STABILISATION OF POLYPROPYLENE USING POLYMER-BOUND ANTIOXIDANTS

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SUMMARY

A variety of hindered phenol and hindered piperidine antioxidants containing vinyl or vinyline functional groups have been synthesised and some of these were successfully bound to Polypropylene backbone during processing operations in presence of a radical generator.

Up to 20% concentrates were prepared using this technique. Commercially acceptable concentrates (MASTERBATCHES) can only be prepared with antioxidants that are only weakly chain breaking such as hindered piperidines.

One of the antioxidants, AATP was found to polymerise as well as bind to Polypropylene. Bound antioxidants were found to be resistant to such channels of physical loss as solvent extraction. Temperature and concentration of the additive and radical generator were found to be important parameters in the preparation of the concentrates. The stabilising efficiencies of the diluted bound antioxidants alone,and in combination (synergistic) with other antioxidants have been evaluated. Results of both thermal and photo-oxidative stabilities of the bound samples in Polypropylene show that the restriction on free mobility of the bound antioxidants in the polymer has virtually no effect on its stabilising efficiency.
Bound AATP was found to generate nitroxyl radicals during the course of its stabilisation activities, and in combination with a small amount of Irganox 1076,it was shown to be highly synergistic thermally. A mechanism of catalytic phenol regeneration by the resultant piperidine hydroxylamine was proposed.
Although the mechanical properties of the masterbatches were affected by the transformation, this was not found to be carried over to the diluted samples.

This work has shown that bound concentrates can be effectively prepared in saturated polymers for subsequent dilution to normal concentrates used in commercial stabilisation.

Key words

BOUND ANTIOXIDANTS,RADICAL GENERATORS,POLYPROPYLENE,MASTERBATCH, SYNERGISM,HINDERED PIPERIDINES, STABILISATION.

To My Mother, Aminatu and Jummai, My Wife

ACKNOWLEDGEMENTS

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CONTENTS

CHAPTER 1

INTRODUCTION

1.1 POLYMER AUTOXIDATION

The second half of the 20th Century has witnessed the unrelenting dominance of man-made high molecular weight materials termed synthetic polymers in all aspects of human endeavour. The reasons for their success over such "traditional" materials as metals, paper, leather, wood, ceramics etc, are their versatility, cheapness and ease of processing. They were originally used as substitutes but now they are generally recognised to have unique advantages over these traditional materials. These obvious advantages are however limited to varying extents by the susceptibility of polymers to oxidative degradation, primarily by heat and light. Polymeric articles therefore need to be protected if a reasonable service life is to be expected.

Degradation results from oxidative attack in three main circumstances.[1]

I) during processing operations (melt degradation)

II) when the solid polymer is exposed to air at elevated temperatures during use, eg. in under-the-bonnet applications in the automotive industry (thermal oxidation)

iii) when polymer is exposed to both oxygen and sunlight, particularly near u.v. component, (photo oxidation)

As a result of these degradative reactions 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 and physical structure of the polymers, the presence of impurities and the environment to which they are exposed.

1.1.1.DEGRADATION & STABILISATION OF POLYOLEFINS

Most of the degradation problems associated with polyolefins are not intrinsic to the structure of the repeat unit, but arise from adventitious impurities which could, at least in principle, be eliminated. Inpractice, the solution to the problem is to incorporate additives in the polymer to eliminate or retard some of the undesireable reactions that bring about macromolecular breakdown. Additives that perform this function in polymers during service are normally called ANTIOXIDANTS. [2]

Typical commercial polyolefins may contain added dyes and pigments, catalyst residue from polymerisation, hydroperoxides, carbonyl groups and other oxidation products.[3,4] Additionally, they may contain traces of polynuclear aromatics from polluted urban atmospheres. Polymer-oxygen charge transfer complexes[3,5] and singlet oxygen [6] produced by the photoinitiation action of

pigments have been implicated as photoinitiators. All of the factors mentioned above, can be important in particular cases but attention has been focussed on hydroperoxides and carbonyl groups.[1,3,7,8,]

Carbonyl groups have been widely implicated because they have higher extinction coefficients in the near uv than do hydroperoxides.[1]

However, the quantum efficiency for radical production by $\rangle C{=}O$ groups is extremely low, probably because macroradicals are produced in the solid polymer and recombine within the cage before they can react with oxygen. In contrasts, hydroperoxides are weaker u.v. absorbers but decompose on excitation with virtually 100% efficiency to yield radicals, one of which is mobile enough to diffuse away very rapidly. They are therefore the favourite candidates as the major initiating impurities in most situations.[2,9,10]

1.1.2 INITIATION BY MACRO HYDROPEROXIDES

The mechanism of hydroperoxide initiation was originally proposed, primarily as a result of studies on polyunsaturated polymers.[10,11]

It is now accepted as applicable to most hydrocarbon polymers and organic compounds. In all cases, hydroperoxides are considered to play a key role in the initiation steps of the oxidative chain reactions.

Mounting evidence provided by several workers over the last two decades has left very little doubt about the initiating role of macro hydro-peroxides.[12-31]

The generalised reaction scheme for the oxidative degradation or autoxidation of polymers is as follows.

Initiation

$RH+O_2 \longrightarrow R^{\cdot} + {}^{\cdot}OOH$ .....(1)

$ROOH \xrightarrow{h\nu} RO^{\cdot} + {}^{\cdot}OH$ .....(2) or

$2ROOH \longrightarrow ROO^{\cdot} + RO^{\cdot} + H_2O$.....(3)

Propagation

$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$.....(4)

$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$ .....(5)

Termination

$2ROO^{\cdot} \longrightarrow$)

$ROO^{\cdot} + R^{\cdot} \longrightarrow$ } INERT PRODUCTS .....(6)

$2R^{\cdot} \longrightarrow$ }

It is now generally accepted that both photodegradation and thermal oxidative degradation involve the same free-radical mechanism.[32,33] The main difference lies in the nature and rate of the initiation step, which is very much faster in

photoinitiation than the bimolecular interaction of hydroperoxides, which is the main process involved in thermal initiation.

Other sources of initiation include transition metal ions, in-chain ketones [34,35] and sensitisation of triplet carbonyl by singlet oxygen [36-39].

1.2. ANTIOXIDANTS & THEIR MECHANISMS OF ACTION

From the sequence of initiation and propagation reactions given above, it is apparent that inhibition of polymer oxidation can be achieved in two or three main ways:

I) by scavenging the reactive radicals formed, thus terminating the kinetic chain (reactions 4&5)

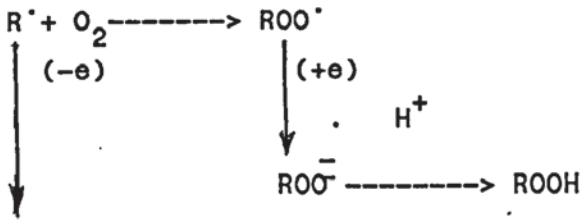
II) by decomposing hydroperoxides formed in a non-radical process, thus preventing initiation (reactions 2&3) and

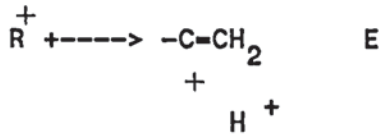
III) by preferentially absorbing the deleterious part of u.v. light by u.v. screeners, also preventing initiation.

1.2.1 THE CHAIN BREAKING (CB) MECHANISM

Free radical oxidation chain reaction in polymers can be interrupted in two ways, either at the alkyl (R$^{\bullet}$) or alkylperoxyl (ROO$^{\bullet}$) radical stage.

Scheme 1.1 is a summary of such a mechanism [40]





Electron Donor mechanism

(CB-D)

Electron acceptor mechanism

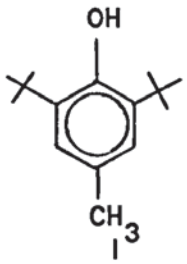
(CB-A)

SCHEME 1.1: Redox mechanism

CB-A mechanism involves the removal of the alkyl radical by an oxidation process to give a carbenium ion or a derived product while CB-D involves the reduction of the alkylperoxyl radical, forming hydroperoxide

1.2.1.1 Chain Breaking (Donor) (CB-D)

Typical antioxidants in this group include hindered phenols (I) and aromatic amines (II).



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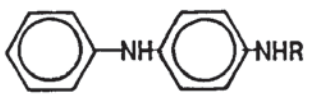
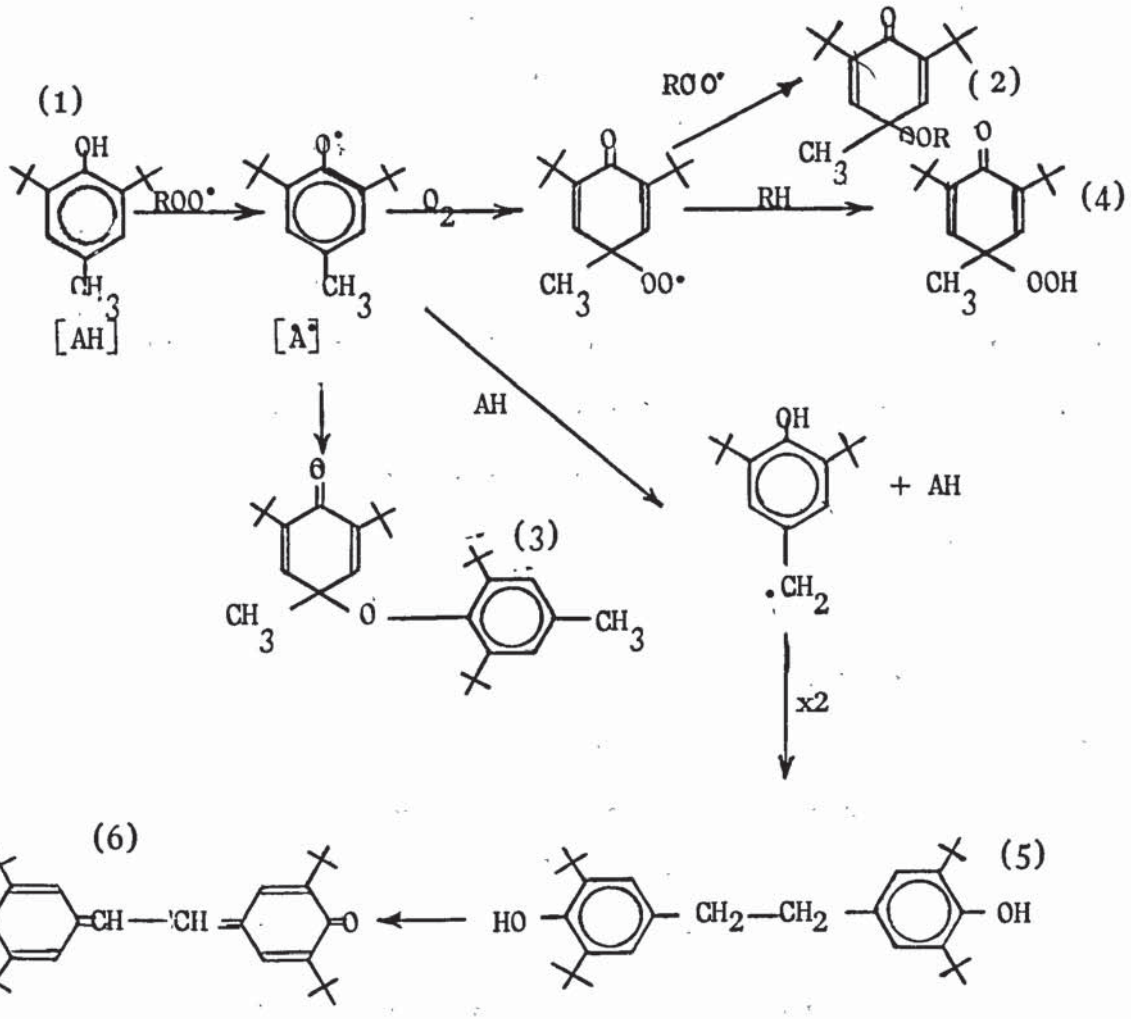


II

Both are able to donate a H atom to an alkylperoxyl radical(ROO·). The products formed by further reaction of the initially formed phenoxyl radical are complex and may have either antioxidant or pro-oxidant activity.

Scheme 1.2 is a summary of a typical hindered phenol reactions and the products formed[2].



SCHEME 1.2 Oxidative transformations of Butylated hydroxytoluene.(BHT)

The stilbene quinone (6) is also an effective antioxidant although it functions by a complementary CB-A mechanism. On the other hand, the peroxydienones (2) and (4) are potential prooxidants due to the presence of a labile peroxide bond. The stilbene quinonoid products are less volatile (increased molecular mass) than the parent phenols and are therefore superior antioxidants where volatility is important.[41] Secondary oxidation products formed from aromatic amines are also very powerful antioxidants [42]

1.2.1.2 Chain Breaking (Acceptor) CB-A

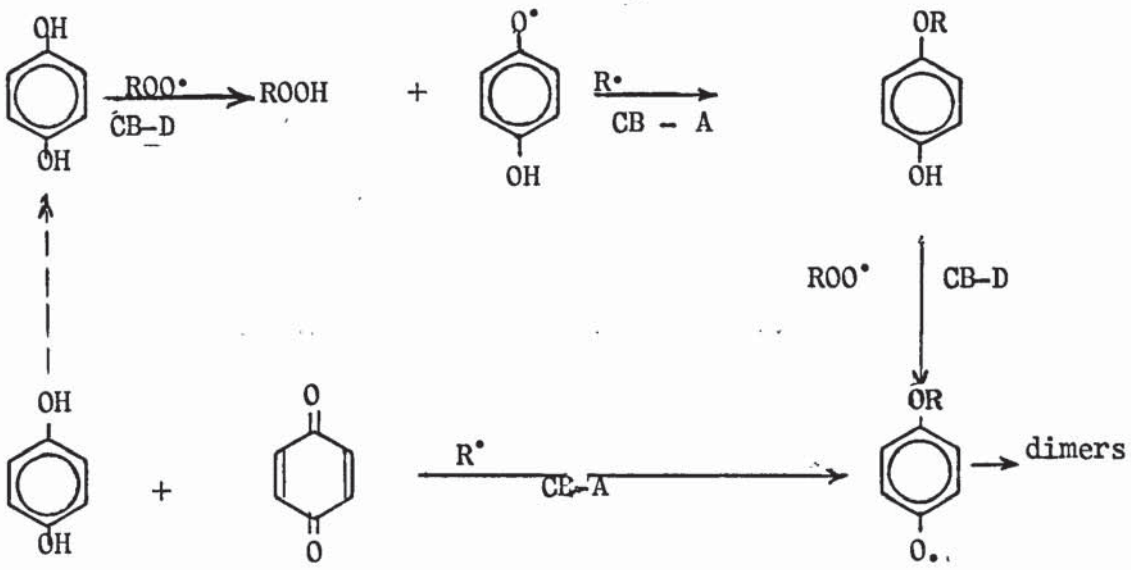
Macroalkyl radicals, unlike alkylperoxyl radicals are not powerful oxidising agents but are themselves readily oxidised by electron acceptors. A variety of oxidising agents are capable of removing alkyl radicals from an autoxidising system, and provided they are able to do this in competition with alkylperoxyl radicals, they have antioxidant activity. In general, the molecular requirement for a CB-A antioxidant are the same as for polymerisation inhibitors. This includes quinones, nitrocompounds and stable free radicals of which nitroxyls[43-48] and phenoxyls[49-51] have been the most studied.

1.2.1.3 Complementary Mechanisms Involving Both CB-D & CB-A

CB-D antioxidants function most effectively in the presence of excess oxygen while CB-A mechanism operates best in oxygen deficiency or at high initiation rates. Antioxidants which exhibit

both kinds of activity clearly have an advantage over those operating by a single mechanism since in most oxidation processes, both alkyl and alkyl peroxyl radicals are present to some extent.

Hydroquinone is the best known example of this type of antioxidants (Scheme 1.3).



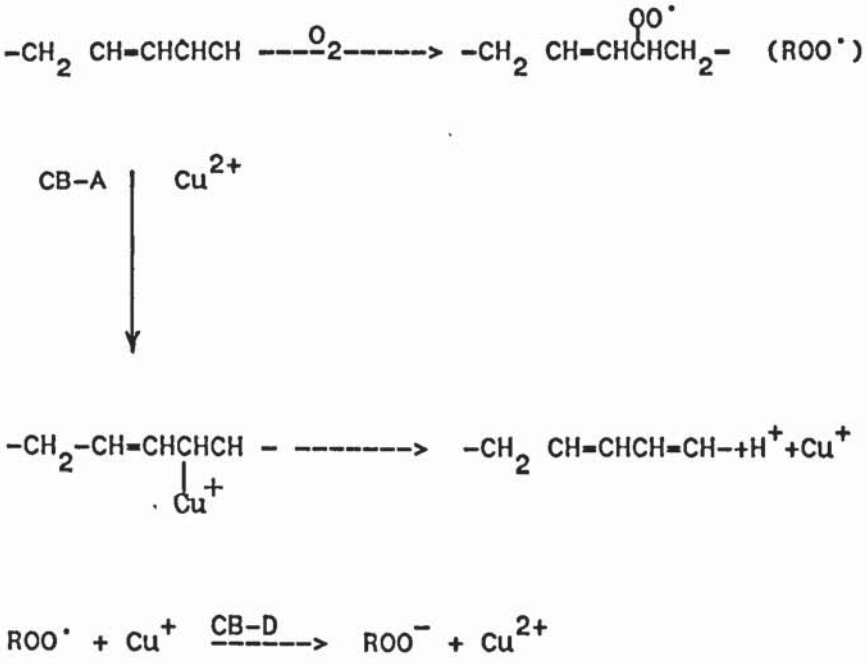
SCHEME 1.3 CB-A/CB-D Mechanism of Hydroquinone

1.2.1.4 Regenerative Chain Breaking Antioxidants

These exhibit catalytic behaviour under conditions where both alkyl and alkylperoxyl radicals are present.[52] The simplest type of catalytic antioxidant is represented by transition metal ions eg.

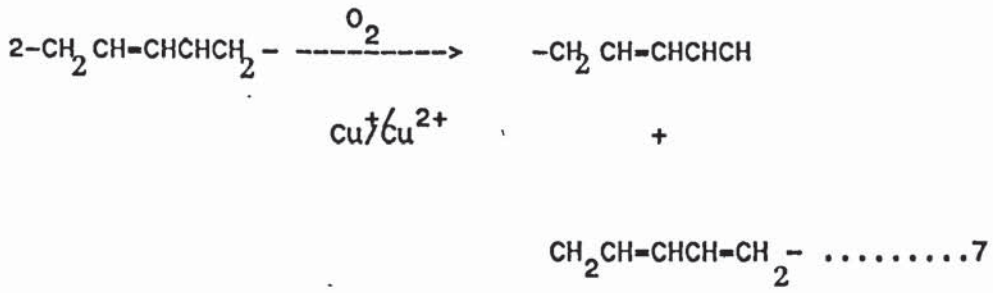
$$Cu^{2+} \underset{-e}{\overset{+e}{\rightleftharpoons}} Cu^{+}$$

The regenerative mechanism (redox) is illustrated in Scheme 1.4



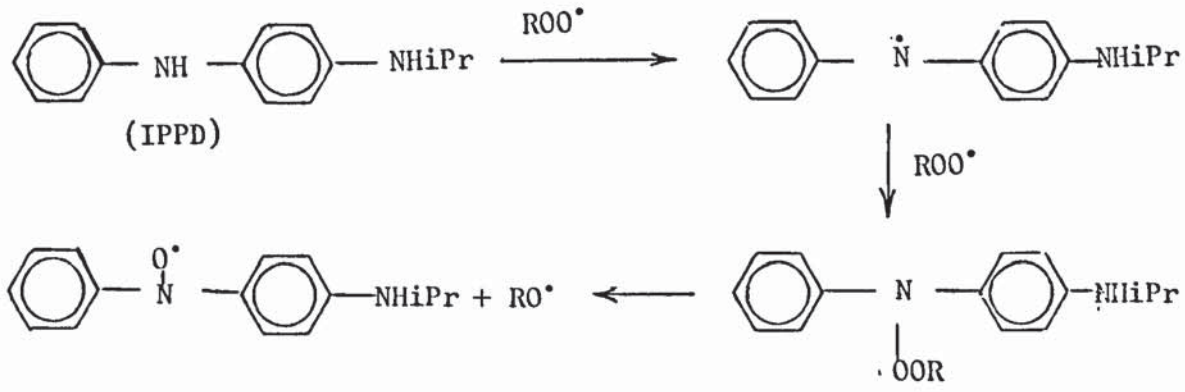
SCHEME 1.4 Regenerative Mechanism

The overall reaction can be summed up as shown in equation 7.

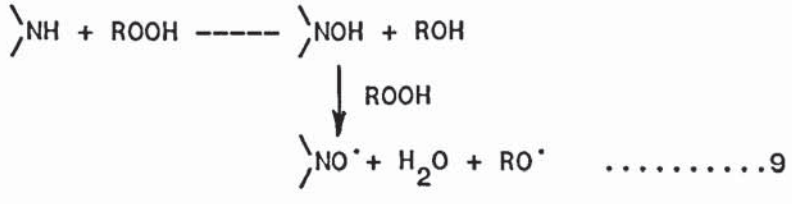


This is of considerable practical relevance to the stabilisation of thermoplastic polymers since Cu^{2+} ions have been found to be effective thermal antioxidants in polyamides and polyesters[53].

Diaryl amines such as N-Isopropyl-N'phenyl-p-phenylene diamine (IPPD) on the other hand, owe their anti-fatigue activity to their conversion to the corresponding nitroxyls.



Hindered aliphatic amines such as bis(2,2,6,6,-tetramethyl-4-piperidinyl) sebacate (Tinuvin 770) behave in the same way although they are less effective as antifatigue agents.[30] In both cases, the parent amines are converted to the corresponding nitroxyl radicals during the mechanochemical process and the concentration of the alkylperoxyl which is intially present falls to an immesurably low value once the nitroxyl radicals begin to be formed in the system.



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The concentration of the nitroxyl then becomes stationary[54] as it converts to hydroxyl amine and its alkyl derivatives.

.....10

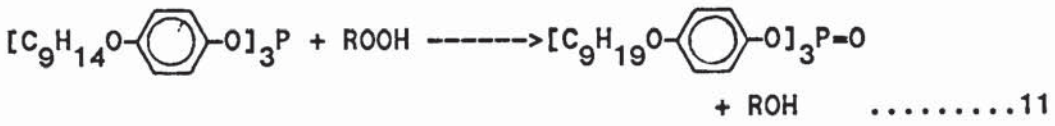
which then acts as a reservoir for nitroxyl radicals.

1.2.2 Peroxide Decomposers (PD)

These fall into two main classes: stoichiometric reducing agents and catalytic peroxide decomposers; (PD-C)

1.2.2.1 Peroxide Decomposers - Stoichiometric (PD-S)

These essentially reduce hydroperoxides to alcohols stoichiometrically, without substantial formation of free radicals. Phosphite esters are examples of such antioxidants, a typical example of which is trisnonylphenylphosphite, which is a commercial stabiliser for raw rubber.



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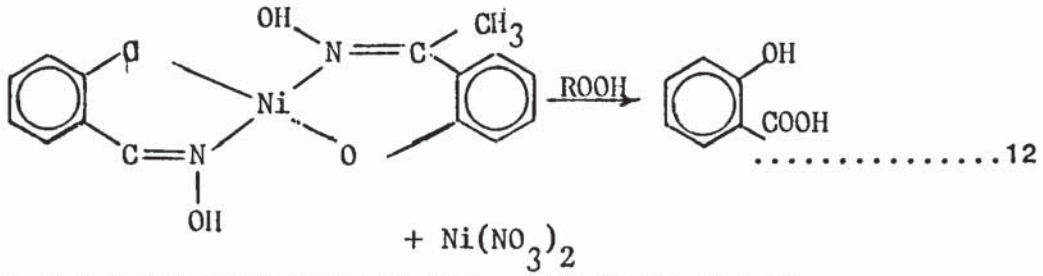
Compounds containing an imino group have also been found to be effective antioxidants. An example is the Nickelphenylhydroxyl imine complex, which consumes 8 molecules of hydroperoxide in being converted to salicylic acid (reaction 12)[30]



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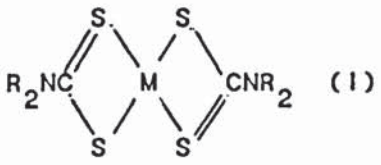
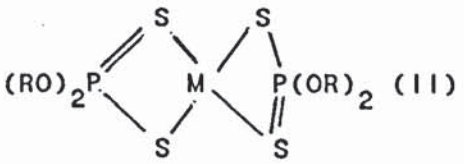
1.2.2.2 Peroxide Decomposers - Catalytic (PD-C)

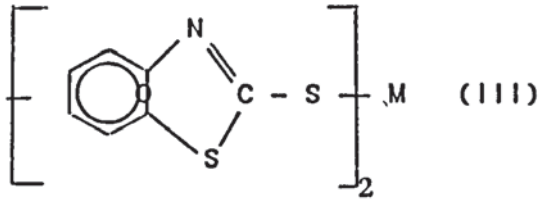
A wide variety of sulphur compounds fall into this class. These compounds have the ability to destroy peroxides through the formation of acidic products in a radical generating reaction involving the hydroperoxide. In all cases, the antioxidant function is preceded by a pro-oxidant stage, and the importance of the pro-oxidant stage is a function of the structure of the sulphur compound.[55] Thus, in the case of the dithiocarbamates[30,56,57,58] (I) the dithiophosphates[55,59,60](II), the mercaptobenzthiazolates[61,62] (III) and the mercaptobenzamidozolates [63](IV), the pro-oxidant effect maybe transient and of no great significance to the long term antioxidant function.



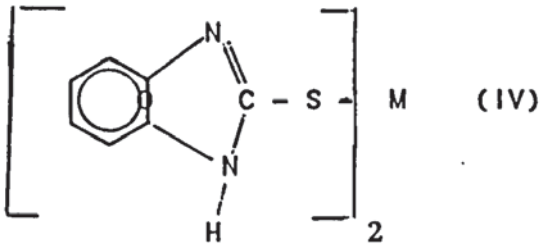
(I)



(II)



(III)

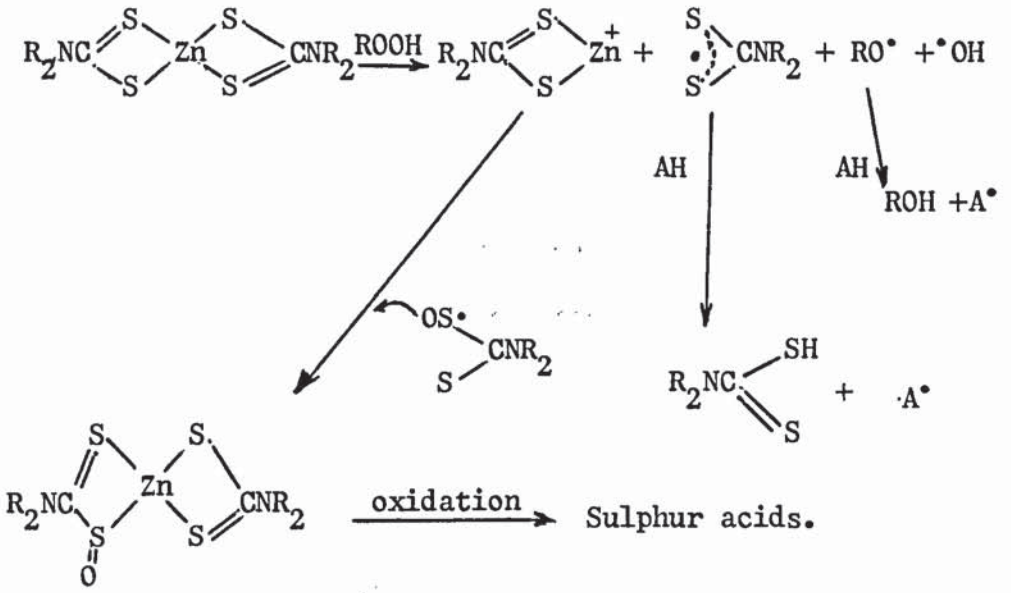


(IV)

In the case of the dialkylsalphides $RSnR^1$(n=1-8) or the diarylsulphides, $RSnR^1$(R,R^1= aryl,n> 1) and the corresponding thiols (RSH), considerable initial pro-oxidant effects are normally observed.[30]

Metal dialkyldithiocarbamates have been used for many years in the plastics industry for both thermal and photostabilisation of polyolefins. Although the steps by which the oxidation inhibition species are generated have not been fully resolved, these stabilising species have been identified as sulphur acids. Recent work[58,64] on the Zn complex, zinc diethyldithiocarbamate now appears to have identified the intermediates, leading to the final oxidation products. However,these intermediates appear to be different from those of analogous Ni II and Fe III complexes[58],at least in model compound studies carried out in this recent work.Two processes were involved; a free radical decomposition of the peroxides, which predominate at molar ratio of 10:1 (CHP/Zn

Complex) and an ionic predominance at higher ratios,although there is a radical contribution at all ratios[58],(Scheme 1.5.).



SCHEME 1.5 Dithiocarbamate Reaction Mechanism

1.2.3 Synergism

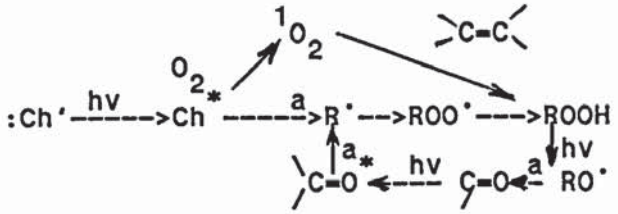
In principle, antioxidants which function by complementary mechanisms should exhibit the phenomenon of synergism. In practice, synergism between CB-D antioxidants and peroxide decomposers has been found to occur in a wide variety of polymers. Combining the two kinds of activity in the same molecule is termed autosynergism. New trends in polymer stabilisation point to a very promising future for this type of antioxidant design.[65]

Homosynergism is the co-operative effect of two mechanistically similar antioxidants of differing reactivity, while

heterosynergism involves two or more antioxidants acting by different mechanisms.

1.2.4 Photo-oxidation & Photostabilisation of Polyolefins

As mentioned earlier, both photo and thermal-oxidative degradation of polymers involve the same free radical mechanism[32,33,66]. The main difference lies in the nature and rate of the initiating step, which is much fasterin photo-oxidation.The key processes in photo-oxidation can best be represented as in Scheme 1.6



'a' indicates processes which can cause backbone scission

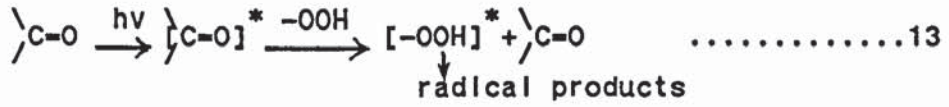
Chromophoric photosensitisation

SCHEME 1.6

An important chromophore (ch) for polymer photodegradation is the hydroperoxide [31] and to a lesser extent, the carbonyl group.

Carlsson and Wiles [15,67] have shown that hydroperoxides formed in polymers during processing and other operations are potentially significant initiators of photo-oxidation of polyolefins [68,69].

They surmised that excited carbonyl species can transfer their energy to hydroperoxide groups according to reaction 13.[70-72]



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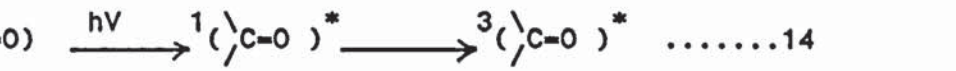
Scott and Co-workers [28,73,74,75] have demonstrated that hydroperoxides formed during processing operations are the main photoinitiators in the early stages of photo-oxidation. In the case of the carbonyl groups either excited singlet or triplet intermediate stages are involved. For chemical purposes, the excited triplet state (formed by intersystem crossing from singlet) is more important than the singlet, since the former has a longer lifetime.



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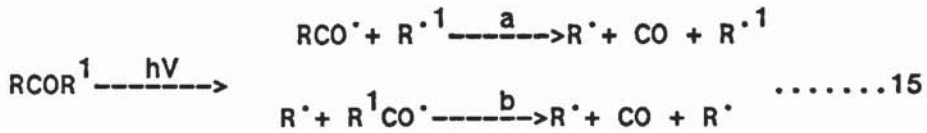
Norrish type I and II reactions are principally involved during the photolysis of aliphatic ketones [76,77]. In the Norrish type I reaction, the bond between carbonyl group and an adjacent carbon is homolytically cleaved producing two radicals.



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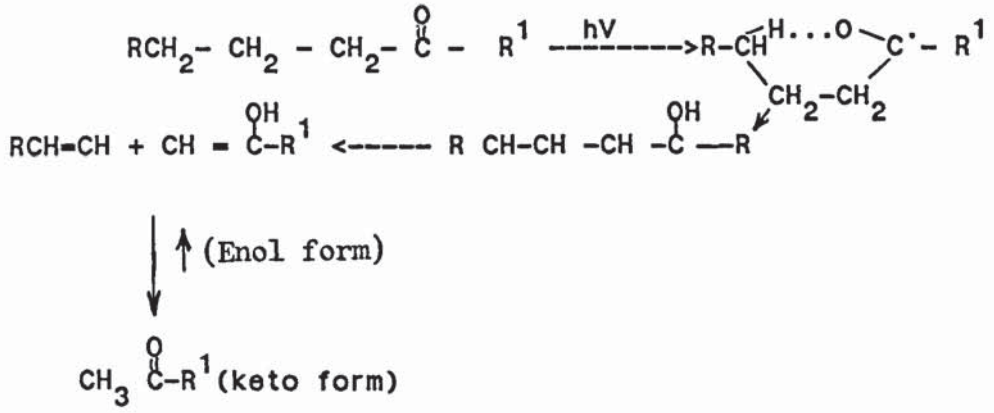
A non-radical intramolecular process which occurs with the formation of a six membered cyclic intermediate is involved in Norrish type II reactions.



Scheme 1.7. Norrish Type II reactions

Although both types I & II lead to scission, only type I has radical products which is therefore the main photoinitiating path.

Direct hydrogen abstraction by an excited triplet carbonyl is also a possible means of intiation [5].

Carlsson & Wiles [7] have concluded in their review that the actual nature of the key chromophore(s) responsible for photo initiation will probably never be unambigiously identified. This is in view of the fact that PP (or PE) samples are seldom identical; the potential chromophoric impurities in a given sample will depend on the conditions of polymerisation and general processing operations as well as deliberately introduced species such as pigments and dyes.

Hydroperoxides undoubtedly play a major part in PP photo-oxidation either from the onset of irradiation or very soon after the start

of oxidation regardless of the photoinitiating species at the early stages.[7,78].

1.3 ANTIOXIDANT SUBSTANTIVITY

1.3.1 Polymer Additive Compatibility

The theory of solution of macromolecular substances is often applied to mixtures of polymers with low molecular mass substances (additives) or to polymer-polymer mixtures. The main factors which determine the effectiveness of stabilisers in polymers, beside the intrinsic behaviour of the stabiliser are solubility, compatibility and permanence.[79-83] The concentration of additive in a polymer is steadily depleted during service primarily as a consequence of chemical reactions of the stabiliser and physical loss (volatilisation) from the polymer. In certain cases, this latter phenomenon may be the major cause of additive disappearance from the system.

For an additive to be effective in its stabilisation function, it must be evenly distributed. Even distribution can only be achieved if the additive is compatible with the polymer. Fertig and co-workers [83] showed the importance of compatibility, to the performance of an additive in a polymer system using polymeric Uv absorbers.

In crystalline polymers such as polyolefins, the distribution of stabilisers is not uniform, owing to the presence of crystalline and amorphous phases.

Low molecular mass compounds (additives) are lodged mainly in the amorphous regions of the polymer. Billingham & co-workers[84-86] investigated the distribution of low molecular mass compounds in different polymers. They found that rejection of the stabilisers into the amorphous regions on the boundaries of spherulites was observed during spherulitic growth. The average concentration in a spherulite was reckoned to be reduced by about 30%.[85]

Such fortuitous preferential distribution of additives in semi crystalline polymers appears to be very advantageous because the amorphous portion of most polymers, especially polyolefins is the region most sensitive to degradation.[87-91]

1.3.2 Additive Volatility

Although typical formulations of an additive in a polymer is usually less than 1% by weight of the additive in most cases, this is enough to produce a supersaturated solution at ambient temperatures. Additives therefore diffuse from the interior of the polymer and are precipitated on the surface. Because they are low molecular mass compounds, they have a measurable vapour pressure

even at this temperature and are easily lost to the environment through a process of blooming and subsequent evaporation.

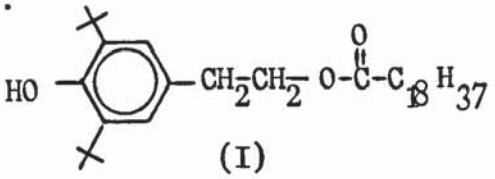
1.3.3 Additive Extractability

The automotive, marine and aerospace industries are making increasing demands on the use of polymeric materials at elevated temperatures out of doors, and in presence of solvents capable of extracting the additives from the polymer.

To meet these challenges of incompatibility, volatility and extractability of additives in polymers, novel methods, some of them empirical have been devised over the last two decades[8] 2,83,92,93

1.3.4 Additive Optimisation

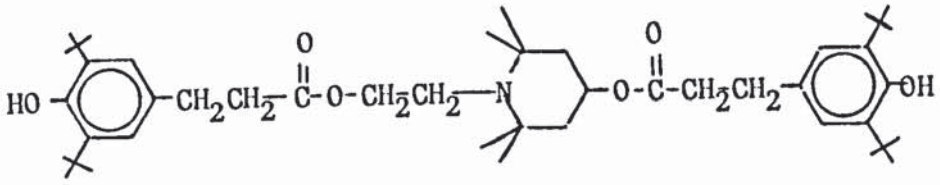
To reduce additive volatility, higher molecular mass compounds were developed to replace their lower molecular mass analogues. A triphenolic antioxidant 1,1,3, Tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane "TOPANOL CA" was designed by ICI while stearyl-B-(3,5-dit-butyl-4-hydroxyphenyl-propionate) (Irganox 1076) (I) and Pentaerythrityl tetrakis (3,5-dit-butyl-4-hydroxyphenyl propionate (Irganox 1010) were chemical products from Ciba Geigy.



(I)

The linear alkyl chain of I was designed to increase compatibility with an esentially non-polar hydrocarbon polymer.

Another technique in stabiliser optimisation is to incorporate more than one, in some cases several stabilising groups in the same molecule, some of them functioning synergistically. SANOL LS -2626 (II) developed by researchers at SANKYO [65] is a good example of an autosynergistic antioxidant incorporating both hindered piperidine and hindered phenol functional groups with both thermal and photostabilising properties.



(II)

Oligomeric and low molecular mass polymeric stabilisers of which SPINUVEX A-36 (III) and Tinuvin 944(IV) are examples, were natural extensions of high molecular mass uv stabilisers, but their use is limited by mobility, solubility and compatibility with polymers.[82]

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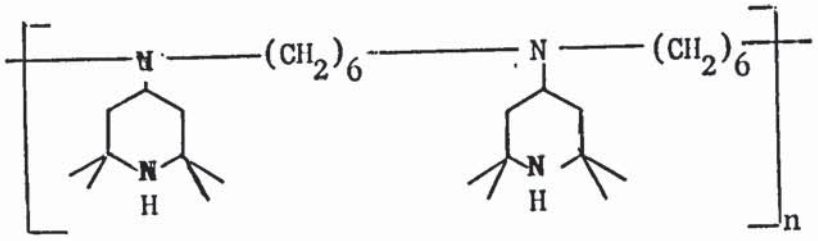
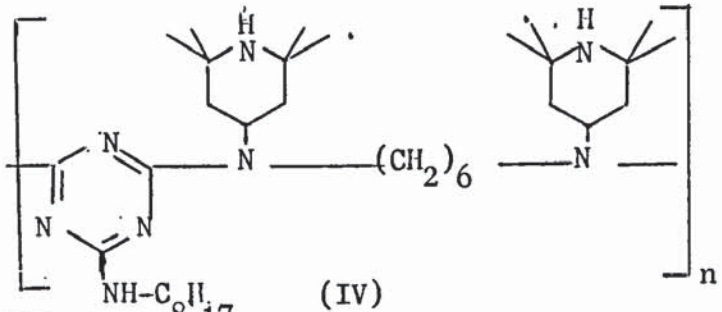


III



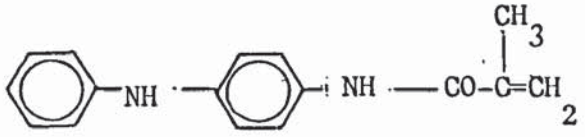
(IV)

1.3.5. POLYMER-BOUND ANTIOXIDANTS

The ultimate solution to antioxidant substantivity is to chemically bind the antioxidant on to the polymer backbone. Polymeric and bound antioxidants do not provide the undesireable characteristics of toxicity, potential carcinogenicity and allergenicity[82,95] and other side effects associated with low molecular mass compounds. But this is only the "icing on the cake" compared to the total non-volatility and non-extractability by solvents.

