Photodegradation and Stabilization of Commercial Polyolefins

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1 Introduction

Polyolefin photochemistry has recently been discussed in a number of papers, reviews, and textbooks,[1,2] and it is evident from these that there are several conflicting views on the nature of the mechanisms involved. Broadly speaking, polyolefin photochemistry can be divided into three major areas (*a*) photodegradation (or oxidation), (*b*) sensitized photodegradation (or oxidation), and (*c*) photostabilization. Although all three areas present problems of considerable technological interest, (*b*) and (*c*) are currently of particular interest because of the ever increasing problem of environmental pollution by plastics litter.

The commercial polyolefins are low- and high-density polyethylene, polypropylene, and poly (4-methylpent-l-ene). Although the end use of the polymer is the main determining factor, in general the major technical photochemical problems are concerned with the sensitized degradation of the polyethylenes and the stabilization of the other two.

2 Photodegradation

A. Absorption and Emission of Light by Polyolefins.—Because of the screening effect of the upper atmosphere, no radiation of wavelengths shorter than about 290 nm reaches the earth's surface.[2] Consequently 'pure' saturated polyolefins should be unaffected by exposure to normal sunlight. However, it is now generally believed that it is the presence of certain impurities in the commercial polyolefins, presumably introduced during polymerization and/or processing, that results in light absorption by the polymer and that may initiate photochemical reaction. The main light-absorbing species are believed to be carbonyl groups, present either in definite impurity compounds or as groups attached to the

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[1] R. B. Fox, *Pure Appl. Chem.*, 1972, **30**, 87; J. F. Rabek and B. Ranby, 'Photodegradation, Photooxidation and Photostabilization of Polymers', Interscience, New York, 1975, and references cited therein.

[2] For recent reviews see D. M. Pinkerton, *Proc. Roy. Austral. Chem. Inst.*, 1972, 33; O. Cicchetti, *Adv. Polymer Sci.*, 1970, **7**, 70; R. B. Fox, *Progr. Polymer Sci.*, 1972, **1**, 47; S. L. Fitton, R. N. Hayward, and G. R. Williamson, *Brit. Polymer J.*, 1970, **2**, 217; Yu. A. Ershov, S. I. Kuzina, and M. B. Neiman, *Russ. Chem. Rev.*, 1969, **38**, 12; A. King, *Plastics and Polymers*, 1968, 195.

polymer chain,[3–7] aromatic compounds,[3,8] metallic impurities,[9] dienes,[10] trienes[11], hydroperoxides,[4,10,12,13] and oxygen–polymer charge-transfer complexes.[14] The commercial polyolefins exhibit both fluorescence and phosphorescence emissions,[3,5,6,8] and these are also due to the presence of impurities that may initiate photochemical reaction in the polymer.[15–17]

B. Initiation and Propagation Mechanisms for Polyolefins.—(*i*) *By Carbonyl Groups.* Two main primary photochemical processes are believed to be responsible for the carbonyl-initiated photodegradation of polyolefins. Their definition originates from the early work of Norrish on the photochemistry of aliphatic ketones.[18]

Norrish Type I. This process leads to the formation of free radicals in which the excited singlet or triplet states of the carbonyl group are precursors[2,18] [reaction (1)].

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[3] (*a*) A. Charlesby and R. H. Partridge, *Proc. Roy. Soc.*, 1965, **A283**, 312; *ibid*, p. 329; (*b*) A. Charlesby and I. Boustead, *ibid.*, 1970, **A316**, 291; (*c*) R. H. Partridge, *J. Chem. Phys.*, 1966, **45**, 5, 1679.

[4] (*a*) A. M. Trozzolo and F. H. Winslow, *Macromolecules*, 1968, **1**, 98; (*b*) D. J. Carlsson and D. M. Wiles, *ibid.*, 1969, **2**, 6, 587, 597.

[5] P. J. Briggs and J. F. McKellar, *Chem. and Ind.*, 1967, 662; *J. Appl. Polymer Sci.*, 1968, **12**, 1825; J. C. W. Chien and W. P. Conner, *J. Amer. Chem. Soc.*, 1968, **90**, 1001; J. E. Bonkowski, *Textile Res. J.*, 1969, **39**, 243.

[6] N. S. Allen, J. F. McKellar, and G. O. Phillips, *J. Polymer Sci., Part B, Polymer Letters*, 1974, **12**, 253; N. S. Allen, J. F. McKellar, G. O. Phillips, and D. G. M. Wood, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1974, **12**, 2647; N. S. Allen, J. Homer, J. F. McKellar, and G. O. Phillips, *Brit. Polymer. J.*, 1975, **7**, 11.

[7] K. Tsuji and T. Seiki, *Polymer J.*, 1972, **2**, 606; *J. Polymer Sci., Part B, Polymer Letters*, 1972, **10**, 139.

[8] D. J. Carlsson and D. M. Wiles, *J. Polymer Sci., Part B, Polymer Letters*, 1973, **11**, 759.

[9] (*a*) N. Uri, *Israel J. Chem.*, 1970, **8**, 125; (*b*) P. Richters, *Macromolecules*, 1970, **3**, 262; (*c*) A. T. Betts and N. Uri, *Chem. and Ind.*, 1967, 512; (*d*) C. Kujirai, S. Hashiya, H. Furuno, and N. Terada, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1968, **6**, 589.

[10] M. U. Amin, G. Scott, and L. M. K. Tillakeratne, *European Polymer J.*, 1975, **11**, 85.

[11] J. F. Heacock, F. B. Mallory, and F. P. Gay, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1968, **6**, 2921.

[12] L. Balaban, J. Majer, and K. Vesely, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1969, **22**, 509.

[13] D. C. Mellor, A. B. Moir, and G. Scott, *European Polymer J.*, 1973, **9**, 219; G. V. Hutson and G. Scott, *Chem. and Ind.*, 1972, 725.

