the processing of polypropylene containing nitroxyl radicals. Chemical measurement was carried out on the processed polymer after dichloromethane extraction (see, section 2.3.7). The results shown in Fig. 3.29 indicate an initial rapid rate of formation of unsaturation followed by a lower rate on more prolonged processing, a similar trend was demonstrated earlier for galvinoxyl (see Fig. 3.17).

Fig. 3.27 Relative rates of formation of nitroxyl, B(TM PO)S from Tinuvin 770 (B(TM P)S) during the processing of pp at 180°C in open and closed mixer.

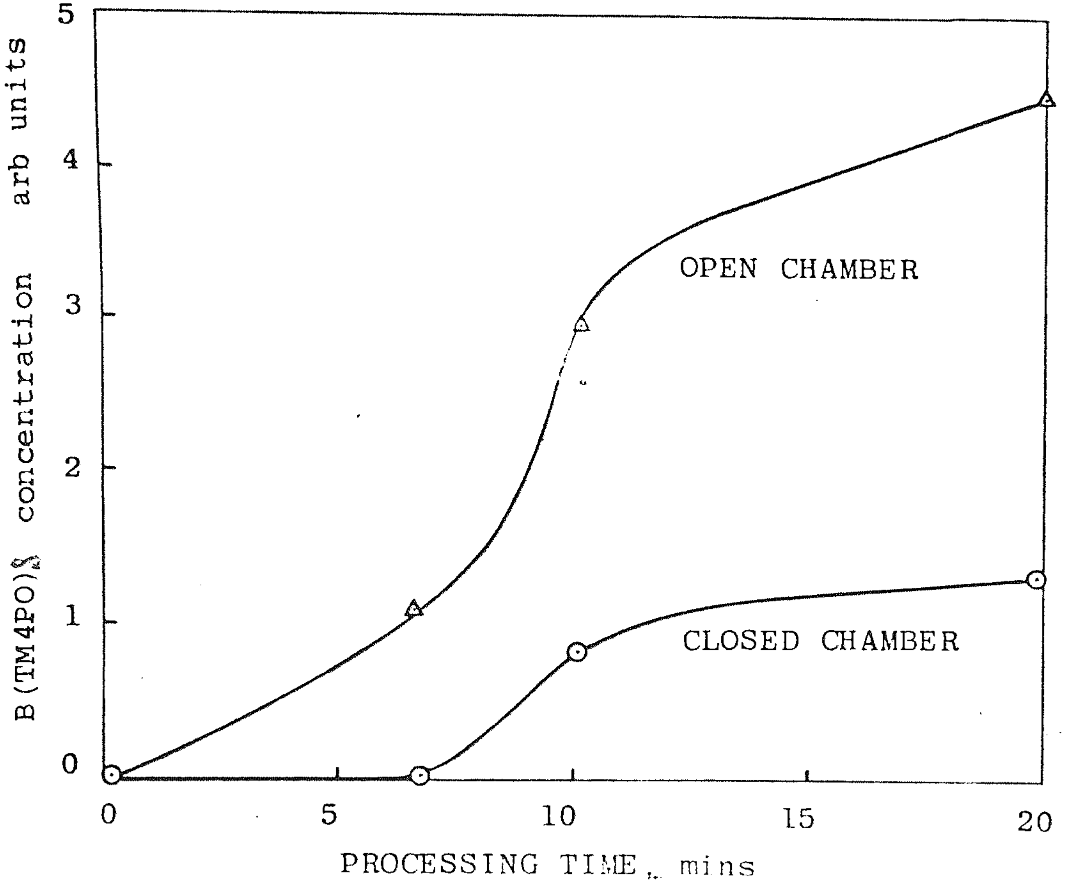


Fig. 3.28 Formation of nitroxyl radical (4OHTMPO) from corresponding hydroxylamine (4OHTMPOH) during processing of pp at 180^{o}C in a closed mixer.

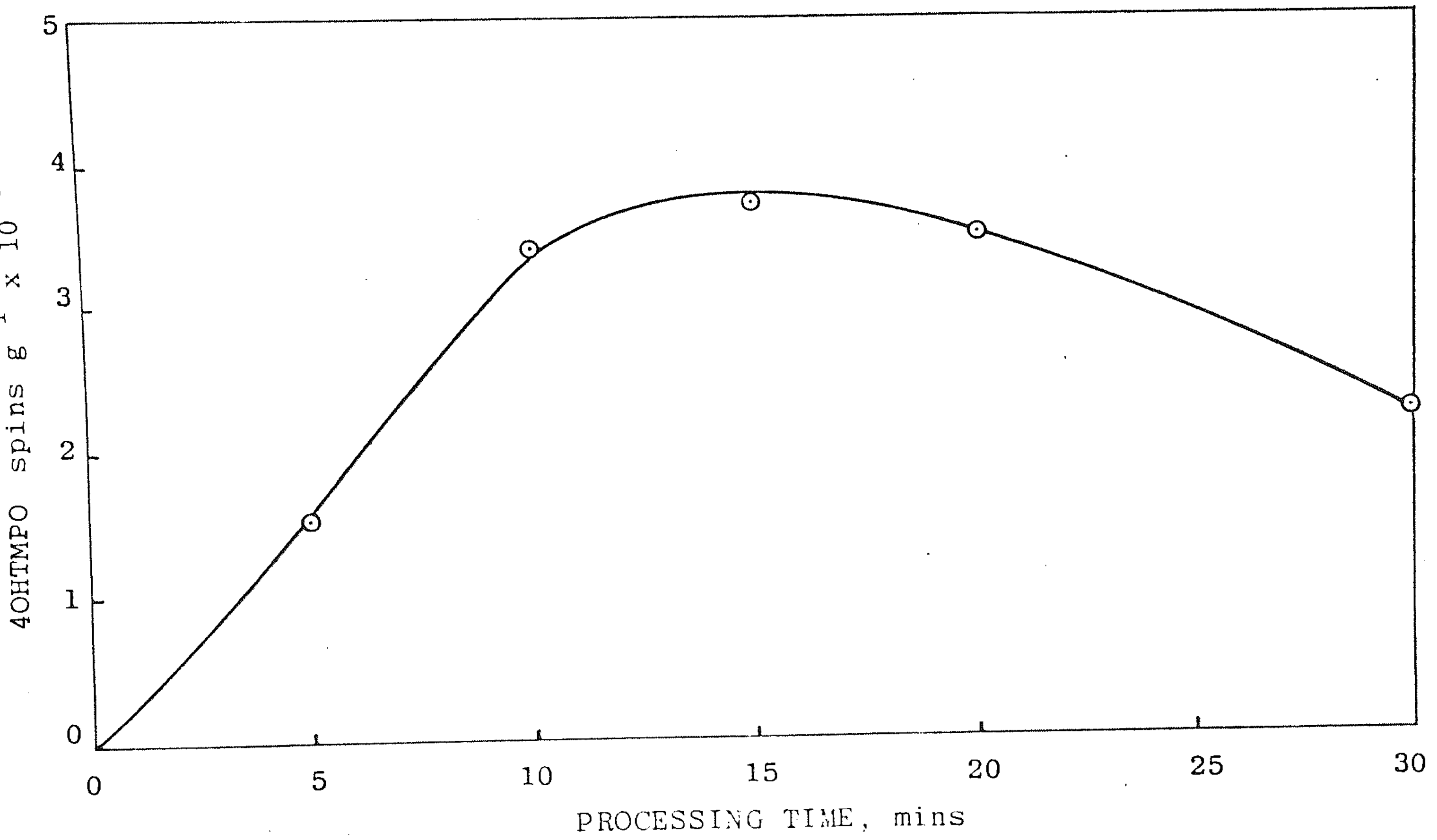
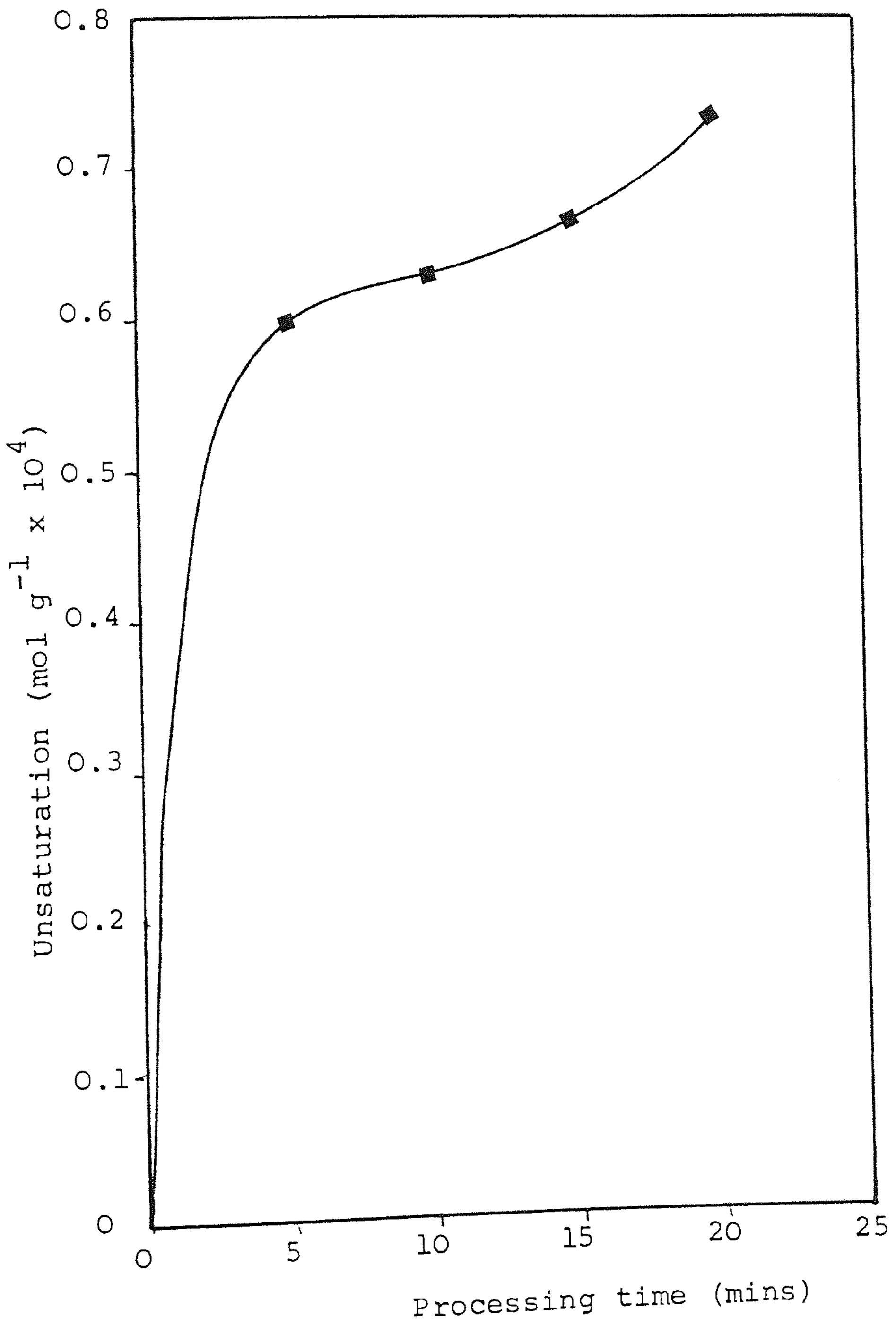


Fig. 3.29 Effect of nitroxyl radical (4OHTMPO) on the formation of unsaturation during processing of pp at 200°C in a closed mixer, nitroxyl radical conc = 1.16 x 10^{-3} mol/100g



No hydroperoxides and carbonyl were formed during processing of polypropylene in the presence of nitroxyl radicals.

E.S.R examination of all processed polypropylene containing nitroxyl radical (4OHTMPO) showed a substantial amount of nitroxyl present in the films.

Variation in nitroxyl radical concentration with time of processing was measured (see 2.3.13).

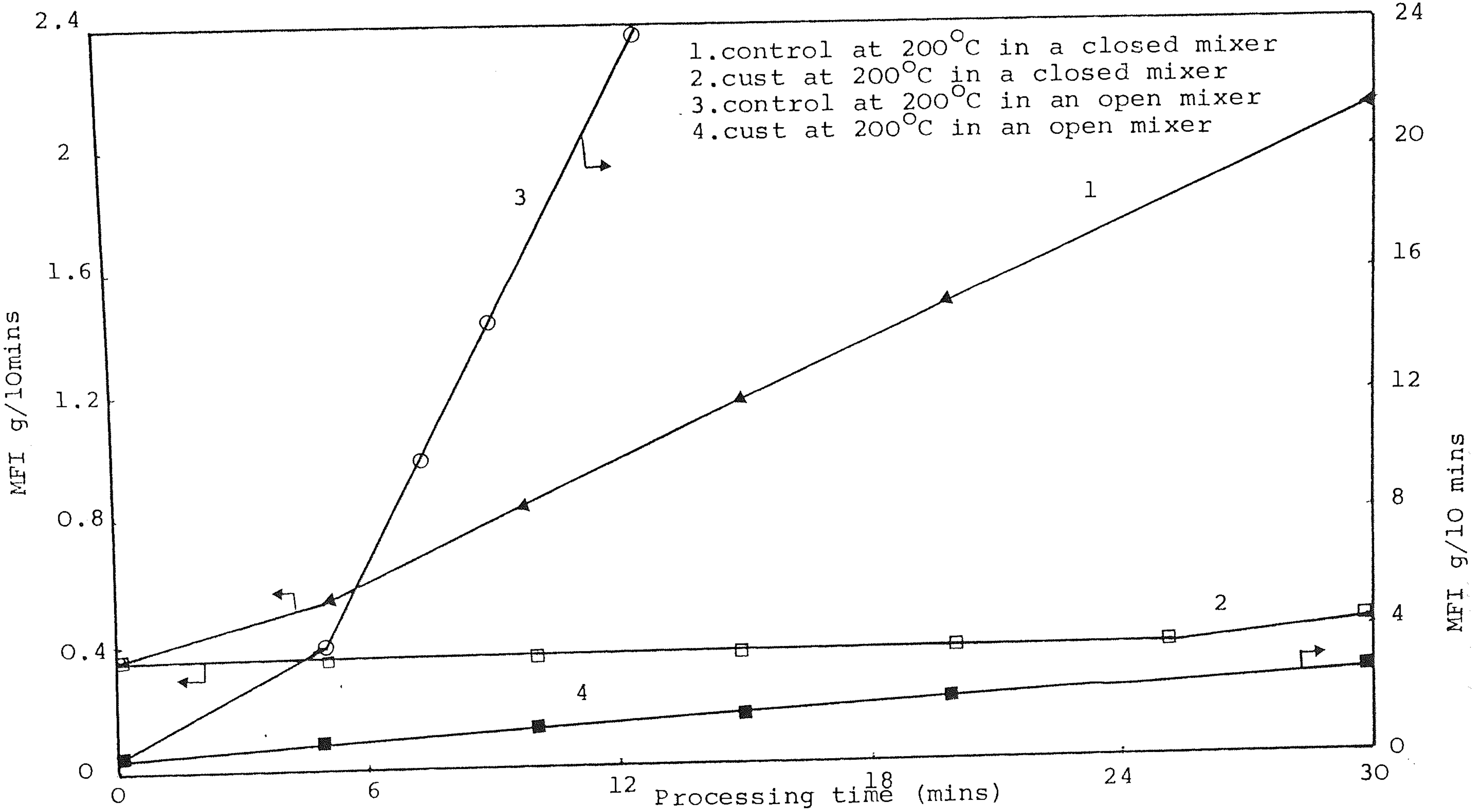
E.S.R results and the detailed mechanisms of melt stabilisation action of nitroxyl radicals will be discussed later.

3.A.4.4 Effect of Cupric Stearate on Melt Stability of Polypropylene.

The effect of cupric stearate as melt stabiliser on the processing of polypropylene was studied and it was found that it acted as an effective melt stabiliser under both severe and mild processing conditions.

Variation of MFI with increasing processing time at 200°C (at 4.5×10^{-4} mol/100g) is shown in Fig. 3.30. After about 25 mins. of processing a slight increase in melt flow index was observed under limited amount

Fig. 3.30 Effect of cupric stearate on the melt flow index of pp processed at 200°C in both closed and open chamber, cust conc = 4.5 x 10^{-4} mol/loog.



of air, but in excess of oxygen the MFI started to increase almost from the beginning at a very slow rate compared with control.

IR spectra of extracted films (benzene used as a solvent) showed no increase in initial carbonyl content until 25 mins. of processing (in closed chamber) which corresponded to the MFI data.

Olefinic unsaturation formed during the processing of polypropylene containing cupric stearate was measured chemically using the procedure described in section 2.3.7 after benzene extraction of the processed polypropylene samples.

The results shown in Fig. 3.31 indicate that an initial rapid rate of unsaturation formation is followed by a very low rate up to 20 mins. of processing and then from 20 to 30 mins. of processing a higher rate of unsaturation formation is again observed.

Discolouration of the samples during processing was observed. At an early stage of processing in deficiency of oxygen, when the shear is high and hence alkyl radicals present in appreciable concentration, the processed sample was blue. As the processing time was increased the blue colour faded and at about 15 mins. it became greenish. Increase in processing

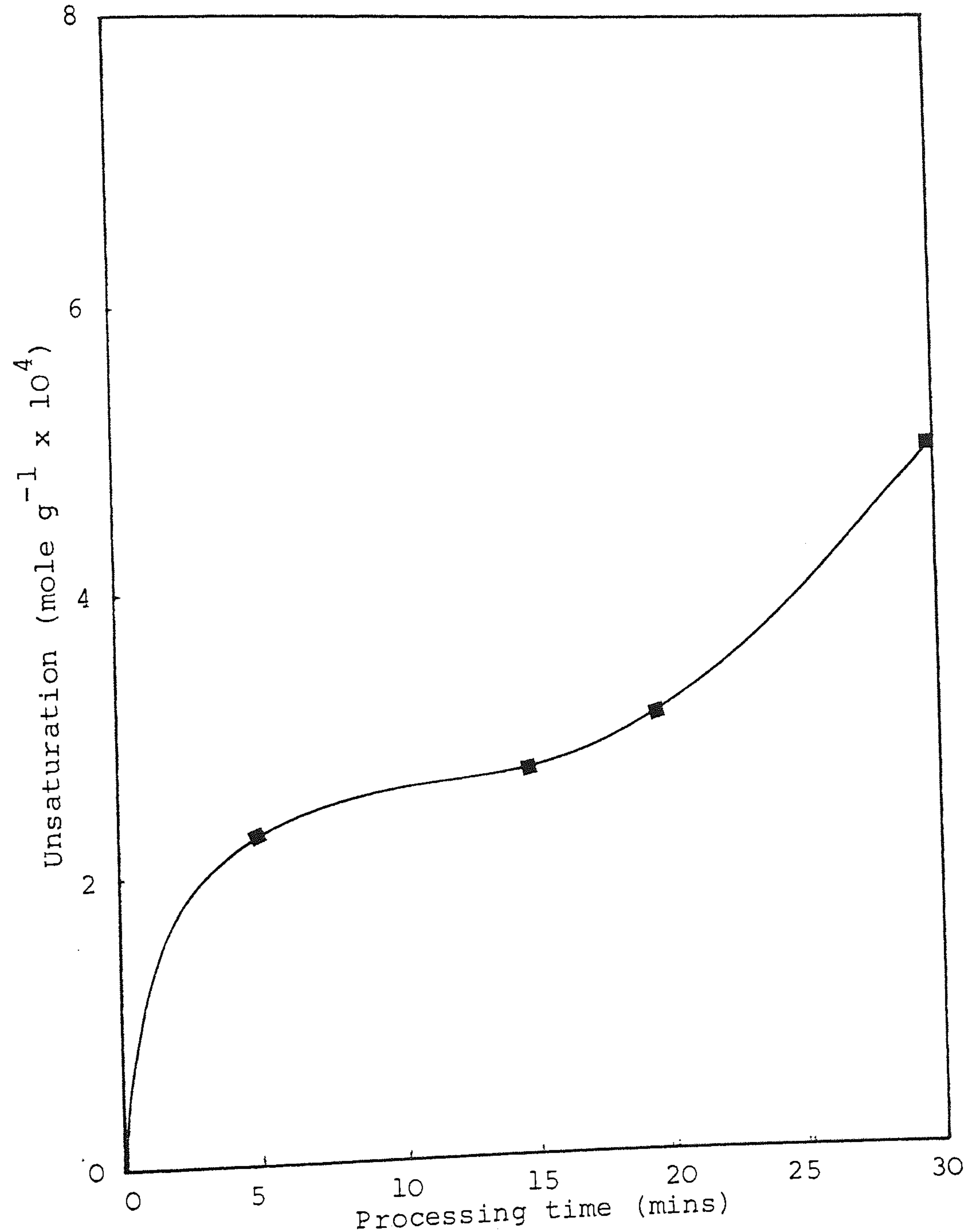


Fig. 3.31 Effect of cupric stearate on the formation of unsaturation during processing of pp at 200°C in a closed mixer, Cust conc = 4.5×10^{-4} mol/100g

time again led to appearance of the blue colour indicating high concentration of Cu^{+2} and therefore suggesting regeneration of Cu^{+2} during the processing.

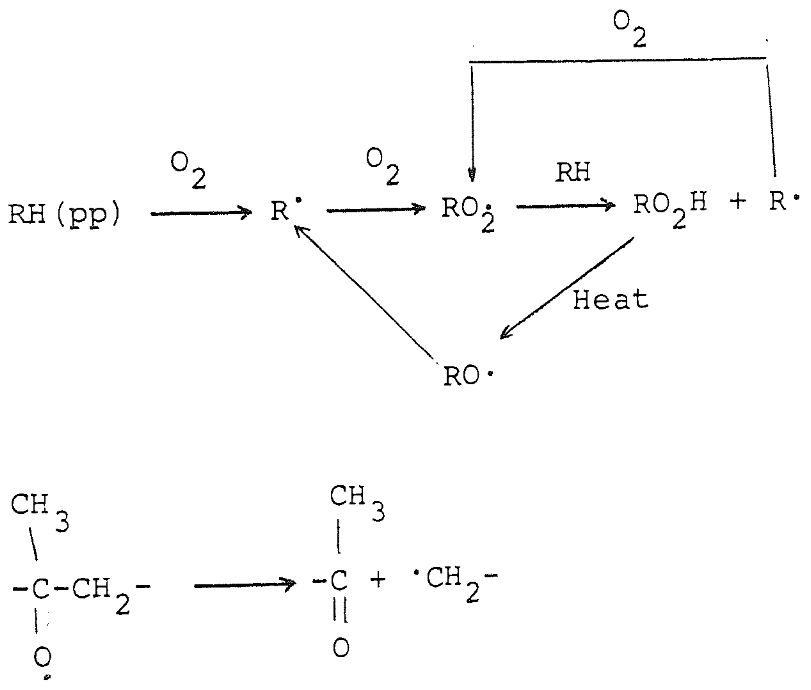
No hydroperoxides could be measured using the procedure described in section 2.3.9.B in the processed polypropylene containing cupric stearate.

Discussion of the mechanism of CuSt action is deferred until Chapter 6.

3.A.5 Discussion

An understanding of the behaviour of different types of antioxidants and stabilisers on thermal processing of polymers will only be possible if the oxidative degradation mechanism of polymer occurring during the processing be elucidated. Our understanding of general inhibition chemistry has greatly improved in recent years, but the processing area has not been fully investigated. It has been generally assumed that the rapid rate of initiation of polymer breakdown during processing necessitates the use of low molecular weight mobile antioxidants. Henman has recently studied(194a) the effect of numerous compounds as melt stabilisers. He has concluded(194a) that neither CB-D antioxidants nor peroxide decomposers could be very effective melt stabilisers and the key to an effective melt stabiliser should be a material that can preferably deactivate alkyl radicals before they react with oxygen.

Figs. (3.1 - 3.5) show that marked changes in melt flow index, torque, molecular weight distribution and chemical changes which occur in polypropylene subjected to both closed and open chamber processing operation. This indicates that chain scission reactions occur during the thermal processing and no cross-linking occurs as shown in the following reactions (scheme 3).



Tertiary alkoxide scission (Scheme 3).

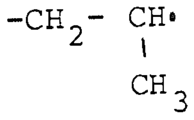
Once an alkyl radical is formed, it will react with oxygen, even at very low partial pressures, to give the alkyl peroxy radical. This is converted by radical exchange to a hydroperoxide, which in turn will cleave to an alkoxy radical. Here reduction in molecular weight is caused principally by fragmentation of tertiary alkoxide radicals to ketones, regenerating primary alkyl radicals which, after rearrangement, can once again take part in the original scheme. Chain-scission takes place in the early stages of processing as is evident by high MFI values (see Figs. 3.1 and 3.2) and change in molecular weight distribution towards lower molecular weight (see Figs. 3.4). This is further supported from an analysis of the IR spectra which shows the formation of carbonyl groups in the early stages of processing (see, Fig. 3.5 curves 1 and 2).

It is observed from Fig. 3.5 curve 3 that the hydroperoxide concentration passes through a maximum when processed in the open chamber, since in the first stage of the oxidation process hydroperoxide formation predominates over its decomposition due to high alkyl radical and hence alkyl peroxy radical concentration in the rate determining step (reaction 4b).

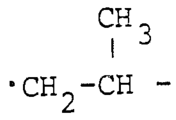
$$\mathrm{RH(pp)} \xrightarrow{\text{shear}} \mathrm{R^{\cdot}} \xrightarrow[\text{(a)}]{\mathrm{O_2}} \mathrm{ROO.} \xrightarrow[\text{(b)}]{\mathrm{RH}} \mathrm{ROOH} \qquad (4)$$

After the maximum the rate of decomposition of hydroperoxide is faster than the rate of its formation which is explained as being due to catalytic effect of carbonyl compounds (e.g. aldehyde, acid etc.), formed during the oxidation, on the rate of hydroperoxide decomposition. Carbonyl groups (e.g. ketone, aldehyde, acid etc.) are formed from hydroperoxide decomposition (i.e. alkoxides). Therefore the significance of hydroperoxide acting as a key initiator during the processing of polypropylene must be accepted.

E.S.R studies have shown(222,223) that during the mechanical destruction of polypropylene the following macroalkyl radicals are formed



$-CH_2-\underset{CH_3}{\underset{|}{CH\cdot}}$



$\cdot CH_2-\overset{CH_3}{\overset{|}{CH}}-$

At the early stage of mechanodegradation the concentration of these radicals is high due to the high shearing forces acting on the polymer. The results obtained from the Fig. 3.1, curve 1 and Fig. 3.2, curve 1 imply the effect of shear on the formation of macroradicals indicating higher concentration of macroalkyl radical formation leading to higher rate of polymer breakdown in the early stage of processing particularly at lower processing temperature.

Scott and co-workers(41-43) have shown that during the processing of PVC the initial degradation is induced by the mechano-chemically formed macroalkyl radicals. The formation of macroalkyl radicals in rubbers during milling and mastication processes due to homolysis of the carbon-carbon bonds in the polymer has also been inferred by a number of workers from the rheological changes in the polymer(224) and from the chemical reactions which can be initiated under conditions of shear(225-227), providing more evidence of macroalkyl radical formation during mechano chemical degradation.

Therefore it is obvious that during processing operation macroalkyl radicals form which have a very short life and because Galvinoxyl is a highly efficient radical scavenger(228-230), coupling might possibly take place between alkyl radicals and Galvinoxyl both on oxygen and on ortho or para carbon atoms as would be expected from Galvinoxyl mesomeric structures. However, extraction of the films showed that the Galvinoxyl did not become bound to the polymer using IR and UV spectroscopic methods.

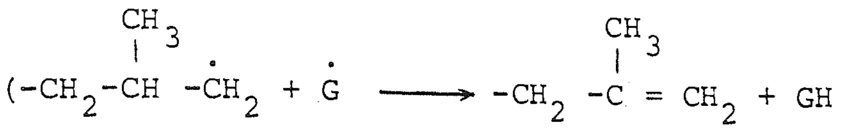
Hydrogalvinoxyl is formed during the processing of polypropylene containing galvinoxyl (see Fig. 3.13 solid curve). In the early stage of processing the

GH concentration reached maximum and then fluctuation in concentration of GH was observed on prolonged processing (see Fig. 3.15). The first peak in GH concentration can be accounted for by the high initial alkyl radical concentration resulting from the high initial shear in the mixer. The second increase is probably owing to the depletion of oxygen in the mixer which is seen (Fig. 3.15) to lead to an increase in GH concentration. An increase in processing temperature from 190^{o}C to 200^{o}C also led to an increase in GH concentration under condition of limited air access (see Fig. 3.15, curve c). This is due to increase in the rate of interaction between Galvinoxyl and polypropylene radicals.

Another significant factor is oxygen concentration, as the oxygen concentration decreases, more GH is formed in the system (Fig. 3.15, curve b) which is explained as being due to increase in alkyl radical concentration.

The results obtained from unsaturation measurement (see Fig. 3.17) are in agreement with the above results, i.e. the initial rapid rate of unsaturation formation which is due to transfer of hydrogen from mechanoalkyl radicals to the Galvinoxyl (reaction 5) parallels GH formation.

As processing continues the olefinic unsaturation increases at a lower rate



$$(-CH_2-\overset{CH_3}{\overset{|}{C}H}-\dot{C}H_2 + \dot{G} \longrightarrow -CH_2-\overset{CH_3}{\overset{|}{C}} = CH_2 + GH \qquad (5)$$

E.S.R examination of the films and measurement of galvinoxyl concentration showed fluctuation of radical concentration with increasing processing time which indicated a cyclic regeneration of Galvinoxyl by oxidation of GH by alkylperoxy radicals(45,136) (reaction 6).

$$GH + RO_2^{\cdot} \longrightarrow ROOH + \dot{G} \qquad (6)$$

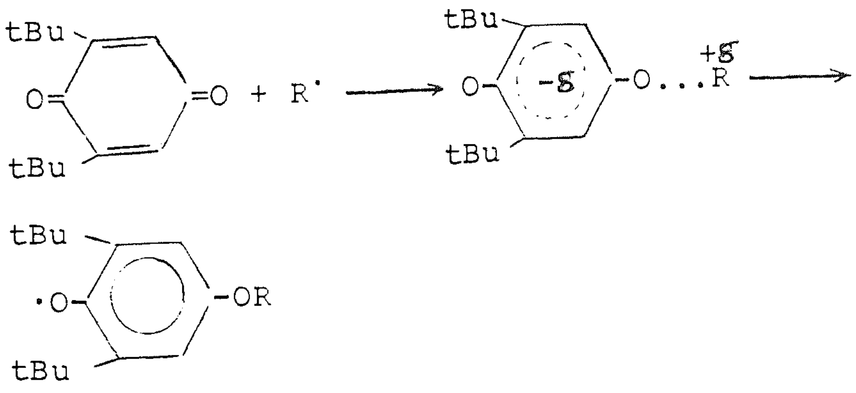
Galvinoxyl repeats its antioxidant function as hydrogen abstractor from the polymer alkyl radicals leading to regeneration of GH. The mechanism of Galvinoxyl action during the processing will be discussed in more detail in Chapter 6.

It is now clearly evident from the measurement of MFI changes (Fig. 3.6 and 3.7), molecular weight distribution (Fig. 3.9), carbonyl content (Fig. 3.10) that galvinoxyl acts as a very powerful melt stabiliser in polypropylene when processed in a closed system. It also acts as a very effective melt stabiliser when processed in the presence of excess air. However, in the later stages of processing degradation of polypropylene occurs to some extent.

The melt stabilising results together with the formation of GH and unsaturation suggest that the stoichiometric coefficient of Galvinoxyl is high due to the presence of both alkyl and alkylperoxy radicals in the system (and has a tendency to increase with decreasing alkylperoxy radical concentration).

2,6 di-tert-butyl 1,4 benzoquinone forming during processing (see, section 2.3.12) is also capable of removing alkyl radicals from an auto-oxidising system$^{(56)}$.

Reaction of an alkyl radical with a quinone is shown as follows (reaction 7)



(7)

The transition state involves partial transfer of an electron to the aromatic π bonds.

The behaviour shown by iodine in polypropylene during melt stabilisation is very similar to that of Galvinoxyl. Figs. 3.19 and 3.20 show the powerful melt stabilisation activity of iodine in polypropylene. The relatively lower effectiveness of iodine as melt stabiliser in polypropylene during processing in the open chamber is almost certainly due to loss of iodine by volatilisation. The molecular weight distribution results from GPC analysis (Fig. 3.21) confirmed the above results (i.e. action of iodine as an effective melt stabiliser). Hydrogen iodide was formed during processing of polypropylen with iodine. It was detected chemically using the procedure described in section 2.3.8B and its formation was confirmed by measuring acidity of aqueous extracted solution of the processed samples using a PH meter. The quantitative measurement of hydrogeniodide formation at different processing time could not be accurate due to high temperature processing (190°C).

Hydrogen iodide formation is presumably due to interaction of macroalkyl radicals with iodine leading to olefinic unsaturation (reaction 8). This is confirmed by the unsaturation formation during the processing which is shown in Fig. 3.22 curve 1.

propagating species present in highest concentration in an autoxidising system. This process is therefore favoured at relatively high oxygen concentrations and low rates of initiation(136,232). Hindered phenols and aromatic amines (AH) which are able to transfer a hydrogen readily to alkylperoxy radicals with the formation of a resonance stabilised radical ($A^\bullet$) are effective in this situation (reaction 11) whereas aliphatic amines are not chain breaking donor (CB-D) antioxidants.

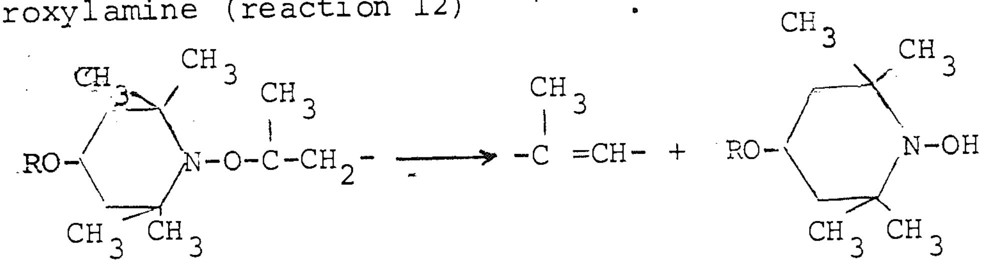
$$ROO\cdot + AH \longrightarrow ROOH + \dot{A} \qquad (11)$$

It has been shown(233) that oxidation products of aliphatic amines notably nitroxyl radicals are effective chain-breaking acceptor (CB-A) antioxidants in an oxygen deficient system(136).

During high temperature processing of polyolefins in a shearing mixer, both alkyl and alkylperoxy radicals are present(27,136). Under these conditions, the hindered piperidine (B(TMP)S) is ineffective as a melt stabiliser (see Figs. 3.24, 3.26) but is partially converted to the corresponding nitroxyl radical (B(TMPO)S, see Fig. 3.27).

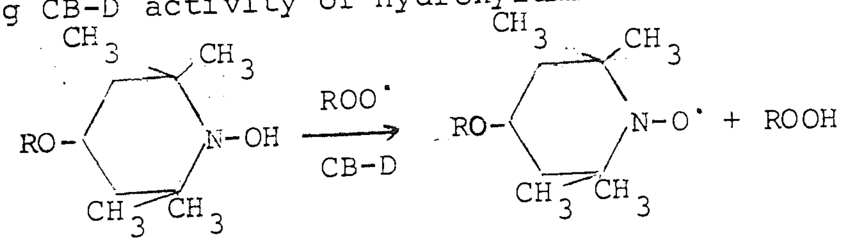
Evidence has previously been put forward(162,234) to

suggest that this occurs at least in part by reaction with hydroperoxides in a radical forming process (162) which is inhibited by both peroxide decomposing (PD-C) antioxidants (162) and CB-D antioxidants (234).
The nitroxyl radical formed in the above process is an effective melt stabiliser as is the hydroxylamine (4OHTMPOH, see Fig. 3.24) which the latter has been shown to be formed by elimination from the alkylhydroxylamine (reaction 12) 235,236).



(12)

The hydroxylamine (4OHTMPOH) was found to be better melt stabiliser compared with its corresponding nitroxyl (4OHTMPO, see Fig. 3.25) in excess of oxygen indicating CB-D activity of hydroxylamines (reaction 13)

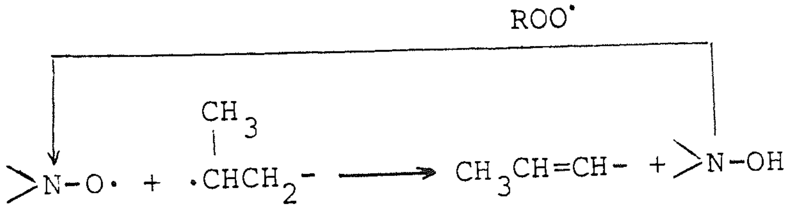


(13)

Since nitroxyl radicals are effective alkyl radical trap, this reaction 13 together with 12 shows a cyclic regenerative process.

The participation of hydroxylamines in this process was confirmed by the fact that when the hydroxylamine (4OHTMPOH) was used as a melt stabiliser the nitroxyl radical concentration increased steadily during the first 15 mins. (see Fig. 3.28) whilst it functioned as a powerful melt stabiliser (see Fig. 3.24).

In addition hydroxylamine was detected from the processed polypropylene containing nitroxyl radical (4OHTMPO) (see 2.3.8A). Additional evidence for the formation of hydroxylamine came from the formation of olefinic unsaturation (see Fig. 3.29) in the polymer. It showed an initial rapid rate of unsaturation formation followed by a low rate. The results could be shown in the reaction 14.



$$>N{-}O\cdot + \cdot\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2{-} \longrightarrow CH_3CH{=}CH{-} + >N{-}OH \qquad \text{(ROO}^\cdot\text{)} \qquad (14)$$

Similar results have been found in the rubber (NR) during fatiguing(237). Bolsman and co-workers(236) and more recently Carlsson and co-workers(238) have shown that hydroxylamines are readily eliminated from alkyl hydroxyl amines at elevated temperatures. The mechanism of anitoxidant action of nitroxyl radicals will be discussed in detail in Chapter 6.

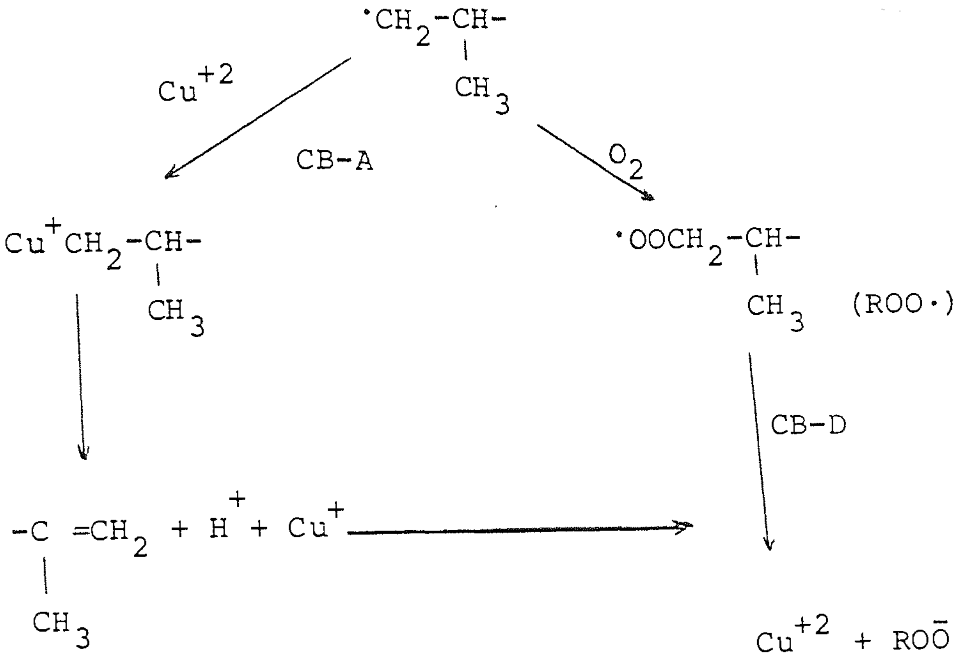
Melt stabilisation results obtained from the effect of CuSt on polypropylene during processing (see Fig. 3.30) provide evidence supporting the view that the reaction of CuSt with the polymer inhibits the chain scission reaction and leads to polymer stabilisation.

A rapid rate of unsaturation formation in the early stages of processing under limited amount of air (Fig. 3.31) indicates that a high rate of termination occurs. This could be due to the interaction of CuSt with macroalkyl radicals which are present at high concentration as the result of high shearing force in the mixer (a redox reaction).

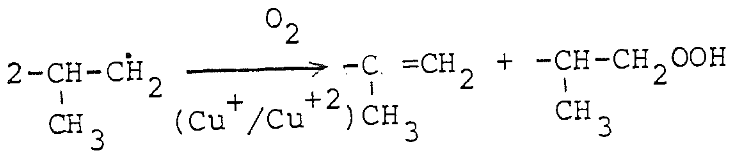
A lower rate of unsaturation formation in the later stages of processing (in closed mixer, Fig. 3.31) could be explained as being due to a lower rate of alkyl radical formation due to reduction in viscosity.