Antioxidants can be incorporated during polymer synthesis by co-polymerisation of vinyl antioxidants with vinyl monomers.

Workers at Goodyear[95,96] claimed to have successfully emulsion polymerised a vinylic antioxidant of the structure



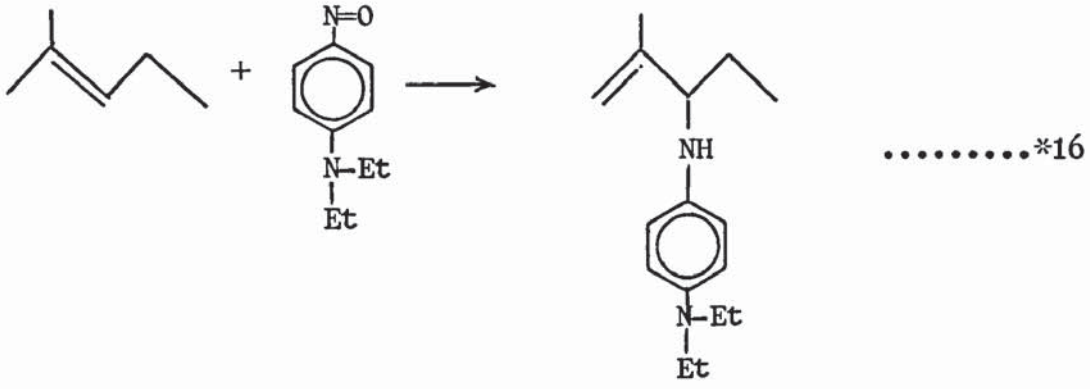
to give antioxidant modified SBRs and NBRs.

However, this method of copolymerisation is not presently commercially attractive, so attention is now directed at chemical binding with an already manufactured polymer.

There are broadly three main approaches to chemical binding, but for convenience, these methods can be classified into eight (8) distinct areas of binding techniques. These will be briefly discussed in the following section.

1. Use of Nitroso Compounds

Cain and Co-workers[97] showed that during vulcanisation, nitroso compounds were successfully bound to natural rubber as evidenced by the high antioxidant activity after the azeotrope extraction process. Based on model compound studies on 2-methylpentene[97,98] N,N-diethyl-p-nitrosoaniline is thought to undergo the following reaction during the vulcanisation of natural rubber.



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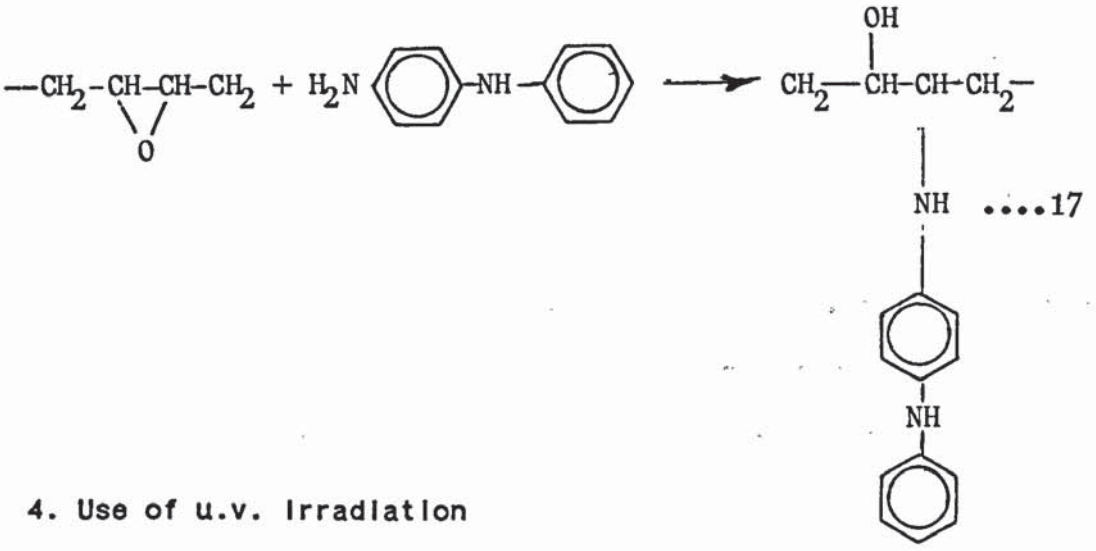
Results of antioxidant effectiveness after binding shows that the reduction in mobility as a result of binding does not significantly reduce its effectiveness. The binding reactions have also been carried out successfully with SBR, NBR and chloroprene rubber[99].

2. Use of Polymerisable Compounds

Polymerisable compounds containing an antioxidant function could be grafted to polymers. Grafted compounds on natural rubber latex include 3,5-di-tert,butyl-4-hydroxybenzyl acrylate (DBBA) and N-(4-anilinophenyl) acrylamide by Cooray[100] and Amarapathy[101].

3. Epoxy Modification of polymer Chains

The principle of this process involves the introduction of a reactive epoxy group into unsaturated polymers. (eg. polybutadiene) and reacting the epoxidised polymer with the additive[102,103].



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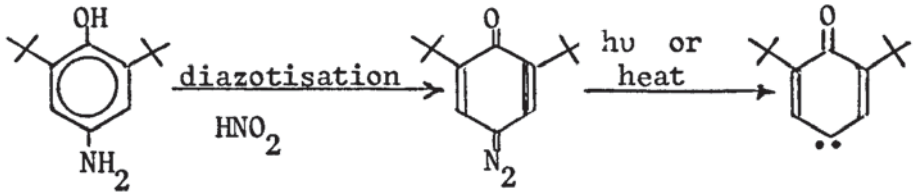
4. Use of u.v. Irradiation

All the methods mentioned so far can only be applied to rubbers and other unsaturated polymers. Saturated polymers such as PP can also be stabilised with a bound antioxidant using a variety of techniques. One of these is the use of u.v. irradiation.

Evans and Scott[94] grafted DBBA onto PP artefact by u.v. irradiation in presence of a benzophenone initiator. Scott and Yusoff[41] also used u.v. irradiation to bind a benzyl mercaptan, BHBM to PP successfully.

5. Use of Reactive Carbene Derivatives of an Antioxidant

The reactive species here is a divalent carbon known as carbene which is obtained by diazotising aniline and subsequent heating or photochemical reaction of the resultant diazooxide into a carbene.



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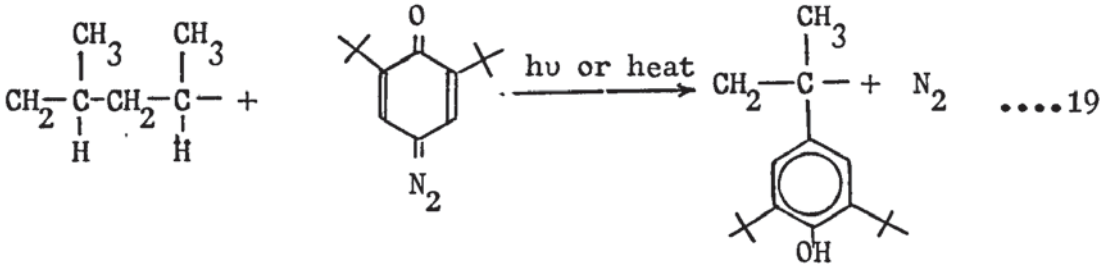
It is known that carbenes can insert themselves into C-H bonds, and it is this reaction which has been exploited by Kaplan & co-workers[104,105] to produce a polymer-bound antioxidant in saturated polymers such as PP.



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It is significant that the binding could be achieved during any heat treatment in the conventional processing of polymers.

6. Use of Mercapto Compounds

A lot of work has been done here by Scott & co-workers[106-120] especially on ABS[114,116,117] SBR[118,120], PP modified EPDM and latterly with polyolefins[121].

Antioxidants containing alphatically linked sulphur, either as free thiol or sulphide can be readily combined chemically with unsaturated rubbers during a shearing operation in a closed internal mixer. This mechanochemical binding process was recently used to bind BHBM and MADA to PP backbone[118].

$$P\ P \longrightarrow 2P^{\cdot}$$

$$ASH + P^{\cdot} \longrightarrow AS^{\cdot} + PH \qquad \ldots\ldots\ldots 20$$

$$P^{\cdot} + AS^{\cdot} \longrightarrow PSA$$

The high extent of binding formed here could not be explained solely on the basis of production of macroalkyl radicals by shear. It was therefore thought that the hydroperoxyl radicals formed initially in the polymer, abstract hydrogen from the polymer chain to give more macro alkyl radicals, which then combine with thiyl radicals to give a bound additive.

$$POO^{\cdot} + P\ H \longrightarrow POOH + P^{\cdot}$$

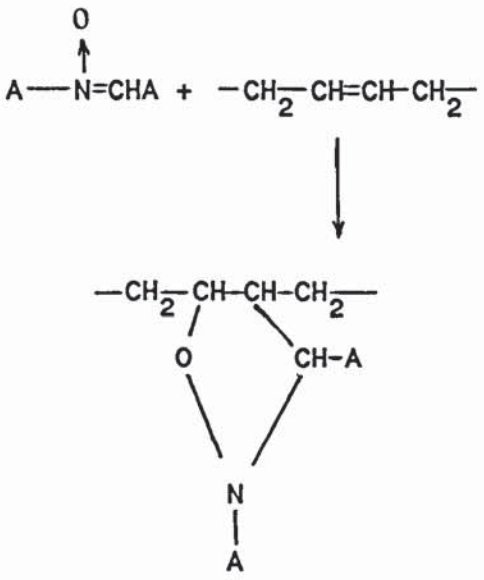
$$POO^{\cdot} + ASH \longrightarrow POOH + AS^{\cdot} \qquad \ldots\ldots\ldots\ldots 21$$

$$AS^{\cdot} + P^{\cdot} \longrightarrow PSA$$

Up to 1.4g in 100g PP of bound antioxidant was obtained using this mechanochemical technique.

7. Use of Nitrones

The 1,3-cycloaddition of nitrones to the double bonds in elastomers provides a general technique for introducing an antioxidant group (A or A') into rubbers. This technique has been successfully applied to cis-polybutadiene and cis-polyisoprene during vulcanisation, using a variety of curing systems[106,120].



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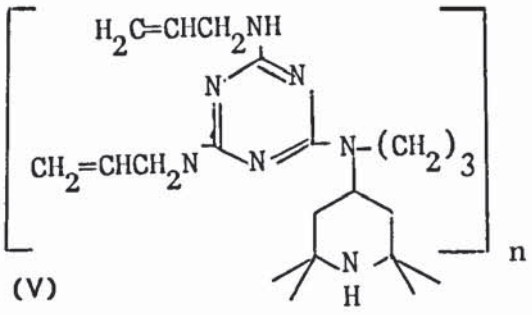
Amine and phenolic nitrones of the structure $R-\overset{O}{\overset{\uparrow}{N}}=CHA$ were found to react readily with rubber during vulcanisation.

8. Using Radical Generators

The use of radical generators to bind antioxidants containing unsaturated groups with saturated polymers is a logical extension of all the above methods. Whether the binding process is mechano-chemical, thermal or UV induced, the technologically useful process taking place is the generation and subsequent reaction of a free radical. If such free radicals can be created in situ in both the antioxidant and polymer substrate without substantial unwanted side reactions, then even higher polymer bound concentrates can be prepared using this technique. This is therefore potentially the most important route to polymer-bound antioxidants.

Researchers at Ciba-Geigy[121] exploited this technique to bind a substantial amount of a triazine derivative (V) containing four ethylinically unsaturated groups on to PE backbone, using dicumyl peroxide as an initiator.



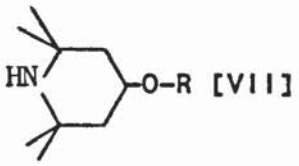
(V)

The mechanical properties (% elongation) of the bound PE were reported to be greatly improved during oven ageing compared to the control.

1.4 MECHANISM OF ACTION OF HINDERED PIPERIDINE UV STABILISERS

Hindered piperidine U.v. stabilisers and related compounds are a new class of light stabilisers that have come into prominance only during the last decade.[65]

They have the general structure [VII].



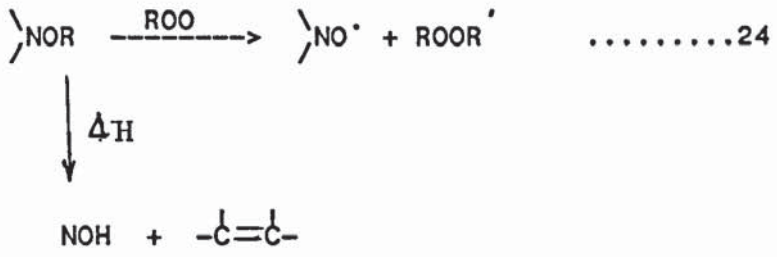
[VII]

They are presently the most widely spread polymer stabilisers found to be effective more especially for polyolefins, but also for polystyrene, polydienes, SBR, ABS, PVC, Polyacetals, polyethers, polyamides and polyurethanes.[122]

The mechanism of action of this class of compounds cannot be discussed separately from that of the related compounds, the stable nitroxyl radicals, their hydroxylamines and ethers. It is known that the amine itself is only a weak antioxidant [30,52] but generates a powerful antioxidant, the stable nitroxyl radical which is an efficient scavenger of alkylradicals [30].

$$\text{>NO}^{\cdot} + \text{R}^{\cdot} \longrightarrow \text{NOR} \qquad \text{.....23}$$

The combination product NOR traps alkyl peroxyl radical and regenerates the nitroxyl radical or otherwise disproportionates, giving an olefin and the hydroxylamine [123].



1.5 BASIC FREE RADICAL CHEMISTRY

Free radical chemistry came into its own as a tool of organic synthesis only during the last 50 years. The accidental synthesis of triphenylmethyl radical by Gomberg,[124] in 1900, probably opened a whole new chapter in "reactive intermediates", although their potential was not realised until long after that discovery.

The class of radical generators of relevance to this work include dialkylperoxides and azo compounds that are stable enough to be handled at ambient temperatures and reactive enough to decompose at greater than 99.9% at normal processing temperatures and times.

1.5.1. Dialkylperoxides

Primary alkylperoxides are unstable. The lowest members (eg dimethylperoxide) are sensitive to shock and are explosive when pure. Ditert-butylperoxide (D^tBP) on the other hand can be distilled at atmospheric pressure, but in the case of peroxides with higher molecular mass, distillation must be carried out under vacuum.

Dialkylperoxides decompose homolytically either thermally or photolytically.

$$ROOR \xrightarrow{h\nu, \Delta} 2RO^{\bullet} \quad .....25$$

The fate of the initially formed alkoxyl radical ($RO^{\bullet}$) depends on the environment, temperature and structure of the R group. In the absence of a substrate, tert-alkyl peroxides give tert-alcohols, ketones and lower hydrocarbons along with epoxides ethers and carbon monoxide.

Tert-alkoxyl radicals, $RO^{\bullet}$ are also efficient hydrogen abstractors.

$$RO^{\bullet} + R'H \longrightarrow ROH + R'^{\bullet} \quad .....26$$

This reaction is extensively utalised in the polymer industry, especially in polyolefin crosslinking[125].

With reactive substrates, thermal or photoinduced decomposition of ROOR offer many synthetic possibilities.

In the gas phase, D^{t}BP decomposes unimolecularly to give tert-butoxyl radicals which fragment further to give ethane and acetone.

$$^{t}Bu\ O\text{-}O\text{-}{}^{t}Bu \longrightarrow 2\ {}^{t}BuO^{\cdot} \longrightarrow 2CH_3^{\cdot} + 2CH_3\overset{O}{\overset{\|}{C}}CH_3 \quad \text{.....27}$$

$$2CH_3^{\cdot} \longrightarrow C_2H_6$$

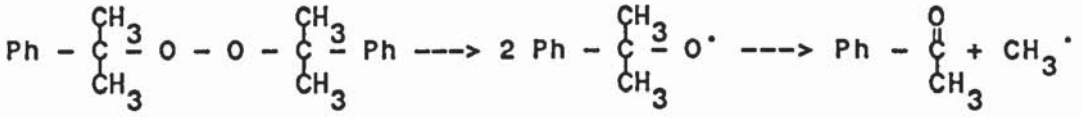
Decomposition in solution often yields ^{t}BuOH, indicating that H atom abstraction by the tert-butoxyl radical from the solvent competes with fragmentation reaction.

$$^{t}BuO^{\cdot} + S\text{-}H \longrightarrow {}^{t}BuOH + S^{\cdot} \quad \text{.....28}$$

where S$^{\cdot}$ is a solvent radical

The ratio of alcohol: acetone indicates the ease of abstractability of H from the solvent[126] . If the solvent is a molten polymer such as PE or PP, then crosslinking or chain scission could be the likely end of the radicals. In presence of a reactive additive, such as a vinyl type antioxidant, a coupling reaction between S$^{\cdot}$ and the additive could result.

Dicumyl peroxide (DCP) decomposes at about the same rate as D^tBP. Fragmentation of the cumyloxyl radicals yields acetophenone, indicating a preference for β-elimination of a methyl radical rather than a phenyl radical.



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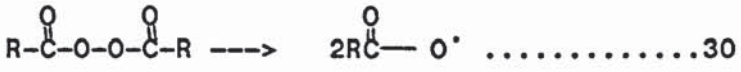
1.5.2. Diacylperoxides

The primary decomposition mechanism, under the same conditions are similar to dialkylperoxides.



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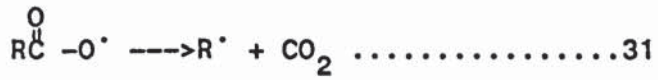
The acyloxyl radicals then fragment to give alkyl radicals and CO_2, in the absence of an easily abstractable hydrogen.



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Acyloxyl radicals, especially the lower homologues resulting from the homolytic cleavage of the peroxide linkage decompose to CO_2 and alkyl radicals more rapidly than they react with the solvent.

Acetic acid is therefore not observed as a reaction product in the decomposition of acetylperoxide in inert solvents[127].

Unimolecular decomposition of benzoylperoxide on the other hand yields benzoyloxy radicals, which are stable enough to react with many substrates at rates comparable to the decarboxylation rate.

1.5.3 Induced Decomposition

Decomposition of most peroxides either neat or in presence of a solvent with an easily abstractable hydrogen gives a half life considerably shorter than that given in Fig 2.9 because of induced decomposition.

The rates of decomposition of diacylperoxides are especially enhanced in certain solvents. This enhancement, in some cases is the result of direct interaction of solvent with the peroxide in polar reactions. Solvents such as ethers and alcohols enhance the decomposition of diacylperoxides by up to six orders of magnitude. In certain amines, reaction with diacylperoxides are spontaneous even at room temperature and apparently do not require any unimolecular decomposition of the peroxide to start a chain process. The reaction of benzoyl peroxide with dimethylaniline proceed readily at temperatures as low as $0^{o}C$[126]

1.5.4 Azo Compounds

These decompose thermally, yielding free radicals and N_2.

$$RN{=}NR \xrightarrow{\Delta} 2R^{\cdot} + N_2 \quad \text{.....32}$$

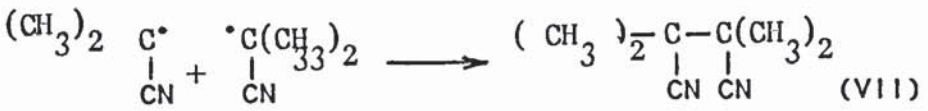
The rate of the decomposition reaction is markedly influenced by the stabilities of the radicals produced.

Azobisisobutyronitrile (AIBN) decomposes readily in the temperature range of 60-90^{o}C and its decomposition is not induced by solvent derived radicals. However, the isobutyronitrile radicals are generally less reactive than the radical fragments encountered in the decomposition of most peroxides.

$$(CH_3)_2\underset{\displaystyle CN}{\underset{|}{C}}{-}N{=}N{-}\underset{\displaystyle CN}{\underset{|}{C}}{-}(CH_3)_2 \longrightarrow 2(CH_3)_2\underset{\displaystyle CN}{\underset{|}{C^{\cdot}}} + N_2 \quad \text{.....33}$$

The isobutyronitrile radicals add readily to most reactive double bonds. AIBN is therefore widely used as an initiator in vinyl polymerisation.

The radicals often couple to form either tetramethyl-succinonitrile (I) or the ketenimine (II).



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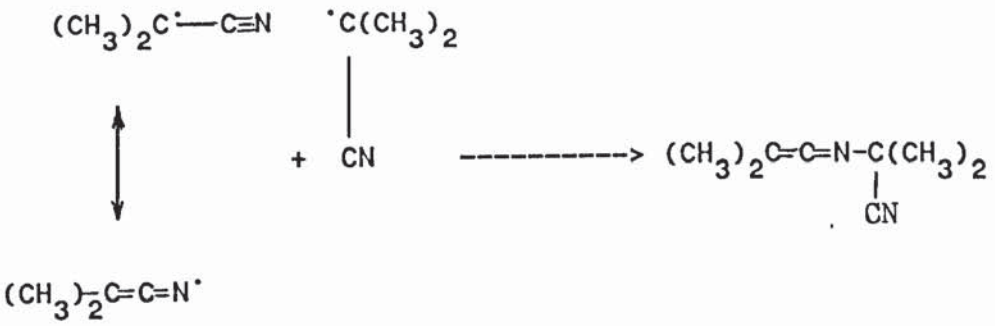


Coupling reactions of the radicals often occur in the solvent cage.

1.6 OBJECTIVE OF THE PRESENT WORK

Polypropylene is the fastest growing general purpose thermoplastic in existence today.[127] It is extensively used as a copolymer and as modified polypropylenes in engineering applications and as general purpose plastics. It is the only high volume thermoplastic that is processable by all four major fabrication methods: moulding, extrusion, film and fibres. However, the choice of PP as a base polymer in stabilisation goes further than that. Experience has shown that antioxidants and stabilisers found to be effective in PP are also generally effective on other polyolefins and in many

cases other saturated polymers. The development of a stabilisation technique on PP therefore, has a wider application potential.

The loss of additives through volatilisation, exudation and solvent extraction has put a great constraint on the use of polymers in more specialised areas of application.

The commercial production of bound antioxidants in saturated polymers could dramatically reduce the constraint presently imposed on the use of polymers as a result of physical loss of the additives to the environment.

The objective of this work is to devise a technologically feasible, economically viable and commercially competetive method of producing concentrates of bound antioxidants (MASTERBATCHES) that could be used in diluted form for the stabilisation of polymers. The final product has to be resistant to solvent extraction and must generally compare favourably with conventional thermal antioxidants such as Irganox 1076 and u.V. stabilisers such as Tinuvin 770

The production of concentrates for subsequent dilution in commercial saturated polymers clearly implies that not all the methods elaborated upon in Section 1.4 could be employed.

Methods 1,2,3, & 6 could only be used with unsaturated polymers (rubbers) as the π bond is necessary as a reactive site. The technique of u.v. irradiation (method 4) has to contend with the constraint imposed by Lambert-Beers' Law, as only thin films can be used, invariably on finished products, this technique has a very limited application potential and unsuitable for masterbatch production. Because of the multitude of reactive sites with the consequent cross-linking tendency, method 7 is also unsuitable for masterbatch production as subsequent uniform dilution would be impossible with a crosslinked polymer. Method 5 is potentially attractive but has several steps which reduces the final yield of product. Only 1.4g of additive in 100g polymer was reportedly achieved.

The method used in the present work has taken cognisance of all the above constraints with the ultimate objective of producing a high enough concentrate that can be homogenously distributed in diluted form in a base polymer, a target not presently attainable by any of the other techniques.

CHAPTER 2

2. EXPERIMENTAL

2.1 GENERAL EXPERIMENTAL TECHNIQUES

2.1.1 Materials: Sources & Purification Methods

Polypropylene (PP) was supplied in powder form and unstabilised under the trade name PROPATHENE HF 22 by I.C.I. It was stored in a refrigerator at -5 C .

The parent hindered amine, 2,2,6,6-tetramethyl-4-piperidinol was kindly donated by Ciba Geigy SA of Switzerland and was used without further purification.

The following chemicals and reagents were used as general purpose grades: Mercaptoacetic acid, acryloyl chloride, tetraisopropyltitanate, triethylamine, 2,6-ditert. butylphenol, allylbromide, maleic anhydride and acrylic acid (ex Aldrich Chemicals). Sodium hydroxide, ethanol and sodium metal (ex BDH).

For spectroscopic measurements, the following spectrograde solvents were used: methylcyclohexane, isooctane, dichlorobenzene and tetrahydrofuran (THF) (ex Aldrich) and dodecane (ex Koch Light).

All other solvents were standard laboratory reagents. These include hexane, diethyl ether, petroleum ether, chloroform, dichloromethane, toluene, benzene and acetone.

The following radical generators used were purified as follows:

Azobisisobutyronitrile (AIBN) was recrystallised from diethyl ether . Dicumylperoxide (DCP) was recrystallised from methanol. Benzoylperoxide (BP) was recrystallised as follows:

It was dissolved in chloroform and separated frorm the aqueous layer (top) used to dampen the peroxide for safe storage and handling. The chloroform was then evaporated at low temperature ($<40^{o}C$). It was then dissolved in methanol, filtered and dried in the oven at room temperature.

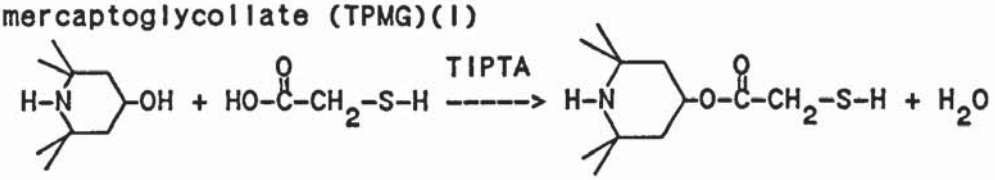
Tertiary butylhydroperoxide (TBH) and di-tert-butyl peroxide (DtBP) were used as supplied.

A phenolic antoxidant, n-octadecyl-3-(3',5'-di-tert-butyl-4-hydroxyhenyl) proplonate under the trade name Irganox 1076 and Bis(2,2,6,6,-tetramethylpiperdinyl) sebacate (Tinuvin 770) were supplied by Ciba Geigy.

The commercial u.v. stabiliser, 2-hydroxy-4-octyloxy-benzophenone (UV531) was supplied by American Cynamid.

2.2 SYNTHESES

2.2.1 Synthesis of 2,2,6,6-Tetramethylpiperidinyl mercaptoglycollate (TPMG)(I)



31.5g (0.2 moles) of 2,2,6,6-tetramethylpiperidinol was placed into a one litre 3 neck flask containing 600ml toluene, previously dried with anhydrous calcium chloride.

A solution of mercaptoacetic acid (0.25 moles) in 200ml toluene was then carefully added into the flask while it was heated in an oil bath and mechanically stirred.

The equipment was then assembled with a thermometer, Dean & Stark apparatus with a condenser and purged with nitrogen. When it started refluxing, 0.02 moles of tetraisopropyltitanate[128](TIPTA) was added as a catalyst. After 30 hours, the stoichiometric amount of water (3.6g) was collected in the water trap. Toluene was removed using a rotary evaporator, leaving a yellow sticky solid which hardened when cool. This was then dissolved in chloroform and filtered. The filtrate was precipitated in isopropyl ether, giving pale yellow crystals. These were further purified by recrystallisation from chloroform

and isopropylether or through column chromatography using alumina column and methanol as the eluent. Methanol was then evaporated giving white crystals of the ester, with a melting point of 118°-120°C.

TLC of the product in methanol on alumina support gave one spot.

Analysis

(a) Infra-red (KBr disc) Fig 2.1

N-H (hydrogen bonded)	3400 cm^{-1}
S-H (")	2480 cm^{-1}
Ester carbonyl (c=0)	1735 cm^{-1}

(b) ^{1}Hnmr

Piperidine proton	:	3.955 (singlet)
Methyl protons	:	1.6-1.75 (doublet)
Ring Sec. protons	:	2.15-2.255 (doublet)
Ring Tert. protons	:	5.50-5.55 (triplet)<
Sec protons	:	2.75
Thiol protons:	:	3.55

(c) Elemental Analysis

C=57% (Calc.57) H=9.1% (Calc. 9.0) N=5.9% (Calc. 6.0)

2.2.2. 1-Acryloyl-4-acryloyloxy-2,2,6,6-tetramethylpiperidine (AATP)

This compound was prepared according to literature[129] as follows:

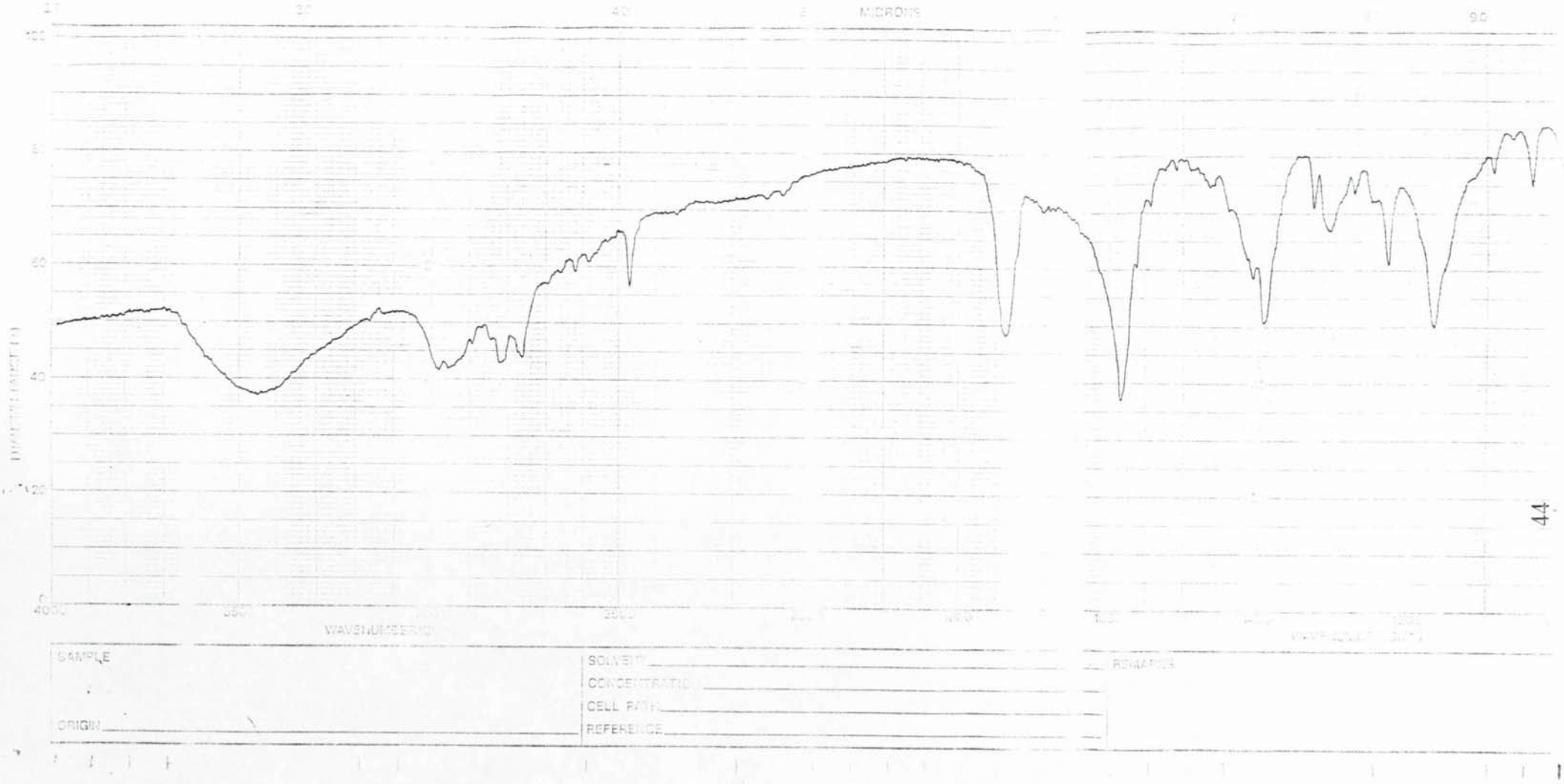
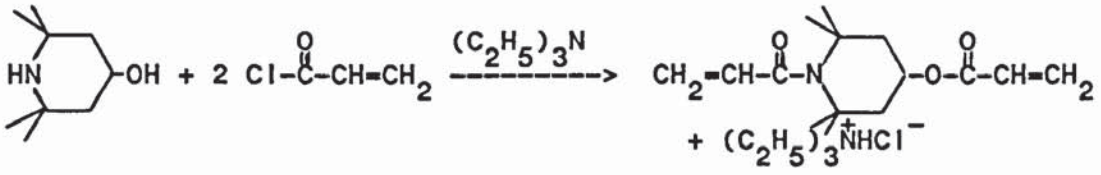


FIG. 2.1 I.R. Spectrum (KBr disc) of 2,2,6,6-Tetramethylpiperidinylmercaptoglycollate (TPMG)



A solution of 60g of acryloyl chloride in 800ml of dry toluene was added dropwise with stirring and ice cooling to a solution of 52g of 2,2,6,6-tetramethylpiperidinol and 70g of triethylamine in 1litre of benzene. The resulting mixture was stirred for 1 hour under ice cooling and then at room temperature for an additional 8h.

The precipitated triethyamine hydrochloride was removed by filtration and the filtrate washed with an aq. sodium bicarbonate and then dried over K_2CO_3. The toluene was distilled off under reduced pressure and the concentrate was then dissolved in either iso octane or hexane to precipitate any remaining reactant or by-product impurity. The clear solution was then decanted, the solvent evaporated with a rotary evaporator, leaving the product as a colourless oily liquid.

2.2.2.1. Analysis

(a) Infra red. (Na Cl cell) See fig 2.2

Ester C = O .....1725cm^{-1}

Unsaturation (vinyl) .....1640cm^{-1}

Acryloamide C = O .....1610cm^{-1}

(b) ^{1}H nmr (Fig 2.3) Ref TMS

Proton No.	1	2	3	4	5	6	7	8	9	10	11
δ (ppm)	6.20 to 6.14	6.35 to 6.20	5.47 to 5.44	1.57	1.54	2.06 to 1.90	2.30 to 2.20	5.32 to 5.20	6.25 to 6.22	5.90 to 5.70	6.5 to 6.42
	d	d	d	s	s	t	d	t	d	d	d

(c) ^{13}C (proton decoupled) nmr (Fig 2.4) Ref TMS

C No.	1	2	3	4	5	6	7	8	9	10	11
δppm	165	131	124	30.6	30	55.6	43	66	128	135	169

(d) Mass spec. Fig 2.5

Fragment	Mass	%Int.
M^+	265.9	0.7
M^+-15	251.0	12.3
M^+-65	210.9	0.5
M^+-88(BASE)	178.0	100

(e) Elemental Analysis

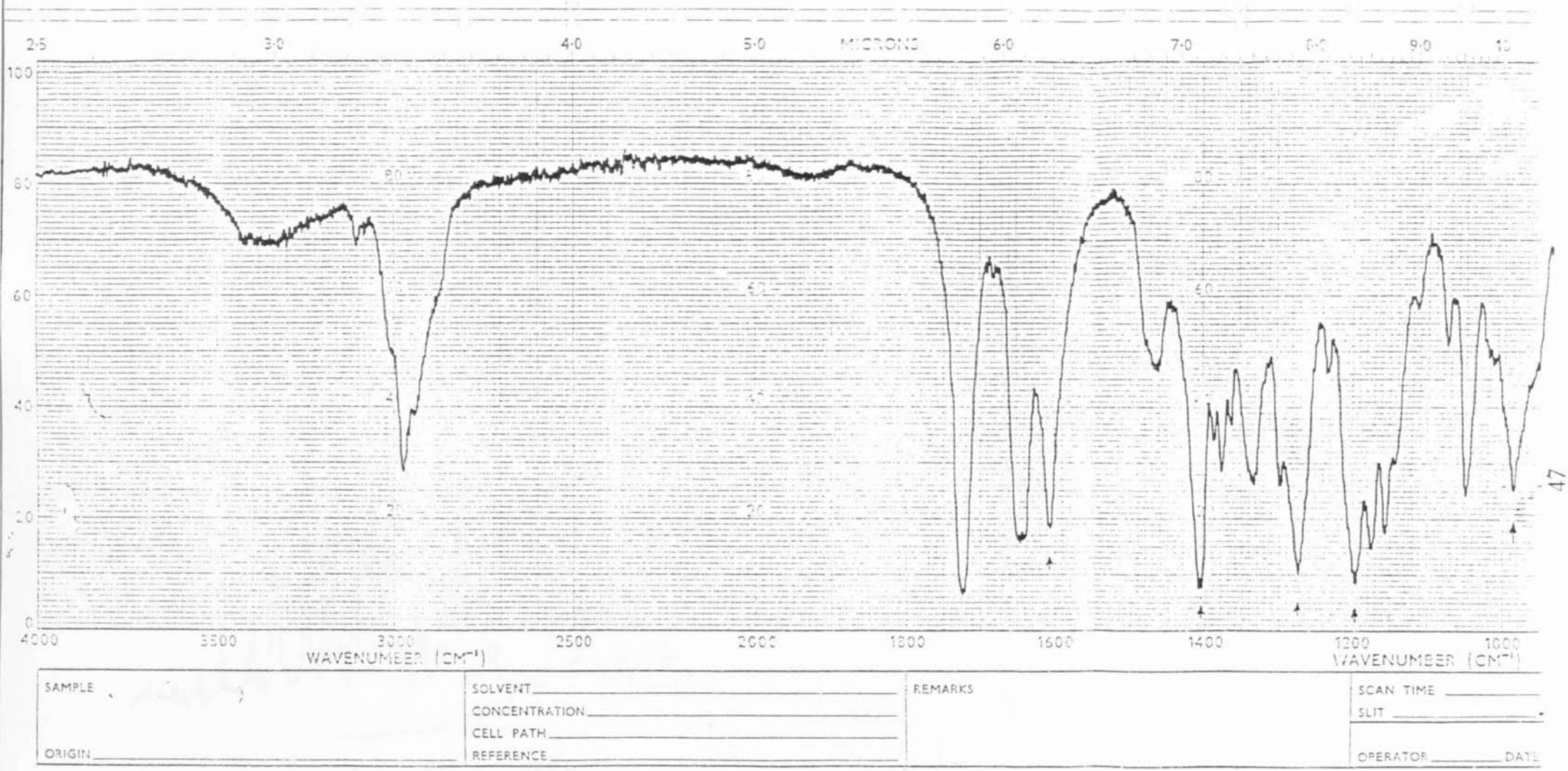


FIG. 2.2 I.R. Spectrum (NaCl cell) of 1-acryloy-4-acryloyloxy-2,2,6,6-tetramethylpiperidine (AATP)