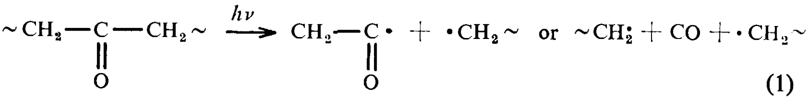
[14] D. G. M. Wood and T. M. Kollman, *Chem. and Ind.*, 1972, 423; (*b*) V. K. Milinchuk, *Vysokomol. Soedineniya*, 1965, **7**, 1293; (*c*) K. Tsuji and T. Seiki, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1971, **9**, 3063; *J. Polymer Sci., Part B, Polymer Letters*, 1970, **8**, 817.

[15] N. S. Allen, J. F. McKellar, and G. O. Phillips, *Chem. and Ind.*, 1974, 300.

[16] N. S. Allen, J. F. McKellar, G. O. Phillips, and D. G. M. Wood, *J. Polymer Sci., Part B, Polymer Letters*, 1974, **12**, 242; N. S. Allen, J. F. McKellar, and D. G. M. Wood, *J. Polymer Sci., Part A-1, Polymer Chem.*, in the press.

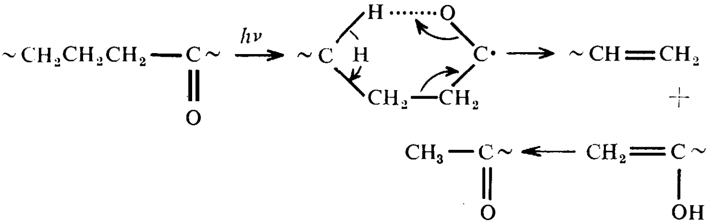
[17] (*a*) A. P. Pivovarov, Yu. A. Ershov, and A. F. Lukovnikov, *Plast. Massey*, 1966, **10**, 7; *Vysok. Energii*, 1968, **2**, 3, 220; (*b*) D. J. Carlsson and D. M. Wiles, *Macromolecules*, 1974, **7**, 259; (*c*) D. J. Harper, J. F. McKellar, and P. H. Turner, *J. Appl. Polymer Sci.*, 1974, **18**, 2805.

[18] J. G. Calvert and J. N. Pitts, 'Photochemistry', New York, John Wiley, 1966; H. J. Heller, *European Polymer J., Supplement*, 1969, 35.

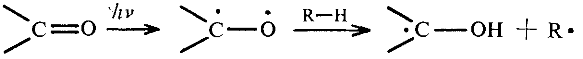


$$\sim CH_2-\underset{\underset{O}{\|}}{C}-CH_2\sim \xrightarrow{h\nu} CH_2-\underset{\underset{O}{\|}}{C}\cdot + \cdot CH_2\sim \quad \text{or} \quad \sim CH_2^{\cdot} + CO + \cdot CH_2\sim \qquad (1)$$

Norrish Type II. This process only occurs when the ketone possesses at least one hydrogen atom on the γ-carbon with respect to the carbonyl group. The reaction occurs *via* a six-membered cyclic intermediate involving intramolecular hydrogen atom abstraction and produces one olefinic and one enolic group in the polymer[2,18,19] [reaction (2)]. A further possible primary process involving photoreaction of carbonyl groups in the polymer is that of intermolecular hydrogen abstraction from adjacent polymer chains. As in the Norrish type I process, this would result in the formation of macroradical centres in the chain[2,18] [reaction (3)].



(2)



(3)

Carlsson and Wiles[4b] studied the photolysis of the main ketonic oxidation products of polypropylene [*i.e.* (1) and (2)]. They found that whereas ketone (1) was photolysed by a Norrish type I process to give carbon monoxide and two macroradicals, ketone (2) was photolysed by a Norrish type II process to give acetone and an unsaturated polymer chain end [reactions (4) and (5)]. Both processes had similar quantum yields of 0.08.

Carbonyl groups may also participate in the oxidative photodegradation of polyolefins by a less direct route. Trozzolo and Winslow[4a] postulated a mechanism for polyethylene photo-oxidation in which the Norrish type II process is dominant. The photoexcited triplet carbonyl groups are quenched by triplet ground-state oxygen and the resultant excited singlet oxygen ($^1O_2$) then reacts with the vinyl groups produced by the Norrish type II process [reactions (6a—c)].

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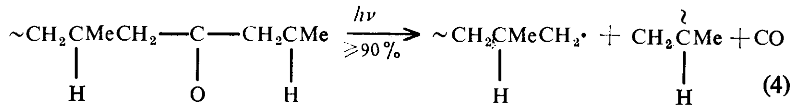
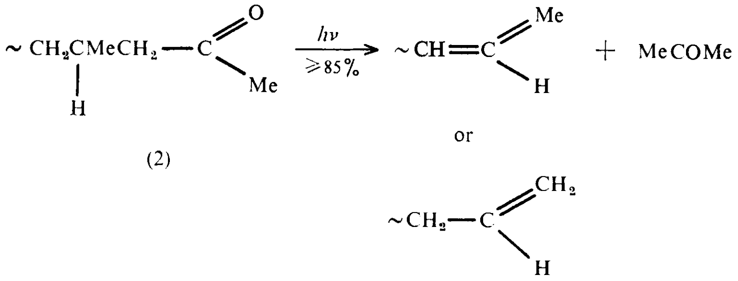
[19] J. E. Guillet, *Naturwiss.*, 1972, **59**, 503.