During the processing of polypropylene with CuSt there will be a competition between oxygen and Cu^{+2} for macroalkyl radicals leading to the regeneration of Cu^{+2} in a cyclic mechanism (reaction 15).

The overall process is the formation of unsaturation and hydroperoxide.



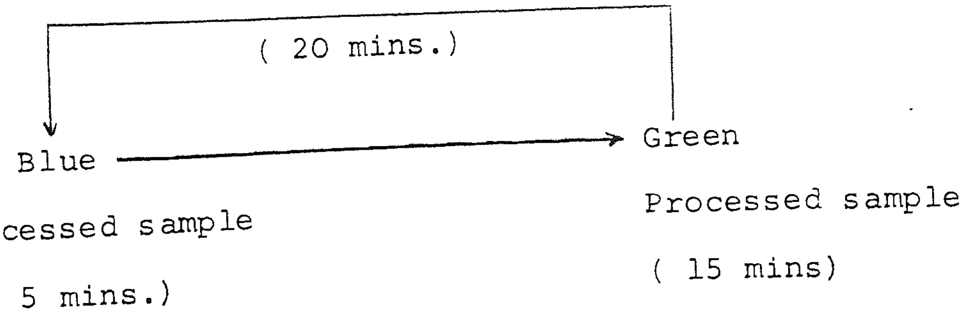
Overal reaction



$$2\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{-CH}}}\mathrm{-\dot{C}H_2} \xrightarrow[(Cu^{+}/Cu^{+2})]{O_2} \underset{\mathrm{CH_3}}{\underset{|}{\mathrm{-C}}}\mathrm{=CH_2} + \underset{\mathrm{CH_3}}{\underset{|}{\mathrm{-CH}}}\mathrm{-CH_2OOH}$$

(15)

Discolouration of the processed samples provides further evidence for the above conclusion which is shown in the following scheme



the above scheme suggests the regeneration of Cu^{+2} during the processing. The relatively high rate of unsaturation formation in the second stage (after 20 mins. processing, see Fig. 3.31) might be due to regeneration of Cu^{+2} (i.e. high conc^{n}. of Cu^{+2}) in this stage.

3.B Low Density Polyethylene (LDPE)

The structure of LDPE, prepared by the high pressure process, contains not only methylene groups but also both short and long chain branches. Infra-red spectroscopy(234) indicates the presence of about 20 to 30 methyl groups per 1000 carbon atoms in LDPE prepared by high pressure process. There is no doubt that branching in polyethylene, whatever its structure, greatly affects the physical and chemical properties of the polymers. The short chain branches are known to give a low degree of crystallinity(239), since branches prevent the close approach of molecules in the unit cell. Other properties like density, melting point, modulus, yield stress, elongation at break etc. are also dependent on short chain branching. The long chain branching mainly affects the rheological properties such as MFI, viscosity etc. and leads to broad molecular weight distribution. Infra-red spectroscopy investigation has indicated that there are three different olefinic double bonds in LDPE namely terminal or vinyl group ($RCH=CH_2$ absorbs at 909 and 1640 cm^{-1}), internal ($RCH=CHR'$, absorbs at 964 cm^{-1}) and vinylidene or side chain methylene group ($R_1R_2C=CH_2$ absorbs at 888 cm^{-1}, it is about 58% by weight of the total unsaturation)(240). Peroxides and carbonyl groups formed by thermal oxidation during polymerisation or during subsequent processing are also present in LDPE.

3.B.1 Experimental Procedures

Low density polyethylene with and without additives was processed at two different temperatures (180°C, 190°C) in the RAPRA torque rheometer for various lengths of time either with the chamber left open to the atmosphere (when 20g charge was used) or in the closed chamber (when 35g charge was used). On completion of processing the polymer sample was rapidly removed and quenched in cold water to prevent further thermal oxidation. The polymer samples were then compression moulded at 150°C for 2 mins. into sheets of thickness 1.8×10^{-2} cm as described in the experimental chapter (see 2.3.2)

Gel content, hydroperoxide content and carbonyl formation of the processed LDPE samples were determined as described in sections 2.3.6, 2.3.10.

3.B.2 Structural Changes occurring in LDPE During Melt Processing

Chakraborty and Scott(27) have found that the melt flow index (MFI) behaviour of LDPE depends on availability of oxygen during the processing. In a closed mixer it decreases from the beginning of processing suggesting a crosslinking reaction. This is confirmed by molecular weight distribution curves which showed an increase in weight average molecular weight (i.e. molecular weight broadening). In an open mixer it showed an induction period before a significant increase in MFI (chain scission) could be observed. They also found that no rheological and chemical changes took place in the absence of oxygen. Chakraborty and Scott have shown(27) that the amount of gel increases with increasing processing time in a limited amount of air and no gel is formed in LDPE samples processed in an open chamber.

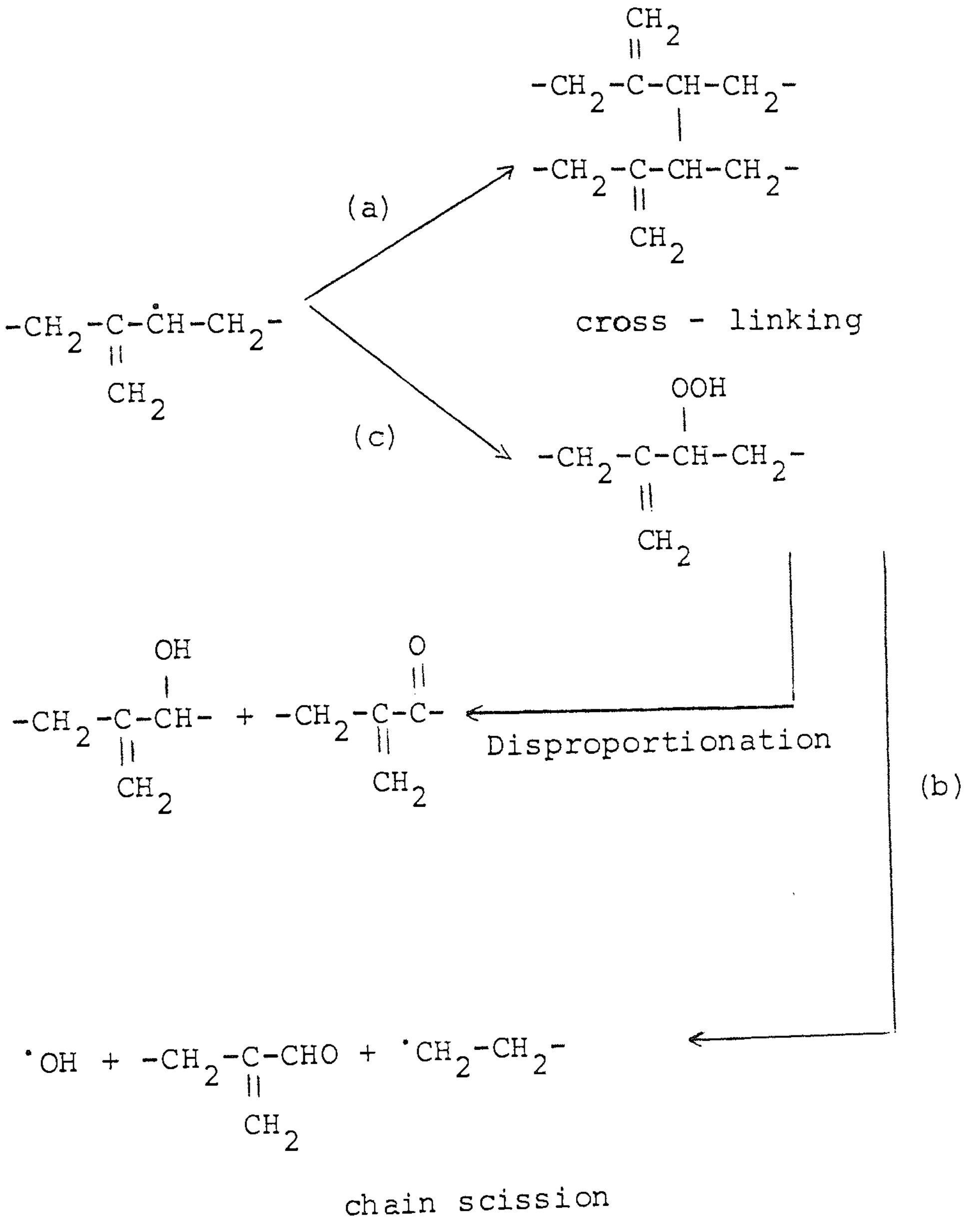
Gel content measurement was carried out in LDPE samples processed both in the closed mixer and open mixer in the present work and the above results were confirmed.

It has also been reported(27) that the hydroperoxide formation (measured chemically as well as by IR method expressed as index A_{3555}/A_{1895} cm^{-1}) in thermally processed LDPE increases rapidly to a sharp maximum and then declines and as the processing temperature is increased, the time taken to reach maximum hydroperoxide formation is reduced.

IR spectra of the samples processed in the excess of oxygen showed that initially the main carbonyl peak is at 1720 cm^{-1} (ketonic carbonyl) and in the later stages of processing the main carbonyl band shifts toward 1710 cm^{-1} (acid) having the following shoulders: 1785 cm^{-1} (peracid), 1765 cm^{-1} (per ester), 1745 cm^{-1} (ester), 1730 cm^{-1} (aldehyde) and at 1685 cm^{-1} conjugated carbonyl. The vinylidene (band at 888 cm^{-1}), internal double bond (band at 964 cm^{-1}) and vinyl content (band at 910 cm^{-1}) which are initially present in the polymer remain constant during processing (up to 30 minutes).

Therefore in a sealed system from which oxygen is physically excluded, except that dissolved in the polymer or trapped between the particles of the polymer, a decrease in MFI occurs during processing. This behaviour contrasted with that in an open mixer when no initial reduction in MFI occurred but instead the MFI increased after an induction period. The explanation proposed(27) to explain this divergent behaviour is that the allylic radicals formed in the polymer by mechano-chemical and oxidative reactions during processing either dimerise in an oxygen deficiency or forms hydroperoxides in an oxygen excess (reaction scheme 16)(27). The former leads to crosslinking(16a) and the latter to chain scission (16b) following thermolysis of the hydroperoxide(16c). The presence of some O_2 is necessary for both reactions to occur, since in the complete absence of O_2 neither reaction takes place(27). The answer to the question as to which reaction predominates will depend on the availability of oxygen. The decrease in MFI reflects an increase in molecular weight due to crosslinking,a practical consequence of which is an increase in torque during the later stages of processing. Crosslinking is also reflected in the rapid increase in solvent insoluble gel in the polymer leading to an initial increase in tensile strength and elongation at break of the polymer(27).

The chain scission process is also supported from IR spectra which show the formation of peracid, perester, acid and ester in the later stages of processing.



(16)

3.B.3 Effect of Melt Stabilisers on Processing of Low Density Polyethylene (LDPE)

Results and Discussions:

The effect of Galvinoxyl, iodine and cupric stearate on the melt stabilisation of LDPE was studied.

Rheological and chemical changes occurring during processing have been estimated.

Figure 3.32 shows the melt stabilisation effectiveness of galvinoxyl and iodine in LDPE during processing under the both severe (air excess) and mild conditions (limited air) at 180°C. It is apparent from the figure that both galvinoxyl and iodine inhibit carbonyl formation in LDPE during processing under the above conditions whereas the control samples particularly processed in the open chamber shows linear growth of carbonyl almost from the very beginning of processing. No increase in carbonyl formation in LDPE is observed even up to 30 minutes when processed in the closed chamber containing galvinoxyl and iodine. In an open chamber processing galvinoxyl again inhibited carbonyl formation up to 30 minutes of processing, but iodine showed induction period to carbonyl formation up to 15 minutes and then carbonyl started to form. This is certainly due to loss of iodine by volatilisation in

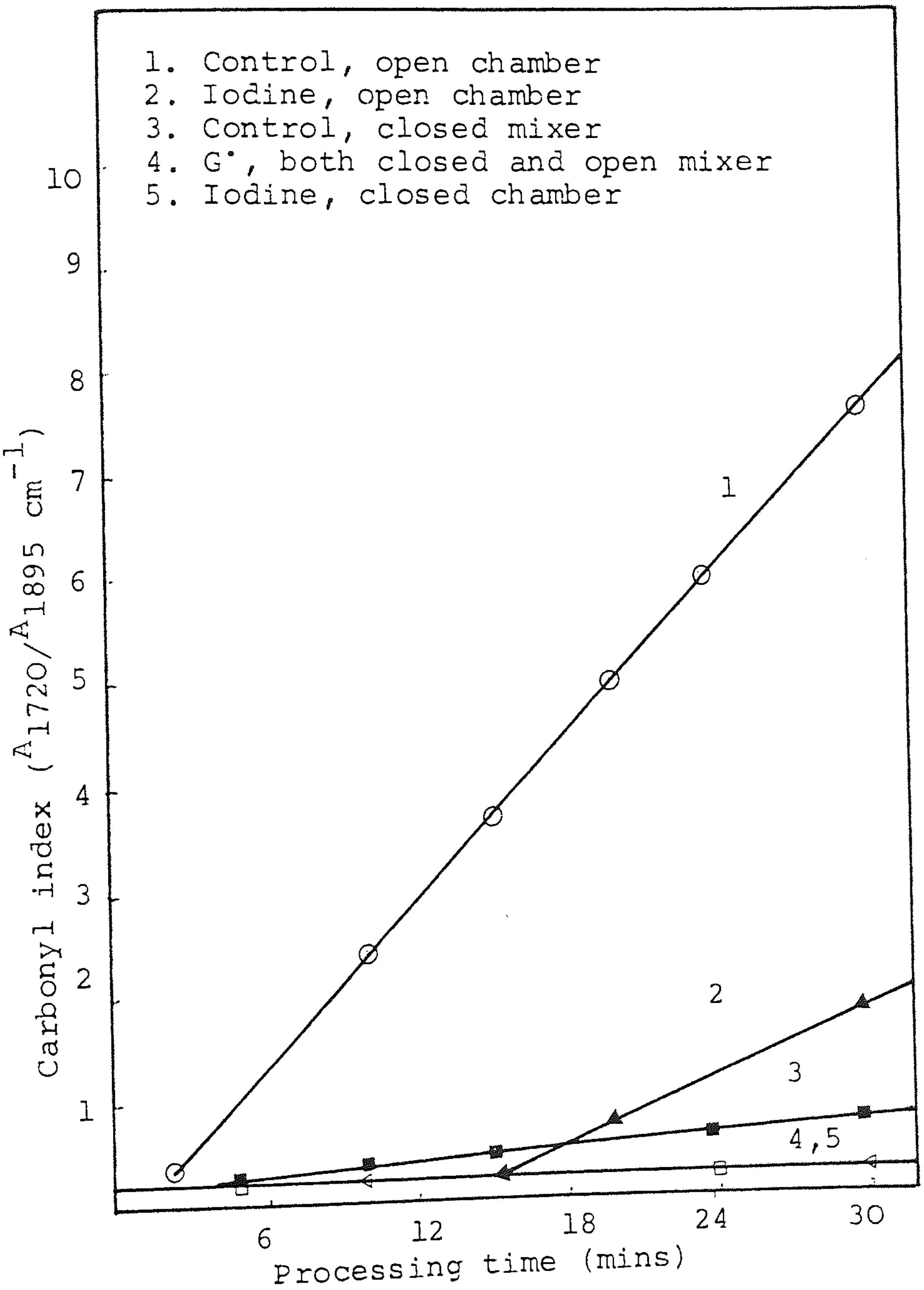


Fig. 3.32 Effect of galvinoxyl and iodine on the formation of carbonyl during processing of LDPE at 180°C in both closed and open chamber, I_2 conc = 1.57×10^{-3} mol/100g, G·conc= 4.75×10^{-4} mol/100g

an open chamber.

No hydroperoxide could be detected in processed LDPE containing galvinoxyl or iodine (Fig. 3.33) whereas hydroperoxides are formed in the control samples particularly processed in the open chamber (Fig. 3.33 curve 1) from the beginning of processing reaching a maximum (i.e. rate of -OOH formation predominates over the rate of its decomposition) and then declines. On decomposition of hydroperoxides various carbonyl groups are produced (detected by IR), ketonic(1720 cm^{-1}), acidic (1710 cm^{-1}), esteric (1745 cm^{-1}) and aldehyde (1730 cm^{-1}).

Gel content measurement of LDPE samples containing galvinoxyl and iodine processed under both conditions was carried out. No gel formation was detected in the samples. This is also supported by measuring MFI of the processed samples which has been found to be simply constant up to the processing times used in the experiment.

The above results clearly show that both galvinoxyl and iodine act as powerful melt stabilisers in low density polyethylene under the processing conditions used.

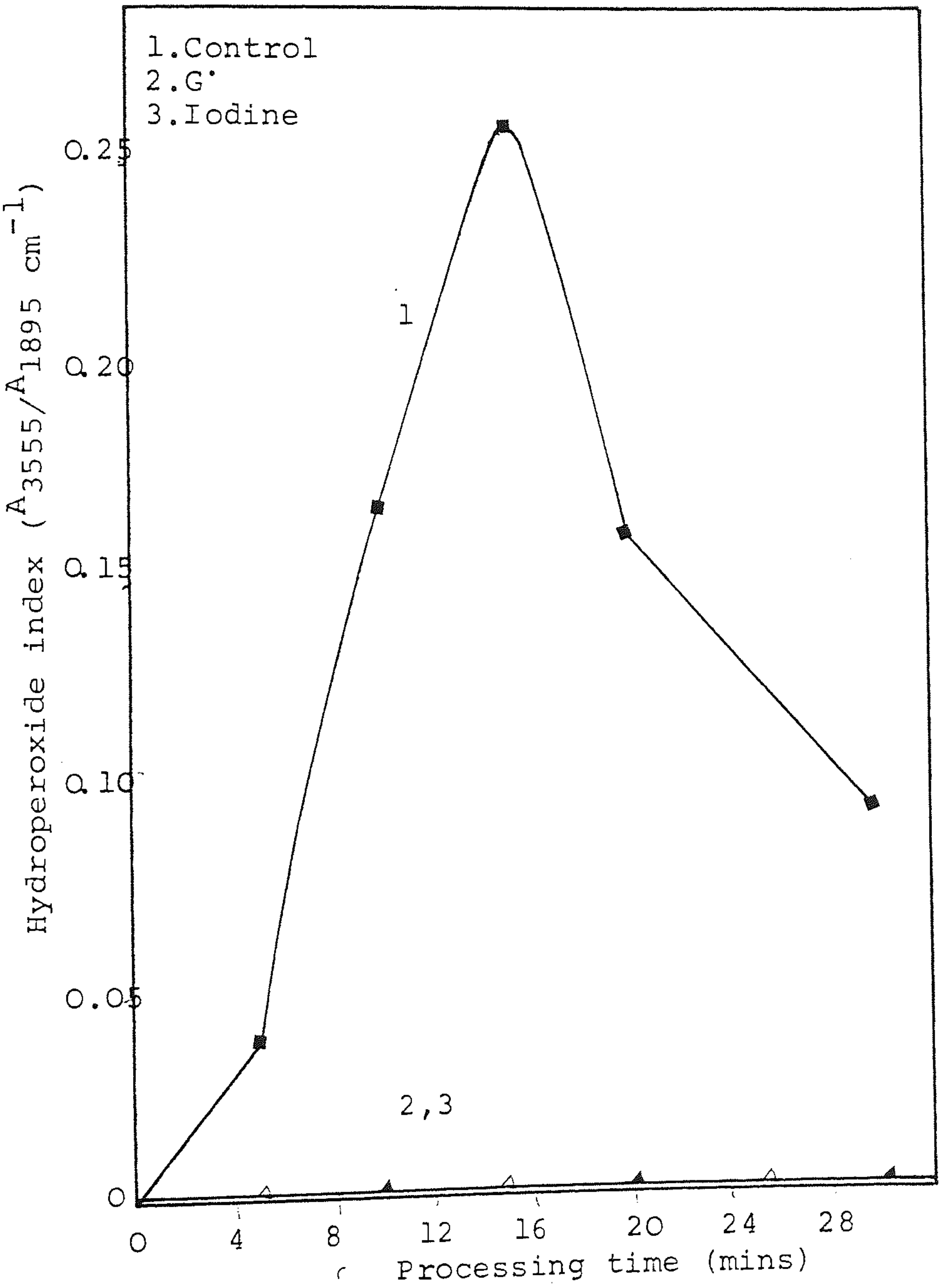


Fig. 3.33 Effect of galvinoxyl and iodine on the formation of hydroperoxide (3555 cm^{-1}) during processing of LDPE at 190°C in an open chamber, G˙ conc = 4.75 x 10^{-4} mol/100g, Iodine conc = 1.57 x 10^{-3} mol/100g.

Since both chain scission and crosslinking occurring during the processing of the unstabilised LDPE which are radical in nature (see reaction scheme 16) galvinoxyl and iodine terminate these radicals and prevent both chemical changes (e.g. carbonyl, peroxide formation) and rheological changes (MFI, m.wt) in the polymer.

IR and UV spectra of all processed LDPE containing galvinoxyl showed a phenolic O-H absorbance at 3640 cm^{-1} and a strong UV absorbance at 380 nm respectively indicating GH formation during the processing.

Fig. 3.34 shows the variation of the UV absorbance of GH with processing time (samples processed in closed mixer). Similar characteristic fluctuation of GH concentration was observed for LDPE samples as it was shown in the case of polypropylene samples (see Fig. 3.15). Thus the results obtained from LDPE samples could be the same as those shown and discussed for polypropylene (see Section 3.A.4).

Olefinic unsaturation (measured by IR as index A_{964}/A_{1895} cm^{-1}) was found to increase during the processing (Fig. 3.35). It shows an early rapid increase in double bond formation followed by a low rate of formation.

Fig. 3.34 Changes in UV absorbance s of hydrogalvinoxyl (at 380 nm) and galvinoxyl concentrations during the processing of LDPE with galvinoxyl at 190°C in a closed mixer.
$G^{\cdot}$ conc = 4.75×10^{-4} mol/100g

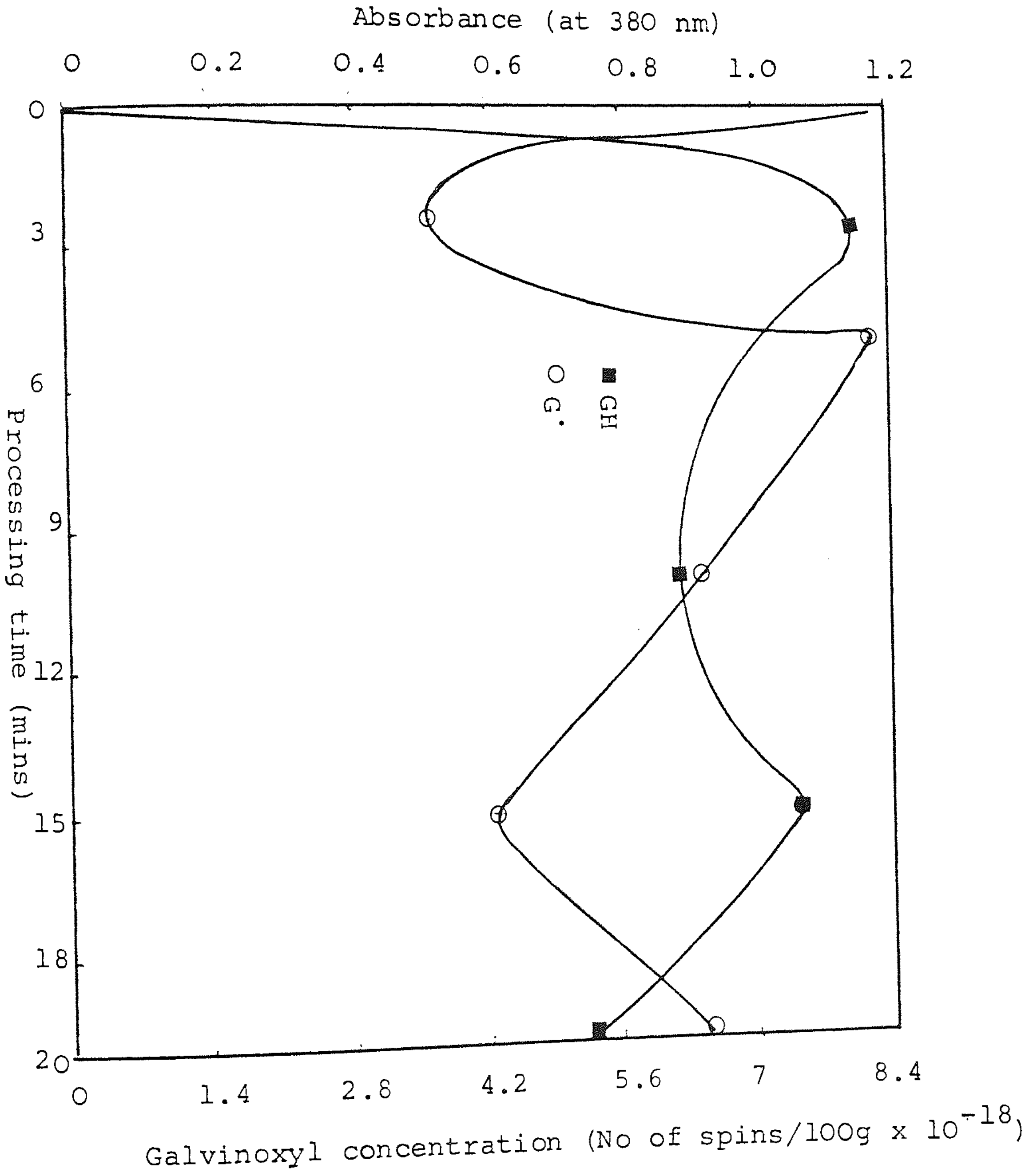
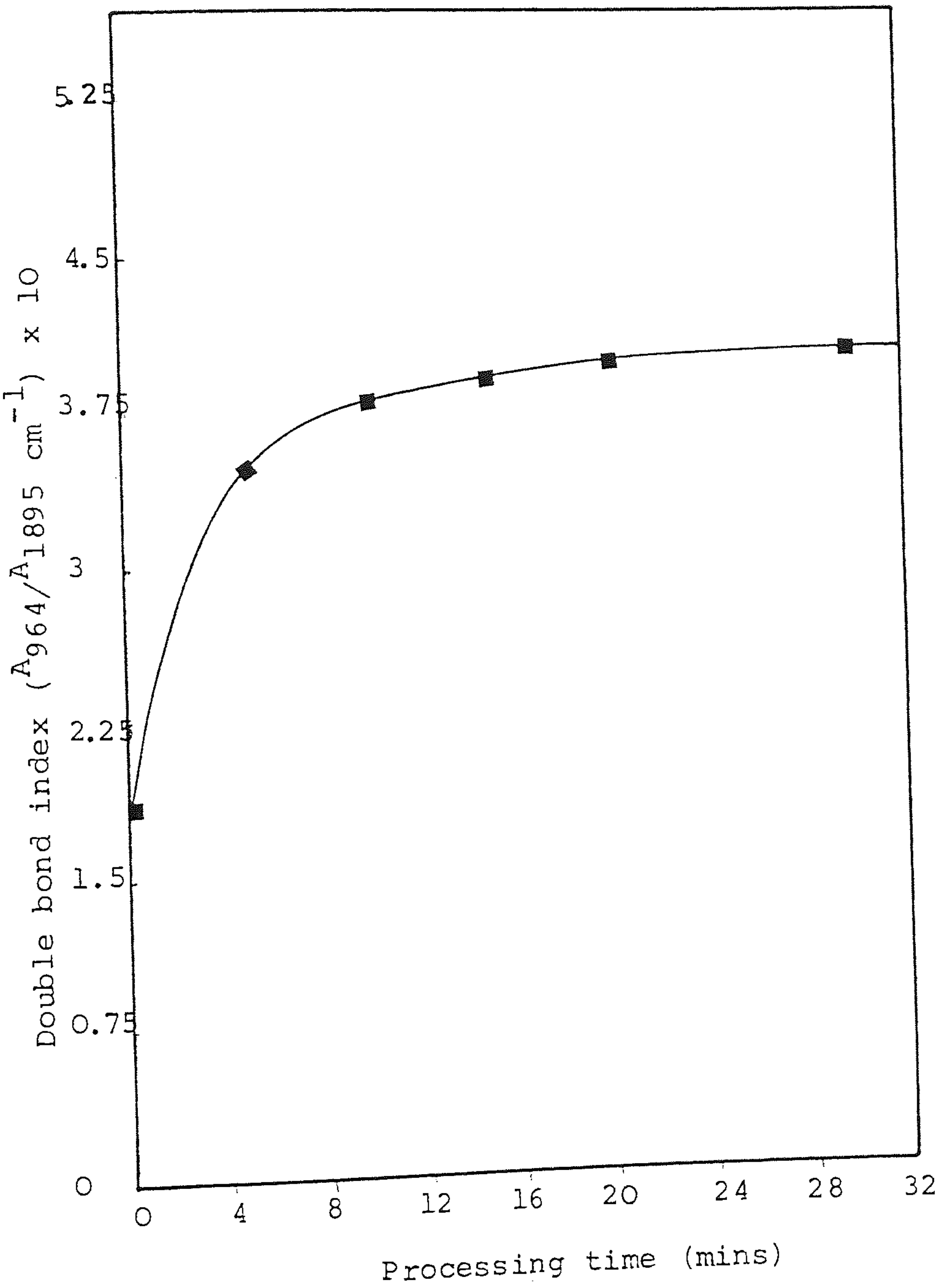


Fig. 3.35 Effect of galvinoxyl on the formation of unsaturation (964 cm^{-1}) during processing of LDPE at 180°C in a closed mixer, G conc = 4.75×10^{-4} mol/100g



This exactly corresponds to the hydrogalvinoxyl formation.

At the early stage of processing macroalkyl radical concentration is higher than alkylperoxy radical (in deficiency of oxygen) and due to interaction of alkyl radicals (e.g. allylic) with galvinoxyl hydrogalvinoxyl is formed leading to a rapid unsaturation formation in the polymer backbone, then reaction continues with a lower rate (lower rate of C=C formation).

Hydrogalvinoxyl is oxidised by alkylperoxy radicals acting as a CB-D antioxidant resulting in galvinoxyl regeneration. This is supported by e.s.r technique, i.e. galvinoxyl was detected and measured quantitatively in the processed samples (see section 6.2).

Fig. 3.36 shows that during the processing of LDPE with iodine, the vinylidene (band at 888 cm^{-1}) decreases rapidly in the early stage of processing followed by a low rate with increasing processing time. This may be explained as a rapid addition of iodine to the double bonds in the polymer.

The double bond was found to reappear on treatment of the processed films containing iodine with alcoholic silver nitrate. The above observations and other

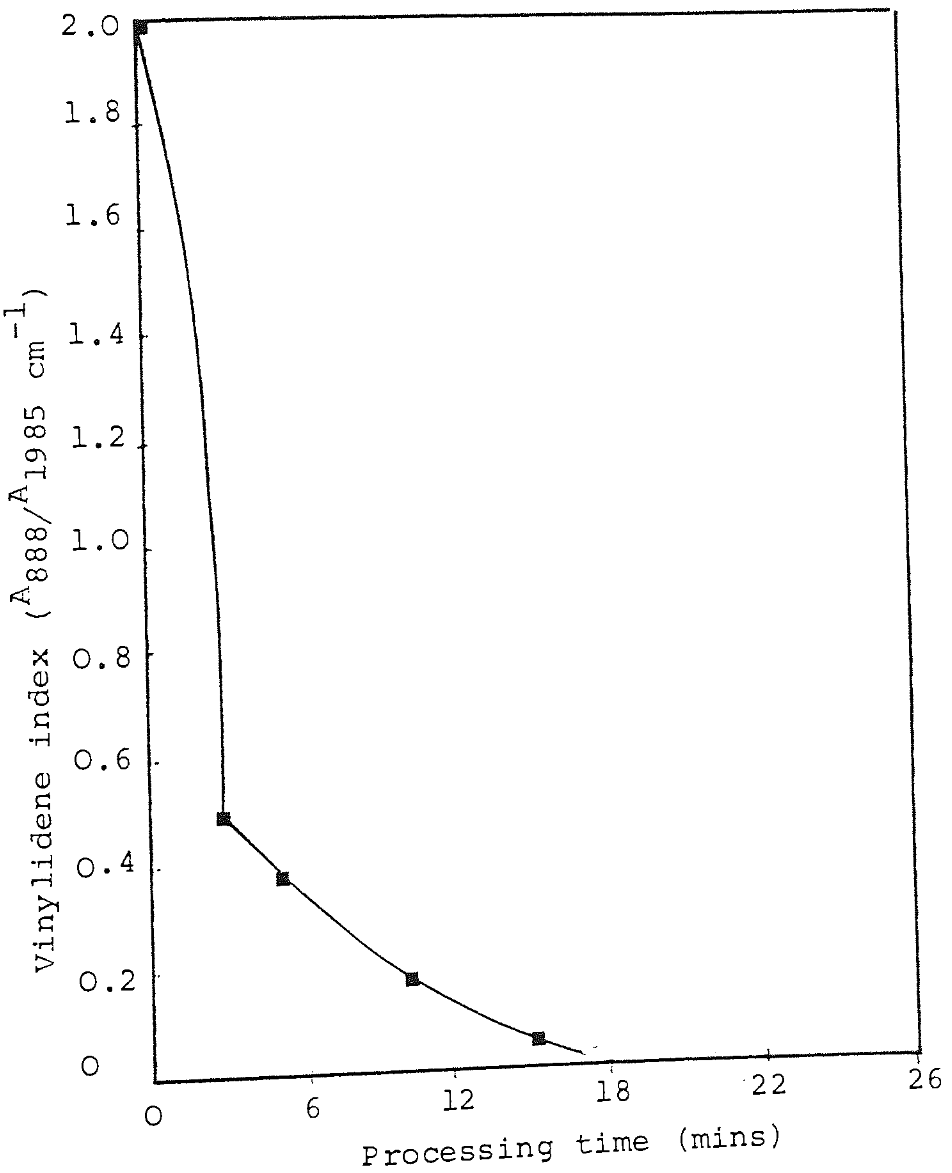


Fig 3.36 Changes in vinylidene double bond (at 888cm^{-1}) during processing of LDPE with iodine at 180°C in a closed mixer, iodine conc = 1.57×10^{-3} mol/100g

chemical tests performed in the system shows that the behaviour of iodine is very similar to that in polypropylene.

The effect of cupric stearate on LDPE during the processing was also studied. No hydroperoxide formation and carbonyl growth were detected in LDPE up to 30 mins. during processing both in an open chamber and in closed chamber (Fig. 3.37).

No gel content was found in the processed LDPE samples containing CuSt. The behaviour of CuSt as melt stabiliser in LDPE is very similar to galvinoxyl and iodine and it acts efficiently as in polypropylene.

It eliminates chemical reaction by interaction with the polymer presumably through the same mechanism as discussed in section 3.A.4.4.

Discolouration of the samples from blue in the early stage of processing (in deficiency of oxygen) to brownish (in 20 minutes) is probably due to formation of conjugated double bonds in the chains(241).

Two bands at 1585 cm^{-1} and 1550 cm^{-1} in the IR spectra could be detected indicating the possible co-ordination of copper with unsaturation(241).

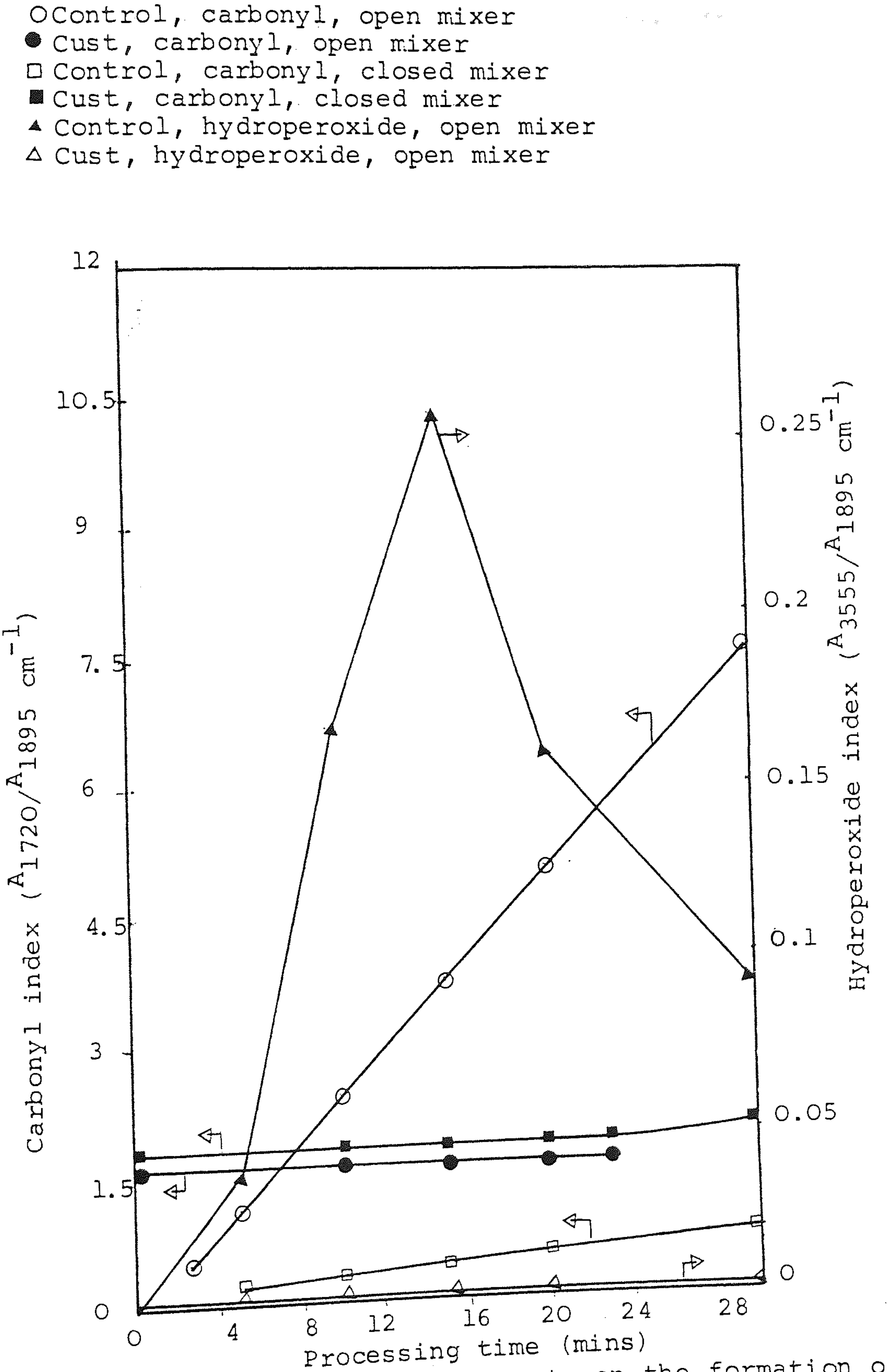


Fig. 3.37 Effect of cupric stearate on the formation of carbonyl and hydroperoxide during processing of LDPE at 180°C in both closed and open mixer, cust conc = 4.5 x 10^{-4} mol/100g

Other mechanistic studies will be discussed in Chapter 6.

CHAPTER FOUR

Thermal-Oxidative Stability of Polyolefins

The behaviour of galvinoxyl, iodine, nitroxyl radicals and cupric stearate as melt stabilisers in polyolefins were studied in detail in the preceding chapter. It has been shown that all the compounds act as very powerful melt stabilisers in polyolefins under various processing conditions. This chapter deals mainly with the subsequent behaviour of the additives during thermal oxidation of polyolefins.

4.1 Experimental

The accelerated thermal oxidations of compression moulded samples (thickness=1.8 x 10^{-2} cm) were carried out in a Wallace oven at 140°C (for pp samples) and 110°C (for LDPE samples) in the presence of air. Each sample was suspended in a separate cell to prevent the cross-contamination of the additives by volatilisation and was subjected to an air flow of 2.5 ft/hr (see also section 2.3.15).