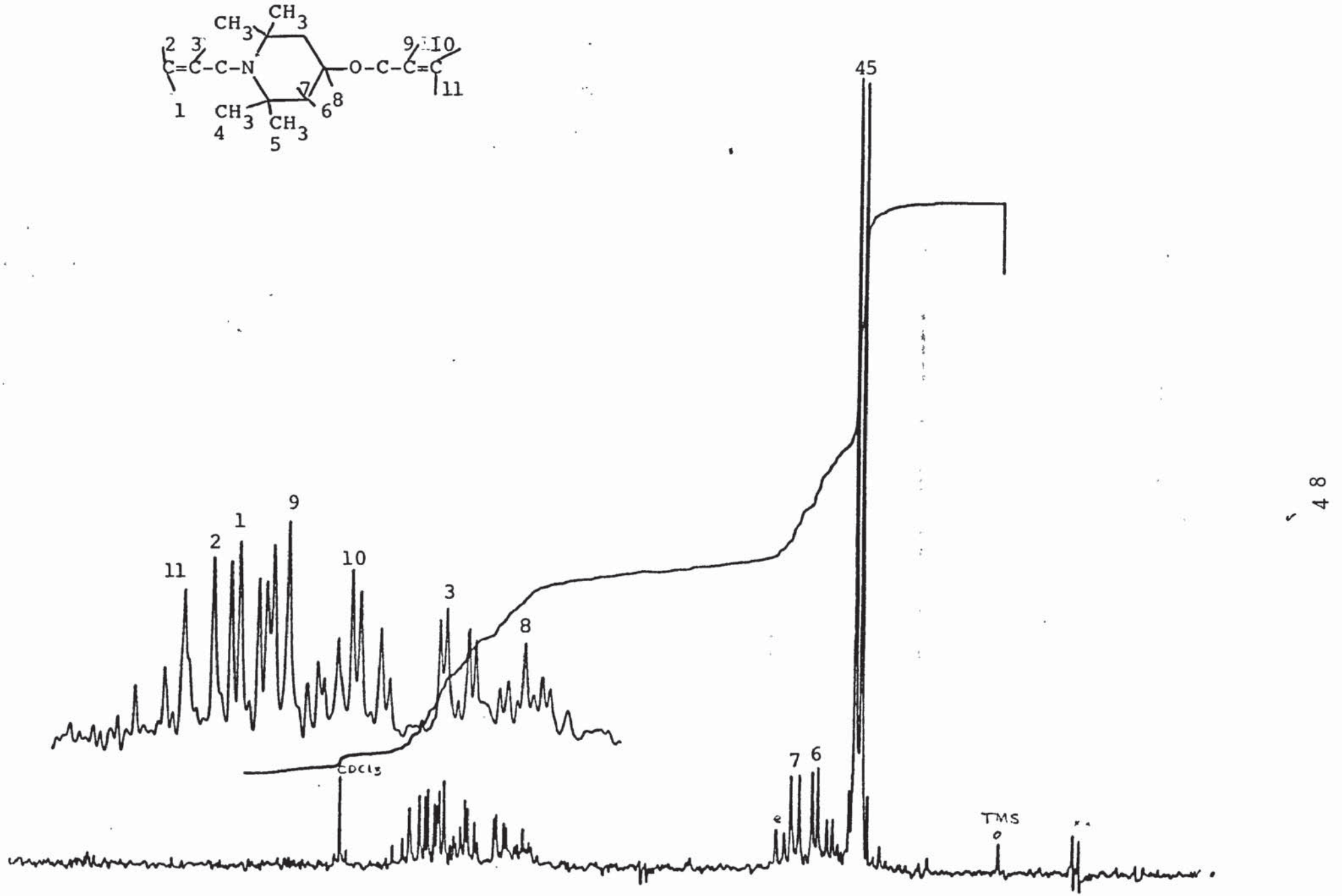


FIG. 2.3 ^{1}H n.m.r. Spectrum of AATP

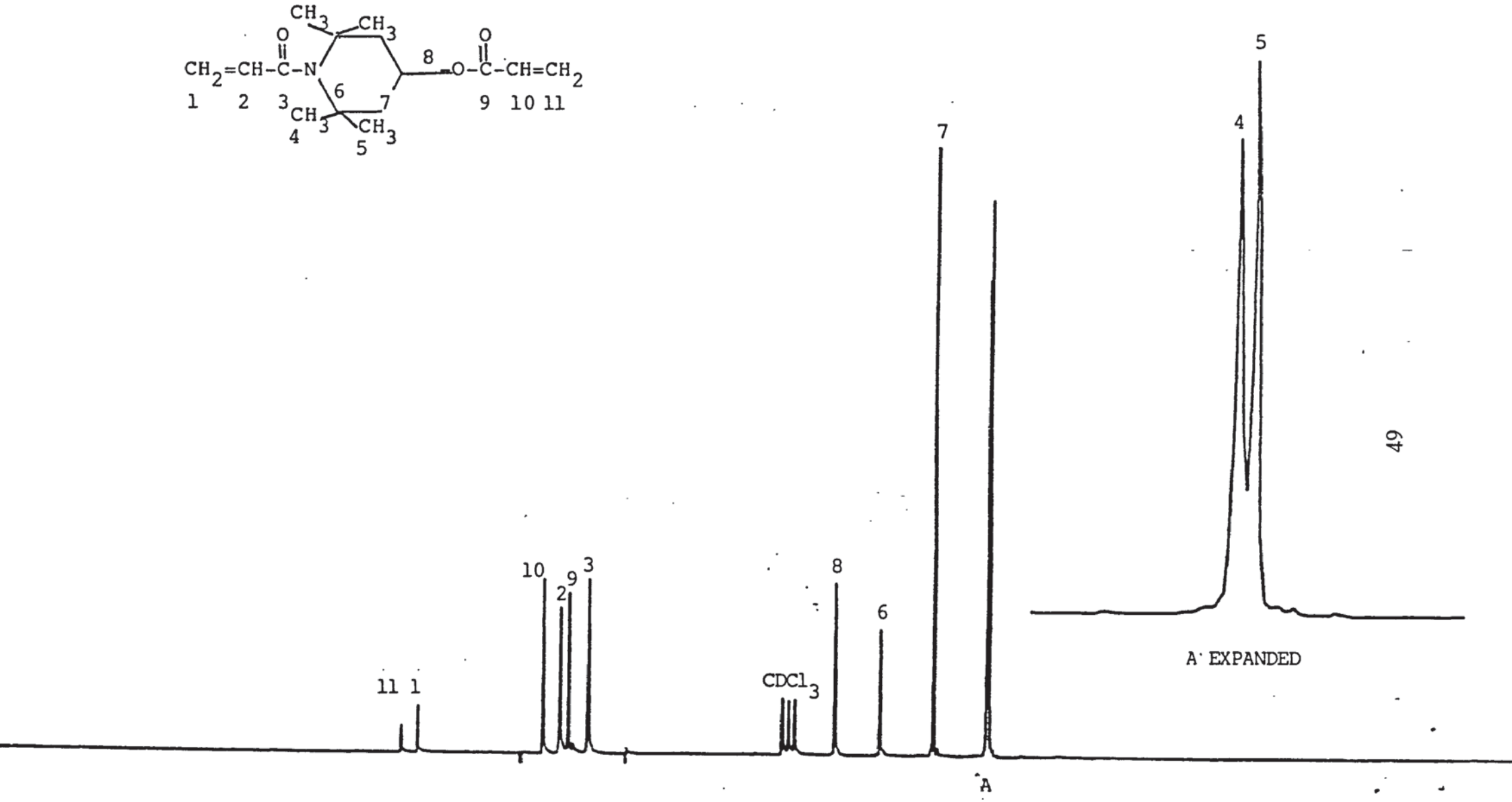


FIG.2.4 ^{13}C n.m.r. Spectrum of AATP (Proton decoupled)

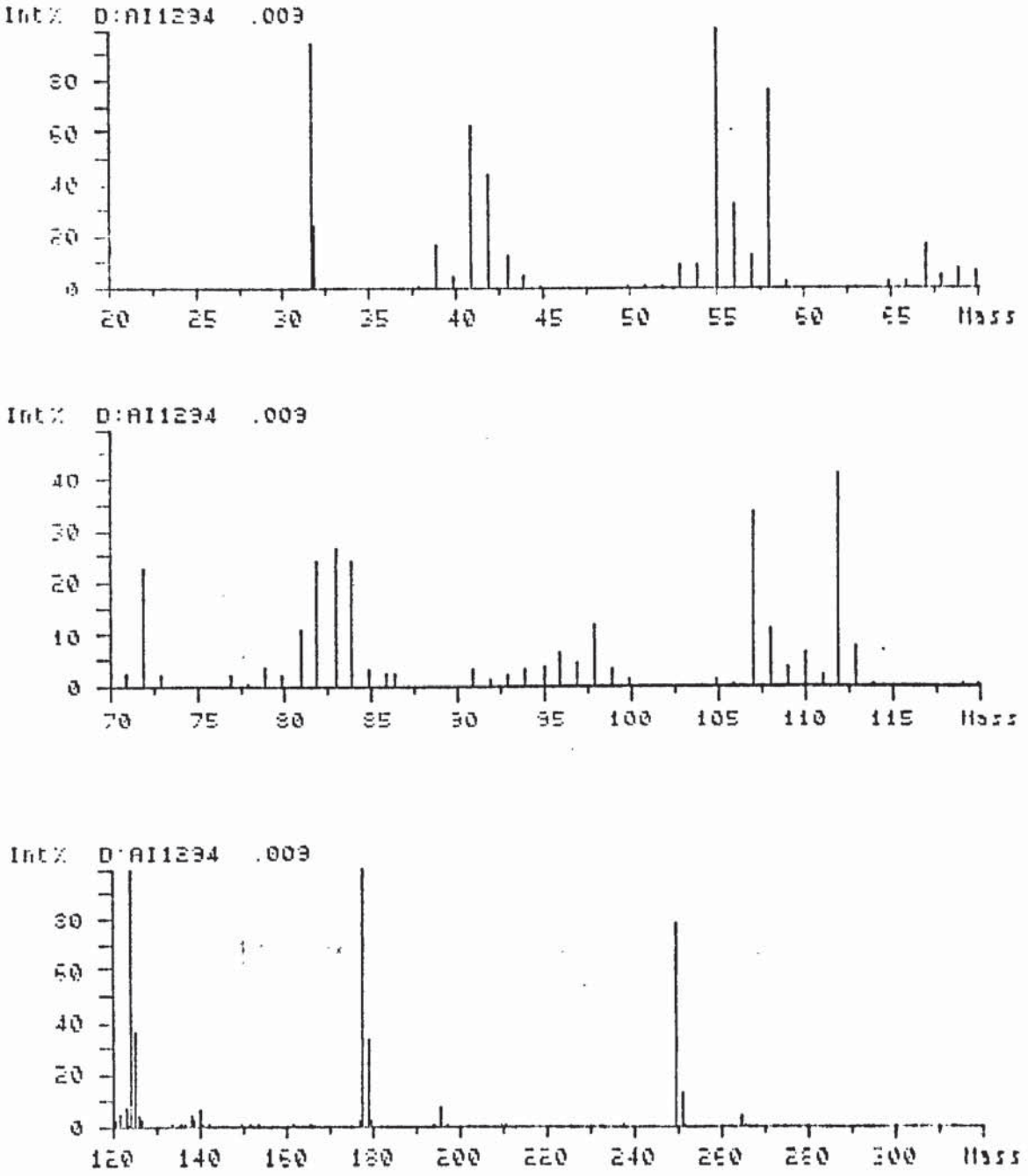
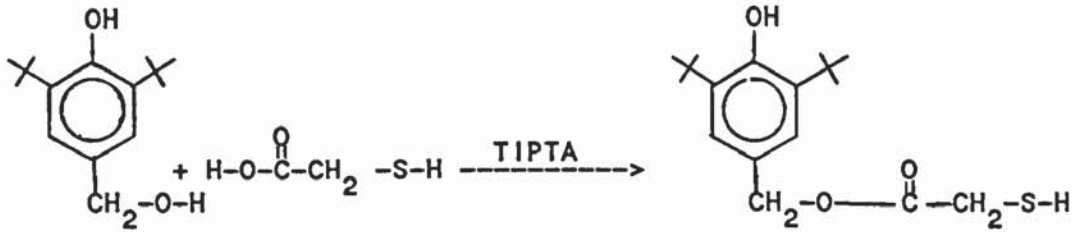


FIG. 2.5 Mass Spectrum of AATP

Element	C	H	N
Found	67.9	8.62	5.20
Calc.	67.7	8.66	5.27

2.2.3 3,5-di-tert.butyl-4-hydroxybenzylmercaptoglycollate(DBBM)

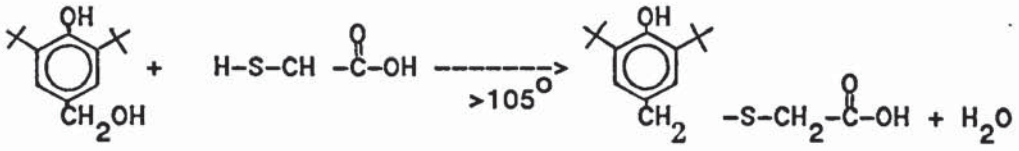


The alcohol used for this reaction was prepared according to the method given in 2.2.4a below.]

To a 0.1 mole (23.6g) of the alcohol in 600 ml toluene, was added 0.1 mole (9.2g) of mercaptoacetic acid in 100 ml benzene into a one litre 3 neck flask. Finally, 3 ml of TIPTA was added as a catalyst. The flask was then placed in an oil bath on a hot plate with a magnetic stirrer. Dean and stark apparatus with a condenser and thermometer were then placed in position. Nitrogen was purged into the reaction flask while it was heated. After 5 hours, 1.8g

of water was removed from the reaction mixture, which was exactly the theoretical amount of water.

The 6:1 toluene/benzene mixture ensured a mild refluxing temperature of 102°C, to minimise an alternative reaction between the alcohol and the thiol of the acid.



2.2.3.1 Purification

Even at such a mild temperature, some of the phenol-sulphide was formed.

The solvent was removed from the reaction mixture by rotary evaporation and the product washed several times with distilled water to remove any remaining acid. The product was then dissolved in hexane where the biproduct precipitated as a white solid. The pale yellow filtrate was then dried with K_2CO_3 and filtered. Hexane was then evaporated, giving a pale yellow oily liquid. This was further purified through column chromatography using a silica gel column and chloroform as eluent. The chloroform was then evaporated giving a thick oily liquid.

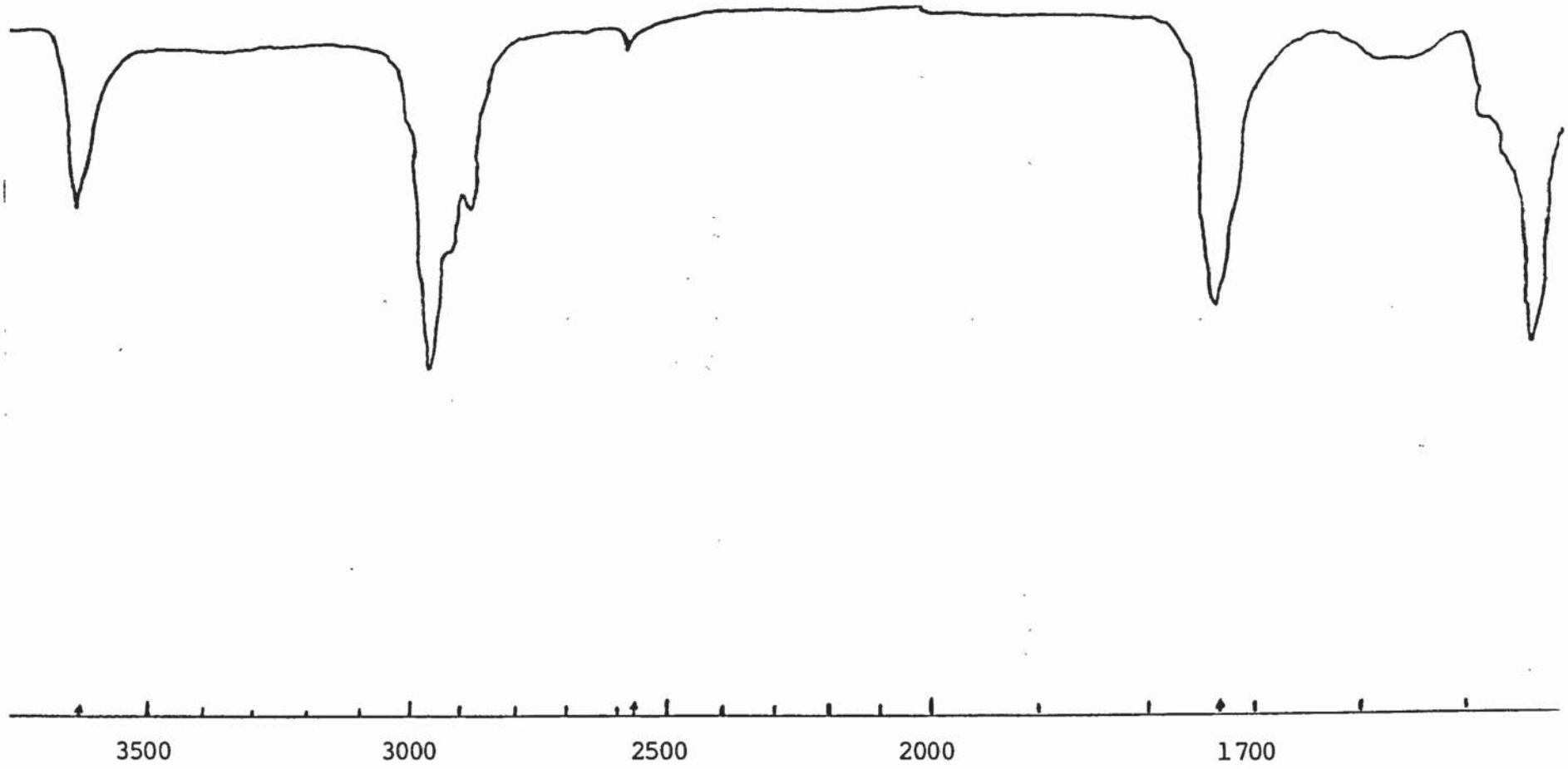


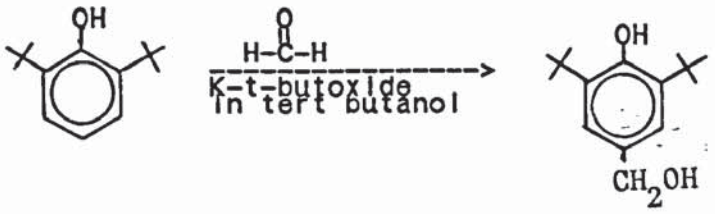
FIG. 2.6 I.R. Spectrum (NaCl cell) of 3,5-Di-tert-butyl-4-hydroxybenzylmercaptoglycollate (DBBM)

Its purity was confirmed by TLC

Infra-red Analysis (Fig 2.6)

Phenolic O-H (free)	:	3640 cm^{-1}
S-H	:	2560 cm^{-1}
Ester C=O	:	1735 cm^{-1}

2.2.4a. 2,6-di-tert.butylhydroxybenzyl alcohol.



A solution of 50g of 2,6-di-tert.butylphenol in 170g tert.butanol was charged into a 500 ml flask, purged with nitrogen. A well dispersed slurry of 8 grams of paraformaldehyde in 100 ml tertiary butanol was also added into the flask which was continuously stirred under ice cooling.

A solution of 1.4g potassium tertiary butoxide in 28g of tertiary butanol was then added gradually from a funnel, keeping the temperature below 10°C.

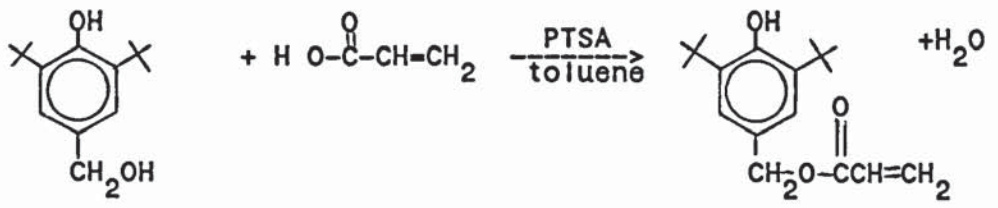
Stirring was continued for about 45 minutes by which time the mixture had turned into a thick red liquid. This mixture was then poured into a bowl of ice and left in the refrigerator overnight. The yellow crystals formed were washed with water and then with

hexane, giving purplish-white powder, which was recrystallised from chloroform and hexane, giving white crystals with an m-p of 129°C.

Infra-red Analysis

Phenolic O-H (free)	:	3640 cm^{-1}
Alcohol O-H (H-bonded)	:	3525 cm^{-1}

2.2.4 3,5-di-tert.butyl-4-hydroxybenzylacrylate (DBBA)



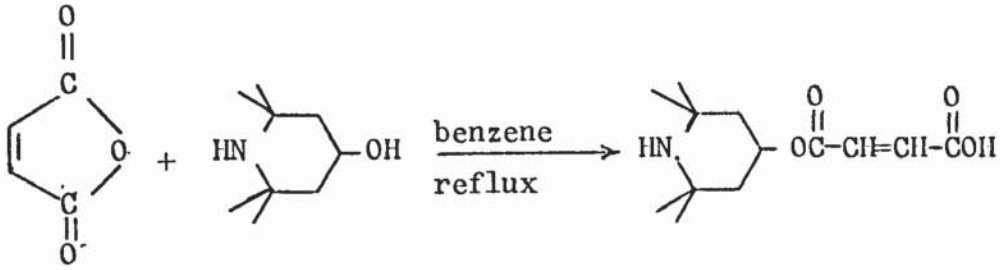
To a 0.1 mole (23.6g) of 2,6-di-t.butylhydroxybenzyl alcohol in 500 ml toluene, 0.15 mole (10.82g) of acrylic acid was added along with about 0.1g of p-toluene sulphonic acid (PTSA) as a catalyst. The apparatus was then assembled for refluxing, complete with Dean and Stark trap. After 2.5 hours of refluxing, 1.8g of water, the expected amount, was collected. The solvent was then evaporated and the product dissolved in hexane. It was then filtered to remove unreacted material and the PTSA catalyst. Any remaining acid was then washed by several washings with distilled water. The product was then dried with $MgSO_4$ for twenty-four hours and

filtered. The solvent was then evaporated, using a high vacuum pump. A thick red oily liquid was obtained. Its purity was confirmed by TLC.

Infra-red Analysis (Fig 2.7)

Hindered phenolic O-H (free)	:	3640 cm^{-1}
Ester C=O	:	1725 cm^{-1}
Vinyl unsaturation (conjugated)	:	1640 cm^{-1}

2.2.5a. Mono (2,2,6,6-tetramethylpiperidinyl)maleate



To a 9.8g (0.1 mole) of maleic anhydride in benzene in a 500ml reaction vessel was added 15.7g (0.1 mole) of 2,2,6,6-tetramethylpiperidinol. The reaction mixture was then refluxed for 1.5h when a white precipitate of the half ester completely replaced the clear solution.

The product was filtered,and washed several times with dichloromethane,to remove remaining reactants. M.p.260^{o}- 262^{o}C

Infra-red analysis.

Carbonyl (C=O)	:	1720cm^{-1}
Conjugated unsaturation:		1635cm^{-1}

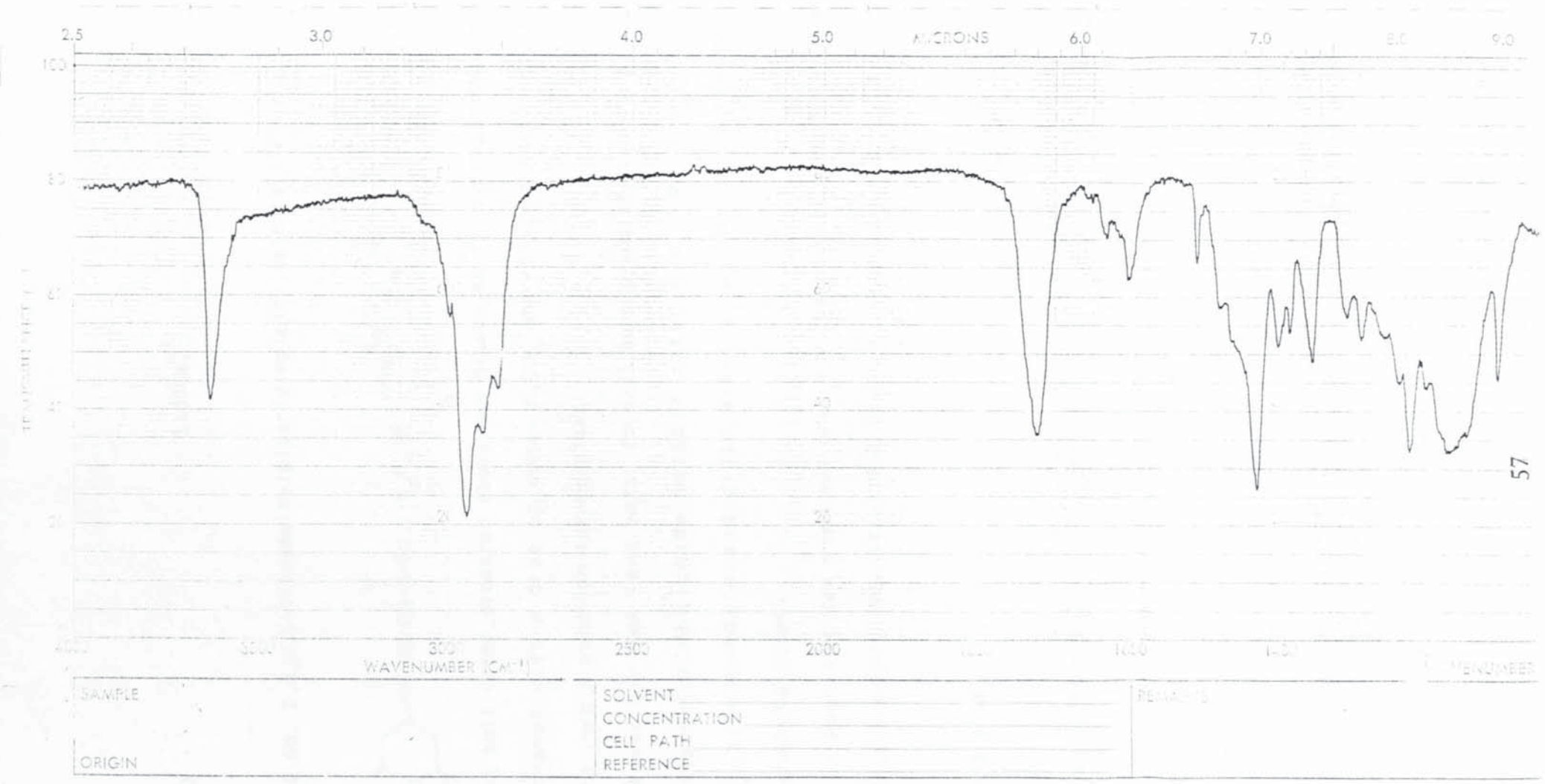
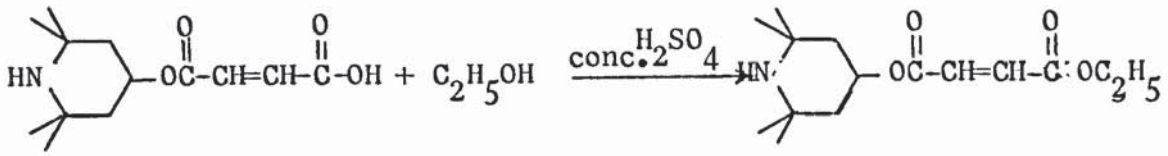


FIG. 2.7 I.R. Spectrum (NaCl Cell) of 3,5-Di-tert-butyl-4-hydroxybenzyl acrylate (DBBA)

N-H : $3400cm^{-1}$

2.2.5b. 2,2,6,6-tetramethylpiperidinylethylmaleate (TPEM)



The half ester,prepared above was dissolved in a large excess of ethanol with a drop of conc. H_2SO_4 and refluxed overnight, when the turbid solution turned clear.

Excess ethanol (and water formed) were evaporated using a rotary evaporator.The crude maleate ester was then dissolved in dichloromethane and dried with Mg SO_4 for 8h to remove the remaining water.

The solution was then filtered and the product precipitated with diethylether. (Mp. 137-139°C.

Analysis.

(a) Infra-rec

Ester C=O : $1725cm^{-1}$

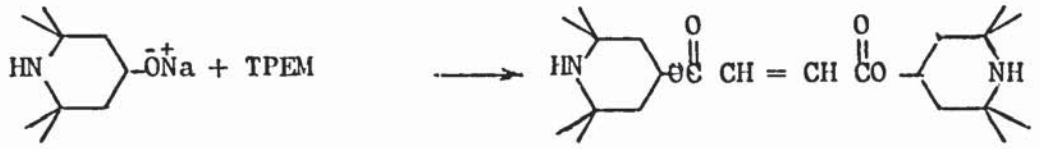
Unsaturation : $1640cm^{-1}$

(b) Elemental Analysis

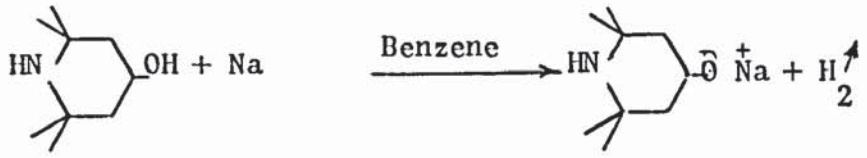
C= 64% (63.5 calc.) H=8.2% (8.8% calc.) N=5.2% (4.9 calc.)

2.2.5. Bis(2,2,6,6-tetramethylpiperidinyl)maleate.

This was prepared by transesterification of the ethyl maleate(TPEM) with sodium piperidinoxide.



The sodium piperidinoxide was prepared as follows:



Benzene (200ml) was dried with anhydrous $CaCl_2$ and filtered.In to this dry benzene was added 4.71g (0.03mole) of 2,2,6,6-tetramethylpiperidinol.

Sodium metal (0.69g) was then freshly cut in to fine pieces and added to this mixture. The mixture was then warmed (40^{o}C) for about an hour,until the rapid evolution of hydrogen had ceased.This freshly prepared sodiumpiperidinoxde was then transfered to a reaction vessel containing TPEM and an excess of 2,2,6,6-tetramethylpiperidinol in benzene. The mixture was refluxed overnight.

The product was then filtered hot. Benzene was evaporated from the filtrate,and the product dissolved in dichloromethane.

Ethylmaleate was precipitated out of this concentrated solution on cooling overnight, leaving the bismaleate in solution.

Benzene was removed by evaporation, leaving the final product as a white solid. (M.p.67-69^{o}C)

Analysis

(a) Infra-red (Fig.2.8)

Ester C=O	1725cm^{-1}
Unsaturation	1640cm^{-1}

(b) Elemental

C =66%(calc.66.8);H =10.4%(calc.9.6);N =6.9%(calc.7.1)

2.3 COMPOUNDING, FILM PREPARATION & EXTRACTION OF PP

2.3.1 Processing of PP & Additives in the Torque Rheometer

PP and additives were processed using a HAMPDEN-RAPRA torque rheometer. This is essentially a small mixing chamber containing mixing screws contra rotating at different speeds. The motor has adjustable speed knobs so that the speed of rotation can be adjusted from very slow to very fast. All the processings were done using a speed of 60 rev/min. A good temperature control and a

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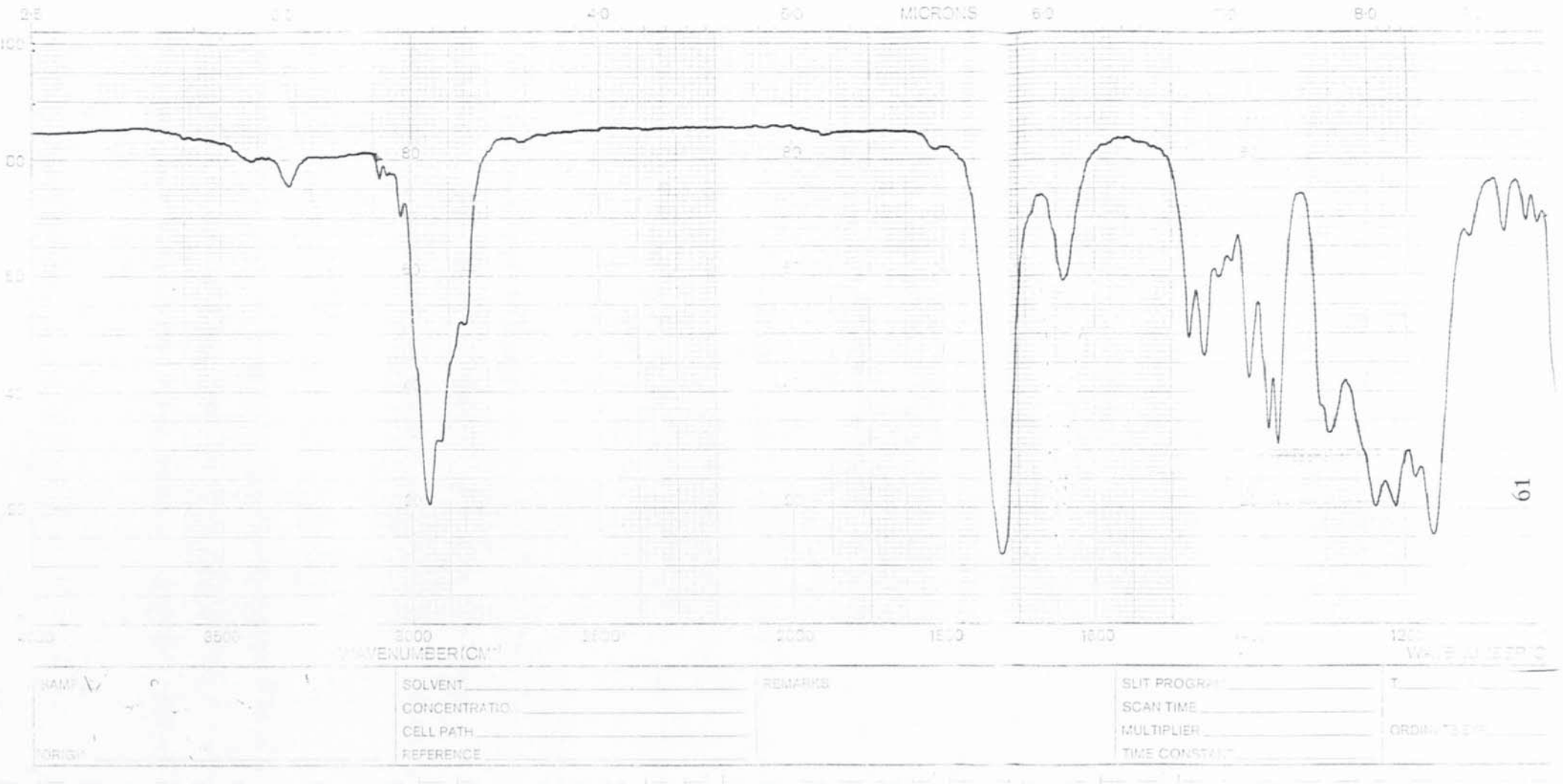


FIG. 2.8 I.R. Spectrum (KBr disc) of Bis(2,2,6,6-tetramethylpiperidinyl)maleate (BPM)

continuous readout of both melt temperature and the torque required for the mixing is provided. The processing chamber may be operated either open to the atmosphere or sealed by a pneumatic ram.

A full charge of 35g (polymer + additive) was used for each sample and the chamber could be open, closed, or under inert atmosphere by prior purging with N_2 or Ar and again purged after the charge, before closing.

The additives (and radical generators) were thoroughly mixed with the polymer at room temperature by tumble mixing before introducing into the torque rheometer chamber.

The hot polymer melt was removed as soon as the chamber was opened and chilled in cold water to avoid thermal oxidation.

2.3.2 Preparation of Bound Concentrates

Concentrates of 5,10 & 20% "masterbatch" of additive/polymer were prepared with varying initiator molar ratios in the torque rheometer at temperatures between 170°C-190°C for ten minutes. These compounding conditions ensure that even without induced decomposition, greater than 99.9% of the initiator was decomposed (see Fig 2.9) for maximum binding, and to guard against any

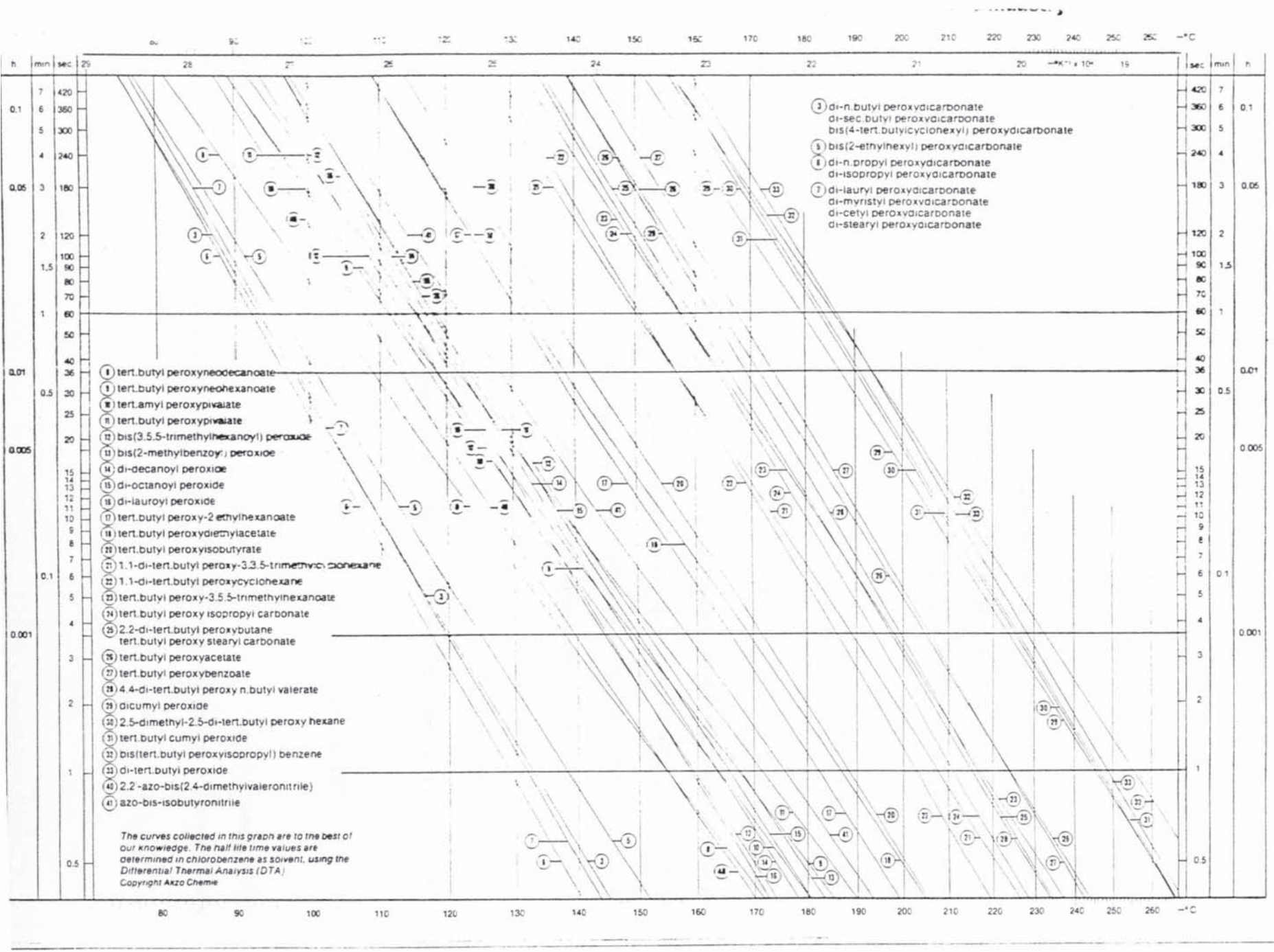


FIG.2.9 Half-life/Temperature Curves of Radical Initiators
[Courtesy Akzo Chemie]

subsequent deleterious effect of unreacted peroxide in a stabilised sample.

2.3.3 Evaluation of Binding

Samples of 10% and 20% were diluted down to 5% for this evaluation using i.r. spectroscopy.

As all the graftable additives were esters in this work, the ester carbonyl absorption was used to measure the amount of bound material in the fashion of "carbonyl index", commonly employed in measuring the amount of carbonyl formation in oxidising polyolefin samples.

2.3.4 Film Preparation

Polymer films for U.V. and thermal ageing and for spectroscopic studies were prepared by compression moulding using an etectric press. The polypropylene samples were placed between two stainless steel glazed plates. The plates were thoroughly cleaned before use to ensure smooth surfaces and a special grade (heat resistant) cellophane film was used to prevent the film sticking to the plates. Control of film thickness was achieved by using a standard quantity of polymer (about 7g) for producing a film thickness of 1.8×10^{-2}cm (0.007"). The weighed amount of the polymer was placed between the plates and inserted into an electric press

whose platens were maintained at 180°C. The sample was pre-heated for 30 seconds without applying any pressure. Pressure of 85kg/cm^2 was then applied for a further 1.5 minutes.

The platens were then cooled to about 40°C by running cold water around them while maintaining the full pressure. Pressure was then released, the plates removed, the films obtained were stored in a refrigerator. Portions of uniform thickness were cut for testing.

