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**A Review of the Effect of Impurities on
the Photostability of Polypropylene**

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A REVIEW OF THE EFFECT OF IMPURITIES ON THE PHOTOSTABILITY OF POLYPROPYLENE

by N.G. TROLLIP

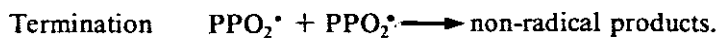
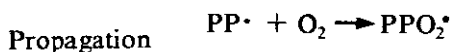
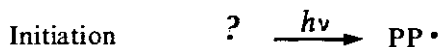
1. INTRODUCTION

The discovery of heterogeneous stereospecific catalyst systems by Ziegler and Natta in 1953 heralded the birth of a wide variety of new polymers such as highly crystalline (isotactic) polypropylene.

The exceptional success of polypropylene in a highly competitive market can be ascribed mainly to its versatility in terms of processing and the physical form of the resultant product (monofilaments, tapes, films and an unlimited variety of compression moulded articles). Other favourable properties of polypropylene include its relatively low cost, high chemical and abrasion resistance, high tensile strength and high elastic recovery.

Polypropylene (PP) is now firmly established in the textile industry in applications such as carpets, ropes and twines and upholstery fabric, and has a foothold in the apparel market. A low thermal conductivity, low specific gravity (allowing a high volume of fibre per unit mass) and an ability to "wick" moisture from a liquid source (contributing towards comfort) are additional properties of PP that make it suitable for textile fabrics. On the other hand, the low melting point and problems associated with dyeing of the polymer have limited its penetration into apparel markets.

A further problem associated with polypropylene is its poor resistance to sunlight, which causes a rapid deterioration of its useful properties (photodegradation). Complete embrittlement is the result of sustained outdoor exposure. An early priority, therefore, for the PP industry was to develop suitable means for increasing the resistance of the polymer to attack of this kind. An understanding of the chemistry of the photodegradative process became essential and the resultant flurry of industrial and academic interest soon established that a free radical, oxidative mechanism, essentially the same as that proposed by Bolland and Gee for liquid hydrocarbons¹, was operative:



However, according to a fundamental principle of photochemistry, light of sufficient energy must first be absorbed by some component of the system before a photochemical reaction such as free radical formation can occur. "Pure" PP, being a fully saturated hydrocarbon should not absorb energy of wavelengths beyond 180 nm² and should therefore be indefinitely stable to the solar energy reaching the earth's surface (lower wavelength limit approximately 290 nm). The initiation of free radical reactions resulting in polymer degradation is therefore attributed to chromophoric (light absorbing) impurities which are fortuitously included at various stages in the production of the finished article (polymerisation, extrusion, etc.), as well as during its storage and use. However, identifying and assigning relative degrees of importance to these photo-initiating impurities has become a subject of considerable controversy in the scientific literature.

In this review, the various chromophoric impurities identified in PP containing no commercial additives are discussed with special reference to experimental evidence presented for the photo-initiating role of each. This will be preceded, however, by a brief introduction to the reasons for the particularly poor resistance of PP to degradation by free radical attack, once these reactive species have been generated within the polymer matrix.

2. THE PHOTOSENSITIVITY OF POLYPROPYLENE

The photosensitivity of PP can largely be ascribed to the fact that its glass transition temperature is well below room temperature. Thus, the molecular mobility within the polymer matrix is sufficiently great to enable a high concentration of radical pairs to escape from the primary reaction "cage" and propagate destructive secondary reactions. Poly (ethylene tetrathalate), on the other hand, with a glass transition temperature of 60° C³, is much more stable to sunlight, even though it contains a much higher concentration of chromophoric groups than PP. In this case, radical-radical recombination is favoured by molecular mobility restraints within a rigid polymer matrix.

The fact that PP is more prone to oxidative degradation than polyethylene (PE) although both are thermoplastic, fully saturated hydrocarbons, is due mainly to the number of tertiary bond sites in each of these polymers. The dissociation energy of a C-H bond decreases in the order primary (410 kJ/mol) > secondary (393 kJ/mol) > tertiary (380 kJ/mol)⁴.

Since hydrogen abstraction from the polymer matrix is an important chain propagating reaction in the oxidative scheme¹, the decrease in the number of relatively weak tertiary bonds in the order

PP > low density (LD) PE (branched) > high density (HD) PE (linear)

explains the decrease in photo-oxidation rate in the same order.

In addition, the degree of crystallinity helps determine the effect that photo-oxidative reactions have on polymer properties⁵. The deterioration of mechanical properties resulting from the same extent of photo-oxidation is likely to be greater in semi-crystalline than non-crystalline polymers. Thus, while a relatively small amount of photo-oxidation renders unstabilised isotactic PP brittle, low density PE, with little or no crystallinity, is not brittle after exposure to light for much longer periods.

The combined result of these factors is a polymer the useful outdoor life of which is limited to only a few months, if left unstabilised.

3. POLYOLEFIN LUMINESCENCE

A variety of experimental tools have been used to detect trace impurities in polypropylene. Thus, techniques such as u.v.-visible, infra-red, atomic absorption and luminescence spectroscopy have identified chromophoric species such as carbonyls, hydroperoxides, olefins, metals and large aromatic molecules⁶⁻¹³.

Of these techniques the extreme sensitivity of luminescence spectroscopy has proved particularly useful in the detection and identification of impurities. However, although a number of independent workers have reported similar luminescence properties of polypropylene, little accord has been reached on the interpretation of these data. Since these studies form an integral part of the controversy surrounding the photo-initiation of polypropylene oxidation, they are expounded in some detail here.

The delayed emission of light (luminescence) from irradiated polyethylene samples was first observed by Charlesby and Partridge¹⁴ and ascribed to aldehydic impurities. Isolated ketonic groups were discounted since these would be virtually non-luminescent, an interpretation later supported by Briggs and McKellar¹⁵.

Partridge¹⁶ then demonstrated that certain peaks in the absorption spectrum of PE could be removed by soaking the films in cold hexane. The hexane extract exhibited fluorescence and long-lived phosphorescence which was ascribed to aromatic molecules on the basis of similarities between the spectra of the extract with those of phenanthrene. Carbonyl oxidation products were dismissed as the luminescent species, since it was considered unlikely that such a mild treatment would remove groups attached to the polymer chains. In addition, the PE absorption removed in this way was shown to gradually return if the PE was stored in air at room temperature. The oxidation of simple benzene derivatives, present as impurities in the ethylene gas during polymerisation, was suggested as the main source of complex aromatic molecules in the polymer.

Boustead and Charlesby¹⁷ confirmed that most of the luminescent centres in LDPE are unattached to the polymer chains and identified

anthracene, phenanthrene and naphthalene as the principal centres. Further evidence for aromatic impurities in PP and PE was supplied by Russian workers¹² who attributed the fluorescence to a combination of various alkyl substituted derivatives and the unsubstituted parent aromatics. They also demonstrated the ability of certain aromatic hydrocarbons to accumulate in PE films from the atmosphere¹⁸ and identified the concentration limit for naphthalene and phenanthrene in these films as $\sim 10^{-3}$ mol/dm³ and that for anthracene as $\sim 10^{-4}$ mol/dm³. Carlsson *et al*¹¹ later confirmed these findings.