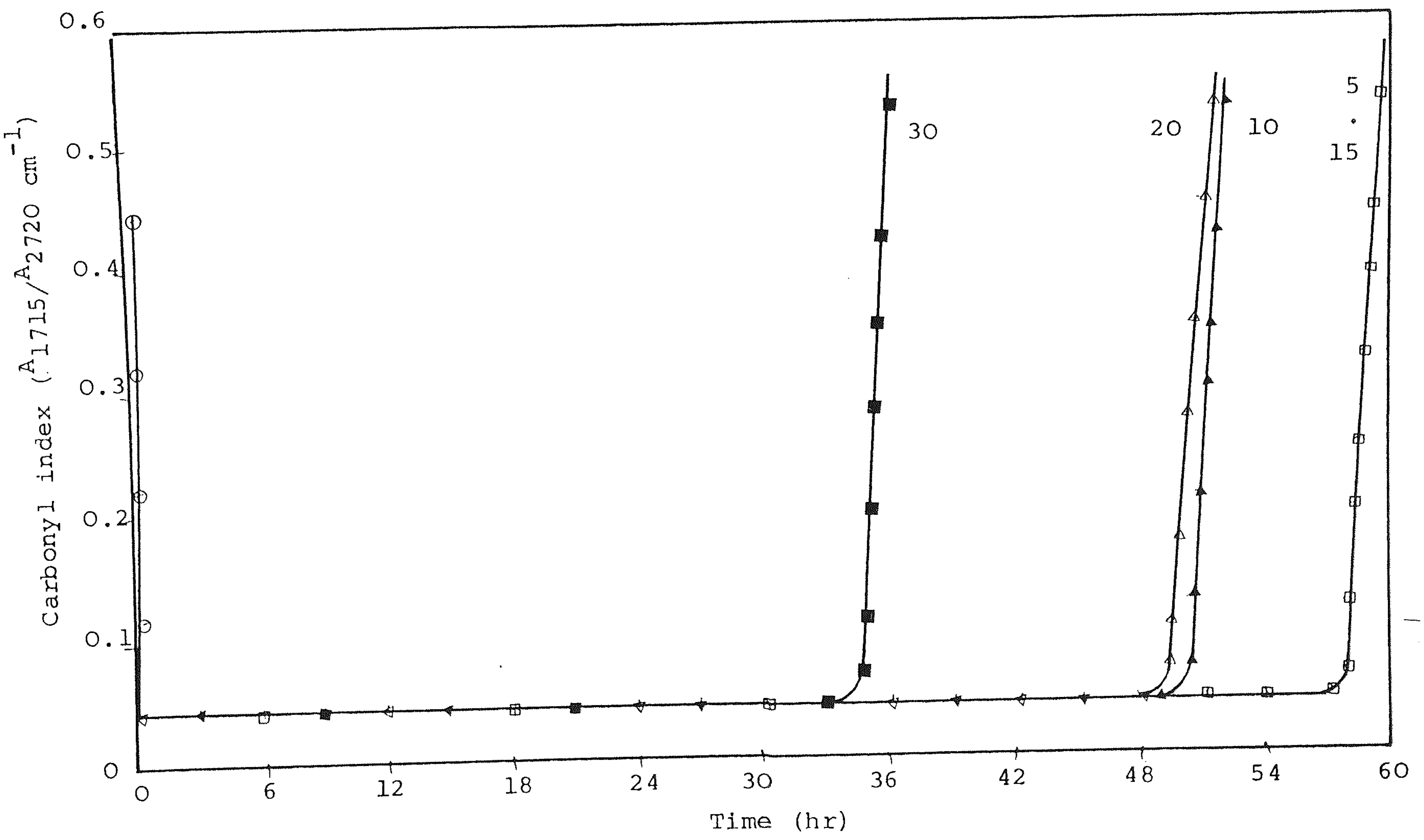
4.A.1 Effect of Melt Stabilisers on the Subsequent Thermal Oxidative Stability of Polypropylene (pp). Results and Discussion

4.A.1.1 Effect of Galvinoxyl

It was shown in preceding chapter that melt degradation is completely inhibited during the processing of polypropylene with galvinoxyl and hydrogalvinoxyl is formed as one of the main products from galvinoxyl. The quantitative formation of hydrogalvinoxyl during the processing of polypropylene with galvinoxyl was also estimated and discussed (see chapter 3, section 3.A.4.1, Fig. 3.15).

Fig. 4.1 illustrates the effect of processing time on the subsequent thermal oxidative stability of polypropylene in the form of compression moulded film containing galvinoxyl at 140°C (oven temperature). All the samples showed an induction period to carbonyl formation during thermal oxidations and the induction period was found to depend on the prior processing time. The length of the induction period seems to correlate with hydrogalvinoxyl concentration formed during processing (see, chapter 3, Fig. 3.15). 5 and 15 minutes processed samples, containing higher concentration of hydrogalvinoxyl, showed longer induction periods compared

Fig. 4.1 Changes in thermal oxidation of pp films (at 140°C) containing galvinoxyl(all samples processed at 200°C in a closed mixer, numbers on curves refer to processing times in mins), G' conc = 4.75×10^{-4} mol/100g.



to 10 and 20 minutes processed samples containing less hydrogalvinoxyl (Fig. 4.1). It is also noted from this figure that samples containing equivalent amounts of hydrogalvinoxyl after processing (e.g. 5 and 15 minutes) showed very similar thermal oxidative stability.

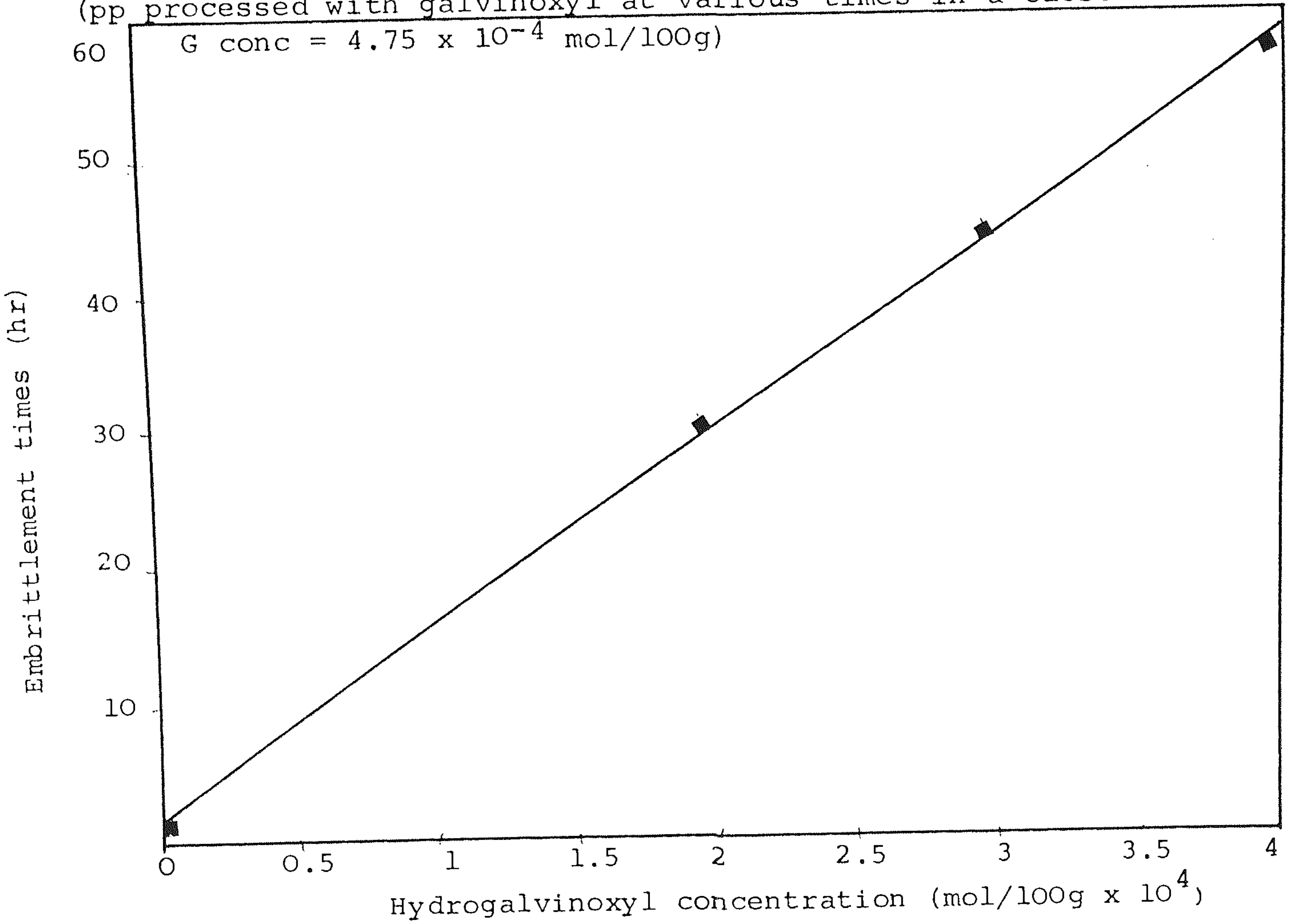
Table 4.1 summarises the thermal oxidative stability of the polymer films at different processing times, processing temperature and initial galvinoxyl concentration as well as hydrogalvinoxyl concentration (formed during processing). Increase in galvinoxyl concentration leads to an increase in thermal oxidative stability of the polymer due to formation of larger amounts of hydrogalvinoxyl during processing (see, Fig. 3.15, curve a). If the embrittlement times of the polymer films are compared at two different processing temperatures (190°C, 200°C) at the same molar concentration of galvinoxyl, better stability is observed at the higher temperature. This is also due to the higher amount of hydrogalvinoxyl formed during processing at higher temperature (see, chapter 3, Fig. 3.15, curve c).
A direct relation between hydrogalvinoxyl concentration in the samples and thermal stability is observed (Table 4.1) which is also shown in Fig. 4.2 (a linear relation).

Fig. 4.3 follows the decay of the phenolic hydroxyl absorbance (at 3640 cm^{-1}, due to GH) in the polymer

Table 4.1 Effect of Galvinoxyl on the Thermal Oxidative Stability of pp at 140°C

Processing time (mins)	Embrittlement time(hr), E.T $[G] = 4.75 \times 10^{-4}$ mol/100g, Processing temp. = 200°C	E.T (hr) $[G] = 2.37 \times 10^{-4}$ mol/100g, Processing temp. = 190°C	E.T (hr) $[G] = 2.37 \times 10^{-4}$ mol/100g, Processing temp. = 200°C	Hydrogalvinoxyl concentration (mol/100g $\times 10^{4}$) initial $[G] = 4.75 \times 10^{-4}$ mol/100g, temp. = 200°C
5	57	26		3.95
10	49	22.5	27	3.06
15	57	26		3.95
20	48	21		3.06
30	33	12	18	1.96
Control	0.5			

Fig. 4.2 Changes in embrittlement times of pp films containing galvinoxyl with hydrogalvinoxyl concentrations present in the samples during oven ageing at 140°C, (pp processed with galvinoxyl at various times in a closed mixer at 200°C, G conc = 4.75 x 10^{-4} mol/100g)



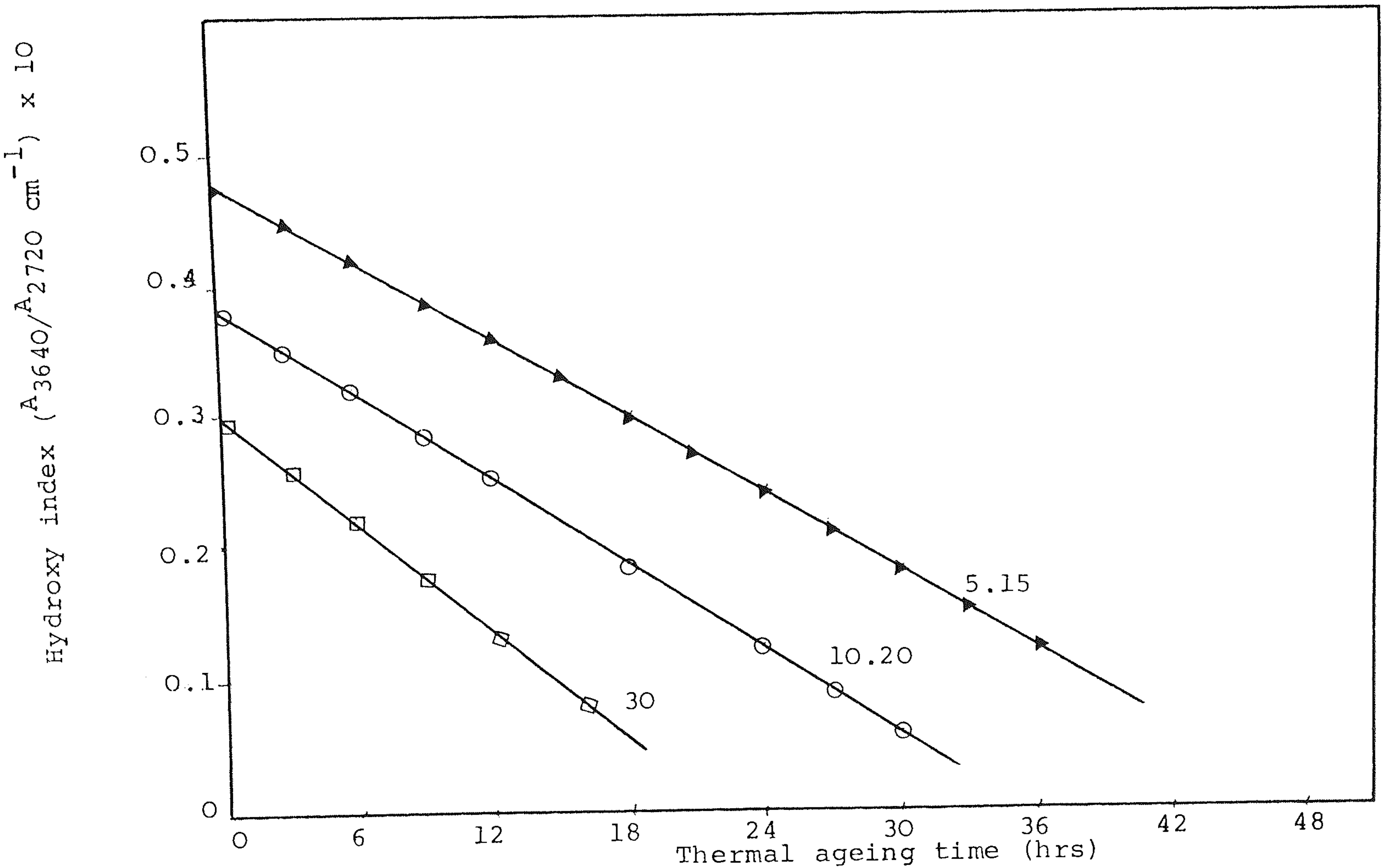


Fig. 4.3 Decay of phenolic hydroxyl (at 3640cm^{-1}) during thermal oxidative ageing (at 140°C) of polypropylene films (pp processed with galvinoxyl at 200°C in a closed mixer, G' conc = 4.75×10^{-4}mol/100g, Numbers on curves are processing times in mins)

films during the thermal oxidative process at 140°C indicating that hydrogalvinoxyl is the main cause of thermo oxidative stability of the polymer.

Fig. 4.4 illustrates the thermal oxidative stability of the polymer films subjected to oven ageing at 110°C. A long induction time to carbonyl formation is seen. The effect of processing time on the thermal stability of polypropylene is the same as was shown in Fig. 4.1 (i.e. oven ageing at 140°C). Since it was shown in chapter 3 that the hydrogalvinoxyl concentration is almost the same for 5 and 15 minutes as well as for 10 and 20 mins respectively and it is much lower in 30 mins processed samples (see,Fig. 3.15, Table 3.1). This confirms that the high thermal stabilising ability of the samples corresponds to the hydrogalvinoxyl concentrations in the samples. Table 4.2 also lists the embrittlement times of the polypropylene films during the thermal oxidation at 110°C. The results are similar to those shown at 140°C (see, Table 4.1). The thermal oxidative stability has increased by almost ten times at 110°C compared with 140°C.

Hydrogalvinoxyl acts as a powerful CB-D antioxidant removing alkylperoxy radicals from the system and resulting in the formation of galvinoxyl which is also a very effective ($ROO^{\cdot} + GH \longrightarrow G^{\cdot} + ROOH$) CB-A

Fig. 4.4 Changes in thermal oxidative stability (at 110°C) of polypropylene films, containing galvinoxyl (pp processed with galvinoxyl at 200°C in a closed mixer, G' conc = 4.75 x 10^{-4} mol/100g, numbers on curves refer to processing times)

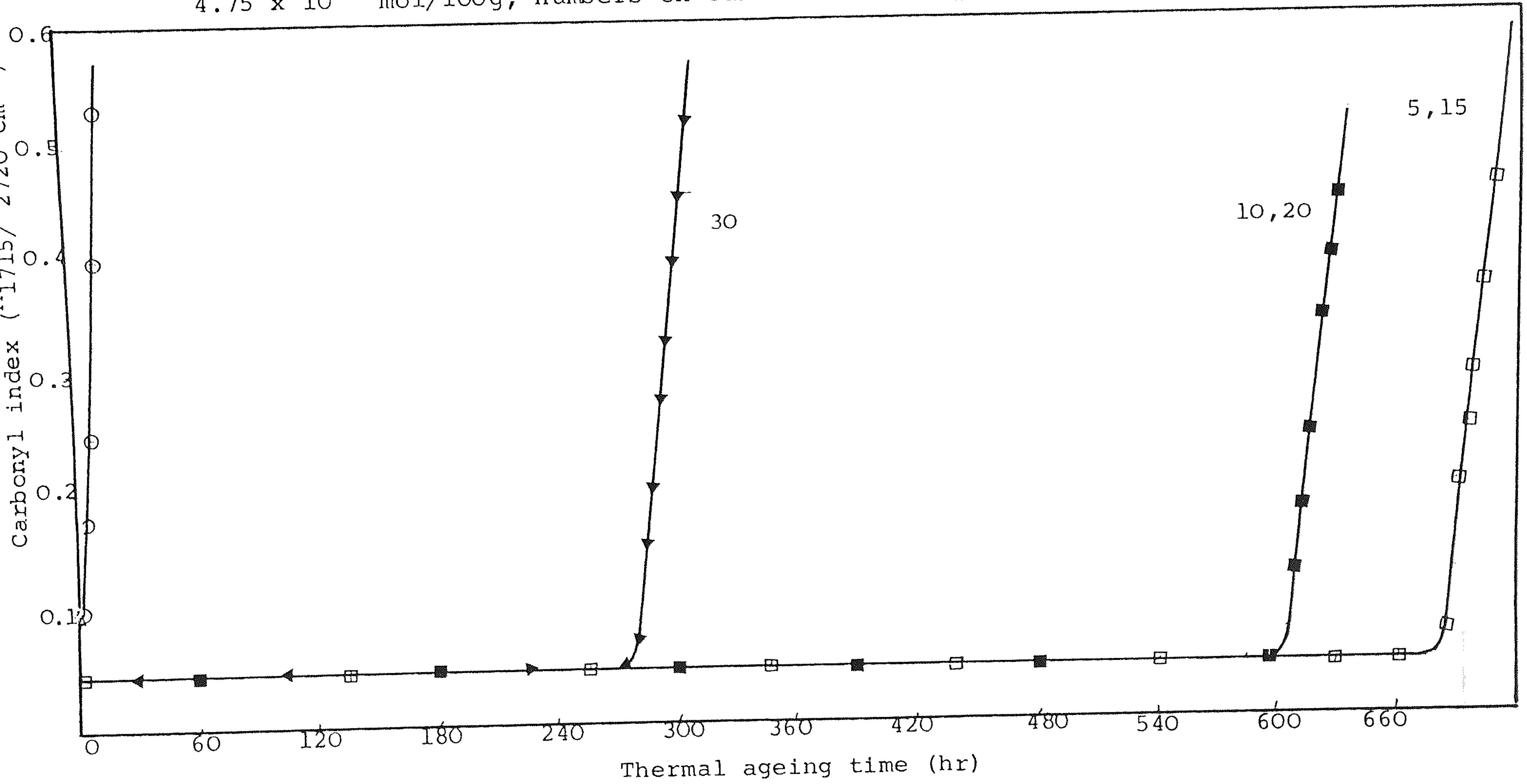
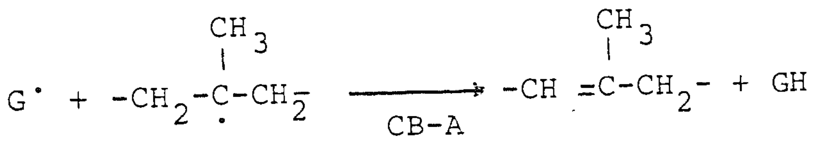


Table 4.2 Effect of Galvinoxyl on the Thermal Oxidative Stability of pp at 110^{o}C (oven temp.).

Processing time (mins)	E.T (hr) [G] = 4.75×10^{-4} mol/100g, Processing temp. = 200^{o}C	E.T (hr) [G] = 2.37×10^{-4} mol/100g, Processing temp. = 190^{o}C	Hydrogalvinoxyl concentration (mol/100g x 10^{4}) initial [G] = 4.75×10^{-4} mol/100g, temp. = 200^{o}C
5	672	280	3.95
10	600	194	3.06
15	672	294	3.95
20	576	185	3.06
30	274		1.96
Control	4.5		

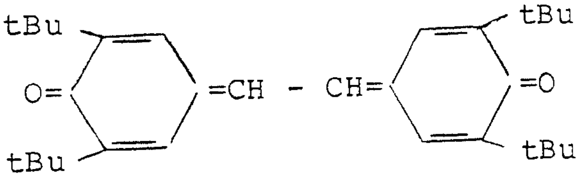
antioxidant. In chapter 3 the role of galvinoxyl in thermal processing stabilisation was discussed and it was shown that hydrogalvinoxyl is formed even in severe processing conditions, (i.e. high oxygen concentration). In oven ageing because of the presence of high concentration of oxygen, there is a competition between oxygen and galvinoxyl for macroalkyl radicals forming both alkylperoxy radicals and hydrogalvinoxyl. Therefore hydrogalvinoxyl is regenerated by a CB-A mechanism and peroxyl radicals oxidise the hydrogalvinoxyl by a CB-D mechanism. The unsaturation formation is also probable during the thermal oxidation.



$$G^{\cdot} + -CH_2-\overset{CH_3}{\underset{\cdot}{C}}-CH_2- \xrightarrow[CB-A]{} -CH=\overset{CH_3}{C}-CH_2- + GH$$

Both CB-A and CB-D mechanisms could be involved in the thermal stabilisation process of pp with galvinoxyl explaining its high stabilising effectiveness. Since the concentration of oxygen in the system is high, the role of hydrogalvinoxyl (CB-D) is predominant. However, there is also a possibility of loss of galvinoxyl from the system by its reaction with alkylperoxy radicals resulting in quinone compounds (e.g. benzoquinone)[194]. 2,6 di-tert-butyl,1,4 benzoquinone was found to be formed during thermal processing of pp with galvinoxyl (see, 3.A.4.1). These quinone compounds might act as a secondary antioxidant e.g. 2,6,di-tert-butyl 1,4,benzoquinone may compete with oxygen for alkyl radical trapping(45) contributing to the thermal antioxidant function.

Kularatne and Scott(249) have shown that TBC (2,6 di-tert-butyl 4-methyl phenol) under appropriate conditions undergoes facile reactions resulting in the formation of coloured quinonoid compounds, notably stilbene quinone of type (I). Stilbenequinone compounds have been found(250) to act as thermal stabilisers.



(I)

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

Henman has also shown(194a) that (I) is formed when TBC is used as a melt stabiliser for polypropylene and is itself much more effective than TBC as a melt stabiliser.

4.A.1.2 Effect of 4-hydroxy -2,2,6,6, tetramethyl piperidine oxyl (4OHTMPO), Tinuvin 770, Iodine and Cupric Stearate (Cust) on Thermal Oxidative Stability of pp.

A similar investigation was carried out with the other melt stabilisers discussed in section 4.A.1.1 in the thermal oxidation of polypropylene (oven ageing at 140°C).

The above compounds did not show any significant thermal antioxidant effect during the oven ageing of polypropylene compared with typical heat ageing antioxidants (see, Table 4.3) although nitroxyl radicals, iodine and cupric stearate are all very powerful melt stabilisers for polypropylene when processed in a limited amount of air (see, section 3.A.3, 3.A.4). However,it has been found (see, chapter 3) that the melt stabilisation effectiveness of both nitroxyl radicals and iodine are very much reduced when processed in an excess of air.

Nitroxyl radicals are very effective alkyl radical scavengers (i.e. CB-A antioxidants)$^{(136,233)}$. Since in thermal oxidation condition (oven ageing) oxygen is able to compete with nitroxyl radicals for alkyl radicals, nitroxyl radicals are ineffective under this condition.

The I.R spectrum of the processed sample containing iodine showed almost no carbonyl formation compared with the control after 0.5 hr oven ageing at 140°C.

Table 4.3 Thermal Oxidative Stability of pp in the Presence of Antioxidants (oven temp = 140°C). Samples, Processed at 180°C/10 mins in a Closed Mixer

Antioxidant	Embrittlement time (hr)
None	0.5
Tinuvin 770	0.5
Iodine	0.75
4 OHTMPO	1
Cust	0.5
Irganox 1076	54
NIDBC	32

Concentration of all antioxidants = 3×10^{-4} mol/100g

Discolouration of the sample was observed after about 0.5 hr heating (towards the colour of the control), indicating loss of iodine by volatilisation. This seems to suggest that if iodine persisted in the sample, there would be no oxidation but when iodine is lost or its concentration falls below the critical concentration in the samples, rapid oxidation occurs.

Cupric stearate is also shown to react with alkyl radicals (oxidation - reduction reaction, see 3.A.4)$^{(241)}$, but because of the high concentration of alkyl peroxy radicals in the thermal oxidation condition CuSt does not act as an efficient antioxidant under this condition.

In oven ageing of the samples containing CuSt oxygen competes with Cu^{+2} for alkyl radicals leading to inactivity of CuSt under these conditions.

During melt processing of polypropylene with CuSt Cu^{+} was found to be formed (see, 3.A.4.4) due to oxidation of alkyl radicals with Cu^{+2} but Cu^{+} oxidises rapidly to Cu^{+2} due to the presence of peroxides in the system. Therefore, there is a low concentration of Cu^{+} in the samples subjected to thermal oxidation which could react with alkyl peroxy radicals.

$$(ROO^{\cdot} + Cu^{+} \longrightarrow RO\bar{O} + Cu^{+2})$$

It therefore has insignificant effect on thermo-oxidative stability of the polymer. Redox reactions between hydroperoxides and copper carboxylate leading to radicals are also involved(248).

It was shown that Tinuvin 770 had a pro-oxidant effect during the melt processing operation (see, 3.A.3, Fig. 3.27) leading to hydroperoxide formation(167). In accelerated thermal oxidation these hydroperoxides initiate The degradation process resulting in a rapid rate of polymer destruction.

A typical commercial CB-D antioxidant (Irganox 1076) and a peroxide decomposer (nickel dibutyl dithio carbamate) at the same molar concentration (3×10^{-4} mol/100g) were found to be very effective during thermal oxidation (at ambient oxygen pressure). The former acted by electron or hydrogen atom donation to the peroxy radicals(45) (CB-D) and the latter by destruction of hydroperoxides in a non free radical process(45,110,167) (see, Table 4.3).

It is clear from the above results that nitroxyl radicals, iodine and cupric stearate which are very effective in an oxygen deficient system are almost ineffective at normal concentrations of oxygen whereas galvinoxyl is effective under both conditions. This shows the importance of CB-A and CB-D antioxidant mechanisms in thermal oxidation processes. CB-A antioxidants are effective when alkyl radicals are the major propagating species present (oxygen deficiency), however, in an autoxidising system containing abundance of alkyl peroxy radicals, CB-D antioxidants operate effectively. Since in many antioxidant processes in polymers both species ($R^\cdot$,$ROO^\cdot$) are present to some degree, antioxidants involving both kinds of activity (CB-A and CB-D) are expected to be superior to those acting by a single mechanism only.

The oxygen molecule is a powerful radical scavenger and competes with CB-A antioxidants (melt stabilisers) for alkyl radicals at ambient oxygen pressure (oven ageing). Since there is higher probability of efficient collisions between oxygen and alkyl radicals compared with CB-A antioxidants, alkyl peroxy radicals are formed predominantly. The presence of an effective CB-D antioxidant (e.g. GH as derived products from $G^\cdot$) can terminate propagating species resulting in stabilisation of the polymer.

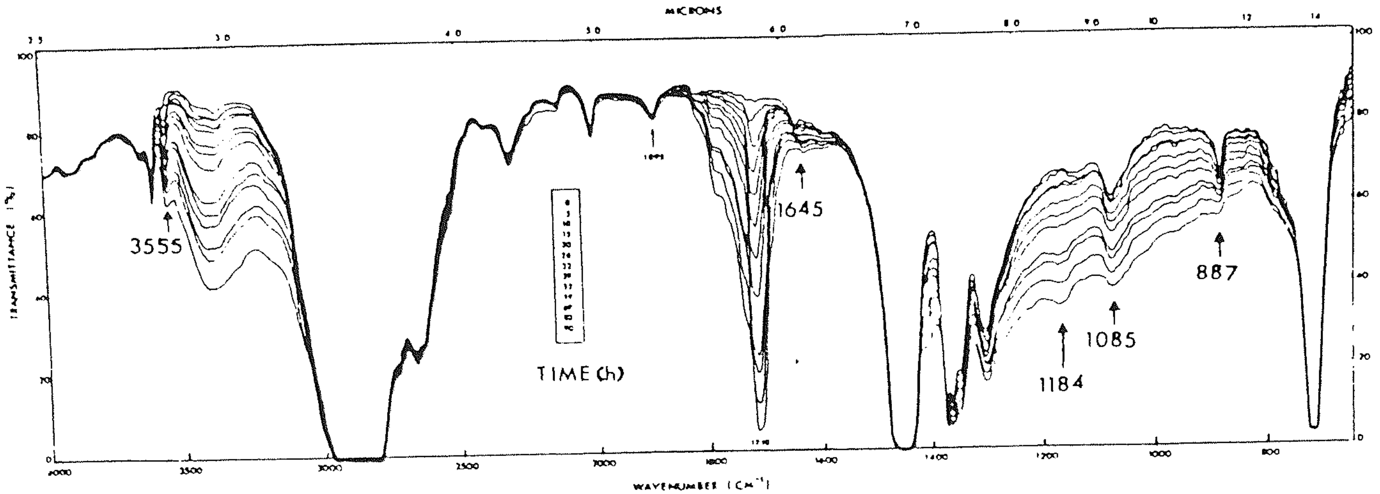
Oxidation of a CB-D antioxidant to the parent CB-A antioxidant necessitates the presence of oxygen in the system, but high concentration of oxygen could lower the efficiency of CB-A antioxidant. Thus a certain concentration of oxygen in the oxidation system is needed to obtain the highest efficiency of stabilisation involving both CB-A and CB-D mechanisms.

4.B.1 Consideration of Thermal Oxidative Stability of Low Density Polyethylene (LDPE)

Fig. 4.5 illustrates I.R spectra of processed LDPE film after being thermally oxidised for various lengths of time at 110°C in a flowing (air) atmosphere.

The effect of thermal oxidation on LDPE in the presence of air (at 110°C) is observed in the three regions of the spectrum (viz. hydroxyl region 3600 - 3000 cm^{-1}, carbonyl region 1850 - 1600 cm^{-1}, and olefinic unsaturation region 1200-850 cm^{-1}).

In the hydroxyl region the intensity of a band at 3380 cm^{-1}, which is typical of hydrogen bonded alcohol and hydroperoxide groups(251), increases during the thermal oxidation and finally becomes very broad. Hydroperoxide formation is characterised by a band at 3555 cm^{-1} (252). In the carbonyl region, the initial carbonyl absorption at 1725 - 1720 cm^{-1} (ketone) shifted towards 1710 cm^{-1} (acid) with increasing heating time. Other carbonyl products were also



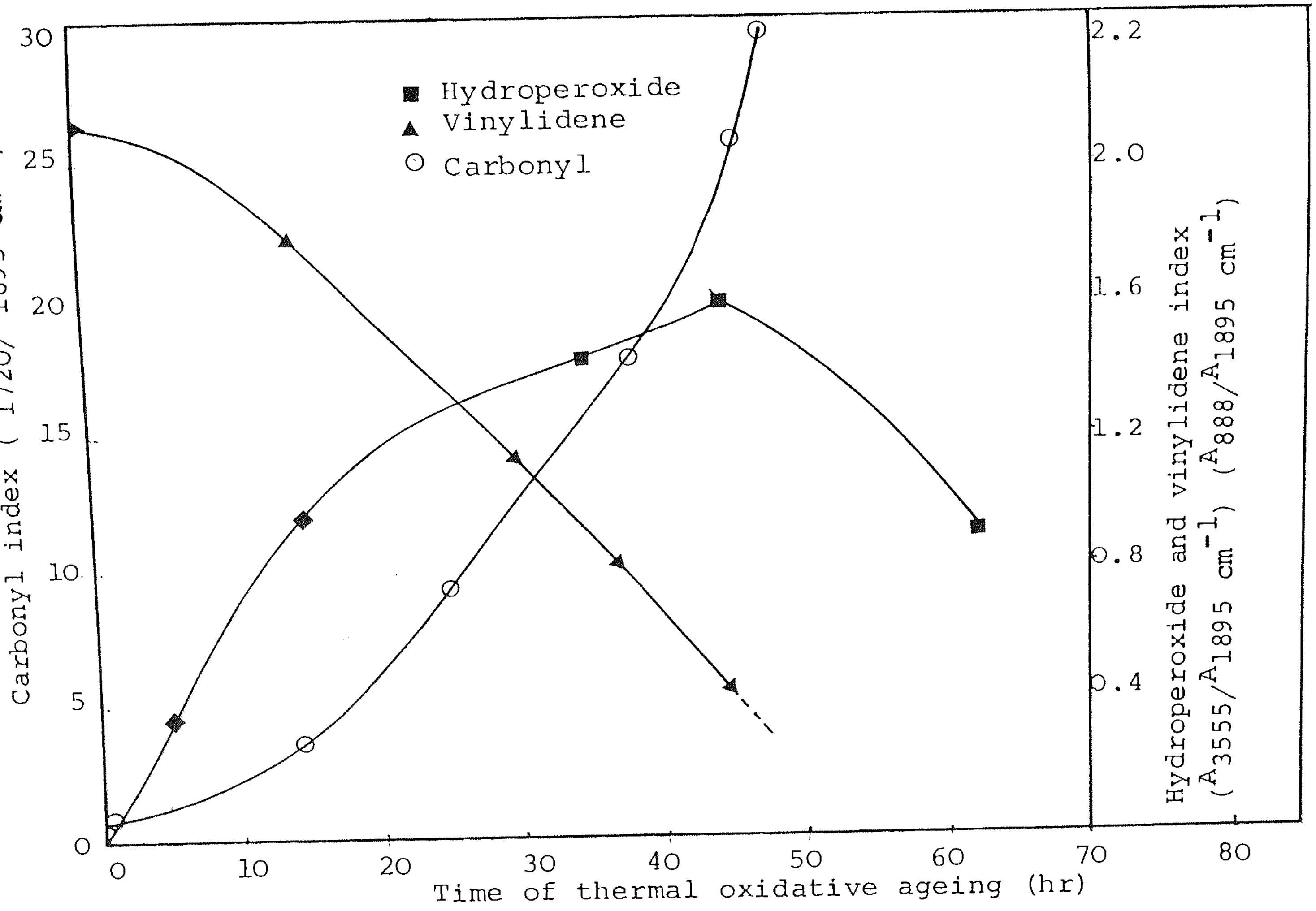
4.5 Changes in the I.R Spectra of unprocessed LDPE during thermal oxidation at 110°C.

observed as shoulders in the later stages of thermal oxidation (e.g. peracid at 1785 cm^{-1}, ester at 1745 cm^{-1}, conjugated carbonyl at 1685 cm^{-1}, etc.). It has been suggested that(252) all oxygen containing groups formed are the result of hydroperoxide decomposition.

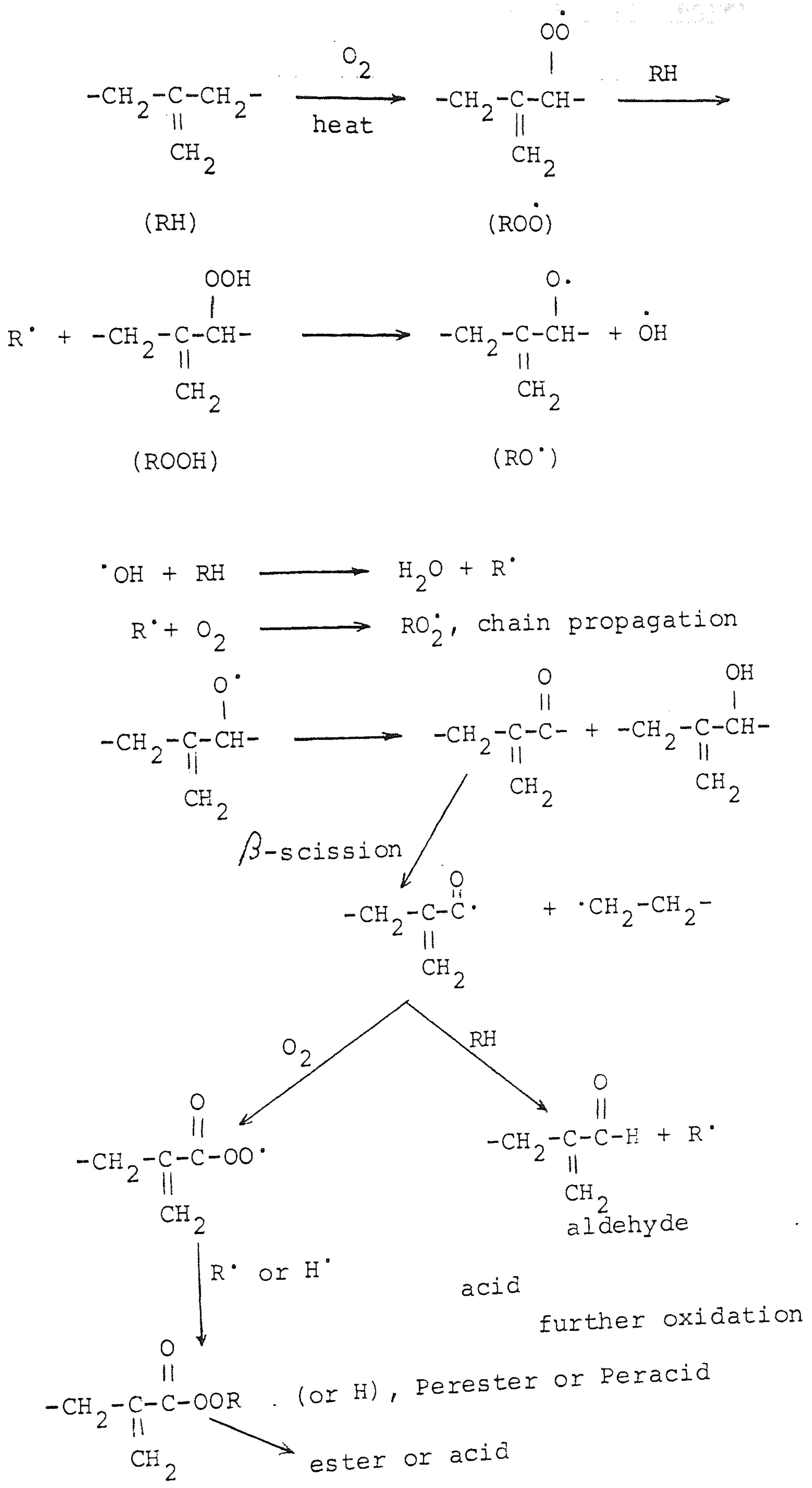
In the region 1200-850 cm^{-1} which corresponds to the absorption due to various types of olefinic unsaturation, the vinylidene unsaturation (at 888 cm^{-1}) initially present in the polymer decreases during the thermal ageing. Other types of unsaturation (viz. vinyl at 910 cm^{-1}, vinylene at 964 cm^{-1}) which are present in very minute quantities in the polymer remained almost constant during thermal oxidation (Fig. 4.5). Fig. 4.6 reveals the effect of thermal oxidation on LDPE film at 110°C. It shows that the hydroperoxide concentration rises to a maximum and then decays with increasing heating time. Change in vinylidene concentration with heating time (at 110°C) shows an initial slow rate of decay followed by a rapid rate of decay (Fig. 4.6).

The carbonyl is also formed in an autoaccelerating manner (Fig. 4.6) which is associated with high rate of hydroperoxide formation during thermal oxidation(252). The following reaction scheme has been suggested(27,39)

Fig. 4.6 Effect of thermal oxidation (at 110°C) on the formation of carbonyl, hydroperoxide, and vinylidene decay of LDPE, Processed in a closed mixer at 180°C/30 mins.



for thermal oxidation of LDPE.



4.B.2 Effect of Melt Stabilisers on the Subsequent Thermal Odiative Stability of LDPE, Results and Discussion

Fig. 4.7 illustrates the effect of galvinoxyl, iodine and cupric stearate on thermal oxidative stability of LDPE. The samples containing galvinoxyl showed very high thermal oxidative stability (Fig. 4.7, curve 4).