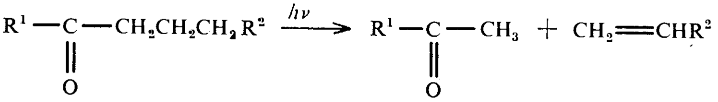
$$\sim CH_2\underset{H}{C}MeCH_2-\underset{O}{C}-CH_2\underset{H}{C}Me \xrightarrow[\geqslant 90\%]{h\nu} \sim CH_2\underset{H}{C}MeCH_2\cdot + CH_2\overset{\wr}{\underset{H}{C}}Me + CO \quad (4)$$

(1)

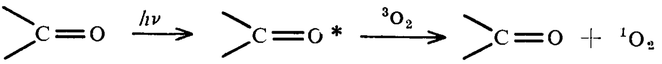


(5)

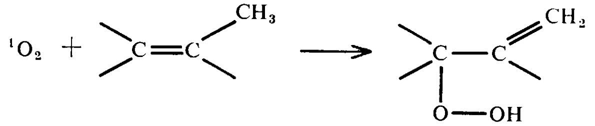
(2)



$$R^1-\underset{O}{\overset{}{\underset{\|}{C}}}-CH_2CH_2CH_2R^2 \xrightarrow{h\nu} R^1-\underset{O}{\underset{\|}{C}}-CH_3 + CH_2{=}CHR^2 \quad (6a)$$



(6b)



(6c)

The validity of this mechanism has recently been questioned by the work of Mill *et al.*[20a] It is seen that the reaction scheme predicts the formation of hydroperoxides. These workers studied the dye-sensitized photo-oxidation of atactic polypropylene in solution using dyes that are well known to generate singlet oxygen on photolysis. However, no hydroperoxide formation was detected. This crucial observation is supported by the recent work of Breck *et al.*[20b] They exposed samples of commercial polyolefins to a gas stream containing singlet oxygen and again, no hydroperoxide formation was detected.

Studies of the luminescence from commercial polyolefins have made a significant contribution to our understanding of the mechanisms involved in photo-

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[20] (*a*) T. Mill, H. Richardson, and F. R. Mayo, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1973, **11**, 2899; (*b*) A. K. Breck, C. L. Taylor, K. E. Russell, and J. K. S. Wan, *ibid.*, 1974, **12**, 1505.

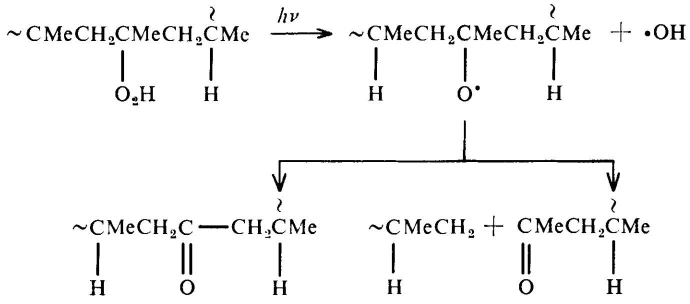
initiation by carbonyl impurities. Charlesby and Partridge[3a] first reported the phosphorescence emission from polyolefins and this was attributed to the presence of impurity carbonyl groups attached to the polymer backbone. Later Charlesby and Boustead[3b] identified other phosphorescent impurities in polyethylene. They found benzoic acid in the crystalline region and several polynuclear aromatic hydrocarbons in the amorphous region of the polymer.

Allen *et al.*[6,15,16] examined the role of these phosphorescent species in the thermal and photochemical degradation of the commercial polyolefins. The phosphorescent species with excitation wavelengths greater than 290 nm were concluded to be potential photoinitiators. These species were formed only on thermal oxidation of the polymer, extending its light absorption into the u.v. region of natural sunlight. Ketonic/aldehydic type carbonyl impurities were concluded to be responsible for this particular emission.

Further information on the nature and reactivity of the luminescent carbonyl impurities in polyolefins has come from studies of other commercial polymers. For example, the phosphorescent species in Nylon-6,6 were concluded to be carbonyl groups conjugated with ethylenic unsaturation.[21] A similar conclusion was reached from phosphorescence studies of the thermal and photochemical oxidation of polybutadiene.[22]

(*ii*) *By Hydroperoxides.* Alkyl hydroperoxides have continuous absorption spectra that extend from the far-u.v. to *ca.* 320—330 nm in the near-u.v. They are therefore capable of absorbing sunlight of wavelengths photochemically harmful to the polyolefins.[2]

Carlsson and Wiles[4b] studied the photolysis of polypropylene hydroperoxides generated by prior thermal oxidation of the polymer. Ketones (3) and (4) were the main carbonyl species formed [reaction (7)]. These workers found a quantum



$$\sim\text{CMeCH}_2\underset{\text{O}_2\text{H}}{\text{CMe}}\text{CH}_2\underset{\text{H}}{\overset{\wr}{\text{CMe}}} \xrightarrow{h\nu} \sim\underset{\text{H}}{\text{CMe}}\text{CH}_2\underset{\text{O}^\bullet}{\text{CMe}}\text{CH}_2\underset{\text{H}}{\overset{\wr}{\text{CMe}}} + {}^\bullet\text{OH}$$

$$\sim\underset{\text{H}}{\text{CMe}}\text{CH}_2\underset{\text{O}}{\overset{\|}{\text{C}}}\text{—CH}_2\underset{\text{H}}{\overset{\wr}{\text{CMe}}} \qquad \sim\underset{\text{H}}{\text{CMe}}\text{CH}_2 + \underset{\text{O}}{\overset{\|}{\text{CMe}}}\text{CH}_2\underset{\text{H}}{\overset{\wr}{\text{CMe}}}$$

(7)

(3) (4)

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[21] N. S. Allen, J. F. McKellar, and G. O. Phillips, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1974, **12**, 1233, 2623; *ibid.*, in the press.