Convincing evidence has therefore been submitted for the presence of aromatic impurities in polyolefins based on their assignment as the luminescent centres in these polymers.

This assignment has not been unanimously accepted, however, and Allen *et al*^{13,19-23} have recently attempted to reinstate carbonyl oxidation products as the luminescent species in PP. By spectral matching these authors assigned the fluorescence to α , β unsaturated carbonyls of the enone type and the phosphorescence to dienones²¹. Naphthalene was discounted on the basis of the shape of its fluorescence excitation spectrum^{22,23}.

A slow decrease in the intensity of the fluorescence emission from PP has been reported to accompany the build-up of carbonyl groups during the photo-oxidation of the polymer^{24, 25}. This implies that carbonyl species are not responsible for the fluorescence observed. However, Allen *et al* have ascribed this observation to the conversion of α , β unsaturated carbonyls to saturated carbonyl groups during the initial stages, followed by reaction to form non-luminescent products such as carboxylic acids^{13, 21}. The fact that PP phosphorescence is long-lived (~ 1 sec), a characteristic feature of aromatic molecules, was attributed to steric hindrances within the polymer matrix, thus inhibiting rotational deactivation and resulting in a longer lived carbonyl excited triplet state²². These workers have, however, been unable to explain the ease with which the luminescence is transferred to a cold hydrocarbon solvent and the fact that the luminescence returns upon exposing the same samples to urban air, even in the dark²⁶.

Furthermore, the intensity of the fluorescence initially exhibited by PP samples has been found to be directly related to the rate at which the samples were subsequently photo-oxidised^{19,17}. In fact, the time to embrittlement of a PP film that showed an initial fluorescence intensity four times that of a control, was reduced by more than 50%²⁷. This implies that the fluorescent impurities in PP play an important photo-initiatory role. Although evidence for the relatively minor photo-initiatory role of saturated ketones will be presented in the next section, to the best of the author's knowledge, no experimental evidence exists for or against an important initiatory role by unsaturated ketones. The true nature and photo-initiatory role of the luminescent species therefore remains speculative.

Luminescence studies are restricted by the fact that PP samples are seldom identical. Thus, the nature and concentrations of luminescent impurities are likely to depend on such factors as the extent of thermal oxidation during processing and the atmosphere to which the samples are exposed during storage and use. These restraints apply to all studies of the initiation of polypropylene photo-oxidation.

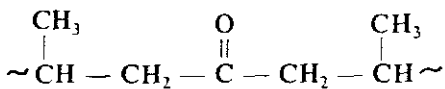
4. PHOTO-INITIATING CHROMOPHORES IN POLYPROPYLENE

A wide variety of chemical groupings has been identified in PP and assigned photo-initiatory roles. In this section, each of these chemical species is discussed with respect to its source of origin in the polymer, its absorption characteristics, its mode of photo-initiating action and the experimental evidence for its contribution to polypropylene photo-oxidation.

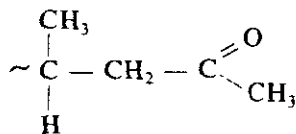
It should be noted that this discussion is limited to the impurities occurring in "natural" PP, i.e. those included fortuitously during polymer production, processing and storage. Further contributions by the wide range of commercial additives such as fillers, pigments, dyes and anti-oxidants are possible in commercial polyolefin articles but are beyond the scope of this review.

4.1 Carbonyl groups

The formation of carbonyl oxidation products during the high temperature processing of PP appears unavoidable⁸. Winslow *et al*⁸ have suggested that carbonyl groups are also introduced during polymerisation as a result of carbon monoxide impurities in the monomer. Macroketones, of the types A and B below, have been shown to be the major carbonyl compounds resulting from short periods of thermal oxidation at temperatures similar to those used during processing⁸. Carboxylic acids and esters were also detected in smaller quantities.



A

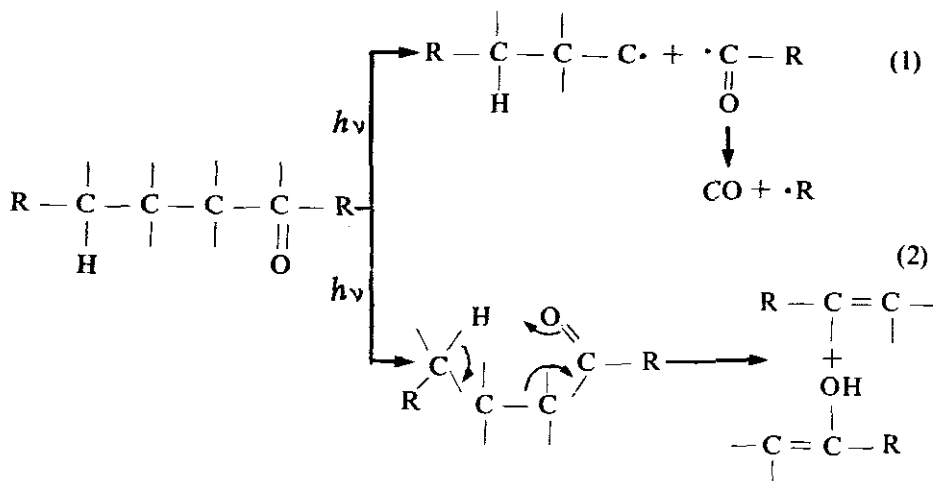


B

Aliphatic ketones absorb relatively weakly in the near u.v. with a maximum in the region of 280 nm and with a tail that extends beyond 300 nm⁴ and upon excitation can undergo two dominant photocleavages, the Norrish type I and II reactions^{6,7}. Type I is a homolytic cleavage yielding free radicals

(reaction 1). The type II cleavage occurs only when the ketone possesses at least one α -hydrogen atom and yields non-radical products via a six-membered ring intermediate (reaction 2).

Whereas macroketone A is photolysed primarily by the type I scission, macroketone B is photolysed mainly by the type II process. Both quantum yields are approximately 0.08⁸.



The macroalkyl radicals formed in the type I process can react with oxygen to give peroxy radicals (reaction 3) which in turn may abstract H atoms from the polymer matrix, PPH, yielding hydroperoxides (reaction 4). These reactions form the basis of the Bolland and Gee auto-oxidation mechanism for aliphatic hydrocarbons described previously.



Although carbonyl groups have for long been considered key photo-initiators in polyolefins¹¹, experimental evidence now suggests otherwise. For example, the inclusion of a long-chain aliphatic ketone in PP failed to accelerate the photo-oxidation²⁹ and an ethylene-carbon monoxide polymer containing 0.3 mole/dm³ of carbonyl groups was found to oxidise only twice as fast as a low density PE of the same crystallinity³⁰.