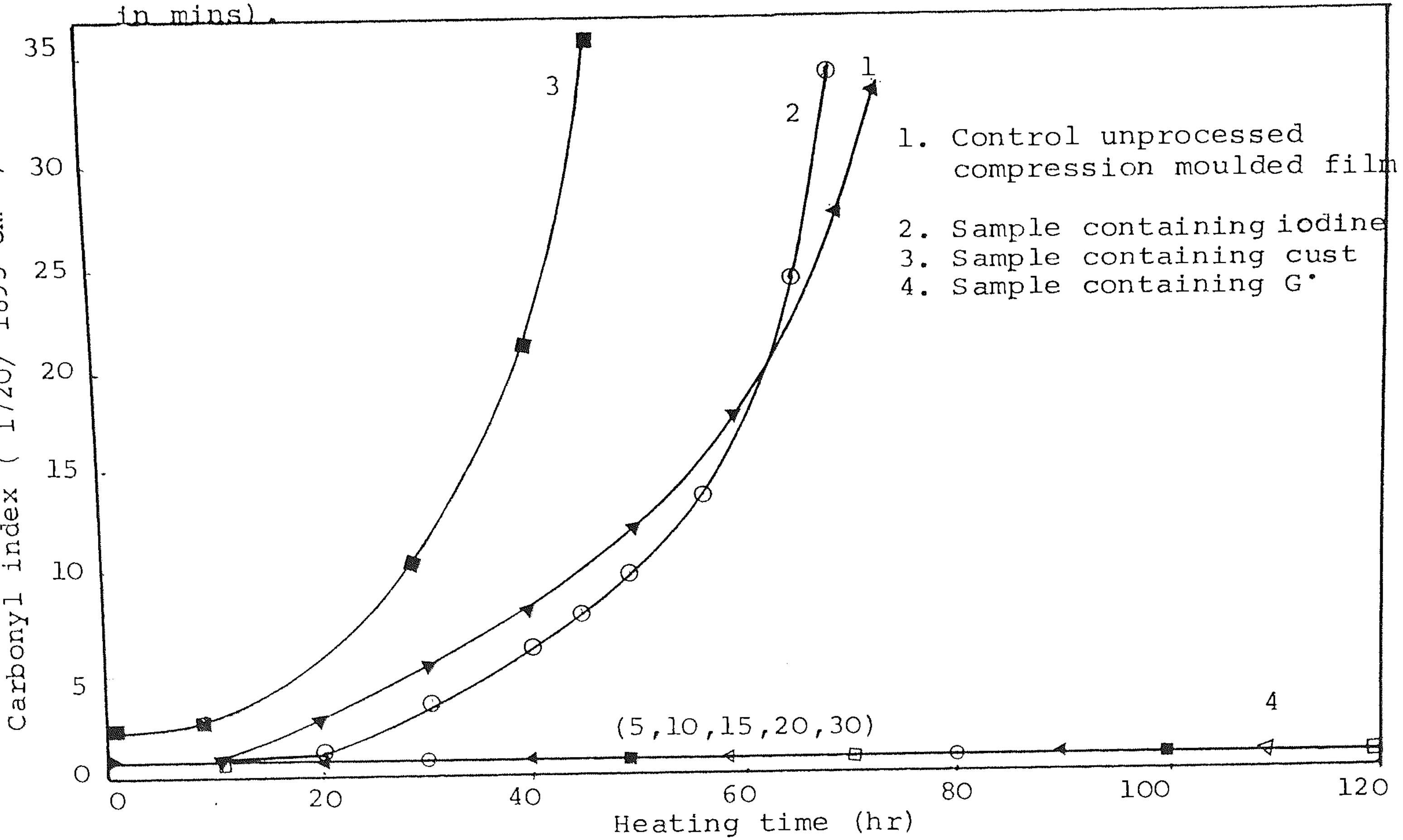
No structural changes (carbonyl, hydroperoxide formation or vinylidene decay) were detected in the films for a long period of time (= 1600 hrs).

The behaviour of galvinoxyl in the case of LDPE is very similar to that for polypropylene (see,section 4.A.1.1). High thermal oxidative stability of the polymer films could be mainly due to the presence of galvinoxyl and hydro-galvinoxyl in the samples. Hydrogalvinoxyl (GH) acts as a CB-D antioxidant removing alkylperoxy radicals from the system.

$$GH + ROO^{\cdot} \longrightarrow HOOR + G^{\cdot}$$

Galvinoxyl ($G^{\cdot}$) also is an effective CB-A antioxidant and competes with oxygen for alkyl radicals leading to the formation of hydrogalvinoxyl as it was shown during thermal processing operation (see, chapter 3,

Fig. 4.7 Effect of galvinoxyl, iodine and cupric stearate on the thermal oxidation of LDPE at 110^{o}C (samples processed at 190^{o}C in a closed mixer for 10 mins, all additives at 4.5 x 10^{-4} mol/100g, numbers on curve 4 in bracket are processing times in mins).



3.B.3) Derived products (e.g. 2,6 di-tert-butyl,1,4 benzoquinone) formed during processing and possibly during thermal oxidation might also contribute to the thermal stabilisation to some extent as it was shown in the case of polypropylene (see, section 4.A.1.1). Iodine and cupric stearate showed no antioxidant effect during thermal oxidation of LDPE (Fig. 4.7, curves 2 and 3). Moreover, the film containing CuSt oxidised more rapidly than the control. This behaviour is similar to that found in the case of polypropylene containing CuSt. Although iodine showed an initial antioxidant effect, subsequent rate of thermal oxidation is again faster than the control. The overall thermal stabilisation activity of both CuSt and iodine during oven ageing is not significant.

CHAPTER FIVE

Photo-Oxidation of Polyolefins

The effectiveness of the melt stabilisers discussed in chapter 3 (see, 3.A.4 and 3.B.3), as photo-stabilisers will be considered in this chapter.

5.1 Experimental

Polypropylene and low density polyethylene with (after tumble mixing) and without additives were processed in the RAPRA torque rheometer (pp at 200°C, 190°C and LDPE at 180°C, 190°C) for various lengths of time in both open chamber and closed chamber. The polymer samples were then compression moulded (pp at 190°C and LDPE at 150°C) for two minutes into films of thickness 1.8×10^{-2} cm. The polymer films were exposed in the U.V exposure cabinet (see, sec 2.3.14).

The rates of photo-oxidation of pp and LDPE films were measured by following carbonyl index(17) expressed as

$$\frac{A_{1715\ -\ 1710\ \text{cm}^{-1}}}{A_{2720\ \text{cm}^{-1}}} \quad \text{and} \quad \frac{A_{1715\ -\ 1710\ \text{cm}^{-1}}}{A_{1895\ \text{cm}^{-1}}} \text{ respectively.}$$

In the case of LDPE vinyl index = $\frac{A_{910\ cm^{-1}}}{A_{1895\ cm^{-1}}}$ and vinylidene index = $\frac{A_{888\ cm^{-1}}}{A_{1895\ cm^{-1}}}$ were also used as a measure of photo-oxidation.

Screening experiments were also carried out as follows:

the sample under investigation was superimposed by a film of identical thickness and size containing additives, thus the samples to be investigated received light which has been screened through the stabiliser containing film.

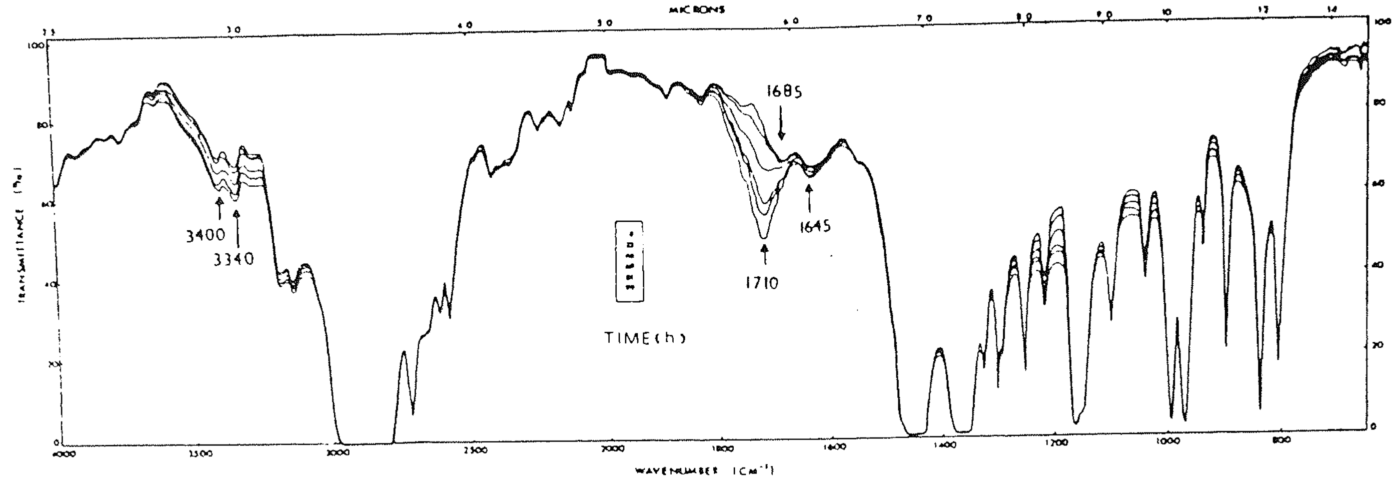
5.A Polypropylene (pp)

5.A.1 Effect of Processing on the Photo-Oxidation of Polypropylene

I.R analysis of irradiated polypropylene film shows that in the hydroxyl stretching region (4000 - 3000 cm^{-1}) a broad band from 3500 - 3300 cm^{-1} with two peak heights at 3400 cm^{-1} and 3350 cm^{-1} increases with increase in irradiation time (Fig. 5.1).

In the carbonyl region (1650 - 1850 cm^{-1}) conjugated

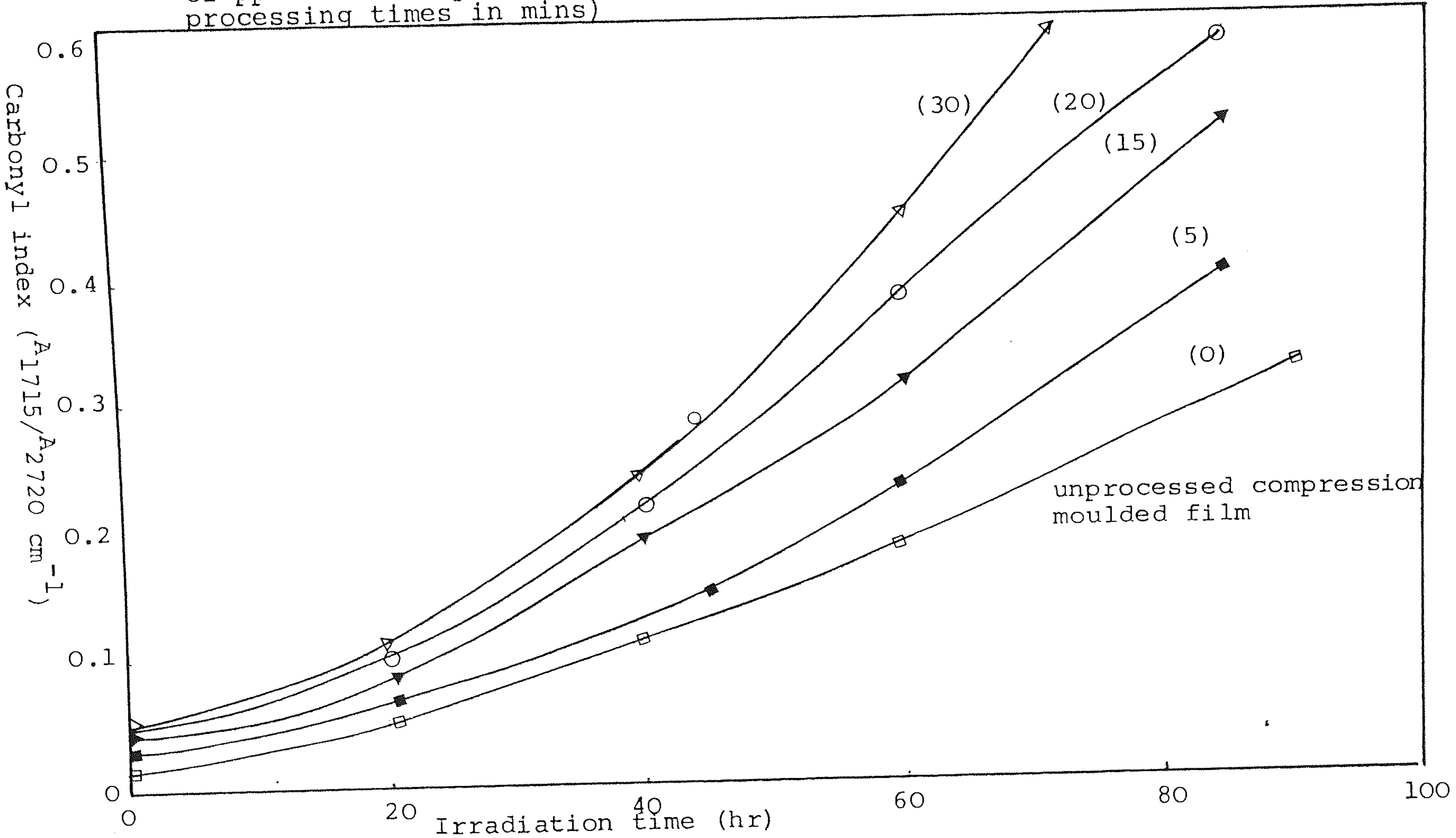
Fig. 5.1 Changes in the I.R spectra of unprocessed pp during photo-oxidation.



carbonyl (at 1685 cm^{-1}) which is initially present in the polymer disappears and a main carbonyl peak at 1715 cm^{-1} (due to ketonic carbonyl) starts to grow rapidly (Fig. 5.1). The main carbonyl peak contains many shoulders indicating the presence of various carbonyl species (aldehyde, ester, ketone etc.) especially a band for acid at 1710 cm^{-1}. The latter peak due to carboxylic acid begins to form from the beginning and remains the strongest during and after oxidation, showing the acid groups to be one of the major oxidation products of polypropylene. A broad band at 1645 cm^{-1} which indicates the presence of olefinic unsaturation in polypropylene remains almost constant during photo-oxidation (Fig. 5.1). To show the effect of processing on photo-oxidative stability of polypropylene the rate of photo-oxidation of three samples (processed in closed mixer for 5, 15, 30 mins at 200°C) are compared with a control (compression moulded of unprocessed pp).

Fig. 5.2 indicates that as processing time increases the rate of photo-oxidation increases. The higher rate of photo-oxidation is the result of higher amount of hydroperoxide which is formed with increased processing time (see, chapter 3, Fig. 3.5), (i.e. hydroperoxides formed during processing are the main photo-initiators).

Fig. 5.2 Effect of processing time on the formation of carbonyl during photo-oxidation of pp films (samples processed at 200°C in a closed mixer, numbers on curves are processing times in mins)



It has previously been reported(28) that there is a linear relationship between initial photo-oxidation rate and initial hydroperoxide concentration during photo-oxidation of polypropylene which implies that hydroperoxide formed during processing can account for the photo-initiation. Further evidence supporting this was also provided(28) by an experiment during which hydroperoxides were removed from a processed sample(by heating in argon at 110°C for 50 hrs before UV exposure). It has been found(28) that in spite of the high concentration of ketonic carbonyl the initial photo-oxidation rate is reduced to zero. When substantial amount of carbonyl groups is present in the polymer either by thermolysis or photolysis of hydroperoxides they are intimately involved as initiator in the later stages of photo-oxidation(28,122).

The presence of carbonyl actually causes photolysis rather than photo-initiation during the early stages of photo-oxidation(21).

5.A.2 Effect of Processing Conditions and Melt Stabilisers on the Subsequent Photo-Oxidation of Polypropylene. Results and Discussion

5.A.2.1 Effect of Galvinoxyl

The effects of galvinoxyl and processing conditions on photo-oxidation of polypropylene in the form of compression moulded film are illustrated in Fig. 5.3. Polypropylene was processed with galvinoxyl ($G^{\cdot}$) = 4.75×10^{-4} mol/100g) at 200°C in a closed mixer and in an open chamber for various lengths of time. On UV irradiation all the samples showed an initial rapid rate of carbonyl formation followed by a period of effective stabilisation (an induction time). At the end of induction period the rate of carbonyl formation was lower compared to the unprocessed control without additive. Fig. 5.3 also shows that when polypropylene is processed with galvinoxyl in a closed chamber (i.e. restricted air access) prolonged processing time up to 20 minutes does not appear to affect the photo-stability of polypropylene to any significant extent (Fig. 5.3, curves 2 and 3, Table 5.1). However, the 30 mins processed sample showed a slight decrease in the level of carbonyl formation in the initial stages (Fig. 5.3,curve 4) followed by similar induction period to the others. It also gave a slightly lower embrittlement time than the samples processed for a shorter time (see, Table 5.1).

The photo-stabilisation effectiveness of galvinoxyl when processed with polypropylene in an open chamber (i.e. in excess air) is very much reduced compared to

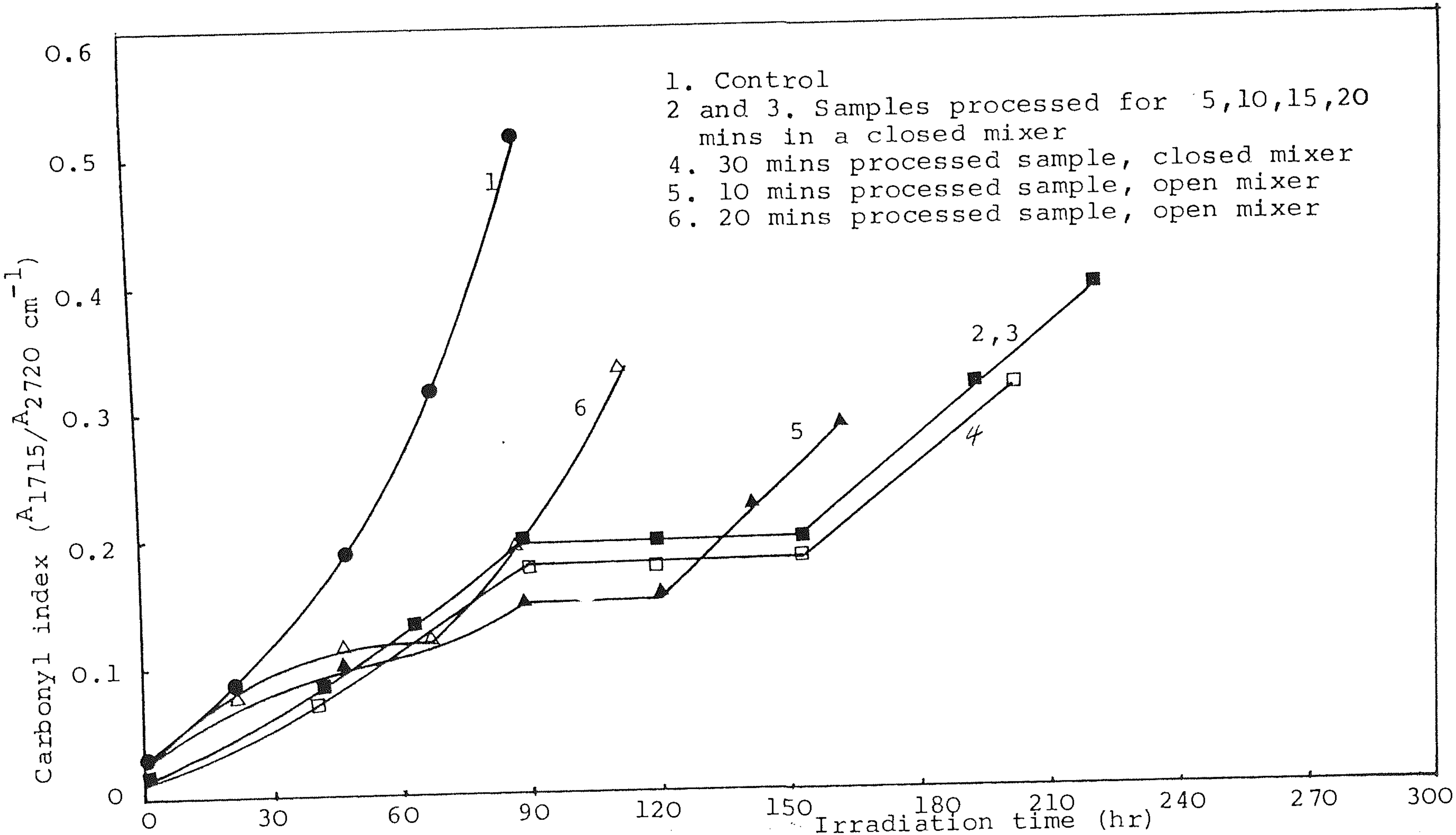


Fig. 5.3 Effect of galvinoxyl and processing time on photo-oxidation of pp as measured by the formation of carbonyl (1715 cm^{-1}), (All the samples processed at 200°C in both closed and open mixer and compression moulded films used, G·conc=4.75 x 10^{-4}mol/100g.

the closed chamber processing (Fig. 5.3 curves 5 and 6). Moreover the photo stability of polypropylene is very much decreased with increased processing time (Fig. 5.3, curve 6).

Fig. 5.4 shows the effect of galvinoxyl concentration on photo-oxidation of polypropylene. As the galvinoxyl concentration was increased a higher initial pro-oxidant effect was observed followed by a longer induction period (Fig. 5.4, curves 2, 3 and 4). UV embrittlement times were found to increase with increasing galvinoxyl concentration (Table 5.2). The above results show that galvinoxyl which is very powerful melt stabiliser for polypropylene (see, section 3.A.4.1) also stabilises polypropylene against photo-oxidation at all concentrations. However, increase in galvinoxyl concentration leads to a yellow colouration of the samples after processing, which fades during photo-oxidation and embrittlement occurs after loss of colour. UV embrittlement times of polypropylene containing galvinoxyl are listed in Tables 5.1 and 5.2.

Results obtained from photo-oxidation of the samples show that two main steps are involved

(1) initial photo-oxidation

(2) followed by a stabilisation.

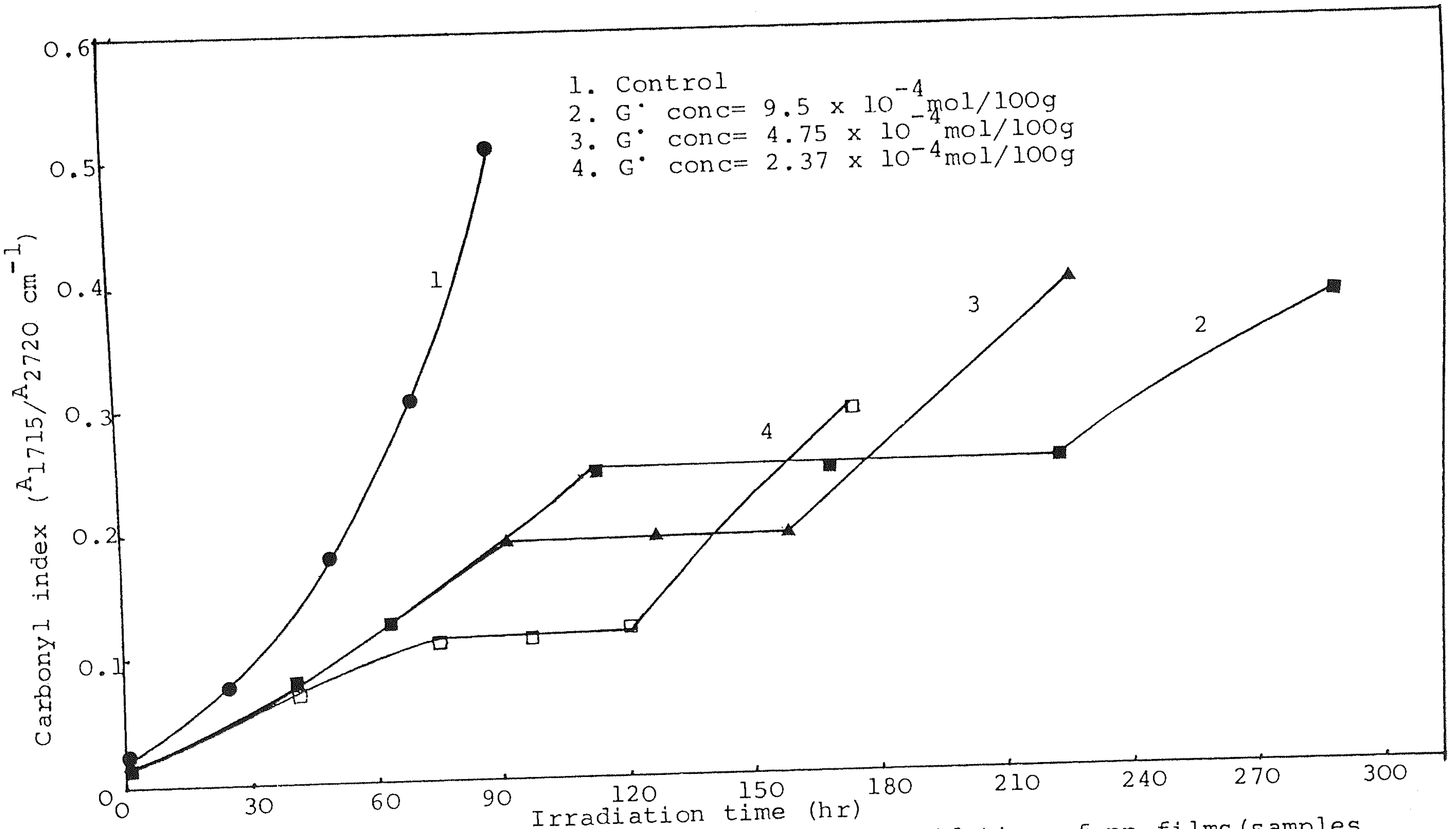


Fig. 5.4 Effect of galvinxoyl concentrations on photo-oxidation of pp films (samples processed at 200^{o}C/10 mins in a closed mixer)

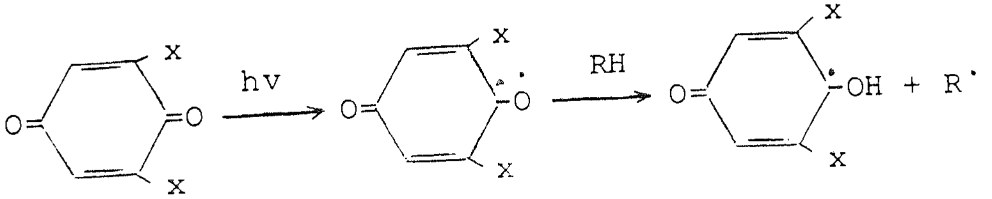
Table 5.1 Effect of processing time on UV lifetime of pp containing galvinoxyl (all samples processed at 200°C in both closed mixer and open mixer, (G) = 4.75×10^{-4} mol/100g)

Processing time (mins.)	Embrittlement time (E.T) (hr.)	
	Closed mixer	Open mixer
5 (control)	95	
5	220	
10 (control)	85	45
10	220	163
15 (control)	80	
15	220	
20 (control)	80	20
20	220	117
30 (control)	70	
30	195	

Table 5.2 Effect of galvinoxyl concentration on UV lifetime of pp (all processed at 200°C for 10 mins. in the closed mixer).

$(G^{\cdot}) \times 10^4$ mol/100g	Embrittlement time (E.T)
2.37	171
4.75	220
9.5	286

Galvinoxyl and hydrogalvinoxyl both are present to some extent in the samples prior to photo-oxidation as it was shown in chapter 3 (see 3.A.4.1). In photo-oxidation of the polymer alkyl radicals predominate owing to the high rate of initiation(167) and oxygen diffusion limitation and galvinoxyl, an effective CB-A antioxidant,may compete with oxygen for alkyl radicals resulting in hydrogalvinoxyl formation as well as unsaturation in the backbone of the polymer chains. Hydrogalvinxoyl also acts as a CB-D antioxidant removing alkylperoxy radicals from the system. These two components lead to photo-stabilisation. Since during the processing quinone compounds are also formed as by products (e.g. 2,6 ditert-buty, 1, 4, benzoquinone shown in chapter 3), they probably cause initial rapid photo-oxidation by a process of hydrogen atom abstraction from the polymer by the triplet state of the aromatic ketones (quinones).



(1)

x = R'(e.g. t-but)   triplet state

Therefore, initial rapid photo-oxidation is in line with involvement of a free radical generation step. Scott has also shown(14) the photosensitising action of benzophenone and its derivatives in polyethylene.

5.A.2.2 Effect of Iodine on Photo-Oxidation of Polypropylene

Fig. 5.5 shows the effect of iodine at various processing time on UV stability of polypropylene. All the samples showed an initial induction period followed by rapid photo-oxidation. The samples processed up to 30 mins showed almost similar behaviour in photo-oxidation (Fig. 5.5, curves 2,3 and 4, Table 5.3). However, longer processing times (60 mins, 90 mins) lead to lower U.V stabilisation effectiveness (Fig. 5.5, curves 5, 6, Table 5.3). Although polypropylene containing iodine showed an initial induction period to carbonyl formation on photo-oxidation, the overall photo-stabilising effect of iodine is not of practical significance (Table 5.3).

Carbon-iodide bonds (which are formed during processing) have a low bond energy (50 k cal/mol)$^{(194a)}$, thus U.V irradiation causes C-I bond cleavage generating free radicals in the polymer$^{(242a)}$

$$(R\text{-}I \xrightarrow{UV} R^{\cdot} + I^{\cdot})$$

This causes rapid photo-oxidation of the polymer.

On UV irradiation of the films containing iodine owing

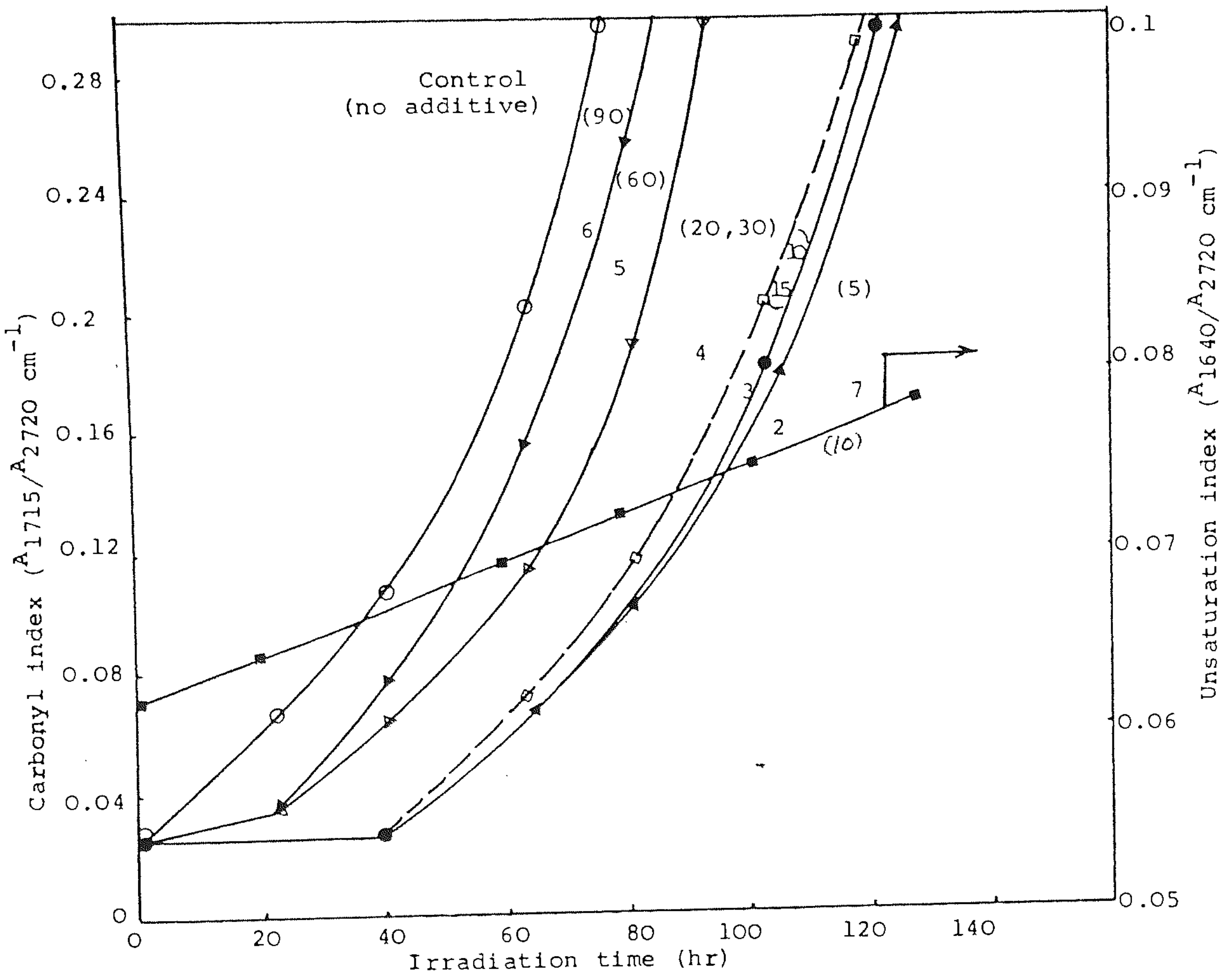


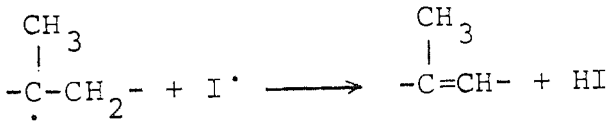
Fig. 5.5 Effect of iodine on photo-oxidation of pp(carbonyl and unsaturation formation), all samples processed at 190^{o}C in a closed mixer, iodine conc= 1.57 x 10^{-3}mol/ 100g, numbers on curves (in parenthesis) are processing times.

to low dissociation energy of iodine molecules (36 k cal/mol)(194a), iodine atoms are formed

$$I_2 \rightleftharpoons 2I^{\bullet}$$

Fig. 5.5 (curve 7) shows the unsaturation formation during the photo-oxidation of a polypropylene film containing iodine (processed for 10 mins).

The unsaturation grows linearly, with irradiation time (Fig. 5.5, curve 7). It seems to suggest that iodine radicals abstract hydrogen from macroalkyl radicals forming unsaturation in the polymer chains.



$$-\underset{\bullet}{\overset{CH_3}{\overset{|}{C}}}-CH_2- + I^{\bullet} \longrightarrow -\overset{CH_3}{\overset{|}{C}}=CH- + HI \qquad (2)$$

Then hydrogen iodide reacts with alkyl peroxy radicals

$$ROO^{\bullet} + HI \longrightarrow I^{\bullet} + ROOH \qquad (3)$$

resulting in regeneration of iodine radical. Therefore a cyclic regenerative process could be involved in photo-oxidation of the polymer films containing iodine. This could account for photo-stabilising activity of iodine in the polymer.

Table 5.3 Effect of processing time on UV lifetime of pp containing iodine (all samples processed in a closed mixer at 190°C, $[I_2] = 1.57 \times 10^{-3}$ mol/100g.

Processing time (mins.)	Embrittlement time (E.T.) (hr)
5 (control)	95
5	129
10 (control)	90
10	129
20 (control)	85
20	129
30 (control)	80
30	115
60	90
90	85

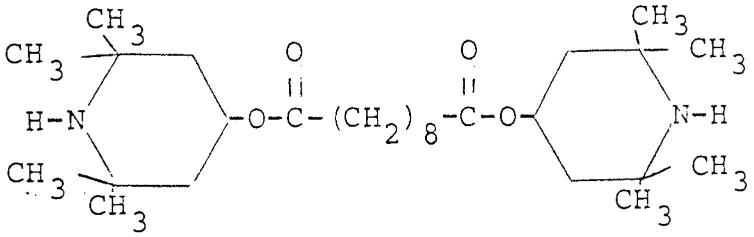
Table 5.4 Effect of hindered amine and related nitroxyl and hydroxylamine on the UV lifetime of polypropylene (conc. = 6×10^{-4} mol/100g)

Additives	Time to embrittlement (E.T.) (hr)
None	90
B(TMP)S	750
B(TMPO)S	960
4OHTMPO	920
4OHTMPOH	1040

5.A.2.3 Effect of Tinuvin 770 and its Related Bis nitroxyl Radical, 4-hydroxy,2,2,6,6 tetramethyl piperidineoxyl and its Related hydroxylamine on Photo-oxidation of Polypropylene

The following additives were used during photo-oxidation of polypropylene.

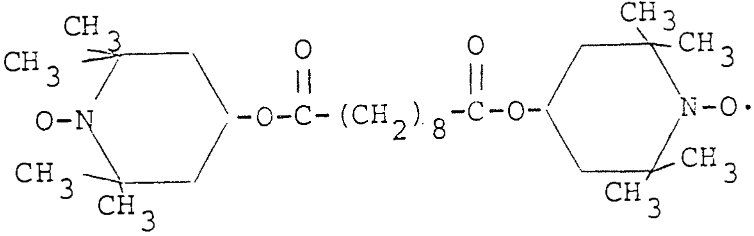
Additives Codes



B(TMP)S

(1)

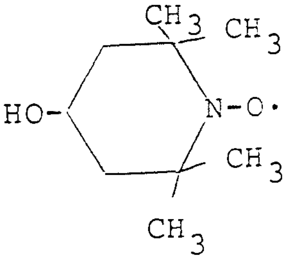
Bis (2,2,6,6 tetra methyl - 4 - piperidininy) Sebacate, Trade name Tinuvin 770



B(TMPO)S

(2)

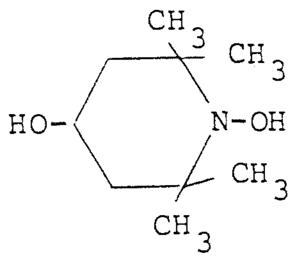
Bis(2,2,6,6-tetramethyl-4-piperidinyl N-oxyl) sebacate



4OHTMPO

(3)

4-hydroxy 2,2,6,6,tetramethyl piperidinoxyl



4OHTMPOH

(4)

4-hydroxy 2,2,6,6, tetramethyl piperidine,N-hydroxy

Fig. 5.6 shows the effect of Tinuvin 770 and its related bisnitroxyl, 4-hydroxy ,2,6,6,tetramethyl piperidine oxyl and its related hydroxylamine on the photo-oxidation of polypropylene. They all show similar behaviour during the photo-oxidation of the polymer. All the additives give long induction periods to carbonyl formation at the same molar concentration and these correlate closely with the embrittlement times of the polymer (Table 5.4). The highest UV stabilsing activity is observed with the hydroxylamine. Fig. 5.7 shows that there is a steady increase in unsaturation in the polymer during the carbonyl induction period in each case as measured by the growth of a band at 1640 cm^{-1} (i.r. method). Initial unsaturation after processing is higher for the nitroxyl radical (4OHTMPO) and its related hydroxyl amine (4OHTMPOH) than it is for the Tinuvin 770 (Fig. 5.7). It has recently been reported$^{(242)}$ the formation of unsaturation in polypropylene containing Tinuvin 770 and its related nitroxyl radical during

Fig. 5.6 Effect of Tinuvin 770 (B(TMP)S) at 3 x 10^{-4} mol/100g, B(TMPO)S at 3 x 10^{-4} mol/100g, 4OHTMPO at 6 x 10^{-4} mol/100g and 4OHTMPOH at 6 x 10^{-4} mol/100g on photo-oxidation of pp (all samples processed at 180°C/10 mins in a closed mixer prior to UV exposure).

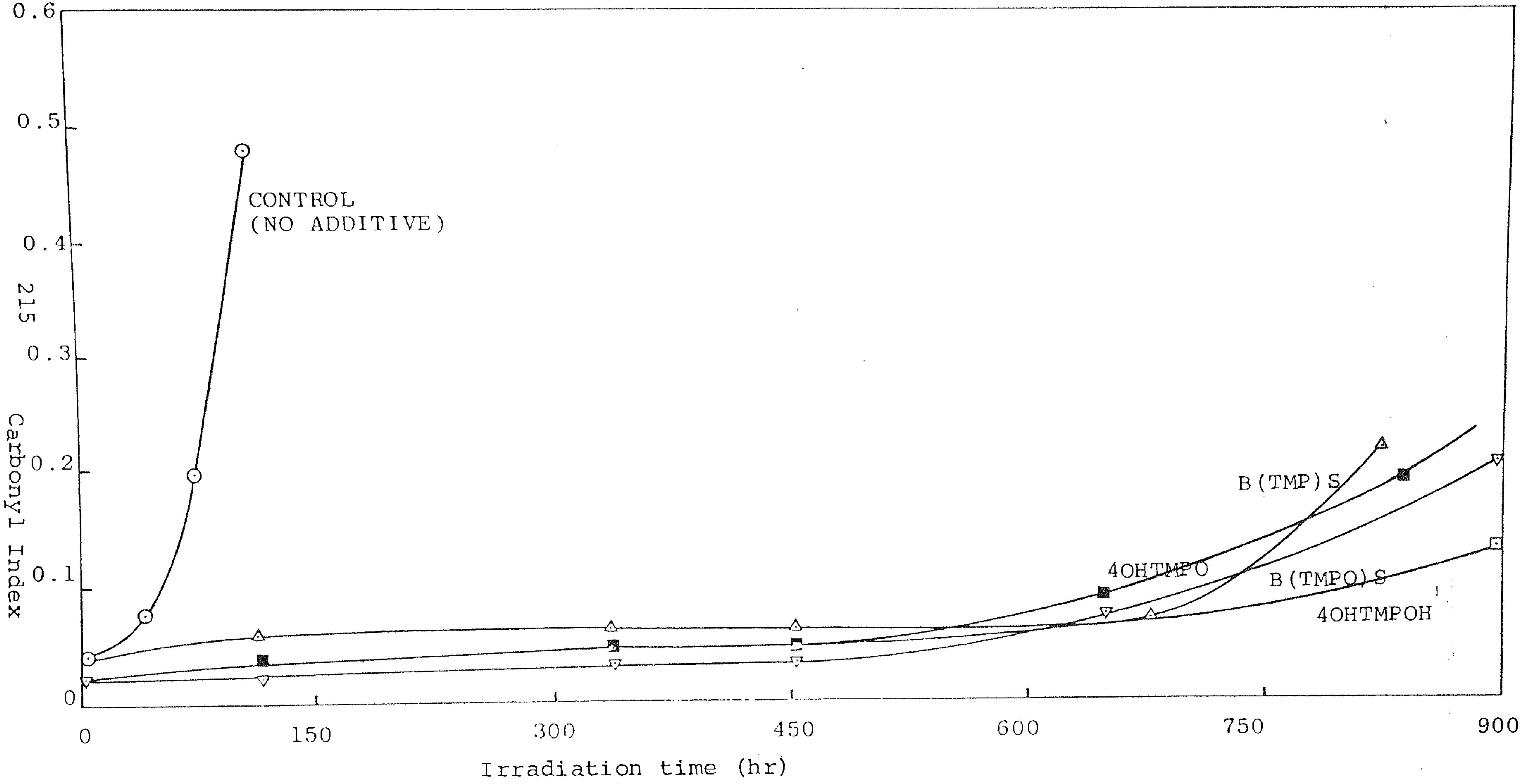


Fig. 5.7 Effect of B(TMP)S (3 x 10^{-4}mol/100g), 4OHTMPO (6 x 10^{-4}mol/100g), and 4OHTMPOH (6 x 10^{-4}mol/100g) on the formation of unsaturation (1640 cm^{-1}) during the photo-oxidation of pp (samples processed at 180°C/10 mins in a closed mixer prior to UV exposure.