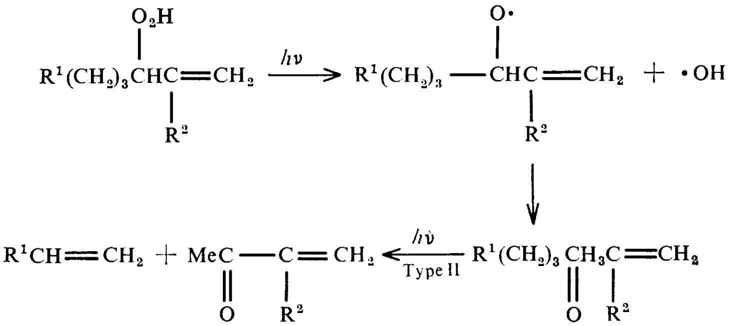
[22] S. W. Beavan, P. A. Hackett, and D. Phillips, *European Polymer J.*, 1974, **10**, 925; S. W. Beavan and D. Phillips, *J. Photochem.*, 1974, **3**, 349.

efficiency of about four for hydroperoxide photolysis in polypropylene. Such a high quantum yield would cause appreciable chain scission in the polymer. Carlsson and Wiles postulated that photolysis of tertiary hydroperoxides present in the polymer is a key step in the photodegradation mechanism. In peroxide-free polypropylene, however, they suggested that the photolysis of ketonic impurities produces alkyl radicals that combine with oxygen to give hydroperoxide groups. Their postulation of hydroperoxide-initiated photodegradation of polypropylene was later supported by evidence from e.s.r. studies.[17b]

According to Scott and co-workers,[13] the hydroperoxides formed during processing are the main photoinitiators in commercial polyolefins. They found that during processing the most rapid increase in the photodeterioration of polypropylene occurred under the conditions where there was no significant change in carbonyl concentration as monitored by i.r. spectroscopy. From his observations Scott also concludes that the hydroperoxides formed during thermal processing of the polymer are the precursors to carbonyl formation.

In contrast to these conclusions on the role of hydroperoxides in polyolefin photodegradation, Mill *et al.*[20a] found that when model peroxides were added to pure atactic polypropylene they were ineffective as photosensitizers. For example, the photolysis of 10-methyl-10-nonadecyl hydroperoxide gave only the analogue of (4) and also the alcohol 10-methyl-10-nonadecanol. There was no evidence for the formation of (3) expected from the mechanism of Carlsson and Wiles. Mill *et al.*[20a] attributed the absence of ketone (3) to 'a phase effect' in which the restricted motion of the tertiary polymeric hydroperoxides in an isotactic polypropylene environment would inhibit alcohol formation.

Recently, Scott[10] has modified his earlier views on the role of hydroperoxides, and now suggests that unsaturated and not saturated hydroperoxides are mainly responsible for the photoinitiated degradation of polyethylene. Only in the later stages of photodegradation does he consider that the Norrish type II mechanism of photolysis of a carbonyl group becomes an important process [reaction (8)].



$$R^1(CH_2)_3\overset{O_2H}{\overset{|}{C}}H\underset{\overset{|}{R^2}}{C}{=}CH_2 \xrightarrow{h\nu} R^1(CH_2)_3{-}\overset{O\cdot}{\overset{|}{C}}H\underset{\overset{|}{R^2}}{C}{=}CH_2 + \cdot OH$$

$$\downarrow$$

$$R^1CH{=}CH_2 + Me\underset{\overset{\|}{O}}{C}{-}\underset{\overset{|}{R^2}}{C}{=}CH_2 \xleftarrow[\text{Type II}]{h\nu} R^1(CH_2)_3\,CH_3\underset{\overset{\|}{O}}{C}\underset{\overset{|}{R^2}}{C}{=}CH_2 \qquad (8)$$

(*iii*) *By Aromatic Impurities*. Both luminescence and u.v. absorption studies have indicated the presence of aromatic impurities in the polyolefins.[3] For example, Carisson and Wiles[8] have shown that naphthalene is present in polypropylene. They have suggested that on photolysis of the polymer any polynuclear aromatic impurity could efficiently generate singlet oxygen by the quenching of its photoexcited triplet state by ground-state oxygen. The excited singlet oxygen thus produced would then be able to attack any nearby double bonds, forming potentially photoreactive peroxides by reaction (6).

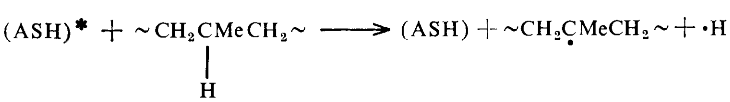
However, evidence against this being an important mechanism in photodegradation comes from e.s.r. studies.[23] These have shown that there is a definite suppression of free-radical formation when the polyolefin is doped with polynuclear aromatic compounds.

(*iv*) *By Metallic Impurities*. It is believed that certain metallic impurities, particularly Ti and Fe, can efficiently sensitize the photo-oxidation of polyolefins.[9] These metallic impurities can absorb near-u.v. radiation, causing them to react with the polymer and producing free radicals *via* electron-transfer processes such as reaction (9). Evidence for this mechanism is given by Kujirai *et al.*,[9d] who

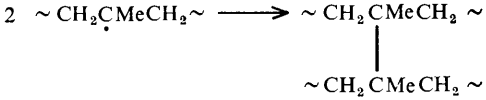
$$Fe^{3+}OH \xrightarrow{h\nu} Fe^{2+}OH \longrightarrow Fe^{2} + \cdot OH \qquad (9)$$

found that the ash residue from a Ziegler–Natta catalyst (composed mainly of TiO_2 and Al_2O_3) caused photochemical cross-linking in polypropylene. Initially the photo-excited ash residue abstracts a hydrogen atom from the polymer, which then allows cross-linking to occur as shown in reactions (10a—c). If

$$(ASH) \xrightarrow{h\nu} (ASH)^{*} \qquad (10a)$$



$$(ASH)^{*} + \sim CH_2\underset{\displaystyle H}{\underset{|}{C}}MeCH_2\sim \longrightarrow (ASH) + \sim CH_2\overset{\bullet}{C}MeCH_2\sim + \cdot H \qquad (10b)$$



$$2\ \sim CH_2\overset{\bullet}{C}MeCH_2\sim \longrightarrow \begin{array}{c} \sim CH_2CMeCH_2\sim \\ | \\ \sim CH_2CMeCH_2\sim \end{array} \qquad (10c)$$

conditions are such that the macroradicals formed in the polymer can react extensively with oxygen then these metallic impurities could act as efficient sensitizers of photo-oxidation.