On the other hand, Carlsson and Wiles⁸ have shown that the photocleavages of macroketones A and B, yielding free radicals in the Norrish

type I reaction, are fairly rapid. They attempted to rationalise the apparent anomaly of relatively high type I quantum yields and inefficient photosensitisation in terms of the rigidity of the polymer matrix compared with liquid systems. Thus a pair of macroalkyl radicals resulting from type I cleavages is likely to combine in the polymer "cage" before oxygen can react with one of them. The high reactivity of these radical species aided by the rigidity of the environment will favour a very rapid combination.

An indirect mode of participation by carbonyl groups in polyolefin oxidation has been postulated by Trozzolo and Winslow³¹. They propose the formation of singlet oxygen (¹O₂) by quenching of the n - π* triplet excited state of carbonyls by molecular oxygen, followed by reaction of ¹O₂ with the double bonds arising from Norrish type II cleavages, to form hydroperoxides. This reaction sequence is given in section 6.4.

4.2 Hydroperoxides

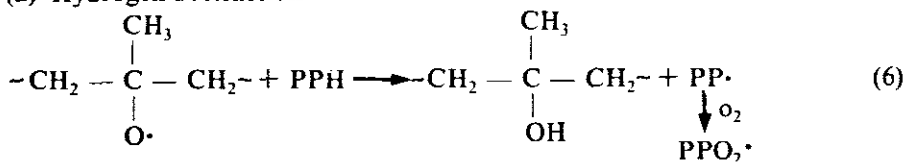
Polymeric hydroperoxides are formed in addition to carbonyl compounds as a result of thermal oxidation during the melt processing of PP (moulding, extrusion, etc.), and in fact would appear to be the primary oxidation products^{9,32,33}. Hydroperoxides may also build up as the result of slow metal-catalysed oxidation at room temperature¹⁰.

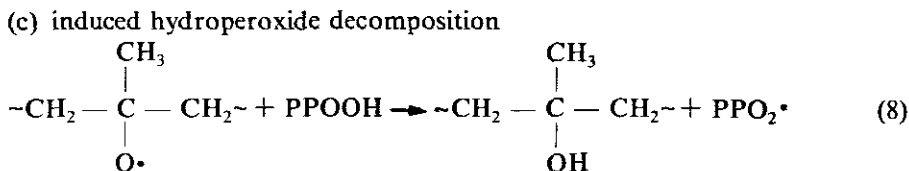
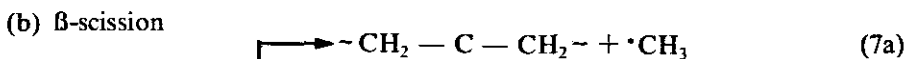
Alkyl hydroperoxides have an absorption band in the far u.v. at about 200 nm, but this band has a tail that extends to about 330 nm in the near u.v.⁷. Their excited states have never been detected, however, presumably because of immediate scission of the weak O - O bond (dissociation energy ~175 kJ/mol)³⁴ yielding two free radicals with a quantum yield close to unity⁶. The very high efficiency of this cleavage can be appreciated if one considers that the photon energy corresponding to a wavelength of 300 nm is ~400kJ/mol.



Reaction 5 is expected to be the dominant primary photolysis step since the bond dissociation energies of the R-O and O-H bonds are significantly larger (~290 kJ/mol and 380 kJ/mol, respectively)³⁴. PP hydroperoxides and peroxides have been shown to photocleave with 100% efficiency, even when irradiated at 365 nm³⁵ and the resultant alkoxy radicals (RO•) can react in one of three ways:

(a) Hydrogen abstraction





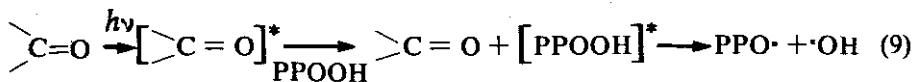
It is β -scission via reaction 7b that is largely responsible for polymer degradation since this reaction causes random cleavage of the main polymer chains with a drastic reduction in molecular mass. Reaction 7a, on the other hand, eliminates only a methyl side chain with minimal reduction in molecular mass.

The $\cdot\text{OH}$ radical produced by reaction 5 may abstract a hydrogen to give water in a manner analogous to reactions 6 and 8. In fact, an analysis of the products resulting from the photolysis of PP hydroperoxides identified various alcohol groups and water in large yields³⁵. These results tend to support an extensive attack on the polymer matrix, generating many new radical species.

Evidence for hydroperoxides rather than carbonyl species being mainly responsible for the photosensitivity of PP has been presented³⁶. A slightly oxidised PP film containing a relatively high concentration of hydroperoxide groups, was heated under an argon atmosphere. This process destroyed the hydroperoxides with a corresponding increase in the ketonic carbonyl concentration. In spite of the high carbonyl concentration, the initial photo-oxidation rate of the film was greatly reduced. In addition, the initial rate was proportional to the initial hydroperoxide concentration while no such correlation could be found between photo-oxidation rate and carbonyl concentration.

Further proof of the vital photo-initiating role of PP hydroperoxides has recently been presented by Allen *et al*³⁷, who demonstrated that the sulphur dioxide treatment of thermally oxidised PP films resulted in significant stabilisation to subsequent photo-oxidation. SO_2 is known to destroy hydroperoxides by reaction to form alkyl hydrogen sulphates³⁸ (reaction 15).

In view of the low absorption coefficients, ξ , of hydroperoxides ($\sim 0,31, \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 300 nm), the sensitised decomposition of hydroperoxides by excited carbonyl groups has recently been suggested as an important initiation route for some polymers^{39,40};

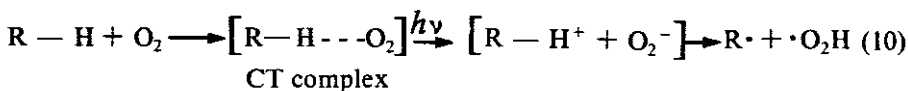


Another group of extraneous impurities, the photo-initiating action of which is closely related to that of hydroperoxides, comprises alkyl peroxides (PP-OO-PP), also generated by thermal oxidation during high temperature processing but in relatively small quantities. Photolysis of the peroxidic linkage also occurs with quantum yields close to unity⁶.

In view of the preceding discussions on carbonyls, hydroperoxides and peroxides, it is not surprising that the u.v. stability of polyolefins has been shown to be profoundly dependent on their thermal histories⁴¹.

4.3 Oxygen-polymer charge transfer complexes

Chien⁴² has shown that purified saturated and unsaturated hydrocarbons can be photo-oxidised with radiation of wavelengths beyond the absorption limits of these compounds. In the absence of chromophoric impurities, he ascribed the photo-oxidation to charge transfer (CT) complexes involving oxygen, based on observed shifts to longer wavelengths in the u.v. absorption spectra of these hydrocarbons, in the presence of O₂. After absorbing light, these complexes may dissociate into free radicals:



Tsuji and Seiki⁴³ have proposed O₂-polymer charge transfer complexes as potential sources of the photo-instability of PP, after their observation of a weak red shift in the u.v. absorption spectra of O₂ saturated samples. However, this absorption was undetectable beyond 240 nm. These authors also reported a higher radical yield from the u.v. irradiation, at -196°C, of air saturated PP as compared to nitrogen saturated samples. This was also attributed to absorption by O₂-polymer charge transfer complexes. Milinchuk⁴⁴ obtained similar results on irradiating polyolefins in the presence and absence of oxygen.