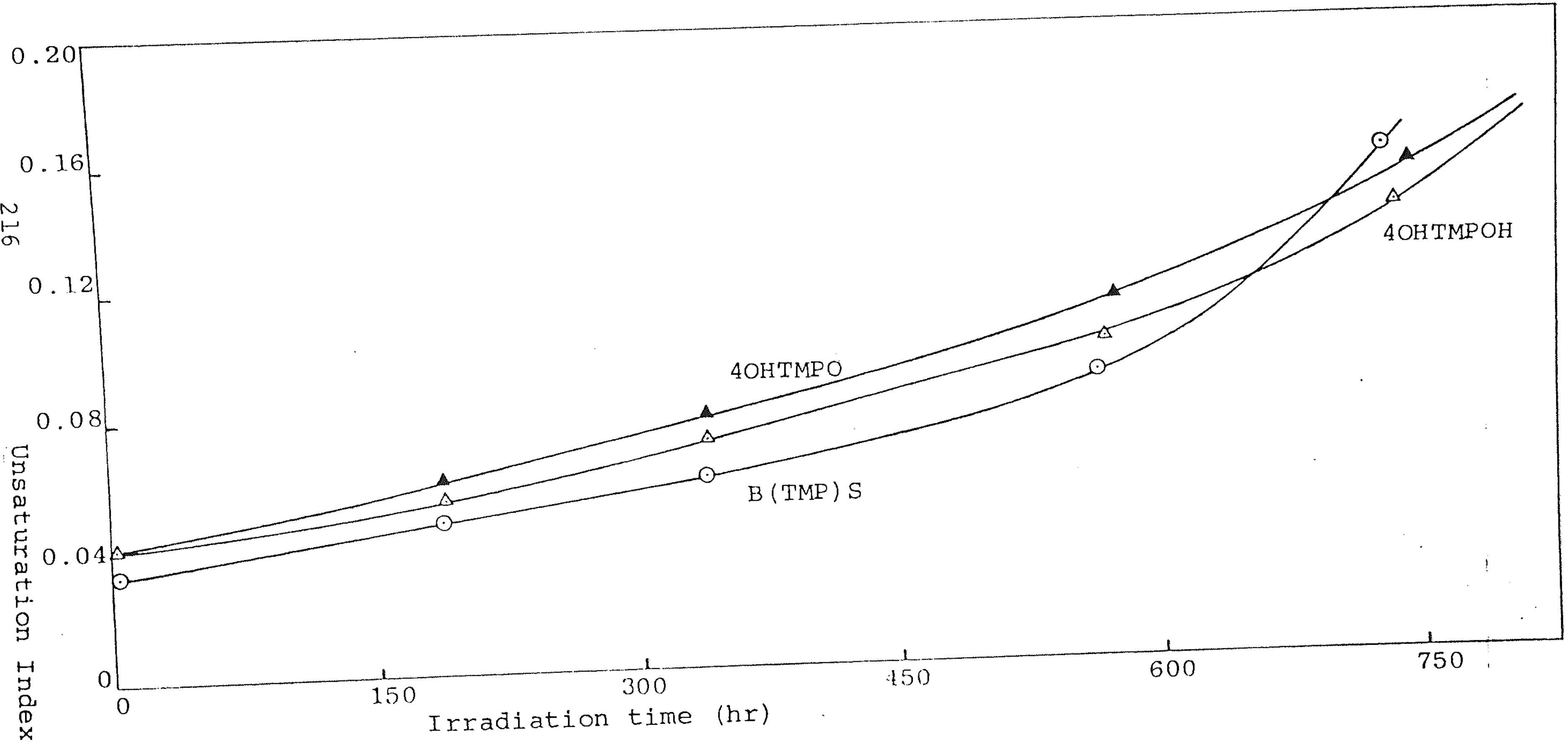
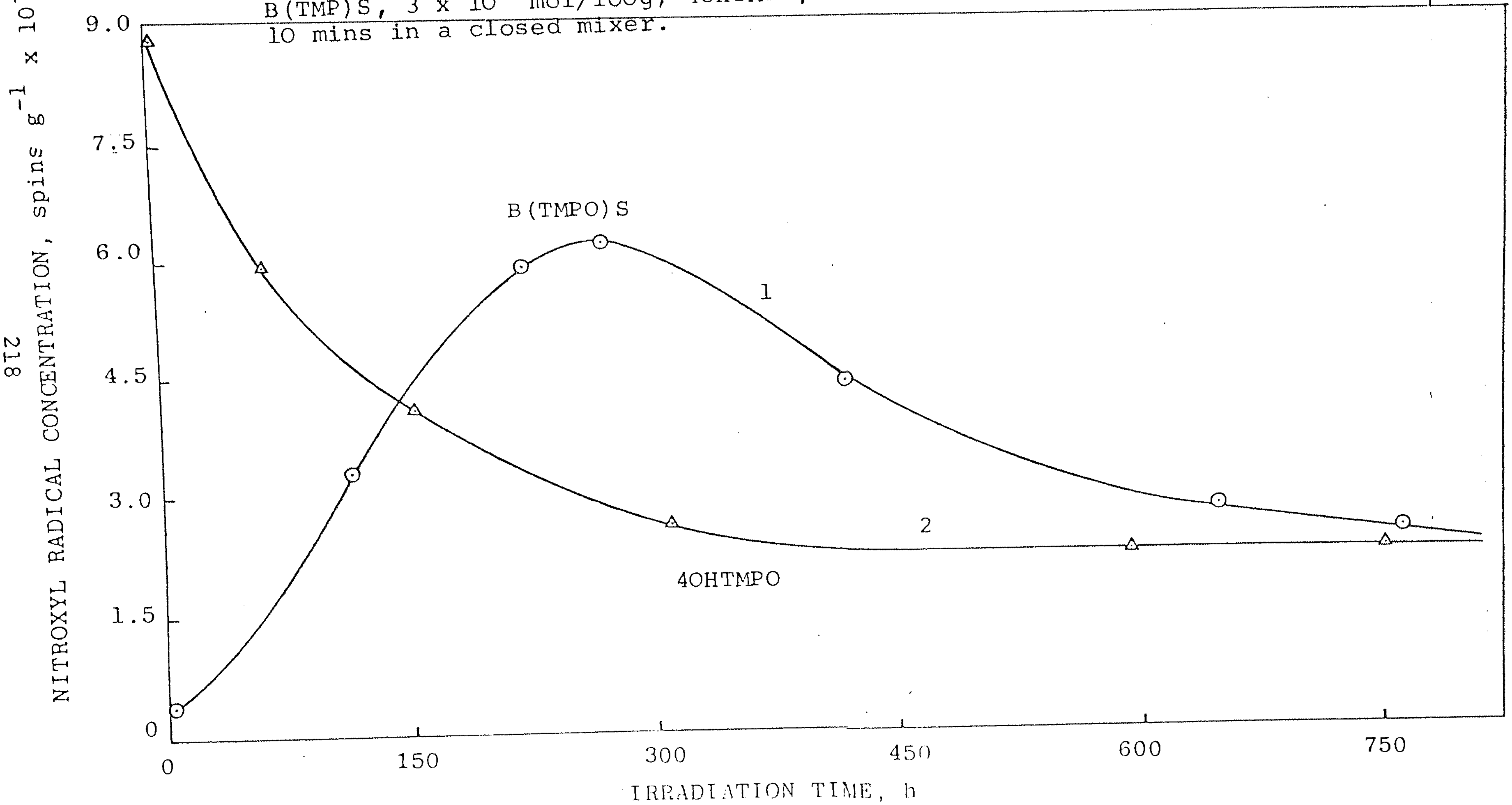


photo-oxidation.

E.S.R examination of the films containing Tinuvin 770 showed (Fig. 5.8 curve 1) the formation of the nitroxyl radical in an auto-accelerating mode during the early stages of photo-oxidation and after rising to a maximum the radical species subsequently decayed to a lower stationary concentration which then persisted until the end of the carbonyl induction period. At embrittlement, the nitroxyl radical could no longer be detected.

Fig. 5.8 (curve 2) also shows that at the same molar concentration nitroxyl radical (4OHTMPO) decays rapidly to the same stationary concentration during U.V. irradiation in polypropylene and again the stationary concentration of nitroxyl radical is maintained until the end of the induction period. The effect of processing time and processing conditions (open and closed mixer at 200°C) on the photo-stabilising ability of mono nitroxyl radical (4OHTMPO) in polypropylene is shown in Fig. 5.9. All the samples gave long induction periods to carbonyl formation followed by low rate of photo-oxidation. Table 5.5 shows that U.V stability of polypropylene containing nitroxyl radical ,processed in closed chamber prior to U.V exposure ,does not seem to depend significantly on the processing time.

Fig. 5.8 Concentrations of nitroxyl radicals B(TMPO)S (formed from Tinuvin 770) and 4OHTMPO in pp during U.V exposure. Concentration of additives incorporated, B(TMP)S, 3 x 10^{-4} mol/100g; 4OHTMPO, 6 x 10^{-4} mol/100g; samples processed at 180°C/ 10 mins in a closed mixer.



However, at high processing time U.V stability of polypropylene decreases which corresponds to the concentration of nitroxyl radical.

Similar result has been observed by Allen and coworkers(255a).

The results correlate closely to the embrittlement time of the samples (see, Table 5.5).

The photo-stabilising activity of mononitroxyl is very much reduced when processed in the open chamber prior to U.V exposure. Comparison of curves 5 and 6 (Fig. 5.9) shows that increase in processing time leads to a rapid decrease in photo-stability and the U.V lifetime of the polymer, also corresponds to the initial nitroxyl radical concentration in the samples before irradiation (see, Table 5.5). Thus, the photo-stabilising behaviour of nitroxyl radicals is very much dependent on the prior processing operation. The effect of processing time and processing conditions on U.V lifetime of polypropylene samples containing mononitroxyl radical (4OHTMPO) is shown in Table 5.5.

Fig. 5.6 shows that initial carbonyl concentration in polypropylene containing Tinuvin 770 is higher than it is for either the nitroxyls or the hydroxylamines.

Fig. 5.9 Photo-oxidation of pp as measured by the formation of carbonyl (1715 cm^{-1}) in the presence of nitroxyl radical (4OHTMPO) at 1.16 x 10^{-3} mol/100g, all samples processed at 200^{o}C in both closed and open chamber for various lengths of times.

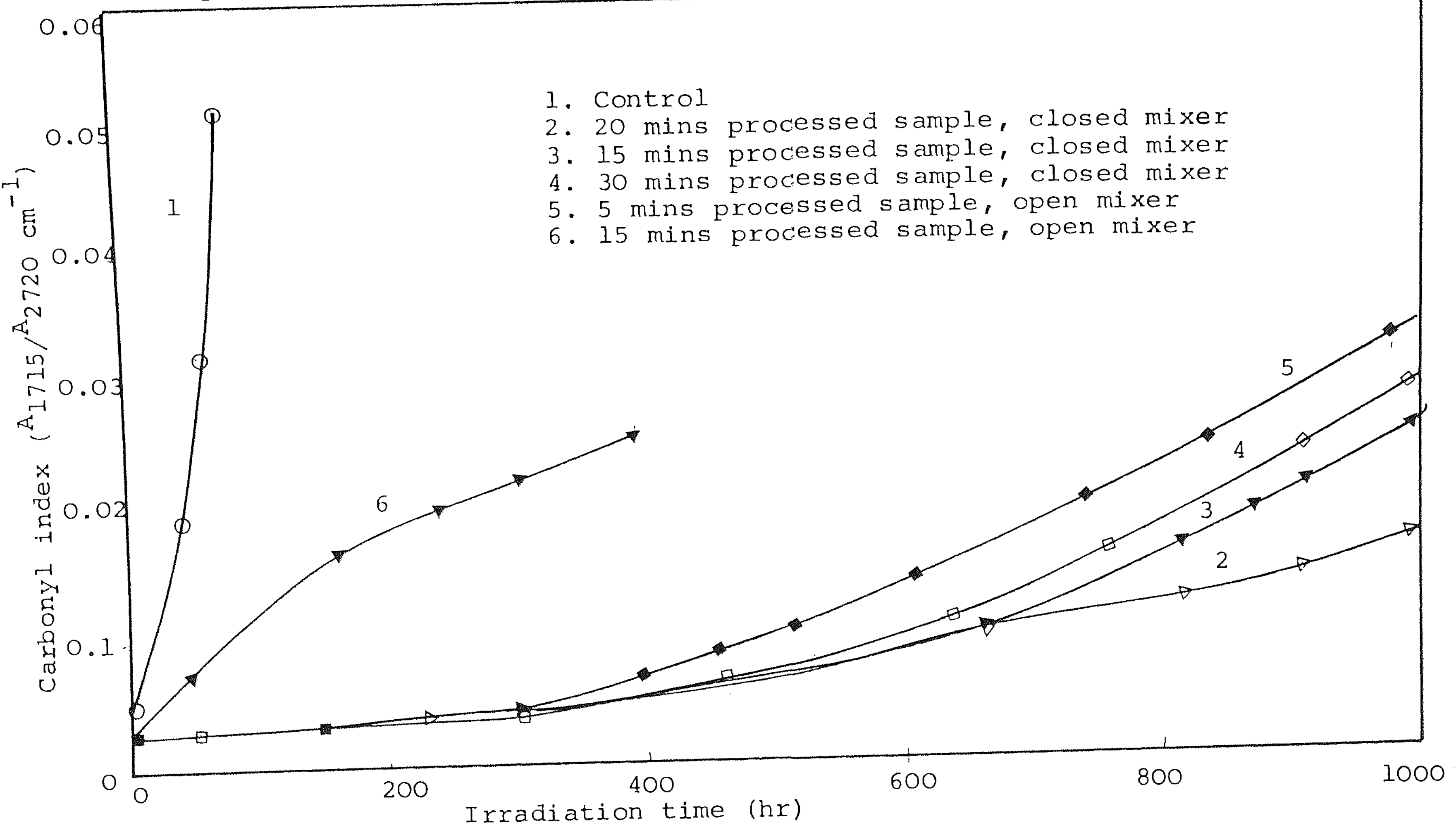
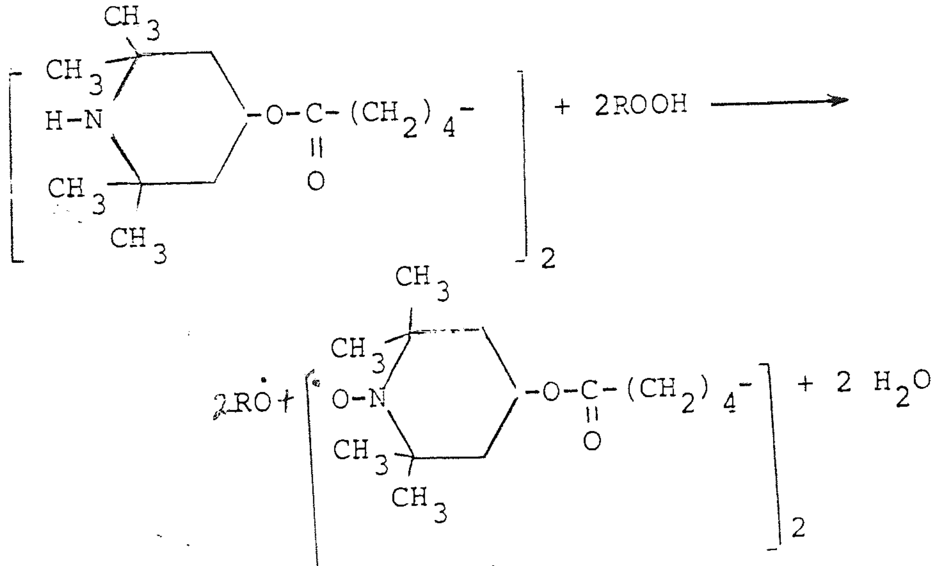


Table 5.5 Effect of processing time and processing conditions on the UV lifetime of pp containing 4-hydroxy , 2,2,6,6 tetramethyl piperidineoxyl (all samples processed at 200^{o}C, conc. = 1.16 x 10^{-3} mol/100g)

Processing time (mins)	Closed chamber		Open chamber	
	Nitroxyl concentration (No spin/ g x 10^{-18}	Embrittlement time (E.T.)hr.	Nitroxyl concentration (No spin/ g x 10^{-18})	Embrittlement time (E.T.) hr.
5	6.87	1358	2	977
10	5.01	1269	1.5	726
15	4.2	1250	0.21	395
20	6.35	1361		
30	3.64	1090		

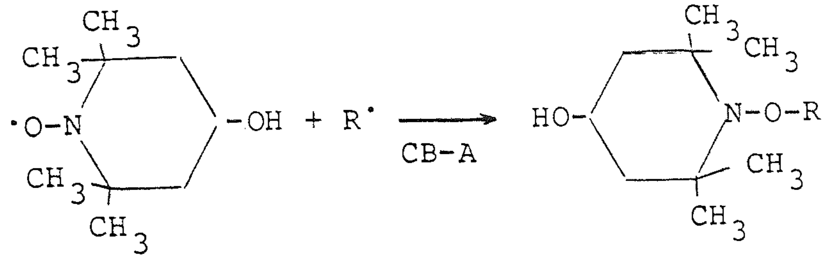
Moreover its formation during U.V irradiation is auto-retarding.

A similar phenomenon has been observed even more sharply during the photo-oxidation of methylcyclohexane$^{(242)}$ containing Tinuvin 770. In the latter case, no prior thermal oxidation of amine to nitroxyl had occurred and consequently the rate of oxidation was actually higher than the control initially due to a pro-oxidant reaction (4).

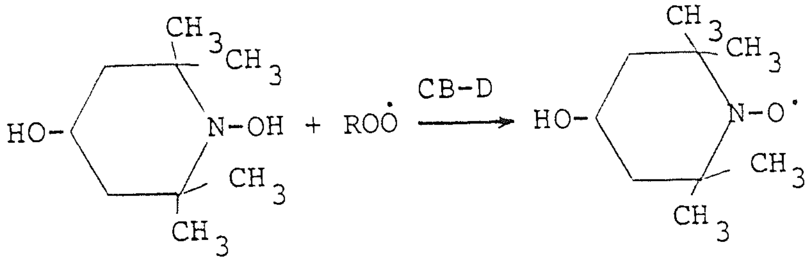


(4)

Such a pro-oxidant reaction would not be expected and indeed is not observed in practice with either the nitroxyl (4OHTMPO) or hydroxylamine (4OHTMPOH), since these are both effective antioxidants; the first by a CB-A mechanism (reaction 5) and the second by a CB-D mechanism (reactions 5 and 6).

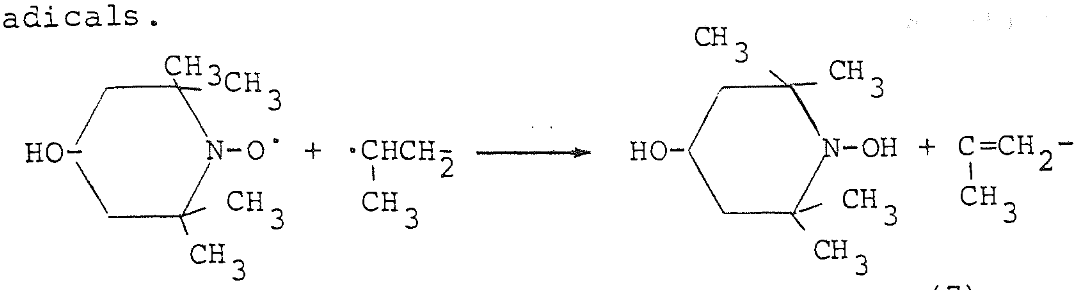


(5)



(6)

In chapter 3 it was shown that no bonding of nitroxyl radicals to the polymer occurs during processing (see, section 3.A.4.3). This seems to suggest that alkyl hydroxylamines are not thermally stable, (more evidence will be given in the next chapter). However, the picture is not clear during photo-oxidation. There is no doubt that nitroxyl radicals can react with low molecular weight alkyl radicals to give alkyl-hydroxylamine (243-244), but no evidence has so far been adduced to suggest that they are present to any extent during the photo-oxidation of polypropylene. On the other hand, the corresponding hydroxylamines have been shown to be formed together with olefinic unsaturation. A possible explanation for this is that reaction (5) is reversible under these conditions. However, this is not a termination process and it is necessary to postulate reaction (7) to remove the radicals.

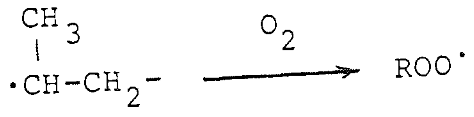


(7)

If the rate of photo-dissociation (reaction 5') is high, as suggested by Shlyapintokh$^{(244)}$, the rates of reaction (7) and (6) will determine the relative concentration of nitroxyl and hydroxylamine in the system.

$$>N\text{-}OR \xrightarrow[h\nu]{} >N\text{-}O^{\cdot} + R^{\cdot} \qquad (5')$$

Carlsson and Wiles and co-workers$^{(245)}$ have reported that the nitroxyl is regenerated from alkyl hydroxylamine much more rapidly in the presence than in the absence of oxygen. This can be accounted for by the above reactions (6,7) since reaction (8) leads to the removal of one of the reactive species formed by reaction (5'). However,



$$\underset{(R\cdot)}{\cdot\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{-}CH_2\text{-}} \xrightarrow{O_2} ROO^{\cdot} \qquad (8)$$

this again is a non termination process and is consistent with the known inefficiency of nitroxyl radicals as antioxidants at relatively high oxygen concentrations (see, Fig. 3.27).

It must be concluded then that the formation of the derived hydroxylamine is necessary for the alternating CB-A, CB-D regenerative cycle to operate effectively.

5.A.2.4 Effect of Cupric Stearate on the Photo-Oxidation of PP.

Fig. 5.10 shows the effect of CuSt as additive on photo-oxidation of polypropylene (at molar conc 4.5 x 10^{-4} mol/100g). All the samples were processed under two different conditions prior to UV exposure at various processing times (at 200°C) and showed an initial induction period to carbonyl formation followed by a higher rate of photo-oxidation compared to the control. A slight decrease in initial carbonyl content (due to CuSt) is observed which could be due to photolysis of CuSt. Fig. 5.10 (curves 7,8) also shows the formation of unsaturation during the irradiation of the films containing CuSt. The unsaturation (measured at 1630 cm^{-1}) increases linearly with time of irradiation.

Comparison of the curves (2,3,4,5 and 6) in Fig. 5.10 and also embrittlement times in Table 5.6 shows that

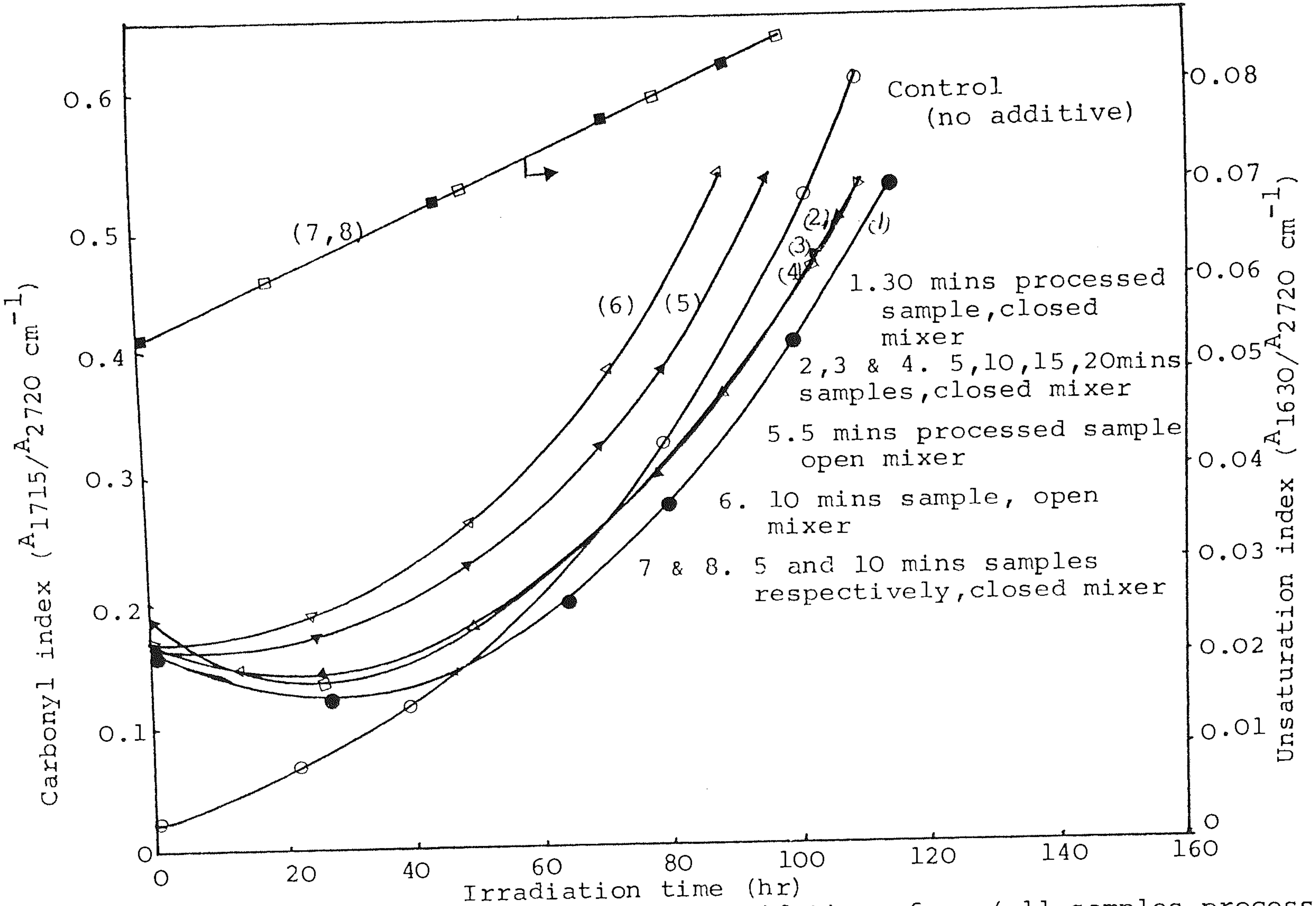


Fig. 5.10 Effect of cupric stearate on photo-oxidation of pp (all samples processed in both closed and open mixer at 200°C for various lengths of time, CuSt conc = 4.5 x 10^{-4} mol/100g

increase in processing time does not affect the photo-stability of polypropylene containing CuSt. However, the photo stabilisation effectiveness of CuSt in poly-propylene is not of practical significance. The photo-stabilising activity of CuSt in polyethylene has recently been reported$^{(253)}$. It has also been shown$^{(241)}$ that CuSt photo-stabilises paint media.

Fig. 5.11 shows UV screening effect of CuSt in poly-propylene. In the screening experiment an unstabi-lised (control) film is exposed behind a film which is identical with former except that it contains CuSt (conc. = 6.3×10^{-4} mol/100g). Now the unstabilised film can only receive light which has passed through the stabiliser containing film. The photo-stability of unstabilised film is determined and is compared with the photo-stability of a film containing CuSt as additive which is screened by an unstabilised film (Fig. 5.11, curves 1 and 3). It seems that the photo-stabilising activity of CuSt in polypropylene is mainly due to UV screening effect.

Screening of UV light is caused by the UV absorbing species in the samples. Since blue colour of all compounds of copper is due to the presence of an absorption in the 600-900 nm region of the spectrum$^{(254)}$, thus Cu^{+2} does not act as an effective screening species.

Fig. 5.11 Effect of CuSt on photo-oxidation of pp(All samples processed in a closed mixer at 180^{o}C/10 mins, CuSt used as screen and additive) cust conc=6.3 x 10^{-4}mol/100g

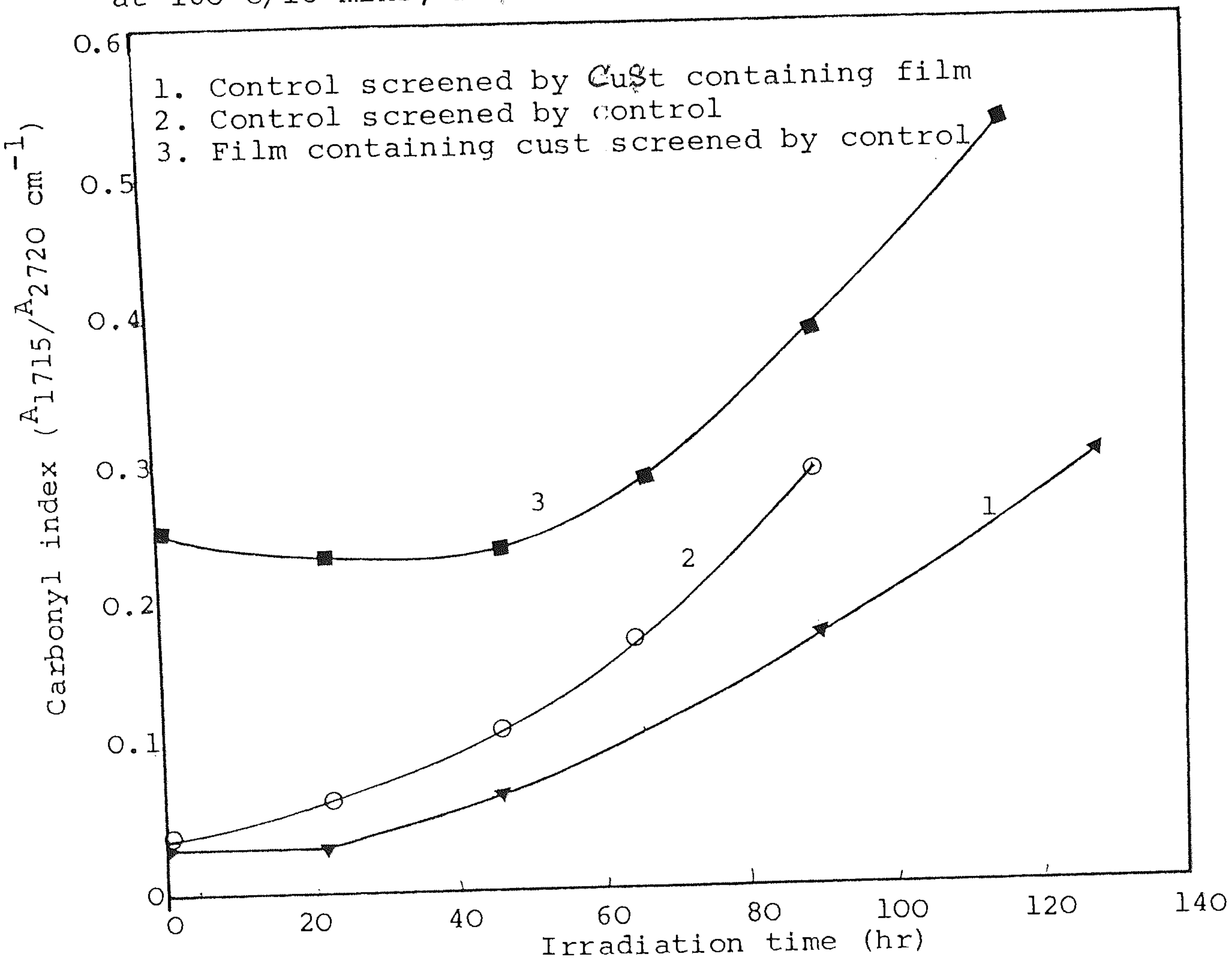


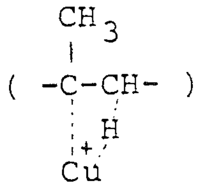
Table 5.6 Effect of CuSt on photo-oxidation of pp (all samples processed in closed mixer at 200^{o}C, (CuSt) = 4.5 x 10^{-4} mol/100g)

Processing time (mins)		Embrittlement time (E.T.) (hr)
(5 - 10)	control	90
(5 - 10)		110
(15-20)	control	80
(15-20)		110
30	control	70
30		110

Table 5.7 Effect of galvinoxyl on UV lifetime of LDPE samples processed in both closed and open mixer for 10 mins. at 180^{o}C, (G$^{\cdot}$) = 4.75 x 10^{-4} mol/100g).

	Embrittlement time (hr) (closed chamber)	Embrittlement time (hr) (open mixer)
Control	1649	1440
Samples	2182	1751

On the other hand Cu^+ which is in the form of a complex with alkyl radicals



$$(\ -\overset{\displaystyle CH_3}{\underset{\displaystyle \vdots\ H \atop \displaystyle Cu^{+}}{C}}-CH-\ )$$

could account for the UV screening activity of the samples. On UV exposure of the samples this complex breaks down resulting in unsaturation formation in the polymer.

The rapid rate of photo-oxidation observed after stabilisation period results from the redox reactions between copper carboxylate and hydroperoxides (248).

5.B Low Density Polyehtylene (LDPE)

5.B.1 Effect of Processing on the Photo-Oxidation of LDPE.

Fig. 5.12 illustrates the structural changes occurring during UV irradiation in the infra-red spectrum of low density polyethylene film. It shows that in the hydroxyl region the intensity of absorption around 3400 cm^{-1} increases gradually and becomes broad indicating the formation of hydroxyl compounds as a result of photo-oxidation (due to hydrogen bonded

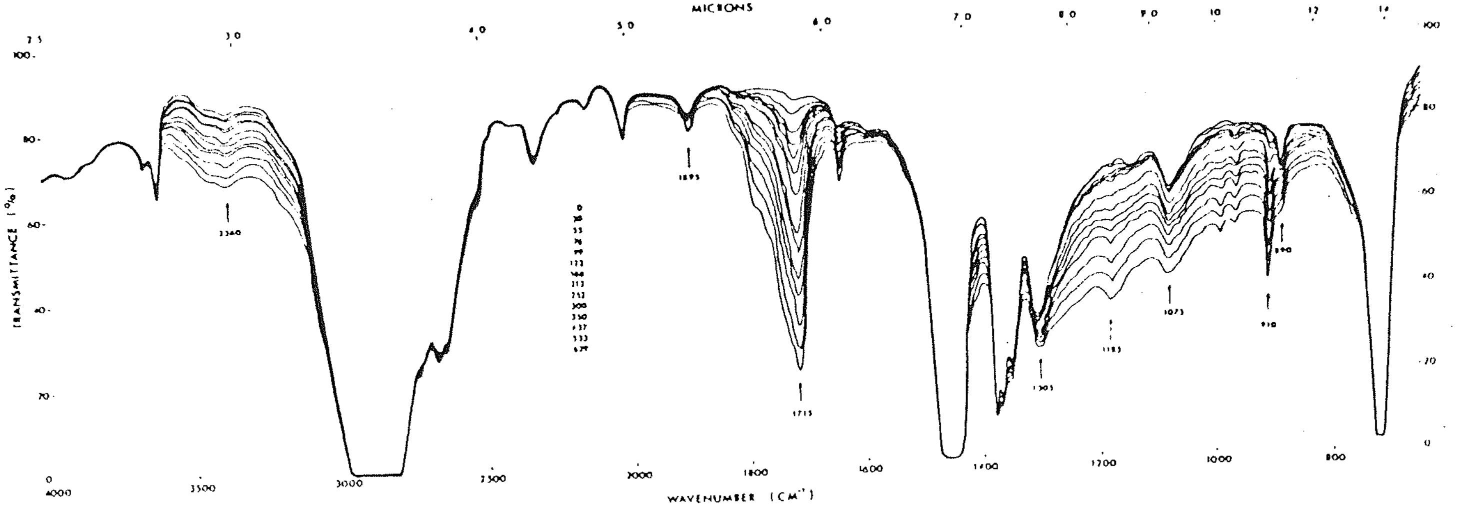


Fig. 5.12 Changes in the I.R spectra of unprocessed LDPE during UV irradiation.

alcohols). No hydroperoxide band at 3555 cm^{-1} is observed since the rate of hydroperoxide decomposition is much higher than the rate of its formation during photo-oxidation$^{(27)}$. In the carbonyl region (1800 - 1650 cm^{-1}) on prolonged UV irradiation the main peaks are dominant by doublets at 1715 - 1710 cm^{-1} and 1730 cm^{-1} due to acid and aldehyde respectively.

A band at 1185 cm^{-1} (due to single bond C-O vibration within the carbonyl group in carboxylic group) is formed and increases on UV irradiation confirming the acid formation.

Vinylidene groups (band at 888 cm^{-1}) initially present in LDPE and decays rapidly on UV irradiation. The increase in the vinyl band at 910 cm^{-1} (present to a much smaller extent initially in the polymer) is also observed during UV irradiation. Some increase in internal double bond (band at 964 cm^{-1}) is also observed during UV irradiation.

Figs 5.13 and 5.14 show the changes in carbonyl, carboxyl, vinylidene and vinyl groups during UV irradiation of LDPE films.