(*v*) *By Oxygen–Polymer Charge-transfer Complexes*. Chien[24] investigated the

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[23] T. Takeshita, K. Tsuji, and T. Seiki, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1972, **10**, 2315, 3119.

[24] J. C. W. Chien, *J. Phys. Chem.*, 1965, **69**, 4317.

photo-oxidation of pure alkanes and alkenes. When saturated with oxygen, these hydrocarbons exhibit absorption bands which extend beyond 300 nm into the photoactive wavelength region for the polyolefins. Of the two hydrocarbons studied, the alkenes exhibited the more intense light absorption. To explain these interesting observations in the context of polyolefin photo-oxidation, Chien[24] proposed the following mechanism, in which the ionic species formed by charge transfer are responsible for the initial light-absorption process (11).

$$\mathrm{R{-}H} + \mathrm{O_2} \xrightarrow{h\nu} (\mathrm{RH^+} + \mathrm{O_2^-}) \qquad (11)$$

Milinchuk[14b] carried out an e.s.r. study of polyolefins irradiated by light of wavelengths greater than 300 nm. The polymers were irradiated in the presence of oxygen and also under high-vacuum conditions. Only when they were irradiated in the presence of oxygen were free radicals detected. These observations were later confirmed by Tsuji and Seiki,[14] who tentatively attributed free-radical formation to occur *via* oxygen–polymer charge-transfer complexes.

Wood and Kollman[14a] compared the rate of photo-oxidation of samples of polypropylene powder and sheet which had been stored in the presence and absence of oxygen. The sheet samples had been compression-moulded in air at 220 °C. No significant difference was observed in their induction periods. Oxygen–polymer charge-transfer complexes were proposed as the photoinitiators.

3 Sensitized Photodegradation

Ultraviolet-sensitized photodegradation shows considerable promise as a method of combating environmental pollution by plastics litter.[25] Although unstabilized polyolefins such as polypropylene and poly(4-methylpent-l-ene) are themselves light-sensitive, if u.v. deterioration by sunlight exposure is desirable then it is important to be able to control and indeed monitor this effect. At present there are two promising ways of achieving this aim; one is the use of specially prepared photosensitive polymers and the other appropriate selection of photoactive additives which are incorporated in the commercial polymer during processing.

A. Photosensitive Polymers.—Guillet,[19,25] has synthesized carbonyl-containing polyolefins which will degrade when exposed to outdoor sunlight but will remain intact if kept indoors. The polymers are made by polymerizing the olefin in the presence of variable amounts of carbon monoxide or a vinyl ketone monomer. The resulting copolymer is relatively stable behind window glass. This is because the ketonic groups introduced into the polymer structure do not absorb light of wavelengths greater than about 330 nm. On exposure out of doors, where the light also contains radiation in the region 290–330 nm, the

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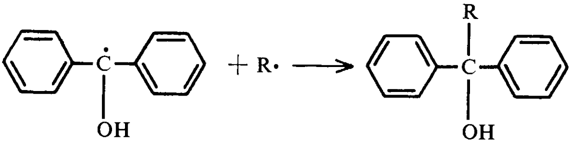
[25] Plastics Institute (London) Conference, 'Degradability of Polymers and Plastics', November, 1973, and references cited therein.

same ketonic groups are photoactive and can initiate degradation of the polymer by the Norrish type II process [reaction (2)].

B. Photoactive Additives.—During the past few years a large number of additives have been claimed in the patent literature to be effective in accelerating the photodegradation of polyolefins[2,25] (prodegradants). Thus only a brief discussion of the distinctive mechanistic features of prodegradants will be given here.

A wide range of derivatives of aromatic aldehydes, ketones, and quinones effectively sensitize the photodegradation of polyolefins by primary processes of hydrogen-atom abstraction[26] [reaction (12)]. The radical R· initiates the oxidative chain processes. However, Scott and Amin[26] have shown that some benzophenone derivatives retard the degradation processes during the later stages of photo-oxidation. This retardation is ascribed by Scott to the relative stability of the ketyl radicals formed, which, in turn, leads to favourable competition between chain-initiation and -termination processes in the mechanism (13).

$$\mathrm{Ph_2C{=}O} \xrightarrow{h\nu} \mathrm{Ph_2C{=}O}^{*} \xrightarrow{\mathrm{RH}} \mathrm{Ph_2\dot{C}OH} + \mathrm{R}^{\bullet} \qquad (12)$$



(13)

Retardation

Apart from the carbonyl-based prodegradants, certain types of transition-metal complexes and salts have also been shown to be effective as prodegradants for the polyolefins.[25] Of these, the ferric complexes are particularly favoured because of their cheapness and low toxicity. According to Brackman and Birley,[25] ferric stearate sensitizes the photo-oxidation of polyolefins by first absorbing u.v. light, then undergoing electron transfer to give a carboxylic acid free radical. This species decarboxylates to give an alkyl radical, which initiates polymer degradation [reaction (14)].

$$\mathrm{Fe^{3+}(\bar{O}_2CR)_3} \longrightarrow \mathrm{Fe^{2+}(\bar{O}_2CR)_2} + \mathrm{\dot{O}_2CR} \longrightarrow \mathrm{CO_2} + \mathrm{R}\cdot \qquad (14)$$

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[26] (*a*) A. R. Burgess, *J. Nat. Bur. Standards*, 1953, Circular 525, p. 149; (*b*) D. J. Harper and J. F. McKellar, *J. Appl. Polymer Sci.*, 1973, **17**, 3503; (*c*) M. U. Amin and G. Scott, *European Polymer J.*, 1974, **10**, 1019.