Allen⁴⁵ has demonstrated that prior irradiation (λ 's > 300 nm) in an inert atmosphere, a process that destroys most of the carbonyl and hydro-

peroxide oxidation products, has little effect on the subsequent u.v. stability of PP and LDPE. This was interpreted as further evidence for oxygen-polymer CT complexes as important photo-initiators. However, the relatively long period (100 hr) of prior irradiation in an inert atmosphere led to increased PP absorption in the near u.v. region which may have influenced the subsequent rate of photo-oxidation.

Despite using the highest quantum yield and most intense u.v. absorption published for model alkanes, Carlsson, Garton and Wiles⁴⁶ have calculated a very low rate of radical generation from O₂-PP CT complexes. Although olefins have much more intense charge transfer absorptions that extend beyond 330 nm, the concentration of unsaturation sites in commercial PP was considered too low to allow significant contributions by these complexes to photo-initiation.

Charge transfer complexes are therefore only likely to play a significant photo-initiating role in unprocessed PP which is relatively free of chromophoric impurities. In the presence of photolabile hydroperoxides and other initiating species, introduced mainly during thermal processing, the contribution by CT complexes is likely to be insignificant.

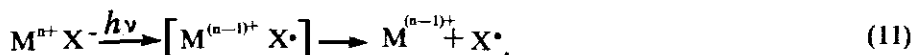
4.4 Metal impurities

Commercial PP is usually polymerised in the presence of Ziegler-Natta (ZN) catalysts (organo-aluminium-titanium complexes) and as a result contains Ti and Al residues that cannot easily be removed. Although their concentrations can be reduced by alcohol extraction, Ti and Al are usually present in concentrations of 5 to 50 ppm.

Catalytic residues of Ti probably exist in a variety of forms, including TiO₂ and Ti(OR)₄⁴⁷, where R is PP or an alkyl group. Whereas compounds such as these absorb strongly in the solar spectral region (up to ~350 nm)¹⁸, Al₂O₃ only absorbs strongly below 300 nm and is therefore unlikely to contribute to photo-initiation under terrestrial sunlight (λ 's > 290 nm).

Kujirai *et al*⁴⁸ have reported that the photostability of PP decreases with increasing catalyst residue content. Inclusion of 170 ppm of TiO₂ in fact caused a ten-fold increase in the initial photo-oxidation rate of PP powder. This photosensitising effect of TiO₂ in PP was confirmed later by Irich⁴⁹.

Cichetti¹⁰ has suggested that transition metal compounds exert their sensitising action by u.v. absorption followed by the generation of free radicals, according to the reaction:

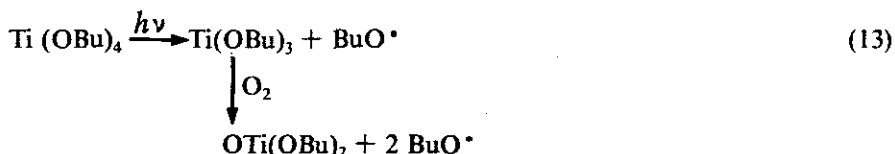


The photosensitising action of TiO_2 in PP may therefore be described as follows⁴⁹:



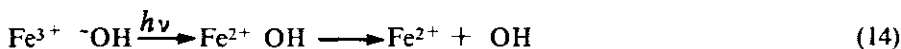
The two crystalline forms of TiO_2 have been reported to exhibit different photo-activities in polymer media. Thus, while the rutile form is relatively inactive in polyolefins, the anatase form markedly sensitises these polymers⁵⁰. This difference has been attributed to the difference between the energies of their photo-excited states⁵¹.

$\text{Ti}(\text{OBu})_4$, found in PP that has been treated with butanol following polymerisation with ZN catalysts, has been shown to generate butoxy radicals quite efficiently in the liquid phase⁴⁷. Ti^{3+} compounds are produced which absorb even more intensely in the near u.v. region than do Ti^{4+} compounds and can further initiate, probably by the cleavage shown below. The overall quantum yield for BuO[•] production is high (0,14 mole/einstein)⁴⁷.



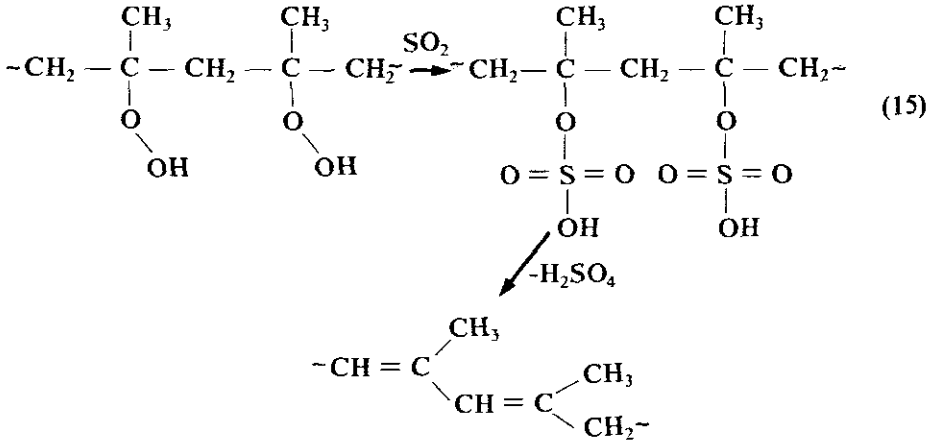
These findings, however, contradict those of Balaban *et al*⁵² who found that the termination of a ZN polymerised PP with isopropanol, gave relatively inactive Ti residues over a range of 100 to 400 ppm. In addition, Carlsson *et al*⁴⁶ have reported that incorporating up to 100 ppm of various Ti compounds caused only a negligible increase in the photosensitivity of PP film.

It is apparent that photo-initiation by catalyst residues is not yet clearly understood. These residues, however, are not the only source of metal impurities in polymer films. Processing steps such as extrusion and milling can introduce traces or even particles of metals such as Fe, Ni or Cr into the polymer. These transition metals are well-known photosensitisers by reactions such as⁵³:



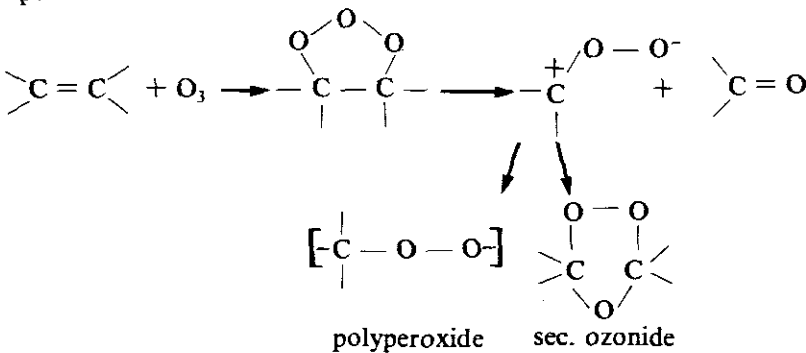
4.5 Unsaturation

Termination of the polymerisation process leaves vinylidene groups at the end of most PP chains. This results in a concentration of unsaturation sites in commercial polyolefins of $\sim 0,05 \text{ M}^{11}$. Conjugated unsaturation may also result from the attack of atmospheric SO_2 on adjacent hydroperoxide groups in PP^{38, 54}:



Although long chain olefins and dienes of the type found in PP do not absorb in the near u.v.⁴, unsaturation may contribute to the photo-initiation process indirectly in a number of ways.