Fig. 5.13 reveals that as the processing time is increased the rate of photo-oxidation (measured as carbonyl index)

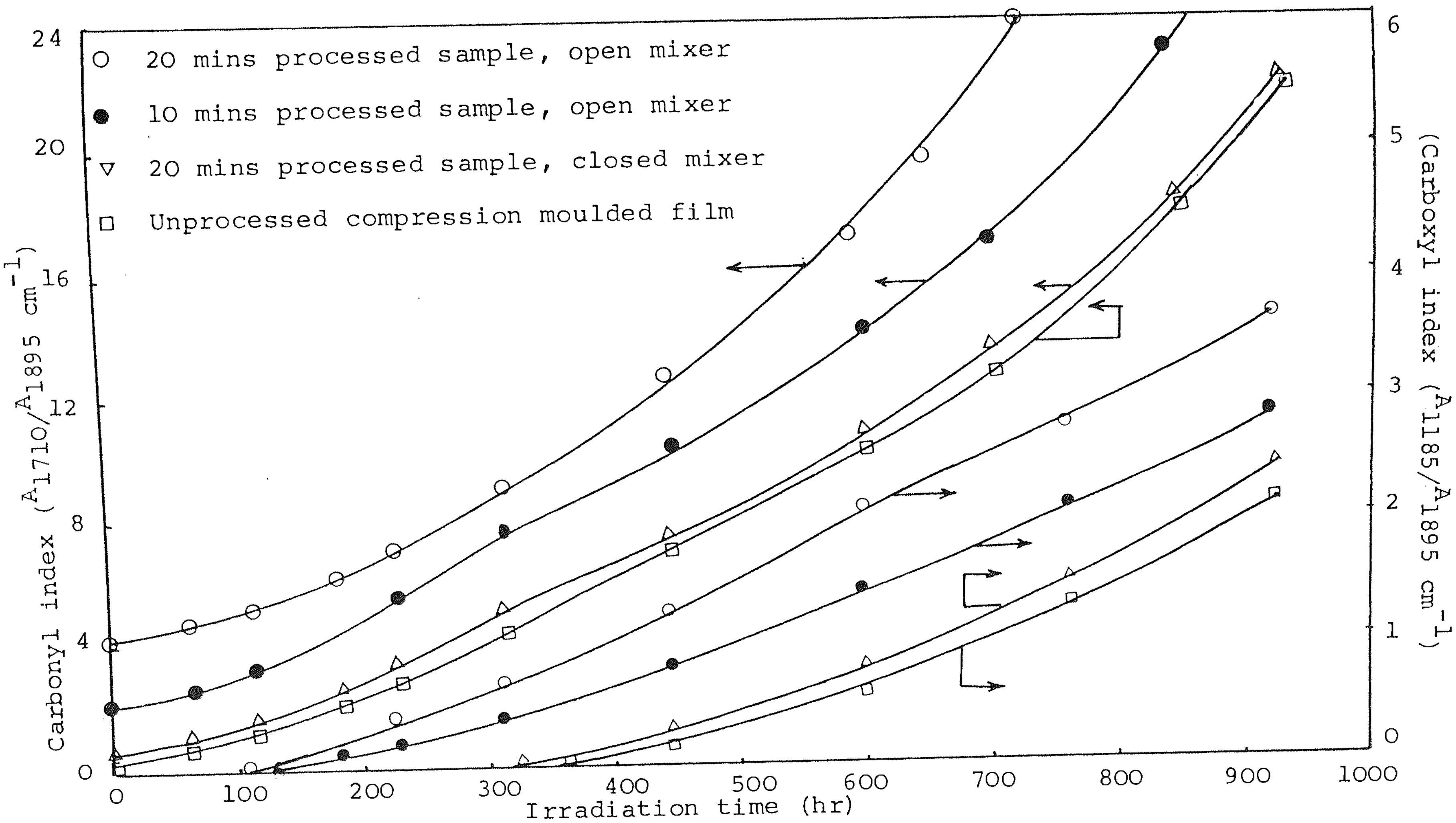


Fig. 5.13 Changes in carbonyl and carboxyl groups of LDPE during photo-oxidation (LDPE processed at 180°C in both closed and open mixer for 10 and 20 mins)

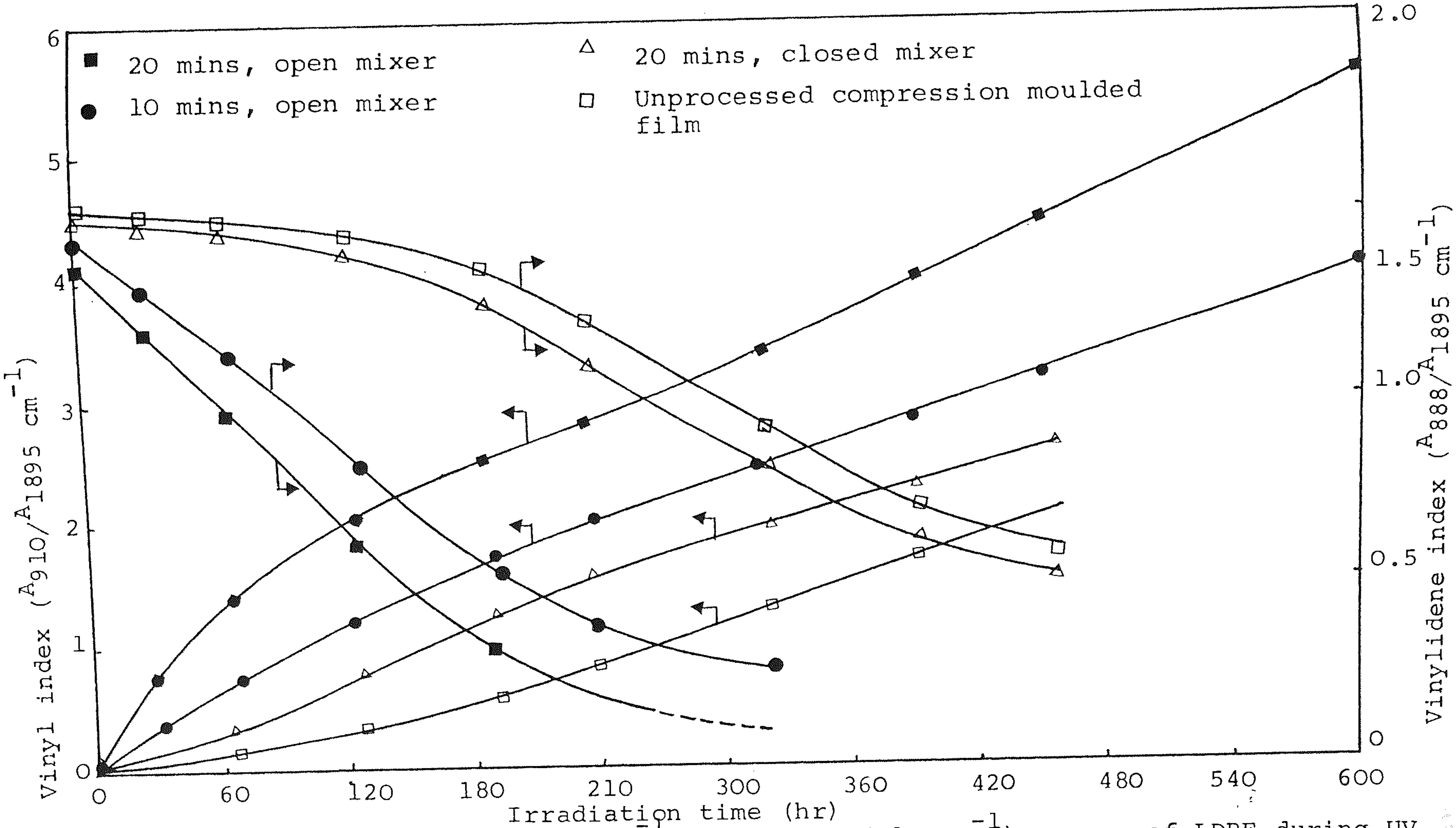


Fig. 5.14 Changes in vinylidene (888 cm^{-1}) and vinyl (910 cm^{-1}) groups of LDPE during UV irradiation. (LDPE processed at 180°C in both closed and open mixer for 10 and 20 mins.

increases and carboxyl group formation in the later stages of LDPE photo-oxidation is one of the main carbonyl products.

Fig. 5.13 also shows that an increase in processing time also leads to higher rate of carboxylic group formation which corresponds with the carbonyl formation.

The rate of photo-oxidation is higher when the polymer is processed in excess of oxygen compared with those in limited amount of air (Fig. 5.13). This is mainly due to the presence of higher hydroperoxide concentration especially at higher processing time which acts as main initiator (as it was shown in preceding chapter).

The mechanism of photo-oxidation of LDPE has been discussed in detail by Chakraborty and Scott(137,24).

5.B.2 Effect of Melt Stabilisers on Photo-Oxidation of LDPE, Results and Discussions

5.B.2.1 The Effect of Galvinoxyl

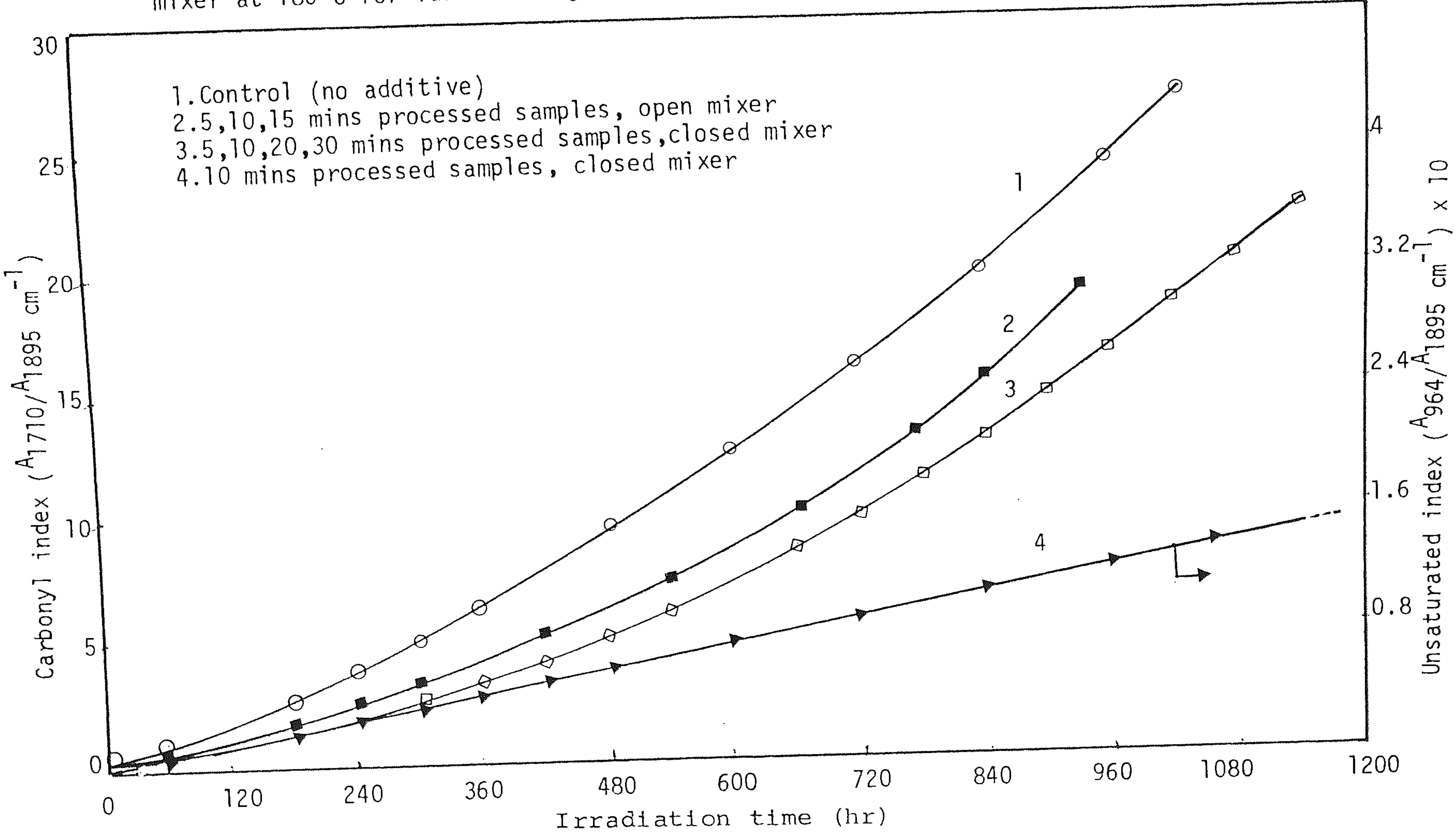
Fig. 5.15 shows the effect of galvinoxyl under different processing conditions on the photo-oxidation of LDPE.

On UV irradiation all the samples (compression moulded films) showed increased photo-stability (Fig. 5.15, curves 2 and 3). Variation in processing time did not affect the photo-oxidative stability of LDPE samples (Fig. 5.15, curves 2 and 3), but the samples processed in an open chamber showed a slightly lower photo-stabilising effect (Fig. 5.15, curve 2) which could be due to presence of lower concentration of hydrogalvinoxyl in the samples after processing (see, sec. 3.B.3).

Although the initial rate of photo-oxidation of LDPE samples, containing galvinoxyl is not very much different from that of the control, the overall photo-stability of the films containing galvinoxyl is higher compared to the control (see, Table 5.7). It seems likely that there are two competition reactions, one stabilisation due to effect of hydrogalvinoxyl and galvinoxyl and another sensitisation due to the effect of quinone compounds present in the samples which is quite similar to those shown in the case of polypropylene (see, sec. 5.A.2.1).

Fig. 5.15 (curve 4) also shows the unsaturation formation during UV exposure of 10 mins. processed sample (closed mixer) containing galvinoxyl measured by a growth of a band at 964 cm^{-1} (after sub-traction of an identical control sample from it). A slow growth of

Fig. 5.15 Effect of galvinoxyl on photo-oxidation of LDPE (all samples processed in both closed and open mixer at 180°C for various lengths of times).



unsaturation is observed (Fig. 5.15, curve 4) which could be the result of hydrogen abstraction from the polymer chains by galvinoxyl leading to hydrogalvinoxyl formation. Then, the latter acts as an effective CB-D antioxidant.

5.B.2.2 Effect of Iodine on the Photo-Oxidation of LDPE

The polymer film containing iodine shows an initial rapid rate of photo-oxidation followed by a slower rate (Fig. 5.16). The effect of processing time on photo-oxidation of LDPE samples is also shown in Fig. 5.16 (numbers on curves are processing times). All samples show a similar rapid rate in the initial stages and a slower rate in the later stages of photo-oxidation. The rapid rate of photo-oxidation of the samples compared to the control is due to presence of a high concentration of C-I bonds in the samples (see, chapter 3, 3.B.3). Since C-I bonds have a low dissociation energy (50 k cal/mol)[194a], on UV irradiation these bonds break down leading to radical formation.

Fig. 5.16 (curve 1) shows the formation of unsaturation (measured at 964 cm^{-1}) in the polymer samples containing iodine (10 mins. processed samples, in a closed mixer) during UV irradiation. (Growth of double bond in an identical control has been sub-tracted from that of

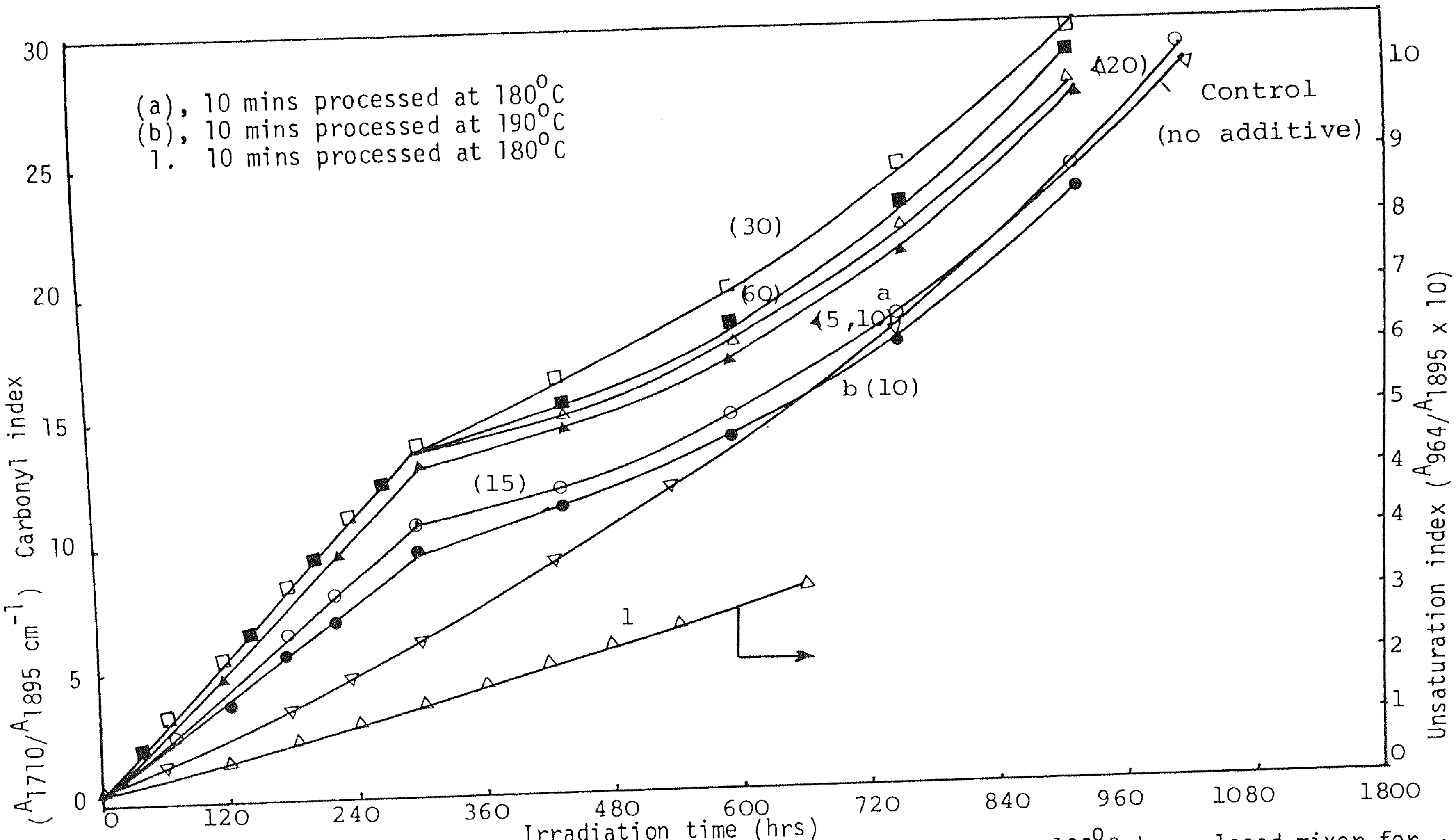


Fig. 5.16 Effect of iodine on photo-oxidation of LDPE (samples processed at 180°C in a closed mixer for various lengths of times, numbers in parenthesis are processing times, iodine conc= 1.57 x 10^{-3} mol/100g)

the sample).

On UV irradiation iodine molecules in the sample also dissociate due to their low bond energy (36 k cal/mol)$^{(194a)}$.

$$I_2 \xrightleftharpoons{hv} 2I^{\cdot}$$

These iodine atoms possibly abstract hydrogen from the alkyl radicals resulting in the unsaturation formation in the polymer

$$-CH_2-\dot{C}H- + I^{\cdot} \longrightarrow -CH{=}CH- + IH$$

Hydrogen iodides could also be oxidised by alkylperoxy radicals.

$$IH + ROO^{\cdot} \longrightarrow ROOH + I^{\cdot}$$

The low rate of photo-oxidation in the second stage is almost the same as control and can be explained as being due to low concentration of C-I bonds or lack of C-I bonds in the polymer chains (Fig. 5.16,).
The effect of the processing temperature is also shown in Fig. 5.16 (curves a and b). Higher processing temperature (190°C) leads to lower level of carbonyl formation compared to lower processing temperature (180°C) which also could be due to lower C-I bond

concentrations at higher temperature (due to volatilisation of iodine).

UV embrittlement times of the LDPE samples containing iodine are listed in Table 5.8. This table shows that although the presence of iodine causes a rapid rate of photo-oxidation in the initial stages overall photo-stability of the films containing iodine is similar to the control.

5.B.2.3. The Effect of Cupric Stearate on Photo-Oxidation of LDPE

Fig. 5.17 compares the behaviour of cust as screen and as additive during the photo-oxidation of LDPE. The samples screened by cust (curve 3) shows an initial induction time to carbonyl formation followed by a lower rate of photo-oxidation compared with control screened by control (curve 2).

Curve 1 (Fig. 5.17) represents the photo-oxidation of LDPE containing cust as additive showing an initial decrease in carbonyl content (due to photolysis of cust). After the decrease in carbonyl, rate of photo-oxidation is slightly higher over the control for a short period of time followed by similar rate to the other samples. Fig. 5.17 (curve 4) also shows the

Table 5.8 Effect of iodine on photo-oxidation of LDPE (sample processed in closed mixer/10 min. at 180°C, $[I_2] = 1.57 \times 10^{-3}$ mol/100g)

Embrittlement time of control (hr) = 1649

Embrittlement time of the sample = 1591

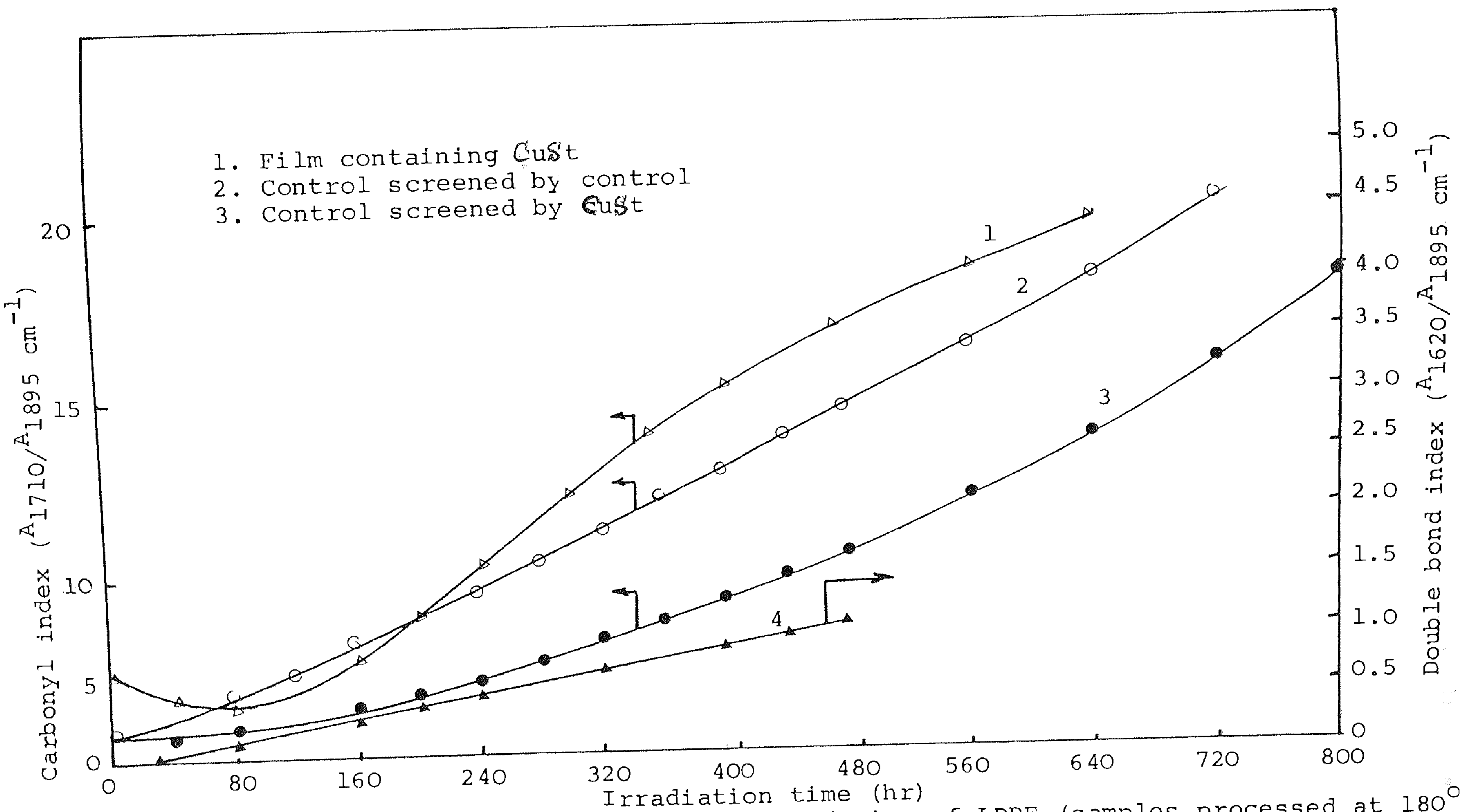


Fig. 5.17 Effect of cupric stearate on photo-oxidation of LDPE (samples processed at 180°C/ 10 mins in a closed mixer, cust conc= 6.34 x 10^{-4} mol/100g, CuSt used as screen and additive).

formation of unsaturation (measured at 1620 cm^{-1}) in the sample containing CuSt. The unsaturation increases linearly with time of irradiation.

The results clearly show that the behaviour of CuSt in LDPE is similar to that in polypropylene (see, sec. 5.A.2.4). The stabilisation ability of CuSt is mainly due to its screening effect.

The high rate of photo-oxidation could be explained as being due to the redox reactions between copper carboxylate and hydroperoxides(248) giving free radical products.

Retardation effect of cust during photo-oxidation of polyethylene containing cust has recently been reported(253). Morover, Scott has also proposed(241) an alkyl trapping by Cu^{+2} followed by regeneration of Cu^{+} in a cyclic mechanism which could be another possible reason for stabilisation effect of CuSt during photo-oxidation of LDPE samples.

CHAPTER SIX

Mechanistic Investigation of Melt Stabilisation of Polyolefins Containing Additives

6.1 Introduction

During the processing of polypropylene and polyethylene the main chain is broken by mechanical shear to produce a pair of mechano radicals$^{(255,256)}$, namely - $CH_2\dot{C}H$-(CH_3) and $^{\cdot}CH_2$ - $CH(CH_3)$ - which have been detected by esr produced from polypropylene$^{(222,223)}$.

One of the characteristics of mechano radicals is high reactivity$^{(257)}$ at low temperature compared with the corresponding radicals formed by ionisation or photo-irradiation. For example, the mechano radicals are more reactive with oxygen than the radicals formed by irradiation (in chain radicals) and this difference in reactivity is mainly due to the fact that the two radical chain ends are rapidly separated by shear whereas radicals formed by other means are formed in a radical cage. The mechano radicals are formed and trapped on the fresh surface which has been created by the shear and therefore oxygen molecules are easily accessible to the mechano radicals. On the other hand, the radical generated by ionising reactions are trapped inside the solid polymer and therefore either an oxygen molecule or a radical has to diffuse into the bulk polymer in order to react with the radical.

It has been shown in the previous chapters (chapters 3 and 4) that mechano radicals produced from polyolefins during processing under high mechanical shear are mainly responsible for the oxidative degradation of polymers. It has also been shown that removal of mechano radicals by efficient free radical scavengers (melt stabilisers viz. galvinoxyl, nitroxyls, iodine) results in powerful melt stabilisation.

In this chapter the behaviour of stable radicals (viz. galvinoxyl, nitroxyls) are studied in detail in a model compound (methyl cyclohexane) and attempts have been made to correlate the model compound results with the results obtained in the polymer medium and mechanisms of antioxidant action of melt stabilisers have been suggested.

6.2 A Study of the Reaction of Galvinoxyl with Methyl Cyclohexane and Polypropylene

A solution of galvinoxyl in dichlorobenzene (4.75×10^{-4} mol/lit) in a two necked round bottomed flask was placed in an oil bath and the temperature was maintained at 70°C and the reaction was carried out under both nitrogen and oxygen. Methylcyclohexane in excess was added to the flask.

The mixture was stirred and as the reaction time increased the colour of the solution changed from violet to yellow. Hydrogalvinoxyl was found to be formed and the kinetics of its formation was followed using UV spectroscopy by following the formation of a new peak at 380 nm which has been shown to be due to hydrogalvinoxyl (see, experimental chapter). Decay of the absorbance at 420 nm due to galvinoxyl was also followed kinetically.

The UV spectrum of the solution containing galvinoxyl before heating was taken and considered as zero time of the reaction and the UV spectra of the reaction mixture were taken at fixed intervals of times during heating.

The decay of galvinoxyl absorbance (at 420 nm) and formation of hydrogalvinoxyl (at 380 nm) during heating under nitrogen as well as in the presence of oxygen are shown in Fig. 6.1).

It is seen from this Fig. 6.1 that galvinoxyl decreases almost linearly with time of reaction both in presence and absence of oxygen (Fig. 6.1, curves 1 and 3). Hydrogalvinoxyl started to form almost from the beginning of the reaction and its concentration increased linearly with time under nitrogen (curve 2),

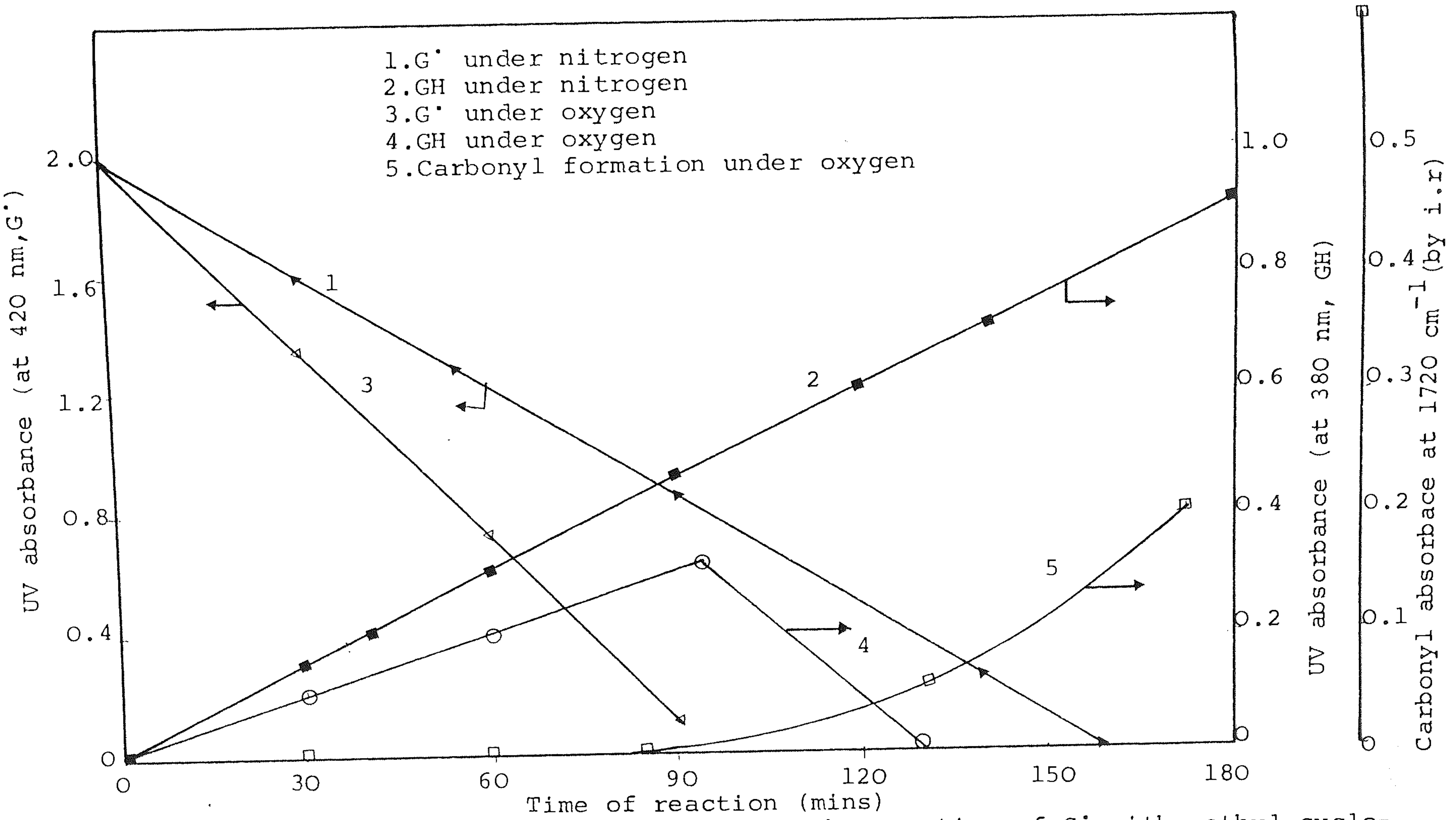
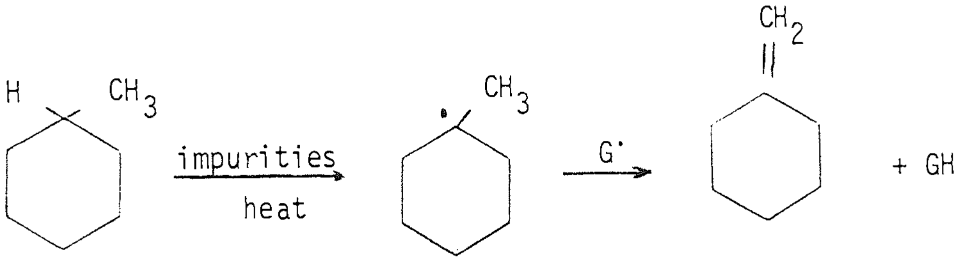


Fig. 6.1 Changes in G˙ and GH concentrations during the reaction of G˙ with methyl cyclohexane at 70°C(C_6H_5Cl used as solvent)

but in the presence of oxygen it reached a maximum and then started to decay (curve 4). It may be noted from Fig. 6.1 that decay of galvinoxyl and formation of hydrogalvinoxyl seem to be related to each other.

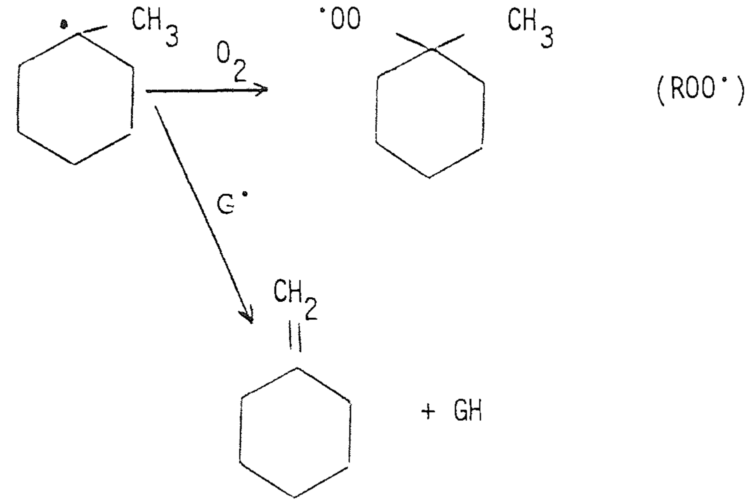
The following reactions (1) are proposed to account for the observations under nitrogen



(1)

Infra-red spectra of the solution at the end of the reaction (under nitrogen) showed a phenolic absorbance at 3640 cm^{-1} and a vinylidene double bond at 890 - 870 cm^{-1}. Formation of unsaturation was also observed at 1640 cm^{-1}.

In the presence of oxygen with increase in reaction time hydrogalvinoxyl reacts with alkyl peroxy radicals resulting in decay of the hydrogalvinoxyl concentration (Fig. 6.1, curve 4), reactions (2).



$$ROO^{\cdot} + GH \longrightarrow G^{\cdot} + ROOH$$

(2)

However, if this were the only reaction galvinoxyl concentration could either increase or remain in equilibrium concentration after reaching a minimum. The fact that galvinoxyl could not be detected at the end of the reaction suggests that galvinoxyl is converted to some other products by reaction with oxygen(194).

No carbonyl was detected when the reaction was carried out under nitrogen (by ir method). However, carbonyl started to form after an induction period under oxygen (Fig. 6.1, curve 5).

It was shown in chapter 3 that galvinoxyl acts as a powerful melt stabiliser during processing with polyolefins even at very low concentration and the results suggest that galvinoxyl is not bound to the polymer but hydrogalvinoxyl and unsaturation in the polymer are formed. The above studies in the model compound confirm the findings in the polymer medium.

The formation of hydrogalvinoxyl during processing of the polymers (pp, LDPE) with galvinoxyl and also variation of hydrogalvinoxyl with processing time were shown in chapter 3 (see, 3.A.4.1, 3.B.3, Fig. 3.15).

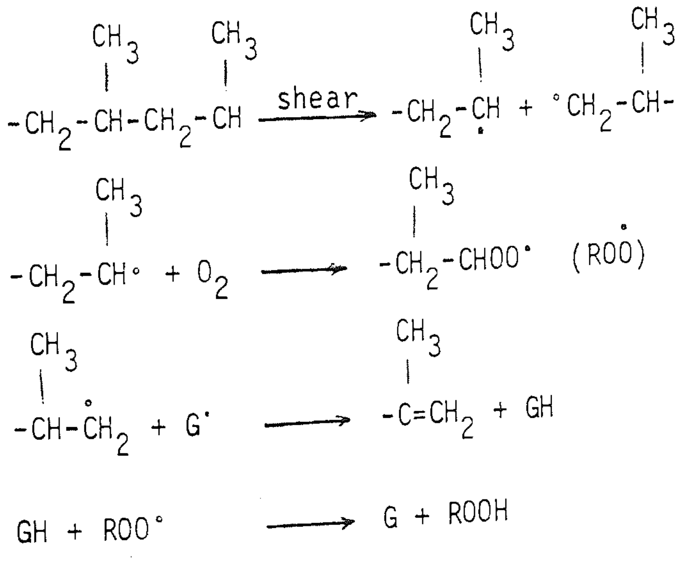
In order to obtain more information about the behaviour of galvinoxyl in the polymer during processing esr examination of the samples was carried out. E.S.R spectra obtained from the samples processed at various times showed a singlet. The value of g-factor of the absorption was measured according to the procedure described in section 2.3.13a and was found to be 2.018 (a typical spectrum is shown in chapter 3, Fig. 3.18). In order to identify the singlet and g-value, galvinoxyl was swelled into the films under nitrogen and esr spectrum of the films showed a similar singlet and g-value. E.S.R spectrum of a solution of galvinoxyl in benzene (0.01 M) was also taken and at low resolution the spectrum appeared as a singlet with a g-value of 2.0185. Therefore the singlet line and g-value obtained from the processed polymer samples containing galvinoxyl is attributed to the galvinoxyl radical (see, Fig. 3.18 in chapter 3).

The concentration of galvinoxyl in the samples (processed at different time, temp. and initial G°conc) was obtained according to the procedure described in section 2.3.13b. It was found that galvinoxyl concentration fluctuates with time of processing corresponding to the variation of hydrogalvinoxyl concentration with time of processing. The results for a particular condition was shown in chapter 3, Fig. 3.13 and also in Table 6.1.

Galvinoxyl concentration in the low density polyethylene was also measured. Table 6.2 shows the variation in the concentration of galvinoxyl during processing of low density polyethylene at 180°C and 190°C respectively with time of processing.

The results are similar to those for polypropylene.

Olefinic unsaturation formed during the processing was shown in chapter 3, Figs. 3.17 and 3.35. Therefore, the mechanism of action of galvinoxyl seems to be analogous to those of hindered nitroxyl radicals during photo-oxidation(168,187,258), involving the cyclic regeneration of galvinoxyl by oxidation of hydrogalvinoxyl by alkyl peroxy radicals(136), reactions (3).



$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}} \xrightarrow{\text{shear}} -CH_2-\overset{CH_3}{\overset{|}{\underset{\bullet}{C}H}} + {}^{\circ}CH_2-\overset{CH_3}{\overset{|}{CH}}-$$

$$-CH_2-\overset{CH_3}{\overset{|}{CH}}{}^{\circ} + O_2 \longrightarrow -CH_2-\overset{CH_3}{\overset{|}{CH}}OO^{\bullet} \quad (RO\dot{O})$$

$$-\overset{CH_3}{\overset{|}{CH}}-\overset{\circ}{C}H_2 + G^{\bullet} \longrightarrow -\overset{CH_3}{\overset{|}{C}}{=}CH_2 + GH$$

$$GH + ROO^{\circ} \longrightarrow G + ROOH \qquad (3)$$

It has also been reported by other workers(194a) that galvinoxyl

Table 6.1 Concentration of galvinoxyl during processing of polypropylene at 200°C in a closed mixer $[G^{\cdot}] = 4.75 \times 10^{-4}$ mol/100g

Time of processing (mins)	Number of spins/100g x 10^{-18}
3	5
7	7.75
15	5.51
20	6
30	6.74

Table 6.2 Concentration of galvinoxyl during processing of low density polyethylene at 180°C and 190°C in a closed mixer, $[G^{\cdot}] = 4.75 \times 10^{-4}$ mol/100g

Time of processing (mins)	Galvinoxyl Conc.	Number of spins/100g x 10^{-18}
	180°C	190°C
3		3.75
5	6.63	8.29
10	4.55	6.45
15	5.8	4.2
20	6.18	6.4
30	9.49	10.1

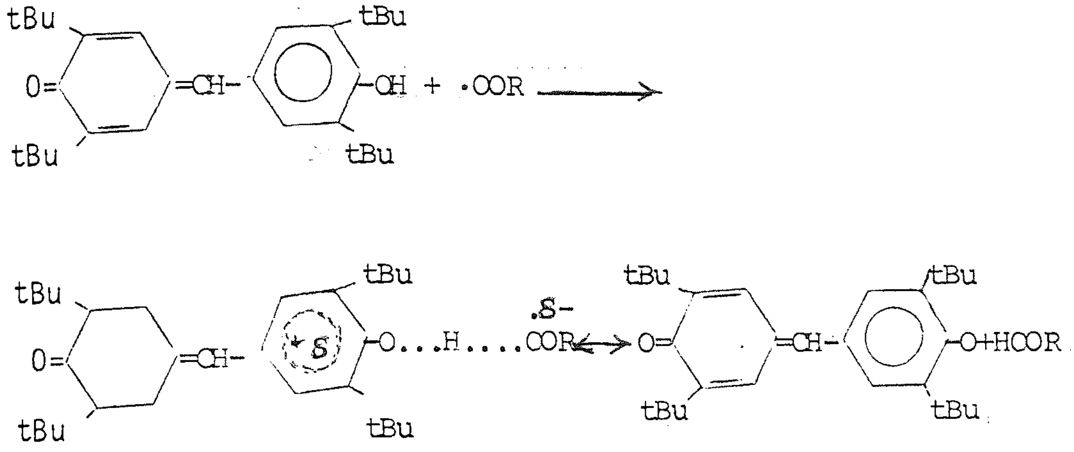
is a more effective melt stabiliser for polypropylene at 270°C than the commonly used hindered phenol, 2,6 di-tert-butyl p-cresol (TBC) when the latter is used in almost ten times the concentration of the former.

The above proposed mechanism could account for the very high activity of galvinoxyl during melt processing.

Hydrogalvinoxyl (CB-D) and galvinoxyl (CB-A) are both involved in melt stabilisation, thermal oxidation (see, section 4.A.1.1) and photo-oxidation (see, section 5.A.2.1) of polyolefins containing galvinoxyl. Thus,it would be useful to review these two mechanisms. The chain breaking mechanism (CB) maybe subclassified into two mechanisms (CB-D) and (CB-A) (see, section 1.2.1 in chapter 1). Hindered phenols and aromatic amines are involved in CB-D mechanism. They do not inhibit the thermal degradation of the polymers and are only effective if oxygen is present(259).

$$GH + ROO^{\cdot} \xrightarrow[\text{CB-D}]{} G^{\cdot} + ROOH$$

The high reactivity of alkyl peroxy radicals in this reaction results from the low activation energy which in turn results from the delocalisation of electron in the transition state due to the highly conjugated system leading to the transfer of electron to the alkyl peroxy radicals (reactions 4a).