Further evidence from the work of Scott and Amin[26c] has shown that certain sensitizers may also act as 'pro-oxidants' during processing. Indeed these workers showed that the prodegradant behaviour of the sensitizers was merely an extension of their 'pro-oxidant activity'. On the other hand, metal complexes containing sulphur ligands showed quite a different pattern of behaviour. In particular, the dithiocarbamates behaved as antioxidants whereas some exhibited u.v. stabilizing effects.

With regard to the factors controlling the rate of prodegradation, the work of Scott and Amin[26c] has also been of considerable interest. For example, the behaviour of the dithiocarbamates was found to depend primarily on the nature of the complexed metal. While the nickel and cobalt complexes were found to be more stable towards u.v. light, and indeed acted as light stabilizers in the polymer, the iron complex was much less stable and acted as an effective prodegradant at low concentrations. Interestingly, at relatively high concentrations the same compound was found to be a light stabilizer. These observations of Scott clearly demonstrate the complexity of the mechanisms involved in both the destabilizing and stabilizing action of the transition-metal chelates to be discussed later.

4 Effect of Pigments on Photostability

The ability to colour thermoplastic polymers such as the polyolefins is, in many cases, necessary for their commercial use. In general, pigments rather than dyes are used to colour the polyolefins. Most of the pigments used for this purpose tend to photostabilize the polyolefins, although there are certain important exceptions.

Papillo[27] carried out an extensive examination of the many ways in which pigments can affect polymer properties. It was noted that the entire additive system rather than any single stabilizer or colourant was responsible for controlling the weatherability of the polymer. This observation was later confirmed by Hill and Martinovich.[28]

To eliminate any pigment–stabilizer interactions, Uzelmeir[29] examined the effect of a number of pigments on the u.v. stability of unstabilized polypropylene. A correlation was found between the screening power of the pigment and its ability to protect the polymer.

It is well known that carbon black affords the most effective protection to u.v. degradation,[2,27] and several theories have been advanced to explain its interesting, as well as its technically important, behaviour in the polymer. For example, apart from acting as an effective screener, which depends on pigment particle size, carbon black is believed to inhibit chain propagation because of the antioxidant properties of its surface phenolic groups.[2,29] Additional theories suggest

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[27] P. J. Papillo, *Mod. Plastics*, 1967, **4**, 45, 31.

[28] G. R. Hill and R. J. Martinovich, *Tech. Papers Reg. Tech. Conf., Soc. Plastics Engineers Phil. Sect.*, Oct. 2-3, 1972.

[29] C. W. Uzelmeir, *Soc. Plastics Engineers Trans.*, 1970, **26**, 69.

that the pigment has a low surface energy[30] and that it may also quench certain photoactive species in the polymer.[31]

Apart from the screening of u.v. radiation above *ca.* 300 nm the high reflection properties associated with the pigment constitute another important factor to be considered. White pigments generally show high u.v. reflectance within the 300–400 nm range. Notable exceptions, however, are zinc oxide and titanium dioxide (titania). Of all the white pigments used in the polyolefins, the anatase and rutile forms of titania provide an interesting contrast in their photochemical behaviour.

It is well known that the two crystalline modifications of titania exhibit markedly different photoactivities when incorporated into a number of commercially important polymers.[32] With the polyolefins, for example, while rutile is relatively inactive, anatase is markedly photosensitive in degrading the polymer.[16,32] Irich[33] has reported that the pigment-sensitized photo-oxidation of isopropyl alcohol can be used as a model for predicting the photochemical activities of different grades of the oxides of titanium and zinc in polypropylene.

It is generally agreed that the photoactivity of titanium dioxide pigments is related to their semiconductor properties.[34] Absorption of near-u.v. light by the titanium results in promotion of electrons into a higher energy conduction band. This leaves a positive hole in the crystal lattice. Those released electrons near the surface of the pigment particle react with oxygen to form O_2 ions and possibly other species that can react with the polymer substrate. The overall result of this process is that the surface of the polymer gradually erodes away. This phenomenon is commonly referred to as 'chalking'.

Recently, Allen *et al.*,[16] by examining titania-pigmented polyolefins by spectrophosphorimetry, found evidence to explain this difference in photoactivity between the two crystalline forms. Only the photoactive form (anatase) quenches the long-lived phosphorescence emitted from impurities native to the polymer, indicating the mechanism shown in reactions (15a and b) for anatase-initiated

$$\mathrm{I} = \text{Polymer Impurity} \xrightarrow{h\nu} \mathrm{I}^{*} \tag{15a}$$

$$\mathrm{I}^{*} + \mathrm{TiO_2(Anatase)} \longrightarrow \mathrm{I}^{\overline{\cdot}} + \mathrm{TiO}_2^{\overset{+}{\cdot}} \text{ or } \mathrm{I}^{\overset{+}{\cdot}} + \mathrm{TiO}_2^{\overline{\cdot}} \tag{15b}$$

photo-degradation. Similar phosphorescence studies were carried out on Nylon-6,6.[32] It was found that manganese compounds, normally coated on the

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[30] H. Schonhorn and P. J. Luongo, *Macromolecules*, 1969, **2**, 4, 364.

[31] M. Heskins and J. E. Guillet, *Macromolecules*, 1968, **1**, 97.

[32] H. A. Taylor, W. C. Tincher, and W. F. Hamner, *J. Appl. Polymer Sci.*, 1970, **14**, 141; N. S. Allen, J. F. McKellar, G. O. Phillips, and C. B. Chapman, *J. Polymer Sci.*, *Part B, Polymer Letters*, 1974, **12**, 723; R. C. Hirt, N. Z. Searle, and R. G. Schmitt, *Soc. Plastics Engineers Trans.*, 1961, **1**, 21; W. L. Dills and T. B. Reeve, *Plast. Technol.*, 1970, **16**, 6, 50.