(a) Ozone (O_3), present in urban atmospheres, reacts very rapidly with olefins to form unstable ozonides which decompose at ambient temperatures, to generate peroxides⁵⁵:



The peroxide and ozonide groups can photolyse to give radicals. The increase in the photosensitivity of polyolefins on storage in the absence of u.v. radiation, is probably due partly to the build up of these types of products⁶.

(b) The role of singlet oxygen in the degradation of polymers is discussed separately in chapter 6. At this stage, it is sufficient to know that singlet oxygen (¹O₂) attacks C-C unsaturation to form allylic hydroperoxides³¹ whose key photo-initiatory role is well documented.

(c) As mentioned previously, charge transfer complexes between O₂ and unsaturation sites may also contribute to photo-initiation, since these complexes show relatively strong absorptions that extend into the solar spectral region⁴².

(d) The ease with which allylic H atoms are abstracted, yielding allylic hydroperoxides after reaction of the allyl radicals with O₂, represents another possible sensitising mode associated with C-C unsaturation, since the bond dissociation energy of allylic H's is ~ 336 kJ/mol⁴ which is ~ 44 kJ/mol lower than that of a tertiary C-H bond.

Allen *et al*^{37,56,57} have reported that removing the unsaturation from PP by various methods has a destabilising and not a stabilising effect as would be expected from the above discussion. The present author suggests that the reasons for this surprising result are to be found in the experimental methods employed to remove unsaturation, namely cold hexane extraction, bromination and prior irradiation (λ 's < 300 nm) in an inert atmosphere:

(a) Cold hexane extraction was claimed to remove unsaturation in the form of α , β unsaturated carbonyls⁵⁶, based on luminescence studies. However, other authors²⁶, have reported that this treatment of PP films causes stabilisation which they attributed to the removal of aromatic impurities.

(b) Although bromination removes unsaturation it leaves weak C-Br bonds (dissociation energy 280 kJ/mol)⁴ in the polymer, which could account for the increased photosensitivity. In addition, examination of the second-order derivative absorption spectrum of the polymer after bromination showed the appearance of a new absorption band at ~ 400 nm⁵⁷, suggested by these authors to be due to brominated catalyst residues, which are also expected to sensitise the photo-oxidation.

(c) Prior irradiation in an inert atmosphere for 50 hours reduced the unsaturation without removing it completely, and also caused slightly increased absorption in the near u.v., as seen from second order derivative absorption

spectra before and after this treatment⁵⁶. The observation of increased absorption following irradiation under an inert gas had previously been reported⁴⁵ and may account for the lower stability.

Allen *et al*⁵⁶ have also reported that doping untreated PP with hexane extracts has a significant stabilising effect which cannot be explained on the present knowledge of the photo-oxidative process.

The above findings are particularly surprising in the light of evidence presented by Scott *et al*^{58,59} that the deliberate incorporation of unsaturation in saturated polymers had a pro-oxidant effect. For example, the addition of ethylene-propylene-diene terpolymer markedly increased the sensitivity of PP to photo-oxidation⁵⁸. These effects were ascribed mainly to the favourable formation of allylic hydroperoxides⁵⁹.

4.6 AROMATIC COMPOUNDS

A large variety of polycyclic aromatic compounds are released into the atmosphere by the combustion and pyrolysis of almost all carbonaceous matter, including fuels⁶⁰. Although diffusion from the atmosphere appears to be the major source of large aromatic molecules in polypropylene²⁶, they may also be included during polymerisation as impurities in the propene gas and during polymer processing from the lubricants used on the processing machinery.

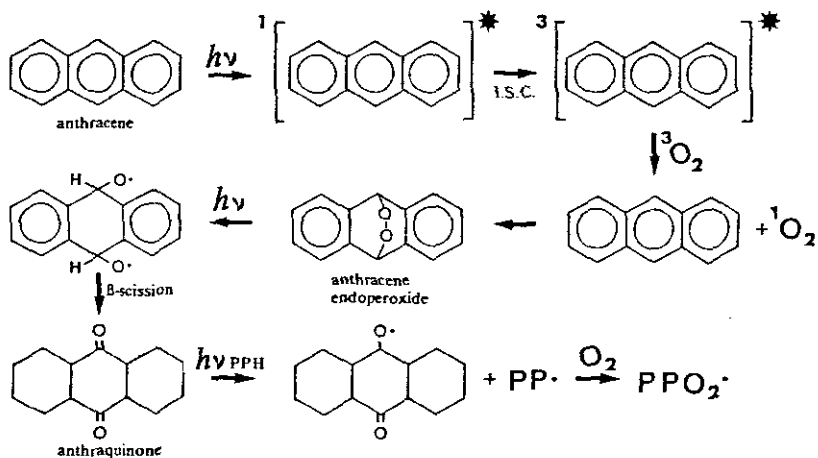
Polycyclic aromatic compounds absorb extremely strongly in the near u.v. (ξ_{\max} for phenanthrene, for example, is $16\,000\text{ l mol}^{-1}\text{ cm}^{-1}$ or 500 times that of long chain saturated ketones) and may contribute to photo-initiation in PP in a number of ways;

(a) Reaction with singlet oxygen to yield photolabile products

Linearly condensed aromatic hydrocarbons containing an anthracene or naphthalene nucleus react readily with singlet oxygen at their *meso* positions to yield photolabile endoperoxides^{61,62}. Autoperoxidation has been demonstrated for anthracene, i.e. the aromatic molecule acts as both sensitiser for $^1\text{O}_2$ formation and as substrate for endoperoxidation⁶³. The reaction sequence leading to photo-initiation in PP is shown below.