2.3.4.1 Thermal Ageing of Polymer Films

The accelerated thermal oxidations of processed polymer films were carried out in a Wallace oven at 140°C in the presence of air. Each sample was contained and suspended in a separate cell to prevent cross contamination of the additives by volatilisation, and was subjected to an air flow of 3 cubic feet/hr (85 litres/h)

2.3.4.2 Ultraviolet Irradiation of Polypropylene Films

All the film samples were irradiated in an ultra-violet light ageing cabinet, cylinderical in shape and composed 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, which was in turn mounted vertically on the circumference of a rotating drum fixed inside the cabinet.

In this manner, the light beam fell perpendicularly on the surface of the film. The distance of the sample from the light source was 10cm and temperature inside the cabinet with the lights on was 30^{o} C ± 1 C

The intensity of uv irradiation at the centre of the drum falling on the surface of the films was calculated[130] to be 5.5 $W.h.m^{-2}$

2.3.4.3 Measurements of Brittle Fracture Time of Polymer Films

Exposed films were tested for embrittlement.Films of identical size and uniform thickness (1.8×10^{-2}cm) containing various additives along with the control sample, both extracted and unextracted were u.v. irradiated or thermally aged at 140^{o}C.

They were periodically checked for embrittlement.

The time to embrittlement was determined by a manual bending of the film onto itself, that is, to an angle of 180^{o}. Each measurement of polymer sample was carried out in triplicate for consitency. The reproducibility of the results was found to be accurate to within plus or minus 5%

2.3.5 Solvent Extraction of Polymer Films

Unbound additives and other low molecular mass materials were removed from the film samples by hot Soxhlet extractions using a

suitable solvent for a duration of between 10-50 hrs. A steady stream of nitrogen was bubbled throughout the extraction period. After the extraction, the samples were dried under vacuum at a maximum temperature of 40^{o}C for 24 hrs.

2.4 Electron Spin Resonance Spectroscopy (e.s.r)

2.4.1 A brief description of e.s.r theory & e.s.r machine[131]

When an electron is in an external magnetic field, its spin generates a magnetic moment. The magnetic moment vector of this small magnet has two possible orientations of the spin vector; parallel and anti-parallel to the applied magnetic field.

The electron energy in the magnetic field is given by

$E = -U_e H$, where U_e is the magnetic moment vector for the unbonded electron which is related to the spin vector, S by $U_e = g_e B_e S$ erg/gauss, where B_e = Bohr magneton and g_e = dimensionless constant called electron freespin g-factor.
The g value of a freely spinning electron is 2.0023.

$E = g_e B_e SH$. S in a magnetic field can have one of two possible values, + 0.5 and - 0.5. Therefore $E_1 = + 0.5\ g_e B_e H$ and $E_2 = - 0.5\ g_e B_e H$. The energy difference between the two stages of electron is given by

$$\Delta E = E_1 - E_2 = g_e B_e H.$$

The measurement of the energy difference is the basis of electron paramagnetic resonance spectroscopy.

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

$$\Delta E = hv = g_e B_e H \text{ (erg)}$$

where h = Plancks' constant

Only electromagnetic waves with the frequency $v = \frac{g_e B_e H}{h}$

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 ΔE 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 millilitre.

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 and
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 of 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.

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 called 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. 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 known as a klystron, producing microwave oscillation in a small frequency range, 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 klystron 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 as a source of static magnetic field.

3. The sample cavity

4. The modulation system at the commonly used frequency of 100kHz.

5. The detection and recording system.

2.4.2. Preparation of e.s.r. Film samples and Detection of Radicals.

All samples analysed were carefully weighed out (0.060g) and cut into small strips with a length of 1.5 cm, and placed in the sample test tube. JEOL (JES-PE) electron spin resonance instrument was used and the machine was callibrated using a marker sample made of MnO powder containing thermally diffused Mn^{+2} ions before the spectrum of the samples were recorded. Test tube containing the sample was inserted into the cavity after adjusting by the insertion length setting device.

The resonance signal was then recorded. If the nature of the radical(s) was not established, its 'g' value can be determined as follows:

Determination of 'g-value'

The line position of an e.s.r. spectrum is denoted in terms of 'g-value', the g-factor or "chemical shift", which 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,

$g = \frac{hv}{BH}$. 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 counted from the low magnetic field side which is g_1 = 1.981 Gauss.

2. Microwave frequency 9300 mHz (mean frequency between 9200 mHz and 9400mHz)

3. $\triangle H$ represents the distance between the measured sample spectrum and the fourth spectrum which can easily be obtained by proportional calculation. (Fg 2.10) and using the equation

$\triangle E = h\nu = g_e B_e H$, for fourth line spectra of marker (a) and measured sample (b)

$$h\nu = g, B\ H_o \quad \text{.....(a)}$$

$$h\nu = gB\ (H_o - \triangle H) \quad \text{.....(b)}$$

$$g = \frac{\frac{h\nu}{B}}{\frac{h\nu}{gB} - H}$$

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

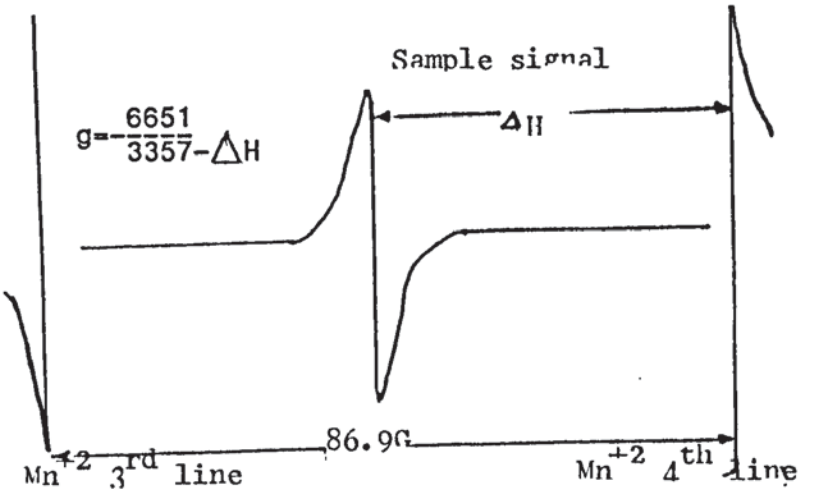


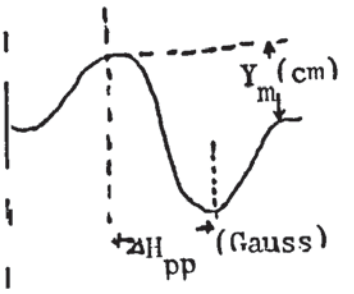
Fig. 2.10

2.4.2.1 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.[132] 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 $(\Delta Hpp)^2$ for the reference sample.

$$\frac{Ym\ (\Delta Hpp)^2 sample}{Ym\ (\Delta Hpp)^2 ref} = \frac{\text{Conc. of radicals in test sample}}{\text{Conc. of radicals in Ref.}}$$



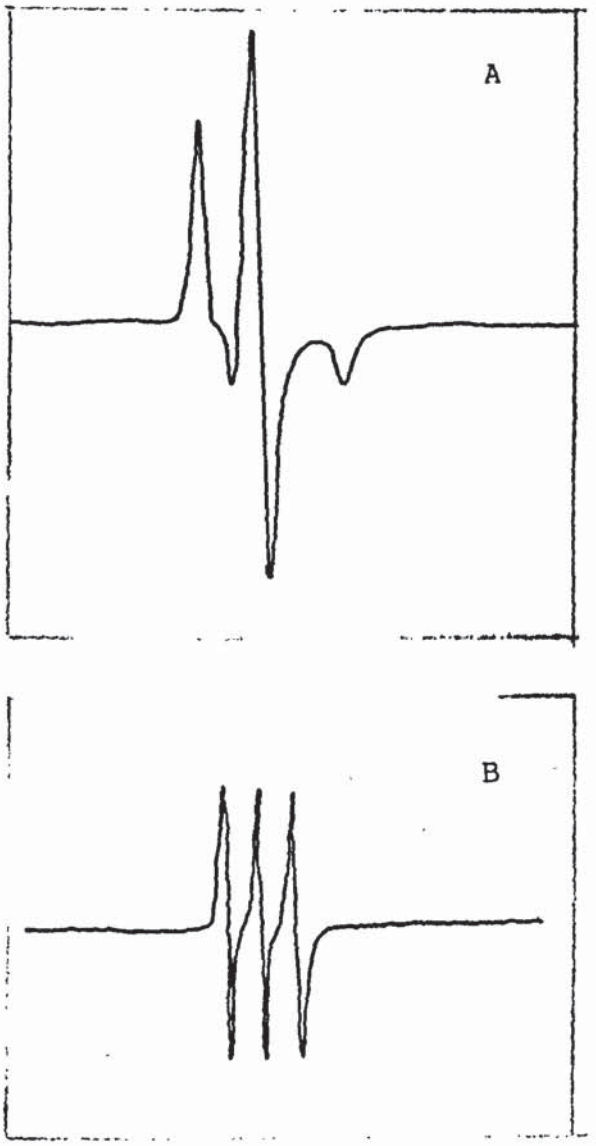


FIG.2.11 E.s.r. Spectrum of Nitroxyl Radical
A: Immobilised in Solid PP
B: Free Tumbling in Dichloromethane Solution

This method was found to be a close approximation of the summation method.[133]

However, because of the multitude of variables involved that could affect the intensity of a free radical signal enumerated earlier on in this section, a more precise and less cumbersome method for the measurement of nitroxyl radical concentration was used in this work. A measured quantity of 2,2,6,6-tetramethyl piperidinoxyl, prepared and purified by the Rozantsev[134] method was used as a standard reference sample. A film of unstabilized PP was pressed and then swelled in a solution of the nitroxyl radical in dichloromethane. The solvent was then evaporated in a vacuum oven at room temperature over a period of 12 hours.

Fig.2.11a,shows the e.s.r. signal of immobilised nitroxyl radical in solid PP while (b) shows that of the free tumbling radical in DCM solution.

The same weight of the sample was prepared and analysed in the same way as other samples.

Since the concentration of the standard sample is known, the ratio of the intensity of the signal of the unknown and the standard sample can be used to calculate its concentration.

2.5. GEL PERMEATION CHROMATOGRAPHY (GPC)

GPC is one of the most important techniques for the determination of Molecular Weight and Molecular Weight distributions of polymer Samples. Polymer molecules are separated according to their random coil dimensions in solution. Separation occurs in one or more columns packed with a crosslinked polymer gel. As a polymer solution passes through the column, the molecules diffuse into the interstices of the packing material according to their size and the pore size distribution in the gel. Hence a sharp separation occurs into fractions of different Molecular Weights the larger molecules being eluted more quickly from the column than the smaller sized molecules which penetrate a larger fraction of the interstices of the gel.

After emerging from the column, the polymer solution passes through a series of detectors which produce a response proportional to the concentration of the polymeric solution. The chromatogram subsequently obtained shows a plot of detector response against retention time.

Quantitative information can be obtained from a chromatogram by calibrating the series of GPC columns with a series of narrow dispersed polystyrene of different known molecular weights. A graph may be made as shown in Fig 2.12.

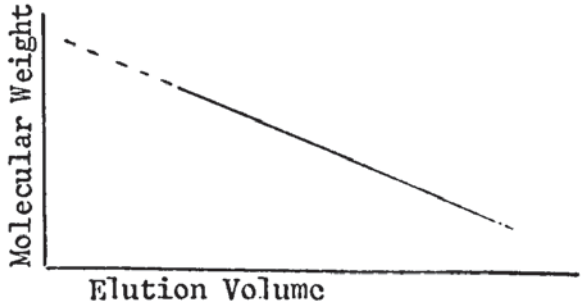


Fig. 2.12. G.P.C. Callibration of $\bar{M}n$ with Polystyrene Standard.

By comparing retention volumes of different polymers, it is possible to obtain a polystyrene equivalent Molecular Weigh t for most linear polymers in solution.

Under conditions of constant temperature, flow rate and concentration for the same physical system, the retention volume is a function only of the molecular size of the polymer molecules in solution. The eluent can be analysed continuously using either an ultraviolet (UV) detector or a differential refrectometer (RI) detector, or a combination of both. The UV detector measures uv absorption of polymers containing chromophores along the backbones of the chain or as the end group. RI detectors detect any change in refractive index between a sample of the pure solvent and a sample of the polymer solution eluting from the GPC columns, the response being proportional to the concentration rather than the nature of the polymer.

From a typical GPC trace, it is possible to obtain all the necessary information for the calculation of molecular weights and their distributions. The molecular weight distributions may be calculated as follows:

By definition,

$$Mn = \frac{\Sigma NiMi}{\Sigma Ni} \quad \text{and} \quad Mw = \frac{\Sigma NiMi^2}{\Sigma NiMi}$$

Where Mn = Number Average Molecular Weight

Mw = Weight Average Molecular Weight

Mi = Molecular Weight of a given fraction

and Ni = Number of moles in a given fraction of molecular mass Mi.

If Wi is the weight of polymer of molecular weight Mi in a given fraction, then

$$Ni = \frac{Wi}{Mi}$$

$$Mn = \frac{\Sigma Wi}{\Sigma Wi/Mi} \quad \text{and} \quad Mw = \frac{\Sigma WiMi}{\Sigma Wi}$$

The differential refractive index gives a relative measure of concentration of polymer units of mass volume^{-1}. Wi may therefore be substituted by hi, the height of the deflection corresponding to the refractive index of the eluent relative to that of pure solvent.

Hence,

$$Mn = \frac{\Sigma hi}{\Sigma hi/Mi} \quad \text{and} \quad Mw = \frac{\Sigma hiMi}{\Sigma hi}$$

GPC analysis of PP and AATP bound PP samples was carried out at RAPRA Polymer Charaterisation Centre while that of polymerised AATP was carried out by the author using WATERS Model 6000 GPC equipment fitted with four 10μ PL gel columns of exclusion limits of 10^2, 10^3, 10^4 and 10^5Å.

250 μl of 2% polymer solution was injected and the resulting chromatographs of the UV and RI recorded on servoscribe potentiometric chart recorders.

Hypergrade THF was used as the eluent and 2% solutions of polymer samples in the same solvent were injected. The results were recorded and analysed.

CHAPTER 3

3. PREPARATION AND ANALYSIS OF CONCENTRATES

3.1 INTRODUCTION

Over the lifetime of a polymer protected by a stabiliser, the overall physical loss of additive could be the single most important factor determining its effectiveness, especially if the material is a thin film or in fibre form.

Binding an antioxidant to a polymer backbone using radical generators is potentially important in the technology of polymer stabilisation. For such a scheme to be successful, both additive and polymer must have active sites for radical reaction. In the case of the polymer, this active site may be an inherent unsaturation such as is found in rubbers, or an easily abstractable hydrogen to provide a radical site for subsequent binding. In the present section of this work, 1-acroyloyl-4-acryloyloxy-2,2,6,6-tetramethyl piperidine,AATP, whose method of preparation and characterisation was given in section 2.2.2. was used both as an additive and a polymer reacted product.

The following radical generators were used: Dicumyl peroxide, (DCP), di-tert-butyl peroxide (D^tBP), benzoylperoxide (BP), and Azobisiso-butyronitrile (AIBN).

Polymers used were PP (HF22) for the stabilisation studies of bound AATP and LDPE for spectroscopic studies of binding mechanism because it has no inherent i.r. absorption in the regions where AATP and its transformed products absorb.

PP was processed with AATP as concentrates of 5%,10%,20% and 30% with varying ratios of radical generators as shown in table 3.1.

Peroxide/AATP Molar ratio	0.0025	0.0033	0.004	0.005	0.01	0.02	0.05	0.1	0.2
Designation	A	B	C	D	E	F	G	H	J

Table 3.1 : Processing ratios of Peroxide / AATP

3.2 SPECTROSCOPIC ANALYSIS OF CONCENTRATES & MODEL COMPOUNDS

3.2.1 RESULTS

The i.r. spectrum of 5% AATP in LDPE processed at 150^{o}C / 10 min without a radical generator is shown in Fig 3.1A and is compared with the spectrum of a similar formulation but processed with DCP at a ratio designated C in table 3.1. This spectrum (3.1B) is compared with A to show the resultant transformation. When sample A was hot Soxhlet extracted with DCM for 5h, all absorptions due

to AATP disappeared. Absorptions of particular interest are 1605cm^{-1}, due to C=O absorption of acrylamide, 1640cm^{-1} with a shoulder at 1630cm^{-1} due to vinyl unsaturations and 1725cm^{-1} due to ester carbonyl, all shown in 3.1A. The i.r. spectrum after extraction is shown in Fig 3.1A(2)
Similar spectra to that in Fig 3.1B were obtained with the same molar equivalent of each of the radical generators in place of DCP.

All film samples processed with radical generators were hot Soxhlet extracted with DCM for 50h, but no additive was found to be measurably extracted as the i.r. spectra were identical to that before extraction.

Fig 3.2 shows the transformation of the i.r. spectrum of AATP in PE in the 1100 cm^{-1} to 800 cm^{-1} region (vinyl absorptions) when processed with radical generators (B) compared with the spectrum of the additive processed without radical generators (A) in the same polymer. AATP was then processed in PP at 180^{o}C for 10 mins with the same molar equivalent of radical generator. The i.r. spectrum of this sample (Fig 3.3) shows the disappearance of the 1605 cm^{-1} (amide C=O) and the broadening of the 1640 cm^{-1} (unsaturations) and 1725 cm^{-1} (ester C=O) absorptions, similar to the AATP spectrum processed in PE with DCP (3.1.B).

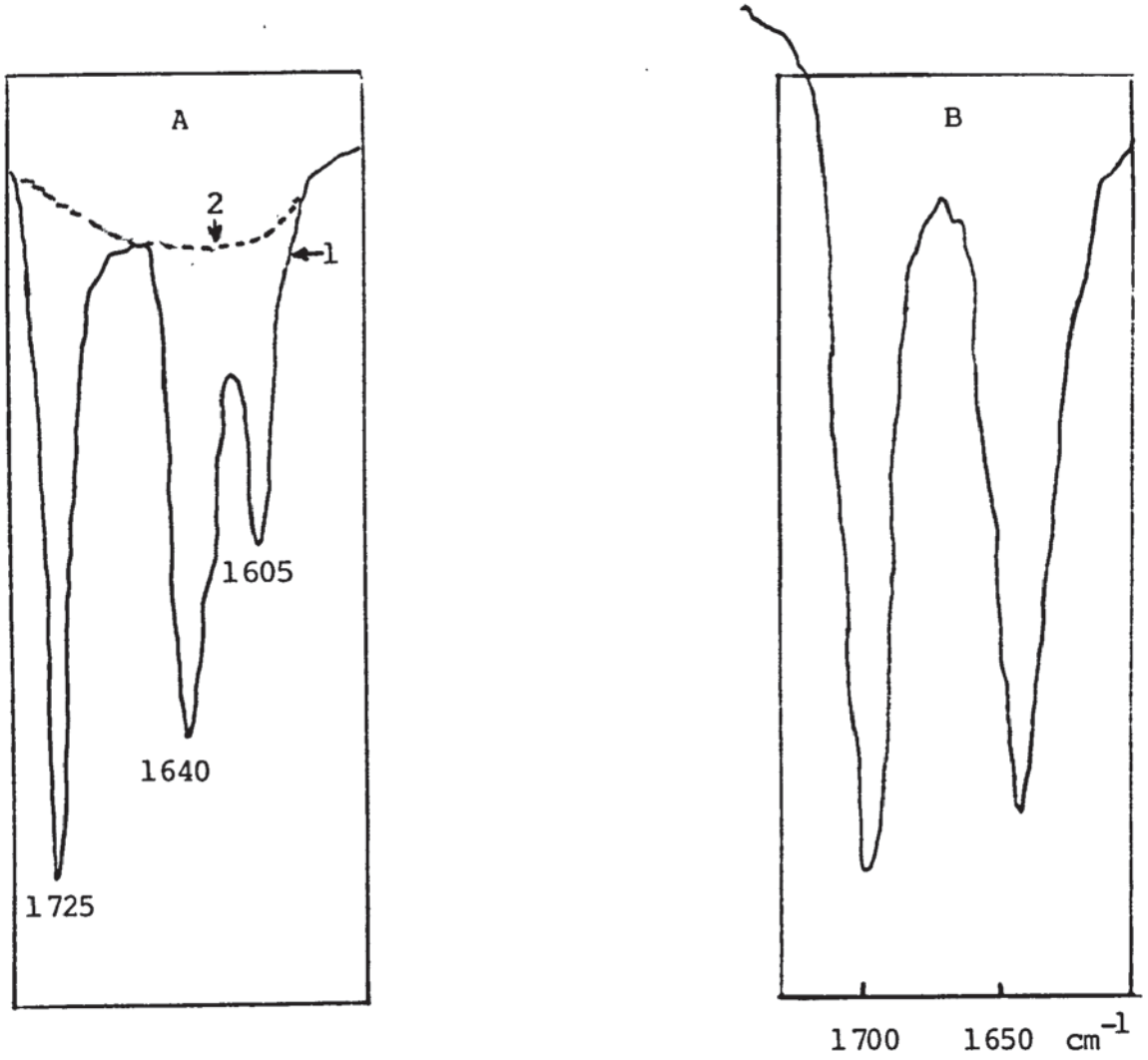


FIG.3.1 I.R. Spectrum of 5% AATP in LDPE processed at 150°C for 10 mins.
A: Without Peroxide 1- Before Extraction; 2- After Extraction
B: With DCP Ratio 'D' (No change in Spectrum after Extraction)

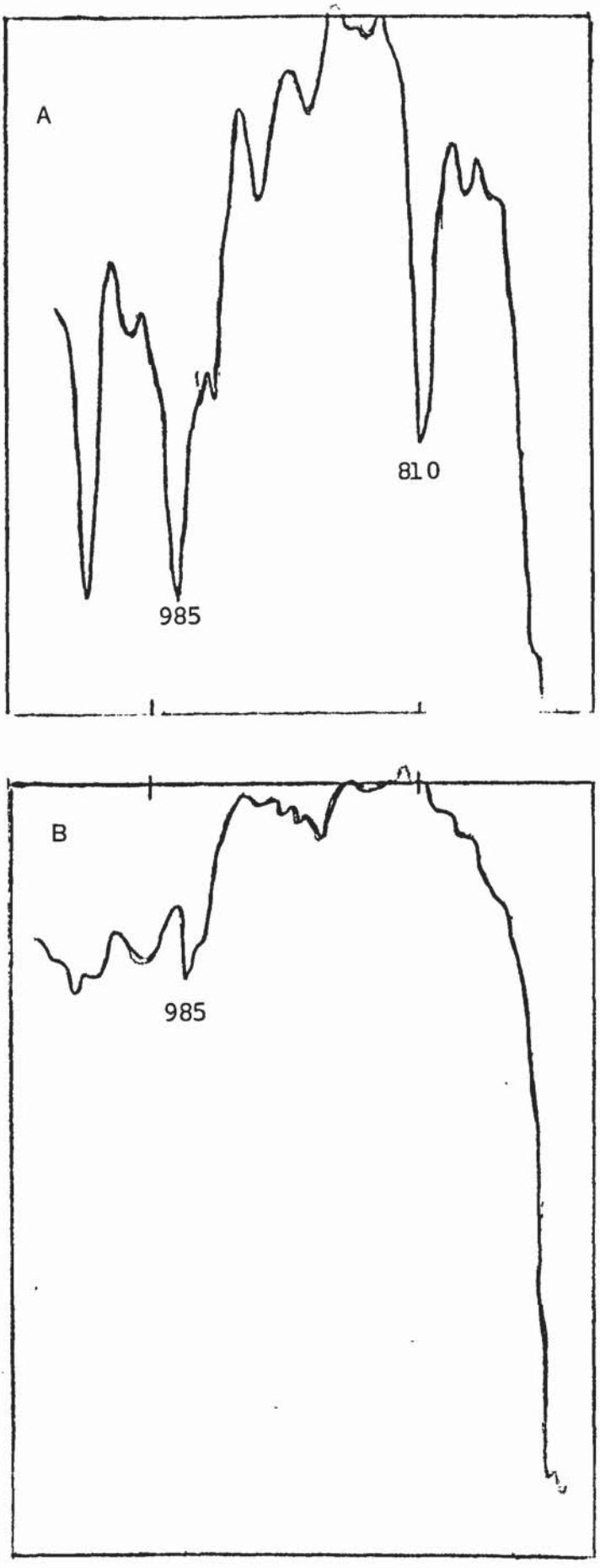


FIG. 3.2 A Segment of ir Spectrum of 5% AATP in PE

A: Processed Without Radical Generators
B: Processed With Ratio 'D' of DCP

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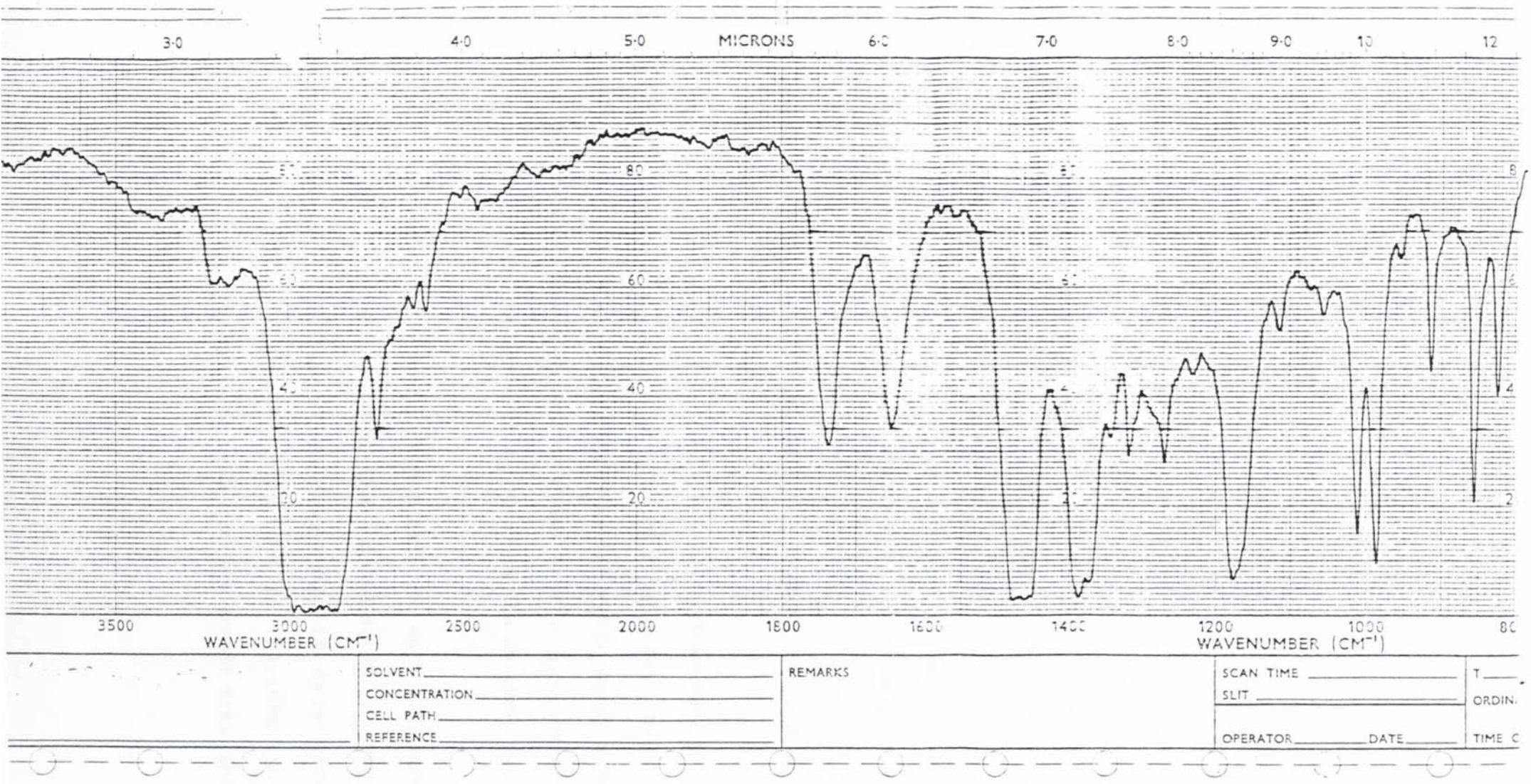


FIG. 3.3 I.R. Spectrum of 5% AATP in PP Processed with 'DCP' (Ratio 'D') at 180°C for 10 mins. Identical Spectrum Obtained After 50h of Soxhlet Extraction.

When this sample was extracted with DCM for 50h, the i.r. spectrum was identical to that before extraction. To investigate the mechanism of the reaction further, a low molar mass model compound, methylcyclohexane (MCH) was used in place of the polymer substrate with DCP initiation.

This reaction was conducted with equimolar quantities of AATP and MCH at 180°C in a sealed ampoule. The ampoule was placed in an oil bath at 180°C and within seconds of immersion, the solution had turned into a white solid product. All the substrate appeared to have reacted with the additive.

The product needed no drying before grinding into a powder (with KBr) for i.r. analysis. One gram (1.00g) of the product was weighed and dried in a vacuum oven at 80°C for 10h without loss of weight. The i.r. spectrum of this product (KBr) disc) is shown in Fig 3.4. The same basic product was obtained with isooctane and dodecane as the substrates. These products were insoluble materials, decomposing at around 350°C without melting. Because of their insolubility they were therefore not susceptable to further spectroscopic analysis. The same ampoule reaction, but this time at a lower temperature of 95°C was carried out for a period of 24h. The product formed here was a soft, wet solid, the wetness due to remaining reactants. The product was washed free of the reactants with hexane and dried. About 15% of this product was found to be soluble in DCM. G.P.C. of this soluble product was

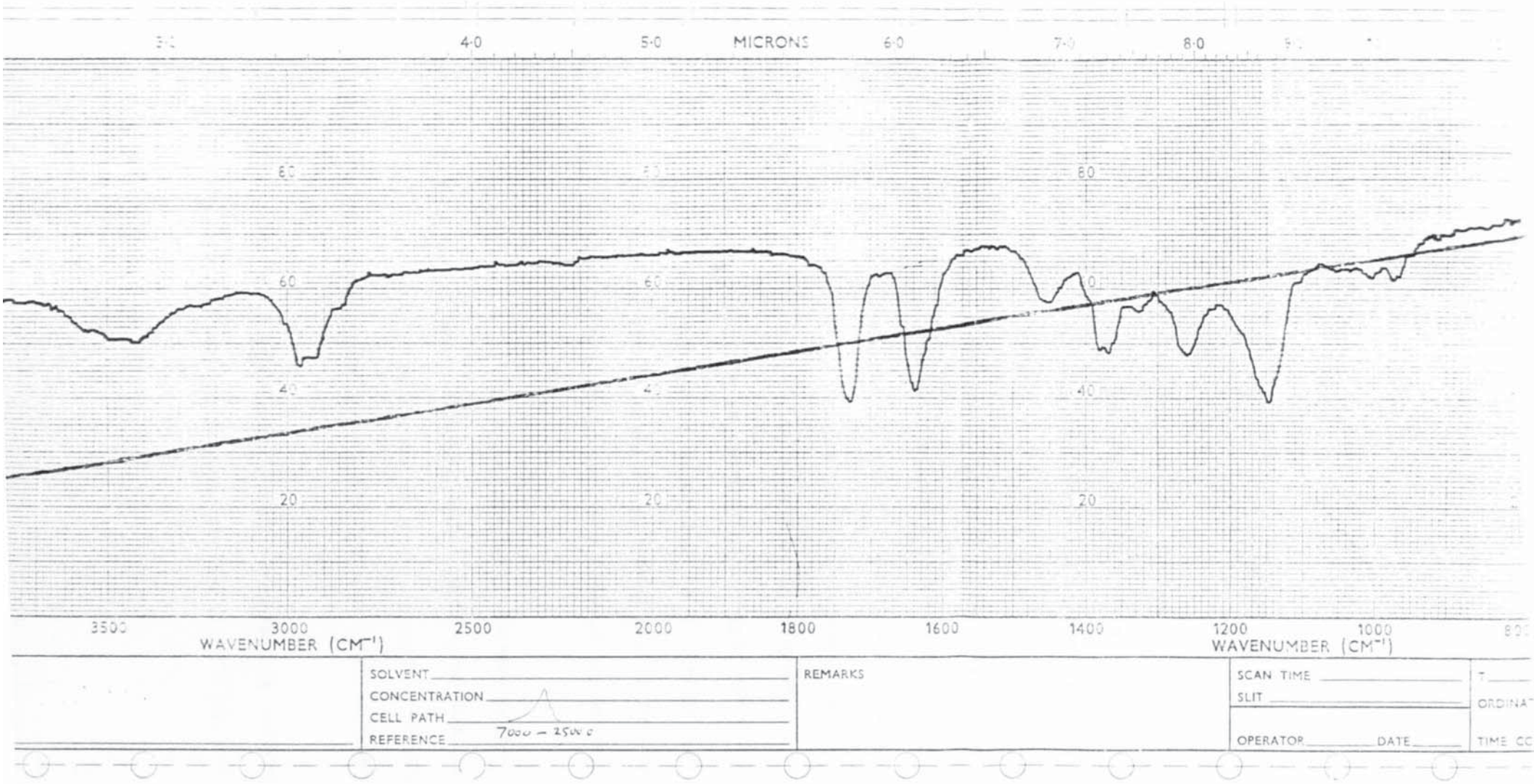


FIG. 3.4 I.R. Spectrum (KBr disc) of the Ampoule Reaction Product of AATP + MCH with Ratio 'D' of DCP

carried out in THF according to the procedure in Sec. 2.5. The product was found to have a Mn of 8000.

Conventional polymerisation of AATP in an open N_2 purged vessel was then carried out with isooctane (101^{o}C) as the solvent,and DCP as the initiator. This reaction was taken to completion, the product washed in hexane and dried in a vacuum oven.

The dried product was then weighed and found to have increased in weight by 10% compared to the original monomer(AATP).This polymer was found to be insoluble in DCM and all other solvents known to dissolve AATP. It decomposed at about 350^{o}C without melting. The i.r. spectrum of this poly AATP is shown in Fig 3.5. This spectrum is very similar to that shown in Fig 3.4, the spectrum of the ampoule reaction product of AATP+MCH with DCP as initiator. The only difference is a peak at 970 cm^{-1} with a shoulder at 960 cm^{-1} in Fig 3.4, which are due to the cyclohexane ring absorption.

Similar results were obtained when MCH and dodecane were used as solvents. When AIBN was used as the initiator in place of DCP, the increase in weight recorded was only 5%.

3.2.2 DISCUSSION

Five hours of hot Soxhlet extraction with DCM was enough to completely remove AATP from LDPE as shown in Fig 3.1B(2), or in

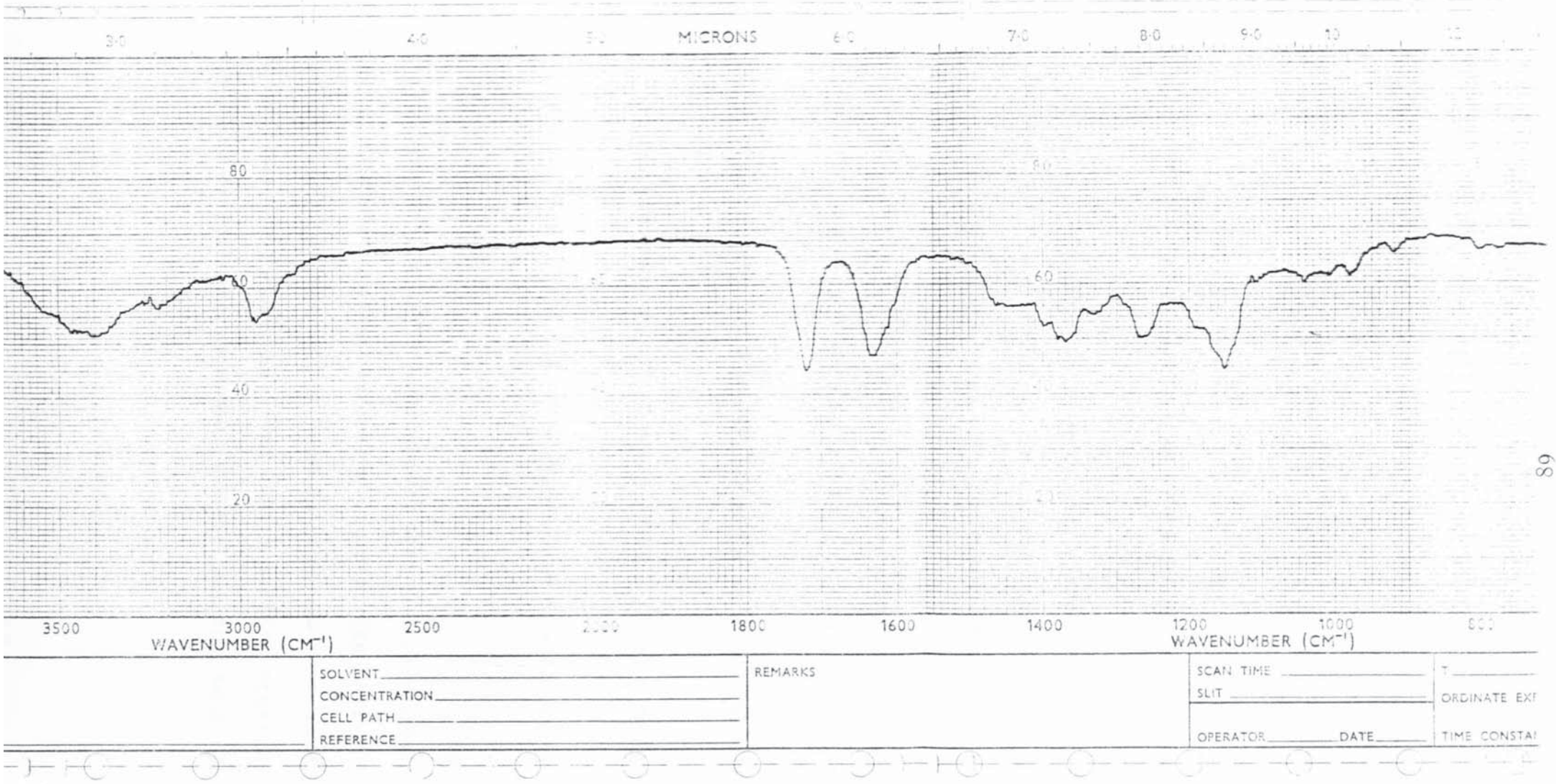


FIG. 3.5 I.R. Spectrum (KBr disc) of Poly AATP (Polymerised in iso octane with DCP as initiator)

PP. When this additive was compounded according to formulation 'A' in table 3.1, in either PE or PP, at a temperature of 150°C or above for a period of 10 mins, a complete transformation of the additive was found to have taken place such that no additive appeared to have been removed even after 50h of extraction with DCM.

In Fig 3.2.A, the following bands are assigned as follows:

985 cm^{-1} (S) Ester vinyl CH out of plane deformation

920 cm^{-1} (m) Vinyl CH_2 out of plane deformation

810 cm^{-1} (S) Vinyl CH_2 out of plane deformation of acrylamide.

In Fig 3.2.B, the spectrum of the transformed product, the 920 cm^{-1} and 810 cm^{-1} absorptions had completely disappeared while the 985 cm^{-1} had reduced in intensity by about 65%.

In Fig 3.1.A, the spectrum of AATP in PE processed without peroxides, the bands are designated as follows:

1725 cm^{-1} (S) Acrylic ester C=O

1640 cm^{-1} (S) Ester vinyl unsaturation with 1630 cm^{-1} shoulder due to amide vinyl unsaturation.

1605 cm^{-1} Acrylamide C=O

Fig 3.1B shows the spectrum of the transformed product. From this spectrum, the following observations can be made:

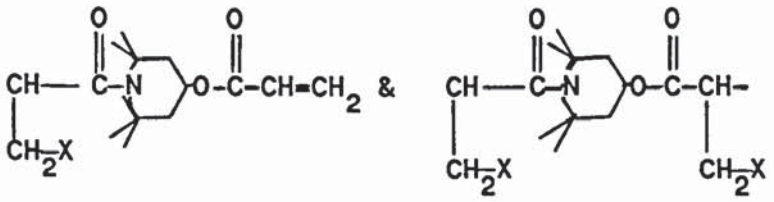
a) the 1605 cm^{-1} band had completely disappeared.

b) both the 1725 cm^{-1} and the 1640 cm^{-1} absorptions had broadened presumably due to superimposition of two absorbances. The 1640 cm^{-1} band also increased in intensity. It can be seen from these figures that the 1640 cm^{-1} absorption in A had broadened towards the lower frequency giving a new peak at 1635 cm^{-1} while the 1725 cm^{-1} had broadened towards higher frequency with a new peak at 1728 cm^{-1} presumably as a result of the contribution of a superimposed band at 1730 cm^{-1}. The intensity of this band however is unchaged.