(4a)

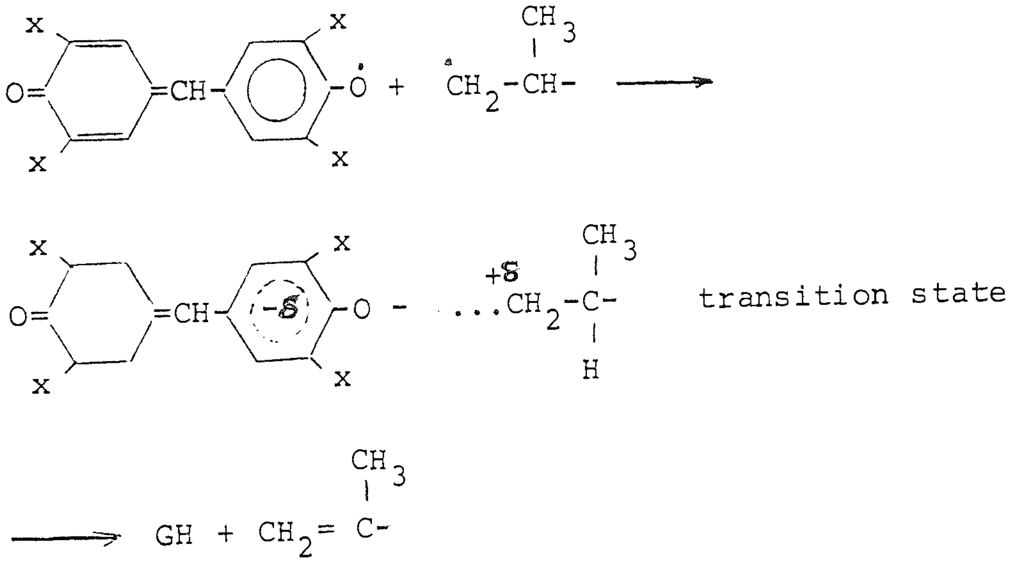
The effects of substituent groups in the aromatic rings is to reduce the energy of the transition state.

The formation of free phenoxy radicals as the primary oxidation products of hindered phenols has been reported(79-81).

Secondary and more stable radicals are formed by further reactions of primary radicals(80b) (e.g. formation of galvinoxyl radical from T.B.C), but actually the products formed by further reaction of the phenoxy radicals are complex and may have either antioxidant or pro-oxidant activity. These have been shown in chapter 1 (see, 1.2.1a).

In the present work it was shown that non-phenolic compounds (e.g. 2,6 di-t-but, 1,4 benzoquinone) formed during processing might contribute in the high thermo-oxidative stabilisation of polyolefins containing galvinoxyl (see, section 4.A.1.1 and 4.B.2 in chapter 4) acting as CB-A antioxidants. Moreover, the sensitisation effect of these compounds during photo-oxidation of the samples was also shown (see, section 5.A.2.1 and 5.B.2.1 in chapter 5).

Galvinoxyl acts as CB-A antioxidant capable of removing alkyl radicals as oxidising agent due to delocalisation of the electron in the transition state and the electrophilic activity of oxygen in the aromatic rings.



(4b)

x = t-Bu

Other stable phenoxy radicals have also been shown as (CB-A) alkyl radical trapping agents(260,261).

Galvinoxyl has been found(262) to have antifatigue activity in rubber suggesting that alkyl radical trapping plays important part in the mechanism of antifatigue agents and a similar regenerative mechanism to that suggested above for melt processing has also been proposed for its action.

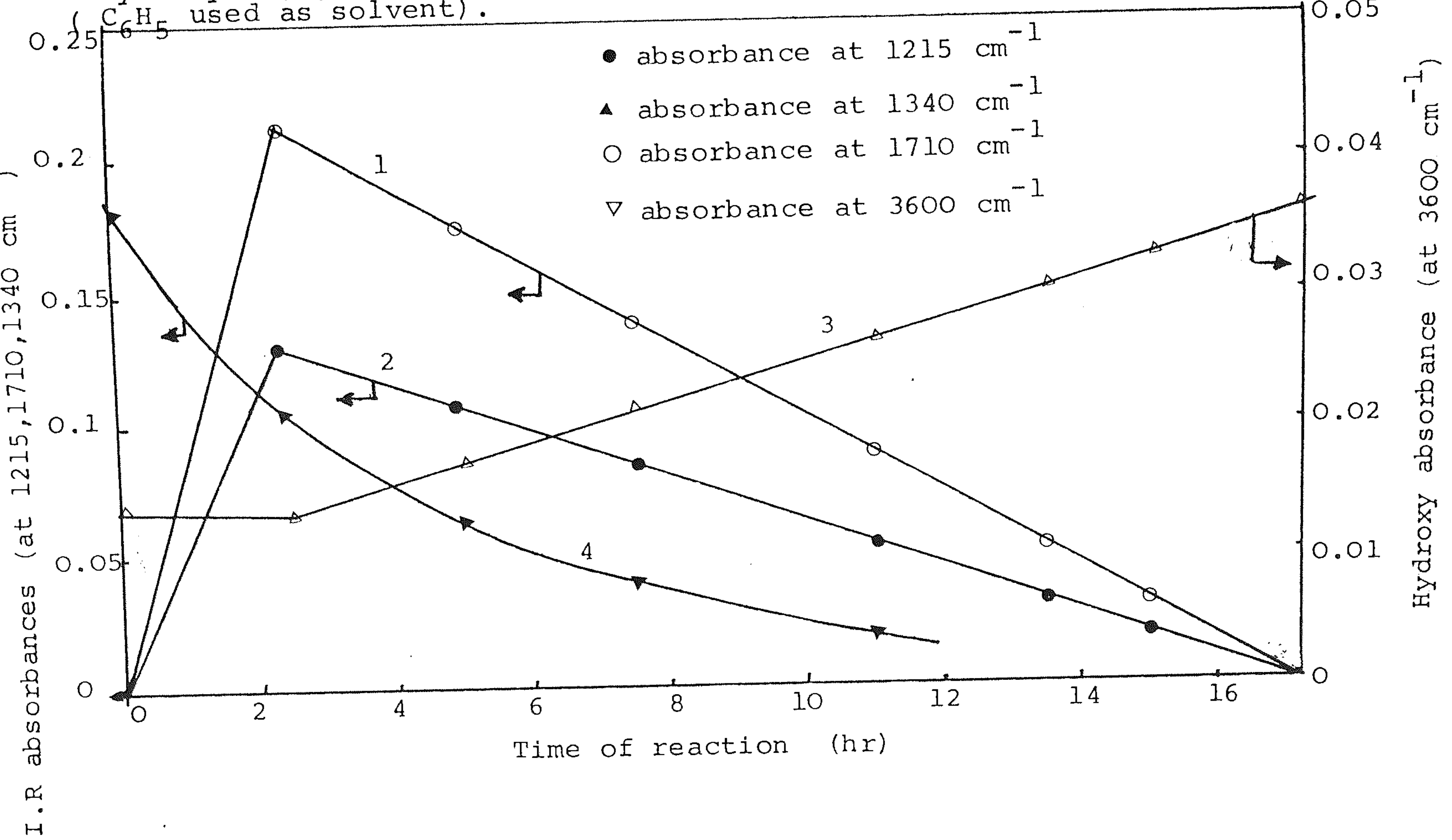
6.3 Reaction of 4-hydroxy, 2,2,6,6, tetra methyl piperidineoxyl with methyl cyclohexane and the Role of nitroxyl radicals as Melt Stabilisers, Photo stabilisers for polypropylene.

Reaction between 4-hydroxy 2,2,6,6,tetra methyl piperidineoxyl (1% solution in C_6H_5Cl) and methyl cyclohexane in excess was carried out at 70°C under nitrogen.

The kinetics of the reaction was studied by following the changes in the i.r. spectra occurring during the reaction (see Fig. 6.2). Two bands at 1710 cm^{-1} and 1215 cm^{-1}, formed during the initial reaction, increased to a maximum and then decreased.

Initial hydroxyl absorbance (3600 cm^{-1}) due to 4-OH present in the compound after an induction period increased. The bands at 1710 cm^{-1} and 1215 cm^{-1} are not observed in either parent amine or its related

Fig. 6.2 Variation in i.r absorbances (at 1215,17103600, 1340 cm^{-1}) due to reaction of 4-hydroxy 2,2,6,6,tetra methyl piperidineoxyl with methyl cyclohexane at 70°C (C_6H_5 used as solvent).



nitroxyl and hydroxylamine.

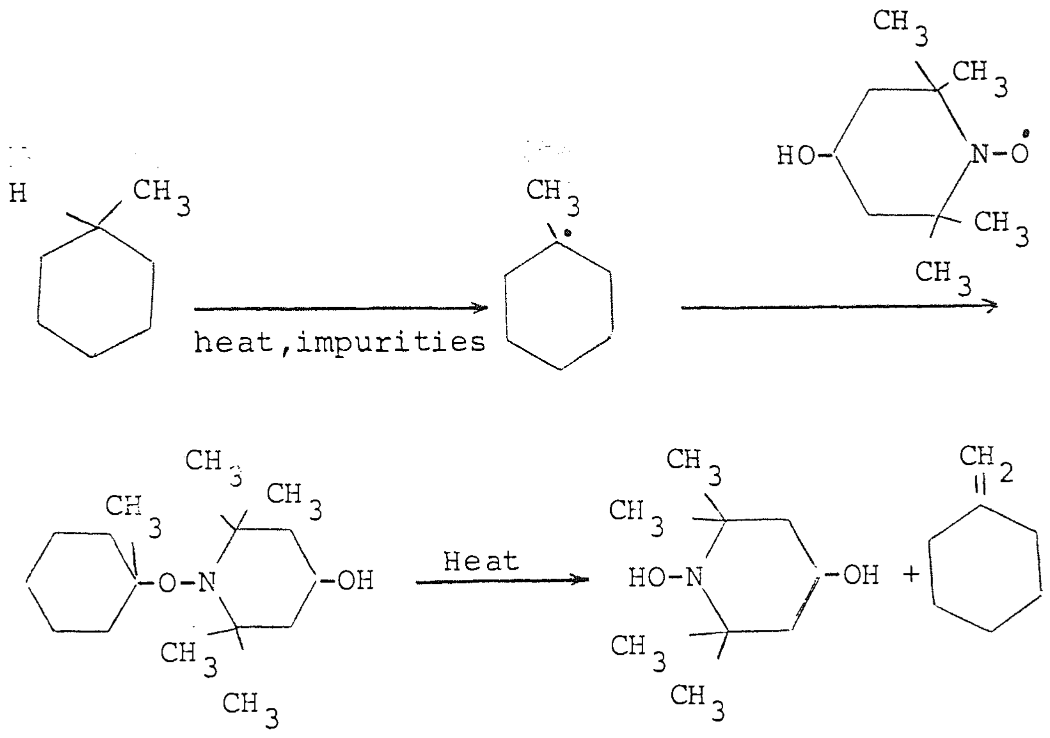
In order to identify the bands, infra-red spectra of 4-hydroxy ,2,2,6,6,tetra methyl, N-methoxyl piperidine in the solid state as well as in solution showed the bands at 1710 cm^{-1} and 1215 cm^{-1} respectively.

This result suggests that these two bands could be due to N-O-C stretching in alkyl hydroxylamine.

Increase in hydroxyl absorbance at 3600 cm^{-1} along with other bands at 2660 cm^{-1}, 2595 cm^{-1}, 2720 cm^{-1} (characteristic to hydroxylamine)(242) and decrease in alkyl hydroxylamine are probably due to hydroxylamine formation. Fig. 6.2 (curve 4) also shows the decay of nitroxyl radical (band at 1340 cm^{-1}, arbitrary units)(242) during the reaction corresponding to the above results. A vinylidene double bond at 890-870 cm^{-1} was found to be formed during the reaction. A band at 1595-1560 cm^{-1} was also detected shortly after disappearance of the bands at 1710 cm^{-1} and 1215 cm^{-1} which could be due to conjugated double bond formation(241).

Other workers(89) have also shown hydroxylamine formation during thermal oxidation of hydrocarbons in the presence of nitroxyl radicals.

The following reactions (5) could account for the above observations.



(5)

In chapter 3 it was shown that nitroxyl radicals are effective melt stabilisers in defincincy of oxygen (see, section 3.A.4.3, in chapter 3).

Compression moulded polymer films containing 4-hydroxy-2,2,6,6,tetra methyl piperidineoxyl (processed at various times, in both closed mixer and open mixer at 200°C) were examined by e.s.r spectroscopy using identical amount of sample and e.s.r conditions (field, amplitude, MOD width, response, power, etc.).

Figs. 6.3 and 6.4 respectively show the e.s.r spectra of the films recorded for various processing times in closed and open chamber. The concentration of the recorded nitroxyl radicals (g-value 2.001, a_H splitting factor 12.5G) were calculated using the procedure described in section 2.3.13.

Fig. 6.5 (curve 1) shows the changes in the nitroxyl radical concentration with time of processing in a closed mixer. During the processing of polypropylene with nitroxyl radical (4OHTMPO), initially the concentration of nitroxyl radical is decreased very much due to high initial shear in the mixer (i.e. high alkyl radical conc, see Fig. 6.5, curve 2) and subsequently nitroxyl radical concentration showed a variation with processing time having two maxima concentrations at about 5 mins. and 20 mins. of processing (see, Fig. 6.5, curve 1). Hydroxylamine (4OHTMPOH) was also found to be formed during the processing (see, section 3.A.4.3) and when it was used as a melt stabiliser the corresponding nitroxyl radical concentration increased steadily during the first 15 mins. of processing whilst it functioned as a powerful melt stabiliser (see, Fig. 3.28 in chapter 3).

Thus, the first maximum peak in Fig. 6.5 could be due

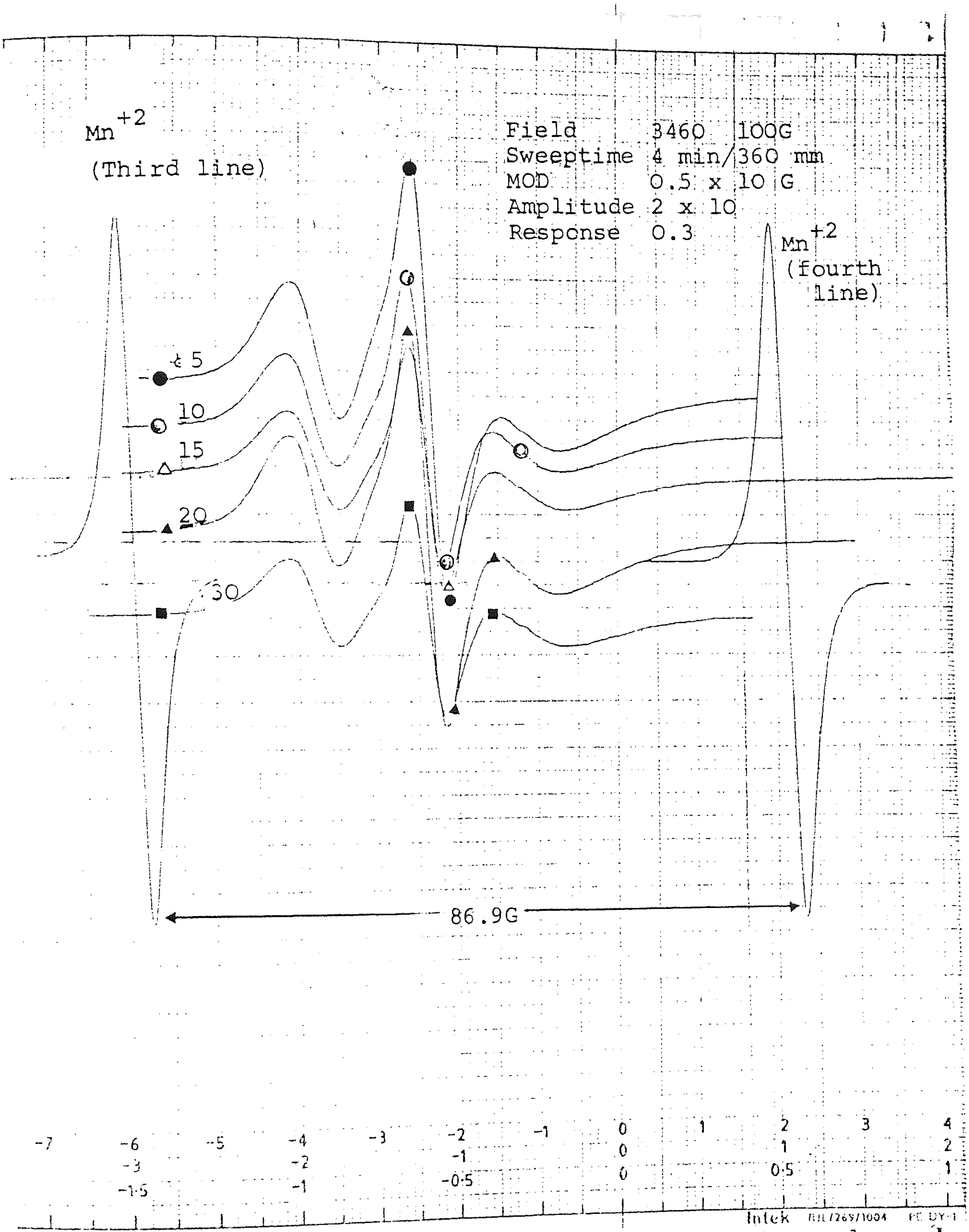


Fig. 6.3 E.S.R spectra of pp films containing nitroxyl radical (4OHTMPO) at room temperature, (samples processed in a closed mixer at 200°C for various lengths of times, 4OHTMPO conc=1.16 x 10^{-3} mol/100g, numbers on curves are processing times, the same amount of sample and condition used in each case.

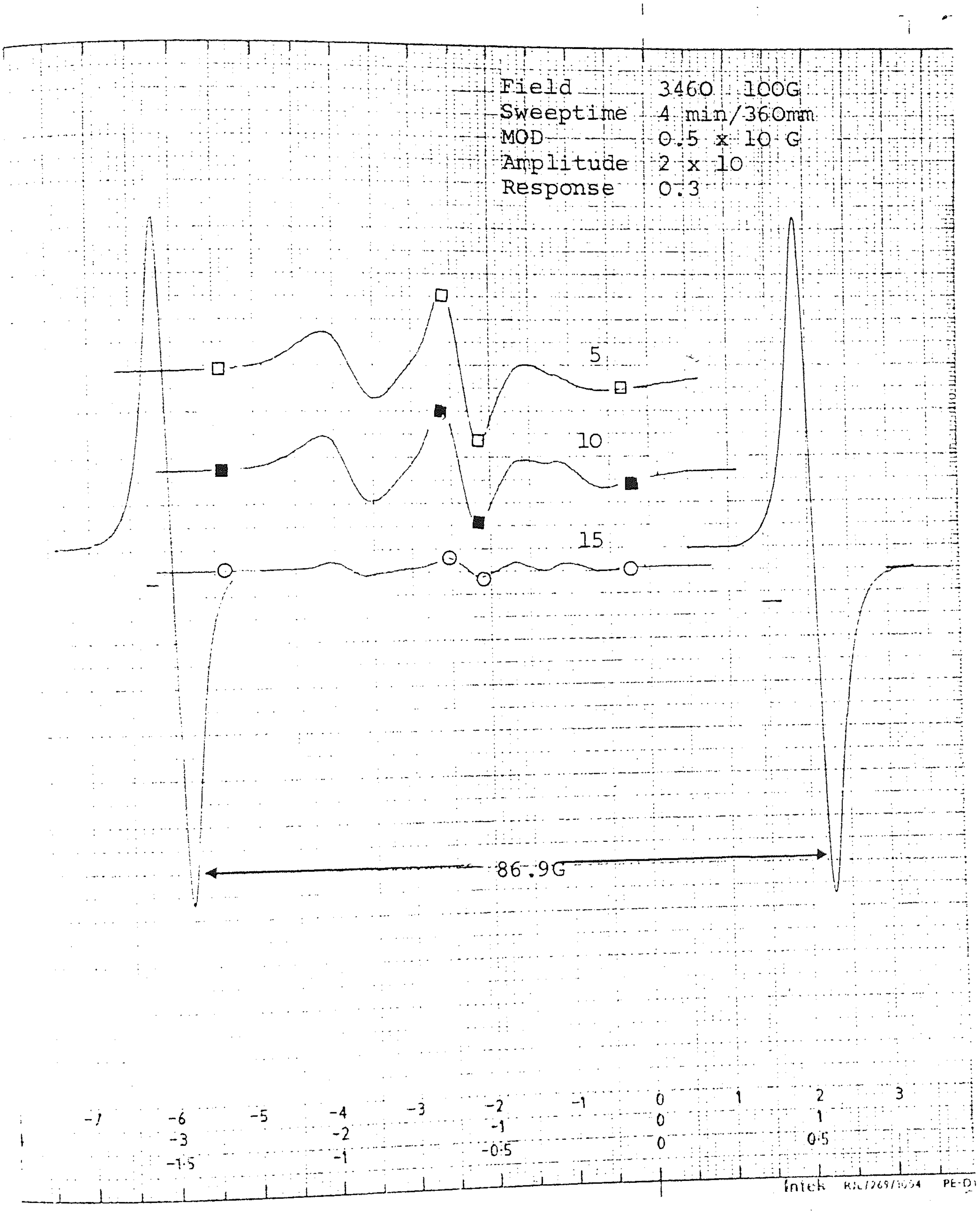


Fig. 6.4 E.S.R spectra of pp films containing nitroxyl radical (4OHTMPO) at room temperature, (samples processed in an open mixer at 200°C for 5, 10 and 15 mins, 4OHTMPO conc=1.16 x 10^{-3}mol/100g, numbers on curves refer to processing times, the same amount of sample and condition used in each case).

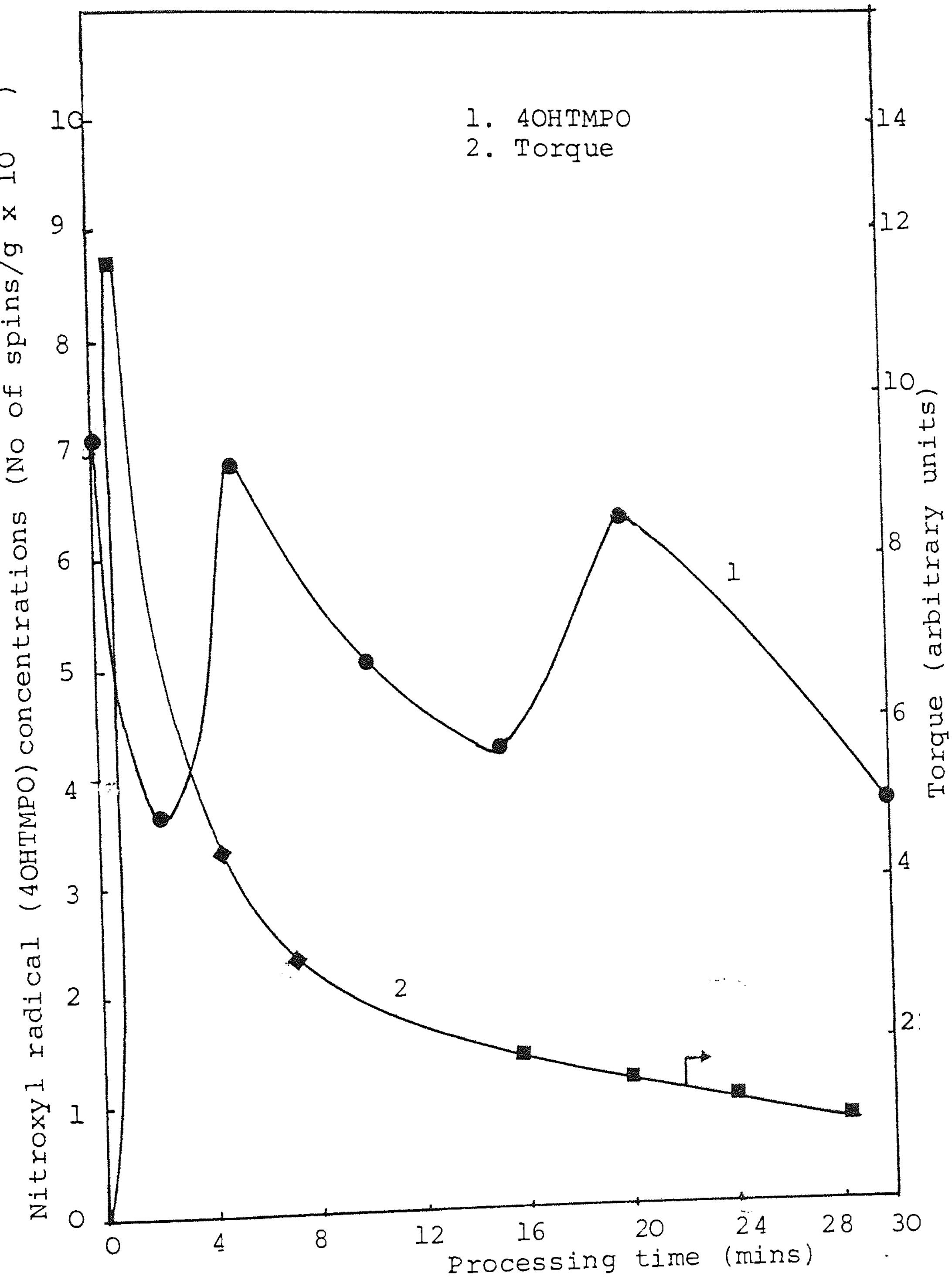
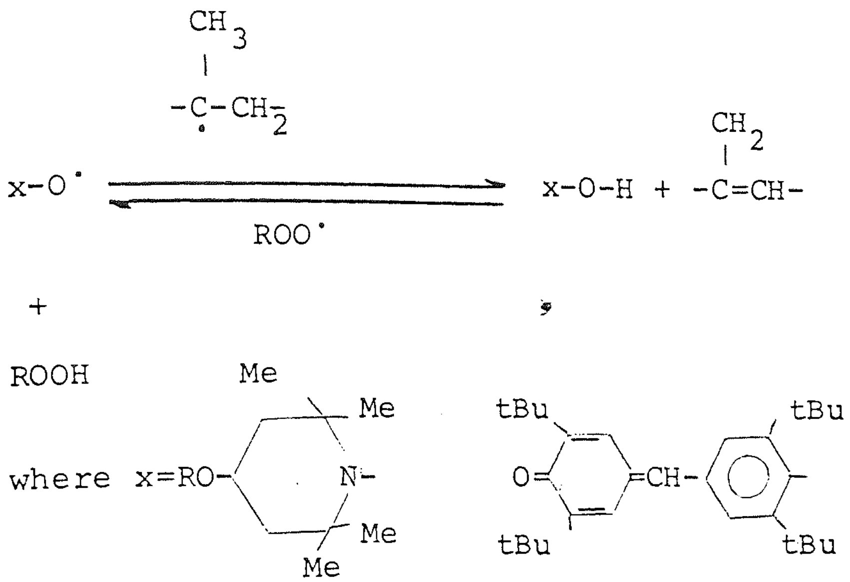


Fig. 6.5 Changes in nitroxyl radical(4OHTMPO) concentration and torque with times of processing (pp processed with nitroxyl radical a closed mixer at 200°C, 4OHTMPO conc=1.16 x 10^{-3} mol/100g).

to regeneration of nitroxyl radical from free hydroxylamine (as intermediate) owing to the effect of alkylperoxy radicals (CB-D type)$^{(136,167)}$. The second maximum peak in Fig. 6.5 is probably due to oxidation of hydroxylamine (CB-D mechnism) by peroxides formed during the processing up to about 15 mins. leading to regeneration of nitroxyl radical.

Fig. 6.4 shows that the intensity of e.s.r spectra of nitroxyl radical decreases with increasing processing time in the presence of air which is certainly due to loss of nitroxyl radical under severe processing conditions.

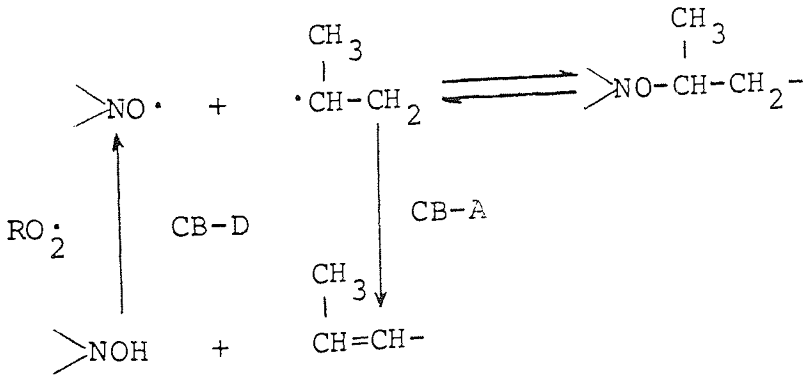
The melt stabilisation mechanism proposed for the stable aryloxy radical (galvinoxyl, see, section 6.1) seems to be analogous to that proposed for nitroxyl radicals. In both cases no bonding of the oxygen radical to the polymer could be detected at any stage during processing and olefinic unsaturation is formed in the polymer (see, section 3.A.4.1 in chapter 3),(reaction 6).



(6)

However, if alkyl hdyroxylamine is at all formed during the processing of polypropylene with nitroxyl radicals, it would be decomposed at processing temperature. Other workers have shown (236,245) that alkyl hydroxylamines are thermally unstable decomposing rapidly at processing temperatures.

On the basis of the above results the following cyclical regeneration mechanism for nitroxyl radicals during melt stabilisation of polypropylene could be proposed (reactions 7).



(7)

This cyclical regeneration process involves both CB-A and CB-D mechanisms.

In chapter 5 photo-stabilisation activity of nitroxyl radicals in polypropylene was shown (see, 5.A.2.3.).

It has been established(174-177,263) that effective photostabilising ability of hindered piperidines (e.g. Tinuvin 770) is due to their rapid conversion to the corresponding nitroxyl radicals.

In chapter 5 changes in nitroxyl radical concentrations during photo-oxidation of pp containing Tinuvin 770 and 4,hydroxy 2,2,6,6,tetra-methyl piperidineoxyl were shown (see,Fig. 5.8 in chapter 5). In both cases,at the same molar concentration, nitroxyl radical reached a stationary concentration which then persisted until the end of the carbonyl induction period.

As nitroxyl radicals are powerful alkyl radical scavengers(188,264), they react with macroalkyl radicals forming alkyl hydroxylamine. To account for the effectiveness of nitroxyl radicals as antioxidants, regeneration of nitroxyl radicals due to reaction of alkylhydroxylamine with alkyl peroxy radicals has been proposed(187).

$$>NO{-}R' + ROO^{\bullet} \longrightarrow\ >NO^{\bullet} + ROOR'$$

Since it has been shown(243) that the rate of this reaction is not high enough to account for high stoichiometric coefficient (f) of nitroxyl radicals, Wiles et al have suggested(180,265) that local association of nitroxyls with hydroperoxide groups present in the polymer could contribute to the overall stabilisation effectiveness in addition to the scavenging of alkyl radicals and the above reaction.

Scott and co-workers have recently reported(242) the intermediate formation of hydroxylamine and associated unsaturation in a substrate containing Tinuvin 770 under photo-oxidation. Hydroxylamine reacts with peroxy radicals by a CB-D mechanism to regenerate nitroxyl radical (reactions 6)(136,167).

It has been proposed therefore that the high efficiency of nitroxyl radicals as UV stabilisers results from the participation of CB-A and CB-D antioxidant mechanisms involving a cyclic regeneration similar to that reported above for melt stabilisation.

Scott and co-workers(237) have also reported the formation of both hydroxylamine and olefinic unsaturation during mechano-chemical degradation (fatiguing) in vulcanised natural rubber containing an aromatic amine (IPPD) or a nitroxyl radical (4OHTMPO) suggesting the similar behaviour of nitroxyl radicals during mechano-chemical oxidation (e.g. processing) and photo-oxidation.

It is now clear that mechanisms of antioxidant action of nitroxyl radicals during melt stabilisation of polypropylene are very similar to those occurring in photostabilisation.

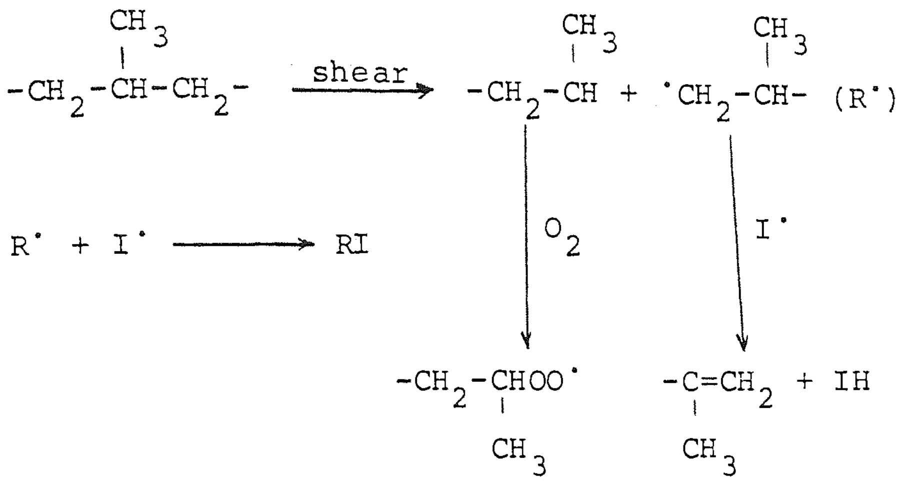
6.4 Mechanism of Antioxidant Action of Iodine and Cupric Stearate in the Melt Stabilisation of Polypropylene

The very powerful melt stabilisation activity of iodine in polypropylene has been discussed in chapter 3.

During the processing of iodine with polypropylene formation of carbon-iodide bonds, hydrogen iodide and olefinic unsaturation were observed and quantitatively estimated (see, 3.A.4.2.).

The following cyclic regeneration mechanism has been suggested for efficient melt stabilising activity of iodine (reactions 8).

$$I_2 \longrightarrow 2I^{\bullet}$$



$$-CH_2-\underset{}{\overset{CH_3}{CH}}-CH_2- \xrightarrow{shear} -CH_2-\overset{CH_3}{CH} + {}^{\bullet}CH_2-\overset{CH_3}{CH}-\ (R^{\bullet})$$

$$R^{\bullet} + I^{\bullet} \longrightarrow RI$$

$$-CH_2-\underset{CH_3}{CH}OO^{\bullet} \qquad -\underset{CH_3}{C}=CH_2 + IH$$

$(RO\dot{O})$

$$2ROO^{\bullet} + 2IH \longrightarrow 2ROOH + 2I^{\bullet}$$

(8)

The regeneration of iodine during the oxidation of cumene with iodine as inhibitor has also been reported(231).

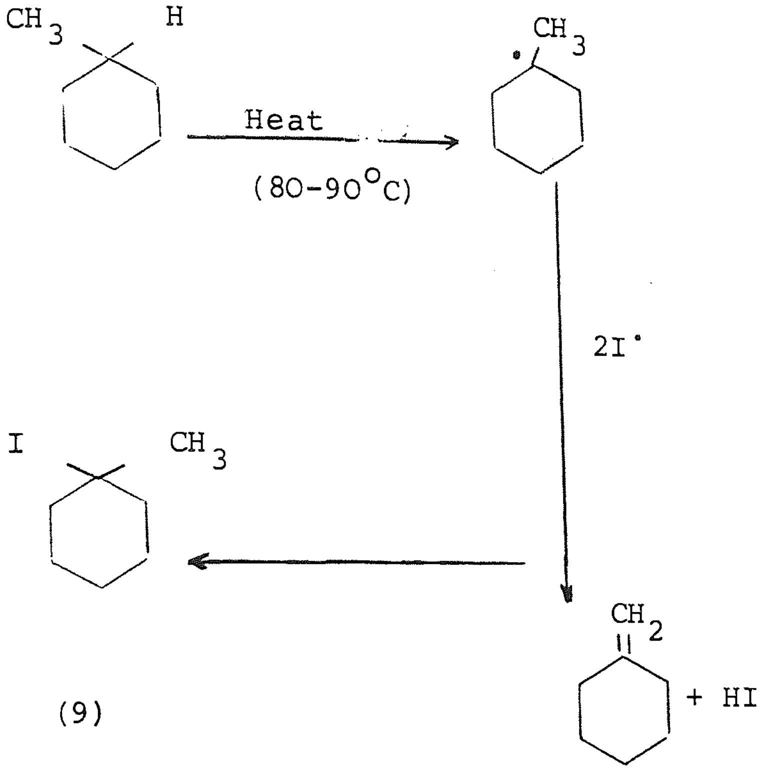
The above proposed mechanism is similar to those described for nitroxyl radical regeneration (see, section 6.3) and galvinoxyl regeneration (see, section 6.2) in the oxidation of polypropylene.

In order to be able to throw some light on the mechanism of melt stabilisation of iodine a reaction between iodine and methyl cyclohexane was carried out. The mixture of iodine and methyl cyclohexane (in excess) in a two-necked round flask (200 ml, C_6H_5Cl used as solvent) was placed in a heat jacket while passing nitrogen through it. The flask was connected to an aqueous solution of $AgNO_3$ by a glass tube. The sol uion was heated very slowly and at 80 - 90°C silver iodide was found to be formed rapidly (precipitation) due to the reaction of hydrogen iodide with $AgNO_3$.

$$IH + AgNO_3 \longrightarrow IAg + NO_3H$$

The unsaturation formation in the substrate was observed by i.r (a band at 1560 - 1640 cm^{-1} and a vinylidene band at 880-870 cm^{-1})

The following reactions are proposed for the above observations under nitrogen (reactions 9).



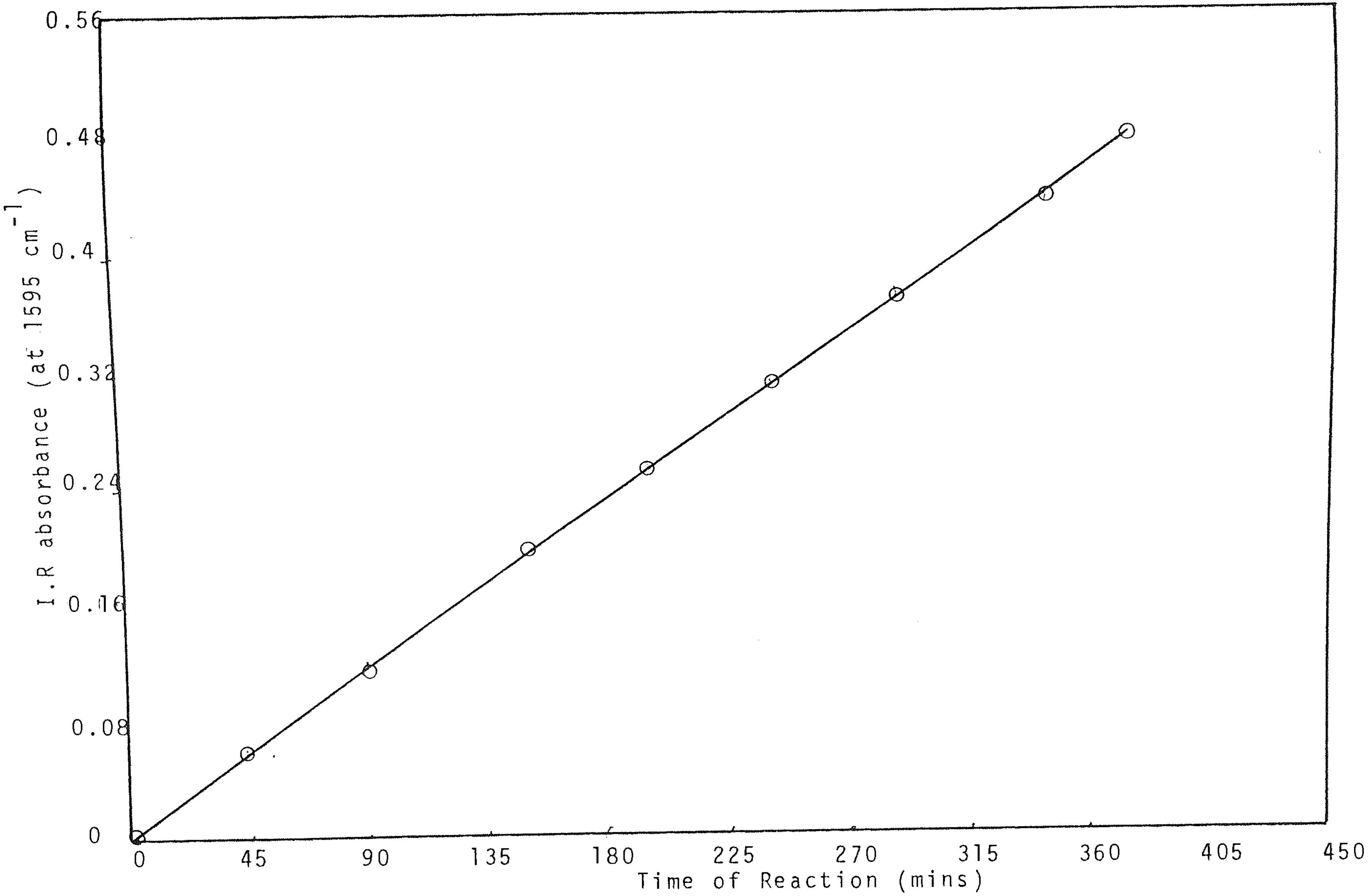
(9)

The kinetics of the reaction between cupric stearate (2% w/v in C_6H_5Cl) and methyl cyclohexane (in excess) under nitrogen at 70°C was carried out using i.r method.