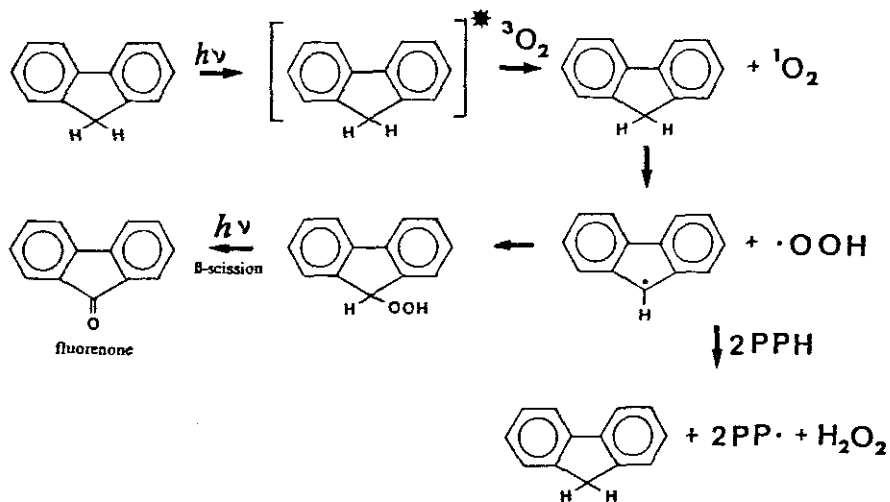
The quantum yield for hydrogen abstraction from the polymer matrix, the polymeric radical generating step, is probably close to unity, as for benzophenone⁶⁴.

Scheme A: Anthracene-sensitised photo-oxidation of PP



In a recent investigation, the author proposed that certain other aromatic hydrocarbons which do not undergo endoperoxidation, may react with oxygen to yield aromatic ketones via a hydroperoxide intermediate. These ketones would then initiate polymeric free radicals in the same manner as anthraquinone. The proposed reaction scheme for fluorene is as follows⁶⁵:

Scheme B: Fluorene-sensitised photo-oxidation of PP



(b) Reaction of singlet oxygen with the polymer matrix

The quenching of excited triplet states of aromatic molecules by triplet oxygen yields excited singlet oxygen with high efficiency⁶⁶⁻⁶⁸. Singlet oxygen may then react with the residual unsaturation in PP to yield allylic hydroperoxides. However, this route to photo-initiation in polyolefins has yet to be conclusively proved (Chapter 6) and appears to be insignificant compared with the aromatic ketone routes discussed above.

(c) Energy transfers between chromophone impurities

Energy transfers between the various chromophoric groups in PP have been largely neglected in photo-initiation studies, probably due mainly to a dearth of reliable energy level data. The sensitised fission of hydroperoxides by photo-excited aromatic impurities has, however, been suggested⁶⁹. In addition, the quenching of excited ketone species by aromatic molecules with low-lying excited states is energetically feasible⁶⁵.

The effects of deliberately incorporated aromatic compounds on the rate of PP photo-oxidation have been studied^{26,65}. In each case, anthracene was shown to be a powerful sensitiser of the oxidative process, an effect ascribed largely to endoperoxidation and subsequent reactions (scheme A). Other aromatic hydrocarbons which exert significant photosensitising effects are fluorene, pyrene and fluoranthene⁶⁵. Phenanthrene is inefficient as a photo-initiator in PP and in fact appears to exert a small stabilising effect. This has been ascribed by some authors to free radical scavenging²⁶ and by the present author to triplet-triplet quenching of excited carbonyl groups⁶⁵. Naphthalene may exert a small sensitising effect but the rapid diffusion of this volatile compound out of polymer samples under irradiation has hampered studies on its role in photo-initiation.

The danger of extrapolating the results of electron spin resonance (e.s.r.) studies to photo-oxidation studies is clearly illustrated by the findings of Pivovarov *et al*¹². These workers have demonstrated that, while naphthalene and phenanthrene sensitise radical formation in PP, anthracene has a retarding effect. These results were ascribed to biphotonic absorptions involving the first excited triplet (T_1) states followed by molecular decomposition yielding radical products. The relatively short T_1 lifetime of anthracene does not favour biphotonic absorptions and explains its lack of sensitisation in this system. It should be remembered, however, that e.s.r. studies are carried out under conditions which are very different from those used for photo-oxidation studies. The above investigation, for example, was performed in the absence of oxygen, at -196°C and under irradiation that included far u.v. energy (wavelengths $< 290\text{ nm}$). Photo-oxidation studies, on the other hand, normally

employ air, ambient temperatures and near u.v. light, i.e. conditions which, by drastically shortening T_1 lifetimes, do not favour biphotonic absorptions.

5. RELATIVE IMPORTANCE OF INITIATORS

The possible sources of the photo-instability of PP and the stages at which they may be introduced are summarised below.

TABLE 1
INITIATORS OF PP OXIDATION

Initiating species	Origin
$>C=O$	Oxidation (processing, O_3 attack, storage), CO copolymerisation.
-OOH	Oxidation (processing, O_3 and 1O_2 attack, storage).
O_2 - PP CT complexes	Inherent property of hydrocarbons.
Transition metals	Catalyst residues, processing, pigment.
-C=C-	Polymerisation, atmospheric SO_2 attack.
Polycyclic aromatics	Polymerisation, processing, absorption from polluted air.

Despite the complications involved, attempts have been made to list the various initiating chromophores in order of importance. Carlsson and Wiles⁶ have calculated rates of radical production for each chromophore during outdoor exposure, from an expression that includes the chromophore's estimated concentration in PP, the published value of quantum yield for its radical generation, the spectral intensity of noon summer sunlight and the u.v. extinction coefficient of the chromophore.

This method, however, has certain limitations that were emphasised by the authors. For example, the quantum yields apply to radical generation in the primary step and not to the formation of PPO_2 radicals in the polymer. Thus chromophores such as macroketones which give caged macroradicals on photolysis, are expected to be poorer initiators than suggested by these calculations, as a result of extensive radical-radical recombination in the polymer matrix before addition of O_2 can occur. Also, some values of quantum yield were derived from model liquid systems and may be appreciably lower in solid polymers.

Within these limitations, the different photo-initiators were arranged in the following order of decreasing importance, for PP that had no previous u.v. exposure and which was free of deliberately added chromophores, such as pigments;

Ti residues \cong PPOOH > polycyclic aromatics > $>C=O$ > RO - OR >>
 O_2 - PP CT complexes

From their subsequent findings that the deliberate incorporation of Ti compounds in PP had little effect on the photostability of the polymer⁴⁶, Carlsson *et al* recently concluded that, in commercial PP, the photo-initiators can be ranked in the order:

-OOH > polycyclic aromatics > $>C=O$

with Ti residues and charge transfer complexes relatively ineffective⁷⁰.

The assignment of the key photo-initiating role to PP hydroperoxides is well supported by experimental evidence that has been described. There is also little doubt that, after short periods of u.v. irradiation, hydroperoxides will be the dominant initiating chromophore since all other initiatory routes lead to -OOH formation.

6. THE ROLE OF SINGLET OXYGEN

Most of the recent studies on PP photo-oxidation have dealt with the contribution by singlet oxygen and, in a fashion typical of the general state of the art, have resulted in controversy.



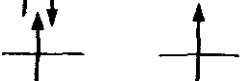
6.1 Historical Background

Ground state molecular oxygen is a triplet (3O_2) since its outermost pair of electrons occupy different orbitals and have their spins parallel. 3O_2 can therefore be considered a stable biradical. Two other arrangements of these outer electrons are possible without involving electron promotion to higher orbitals, resulting in two low-lying singlet states, the $^1\Delta_g$ and $^1\Sigma_g^+$ states⁷¹.