The complete disappearance of the 810 cm^{-1} and the 1605 cm^{-1} absorptions suggest that the acrylamide ($CH_2 = CH-\overset{O}{\overset{\|}{C}}-N$) vinyl group had reacted. The broadening and increase in the intensity of absorption of the 1640 cm^{-1} band (now at 1635 cm^{-1}) is in total agreement with the loss of conjugated unsaturation and therefore the shifting of the 1605 cm^{-1} to 1635 cm^{-1}.

About 65% of the ester vinyl unsaturation had also disappeared based on the absorbance index of the 985cm^{-1} absorption.

The disappearance of conjugated unsaturation here is expected to result in a shift of absorption towards higher frequency at 1730cm^{-1}. Fig 3.1B clearly shows this superimposed absorptions. Based on the above evidences, it might be argued therefore that AATP is essentially transformed into the following structures in the polymer.

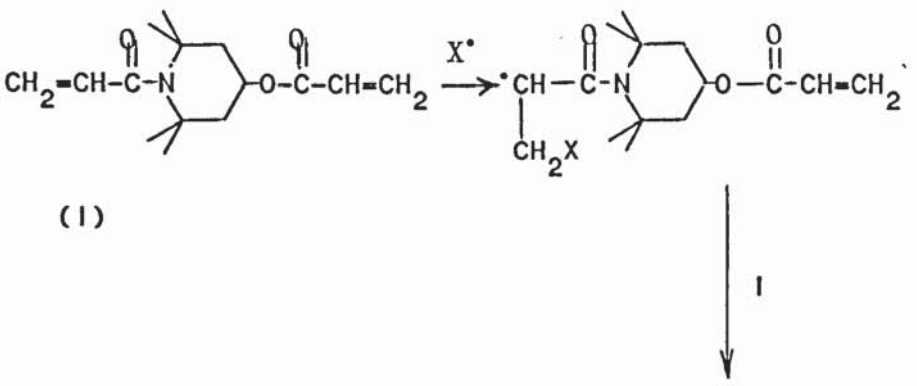


where X is a radical fragment.

Although the region lower than 1500cm^{-1} is masked by the inherent absorbance of PP (Fig 3.3) the transformed spectrum is similar to that in PE at the C=O and C=C stretch region (1730-1600cm^{-1}). It may therefore be presumed that the same transformation had taken place in PP under similar conditions.

The ampoule reactions all produced the same basic product which was similar to poly AATP (Cf Figs 3.4 & 3.5).

In Fig 3.4 however, there was a small absorption at 970cm^{-1} with a shoulder at 960cm^{-1} and these are characteristic absorptions of the methylcyclohexane ring. These two spectra, unlike the reaction products in PE and PP show the complete disappearance of the 985 cm^{-1} ester vinyl absorption. The complete disappearance of all absorptions due to both unsaturations suggests that AATP had reacted from both ends, giving a crosslinked, insoluble polymer.



(I)

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POLYMER .....(1)

Both polyAATP and the products of the ampoule reaction were insoluble in the usual solvents known to dissolve AATP and both decompose at about 350^{o}C without melting, suggesting a heavily crosslinked polymeric product.

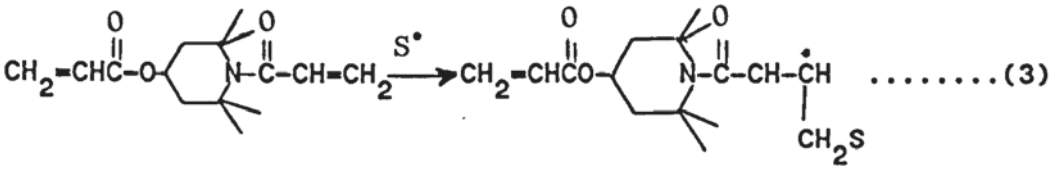
The increase in weight of the products in the ampoule reaction with MCH was 32.5% (Equimolar quantities of reactants) and 10% in the open vessel reaction in isooctane with DCP initiation giving

polyAATP. This increase in weight of the product was the result of incorporation of the solvent into the product polymer.

If S and S$^{\bullet}$ are solvent and solvent radicals respectively and RO$^{\bullet}$ is an alkoxyl radical, then chain transfers can take place as in reaction 2.

$$\left.\begin{array}{ll} RO^{\bullet} + S & ROH + S^{\bullet} \\ P^{\bullet} + S & P + S^{\bullet} \end{array}\right\}\ a,b \quad \cdots\cdots\cdots \quad 2.$$

Where P and P$^{\bullet}$ are polymer and its growing chain respectively. The solvent radical can then initiate the polymerisation of a new monomer, thus becoming part of the polymer.



.....(3)

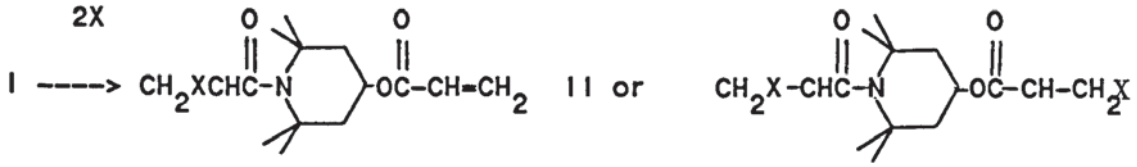
The probability of chain transfer to a solvent is enhanced due to the fact that the polymer may be growing from both ends and a transfer from one end would ensure the production of a linear rather than crosslinked polymer.

In the ampoule reaction with equimolar quantities of AATP and MCH at 180^{o}C, chain transfer to solvent was predominantly from the radical initiator, as the reaction product (Fig 3.4) was a heavily

crosslinked polymer. When the reaction was conducted at 95°C, even after 24h of reaction, 15% of the product was found to be soluble in THF, therefore presumably linear. Temperature therefore is an important parameter in the chain transfer process. Another important reaction parameter presumably responsible for this high rate of transfer is pressure (sealed ampoule, high temperature).

In an open vessel, where the pressure was atmospheric and the temperature was 101°C (b.p. of isooctane) the amount of solvent chemically combined with the product polymer was 10% when DCP was used as the initiator and 5% when AIBN was used. The rate of chain transfer therefore depends also on the temperature and type of radical initiator used.

The proposed reaction mechanism taking place in model compounds is as shown in Scheme 3.1



n I + II ------> Polymer

n I + III -----> Crosslinked Polymer

Scheme 3.1 : AATP reaction in Model compounds.

3.3 EFFECT OF REACTION PARAMETERS IN PP DURING PROCESSING

3.3.1 RESULTS & DISCUSSION

In addition to temperature and pressure, there is a third important parameter that determines the nature of the product in PP.

Unlike low molecular mass (monomeric) liquid model compounds, the viscosity of PP even at melt temperature is very high. Viscosity is therefore a third important parameter that determines the fate of the radicals initially generated by decomposing peroxides. This high viscosity increases the probability of chain transfer to the solvent (PP) from both the radical initiator and a growing chain due to restricted mobility, thus increasing solvent participation in the chain reaction and ensuring minimal crosslinking by radical-radical reactions.

3.3.1.1 TEMPERATURE

Fig 3.6 shows the change of torque with processing time at various temperatures for a 20% AATP in PP processed with ratio C. DCP

Each sample was processed in a closed chamber for 10 mins while the torque developed and displayed on the digital readout was recorded.

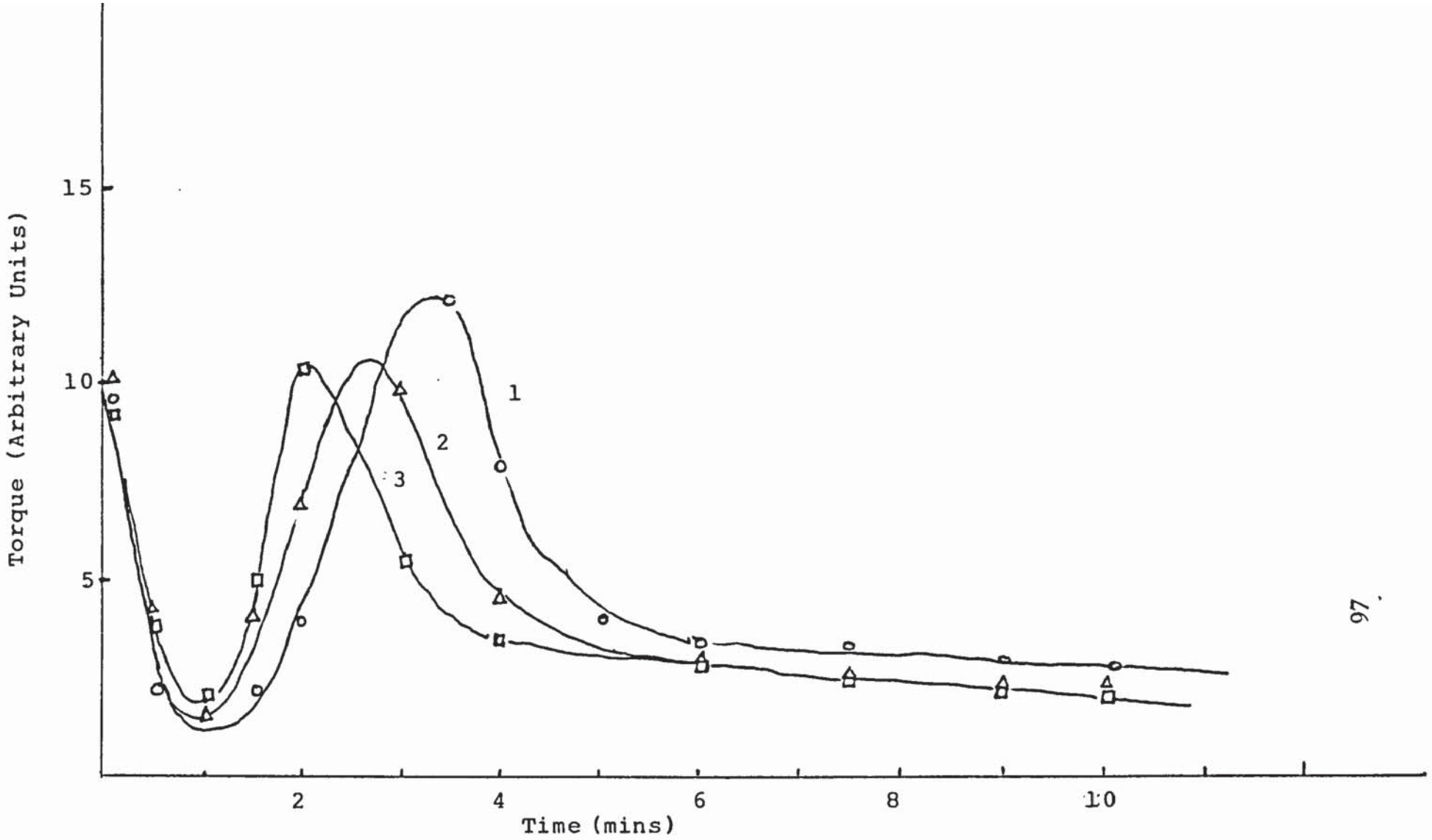


FIG. 3.6 Effect of Temperature on Torque for 20% AATP in PP Processed with DCP (ratio 'D')

1- 150°C; 2- 170°C; 3- 180°C

Since AATP is a liquid, it acted initially as a lubricant and reduced the torque in the chamber before the polymer melted. At the trough (a) three factors were presumably responsible for the minumum torque. The reduction due to lubrication was accelerated further by reduction in molecular weight and change of polymer phase into a molten state. The initial polymer chain scission caused by decomposing peroxides was soon taken over by simultaneous transformation of the additive into bound and polymerised product. The polymer radicals PP$^{\cdot}$ along with alkoxyl radicals initiate the polymerisation of AATP. Monomers initiated by PP$^{\cdot}$ are now bound to polypropylene backbone.

The torque rises sharply as high molecular chains are formed within a very short time.

In certain cases, two growing polymer chains may combine to form an even higher molecular mass polymer. If one end of these chains is already bound to PP, then the resultant polymerised AATP is bound to the polymer. If, on the other hand both ends of the growing chain are bound to PP, then a crosslinked polymer is obtained. Both phenomena should exhibit increased torque at this point.

The peak of the torque at 150^{o}C (curve 1) was reached after 3.5 minutes. A new polymer, essentially a modified PP with some of it in a crosslinked form resulted at this point. At 180^{o}C, this peak

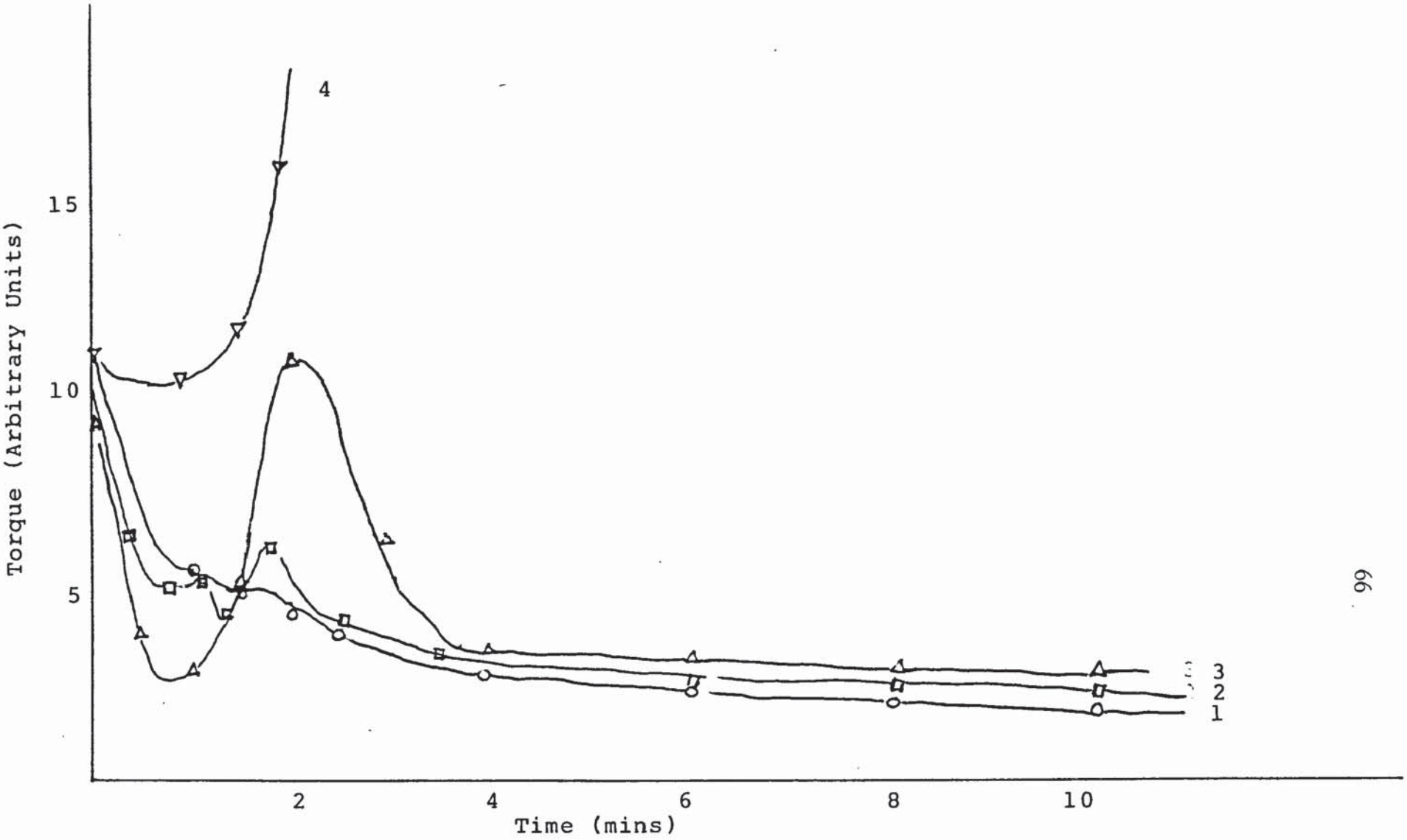


FIG. 3.7 Effect of AATP Concentration in PP on Processing Torque at 180°C
1- 5%; 2- 10%; 3- 20%; 4- 30%

was reached after only 2 minutes and after about 4 minutes, from the start of processing, the reaction was virtually completed. At 170^{o}C, it took more than 6 minutes. The concentrate at this point, was a completely homogenous system with presumably grafted polymeric AATP on the backbone of the PP, thus increasing its molecular weight.

3.3.1.2 CONCENTRATION

Concentration of the additives in masterbatch preparation also plays an important role both on the extent of homopolymerisation and chain transfer to solvent (leading to binding) and crosslinking, which is undesireable in a concentrate whose uniform distribution in a diluted form in the polymer is highly desireable for effective stabilisation.

In Fig 3.7, it can be observed that the 5% curve had virtually no trough or peak as it passed through the lubricating, radical initiating, melting and homopolymerisation and binding stages in PP. The 10% (curve 2) showed a clear evidence of chain scission (stage A) at about 80 seconds after the start of processing, which was soon overtaken by polymerisation, mainly initiated by PP$^{\cdot}$, resulting in a bound polymeric AATP.

$$PP^{\cdot} + n(I) \longrightarrow PP\text{—polymeric AATP} \qquad (4)$$

After about 100 seconds, most of the PP$^{\bullet}$ had initiated polymerisation giving a new modified PP at the peak of the curve, which is then homogenised by subsequent processing, giving a constant final torque reduction due to the effect of the remaining peroxide on the crosslinked polymer. The 20% curve (3) showed the same pattern except that the torque at the peak was much higher. The statistical probability of formation of higher molecular weight, and indeed crosslinked polymer is higher with this concentration. The levelling off of the curve after the reaction (about 4 minutes) near the minimum torque suggests that the amount of crosslinking was minimal. When the concentration was increased to 30% (curve 4), there was a different pattern in torque development. The polymer did not go through the lubricating and melting stages before an auto-accelerating chain reaction developed, presumably giving a heavily crosslinked polymer. After just 2 minutes of processing, the torque developed was 45 units and was approaching 65 after 2.5 minutes (curve 4). The processing was stopped at this stage to avoid possible damage to the torque rheometer. The physical properties of this sample were completely differnt from all the other samples. While all other samples were molten, at 180°, the 30% masterbatch was an infusible powder. An attempt to press a film from this sample at 200°C was largely unsuccessful.

3.3.1.3 Concentration of Radical Initiator

The ratio of AATP/peroxide is very important to effective homopolymerisation and binding of the additive in PP. For a particular AATP/Peroxide ratio in a given PP formulation, increasing the percentage of AATP in PP also increases the percentage of peroxide while actually reducing the amount of PP molecular chains. It follows therefore that the increased peroxide concentration will increase initial chain scission of PP with reduction in molecular mass. A high AATP/DCP ratio on the other hand produces less initiating sites, presumably resulting in higher molecular mass polymer grafting on to PP chains. Fig 3.8 shows the effect of peroxide concentration on torque with processing time for 10% AATP at 180^{o}C. At DCP/AATP ratio 'C', curve 1, shows the typical plasticisation, melting and chain scission, followed by polymerisation and formation of modified PP. High molecular mass grafted polymeric AATP was presumably formed because of the low concentration of DCP in the system. There was less chain scission for the same reason, so the two phenomena may be assumed to have combined to give a high molecular mass product. At ratio F, there was so much initial chain scission so that the final product formed had possibly a lower distribution than the original PP. This is even more pronounced when the ratio was decreased to G (curve 3).

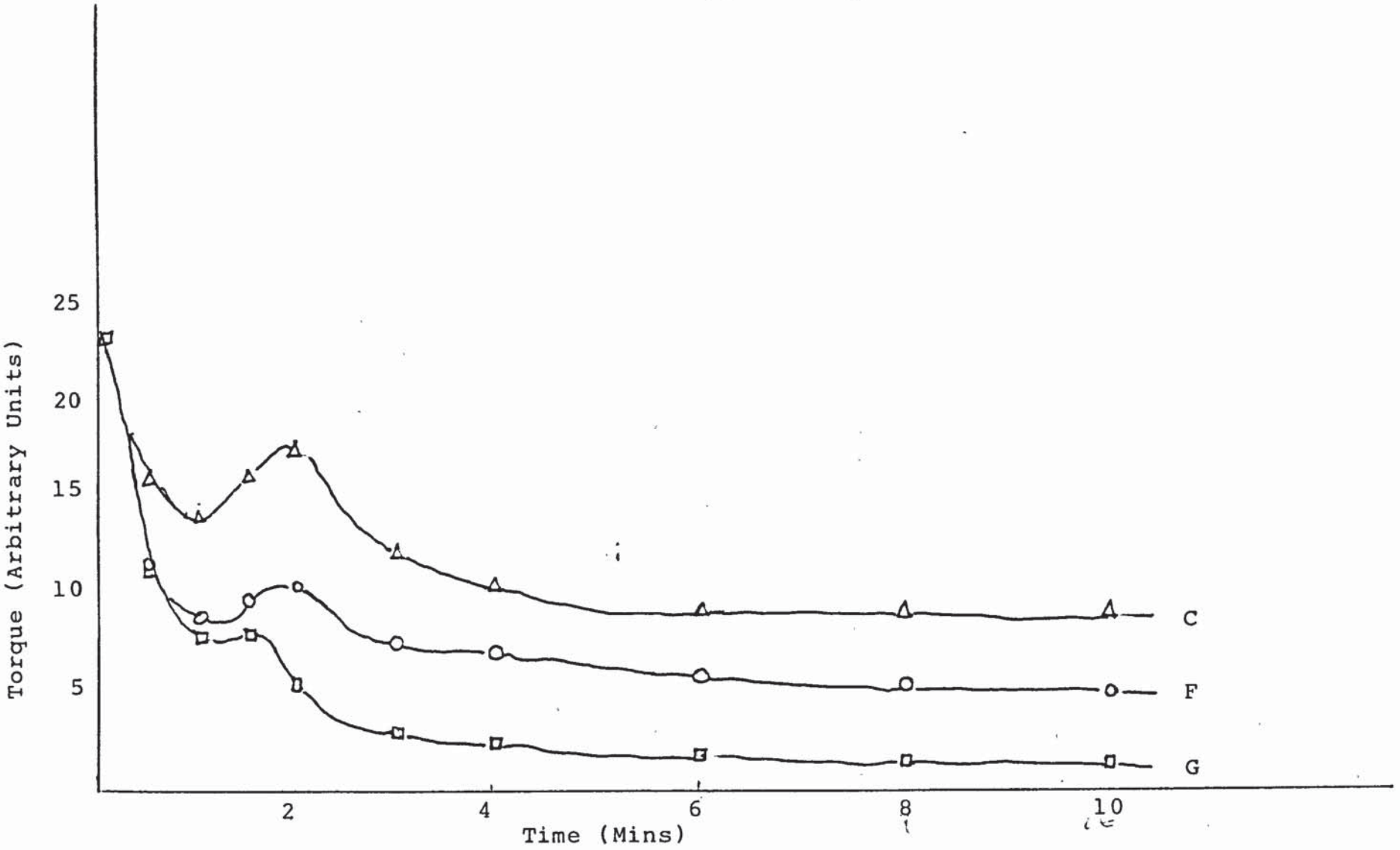


FIG. 3.8 Effect of Increasing Peroxide Ratio on Processing Torque of 10% AATP in PP Processed at 180°C

3.4 EVALUATION OF TRANSFORMED CONCENTRATES

3.4.1 RESULTS & DISCUSSION

The introduction of a second component into a homogenous polymeric material is expected to change such properties of the polymer as molecular weight and its distribution and general bulk properties such as crystallinity and consequently, mechanical properties. In PP, the higher the molecular weight, the lower the crystallinity due to chain entanglement and therefore difficult to rearrange into an ordered crystalline state. Processing of PP with peroxide reduces its molecular mass and a narrowing of its distribution.

Although its ease of processing is improved, most of the desired mechanical properties may be reduced or even lost altogether. Physical properties both microscopic and bulk, can be investigated in a number of ways.

3.4.2 GEL PERMEATION CHROMATOGRAPHY

The analysis of molecular weight and molecular weight distribution of the bound concentrate as shown in Fig 3.9 was carried out by RAPRA Polymer Characterisation Centre. Curve 1 is the distribution of unprocessed PP (HF22) while 2 is the distribution of the same polymer processed with 1.5×10^{-4}mol DCP/100g PP at 180^{o}C for 10mins. Curve 3 is 10% AATP processed with the same amount of DCP

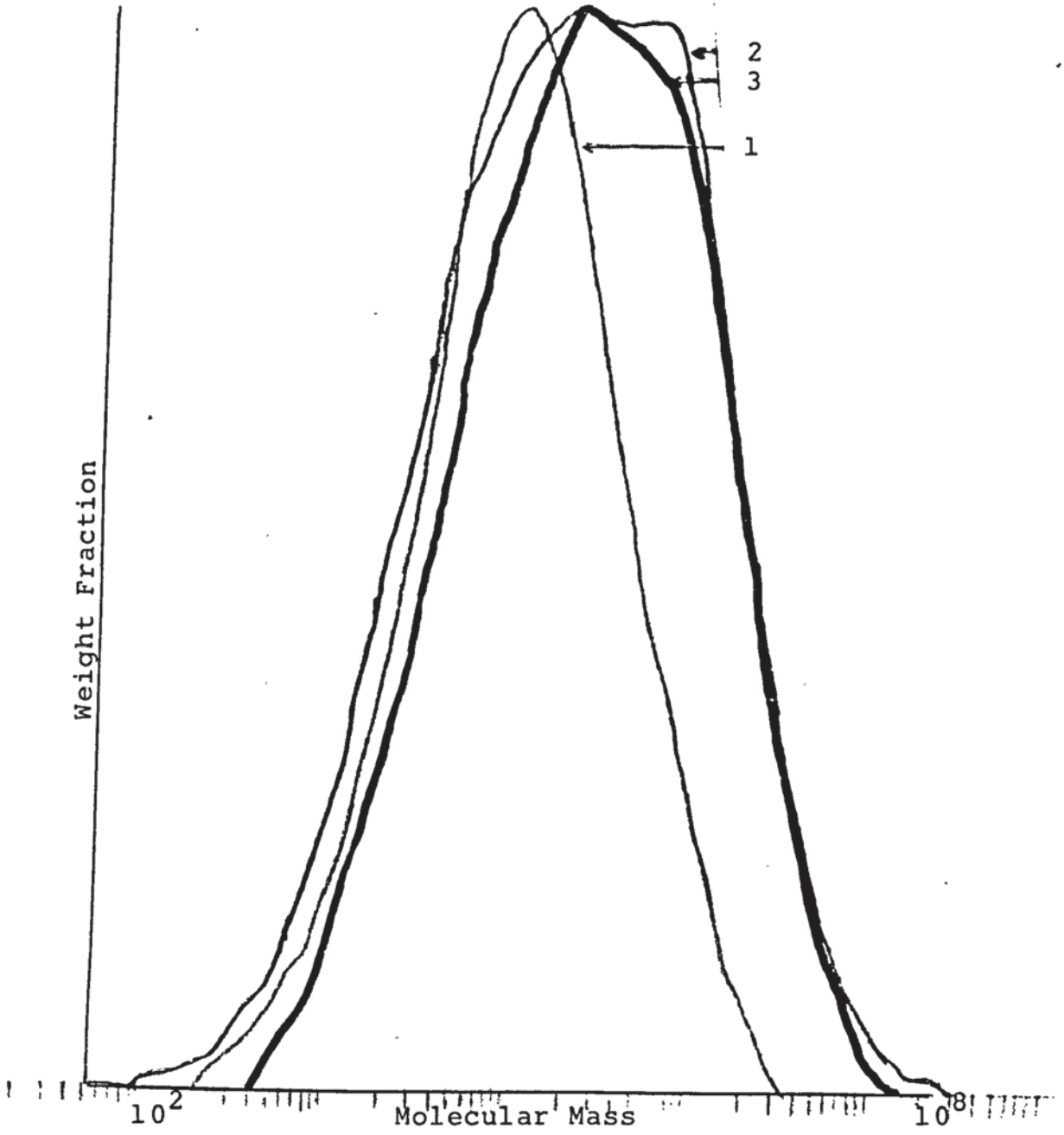


FIG. 3.9 Molecular Mass Distribution of Treated Samples

1- HF22 processed with 1.51×10^{-4} moles DCP/100g PP
2- HF22 Unprocessed
3- 10% AATP in PP (HF22) processed with Ratio 'D' of DCP

as in curve 2 (ratio C). The various properties of the polymer samples are given in table 3.2.

PP type	Mn x 10^4	Mw x 10^5	Mz x 10^6	D
HF 22	4.27	4.48	2.63	10.48
Processed with $1.51x10^{-4}$mol DCP/100g	4.4	1.80	0.7	4.1
10%AATP ratio 'C'	6.52	4.84	2.26	7.43

Mn = Number Average molecular weight

Mw = Weight Average molecular weight

Mz = Mz Average molecular weight

and $D=\frac{Mw}{Mn}$ (Distribution)

Table 3.2 : GPC of treated PP sample

From this table, it can be observed that only $1.5x10^{-4}$ mol DCP per 100g PP reduces the distribution D to less than .5 of its original value (10.48 to 4.1). The same amount of DCP processed with 10% AATP in PP however had a much less dramatic effect on distribution as this was narrowed down to 7.43.

The real effect of the peroxide is more pronounced when Mw, which is most influenced by high molecular weight species in any given polymer is considered. While it reduced the Mw of HF22 to 0.4 of its original value, the presence of 10% AATP in the concentrate increased Mw (from 4.48 x 10^5to4.84x10^5) compared to its original

value. A gel content of 5% which was filtered off before GPC measurement was recorded in this sample.

3.4.3 SOXHLET EXTRACTION OF CONCENTRATES IN XYLENE

5% of poly AATP (see Fig 3.5) was incorporated in PP at 180°C for 10 mins in a torque rheometer. This concentrate, along with5%,10%,&20% masterbatches(Fig.3.7)prepared with 0.004 mol DCP/mol AATP were separately dissolved in xylene in a Soxhlet apparatus for 40h. Table 3.3 shows that the 5% masterbatch was completely dissolved in xylene while insoluble residues remained in all the other extractions.

The 10% concentrate had 5% insoluble gel while the 20% had 12% gel. In the case of 5% polyAATP processed in PP (Fig 3.5) only about 20% of the additive had dissolved in xylene along with PP during extraction. The gel here was polyAATP homopolymer with out PP.

Concentrate	% Gel Content	% AATP retained after recrystallisation
5%	-	> 90
10%	5	90
20%	12	> 80
5% polyAATP	80% of orig.additive	< 5

Table 3.3 : Gel content of Concentrate

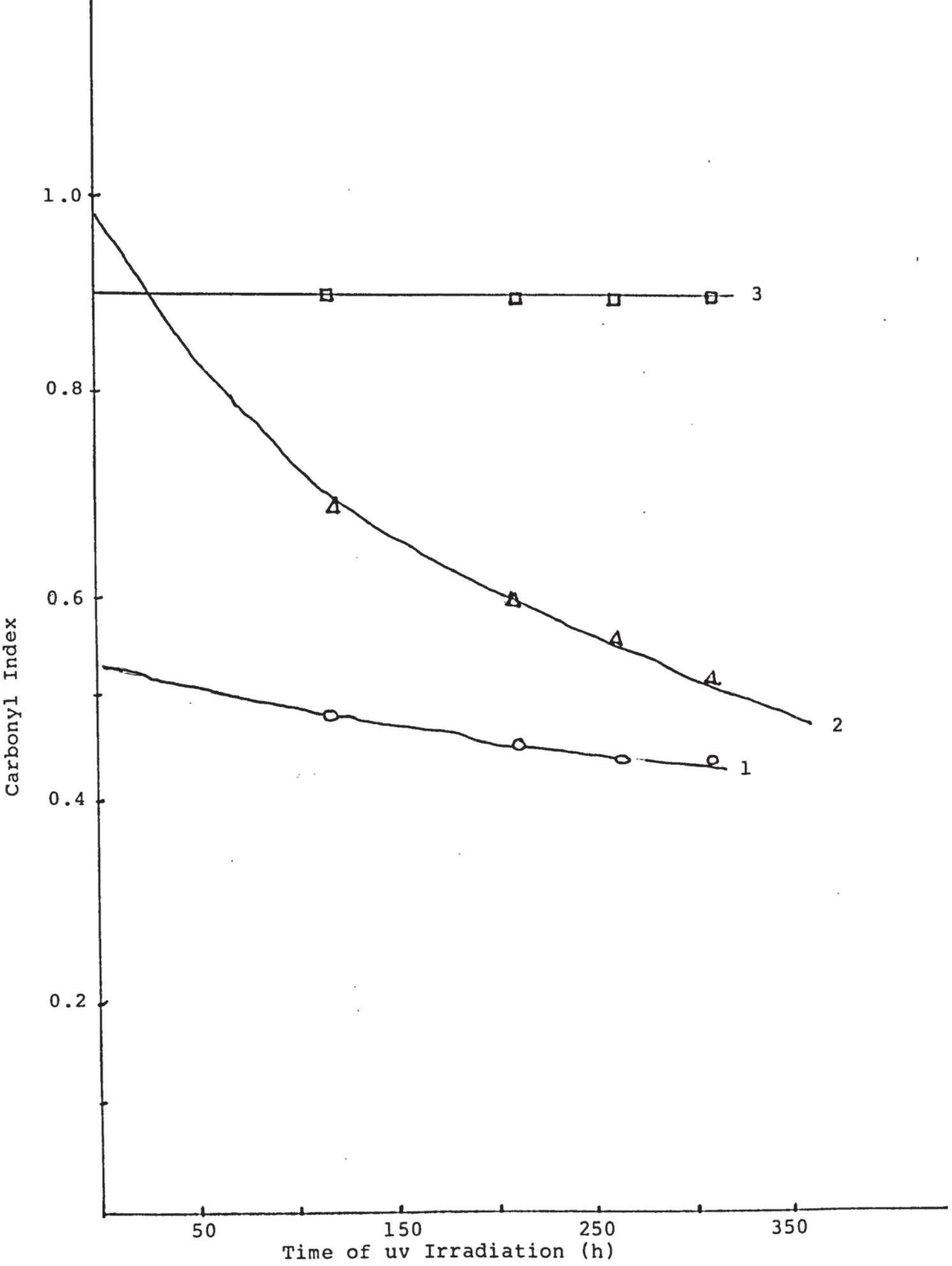


FIG. 3.10 Volatilisation of AATP with Exposure Time
1- 1% AATP in PP; 2- 2% AATP in PP; 3- 2% bound AATP in PP diluted from 10% ratio 'C'

An attempt was made to separate the dissolved additives from PP in this xylene extract by repeated recrystallisation. In the case of 5% polyAATP, the 20% originally retained (dissolved) in PP had been reduced to less than 5% of its original value after 2 recrystallisation procedures. Repetition of this procedure several times could not separate any substantial amount of AATP from these PP concentrate (table 3.3). It can therefore be assumed from all these results that AATP is an integral part of PP.

3.4.4 PHYSICAL LOSS OF ADDITIVES WITH EXPOSURE TIME

Fig 3.10 compares the rate of loss of monomeric AATP with that of the bound antioxidant in PP, exposed in a u.v. cabinet over a 300h period as measured by reduction of ester Carbonyl index. The concentrations used in this study (1&2%) are somewhat higher than what is normally used in the industry, but only a simple comparison is intended here to show the superior substantivity of the bound AATP over the unbound antioxidant.

Although volatilisation is not the only phenomenon causing the loss of this additive, other factors can be neglected over this short time scale. During this exposure period, the 1% concentration of the unbound additive was depleted by about 25% [Fig.3.10.(1)] while over 50% was lost from the 2% unbound additive(2). On the other hand, there was hardly any reduction in concentration of the bound sample [Fig 3.10 (3)].

3.4.5 OPTIMUM CONCENTRATES

From Fig 3.7, it is quite evident that only an AATP concentration of less than 30% in PP could be processed without a build up of an excessively high torque generated as a result of crosslinking and subsequent formation of an infusible gel. Table 3.3 shows a progressive build up of gel with increasing AATP concentration. While no gel was formed with the 5% concentrate and therefore technically the best masterbatch, a balance has to be struck between gel formation (minimum) and additive concentration (maximum). Although the 20% masterbatch can still be effectively diluted to the usual concentration, the 12% gel content may not allow even distribution to provide an effective protective action.

The 10% concentrate with about 5% gel content is therefore preferred as the optimum masterbatch based on these considerations and subsequent u.v. exposure results.

The concentration of radical generators could be as low as in ratio A of table 3.1. If the amount is generally less than this minimum, not all the additive is transformed in the polymer. From this minimum amount to about ratio C some of the transformed (polymerised) additive was found to be substantially separable from PP after xylene dissolution of the masterbatch and repeated recrystallisation. As high as 40% of the polymerised AATP was removed in this way at such a low peroxide concentration.

This polymerised but unbound AATP however, is not extracted by its usual solvents such as DCM or acetone and could therefore be presumably as substantive as the bound additive.

At ratio 'D' only about 10% of the transformed additive could be removed. When this ratio was increased to F [Fig 3.8 (2)] the final processing torque was lower than the minimum at change of phase, which is an evidence of degradation of PP. At ratio 'G' the torque was almost down to zero and the product was a liquid rather than a melt. When this product was incorporated into PP, in a diluted form, the distribution was extremely poor.

As photostabilisation results show in chapter 4.1, the performance of this sample was also very poor.

CHAPTER 4

4. STABILISATION OF POLYPROPYLENE BY AATP

4.1 PHOTOSTABILISATION

It is now well established[122,135-138] that sterically hindered piperidines such as AATP are oxidised to the corresponding nitroxyls during photo oxidation in stabilised polymers and these are now believed to be the species responsible for photostabilisation.

Nitroxyl radical concentration was measured in PP containing AATP as described in Section 2.4.2. Because of the size of the E.s.r. sample tube and the density of the polymer films a maximum of only about 0.06g of the polymer sample can be conveniently inserted into the tube for radical concentration measurement. This has necessarily imposed a limit to the sensitivity of the instrument since the noise to signal ratio becomes too high for accurate measurement at concentrations less than 2.5 $x10^{-5}$mol/100g.

This is therefore the sensitivity limit for Nitroxyl radical concentration in solid PP with the instrument used in this work.

4.1.1 RESULTS

The photostabilising effectiveness of the different formulations of AATP in PP is compared with the control sample in Fig 4.1.