Fig. 6.6 shows that a band at 1595 cm^{-1} is formed and is increased linearly with time of reaction. This is attributed to the co-ordination of copper with unsaturation(241). Similar phenomenon has also been observed during processing of polypropylene containing cupric stearate (see, 3.A.4.4.) while cupric stearate acted as an effective melt stabiliser.

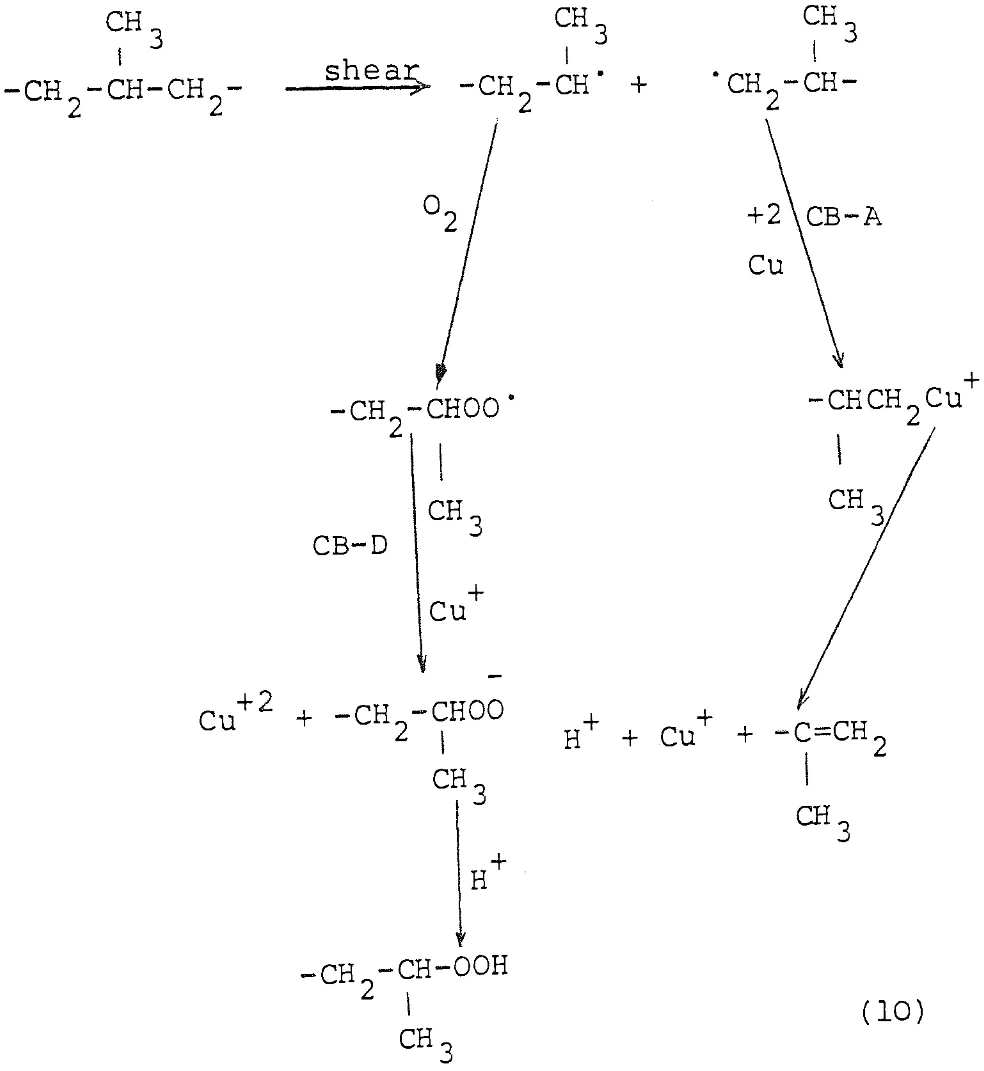
The presence of Cu^{+2} and Cu^{+} has been observed by colour changes both during processing as well as in

Fig. 6.6 Olefinic unsaturation formation due to reaction of cupric stearate with methyl cyclohexane under nitrogen at 70^{0}C (C_6H_5Cl used as solvent)



model compound study. Initially the colour is blue due to Cu^{+2} which changes to green (due to Cu^{+}) and finally becomes bluish green.

Generally, in the presence of Cu^{+2} there will be a competition between Cu^{+2} and oxygen for alkyl radicals (which are predominant in abundance due to high shear in the mixer) during processing leading to the regeneration of Cu^{+2} in a cyclic mechanism (reactions 10).



(10)

The above mechanism suggests that both chain-breaking electron acceptor (CB-A) and chain-breaking electron donor (CB-D) mechanisms are involved in the action of cupric stearate during melt processing of polypropylene.

A very similar cyclic process has been shown to be involved in the photo-stabilisation of paint films by copper ions (241).

CHAPTER SEVEN

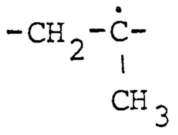
Conclusions and Suggestions for Further Work

7.1 Conclusions

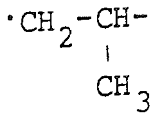
The effect of thermal processing on the chemical and physical properties of polyolefins was found to be strongly dependent on the amount of oxygen present in the mixer.

Since all thermo-plastic polymers are subjected to powerful shearing forces during processing, mechano-chemical scission of polymer chains is a major source of initiating radicals. This has been known for many years in rubbers(224-227) and has recently been shown to be the main source of sensitising species in PVC(41-43).

E.S.R studies have shown that(222,223) during mechanical destruction of polypropylene the following two macro-alkyl radicals are formed.



$-CH_2-\dot{C}(CH_3)-$



$\cdot CH_2-CH(CH_3)-$

At the early stage of mechano-degradation the concentration of these radicals is high due to high shearing forces acting on the polymer. It has been shown in the chapter 3 that mechano-radicals produced from polyolefins during processing under high mechanical shear are mainly responsible for the oxidative degradation of the polymers.

Increase in melt flow index, decrease in torque and molecular weight distribution towards lower molecular weight, along with chemical changes have been observed in polypropylene subjected to both closed (restricted oxygen) and open (excess of air) chamber processing. This indicates that chain scission reactions occur during the thermal processing of polypropylene and no cross linking. Alkyl radicals are formed in abundance in the early stages of processing which react with oxygen even at very low oxygen concentration to give the alkyl peroxy radicals which subsequently abstract hydrogen from the polymer chains to produce hydroperoxides. Hydroperoxides are thermally unstable and decompose to alkoxy and hydroxy radicals.

Reduction in molecular weight is caused principally by fragmentation of tertiary alkoxide radicals to ketones regenerating primary alkyl radicals which can again take part in the auto-oxidation scheme. The initial products of auto-oxidation have been found to be hydroperoxides and derived carbonyl compounds and the initial rates of both thermal oxidation and photo-oxidation, as has been found previously(28), are primarily dependent on the concentration of the former.

Therefore removal of mechano-radicals ($R^{\bullet}$, $RO\dot{O}$) formed in the initial stage of processing by efficient free radical scavengers will lead to effective stabilisation. The former ($R^{\bullet}$) is removed by a CB -A mechanism and the latter ($RO\dot{O}$) by a CB-D mechanism(136). Any anti-oxidant possessing both types of antioxidant activity will be very effective melt stabiliser.

This study clearly shows that galvinoxyl, iodine, nitroxyl radicals and cupric stearate all act as very powerful melt stabilisers for polyolefins by this kind of mechanism.

Galvinoxyl is mainly converted to hydrogalvinoxyl during the processing with polyolefins resulting in olefinic unsaturation formation in the polymer (CB-A mechanism).

Hydrogalvinoxyl concentration reaches a maximum at an early stage of processing due to high initial shear in the mixer (i.e high alkyl radical conc.). Alkyl peroxy radicals react with hydrogalvinoxyl by a CB-D mechanism regenerating galvinoxyl. A synchronous fluctuation of both hydrogalvinoxyl and galvinoxyl concentrations with time of processing is observed due to action of both CB-A and CB-D mechanisms involving a cyclic regenerative process. This results in a very powerful activity of galvinoxyl as a melt stabiliser particularly in a restricted amount of air. No change in melt flow index, molecular weight distribution and chemical structure of the polymers containing galvinoxyl is observed for a prolonged processing time.

The samples containing galvinoxyl also showed very effective thermo-oxidative stability (during oven ageing) involving both CB-A and CB-D mechanisms in a regenerative process. The results obtained from the action of galvinoxyl clearly show the importance of both CB-A and CB-D mechanisms and also the advantages of antioxidants acting by both mechanisms as compared with those acting by a single mechanism. The presence of oxygen is necessary for an antioxidant to act by both CB-A and CB-D mechanisms, but very high concentrations of oxygen lower the efficiency of CB-A type mechanism. Thus, a certain concentration of oxygen in a system is crucial to obtain high efficiency from an antioxidant acting by both CB-A and CB-D mechanisms.

The samples containing galvinoxyl also showed relatively effective photo-stabilising ability due to activity of hydrogalvinoxyl (CB-D) and galvinoxyl (CB-A) in the samples.

Hydrogen iodide and olefinic unsaturation in the polymers are formed during the processing of the polymers with iodine (CB-A mechanism). No chain-scission, change in molecular weight distribution or chemical change occur during the melt processing of the polymers containing iodine, indicating a powerful melt stabilising activity.

Alkyl peroxy radicals oxidise hydrogen iodide regenerating an iodine atom by a CB-D mechanism. Both CB-A and CB-D mechanisms are involved in a cyclical regenerative process during the melt processing of polymers with iodine. In photo-oxidation of the samples containing iodine olefinic unsaturation is formed in the polymer by a CB-A mechanism and hydrogen iodide is evolved followed by oxidation of the hydrogen iodide by alkyl peroxy radicals (CB-D activity).

This leads to a short term stabilising effect of the samples during photo-oxidation. The samples containing iodine show a stabilising effect during thermal-oxidation (oven ageing) as long as iodine persisted in the samples. When iodine is lost by volatilisation the samples are no longer protected against thermal-oxidation.

During the processing of polypropylene with 4,hydroxy, 2,2,6,6,tertra methyl piperidineoxyl olefinic unsaturation in the polymer and related hydroxylamine are formed by a CB-A mechanism. Nitroxyl radical concentration initially decreases due to high initial shear in the mixer (i.e. high alkyl radical conc.) and subsequently gives two maxima with time of processing indicating regeneration of nitroxyl radical during the processing in a closed mixer.

Nitroxyl radicals and hydroxylamine act as effective melt stabilisers in polypropylene and no physico-chemical changes in the polymer occur. 4-hydroxy, 2,2,6,6,tetra methyl,N-hydroxy,piperidine is converted into the corresponding nitroxyl radical during the processing with polypropylene by a CB-D mechanism. Therefore, both CB-A and CB-D antioxidant activities are involved in the melt stabilisation of polypropylene containing nitroxyl radicals in a cyclic regenerative process.

Nitroxyl radicals and hydroxylamine (4-hydroxy,2,2,6,6,tetra methyl,N-hydroxy,piperidine) show powerful photo-stabilising activity acting in a very similar cyclic-regenerative process to that during melt processing involving both CB-A and CB-D mechanisms.

Nitroxyl radicals show almost no stabilising effect during the accelerated thermal oxidation of the samples due to lack of their ability to scavenge alkyl peroxy radicals (a predominant species).

Cupric stearate oxidises alkyl radicals particularly formed during the initial stages of processing of the polymers (due to high initial shear) resulting in olefinic unsaturation formation in the polymers and Cu^+ by a CB-A mechanism. Alkyl peroxy radicals in the system oxidise Cu^+ regenerating Cu^{+2} by a CB-D mechanism. Therefore, both CB-A and CB-D mechanisms are involved in a cyclic regenerative mechanism during the melt processing of the polymers containing cupric stearate. No change in melt flow index and chemical structure of the polymers containing cupric stearate is observed for a long processing time particularly in a restricted amount of air indicating very effective melt stabilising activity of cupric stearate.

On UV exposure of the samples containing cupric stearate a photo-stabilising effect is also observed probably by a similar mechanism to that shown during the melt processing(241). No thermo-oxidative stabilising activity of the samples containing cupric stearate is found, due to free radical generating reaction between copper carboxylate and hydroperoxides.

The mechanisms of melt stabilising action of all melt stabilisers show a similar cyclic regeneration mechanism involving both CB-A and CB-D antioxidant activity and even the mechanisms of photo-stabilising action of most of them also show similar behaviour involving both CB-A and CB-D mechanisms.

This similarity during both melt processing (in a restricted air) and photo-oxidation is due to the presence of alkyl radicals in both cases.

Generally, the work described in this thesis shows the effect of a class of antioxidants which have the ability to alternate between the oxidised and the reduced state and hence exhibit regenerative behaviour under conditions where both alkyl and alkyl peroxy radicals are present during processing and subsequent photo-oxidation.

7.2 Suggestions for further work

Galvinoxyl was shown to be a very effective melt stabiliser for polyolefins. Hydrogalvinoxyl has been identified and quantitatively determined during processing of polyolefins with galvinoxyl. In order to confirm the cyclical regeneration of galvinoxyl via hydrogalvinoxyl (as proposed in chapter 6) during processing it is also necessary to investigate the behaviour of hydrogalvinoxyl in polyolefins during melt processing as well as in thermal and photo-oxidation. 2,6,di-tert-butyl, 1,4 benzoquinone has also been found to form during processing of polyolefins with galvinoxyl. It is also suggested that the study of the behaviour of benzoquinone during melt processing and subsequent photo-oxidation is very useful. Examination of other products, if any, formed during processing of polyolefins with galvinoxyl may be necessary in order to put more light into the mechanisms of antioxidant action of galvinoxyl.

It was found that hydrogen iodide and hydroxyl amines are formed during processing and photo-oxidation of polyolefins containing iodine and nitroxyl radicals respectively.

It would be useful to measure the concentration of these species quantitatively during processing and UV irradiation. Formation of alkyl hydroxylamine was not conclusively found either during processing or U.V irradiation of polypropylene containing nitroxyl radicals. Therefore, it is suggested that attempts should be made to synthesise alkyl hydroxylamines (NOR, R= tert butyl or other alkyl groups) and to study the effect of the above compounds as melt, thermal and U.V stabilisers in polyolefins. The effect of the alkyl hydroxylamines in model compounds as well as thermal and U.V stability of the compounds should be studied in detail.

It would be also interesting to study the effect of a cuprous salt on the melt processing and subsequent photo-oxidation of polyolefins.

REFERENCES

1. G Scott, Europ, Polym J, Supp, p 189, (1969)
2. W L Hawkins in (Polymer Stabilisation), ed, p3, Wiley Interscience, New York (1972)
3. F J Golemba, J E Guillet, SPE Journal, 26, 88 (1970)
4. H P Frank, H Lehner, J Polym, Sci, 31C, 193, (1970)
5. G Scott, Macromolecular Chem, IUPAC, 8, 319 (1972)
6. J E Guillet, J Dhaney, F J Golemba, G H Hartley, Adv. in Chem, 70, (1969)
7. G Scott, Atmospheric Oxidation and Antioxidants, Elsevier, London & New York (1965) Chap. 2.
8. J L Bolland and G Gee, Trans. Faraday Soc., 42, 236-244 (1946)
9. J L Bolland, Trans. Faraday Soc., 44, 669 (1948)
10. J L Bolland, Quart Rev, 3, 1 (1949)
11. J D Holdsworth, G Scott, D Williams, J. Chem Soc, 4692 (1964)
12. G Scott, J. Polymer Sci, Symp, 57, 357 (1976)
13. G Scott, Chem in Britain, 9,267 (1973)
14. M U Amin, G Scott, Europ Polym J, 10,1019 (1974)
15. A Ghaffar, A Scott, G Scott, Europ Polym J, 13, 83 (1977)
16. M U Amin, G Scott, L M K Tillekeratne, Europ Polym J, 11, 85 (1975)
17. D C Mellor, A B Moir, G Scott, Europ Polym J, 9,

219 (1973)

18. A Ghaffar, A Scott, G Scott, Europ Polym J, 11, 271 (1975)

19. G Scott in (Polymers and Ecological Problems) ed E Guillet, p 27, Plenum Pub Corp, New York (1976)

20. C H Chew, L M Gan, G Scott, Europ Poly J, 13, 361 (1977)

21. D J Carlsson, D M Wiles, Macromolecules, 2, 597, (1969)

22. D J Carlsson, A Garton, D M Wiles, Macromolecules, 9, 695 (1976)

23. D J Carlsson, D M Wiles, J Polym Sci, 12, 2217 (1974)

24. D J Carlsson, D M Wiles, J Macromol Sci, Rev, Macromol Chem, C 14, (2) 155 (1976)

25. D J Carlsson, T Suprunchuk, D M Wiles, J App Polym Sci, 16, 615 (1972)

26. J R Shelton, in (Polymer Stabilisation) (ed Hawkins) p 31, Wiley Interscience, New York (1972)

27. K B Chakraborty, G Scott, Europ Polym J, 13, 731 (1977)

28. K B Chakraborty, G Scott, Polymer, 18, 98, (1977)

29. L Bateman and A L Morris, Trans Faraday Soc, 49, 1026 (1953)

30. J L Bolland, Trans Faraday Soc, 46, 358 (1950)

31. G Scott, Atmospheric Oxidation and Antioxidants, Elsevier, London and New York (1965) Chapter 10.

32. N K Baramboim, Mechano, Chemistry of Polymers P.B (ed, W F Watson), MacLaren and Sons Ltd, London (1964)

33. Fred W Bilmyer, J R, text book of Polym Sci, p 212, Wiley & Sons, London, second edition (1971)

34. L Bateman, The Physico Chemistry of Rubber Like Materials, p 460, MacLaren (1963)

35. R J Ceresa and W F Watson, J App, Polym Sci, 1, 101 (1959)

36. W F Watson, M Pike, J Polym Sci, 9,229 (1952)

37. W F Watson, Trans, IRI, 29, 32, (1953)

38. S E Bresler, S N Zhurkov, E M Kazbekov, E M Samiskii and E E Tomashevskii, Rubb Chem Tech, 33, 462 (1960)

39. K B Chakraborty, Ph.D thesis, Aston University (1977)

40. Junkichi Sohma, in Development in Polymer Degradation - 2 (ed, by N Grassie) App Sci, pub (London) Chapter 4, p 99 (1979)

41. G Scott, M Tahan and J Vyvoda, Chem and Ind, 903 (1976)

42. G Scott, M Tahan and J Vyvoda, Europ Polym J, 14, 377 (1978)

43. G Scott, Polym Plast Tech, Eng, 11, 1 (1978)

44. B Cooray and G Scott, Polymer Degradation and Stability, 3, (No 2), p 127 (1981)

45. Reference 7, Chapters 4 and 5

46. J C Ambelang, R H Kline, J R Shelton, Rubber Rev, Rubb Chem Tech, 36, 1497 (1963)

47. P Kovacic, F W Koch, J Org Chem, 28, 1864 (1963)
P Kovacic, L Husus, J Poly Sci, Part A-4,5 (1966)

48. M A Plant, G Scott, Europ Polym J, 7, 1173, (1971)

49. N C Billingham, P D Calvert, P Prentice, T G Ryan, The Weathering of Plastics and Rubbers, in Symp, E1, 1, London (1976)

50. W L Hawkins, F H Winslow, J App Polym Sci, C,No 4, 29 (1967)

51. W L Hawkins, W Matreyek, F H Winslow, J Polym Sci, 41, 1 (1959)

52. Reference 7, Chapter 4, page 115

53. G Scott, Lecture given at the Prague meeting on Macromolecules, 9 - 12 July (1970)

54. Autoxidation and Antioxidants, N. Y, Inters, Publ, (1961)

55. D A Gordon and E C Rothstein, Poly, Eng Sci, 6, 231 (1966)

56. Reference 7, Chapter 4, page 149.

57. J R Shelton in 'Polymer Stabilisation' ed W L Hawkins,p 66-76, Wiley Interscience (1972)

58. J A Howard and K V Ingold, Can J Chem, 40, 1851, (1962); 41, 1744, 2800 (1963); 42, 2324 (1964)

59. J Pospisil in Development in Polymer Stabilisation - 1 (ed, G Scott) App Sci, publ, London (1979)

60. K Adamic, and K U Ingold, Can J Chem, 47,295 (1969)

61. R Hoskins, J Chem Phys, 25, 788 (1956)

62. O L Harle and J R Thomas, J Am Chem Soc, 79, 2973, (1957)

63. J R Thomas and C A Tolman, J Am Chem Soc, 84, 2930, (1962)

64. K Adamic, C Dunn and K U Ingold, Can J Chem, 47, 287 (1964)

65. J R Thomas, J Am Chem Soc, 82,5955 (1960)

66. A T Koriiskii and A F Lukovonikov, Dokl, Akad, Nauk, SSSR, 147,1126 (1962)

67. J C Baird and J R Thomas, J Chem Phys, 35, 1507 (1961)

68. C D Cook, J Org Chem, 18, 261 (1953)

69. C D Cook and R C Woodworth, J Am Chem Soc, 75, 6242 (1953)

70. M S Kharasch and B S Joshi, J Org Chem, 22,1435 (1957)

71. P D Bartlett and C Rüchardt, J Am Chem Soc, 82, 1756 (1960)

72. P D Bartlett and T Funahashi J Am Chem Soc, 84, 2595 (1962)

73. D Kearns and S Ehrenson, J Am Chem Soc, 84, 739 (1962)

74. Review: E R Altwicker, Chem Rev, 67, 475 (1967)

75. G M Coppinger, Tetrahedron, 18, 61 (1962)

76. O Neunhoeffer and P Heitmann, Chem Ber, 96, 1027 (1963)

77. E Müller, H Eggensperger and K Scheffler, Ann Chem, 658,103 (1962)

78. E Müller, H Eggensperger and K Scheffler, Ann Chem, 645, 79 (1961)

79. Review: A I Scott, Quart Rev, (London), 19, 1 (1965)

80a. Review: W A Waters, Progr Org Chem, 5, 26-45 (1961)

80b. J K Becconsall, S Clough and G Scott, Proc. Chem Soc, 308 (1959)

81. Review: B S Thyagarajan, Chem Rev, 58, 439 (1958)

82. D Johnson, M Rogers and G Trappe, J Chem Soc, 1093 (1956)

83. M Rogers, J Chem Soc, 2784 (1956)

84. C Brown and M Rogers, British Patent 850418 (1960) Chem Abstr, 55, 6498 (1961)

85. R M Dupeyne and A Rassat, J Am Chem Soc, 88, 3180 (1966)

86. A L Buchachenko and O P Sukhanova, zh. Strukt Khim, 6, 32 (1965)

87. K Adamic and K U Ingold, Can J Chem, 47, 281(1969)

88. A R Forrester and R H Thomas, Nature, 74, 203 (1964)

89. T A B M Bolsman, A P Blok and J H G Frijns, J Royal, Netherland, Chem Soc, 97/12, 313 (1978)

90. G A Kovtun, A L Aleksandrov and V A Golubev, Bull Acad Sci, USSR, 2115 (1974)

91. A K Hofman, A M Fieldman, E Gelblum and W G Hodgson, J Am Chem Soc, 86, 639 (1964)

92. Reference 7, page 39 et seq.

93. L Bateman and G Gee, Proc Roy Soc, A195, 376, 391 (1948-9)

94. Reference 92, page 88.

95. W L Hawkins and Mrs H Sautter, J Polym Sci, A1, 3499 (1963)

96. E A Oberright, S J Leonardi and A P Kozacik, Additives in Lubricants Symposium, ACS, Div Pet Chem, Atlantic City, 115 (1958)

97. G H Denison and P C Condit, Ind Eng Chem, 37, 1102 (1945), 36, 477 (1944), 41, 949 (1949)

98. Reference 92, chapter 6.

99. L Bateman, Chemistry and Physics of Rubber-Like Substances (ed), p 641 et seq, MacLaren (1963)

100. G W Kennerly and W L Patterson, Ind Eng Chem, 48, 1917 (1956)

101. Brit Pat, 779, 825; U S Pat, 2, 820, 011

102. Brit Pat, 822, 655, 841, 348, U S Pat, 2, 794, 780, 2, 794, 821, 2, 824, 836, 2, 837, 549, 2, 828, 555

103. M T Leffter, U S Pat, 2, 579, 679

104. Hercules, Powder, Co. Brit, Pat, 851, 670

105. N P Neureiter and D E Bown, Ind Eng Chem, (Prod. Res and Dev), 1, 236 (1962)

106. References 34 and 99

107. D Barnard, L Bateman, E R Cole and J I Cuneen, Chem and Ind, 918 (1955)

108. N U Mikhailov, L G Tokareva and A G Popov, Polym, Sci, USSR, 4, 805 (1963)

109. G Scott, Chem Comm, 1572 (1969)

110. G Scott, Mechanisms of Reaction of Sulphur Compounds, 4, 99, (1969)

111. G Scott, P A Shearn, J App Pol Sci, 13, 1329 (1969)

112. J R Shelton and K E Davis, Int J Sulphur Chem, 8, (2), 197 (1973)

113. D W Emerson, A P Craig and I W Potts Jr, J Org Chem, 32, 102 (1967)

114. J L Kice and J D Campbell, J Org Chem, 32, 1631 (1967)

115. T Colclough and J I Cuneen, Chem and Ind, 626 (1960)

116. C Armstrong and G Scott, J Chem Soc, 1747 (1971)

117. M J Husbands and G Scott, Eur Poly J, 15, 879-887 (1979)

118. R P R Ranweera and G Scott, J Poly Sci, Poly Lett, 13, No (2), 71, (1975) ibid 12, 825 (1976)

119. B B Cooray and G Scott, Eur Poly J, 17, 233-38 (1981)

120. G Scott, Pure and Appl Chem, 30, 267 (1972)

121. C Armstrong, M A Plant, G Scott, Eur Pol J, 11, 161 (1974)

122. G V Hutson and G Scott, Chem and Ind, (London)

725, (1972), Eur Poly J, 10, 45 (1974)

123. K J Humphris, G Scott, Pure Appl Chem, 36, 163 (1973)

124. M J Husbands and G Scott, Eur Ply J, 15, 249-53 (1979)

125. C Armstrong, Ph.D thesis, Aston University (1971)

126. J P Fortuin and H I Waterman, Chem Eng Sci, 2, 182 (1953)

127. M J Husbands, Ph.D thesis, Aston University (1977)

128. C Armstrong, M J Husbands and G Scott, Eur Pol J, 15, 241 (1979)

129. V M Farzaliev, W S E Fernando and G Scott, Eur Poly J, 14, 835 (1978)

130. L Jirackova, T Jelinkova, J Rotschova and J Pospisil, Chem Ind (London) 384 (1979)

131. A J Bridgewater and M D Sexton, J Chem Soc, Perkin II, 530 (1978)

132. D Wight, W Chasar, Polym Degradation and Stability, Int J App Sci, pub, 121-25, (1981)

133. G Brunton, B C Gilbert and R J Mawby, J Chem Soc, Perkin II, 1267 (1976)

134. K J Humphries and G Scott, J Chem Soc, Perkin II, 831 (1973), 617 (1974) and 826 (1973); Pure and App Chem, 36, 163 (1973)

135. G V Hutson and G Scott, J Polym Sci, C40, 67 (1973)

136. G Scott, S, Afr J Chem, 32, 137-146 (1979)

137. K B Chakraborty and G Scott, Eur Polym J, 13, 1007 (1977)

138. K B Chakraborty and G Scott, Chem Ind (London) 237 (1978)

139. Reference 7, chapter 3, page 92.

140. W L Hawkins, Polym En g and Sci, 5, 196 (1965)

141. Z M Trozzolo in Polymer Stabilisation (ed W L Hawkins) p 159 et seq, Wiley Interscience, New York (1972)

142. G Scott, Chem and Ind, 7, 271 (1963)

143. D J Carlsson and D M Wiles, Macromolecules, 7, 259 (1974)

144. D J Carlsson and D M Wiles, J Radiation Curing, 2 (4), 2 (1975)

145. D M Wiles and D J Carlsson, Polym Deg and Stability, Inter J App Sci, pub, 3, 61-72 (1980-81)

146. H C NG and J E Guillet, Macromolecules, 11, 937 (1978)

147. G Geuskens and C David, Pure Appl Chem, 51, 233 (1979)

148. G Scott, in Ultraviolet Light Induced Reactions in Polymers, S S Labana, ed, Washington, A.C.S Sym Ser (No 25), 340 (1976)

149. G Scott, Coatings and Plastics, pre-prints, Am Chem Soc Meeting, (philadelphia), 35, 1, 163, (1975)

150. C H Bamford and R G W Norish, J Chem Soc, 1504 (1935)

151. J E Guillet and R G W Norish, Proc Roy Soc, 233, 153 (1955)

152. F H Winslow, W Matreyek and A M Trozzolo, ACS Poly, pre-prints, 10, (2), 1271 (1969)

153. M L Kaplan and P G Kelleher, J Poly Sci, Part B, 9, 563 (1971)

154. A M Trozzolo and F H Winslow, Macromolecules, 1, 98 (1968)

154a. O Cicchetti, Adv Polym Sci, 7, 70 (1970)

154b. B Stevens and B E Algar Ann NY Acad Sci, 171, 50 (1970)

155. J Durmis, M Karvas, P Caucik and J Holcik, Eur Polym J, 11, 219 (1975)

156. J P Guillory and C F Cook, J Polym Sci, A1, 9, 1529 (1971)

157. D J Carlsson, T Suprunckuk and D Wiles, J Am Chem Soc, 94, 8960 (1972)

158. J S Zannucci and G R Lappin, Macromolecules, 7, 393 (1974)

159. R P R Ranweera and G Scott, Chem and Ind, 774 (1974)

160. K B Chakraborty and G Scott, Eur Poly J, 15, 35, (1979)

161. G Scott, H H Sheena and A M Harriman, Eur Poly J, 14, 1071 (1978)

162. K B Chakraborty and G Scott, Chem and Ind, 237 (1978)

163. G Scott, J Poly Sci, C57, 357 (1976)

164. K B Chakraborty and G Scott, Poly Deg and Stability, Inter J App Sci, pub, 1, 37 (1979)

165. J C W Chien and C R Boss, J Poly Sci, Al, 10, 1579 (1972)

166. K B Chakraborty and G Scott, Poly Deg and Stability, 1, 37 (1979)

167. G Scott, Pure App Chem, 1980, 52, 365

168. A Garton, D J Carlsson and D M Wiles, in Developments in Polymer Stabilisation - 1, G Scott, (ed) (Chapter 7, (London), Appl Sci, pub (1979)

169. E C Rothstein, J App Polym Sci, 12, 1279 (1968)

170. B W Evans and G Scott, Eur Poly J, 10, 453 (1974)

171. G V Hutson and G Scott, Eur Poly J, 10, 45 (1974)

172. J H Chaudet and J W Tamblyn, J App Poly Sci, 8, 1949 (1964)

173. Y I Temchin, Y F Burmistrov, L A Skripko, R S Burmistrova, Y V Kokhanov, M A Gushehina and E G Rozantsev, Vysokomol Soedin, Ser A, 15, 1038 (1973)

174. Ustilon, J J and Patel A R, Am Chem Soc, Polym prepr, 18, 393 (1977)

175. Allen N S and McKellar, J F Br Poly J, 9, 302 (1977)

176. D J Carlsson, D W Grattan, T Suprunckuk and D M Wiles, J App Polym Sci, 22, 2217 (1978)

177. K B Chakraborty and G Scott, Chem and Ind, 237

(1978)

178. D W Grattan, D J Carlsson and D M Wiles, Polym Deg and Stability, 1, 69 (1979)

179. H J Heller and H R Blattmann, Pure App Chem, 36, 141 (1973)

180. D W Grattan, A H Reddoch, D J Carlsson and D M Wiles, J Polym Sci, Poly Letters, Ed, 16, 143 (1978)

181. M V Sudnik, M F Romantsev, A B Shapiro and E G Rozantsev, Izv Akad Nauk, SSSR, Ser Khim, 2813 (1975)

182. E G Janzen, Top Stereochem, 6, 177 (1971)

183. J A Howard, Advances in Free Radical Chemistry, 4, 49 (1972)

184. K J Murayama, Synth, Chem, JPn, 29, (4) (1971)

185. K Murayama, S Marimura and T Yoshioka, Bull Chem Soc, Jpn, 42, 1640 (1969)

186. E T Denisov, International Symposium on Degradation and Stabilisation of Polymers, Brussels (September 11-13, 1974), Prepr, p 137.

187. Y B Shilov and E T Denisov, Vysokomol, Soed, A16, 2313 (1979)

188. M V Sudnik, M F Rozantsev, A B Shapiro and E G Rozantsev. Bull Akad Sci, USSR, 2706 (1976)

189. G Scott and M F Yusoff, Polym Deg and Stability 2, 309-319 (1980)

190. G Scott, (ed), in Development in Polymer Stabilisation - 1, App Sci, pub, (London) 309 (1979)

191. G Scott, Plastic and Rubber: Processing, 41 (1977)

192. G Scott and M F Yusoff, Eur Polym J, 16, 497-501, (1980)

193. W S E Fernando, Ph.D thesis, Aston University (1976)

194. F D Greene and W Adam, J Org Chem, 28, 3550 (1963)

194a. T J Henman, Developments in Polymer Stabilisation-1, (ed) G Scott, App Sci, pub p 39-99 (1979)

195. E J Raukman, G M Rosen and M B Aboudonia, Synth, Comm, 5, 409 (1975)

195a. E G Rozantsev, V A Golubev, M B Neiman and Y V Kokhanov, Bull Akad Sci, USSR, 559 (1965)

195b. K S Markley, "Fatty Acids" their Chemistry, Properties, Production and Used, Part 2 (edited) Inter Sci, pub, INC, New York, p 722 (1961)

195c. E G Rozantsev and V A Golubev, Bull Akad Sci, USSR, 852 (1966)

196. E G Rozantsev, V A Golubev, M B Neiman and Y V Kokhanov, Bull Akad Sci, USSR, 559 (1965)

197. K T Paul, RAPRA, Bulletin: 26, 29 (1972)

198. RAPRA Members Journal, p 61 et seq, March (1973)

199. K T Paul, RAPRA Members Journal, p 273 et seq, November (1963)

200. British Standard, 2782, 105C, Pt 1 (1965)

201. S G Gallo, H K Wiese and J F Nelson, Ind Eng Chem, 40, 1277 (1948)

202. R Berg and Becker, E Ber, dtSch, chem Ges, 73, 172 (1940)

202. R G W Hollingshead, Oxine and its Derivatives, Volume (IV) London, Butterworths Sci Pub, p 991 and 1205 (1956)

202a. Wesp and Brode, J Am Chem Soc, 56, 1037 (1934)

203. Z Manasek et al, Rub Chem Tech, 36, 532 (1963)

204. W C Geddes, Eur Poly J, 3, 733 (1964)

205. P Bocek, Chem Prumsyl, 17, 439 (1967)

206. J C W Chien and C R Boss, J Poly Sci, Al, 10, 1579 (1972)

207. J P Luongo, J Poly Sci, 42, 139 (1960)

208. E Wing, Instrumental Methods of Chemical Analysis, M C McGraw-Hill, p 82 (1960)

209. M Berson and J C Baird, An Introduction to Electron Paramagnetic Resonance, W A Benjamin, New York (1966)

210. Biological Application of Electron Spin Resonance New York, Wiley (1972)

211. E Muller, A Aierker, K Scheffler and A Moosmayer, Angew Chem, Int, (ed) 5,6 (1966)

212. W D Potter and G Scott, Eur Poly J, 7 p 489 (1971) 5 [illegible] eHC

213. S J Wyard, J Scient Instrum, 42, 769 (1965)

214. J A Brydson, Plastics Materials, Third Edition, London, Newnes-Butterworths, (1975)

215. G Natta, Macromol Chem, 16, 213 (1955)

216. C Y Liang, M R Lytton and C J Boone, J Poly Sci, 47, 139, (1960)

217. K Abe and K Yanagisawa, J Poly Sci, 36, 536 (1959)

218. T M Yazawa, J Poly Sci, C7, 59 (1964)

219. W Heinen, J Poly Sci, 38, 545 (1959)

220. J P Luongo, J App Polym Sci, 3, 302 (1960)

221. Morison and Boyd, Organic Chemistry, 3rd Edition, Allyn and Bacon, Inc, Boston, London, Sydney (1973)

222. V A Radtsig and P Y U Butyagin, Polym Sci, USSR, 9:12, 2883 (1967)

223. B R Loy, Physical Research Laboratory, the Dow Chemical Company, Midland, Michigan, J Polym Sci, A1, 2251 (1963)

224. W Kauzmen and H Eyring, J Am Chem Soc, 62, 3113 (1940)

225. S N Zhurkov, V A Zakrevskii and E E Tomashevskii, Soviet Phys, Solid State 6, 1508 (1964)

226. S E Bresler, S N Zurkov, E N Kazbekov, E M Saminskii and E E Tomashevskii, Soviet Phys Tech Phys, 4, 321 (1962)

227. P Yu Butyagin, V F Drozdovskii, D R Ruzgen and I V Kolbanov, Soviet Phys, Solid State, 7, 757 (1965)

228a. P D Bartlett and T Funahashi, J Am Chem Soc, 84, 2596 (1962)

228b. P D Bartlett, B H Gontarev, and H Sakurai, ibid, 84, 3101 (1962)

228c. F D Greene, W Adam and J E Cantrill, ibid, 83 3461 (1961)

229. G M Coppinger, J Am Chem Soc, 79, 501 (1957)

230. B S Joshi, Chem Ind, 525 (1957)

231. A L Alexandrov, V V Kharitonov, E T Denisov, J

Fizicheskoi Khimii, 44, 1122 (1970)

232. G Scott, in Developments in Polymer Stabilisation - 4, (Edited by G Scott) App Sci, pub, London (1981)

233. A R Forrester, J M Hay and R H Thomson, Organic Chemistry of Stable Free Radicals, Acad Press (London, New York), p 224 (1968)

234. N S Allen, Polymer Degrad and Stab, 2, (No 3), 179 (1980)

235. K B Chakraborty and G Scott, Polymer, 21, 252 (1980)

236. T A B M Bolsman, A P Blok and J H G Frijns, Rec Trav Chem, Pays, Bas, 97, 313 (1978)

237. A A Katbab and G Scott, Eur Poly J, 17, 559 (1981)

238. D W Grattan, D J Carlsson, J A Howard and D M Wiles, Canad J, Chem, 57, 2834 (1979)

239. Reference 214, Chapter 10, p 189.

240. F M Rugg, J J Smith and L H Waterman, J Polym Sci, 11, 1 (1953)

241. F Rasti, G Scott, Eur Poly, J, 16,1153(1980)

242. K B Chakraborty and G Scott, Polymer, 21, 252 (1980)

242a. E S Huyser, Free Radical Chain Reactions, Wiley-Inter, Science,New York,London, p 115 (1970)

243. D J Carlsson, D Grattan and D M Wiles, In Developments in Polymer Stabilisation - 1 (ed G Scott)

App Sci, pub, p 219 (1979)

244. V Ya Shlyapintokh and V B Ivanov, in Developments in Polymer Stabilisation - 5 (ed G Scott), App Sci, pub, in press.

245. D W Grattan, D J Carlsson, J A Howard and D M Wiles, Canad J Chem, 57, 2834 (1979)

246. F J Golemba and J E Guillet, Macromolecules, 5, 63 (1972)

247. G H Hartley and J E Guillet, Macromolecules, 1, 165 (1968)

248. W H R Chardson, J Am Chem Soc, 88, 975 (1966)

249. K W S Kularatne and G Scott, Europ, Polym, J, 14, 835 (1978)

250. G Scott and M F Yusoff, Polymer Degradation and Stability, App Sci, pub, 3, 13 (1980-81).

251. F M Rugg, J J Smith and R C Bacon, J Polym Sci, 13, 535 (1954)

252. J P Luongo, J Polym Sci, 42, 139 (1960)

253. Zenjiro Osawa, Norio Kurishu and Hideyuki Kuroda, Poly Deg and Stab, App Sci, pub, 3, No 4 July 1981

254. F Albert Cotton and Geoffrey Wilkinson, Advanced Inorganic Chemistry, A Wiley-Inter Science Publication, New York (4th edition), p 814 (1980)

255a. N S Allen, J L Gardette and J Lemaire, Poly Deg and Stability, 3, 199 (1981).

255 J Sohma and T Kudo, The 27th Polymer Symposium,

(Kyoto), The Soc of Polymer Sci, Japan (1978)

256. J Sohma, M Sakaguchi, J Polymer Sci, Part A-2 13, 1233 (1975)

257. J Sohma and M Sakaguchi, Adv Polym Sci, 20, 111 (1976)

258. E T Denisov, in Developments in Polymer Stabilisation - 3 (ed G Scott) London, App Sci, pub, p 1 (1980)

259. A S Kuzminskii, M S Kavun, V P Kipitchev, (Physico-chemical Trends of Preparation, Processing and Application of Elastic Plastics, (1976) Khimia, Moscow

260. B S Joshi, Chem Ind, p 525 (1957)

261. J C McGowan and T Powell, J Chem Soc, p 238 (1960)

262. A Katbab and G Scott, unpublished work.

263. F Gugumus in Developments in Polymer Stabilisation - 1 (ed G Scott), App Sci, pub p 261 (1979)

264. D K C Hodgeman, J Polym, Sci, Polym, Chem, Ed 18, 533 (1980)

265. D J Carlsson, K H Chan, D M Wiles, J Polym Sci, Poly Letters Ed, 18, 607 (1980)