Kautsky⁷² originally suggested singlet oxygen molecules as the reactive intermediate in sensitised photo-oxygenation reactions. He demonstrated that the excitation of sensitiser molecules caused the oxygenation of spatially distant acceptors, which he attributed to the migration of singlet oxygen from sensitiser to acceptor. Kautsky's ideas were not accepted in his lifetime and it was a quarter of a century later when the interest in singlet oxygen as the common intermediate in photo-oxygenation reactions was revived.

Evidence supporting Kautsky's proposal is based on comparisons of the

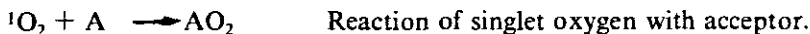
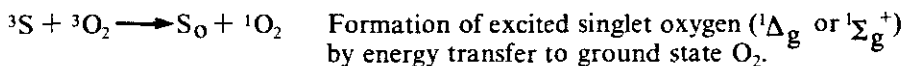
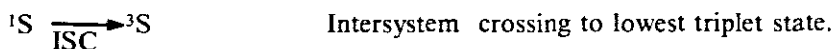
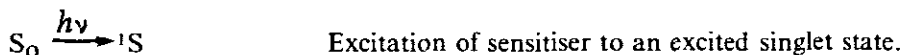
TABLE 2
ELECTRONIC STATES OF O₂^α

State	Electronic configuration in H.O.M.O. ^α	Relative energy (kJ/mol)
¹ Σ _g ⁺		159
¹ Δ _g		92
³ Σ _g ⁻ (ground state)		0

^α: highest occupied molecular orbital.

products obtained from sensitised photo-oxygenations with those formed under reaction conditions where ¹O₂ is known to be present. Thus, when a H₂O₂-NaOCl system⁷³ or a radio frequency discharge⁷⁴ was used as the ¹O₂ source, the same oxygenation products were obtained as from the corresponding photosensitised reactions.

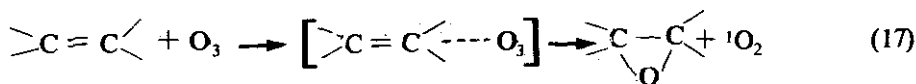
The mechanism which Kautsky proposed and which is now widely accepted is:



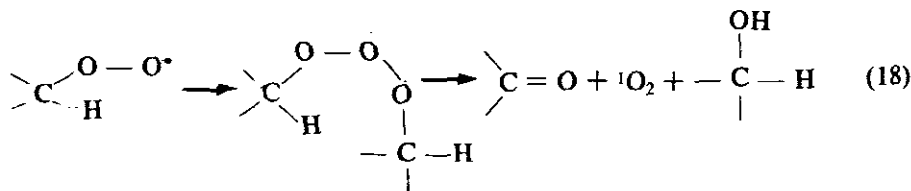
6.2 Sources of ¹O₂ in polypropylene

There are three main sources in polypropylene which raise the level of ¹O₂ within the polymer significantly above that found naturally in the atmosphere (~10⁻⁴ ppm)⁷⁵.

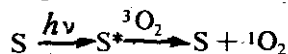
(a) Murray and Kaplan⁷⁶ have shown that complexes between ozone (which diffuses into PP from the atmosphere) and olefins can decompose to give ¹O₂.



(b) ${}^1\text{O}_2$ is also produced in the self-termination of secondary and primary peroxy radicals⁷⁷.



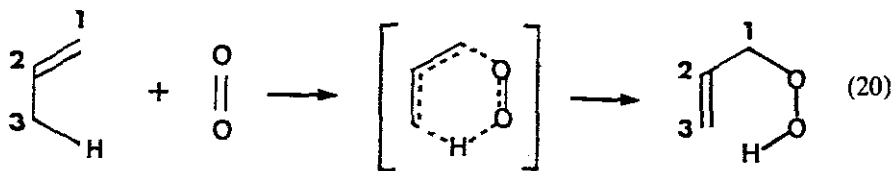
(c) The above sources are of secondary importance compared with the photochemical generation of ${}^1\text{O}_2$ by excited chromophoric impurities, S, in polyolefins. Polycyclic aromatic compounds are particularly important in this respect, as mentioned previously (section 4.6).



Although the phenomenon of elevated levels of ${}^1\text{O}_2$ within the polymer matrix is generally accepted, the importance of its role in photo-oxidation remains a contentious issue.

6.3 The "ene" reaction

At the centre of the controversy surrounding the role of ${}^1\text{O}_2$ in the photo-oxidation of PP is the reaction of ${}^1\text{O}_2$ with olefins possessing an allylic hydrogen to yield allyl hydroperoxides. The "ene" mechanism of concerted addition is generally accepted for this reaction⁷⁸:



Although ${}^1\text{O}_2$ reacts readily with electron rich olefins in this way, its reaction with terminal olefins, as found in PP, has been reported to be much slower⁷⁹. This fact coupled with the low concentration of unsaturated sites in PP

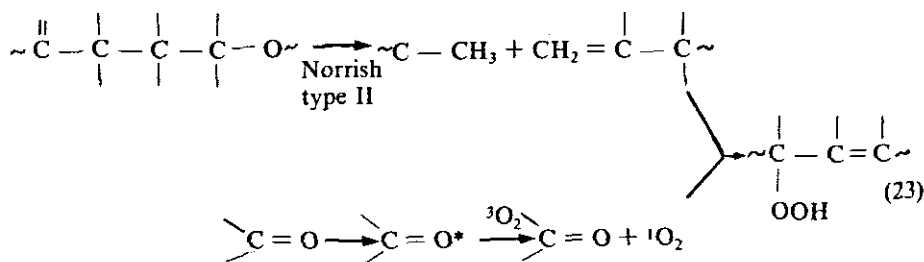
has led to the belief that the reaction of $^1\text{O}_2$ with the polymer matrix cannot contribute significantly to photo-initiation. Others, however, are of the opinion that the level of hydroperoxides generated via the "ene" reaction is sufficient to contribute significantly to photo-oxidation in view of the extreme lability of these species. The experimental evidence which has led to these opposing viewpoints is reviewed below.

6.4 Contribution of $^1\text{O}_2$ to polymer photo-oxidations

The radiative lifetime of $^1\text{O}_2$ in air and liquid alkanes are approximately 0,1 s and 1×10^{-5} s respectively⁸⁰. The lifetime of $^1\text{O}_2$ in saturated polymers is likely to be similar to that reported for liquid alkanes. In spite of this short life, $^1\text{O}_2$ has been shown to penetrate up to 3000 Å into rubber before reacting to yield hydroperoxides⁸¹ and to diffuse through more than 100 Å of hydrocarbon film before 50% deactivation occurs⁸².