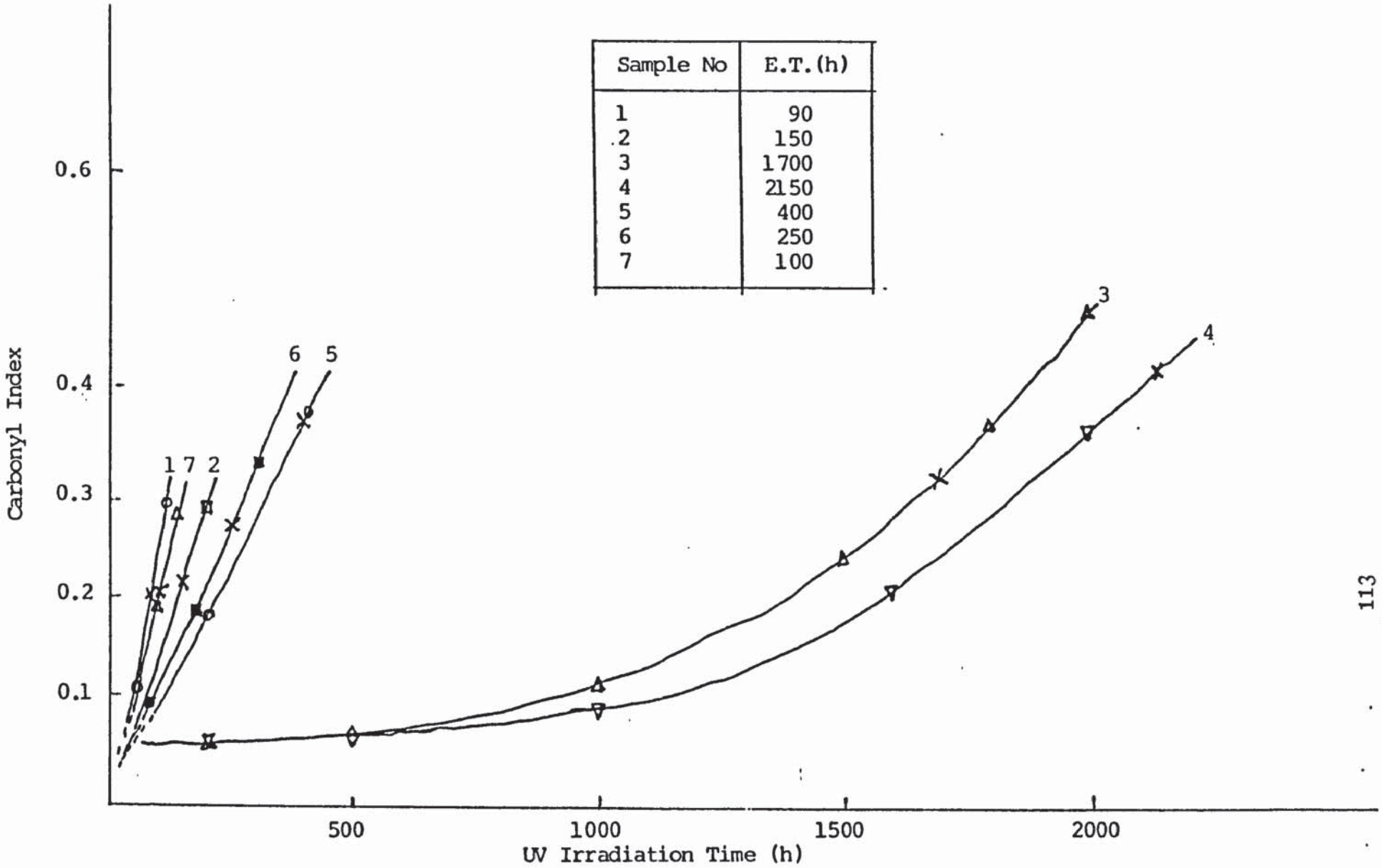


FIG. 4.1 Effect of 1.51×10^{-3} mol/100g AATP(0.4%) on Photo-oxidation of PP . Embrittlement Time (E.T.) is Indicated on the Curves by x
1- Control (No additive); 2- No radical Generator, E; 3- No radical Generator, U; 4- With Ratio 'D' DtBP, U; 5- With Ratio 'D' DtBP, E; 6- Poly AATP; 7- With Ratio 'E' DCP

E=Extracted, U=Unextracted

The control sample (curve 1) containing no additive embrittled at 90h, while a 0.4% sample in PP processed without radical generators and then thoroughly extracted with DCM before exposure embrittled at 150h, suggesting a small residual amount of the additive in the extracted sample. When this same sample was exposed without extraction, (curve 3) it embrittled at 1700h.

The time to embrittlement was extended to 2150h when the same amount (0.4%) of AATP in PP diluted from ratio 'C' (table 3.1) was exposed as an unextracted sample (curve 4). Although no additive was measurably extracted from this bound sample, (Chapter 3, Fig 3.3) a five hour extraction with DCM reduced its effectiveness rather dramatically, giving an embrittlement time of 400h, as shown in Fig 4.1 curve 5. The same amount of polyAATP (chapter 3, Fig 3.6) in PP gave an embrittlement time of only 250h (curve 6) when it was exposed in the uv cabinet. Curve 7 shows the result of 0.4% AATP in PP diluted from 10% AATP processed with (ratio E)DCP. This sample gave the same embrittlement time of 100h with both extracted and unextracted films.

The development of nitroxyl radicals with exposure time for some of the samples discussed in Fig 4.1 is shown in Fig 4.2, where curve numbers refer to the same sample.

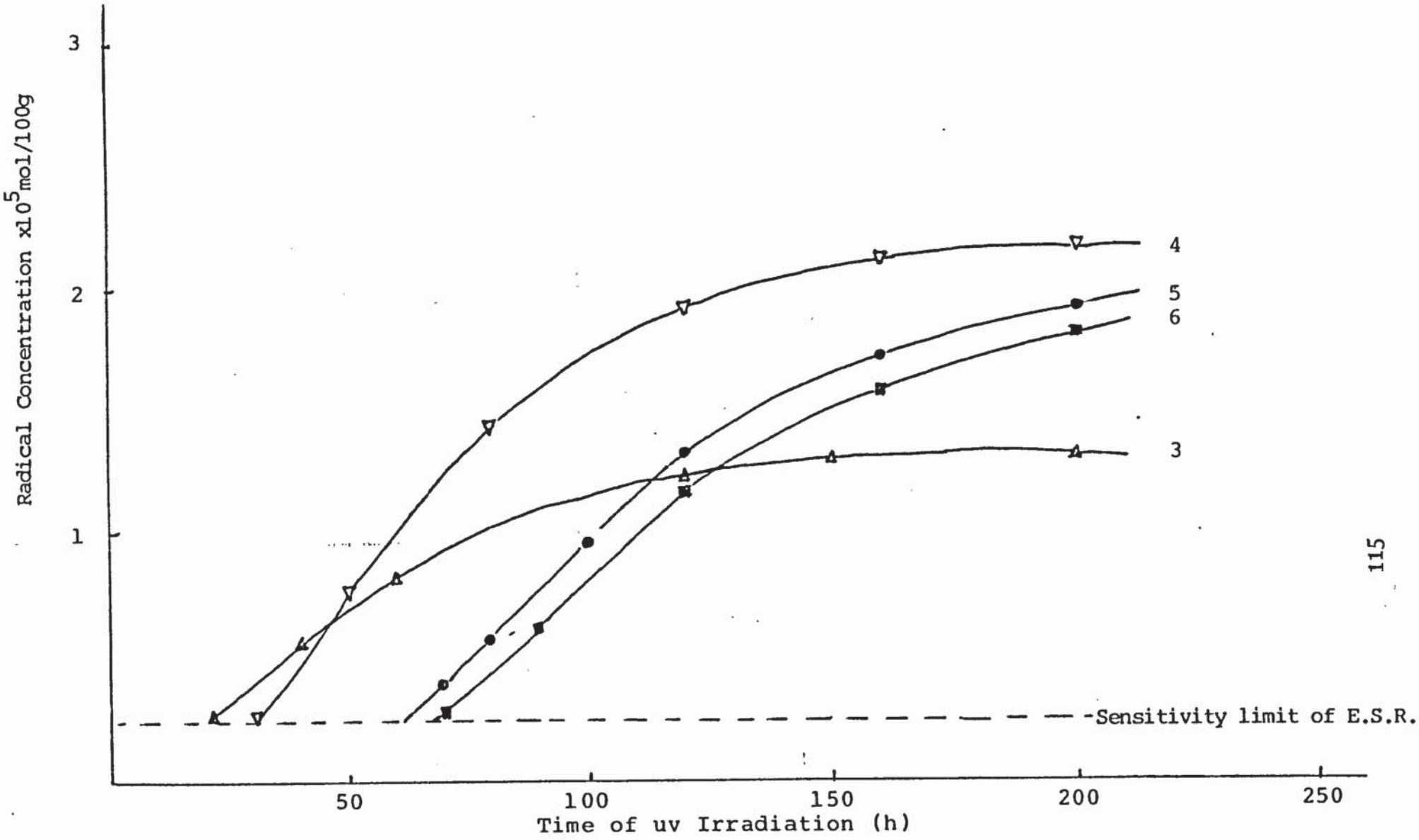


FIG. 4.2 Effect of UV Irradiation on Nitroxyl Radical Development in 1.51×10^{-3}mol/100g (0.4%) AATP in PP
3- No Radical Generator, U; 4- With Ratio 'D' DtBP, U; 5- With Ratio 'D' DtBP, E
6- Poly AATP

E=Extracted sample; U=Unextracted sample

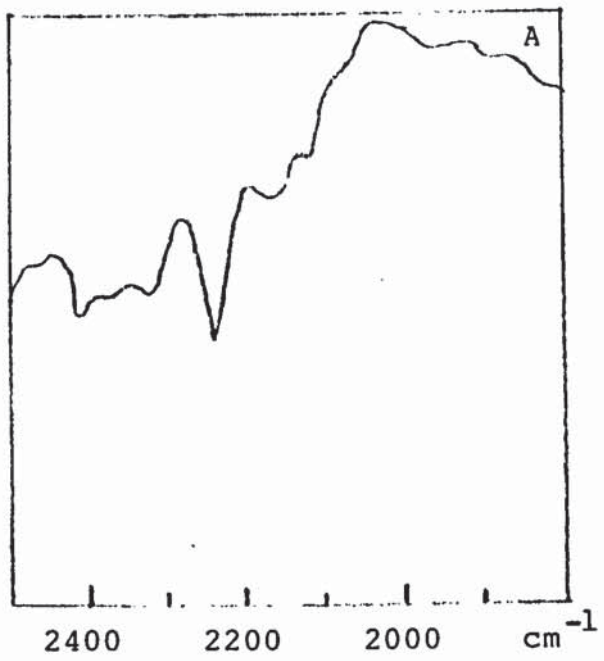
A measureable amount of nitroxyl radicals could be detected in sample 3, after only 20h of u.v. exposure, and a steady state appeared to have been reached after 150h.

No radicals could be detected from sample 4 until after 30h of irradiation, but its steady state concentration appeared to be higher than that of sample 3. Both samples 5 & 6 showed no measureable nitroxyl radical concentration until after 60h of irradiation. The concentration, even after 200h did not appear to have reached a steady state, but both concentrations are higher than the steady state concentrations of sample 3 after 150h. As shown in Fig 4.1, samples 5 & 6 have embrittlement times of 400h and 250h respectively, while 3 & 4 have 1700h and 2150h as their respective embrittlement times.

When the 10% concentrate was prepared with DCP/AATP molar ratio in excess of 0.01, a new band appeared in the i.r. spectrum of the film at 2240 cm^{-1} as shown in Fig 4.3A.

This sharp and strong band became even more intense when most of the soluble part of the polymer was dissolved away with xylene leaving largely an insoluble gel.

A film was pressed from this residual polymer and its i.r. spectrum as given in Fig 4.3B(1) shows the increased intensity of this absorption at 2240cm^{-1}. The soluble part of the polymer showed no absorption in this region.



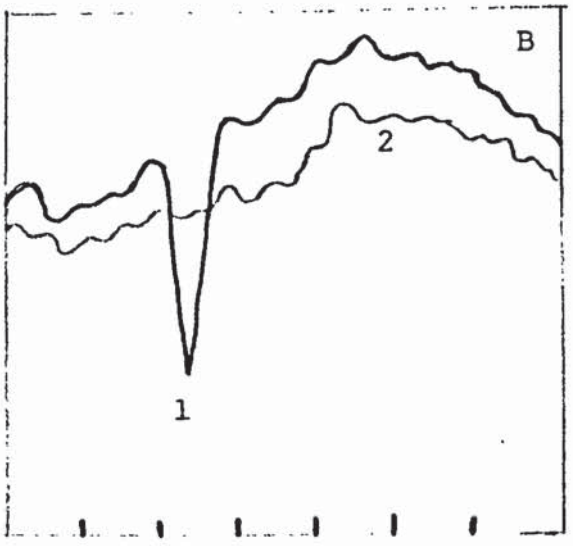


FIG. 4.3 A segment of ir Spectrum of AATP in PP processed with High Ratio (E) of DCP showing the formation of Isocyanate.

A: Spectrum of 10% AATP processed with DCP
B: Spectrum of the largely Xylene insoluble part of the polymer
1- Before warming in n-butylamine
2- After 2 mins of warming in n-butylamine

The 2240cm^{-1} is a characteristic absorption of isocyanates (-N=C=O) and a test for such compounds was carried out by warming the film in n-butylamine for a few minutes.

As shown in Fig 4.3B(2) this band disappeared completely after warming, confirming that it was indeed an isocyanate absorption. This can only form as a result of ring opening of the piperidine ring.

Samples 6 & 7 in Fig 4.1, which embrittled at 250h and 100h respectively were reprocessed each with a very low concentration (0.02%) of monomeric AATP to provide an initial protection during the critical first 50h of nitroxyl radical generation. Fig 4.4 shows the effect of such an addition, compared with 0.02 unbound AATP in PP alone [Fig 4.4(1)].

As shown in this figure, the embrittlement time of PP stabilised with 0.4% AATP (diluted from 10% ratio 'E') which embrittled at 100h in Fig 4.1 has now been extended dramatically to 1850h. The photostabilising effectiveness of the added monomeric AATP alone [Fig 4.4 (1)] was only 320h.

The embrittlement time of PP stabilised with polyAATP was only marginally improved to 550h by the same treatment as shown in the figure, (curve 6a).

The nature of the initial protection given to this totally transformed sample (7) was investigated further by the addition of 0.1% HOBP and Irganox 1076 to 0.4% of this sample in PP before irradiation. The effect of these additives on the stability of the film is shown in Fig 4.5. Curves 1 & 2 show the development of C=O index with embrittlement point of 0.1% Irganox 1076 and HOBP respectively in PP. Curves 7a and 7b show analogous curves for 0.4% AATP in PP (sample 7 in Fig 4.1) after addition of 0.1% Irganox 1076 and 0.1% of HOBP respectively. It is quite evident from this result that initial protection provided by these additives to the totally transformed AATP was responsible for the prolonged photostabilisation of the samples. Sample 3 (0.4% AATP in PP) was diluted from a 10% ratio 'E' and 1% Irganox 1076 added during the preparation of the masterbatch. So it is effectively 0.4% AATP + 0.04% 1076.

The addition of this phenolic antioxidant during masterbatch preparation has a dual function as a melt stabiliser, thus minimising the initial formation of hydroperoxides and presumably as polymerisation regulator, giving an embrittlement time of 1980h.

Sample 4 (0.1% AATP + 0.4% 1076) has a rather high ratio of the potentially photosensitising phenol, giving an embrittlement time of 650h, pointing to a possible antagonism between the two

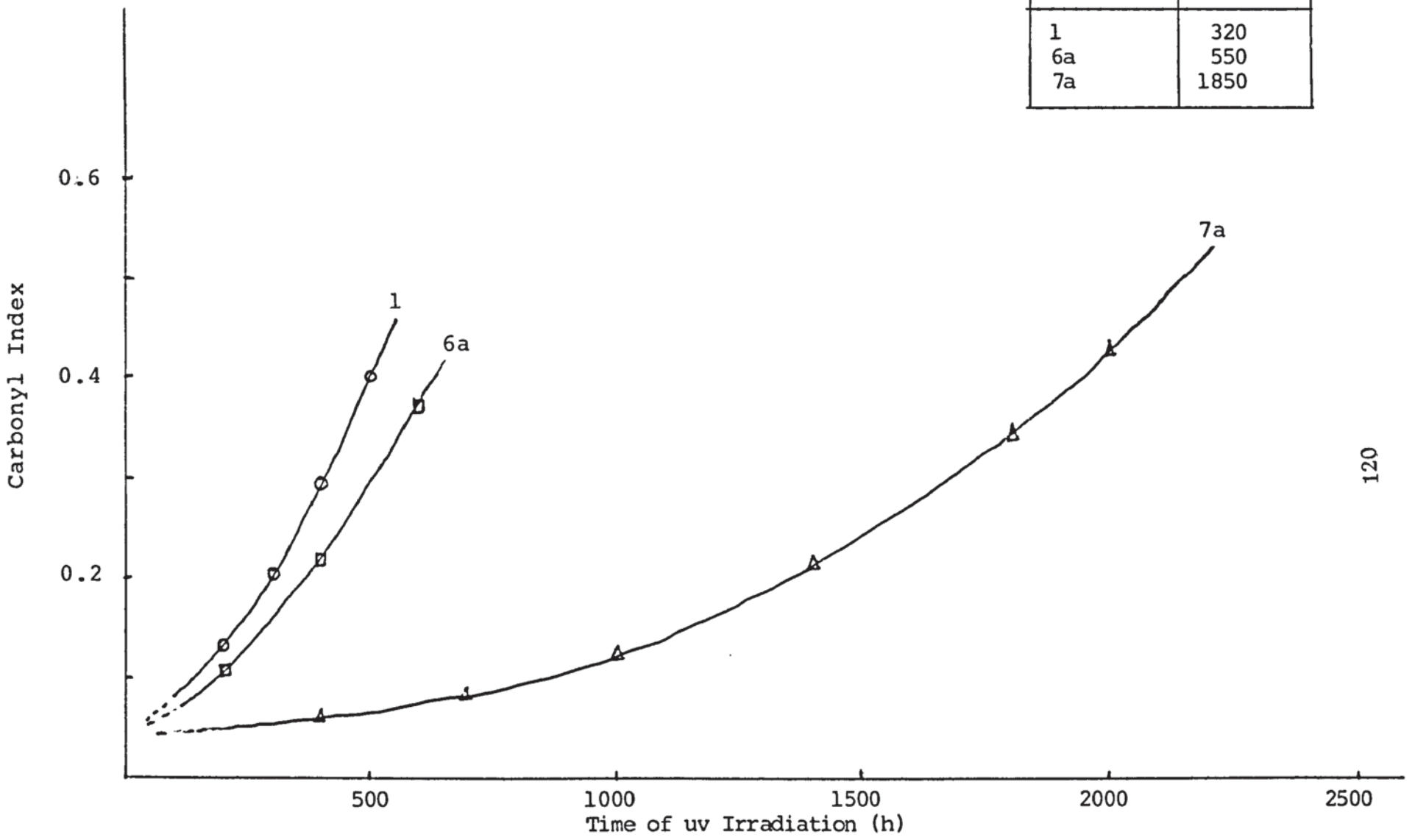


FIG. 4.4 Effect of Initial Protection by Unbound AATP on Bound AATP in PP During UV Irradiation
1 → 0.02% AATP(unbound); 6a → 0.4% PolyAATP + 0.02% AATP(unbound)
7a → 0.4% AATP with Ratio 'E' DCP + 0.02% AATP(unbound)

stabilising species. The concentration of nitroxyl radicals was followed with time of irradiation for the PP samples in Fig 4.5.

As shown in Fig 4.6, a measurable amount of nitroxyl radicals could be recorded from sample 3 after 30h of uv irradiation. After 150h, the concentration of nitroxyl radicals appeared to have reached a steady state. In the case of sample 7a, no nitroxyl radicals were detected until after 120h and no appreciable increase was recorded even after 250h. However, it did not appear to have reached a steady state. The sample containing HOBP synergist (7b) was also slow in nitroxyl radical generation but a measurable amount was in this case recorded after 70h of irradiation and its rate of increase however was higher than that of sample 7a.

In sample 4 (0.1% AATP + 0.4% 1076), no NO·signal was observed even after 250h of u.v. irradiation.

A combination of 0.4% (1.51×10^{-3}mol/100g) AATP and 0.1% (2.82×10^{-4}mol/100g) NIDEC in PP and an equivalent amount of the bound additive but without the Ni complex were exposed in the u.v. cabinet while the development of nitroxyl species was followed by e.s.r. While a measureable amount of this NO·species was generated after 30h of exposure, reaching a stationary level after 150h, [Fig 4.2 (4)], no NO·radical could be detected from the AATP/NIDEC combination up to embrittlement time of 210h.

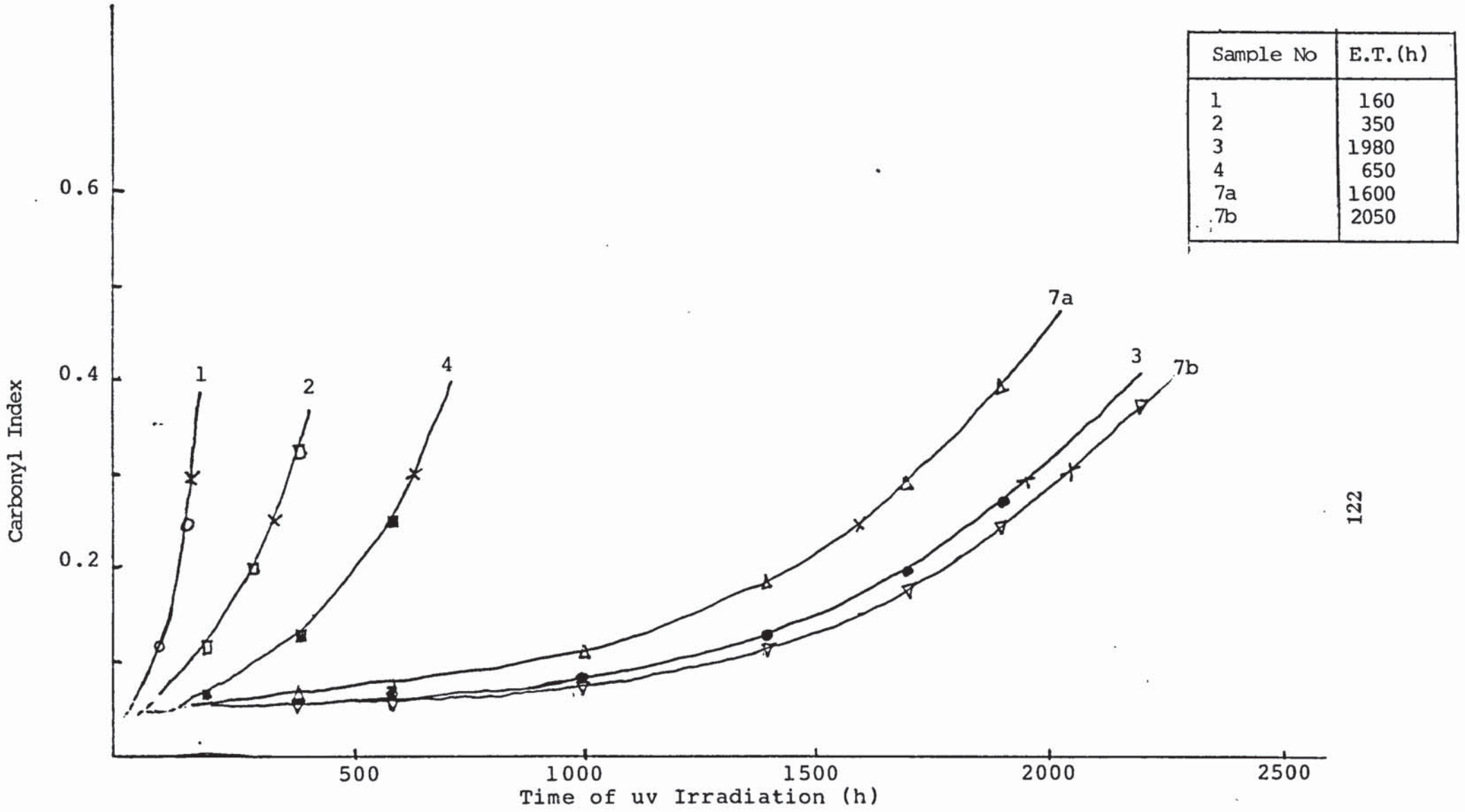


FIG. 4.5 Effect of Combination of Antioxidants (with AATP) on the Photo-oxidation of PP
1→ 0.1%(1.9×10^{-4}mol/100g) Irganox 1076; 2→ 0.1%(2.9×10^{-4}mol/100g)HOBP
3→ 0.4% AATP + 0.04% 1076; 4→ 0.1% AATP + 0.4% 1076
7a→ 0.4%(1.51×10^{-4}mol/100G) AATP + 0.1% 1076; 7b→ 0.4% AATP + 0.1% HOBP

(Numbers correspond to those in FIG. 4.4)

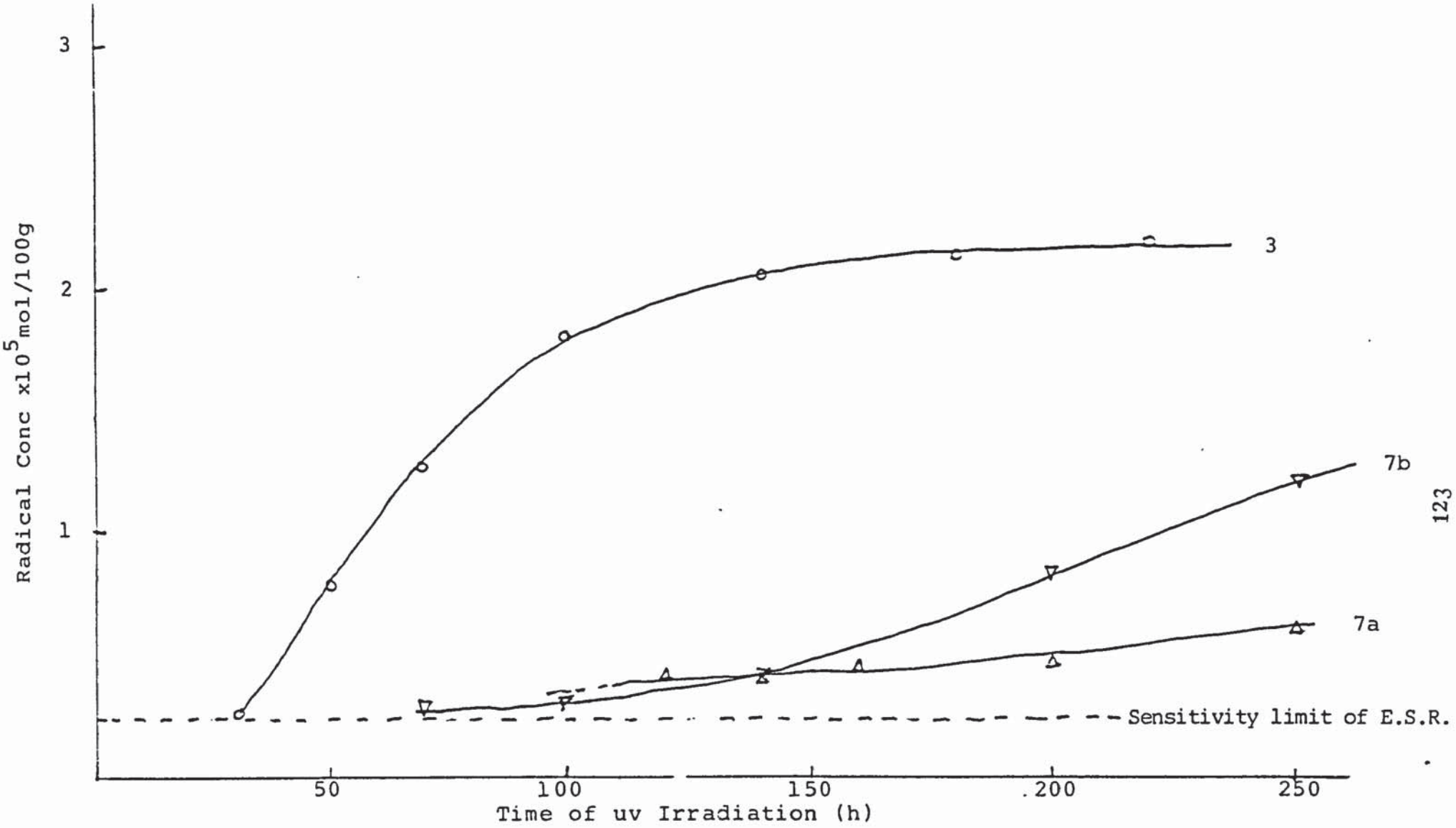


FIG. 4.6 Effect of uv Irradiation on Nitroxyl Radical Development
3→ 0.4% AATP + 0.04% Irganox 1076 added during Masterbatch preparation
7a→ 0.4% AATP + 0.1% Irganox 1076; 7b- 0.4% AATP + 0.1% HOBP
4→ No signal recorded up to 250h.

(Numbers correspond to those in FIG. 4.5)

Table 4.1 gives the embrittlement times (ET) of the separate antioxidants in PP compared to the combination.

Antioxidant	CONCENTRATION Wt.%	Molar/100g	E.T. (h)	Time of first detection of $NO^{\cdot}$ (h)
AATP	0.4	1.51×10^{-3}	1700	30
NIDEC	0.1	2.8×10^{-4}	550	-
AATP+NIDEC			210	Not detected up to E.T.

Table 4.1 : Combination effects of stabilisers

Antioxidant	Wt % Conc.	Mol/100g	E.T
HTMPO	0.1	6×10^{-4}	750
NIDEC	0.2	5.64×10^{-4}	800
HTMPO+NIDEC			380

Table 4.2 :

Table 4.2 compares the E.T. of 0.2% NIDEC and 0.1% 4-hydroxy-2,2,6,6,-tetramethyl piperidinoxyl (HTMPO) in PP separately and in combination. The rate of nitroxyl radical decay (signal) was also followed with irradiation time during the first 50h. The

combination with NIDEC as shown in Fig 4.7, was found to accelerate the decay of nitroxyl radicals.

4.1.2 DISCUSSION

In Fig 4.1, it was shown that the E.T. of the extracted PP samples processed with AATP but without peroxide (2) showed evidence of residual antioxidant even though it was presumably a very small amount, considering the extension of E.T. from 90h (control) to 150h for the extracted sample.

Vinyl monomers are known[139] to undergo thermal polymerisation in some cases in the absence of added free radicals but the extent is obviously very low in the present instance.

This possible transformation from a monomer to a polymer would be expected to change both the physical and chemical properties of the additive. The polymerised antioxidant therefore may not be as readily soluble in DCM as the monomer. It is presumably this retained antioxidant which extended the E.T. of the extracted sample to 150h.

The unextracted sample of this unbound additive (3) embrittled after 1700h while the bound but unextracted sample (4) embrittled after 2150h. The difference between these two values can only be

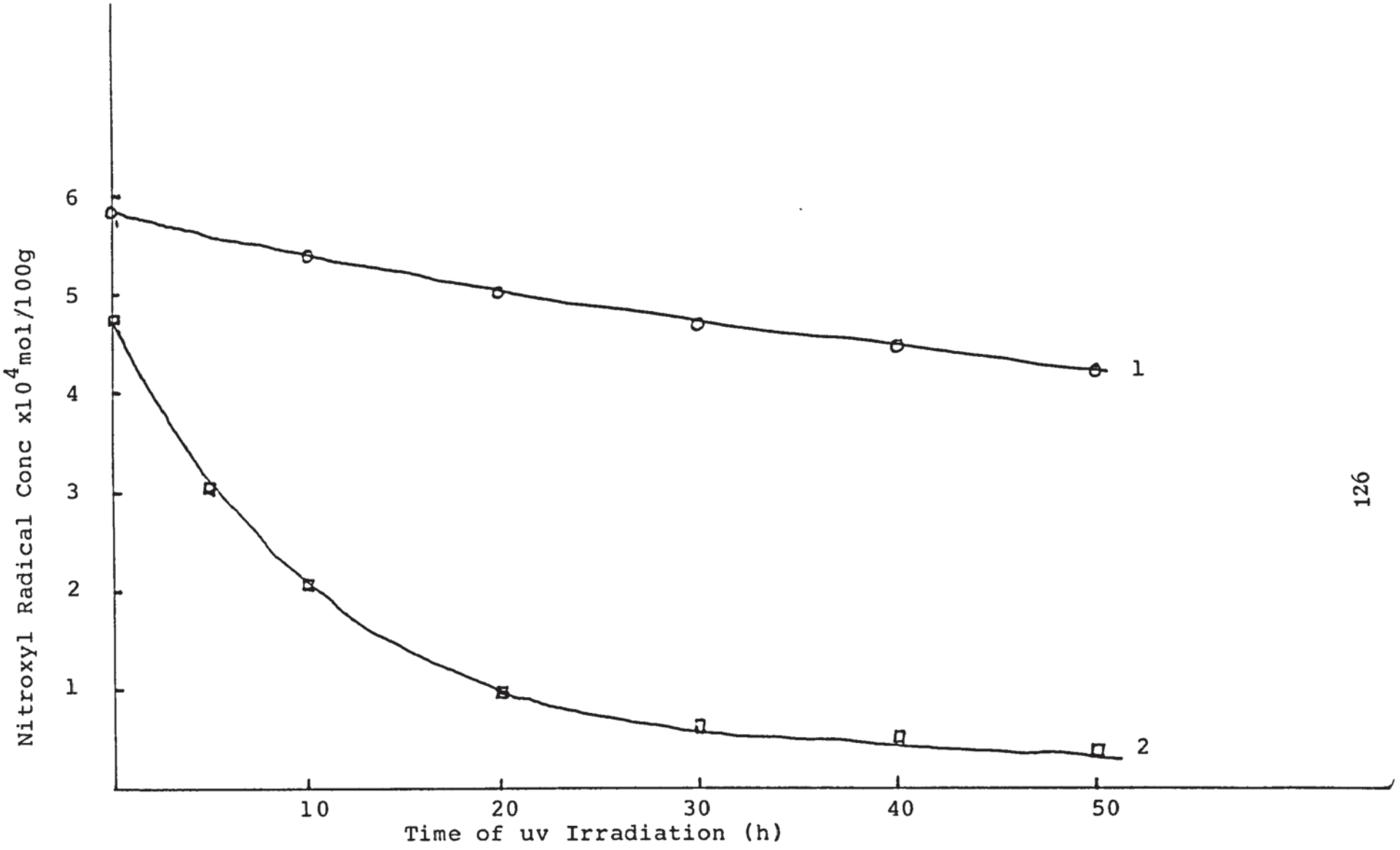


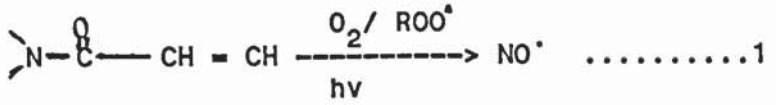
FIG. 4.7 Nitroxyl Radical Decay with Irradiation Time in PP
1-6 x 10^{-4} mol/100g (0.1%) TEMPO
2-5.64 x 10^{-4} mol/100g (0.2%) NiDEC + 0.1% TEMPO

attributed to the mobility and volatility of the former since it was shown in Sec.3.6 (Fig 3.10) that physical loss of the unbound AATP through volatilisation is a major contributory factor to overall antioxidant loss in polymer systems. When this same sample (as concentrate) was hot Soxhlet extracted for 50h, there was no additive measurably removed from the sample (see Fig 3.3). It would have been predicted that extraction would not make any difference to the photostability of the bound sample. However, the extracted sample (5) embrittled after only 400h. The difference in photostability between 4&5 is therefore attributed to the small amount (<1%) of unbound AATP left in the system to provide the much needed initial protection during the first 50h of u.v. irradiation.

In Fig 4.2, the sample containing the monomeric AATP (3) developed a measurable amount of nitroxyl radicals after only 20h of u.v. irradiation while the totally transformed samples (5&6) did not develop a measurable amount until after 60h of irradiation. Sample 5 is sample 4 after extraction and although no additive was measurably removed from the sample, the subsequent behaviour of the two samples was very different in terms of the ease of nitroxyl radical generation and subsequent photostability. While sample 4 embrittled after 2150h, sample 5 failed just after 400h.

The conversion of the acrylamide end of AATP to the Nitroxyl is therefore more facile than that of the saturated amide, because of

the addtional photosensitising effect provided by the vinyl chromophore in conjugation with the amide C=O, which lowers the activation energy for the photo cleavage and subsequent formation of nitroxyl radicals.



The development of the stabilising species, the nitroxyl, depends on the nature of the N substituent on the piperidine ring. For the same period of irradiation, N H was found[140-144] to generate nitroxyl radicals much faster than N CH_3 and other tertiary amines. In transformed AATP, the vinyl unsaturation (acrylamide) was observed to have disappeared from the absence of absorptions at 810cm^{-1}, 1405cm^{-1} and that the 1605cm^{-1} absorbance due to acrylamide C=O had shifted to 1630cm^{-1} (see sec. 3.3). More energy is therefore required to activate the cleavage of the more stable N-C bond, a necessary step in the formation of nitroxyl radicals.

For effective inhibition of photo-oxidation of polymers, a minimum amount of the stabilising species called the Critical Concentration[122,145] must be generated before a critical time. This depends on the degradation chemistry of the polymer and exposure conditions employed. Before the generation of the critical antioxidant concentration, polymer oxidation will proceed

at a substantial rate which can lead to premature embrittlement. The more facile the photo induced nitroxyl generation, the earlier this critical antioxidant concentration is achieved. Samples 3&4 achieved this critical stabiliser concentration while 5 could not, because all the residual unbound AATP had been extracted.

By the time the critical concentration of nitroxyl had been achieved in sample 5, it had already reached an advanced state of degradation. Compared to the control sample (1) this sample (5) had its E.T. considerably extended but it was still well short of the 2150h obtained with sample 4, whose radical development was measureable after 30h.

Although the rate of development of nitroxyl radicals in sample 6 containing poly AATP was very similar to that of sample 5, the former embrittled after only 250h. PolyAATP was an insoluble and infusible product and is therefore not expected to be soluble or distributed uniformly in the polymer. Solubility and hence even distributon[82] are essential for effective stabilisation by any additive in polymer systems.

Sample 7 (Fig 4.1) had the shortest E.T. even though it was not extracted. This is attributed to complete transformation of the additive (polymerised and bound) and the possible formation of

photosensitising isocyanate such as in Fig 4.3 due to the high molar ratio (E) of the peroxide to the additive.

Fig 4.4 shows the significance of initial protection given by monomeric AATP to samples 6&7 which in Fig 4.1 embrittled at 250h and 100h respectively. The addition of 0.02% AATP to sample 7 was enough to provide the necessary initial time for the generation of the critical concentration of nitroxyl, thus extending the E.T. from 100h to 1850h as shown in Fig 4.4 (7a). The effect of this monomeric AATP on sample 6 was only additive rather than synergistic.

The polymeric antioxidant appears to be having little effect.

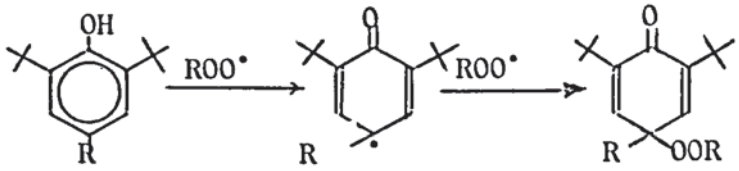
4.1.2.1 SYNERGISM & ANTAGONISM

Various workers[146-148] have reported synergistic action between hindered amines and u.v. absorbers. The effect of HOBP and Irganox 1076 in combination with bound AATP was studied in this work. In Fig 4.5, the addition of 0.1% of HOBP and Irganox 1076 each to sample 7 [see Fig 4.1 (7)] extended the E.T. of the samples from 100h to 2050h (7b) and 1600h (7a) respectively. It is apparent from the result that both the u.v. absorber and Irganox 1076 had essentially the same effect on AATP in that they protected the easily oxidisable PP against photooxidation until the bound additive had developed a high enough nitroxyl radical

concentration to take over the photostabilising function. In sample 3, which was a diluted masterbatch of 10% AATP + 1% 1076 processed with 0.01 mol DCP/mol AATP, the presence of the hindered phenol during the transformation of the AATP provided a regulatory effect by presumbaly ensuring a minimum formation of initial hydroperoxide and leaving a small (less than 1% of original) amount of unbound AATP in the system to provide initial protection. This is manifested by the ease of generation of nitroxyl during the early hours of u.v. irradiation of this sample as shown in Fig 4.6(3). A measureable amount was recorded after 30h of u.v. irradiation and reached a steady state after 150h.

No radicals were detected from sample 7b until after 70h of irradiation and even after 250h, it had not reached a steady state. Initial protection here is provided by the u.v. absorption function of HOBP and subsequent harmless dissipation. Although the shielding of the polymer from u.v. irradiation had protected it from photooxidation it had also retarded the photoinduced generation of $\rangle N0^{\bullet}$ from the bound system. In the case of sample 7a, no radicals were detected until after 120h, and this concentration seemed to be stationary up to 200h of irradiation. The initial protection from photo-oxidation of the system affered by 0.1% ($1.9x10^{-4}$mol/100g) Irganox 1076 is not as effective as that offered by 0.1% ($2.9x10^{-4}$mol/100g) HOBP not just because the concentration of HOBP is higher on a molar basis. Furthermore, hindered phenols are not as effective u.v. stabilisers[135] since

they are said to undergo rapid photodecomposition [42] during irradiation, accompanied by the formation of photosensitising products. Inhibition of oxidation by these phenols produces the cyclohexadienyl radical (I) which is subsequently oxidised to II, a product implicated in the photosensitised degradation of stabilised polyolefins[69].



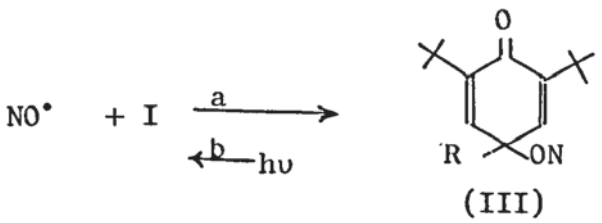
.....(2)

(I) (II)

HOBP on the other hand is photostable, absorbing the harmful uv irradiation and dissipating it harmlessly while at the same time quenching the excited states of carbonyl chromophores[149].