[33] G. Irich, *J. Appl. Polymer Sci.*, 1972, **16**, 2387.

[34] W. F. Sullivan, *Progr. Org. Coatings*, 1972, **1**, 157; H. G. Voltz, G. Kompf, and H. G. Fitsky, *ibid.*, 1974, **2**, 223.

surface of the anatase pigment particles to counteract their photoactivity, quench the pigmented polymer emission.

5 Photostabilization

It is generally accepted that photostabilization of a lightsensitive polyolefin may be achieved in many ways. Indeed a judgement of satisfactory 'photostabilization' to light exposure will primarily depend upon the end-use to which the polyolefin is put. For example, in the case of polypropylene, it is essential that a suitable additive be incorporated in the polymer for it to be satisfactory for most commercial uses out-of-doors. A study of the patent literature will clearly validate this point.

However, over the past few years it has become increasingly clear that these light-stabilizing additives, particularly those for polypropylene, fall into three general categories, and their nature and possible modes of action will now be discussed. It should be clearly understood that of the three major fields of polyolefin photochemistry, photostabilization is undoubtedly the one of greatest controversy on mechanistic grounds.

A. Ultraviolet Screeners.—In this case the light is prevented from being absorbed by the photoactive chromophoric species (PCS) in the polymer by, for example, carbon black or titanium dioxide in its photochemically inactive rutile form. Here the mechanism is believed to be one of simple screening of the PCS from the harmful radiation (see Section 4).

B. Ultraviolet Absorbers.—The u.v. absorbers are believed to operate by a mechanism in which, like the screeners, the stabilizer prevents the light from reaching the PCS. The harmful radiation is directly absorbed by the stabilizer, then harmlessly dissipated. An effective u.v. absorber should thus have high absorbance in the wavelength range which is most harmful to the polymer. For example, a number of commercial light stabilizers based on 2-hydroxybenzophenone have this property. They also dissipate their energy, when photoexcited, by a mechanism that involves the reversible formation of a six-membered hydrogen-bonded ring[2,18] [reaction (16)]. The result of this mechanism of light absorption and dissipation thus leaves the stabilizer chemically unchanged and able to undergo a large number of these activation–deactivation cycles. Direct evidence for such a mechanism is difficult to obtain because the role of the stabilizer is essentially that of a 'passive' nature. However, one feature that serves as indirect evidence for this mechanism is that the more effective of these stabilizers exhibit a correspondingly stronger intramolecular hydrogen bond with the carbonyl group.[35] This is an essential feature of mechanism (16).

A further interesting class of stabilizers that appear to operate by this mechanism are the salicylates, particularly phenyl salicylate. Here, however, the pro-

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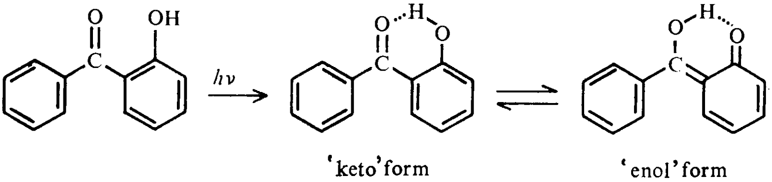
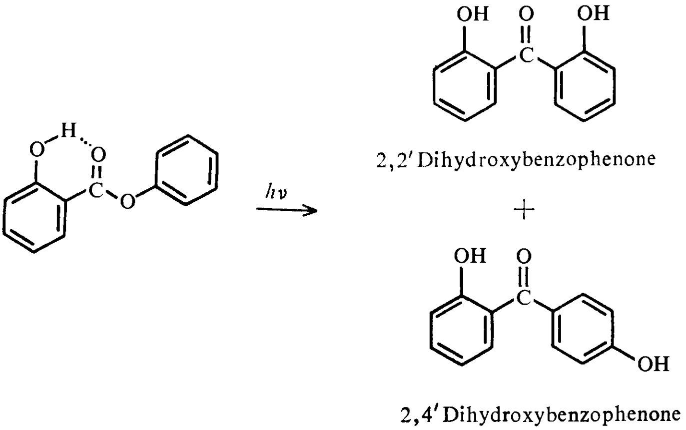
[35] J. H. Chaudet, G. C. Newland, H. W. Patton, and J. W. Tamblyn, *Soc. Plastics Engineers Trans.*, 1961, **1**, 26; K. A. Leitman, T. V. Kreitzer, V. L. Maksinov, and A. F. Lukovnikov, *Vysokomol. Soedineniya*, 1971, **A13**, 1, 86.



(16)

tective mechanism is slightly different in that they are photolysed by the incident radiation into products with high absorbance in the near-u.v.[36] [reaction (17)].



(17)

C. Excited State Quenchers.—Here the mode of action of the stabilizer is to deactivate the PCS in the polymer before it undergoes chemical reactions that result in polymer degradation. In general, these stabilizers are complex chelates of the transition metals, usually nickel. Despite their relatively lower light absorption in the region 300–400 nm, a number of these chelates are much more effective as light stabilizers in polypropylene than the 2-hydroxybenzophenones.[5]

Deactivation of the PCS can be achieved in a number of ways, and this adds a further complicating factor to the assessment of the stabilizing action of the quencher. For example, the photoexcited state of the PCS may be either the singlet or triplet state or it may even indirectly initiate degradation by being quenched in its triplet state by oxygen to form excited singlet-state oxygen [reaction (18)], which may then proceed to attack the polymer matrix.[4,25]

The first evidence that a transition-metal chelate was both an effective light-stabilizer for polypropylene and also an efficient triplet-deactivator was reported

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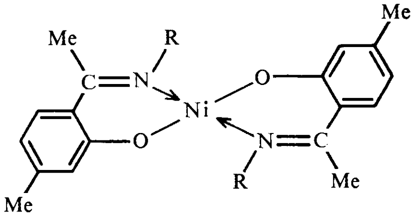
[36] J. Jortner, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1959, **3**, 7, 199; G. C. Newland and J. W. Tamblyn, *J. Appl. Polymer Sci.*, 1964, **8**, 1949.

$$^{3}(\mathrm{PCS}) + {}^{3}\mathrm{O}_2 \longrightarrow {}^{1}(\mathrm{PCS}) + {}^{1}\mathrm{O}_2$$

by Briggs and McKellar.[5] In this case a diamagnetic chelate of structure (5) was studied, and from observing the variation in the efficiency with different substituents for R it was concluded that the triplet quenching efficiency was dependent on the spatial configuration of the ligand around the metal atom (Ni) in the chelate.