The reaction of singlet oxygen with unsaturated polymers is in fact well documented. Kaplan and Kelleher^{81, 83}, for example, have demonstrated the oxidation of polybutadiene by $^1\text{O}_2$. The reaction of $^1\text{O}_2$ with saturated polymers has, however, not been demonstrated conclusively;

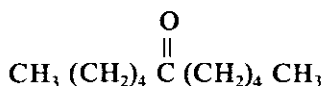
Trozzolo and Winslow³¹ first suggested that $^1\text{O}_2$ takes part in the oxidative photodegradation of PE, according to the scheme below.



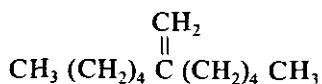
The process can be divided into four stages —

- (i) absorption of light by the carbonyl groups in the polymer,
- (ii) A Norrish type II cleavage of the $n-\pi^*$ excited carbonyl,
- (iii) formation of $^1\text{O}_2$ by quenching of the $n-\pi^*$ triplet state of the carbonyl by ground state O_2 , and
- (iv) reaction of $^1\text{O}_2$ with the vinyl groups formed in the type II cleavage, to yield allyl hydroperoxides via reaction 20.

The quenching of ketone photoreactions and phosphorescence by molecular oxygen is well documented⁸⁴, lending support to this mechanism. However, experimental evidence^{29,30,36}, described earlier (section 4.1) implies that carbonyl groups play an unimportant or at best a minor photo-initiating role in polyolefins. Some doubt therefore exists concerning the significance to the oxidative process of the scheme proposed by Trozzolo and Winslow. In addition, Scott⁸⁵ has reported that diamyl ketone (C) has virtually no effect on the rate of photo-oxidation of 1,1-diamylethylene (D), a low molecular weight model of the vinylidene function in PE. It was suggested that if ¹O₂ was formed by energy transfer from the excited (triplet) ketone to ³O₂, rapid quenching by other small molecules, such as H₂O, prevented reaction of ¹O₂ with the olefin.



C



D

Although gaseous ¹O₂, generated by a microwave discharge, has been shown to react with polyolefins and low molecular mass analogues of the residual unsaturation in these polymers^{11,86}, it has been suggested that other oxygen species in the gaseous stream, such as atomic oxygen or ozone, were the reactive species in these cases⁴⁰.

In addition, other workers^{85,87} have since reported finding no evidence for the reaction of gaseous ¹O₂ with PE and Mill *et al*⁸⁸ failed to detect hydroperoxides after exposing atactic PP to ¹O₂ generated by dye-photosensitisation in solution. Carlsson and Wiles⁶ have, however, offered an explanation for the latter observation. Assuming the atactic PP contained ~0.05M of C=C groups¹¹, the reference solution used (tetramethylethylene) would have been ~80 times richer in double bonds. In addition, fully substituted olefins of this kind will be much more reactive than the terminal olefins found in PP⁷⁹. The failure to detect ¹O₂ attack on PP in this system is therefore not surprising.

The photostabilising action of Ni(II) chelates implies the involvement of ¹O₂ in PP photo-oxidation since these compounds have been shown to be very efficient ¹O₂ quenchers⁸⁹. In addition, Guillory and Cook⁹⁰ have reported a correlation between singlet oxygen quenching by metal chelates and their photostabilising efficiencies. However, these stabilisers probably owe their action to a combination of effects such as hydroperoxide decomposition and radical scavenging⁹¹. Allen *et al*⁹² have in fact presented recent evidence that ¹O₂ quenching is not a major process in the photostabilising action of metal chelates. Similar evidence has also been presented for hindered amine light stabilisers⁹³.

Direct hydrogen abstraction by ¹O₂ from saturated centres has also been

suggested as a mode of photo-initiation. Kaplan and Kelleher⁸⁶, for example, reported the slow attack of $^1\text{O}_2$ on the saturated hydrocarbon, n-tetracosane. This finding was disputed, however, by Carlsson and Wiles¹¹, who detected no hydroperoxides after exposing rigorously purified hexadecane to a singlet oxygen stream. It appears, therefore, that trace impurities were responsible for the reaction of $^1\text{O}_2$ in the former study.

From the available evidence it appears that if $^1\text{O}_2$ reacts at all with PP, this addition will be confined to the unsaturated sites. Furthermore, this route to photo-initiation is likely to be important only in the very early stages of photo-oxidation before the build up of carbonyl and hydroperoxide species which would soon become the dominant initiators for further oxidative chains. It may be safely assumed that the reaction of singlet oxygen with aromatic hydrocarbons to yield aromatic ketones is a far more efficient source of polymeric free radicals than the more direct reaction of singlet oxygen with the polypropylene matrix.

7. CONCLUDING REMARKS

Processed polypropylene, far from being a pure, saturated hydrocarbon entirely transparent to sunlight, contains a wide variety of chromophoric impurities, each of which is capable of initiating free radical reactions which lead ultimately to the erosion of polymer tensile properties.

The generation of polymeric free radicals may occur either directly by the photolysis of the chromophore, or indirectly via one or more reactions involving other species to yield photolabile products. Hydroperoxides, peroxides, carbonyls and metallic impurities are thus capable of direct photo-initiation, while aromatic hydrocarbons, residual unsaturation, and active oxygen species may be classified as indirect photo-initiators.

There is little doubt that hydroperoxides play a key role in both the initiation and propagation of the photo-oxidative process. The contribution by the other chromophoric impurities is less clear, however, and has led to considerable discord in the scientific literature. The role played by singlet oxygen is particularly controversial and its clarification may require a more direct experimental approach, such as the incorporation of specific singlet oxygen quenchers within the polymer. Even the contribution by aromatic impurities, shown by independent workers to possess significant photo-initiating capabilities, is questioned. In this case, however, the very existence of these impurities in polypropylene is under debate in view of conflicting claims regarding the nature of the luminescence observed from the polymer.

The conflicting experimental evidence characterising the broad subject of polypropylene photodegradation must be at least partly due to inconsistencies between polymer samples. Thus, variables such as product manufacturer, extent

of thermal processing and even the atmosphere in which the samples are handled and stored will result in polymer samples of differing purities and hence photo-oxidative stabilities. The controversy surrounding the photo-initiation of polypropylene oxidation is likely to continue until workers in the field include in all publications, full descriptions of polymer samples used. This information should include, inter alia, the trade name of the unprocessed polymer, its catalyst residue content, degree of crystallinity as well as the detailed thermal history of the samples prior to their exposure to light, and a full description of the irradiation conditions employed.

An aspect of photo-initiation that has been largely neglected concerns the importance to the process of the interactions, such as energy transfer, between the different chromophoric groups. These interactions are most likely very complex and represent a daunting challenge to workers in the field.

A number of precautionary measures aimed at limiting the levels of photo-active groups in the polymer should be taken by producers of polypropylene products such as fibres, films and injection moulded articles. These include using polymeric materials with low catalyst residue content, employing the mildest possible thermal processing conditions and storing the polymer in places not affected by exhaust gases from industrial or other machinery. The incorporation of photo-active additives such as dyes and pigments should be accompanied by the addition of highly effective stabiliser systems.

A clearer understand of the photo-oxidative process, apart from being of considerable academic value, will pave the way for the development of improved stabiliser systems which would benefit the polypropylene and related industries markedly.

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