Its synergistic effect on AATP (Fig 4.5) was superior to that of Irganox 1076 (2050h vs 1600h).

The 120h delay before the first evidence of nitroxyl radical generation could be attributed to the reaction of this radical with I, such that it was consumed as soon as it was generated. However, this process should be reversible in the presence of u.v.

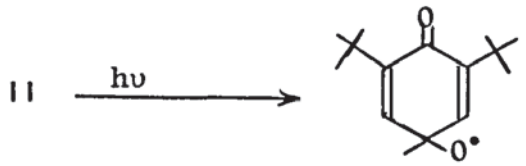


(III)

..... ---- 3.

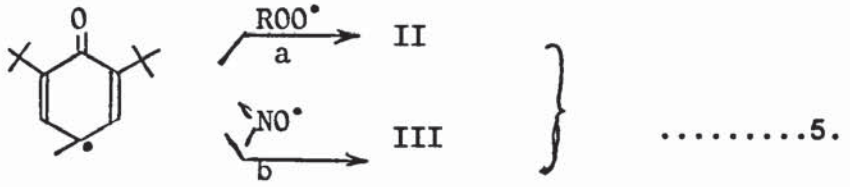
III will serve as a reservoir of both nitroxyl and I so that reaction b takes place, with the release of nitroxyl as it is required.

In sample 4 of Fig 4.5, the concentration of AATP was reduced to 0.1% while that of Irganox 1076 was increased to 0.4%, giving a molar ratio of 0.5. This sample (4) embrittled after 650h, which was less than the additive effect expected of the antioxidants. No NO$^{\bullet}$ radicals were detected from this sample even after 250h of u.v. irradiation. In this sample, where the hindered phenol concentration was high, and in the absence of NO$^{\bullet}$radicals initially, it seems likely that the photounstable phenol produces II which photocleaves according to reaction 4 to give two pro-oxidant species.



.....4

This reaction, presumably contributed to hastening the embrittlement of sample 4. The presence of an appreciable amount of NO$^{\bullet}$ in combination with a hindered phenol could provide an effective check against the formation of II through completing reaction, 5b.

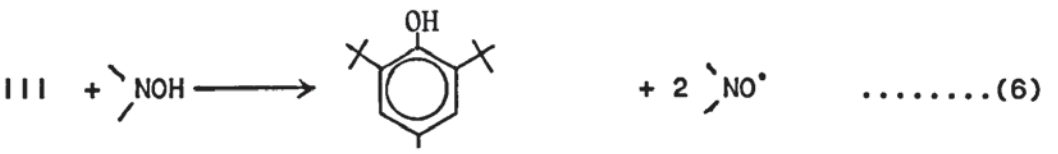


.....5.

For this combination to be effective, the molar concentration of NO•and its precursors must be greater than that of the hindered phenol in the system during photo-oxidation.

Nitroxyl radicals are generated relatively slowly even from secondary amines and less slowly from fully substituted amines, such as bound AATP. On the other hand, hindered phenols are very efficient CB-D antioxidants, readily forming I & II in the course of inhibitive reactions. A high phenol/hindered piperidine ratio could not only suppress the formation of NO• but also result in formation of II resulting in the early failure of the sample. Allen & Co workers[150] found the combination (1:1) of Tinuvin 770 and Irganox 1076 to be antagonistic. As evidence in this work shows, this observation is true only if the molar concentration of the hindered phenol is equal to, or higher than that of the nitroxyl or its precursor. [see Fig 4.5 curve 4].

If the concentration of NO•is high enough in the system, then both hindered phenol and nitroxyl radicals can be regenerated from III as NOH is normally present, though at a later stage of inhibitive reaction in the system.



The right combination could therefore be synergistic [Fig 4.5(3)] rather than antagonistic.

The catalytic scheme for the antioxidant regeneration is given in section 4.2

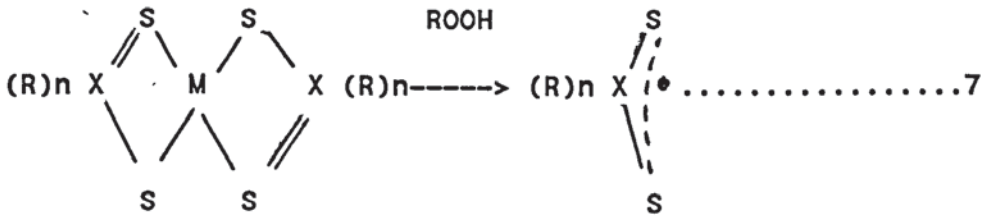
As shown in Fig 4.1 (4) and table 4.1, the E.T. of 0.4% AATP in PP (bound, unextracted) was 2150h while that of 0.1% NIDEC was 550h. If the combination of the two additives were to give an additive effect, the expected E.T. of the combination should be around 2700h (2150 + 550h).

From table 4.1, the actual E.T. found was 210h, less than 10% of the theoretical value.

Chakraborty and Scott[151] found antagonism between hindered piperidines and Ni complexes and attributed this antagonism to the excellent peroxydolytic action of the Ni complex which precludes the generation of NO•from N H by ROO•participation. However, since initially this AATP/NIDEC combination is essentially inert, the stabilised PP sample would be expected to exhibit photostability at least equivalent to NIDEC alone, on the basis of

the above explanation. From table 4.1 this is clearly not the case and as no NO·radicals were detected from this AATP/NIDEC sample up to embrittlement, it may be assumed that the NO·radicals generated were consumed in the system in a destructive manner. It is known[60] that the effective antioxidants in transition metal dithiolates are not the metal complexes but acidic products formed from them by oxidation.

Sulphur centered radicals are normally intermediate species in the formation of these active antioxidants and these are indeed known to be fairly pro-oxidant in certain cases.



where M is the transition metal and X = P or NC

Normally these S centered radicals dimerise to form disulphides which are finally converted to sulphur acids to continue the catalytic antioxidant function.

Murayama & Yoshioka[152] and Al-Malaika & Co workers[153] have shown that S compounds readily reduce NO·, and the latter group have

found the combination of both hindered amine and its derived nitroxyl with Ni thiolates to be antagonistic.

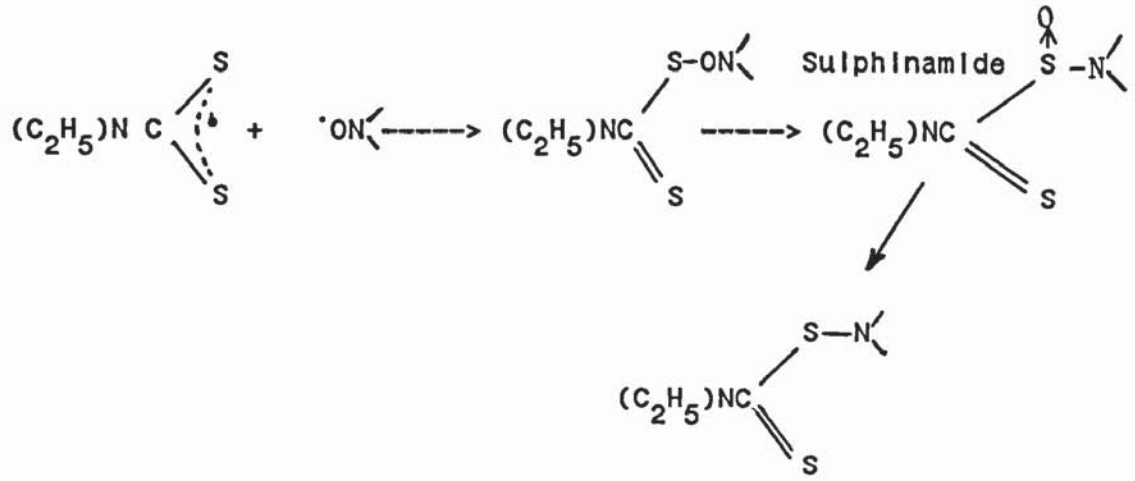
On the basis of the evidence in this work, the combination between AATP and NIDEC is highly antagonistic and as no NO· was detected up to the E.T. of 210h while a steady concentration was formed in PP stabilised with AATP alone, it may be presumed that they partake in a combination reaction with the S radicals.

Fig 4.6 shows clearly that while there was only a decay of about 25% of NO·concentration in 50h of u.v. exposure of a PP sample stabilised with 0.1% ($6x10^{-4}$mol/100g) 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl, the nitroxyl radical decay in the NIDEC/NO·combination was 95%. In only 5 mins of processing the dithiocarbomate reduces the initial NO·concentration by 22% (from $6x10^{-4}$to $4.7x10^{-4}$mol/100g.)

The E.T. of these three samples where the combination gave less than 25% of the theoretical additive effect (table 4.2) suggests that the peroxidolytic function of the Ni dithiolates in preventing the oxidation of the hindered piperidine to the nitroxyl is only one of two major antagonistic reactions.

Murayama & Yoshioka[152] isolated sulphinamides, sulphenamides and the reduced form of the parent amine in their model compound reactions, between S and NO· radicals.

The formation of both sulphinamides and sulphenamides but not the parent amine clearly explains the non-detection of NO radicals during irradiation of AATP-NIDEC combination up to embrittlement time and provides a rational explanation of the decay of up to 22% of NO concentration. In the first 5 minutes of processing and of up to 95% during 50h of irradiation. It would also explain the highly antagonistic nature of the combinations on the basis of reaction scheme 4.1



(Sulphenamide)

Scheme 4.1

The reduction in concentration of the stabilising species by mutual destruction appears to leave the system open to oxidative attack.

4.2 THERMAL STABILISATION

4.2.1 Results and Discussion.

The oxidation products of hindered piperidine compounds are excellent photoantioxidants, but are normally weak inhibitors of polymer oxidation at high temperatures.

Although volatility contributes significantly to antioxidant loss from polymer samples at elavated temperatures (as well as at ambient temperatures over the lifetime of the polymer), improving the substantivity of hindered piperidine compounds generally does not seem to improve their thermal antioxidant activity significantly.

Table 4.3.shows the embrittlement time (E.T.) of PP films containing various hindered piperidine compounds compared to Irganox 1076, a conventional thermal antioxidant, and an oligomeric hindered piperidine compound containing a triazine moiety (Tinuvin 944) which seemed to have improved its thermal stability significantly. From the results in the table, it is clear that Tinuvin 770,AATP (bound and unbound), have no inhibitive action on PP thermal oxidative degradation at this temperature.

The failure time of PP samples containing these additives were only comparable with control samples. The concentrations of these three additives in PP were increased progressively and exposed to this test condition, but up to a concentration of 5% no improvement in the embrittlement time was observed.

Antioxidants	E.T. (h)
Control (No additive)	0.5
Tinuvin 770	0.5
Tinuvin 944	15
Irganox 1076	95
AATP (bound & unbound)	0.5

TABLE 4.3.

Oven Ageing of PP Films containing 0.1% Antioxidants at 140^{o}C
Air flow rate 3cu ft/h

Nitroxyl radicals have been reported to be good melt stabilisers in PP[9,154,155] but showed only marginal activity in thermal antioxidant activity during oven ageing at 140^{o}C.

Unstabilised PP is stable for several hundred hours at moderate temperatures (below about 90^{o}C). This fact was exploited to "pre-age" the AATP stabilised PP films at 85^{o}C for various lengths of time. The films were then oven aged normally at the usual test

temperatures of 140°C and an air flow rate of 3 cu ft/h. The result of this test is shown in Table 4.4.

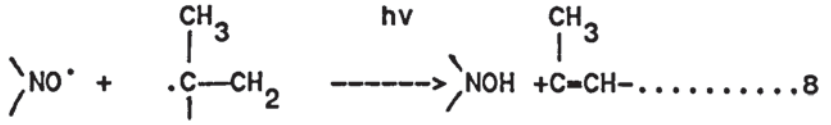
Time of preageing(h) at 85°C	0	100	200	400	500
E.T.at 140°C(h)	0.5	3	8	15	15
[NO·]generated $x10^{-6}$moles/100g	-	-	-	3	3.4

Table 4.4

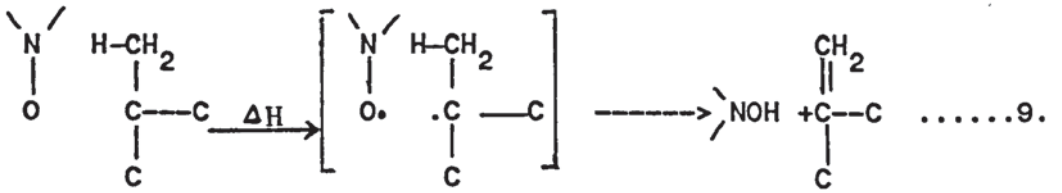
PP films containing 0.4% AATP pre-aged at 85°C prior to ageing at 140°C

The development of nitroxyl radicals from the film was monitored by E.s.r but up to 400h of "pre-ageing", the amount of the radical was too small ($< 10^{-6}$M/100g) to be quantified because of the high noise to signal ratio, approaching the limit of the instruments sensitivity. After 400h of pre-ageing, the amount of NO·radicals generated was $3x10^{-6}$M/100g, which rose to $3.4x10^{-6}$M/100g after 500h. This increase in nitroxyl concentration however, did not bring about a concomitant improvement in embrittlement time compared to that at 400h. Even a 2% AATP-bound PP sample pre aged for 500h gave only a marginal improvement (18h) compared to 15h for the 0.4% samples. The production of higher concentrations of nitroxyl is therefore not commensurate with the achievement of higher thermal oxidative stability beyond a certain limit.

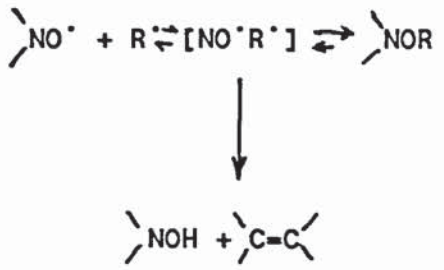
Stable nitroxyl radicals act essentially by a CB-A mechanism. Antioxidants acting by this mechanism are not normally effective in polymers under conditions where the concentration of alkyl radicals (R$^{\bullet}$) is negligible compared to the concentration of alkyl-peroxyl radicals (ROO$^{\bullet}$), so that the catalytic CB-A/CB-D cycle necessary for the stabilisation of the system would not be expected to occur. The reduced form of the nitroxyl ($\rangle$NOH) is an efficient ROO$^{\bullet}$) radical inhibitor[122] acting by a CB-D mechanism. Scott and Co-workers[136,137] have proposed that the excellent photostabilising properties of nitroxyl radicals in PP is through a mechanism of tertiary alkyl radical termination with the generation of hydroxyl amine and ethylenic unsaturation



Various workers[122,156-158] have demonstrated that reaction 8 also occurs during thermal oxidation. Berger and Co-workers[157] also added that the same products can be obtained by the thermal homolytic cleavage (thermolysis) of the O-tert alkyl hydroxyl amine, followed by abstraction of a B-hydrogen atom to produce the decomposition products



The combination of alkyl radical with nitroxyl radical is kinetically favoured while the production of NOH and the ethylenic unsaturation as disproportionation products is thermodynamically favoured.[157]



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If only R• is present in the system, then the CB-A/CB-D mechanism of NO• and its hydroxyl amines can continue to inhibit the onset of degradation. But NO• radicals under thermal oxidative conditions are also in competition for R• with O_2,

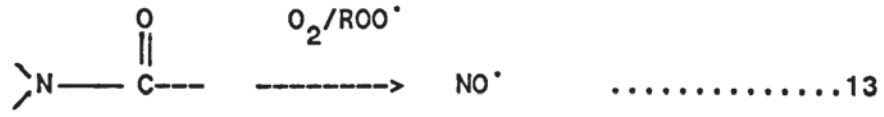
.....11

.....12

and because of the high rate constant of reaction 12(k12) in especially liquid hydrocarbons,alkyl radicals are very rapidly oxidised, and reaction 11 cannot effectively compete[159,160] with 12. The reaction of polymer macro alkyl radical on the other hand is limited by the rate of O_2 microdiffusion, so that the lifetime of the macroalkylradical is many orders of

magnitude longer than that of its analogous radical in liquid hydrocarbons.[52] For this reason, macroalkyl radicals are terminated by efficient CB-A antioxidants such as NO$^{\cdot}$, as well as reacting with O_2 to form ROO$^{\cdot}$

The generation of nitroxyl radicals in PP stabilised with bound AATP under thermal oxidative conditions at 85^{o}C may be assumed to follow the mechanism in reaction 13



.....13

The nitroxyl generated then inhibits oxidation by effectively competing with O_2 at this moderate temperature (reaction 4) giving NOR. This probably explains why no definite NO$^{\cdot}$ signal could be observed from the pre aged samples until after 400h, even though they showed enhanced thermal stability (table 4.4.) when subsequently oven aged. The NOR then generates NOH (reactions 9&10) which is in turn oxidised by ROO$^{\cdot}$ in the system generating >NO$^{\cdot}$

This catalytic cycle could not be sustained beyond about 15h because, as will be shown later, NOH is unstable in presence of O_2 at the test temperature, and therefore could not effectively take part in the cycle.

4.2.2 SYNERGISM BETWEEN AATP-BOUND AND IRGANOX1076

Various concentrations of Irganox 1076 (0.02 - 1.0%) in PP were oven aged at 140°C. A second set of samples was hot soxhlet extracted with acetone for 15h, dried and similarly oven aged, while a third set was aged for 48h before extraction and oven ageing. The results of these treatments on the thermal stability of the samples is given in table 4.5.

Concentration		Time (h)		
Weight%	Mole%x10^{-4}	U	E	48h Oven ->E*
Control	-	0.5	0.5	-
0.02	0.378	5	1.5	-
0.1	1.89	95	>2	2
0.2	3.78	160	>2	3
0.4	7.5	260	<2	3
1.0	18.9	500	2	4

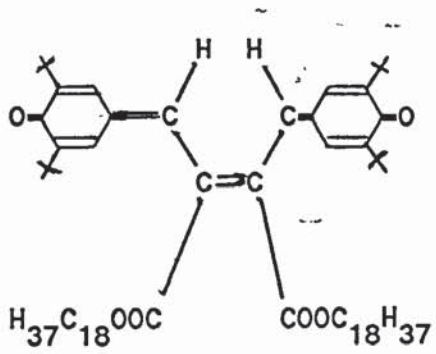
Table 4.5

U = Unextracted, E = Extracted.

Embrittlement Time of Extracted and Unextracted PP containing Irganox 1076 in circulating Air Oven at 140°C.

The above results show that Irganox 1076 or its oxidative product were not bound to the polymer as oven ageing tests after extraction show. The improvement in stability of extracted samples over the control sample could be attributed to the initial melt stability conferred on the polymer by the hindered phenol by minimising the formation of sensitising hydroperoxides during processing. There was however a small improvement (3h) in the stability of the samples initially oven aged for 48h before extraction.

This could be due to acetone insoluble oxidation products of the quinone type such as dioctadecyl-1,4-bis(0-0x0-3,5-di-tert-butyl-2,5-cyclohexadiene-1-ylidene)-2 butene-2,3-dicarboxylate[42](IV).



IV

A combination of bound AATP with Irganox 1076 in varying ratios and concentrations was then processed in PP and similarly tested. The result is shown in Table 4.6.

Weight% AATP/1076 :	Mole%x10^{-4}	U(h)	%Synergism	E(h)	48h Oven -> E*(h)
Control	-	0.5	-	0.5	-
0.2%AATP	7.5/0.0	0.5	-	0.5	-
0.2/0.02	7.5/0.38	50	1200	1.5	3
0.2/0.1	7.5/1.89	650	787	5.5	15
0.2/0.2	7.5/3.80	750	570	4.5	35
0.4/0.1	15/1.89	950	1051	-	30
0.4/0.2	15/3.8	1200	850	-	65
0.4/0.4	15/7.5	1300	600	-	20
0.4/1.0	15/18.9	1500	400	-	5

Table 4.6

* 48h Oven Ageing before extraction

Embrittlement Time of Extracted (E) and Unextracted (U) PP containing combinations of AATP/Irganox 1076 in circulating Air Oven at 140°C

Percentage synergism is calculated using the formula[161].

$$\%\text{Synergism} = \frac{(Es-Ec)-\{(E_1-Ec) + (E_2- Ec)\}}{(E_1-Ec)+ (E_2-Ec)}$$

where Es = the Embrittlement time of the synergistic mixture

Ec = the Embrittlement time of the control sample

E_1 = the Embrittlement time of antioxidant 1

and E_2 = the Embrittlement time of antioxidant 2.

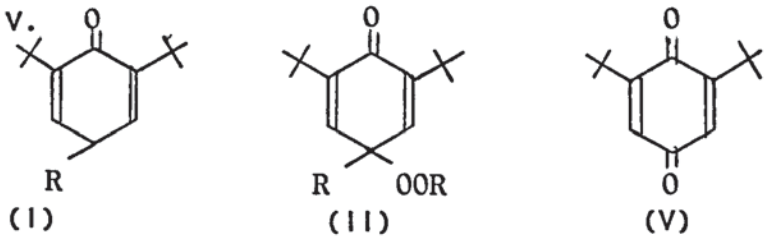
Results from table 4.6. indicate that there must be some kind of interaction between the combination of antioxidants.

Irganox 1076 and its subsequent oxidation products are easily hot soxhlet extracted from PP samples (table 4.5.) after a few hours in a suitable solvent such as acetone. Scott and Co-workers[135] [55,162] found no evidence for the formation of a bound antioxidant or its oxidation products after exhaustive extraction of PP film processed with a hindered phenol.

In table 4.6., there is evidence of residual antioxidant action in extracted films, which seems to depend on the ratio of AATP/1076 in the system. A much clearer evidence of antioxidant substantivity in the extracted polymer was brought about after 48h of oven ageing of the stabilised films prior to extraction.

Belova et al[163] after observing a synergistic effect between hindered phenols and nitroxyls concluded that there must be some kind of interaction between the two antioxidants. PP film samples stabilised with 0.1% Irganox 1076 embrittled in less than 300h (table 4.5.). On the other hand, a combination of 0.2% AATP which has no thermal antioxidant activity on its own, and 0.1% Irganox 1076 embrittled after 650h.

Irganox 1076 is normally transformed into quinonoid products during thermal oxidation. Such products include IV,alkylcyclohexadienonylradical intermediate I, leading to the formation of a pro-oxidant peroxy compound II, and a benzoquinone



(I) (II) (V)

The generation of II in phenol stabilised systems has a deleterious effect on the continued stability of the system and ultimately leads to the destruction of the sample.

In an admixture with AATP in the thermal oxidative stabilisation of PP, radical species of importance include I, macroalkyl ($R^{\cdot}$), nitroxyl ($NO^{\cdot}$) and aminyl ($\rangle N.$), from the cleavage of $N-\overset{O}{C}$ bond prior to the formation of $\rangle NO^{\cdot}$

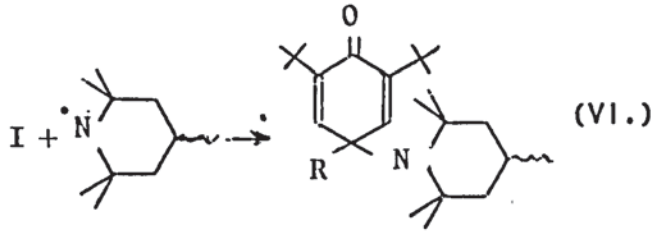
Denisov[164] has shown that the lifetime of macroalkyl radical in solid PP is about 2 orders of magnitude higher than an analogous concentration in liquid hydrocarbons.

The probability of $\rangle N^{\cdot}$ combining with I cannot therefore be ruled out.

However because $\backslash N^{\cdot}$ radicals are highly reactive, their very short lifetime would preclude the formation of a substantial amount of adduct VI.

Also, because of the excellent synergistic effect observed between AATP and Irganox 1076, it could be assumed that transformation products II & V could not have been formed in the system, because II which leads to the formation of V has a prooxidant effect.

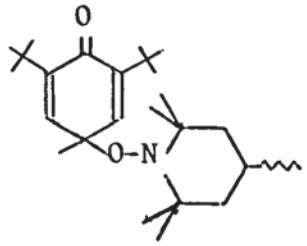
Since II is formed through the intermediate I, it could also be assumed that the reactive aminyl radical could trap I, forming VI.



(VI.)

An even more feasible combination reaction is that of a nitroxyl radical trapping I to give the adduct III.

Diphenyl nitroxyl radicals are reported[165] to react with phenoxyl radicals in a similar manner.



(III)

As the nitroxyl moeity is bound to the polymer, adduct III is unextractable and its formation could retard the alternative formation of the pro-oxidant compound II.

This phenomenon will increase the substantivity of the efficient and thermally stable phenolic antioxidant.

Synergistic action with this combination is the direct result of failure of the hindered phenol to completely inhibit oxidation in the polymer system. AATP is in a bound inactive form and essentially part of the polymer so that at the initial stage, the only active inhibitor is the phenol and its subsequent oxidation products. If the amount of phenol in the combination is above its critical concentration, then it completely swamps the whole polymer giving a "blanket" protection.

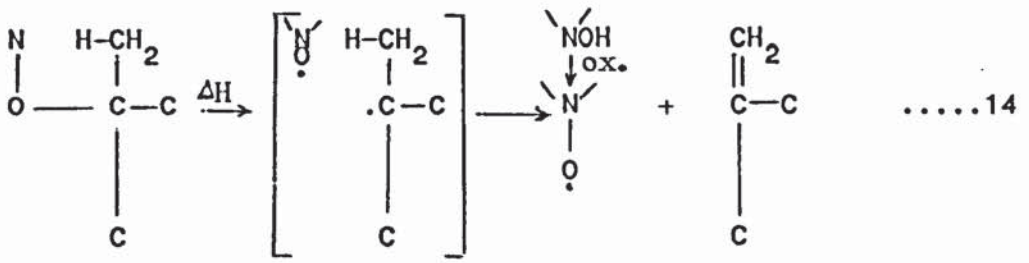
The first product of phenol antioxidation reaction is the formation of a phenoxyl radical. In presence of a nitroxyl radical, the former is readily trapped by the latter to form the adduct III. In the absence of a nitroxyl radical, the phenoxyl radical is oxidised to the pro-oxidant compound II, thus reducing the intrinsic effectiveness in the system. Nitroxyl radicals can only be formed when there is an oxidative attack on the bound AATP (reaction 13). For this to happen to any degree, the phenol moeity must be absent from the immediate vicinity of the site of reaction, requiring a higher ratio of AATP/1076 in the system. This is shown in terms of % synergism in table 4.6.

Oxidation of bound AATP to release the active nitroxyl antioxidant (reaction 13) can be assumed to have the highest probability of

occuring with the sample containing not only the highest ratio of AATP/1076, but also the least amount of 1076 per unit volume of polymer. Subsequent coupling reaction is therefore expected to be highest with this sample, which is expected in turn to give the best performance in terms of synergistic effectiveness. The best measure of this is given by percentage synergism (table 4.6.). The highest % synergism (1200) was given by the sample with the highest AATP/1076 ratio (0.2/0.02), because of the twin reasons enumerated above. In agreement with this postulate, the lowest % synergism (400) was also given by the lowest AATP/1076 ratio (0.4/1.0). The duration of exclusive inhibitive action by the hindered phenol is dependent on its absolute concentration in the system as well as the concentration of AATP. The longer the duration of this exclusive inhibitive action, the higher the chances of unwanted side reactions with the formation of II, and the lower the ultimate % synergism.

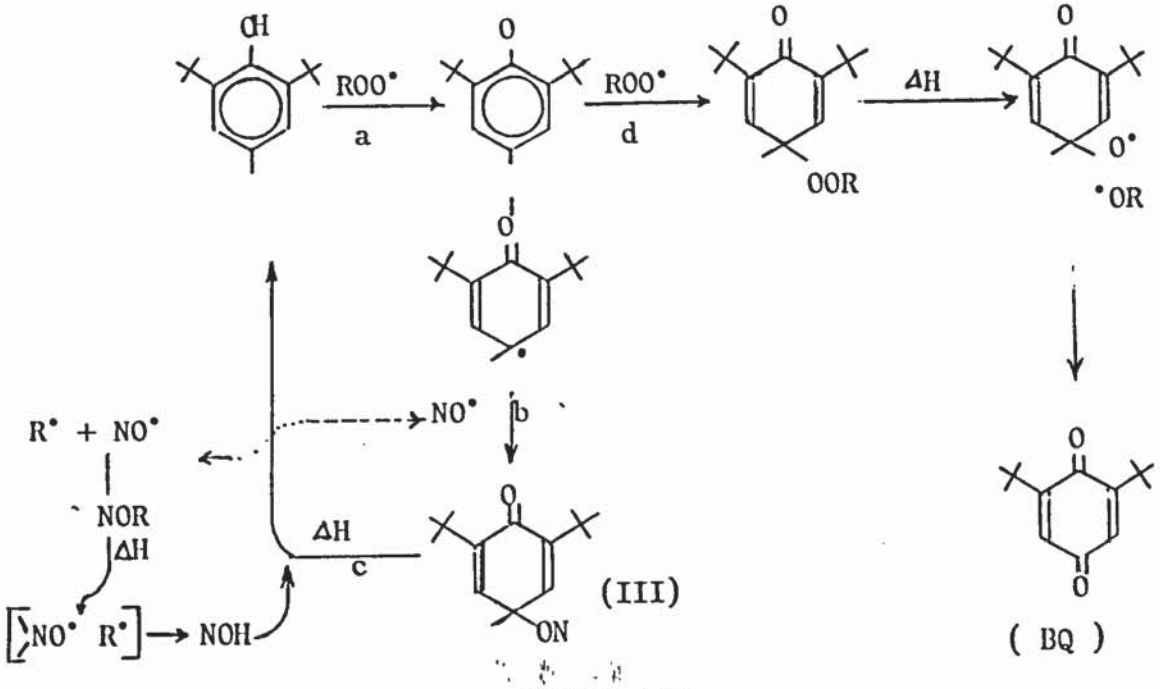
Initial generation of NO$^{\cdot}$ from the bound system is soon depleted by adduct formation with phenoxyl radicals. Nitroxyl radicals start building up in the system only after an equilibrium is reached with the adduct product. Only then, is the mechanism of antioxidant action truly synergistic and catalytic.

The nitroxyl radical generated in the system is an efficient alkyl radical trap, the combination of which gives a substituted hydroxylamine NOR. Berger and Co-workers[157] have shown clearly that this ether undergoes a homolytic cleavage at elevated temperatures (thermolysis) according to equation 14



.....14

The hydroxylamine product of disproportionation is a very efficient CB-D antioxidant but quite unstable in presence of oxidising species in the system at this temperature. Adducts III& VI can be attacked by >NOH at this temperature to release the phenol moeity and a nitroxyl radical so that a catalytic cycle is evolved, terminating many alkyl and alkylperoxyl radicals until the phenol is used up through side reactions outside the cycle, ultimately forming benzoquinones according to scheme 4.2



SCHEME 4.2

Phenol Regeneration by Hydroxylamine

Such regeneration of a complementary antioxidant in a synergistic mixture has been found[19] to occur during hydrocarbon oxidation inhibition.

Fig 4.8 shows the I.R spectrum of extracted PP sample stabilised with a combination of 0.2% AATP and 0.1% 1076 which was oven aged for 48h before extraction, and then aged again (curve 2) until the onset of embrittlement. A considerable amount of unsaturation ($1645cm^{-1}$) was formed in accordance with equation 14 with the radicals taking part in scheme 4.2 reaction.

This pre-heated extracted sample is deemed to have the following antioxidant species: $\rangle NO^{\bullet}$, NO-R, N-C, NO-phenol (III) and probably NOH. These radicals sustain the catalytic cycle as in the scheme, up to embrittlement without measureable carbonyl (ketonic) formation .

The development of $NO^{\bullet}$ radicals in the unextracted synergistic combinations was monitored with e.s.r during oven ageing. Fig 4.9 shows the development of two samples containing 0.4% AATP + 0.1% 1076 (curve 1) and 0.2% AATP + 0.1% 1076 (curve 2).

Nitroxyl growth was recorded much earlier with the 0.2/0.1 combination (200h) compared with the 0.4/0.1 combination (350h). Sample 2 has only half the potential amount of $\rangle NO^{\bullet}$ radicals, yet nitroxyls were detected much earlier with the lower AATP/1076

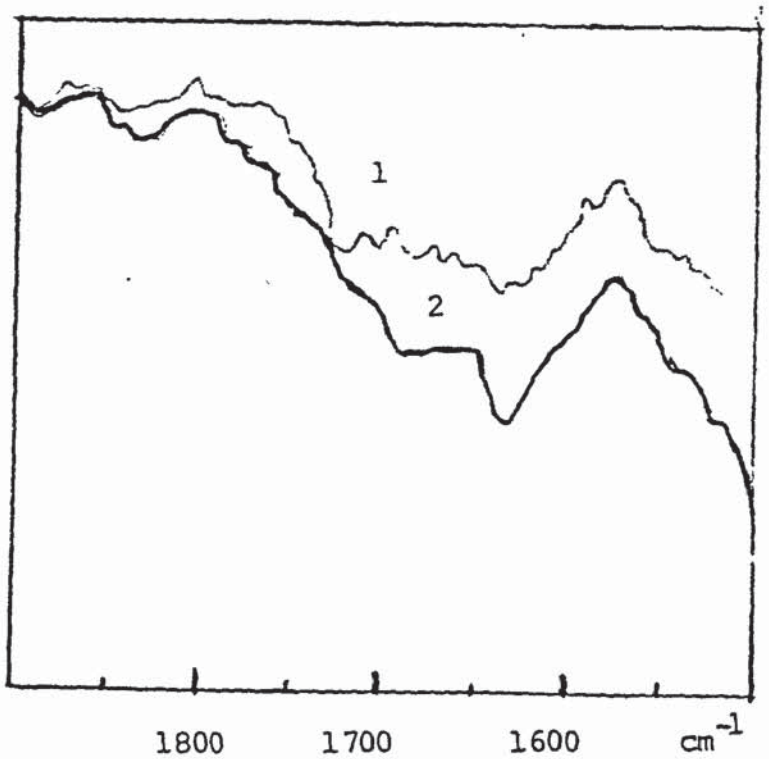


FIG.4.8 A Segment of ir Spectrum of PP Sample Stabilised with a Combination of 0.2% AATP + 0.1% Irganox 1076.
1- Oven aged for 48h and Soxhlet Extracted with DCM
2- Extracted Sample Oven Aged again for Another 48h

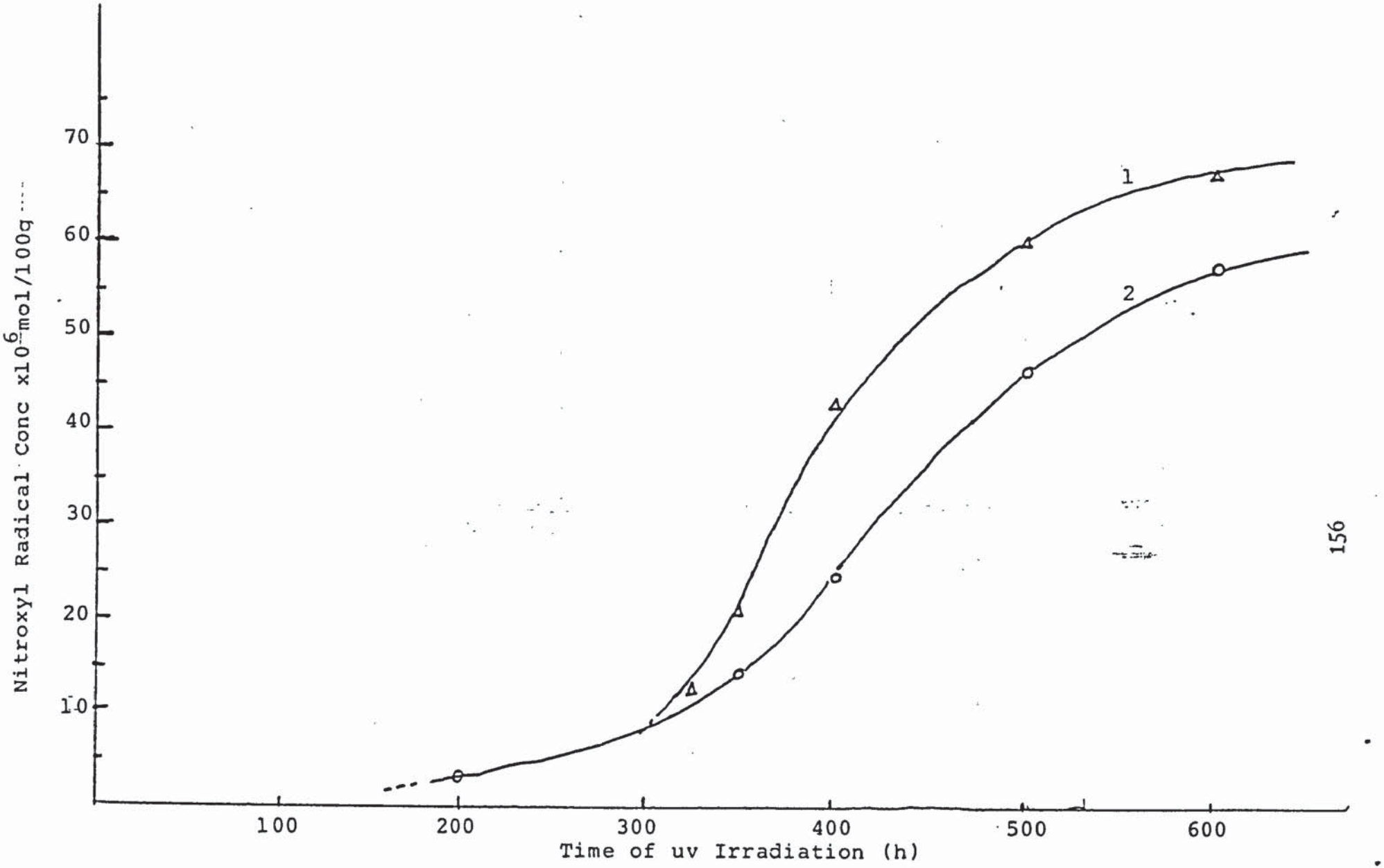


FIG. 4.9 Nitroxyl Radical Development During Oven Ageing of PP Samples Stabilised With a Combination of AATP and Irganox 1076
1→0.4% AATP + 0.1% Irganox 1076; 2→0.2% AATP + 0.1% Irganox 1076

ratio. It is logical to assume that more NO˙ radicals would be generated in sample 1 than in 2. Adduct formation with the hindered phenol would consequently be greater with sample 1 than 2 (see table 4.6).

A substantial amount of the phenol would have left the cycle through reaction d of scheme 4.2, leading to the formation of benzoquinone (BQ). Because of the higher ratio of NO˙ to phenol in sample 1, loss of phenol through this phenomenon would be minimal.

The formation of NO˙ radicals from bound AATP could be detected from the PP sample containing 0.2% AATP alone, in half an hour, during oven ageing. In combination with 0.1% Irganox 1076 however, it took 200h of oven ageing to develop a detectable amount. At 140^{o}C, sample 1 might have developed more NO˙ radicals, but since they were engaged in adduct formation and alkyl radical termination forming the ether, these are not detectable. As very little of the phenol is assumed to be lost in this sample, there is a far higher chance of forming even more phenoxyl- nitroxyl adduct at room temperature with the result that very little of the free NO˙ is left in the system. This retention of phenol through adduct formation and consequent prevention of formation of quinonoid products is primarily responsible for extending the embrittlement time of sample 1 to 950h compared to 650h for sample 2.(See table 4.6.)

4.3 TENSILE MEASUREMENTS

4.3.1 RESULTS

Tensile measurements at room temperature provide a simple and reliable evidence of structural changes taking place in a particular polymer film or fibre.

These changes, following introduction of pendant groups on to the polymer backbone were measured using the Instron Tensile Tester Model TMSM.

Specimens were loaded at a constant rate of crosshead speed of 3cm min^{-1} and the usual force/elongation curves were produced by the chart recorder operated on a similar rate. From the stress/strain curves obtained, parameters such as ultimate tensile strength UTS and elongation at break EAB were determined in accordance with BS 2782: methods 326A to 326C:1977 .

Films of equal thickness (0.020cm) were cut out in the dumb bell shape of a standard mould. Unstabilised PP (USPP) film of equal thickness was also measured. The measurements were conducted in triplicates from which an average value was recorded. The mechanical properties of the antioxidant bound PP were then compared to those of the USPP film in form of a ratio as given in table 4.7.