Using laser flash photolysis, Adamczyk and Wilkinson[37] found that a number of $\mathrm{Ni^{II}}$ chelates effectively quench triplet benzophenone. The square-planar diamagnetic chelates based on structure (5) were found to be the most efficient. Their results correlate well with those of Harper and McKellar,[38] who determined the stabilizing efficiency of the same chelates in polystyrene. Recently, Harper *et al.*[17c] demonstrated that the diamagnetic chelate shown in structure (5) markedly quenches the lifetime of the long-lived phosphorescence from polypropylene. The source (or sources) of this emission are believed to be carbonyl groups capable of initiating photo-oxidation of the polymer.[5,16]



(5)

Several workers[37,39–41] have reported that some nickel(II) chelates are effective quenchers of singlet oxygen, particularly those chelates with sulphur donor ligands, *e.g.* 2,2′-thiobis-(4-t-octylphenolato)-n-butylamine. In this case, therefore, a stabilizing effect by the chelate could be possible by it acting as a scavenging agent for singlet oxygen, preventing the attack of $^{1}\mathrm{O}_2$ on the polymer matrix.[4]

Recently, Carlsson and Wiles[42] studied the effect of various stabilizers on the phosphorescence from thermally oxidized polypropylene film. In contrast to other workers they found that certain nickel(II) chelates did not operate by long-range energy transfer, but by collisional quenching and radical-scavenging

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[37] A. Adamczyk and F. Wilkinson, *J. Appl. Polymer Sci.*, 1974, **18**, 1225.

[38] D. J. Harper and J. F. McKellar, *J. Appl. Polymer Sci.*, 1974, **18**, 1233.

[39] D. J. Carlsson, T. Suprunchuk, and D. M. Wiles, *J. Appl. Polymer Sci.*, 1972, **16**, 615; J. P. Guillory and C. F. Cook, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1971, **9**, 1529.

[40] B. Felder and R. Schumacher, *Angew. makromol. Chem.*, 1973, **31**, 35; D. J. Carlsson, T. Suprunchuk, and D. M. Wiles, *J. Polymer Sci., Part B, Polymer Letters*, 1973, **11**, 61.

[41] J. P. Guillory and C. F. Cook, *J. Amer. Chem. Soc.*, 1968, **95**, 15, 4885; *J. Polymer Sci., Part A-1, Polymer Chem.*, 1973, **11**, 1927.

[42] D. J. Carlsson and D. M. Wiles, *Macromolecules*, 1974, **7**, 259; *J. Polymer Sci., Part B, Polymer Chem.*, 1974, **12**, 2217.

processes. A number of the chelates were found to be efficient scavengers of ·OH and ·OR radicals formed during the thermal and photo-decomposition of model and polymeric hydroperoxides. A similar effect has also been reported by Ranaweera and Scott.[43] It would appear, therefore, that the series of Ni^{II} chelates which have been clearly established as effective stabilizers for polypropylene may function either as PCS quenchers, or as radical scavengers. Indeed, some of the most effective, such as the diamagnetic chelates, may well operate by both mechanisms.[17c]

In addition to their function as u.v. absorbers (Section 5B), a number of investigations on the 2-hydroxybenzophenones and the corresponding hydroxybenzotriazoles indicate that their effectiveness as stabilizers may also be due to their ability to quench PCS in the polymer. For example, early studies by Pivovarov and co-workers[17a] showed that the protective action of 4-t-butylphenyl salicylate and 2,2′-hydroxy(5′-methylphenyl) benzotriazole in a range of polymers is largely due to energy-transfer processes. A similar conclusion has recently been reported by George.[44] However, in contrast to the conclusions of Pivovarov[17a] and George,[44] other studies,[41] in which the unstabilized polyolefin was irradiated by light which was first passed through solutions containing the stabilizers, have shown that the salicylates and the hydroxybenzotriazoles operate purely as u.v. absorbers while the 2-hydroxybenzophenones can also function as PCS quenchers.

6 Conclusions

In this review we have discussed the evidence for the presence of several types of impurities, all of which are believed to be capable of acting as photoinitiators in a polyolefin. In our view it is evident from the literature that all these impurities could participate in the photo-oxidation of commercial grade polyolefins. Further, the relative importance of a particular initiator will obviously depend on the conditions of u.v. exposure, the manufacturing and processing history of the polymer, and even the nature of the polyolefin itself.

During the preparation of this review an excellent book by Ranby and Rabek[2] was published in which the following statement appears (p. 120). 'Frequently the same problem is examined by various authors, using different methods, and the results obtained may refute each other. Hundreds of papers published to date have not yet given a satisfactory answer to the question of the precise mechanism of the degradation and oxidation of polymers'. We firmly believe that this general statement can be applied to the polyolefins for the reasons given above. This should serve as a cautionary guide to future workers in attributing unique mechanisms to additives such as prodegradants and light stabilizers where the evidence emerging from the literature is that several of these additives may well be multi-functional in their mode of operation.

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[43] R. P. R. Ranaweera and G. Scott, *Chem. and Ind.*, 1974, 774; *J. Polymer Sci., Part B, Polymer Letters*, 1975, **13**, 71.

[44] G. A. George, *J. Appl. Polymer Sci.*, 1974, **18**, 419.