Ultimate Tensile Strength (UTS) and Elongation at Break (EAB) of the bound PP samples were compared to those of an equal thickness of USPP

% CONC.	EAB(bound) / EAB(USPP)	UTS(bound) / UTS(USPP)
0.4	1.0	1.1
5	0.7	1.2

Table 4.7 : Ratios of Mechanical Properties.

4.3.2. DISCUSSION.

Table 4.7.shows that the relevant physical properties of diluted samples of bound AATP in PP are not adversely affected. Only 4g of the 10% AATP bound PP is added to 96g of PP to give a 0.4% sample. It is also quite evident that the physical properties of the concentrate are affected by the changes in molecular structure and arrangement. G.P.C. of the AATP bound PP (see Sec. 3.4.2.) shows an increase in Mw and a small narrowing of the distribution by about 20%. The formation of a pendant group on the backbone of a PP chain is expected to change the crystalline arrangement of the molecules to a more random amorphous state. This should in turn increase the percentage elongation and UTS. However table 4.7. shows that the physical properties of the 0.4% diluted sample are not affected by the 4% content of the AATP bound PP.

The properties of the 5% concentrate however,are clearly altered as neither EAB nor UTS was comparable to that of the unstabilised PP. In theory both EAB and UTS are expected to increase with decreasing crystallinity. Although there was increase in UTS (ratio 1.2), there was actually a decrease in EAB(0.7). This apparent anomaly could be attributed to increase in Mw of the AATP bound concentrate. Thus although the desired mechanical properties of concentrates are adversely affected, this is not carried over to the dilute samples, as less than 5% of the bound polymer is generally added to PP samples to provide the necessary protection.

CHAPTER 5

5.1 ATTEMPTED BINDING OF OTHER UNSATURATED AND THIOLATED ANTIOXIDANTS IN PP.

5.1.1 INTRODUCTION

Antioxidants with vinyl or vinylene unsaturations and thiolated groups were synthesised and characterised as described in chapter 2. Attempts were made to bind them using the various radical generators listed in Sec-3.1.

5 and 10% concentrates in PP were prepared with various peroxide molar ratios as given in table 5.1. Processing temperatures used were 170°, 180° and 190°C.

Peroxide/Additive Molar ratio	0.004	0.01	0.05	0.1	0.2
Designation	C	E	G	H	J

Table 5.1

Peroxide/Additive Molar Ratio

Antioxidants used have been given the following codes:

DBBA: 3,5-di-tert-butyl-4-hydroxybenzylacrylate

DBBM: 3,5-di-tert-butyl-4-hydroxybenzylmercaptoglycollate.

TPMG: 2,2,6,6,-tetramethyl piperidinyl mercaptoglycollate

BPM : Bis(2,2,6,6-tetramethylpiperidinyl)maleate

5.1.2 RESULTS

5 and 10% of the TPMG were processed in PP with each of the radical generators at 'C' ratio at a temperature of 170^{o}C. Soxhlet extraction in acetone showed that all the additive was removed. The ratio was then changed to 'G' and the whole operation repeated again. When no binding was achieved the processing temperature was raised to 190^{o}C. Ratios C E & J were tried but no binding was achieved as the additive was easily extracted with acetone. U.v. exposure results of this extracted sample confirmed that no active additive was retained in the film as it embrittled at 90h.

A second mercaptan DBBM was substituted for TPMG and the whole operation carried out again. No binding was achieved here either as all additive was removed by Soxhlet extraction with acetone. The same procedure was then repeated with DBBA. Fig 5.1 shows the I.r spectrum of 5% DDBBA in PP processed with ratio H of benzoylperoxide (BP). The spectrum before extration (1) showed the typical absorptions of DBBA; free phenol O-H at 3630 cm^{-1}, ester C=O at 1725cm^{-1} and the unsaturation at 1640cm^{-1}. All these bands were observed to disappear after extraction (2). The new band that appeared at 1696cm^{-1} after processing, also disappeared after

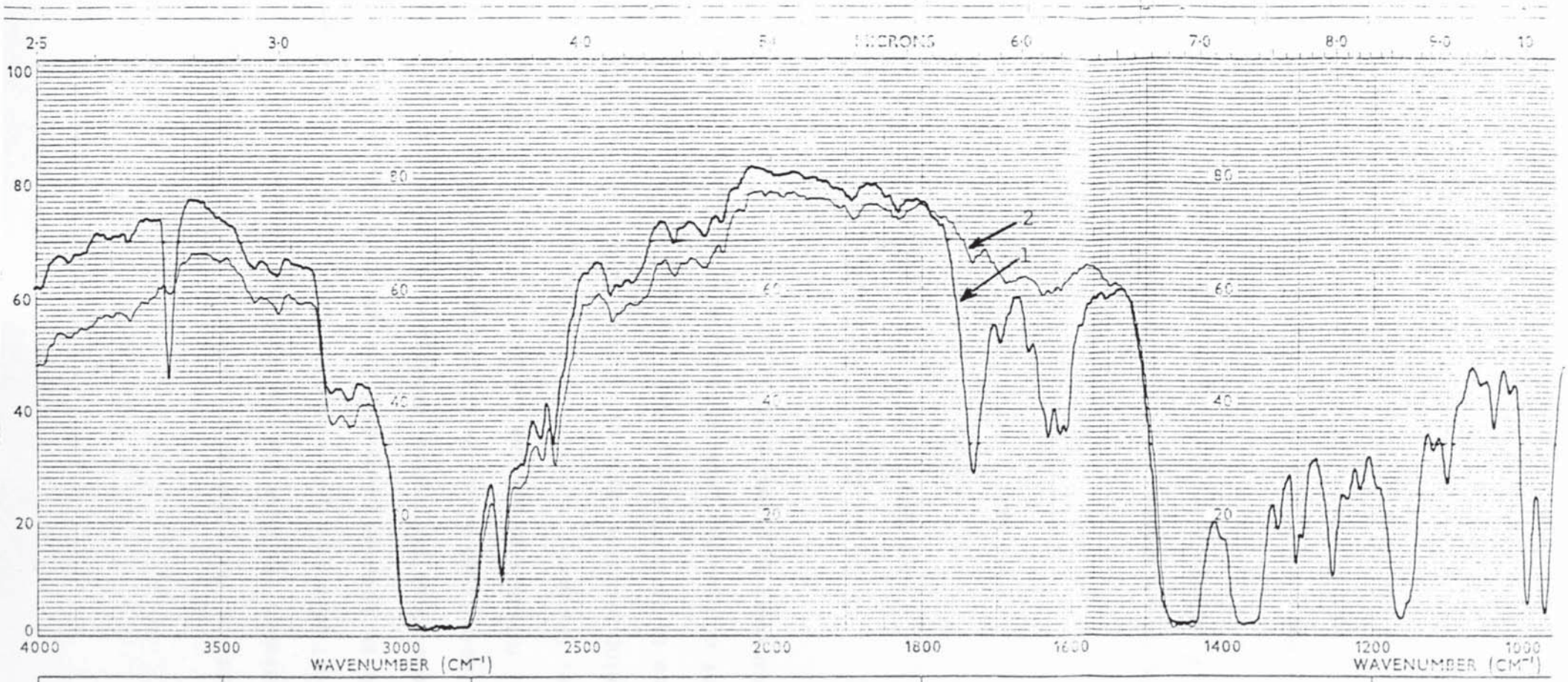


FIG. 5.1 I.R. Spectrum of DBBA in PP processed with Ratio 'H' of Benzoyl peroxide

1- Before Extraction
2- After Extraction

hexane extraction. This absorption is due to quinonoid products of reaction between the DBBA and the peroxide. Processing with DtBP as the radical generator gave a similar peak at this wave number which was also removed along with the additive after extraction. When DCP was used as the radical generator, a different reaction appeared to have taken place. Persistent and exhaustive extraction with hexane, followed by acetone for 24h each could not remove all the additive. The amount of additive retained appeared to increase with increasing peroxide ratio for a 5% masterbatch. The peak at 1735cm^{-1} (due to saturated ester C=O) was used for the measurement of the extent of binding, after exhaustive extractions. The result of this measurement is given in table 5.2

DCP/DBBA	G	H	J
%bound	10	60	15

Table 5.2; Extent of binding of 5% DBBA in PP, using different DCP ratios

Fig 5.2 shows the i.r spectrum of 5% DBBA in PP processed with the optimum ratio (H) of DCP (see table 5.2). The unsaturation disappeared completely after binding and subsequent extraction of the unbound additive. The binding reaction however was accompanied

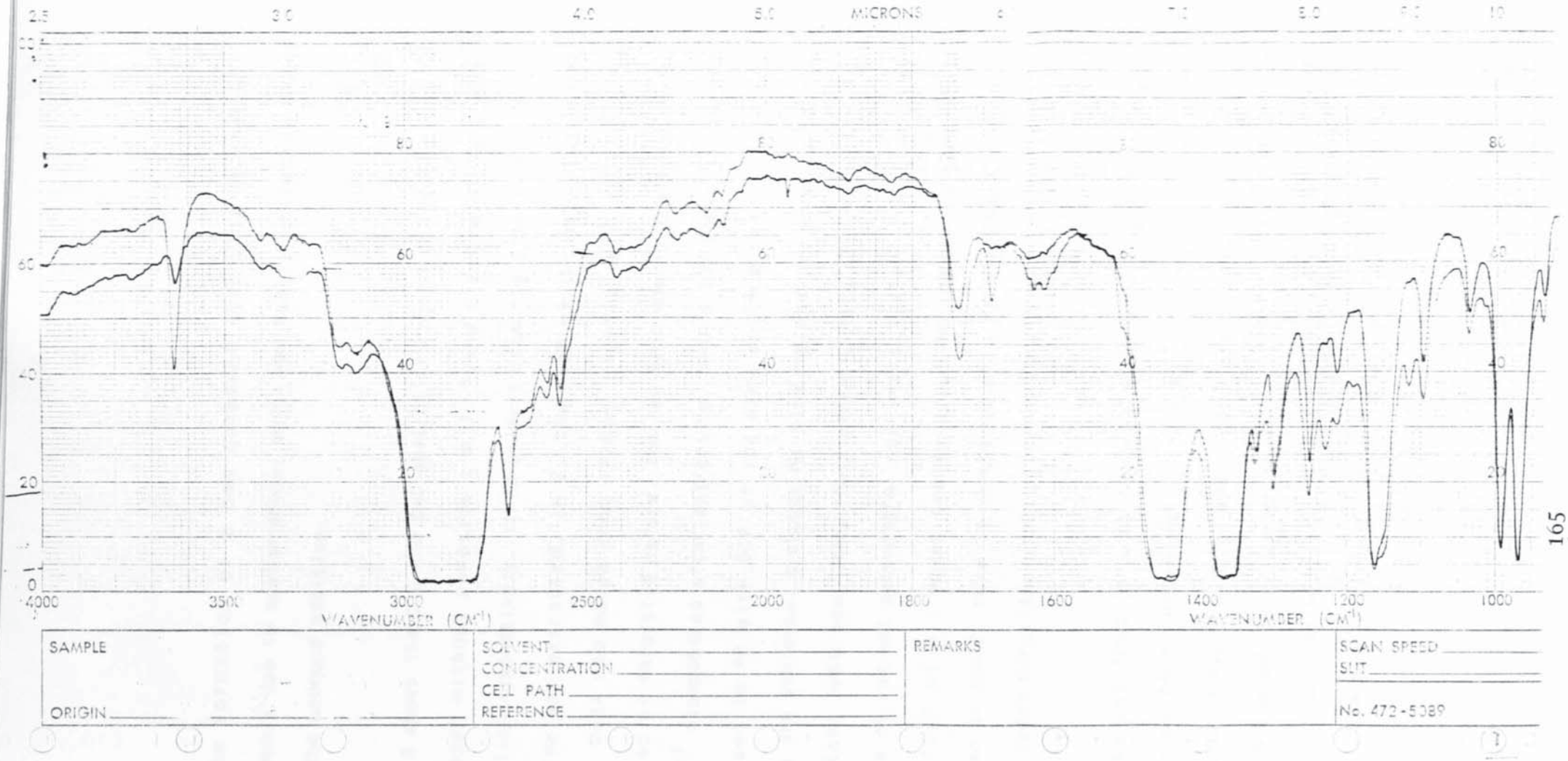


FIG. 5.2 I.R. Spectrum of DBBA in PP Processed with Ratio 'H' of DCP

by the formation of a new compound absorbing at 1690cm^{-1}, presumably due to acetophenone, which was easily extracted along with the unbound additive.

Fig 5.3 shows the C=O and C=C absorption region of 5% DBBA in PP processed without peroxide (A). 1 and 2 are before and after extraction respectively. It is evident from fig 5.3A that all the additive was extracted. In B, the peak of the ester C=O of the bound DBBA had moved from 1728cm^{-1} to 1735cm^{-1} as would be expected of saturated esters. The new band due to acetophenone at 1690cm^{-1} disappeared after extraction. When a 10% concentrate was processed in PP with DCP of the same optimum ratio, only 25% binding was achieved. Although no binding was achieved with the mercaptans DBBM and TPMG, their effect on the stability of PP in presence of radical generators was investigated. Fig 5.4 shows the effect of 0.1 molar (ratio H) of DCP on 5% concentrates processed at 180 C. This is compared with PP samples with, and without added peroxide.

Both DBBM and TPMG (1 & 2) reduced the impact of the added peroxide on PP by efficiently trapping the radicals so that the final torque after 6 minutes was almost comparable to PP sample without peroxide (5). Tinuvin 770 (3) on the other hand could not provide the required stabilising effect in PP, hence the added peroxide effectively reduced the molecular mass of PP to the same degree as unstabilised PP with an equivalent amount of DCP

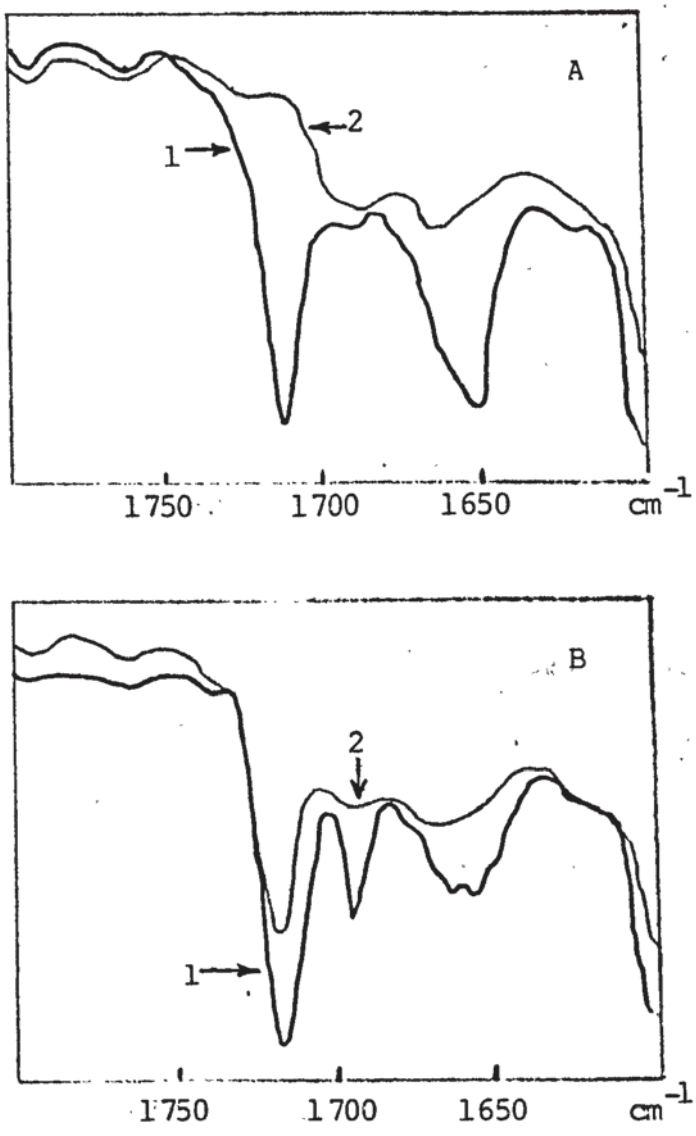


FIG. 5.3 A segment of i.r. Spectrum of 5% DBBA in PP

A: Processed without Peroxide
1-Before Extraction
2-After Extraction

B: Processed with Ratio H of DCP
1-Before Extraction
2-After Extraction

(4).Both samples gave a minimum torque after 3 minutes of processing which is an evidence of extensive degradation of PP by the peroxide.

The thermal stability of PP samples bound with DBBA (optimium) both extracted and unextracted was compared to the samples processed with conventional antioxidant (Irganox 1076) as well as unbound DBBA. The result of this study is presented in table 5.3. The exposed samples $7x10^{-4}$ m/100g diluted from the 5% concentrates.

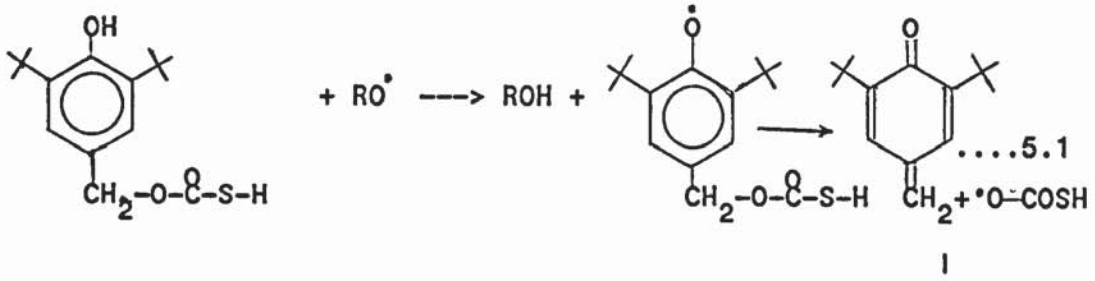
Antioxidants	DBBA unbound	DBBA bound,U	DBBA bound,E	1076,U	1076,E
E.T.(h)	10	80	60	110	1

Table 5.3: Embrittlement Time (E.T.) of stabilised PP Samples, oven aged at 140 C
U=Unextracted, E=extracted.

5.1.3 DISCUSSION

Mercaptans are shown to be bound to unsaturated polymers [116-118,120] during mechnochemical reaction and with less success, to saturated polmers[119], also mechanochemically or by u.v. initiated reactions (see Sec 1.3.1). As reaction 1.16 shows, this is a situation of limited radical generation, with no added

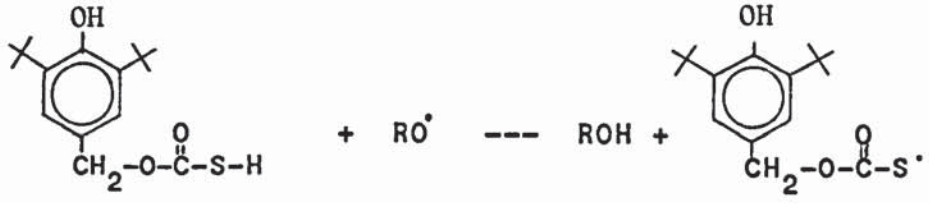
radical generator. In this attempted binding of mercaptans, the presence of peroxides in the system was expected to create a high proportion of both thiyl and macroalkyl (P$^{\cdot}$) radicals and subsequent reaction of the two radicals. However, both the phenol and the mercapto functions of DBBM are good hydrogen donors so that the alkoxyl radicals are reduced as soon as they are formed, before they abstract hydrogen from PP to give a macroalkyl radical.



....5.1

I

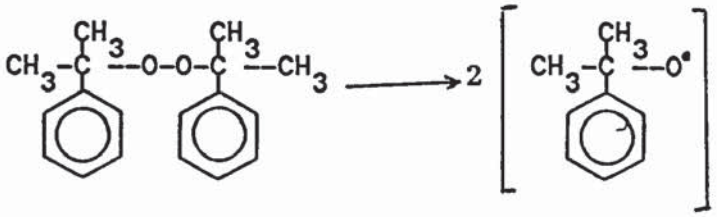
Another possible but parallel reaction is 5.2



The peak of 1696cm^{-1} in Fig 5.1 is presumably due to I and other similar quinonoid products. The same peak was also obtained when DtBP was used as a radical generator instead of BP. DBBM cannot

therefore be bound to PP using radical generators since the main reaction is presumably reduction of the RO$^{\bullet}$radicals by the additive. Fig 5.4 shows that both DBBM and TPMG have efficeintly suppressed alkoxyl radical attack on PP despite the high concentration of such radicals. In Sec 3.4.2 a small amount of $D^{t}BP$ equivalent to ratio C reduced the $\bar{D}$ of unstabilised PP by a factor of nearly 3. Ratio 'H', used in this attempted binding is 25 times as high as ratio 'C', yet its effect on PP samples in the presence of mercapto compounds was very minimal. The final processing torque after 6 minutes was 6 units for DBBM while that of the control sample (without peroxide) was 7 units.

Sample 3,PP processed with 5% tinuvin 770 and sample 4,(unstabilised PP) both containing an equivalent amount of DCP as DBBM, were completely degraded as evidenced by the minimum torque. The decomposition mechanism and reactivity of DCP is similar to that of DtBP[126], yet only DCP was found to initiate binding between DBBA and PP. DCP decomposes to give cumyloxyl radicals, which fragment further to give acetophenone and a very reactive methyl radical $CH_3^{\bullet}$.



5.3a

IV

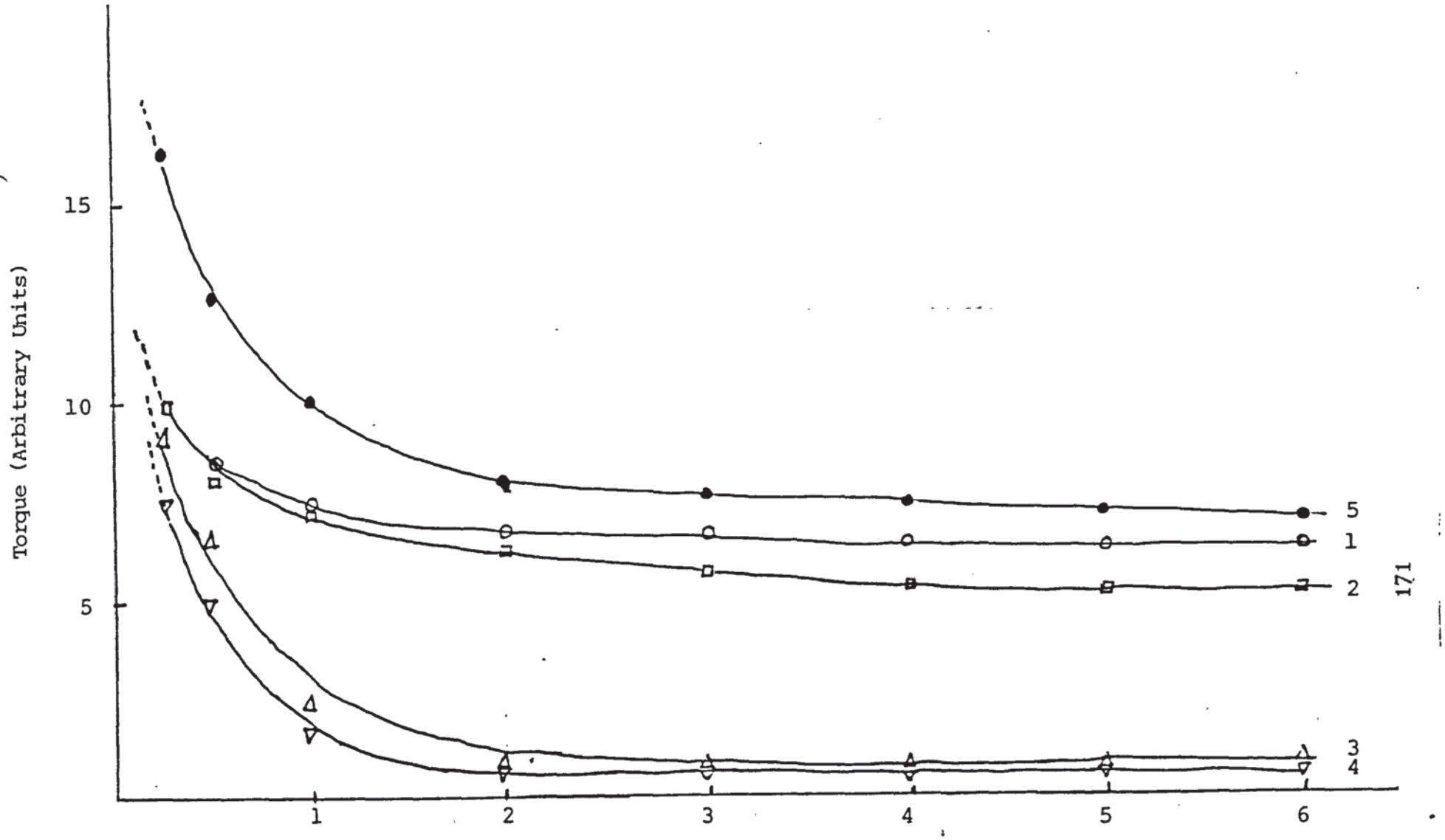
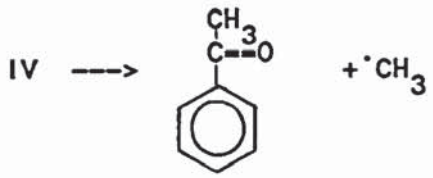
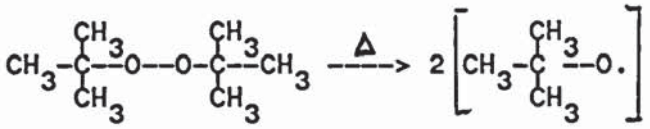


FIG. 5.4 5% Concentrates Processed in PP with Ratio 'H' of DCP at 170°C.
1- DBBM; 2- TPMG; 3- Tinuvin 770; 4- PP with DCP equivalent to ratio 'H'; 5- PP control (No additive)



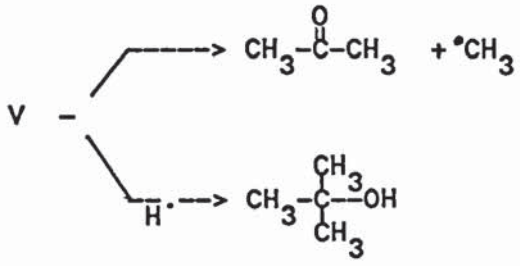
5.3b

DtBP on the other hand, decomposes to give tert-butoxyl radicals which may also fragment further, depending on the H donating ability of the environment.



5.4a

V



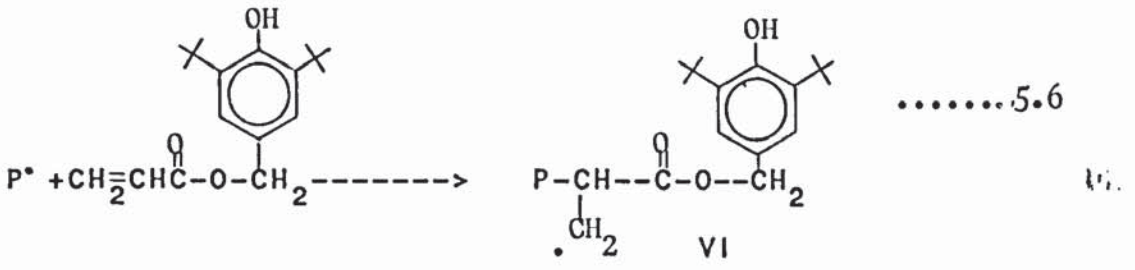
5.4b

5.4c

The molecular fragmentation product, acetone, is too volatile to be retained in a polymer film to be detected by I.r., so a reaction in a model compound, MCH was carried out at 80°C . The products of this reaction were identified by gas chromatography(G-C). Although acetone was identified as one of the products, the major component was tert-butyl alcohol. The reaction was then conducted in a sealed ampoule at 140°C. The result of this reaction product showed an even greater proportion of the alcohol was produced with only a trace of acetone. At 180°C, in presence of an easily abstractable H,such as O-H or DBBA this reaction

could be assumed to produce the alcohol exclusively. From figure 5.2 (and 5.3B) it is quite evident that acetophenone was formed (1690cm^{-1}) as a major fragmentation product, and since the extent of binding was 60%, it may be assumed that this major part of DCP was constructively engaged in the binding process. Since no binding was achieved with DtBP, a peroxide of comparable reactivity, and since only a minimal amount of $CH_3^{\bullet}$ was produced as a fragmentation product with DtBP, it is logical to conclude that the active radical in this process is the methyl radical.

$$^{\bullet}CH_3 + P \longrightarrow CH_4 + P^{\bullet} \qquad 5.5$$



.....5.6

VI may either abstract H from the polymer to start another chain or may initiate another vinyl bond to form an oligomer.

Volatility is a serious drawback to the antioxidant activity of low molecular mass phenolic compounds such as DBBA at test temperatures of 140°C. Table 5.3 shows that a PP film stabilised with $7x10^{-4}$mol/100g unbound DBBA embrittled after 10h while the bound but unextracted sample of the same concentration embrittled after 80h. Even after exhaustive solvent extraction, this sample did not embrittle until after 60h. When this is compared with a sample stabilised with an equivalent concentration of Irganox 1076, the E.T. of the unextracted sample was 110h, higher than the bound DBBA but when extracted, virtually no antioxidant activity was found in the Irganox stabilised sample, giving an E.T. of only 1h. Thus, because of its higher molecular mass, volatility is not an important factor in the antioxidant activity of Irganox 1076, even at the test temperature of 140°C, but it was seen to be easily extracted by solvents such as acetone or DCM.

5.1.4. Bis(2,2,6,6-tetramethylpiperidinyl)maleate

Result and Discussion

Bispiperidinemaleate(BPM),an unsaturated symmetrical diester prepared according to the method described in Sec.2.2.5 was also processed with varying amounts of the radical generators listed in Sec.3.1,in PP.Binding was observed to take place with all the radical generators.

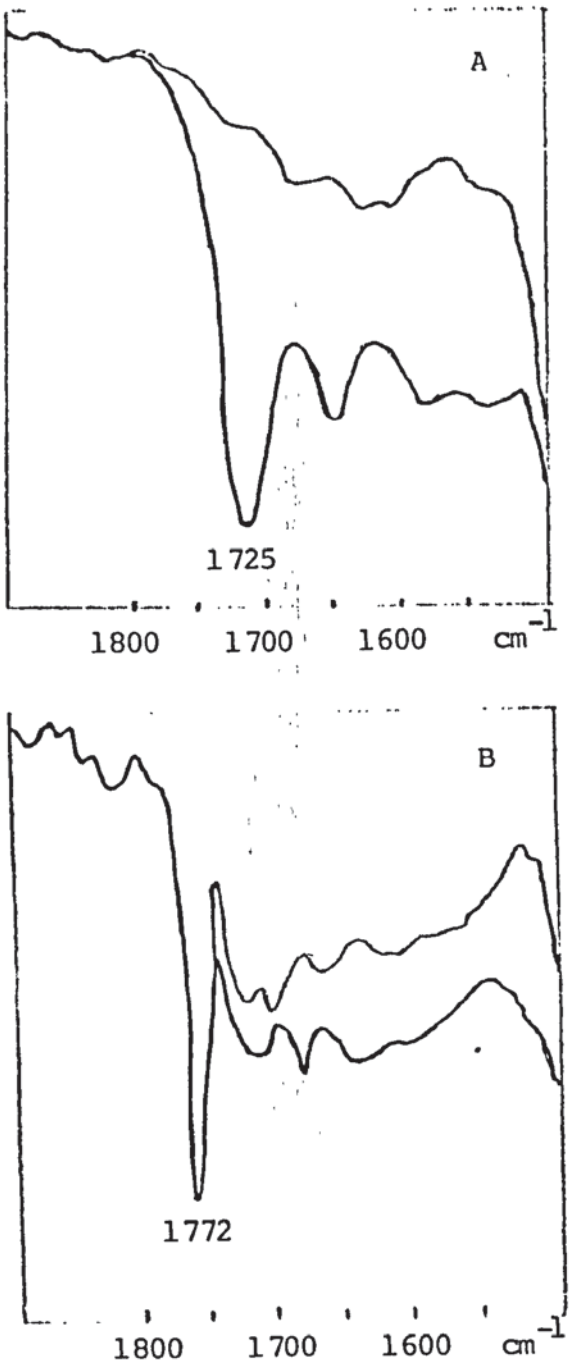


FIG.5.5 A Segment of i.r. Spectrum of 5% BPM in PP
A: Processed Without Peroxide
1- Before Extraction 2- After Extraction
B: Processed With Ratio 'H' of DCP at 180°
1- Before Extraction 2- After Extraction

A 5% masterbatch was therefore processed with various ratios of DCP, the radical generator used for all the results given in the rest of this section.

The i.r. spectrum of 5%BPM (ester C=O and C=C absorption regions) is given in Fig.5.5. When processed without peroxide (Fig.5.5A), 12h of extraction with either acetone or dichloromethane was enough to remove all the additive(2). When the mixture was processed with DCP (Fig.5.5B) there was a shift of the unsaturated ester C=O peak from 1720cm^{-1} to that of a saturated diester at 1772cm^{-1}. The unsaturation at 1640cm^{-1} was also observed to disappear.[Fig.5.5B(2)]. No amount of extraction could remove this new band at 1772cm^{-1}. A peak at 1690cm^{-1} presumably due to acetophenone was also observed in Fig.5.5B(1) which was easily removed after 12h of extraction.

Table 5.4 shows the percentage of the original 5%BPM bound to PP when processed with varying ratios of DCP.

DCP/BPM Molar Ratio	C	E	G	H	J
%Bound	8	20	60	70	90

Table 5.4 :Degree of Binding of 5% BPM in PP in presence of DCP

The degree of binding was found to increase with increasing peroxide ratio such that at ratio C, only 8% of BPM was bound to PP while at ratio J,up to 90% was bound.

The uv stabilising effectiveness of $1.0x10^{-3}$mole/100g (0.4%) of the diluted samples were compared with equivalent samples of the additive processed without peroxide and Tinuvin 770 in Table 5.5. Another set of samples was also Soxhlet extracted before exposure in the uv cabinet. The performance of the extracted samples (E) and unextracted (U) was also compared in the same table.

Sample	C	E	G	H	J	No peroxide	T.770
E.T.[U](h)	2400	2600	2900	2850	2000	2300	2250
E.T.[E](h)	250	650	1200	1400	900	90	90

Table 5.5 Effect of Bound(E&U) BPM on the uv Stability of PP.

All concentrations are $1x10^{-3}$mole/100g.

Sample G which was 60% bound,was found to have the best uv stability (2900h) when the samples were exposed without extraction,but was not as good as sample H when extracted. The extracted PP samples stabilised with both unbound BPM (no peroxide) and Tinuvin 770 embrittled after 90h,but sample H did not embrittle until after 1400h. Even sample C, which was only 8%

bound and which as an unextracted sample did not show any superior performance over the unbound sample,embrittled at 250h after extraction,showing the effectiveness of the residual bound BPM . The highest binding achieved was 90% with sample J but this is not concurrent with the achievement of highest uv stability since unextracted sample J embrittled at 2000h while the extracted sample embrittled at 900h (See table 5.5). Unextracted sample H on the other hand which was only 70% bound embrittled at 1400h. Although the uv stability of bound samples was progressively increasing with increasing DCP ratio the limit appeared to be at ratio H. The poor performance of ratio J may be attributed to poor distribution of the concentrate in the diluted sample, as crosslinks could be formed because of the excessive amount of DCP generating alkoxyl radicals, thus creating a multitude of reactive sites in the system during the binding reaction.

Equimolar quantities of unbound BPM and Tinuvin 770 in PP gave about the same embrittlement time (see table 5.5).
The improvement in uv stability of the bound BPM samples can therefore be attributed not only to the improved substantivity of the bound additive, but also to uniform distribution as the problem of incompatibility is virtually eliminated in the bound system. It is presumably the optimisation of substantivity and uniform distribution of additive that gave sample H (extracted) the highest E.T. in table 5.5, higher than that of sampleJ.

6. CONCLUSIONS & RECOMMENDATION FOR FURTHER WORK

6.1 CONCLUSIONS

Significant amounts of antioxidants can be lost from polymeric materials due to oxidation, volatilisation and solvent extraction during the lifetime of an article, especially if the material is of high surface to volume ratio such as films and fibres. A high proportion of polyolefins produced are used as such, and with the increasing trend towards the use of polymers in automotive and aerospace industries, volatility and extractability of an antioxidant is a serious limitation to further penetration in this area of application.

Low molecular weight compounds easily volatilise at elevated temperatures under air oven ageing conditions or are otherwise easily extracted by solvents in contact with the stabilised articles.

The use of oligomeric and polymeric antioxidants has gone a long way to reducing volatility but even polymeric antioxidants can non-the-less be extracted by solvents, especially at elevated temperatures. If the repeat unit of a polymeric antioxidant is short and polar, then compatibility with essentially non polar

polyolefins is a serious problem. Compatibility can be improved by incorporating a long alkyl chain to the antioxidant with a consequent dilution of the antioxidant function by reducing its activity on a weight basis

The problems of volatility, extractability and solubility can all be avoided if the antioxidant is chemically bound to the polymer. In the food and drinks industry, bound antioxidants are potentially capable of eliminating the hazards of toxicity, carcinogenicity and allergenicity.

Although the physical properties of the concentrates are altered by the transformation of the bound polymer this does not appear to be carried forward to the diluted sample (see sec. 4.3).

Monomeric AATP is easily volatilised at a temperature of 140^{o}C in a circulating air oven. Surprisingly when bound it was found to possess no thermal antioxidant activity at this temperature on its own,even though it was no longer lost from the polymer. However it was found to synergise very effectively with even very small amounts of Irganox 1076 (see Sec. 4.1.) to give a combination which compares favourably with the best combination commercially available.

The effect of volatility of antioxidants cannot be realistically evaluated during accelerated uv tests,but in view of the fact that the actual lifetime of a polymer film or fibre outdoors is between

10 and 100 times that in the uv cabinet,the significance of antioxidant substantivity through binding cannot be over emphasised .

In sec.4.2. more than 50% of monomeric AATP was observed to be lost through volatilisation of the 2% additive in PP within a period of only 300h,while virtually no loss was recorded in the bound sample. Although the 2% monomeric AATP may have been supersaturated the solubility of the bound additive is limited only by the technological extent of binding.

The technique of binding vinyl antioxidants to PP backbone using radical generators appears to be successful only with antioxidants whose precursors are not effective radical scavengers such as hindered piperidines .

The effect of radical generation in presence of effective radical scavengers such as DBBM with 2 radical trapping functional groups is to instantly reduce the alkoxyl radical generated with very minimal attack on PP molecular chains (see Sec. 5.1)

DBBA was found to be bound to PP only to the extent of 60% at 5g/100g and only with DCP initiation. Attempts to bind higher concentrates were unsuccessful.

The actual active radical in this binding process appears to be the methyl radical (fragmentation product) rather than the cumyloxyl radical itself.

It is obvious that binding an antioxidant to a polymer backbone restricts its mobility. This restriction however does not appear to adversely affect the effectiveness of the antioxidants.

6.2.RECOMMENDATION FOR FURTHER WORK

1.Both vinyl groups (acrylate and acrylamide) in AATP are observed to react in presence of a radical generator (see Sec. 3.2.2.) during the polymerisation and binding reactions. From i.r. evidence, not all the vinyl unsaturation disappeared after the reaction, and all the remaining unsaturation was attributed to the acrylate unsaturation. However the reactivity of the 2 vinyl groups (and influence of adjoining groups) cannot be unambiglously ascertained on the basis of this evidence alone. Further work is therefore needed to measure the relative reactivities of the vinyl groups, by preparing and studying the reactivities of the amide (1- Acryloyl-2,2,6,6-tetramethyl piperidinol) and the acrylate (4-Acryloyloxy 2,2,6,6-tetramethylpiperidine).

2. Although the formation of nitroxyl radicals was observed to be more facile with the acryloamide than the saturated ester in AATP (see Sec. 4.1.) the actual mechanism of nitroxyl radical

formation with either of the two groups as substituent on the piperidine nitrogen, needs to be investigated.

3. Isocyanate formation was observed to occur when AATP was processed with high ratios (>C) of either D^tBP or DCP (see Sec.4.1)
The formation of isocynates can only happen as a result of ring opening reaction, with the consequent destruction of the stabilising species. This is therefore an important side reaction whose extent and mechanism need to be further investigated.

4. BPM was shown to be bound to the extent of 90% in PP (see Sec.5.1.4.) from a 5% concentrate in PP. More work is therefore needed here to find the optimum masterbatch concentration and the effect of high ratio of the radical generator on the solubility of the concentrate in a diluted sample.

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