

MECHANISM OF THE PHOTO-INITIATION PROCESS IN POLYETHYLENE*

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ABSTRACT

It is shown that, during the processing of low density polyethylene, the hydroperoxide content increases rapidly to a very sharp maximum and then declines. Vinylidene groups initially present in the polymer, decrease to zero after an induction period and the rate of destruction is related to hydroperoxide concentration.

Carbonyl concentration increases in an auto-accelerating mode in a process which follows the formation and decay of hydroperoxide; when the carbonyl concentration is low, hydroperoxide and vinylidene are the main source of the photo-initiation step. In the later stages of the reaction, Norrish II photolysis of carbonyl is the most important process.

INTRODUCTION

Attempts to explain the activity of u.v. stabilizers have centred on three main mechanisms, *viz.* u.v. absorption (screening) (Heller, 1969; Heller & Blattman, 1973 and Scott, 1965), quenching of photo-chemically excited states (Heller & Blattman, 1973; Briggs & McKellar, 1968; Chien & Connor, 1968; Trozzolo & Winslow, 1968; Guillory & Cook, 1971; Kaplan & Kelleher, 1971; Flood *et al.*, 1973; Adamczyk & Wilkinson, 1972; and Carlsson *et al.*, 1973) and hydroperoxide decomposition (Mellor *et al.*, 1973; Hutson & Scott, 1972, 1974; and Scott, 1973).

The first is well established in the case of 2-hydroxybenzophenones and 2-hydroxybenzotriazoles but most of the arguments for the second and third mechanisms are based on inference rather than direct observation. For example, it is known that many nickel complexes which are effective u.v. stabilizers in polyolefins are effective in quenching carbonyl triplet states (Heller 1969; Trozzolo & Winslow, 1968) or oxygen singlet which can be formed from them by energy transfer to oxygen triplet (Scott, 1965; Briggs & McKeller, 1968; Chien & Connor, 1968). However, there is a lack of correlation between quenching ability and u.v. stabilizing effectiveness; For example, ferric acetylacetonate is an effective quenching agent for triplet carbonyl (Hammond & Foss, 1964) and yet it is a photoactivator for polyolefin photodegradation (Amin & Scott, 1974).

Extensive studies on polymers containing carbonyl groups either forming part of the chain (Hartley & Guillet, 1968 and Plooard & Guillet, 1972) or as pendant groups where the carbonyl is directly attached to the chain (Golemba & Guillet, 1972) have shown that photolysis occurs readily on irradiation with light of wavelength greater than 290 nm leading to molecular weight reduction. This process can be retarded by quenching agents (Golemba & Guillet, 1972) but the evidence suggests that in polyethylene this is a secondary process in the photo-oxidation reaction

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sequence since extensive molecular weight reduction occurs before appreciable carbonyl can be detected in the polymer (Hutson & Scott, 1972, 1974) and in polypropylene subjected to photo-oxidation during processing a very considerable reduction in u.v. lifetime occurs without any associated increase in carbonyl concentration (Mellor *et al.*, 1973).

It has been proposed (Mellor *et al.*, 1973, Hutson & Scott, 1972 & 1974) that hydroperoxide, the initially formed autoxidation intermediate, is responsible for the photo-initiation process and that the effect of some metal complexes with u.v. stabilizing activity (*e.g.* Ni and Co dithiocarbamates) is to remove hydroperoxide initiators (Scott, 1965 ; Holdsworth *et al.*, 1964).

Further doubt has been cast on the importance of aliphatic carbonyl as a sensitizer of photo-oxidation in aliphatic polymers by the finding (Harper & McKellar, 1972) that although aromatic ketones are effective photo-activators for the oxidative degradation of polypropylene, long chain aliphatic ketones are not.

The direct observation and estimation of hydroperoxides formed during processing and fabrication of polymers has in the past proved difficult due to the very low concentrations involved and the fact that they are unstable. A ferrous iron titration technique has been used in the present study to estimate the growth and decay of hydroperoxides in low density polyethylene and the presence of this group is related to the decay and growth of other functional groups in the polymer during processing and u.v. degradation.

EXPERIMENTAL

Materials

Low density polyethylene was commercial material from ICI (Alkathene, WJG 47. MFI, 2.0).

Processing: The polymer was processed at 165°C in an open mixer in the presence of air for various times and was discharged into chilled water. The polymer was compression moulded immediately after discharge to film of thickness 8×10^{-3} in. Infra-red studies were carried out using a Perkin-Elmer 457 spectrophotometer ; u.v. spectrophotometry was carried out using a Perkin-Elmer 137 machine.

Peroxide estimation : Very few methods of peroxide analysis are sufficiently sensitive to measure the very low concentrations found in processed polymers. The method of Bocek (1968) is capable of measuring 10^{-6} moles in polymer samples of convenient size. The method was found to be irreproducible when applied to polyethylene films and two contributory reasons were identified.

1. The iron-phenanthroline complex, which is estimated by u.v. spectrophotometry at 510 nm, is unstable to light of this wavelength and repeat measurement on replicate samples is necessary.

2. Due to the slow penetration of the solution into the polymer film, measurements were reproducible only after the solution was in contact with the film for 2 h. A minimum time of 2.5 h was used in practice. The method was calibrated using pure *tert.*-butyl hydroperoxide.

Ultra-violet irradiation : The alternating fluorescent sun-lamp/black-lamp combination described previously (Amin & Scott, 1972 & 1974) was used to initiate photo-degradation of the polymer,

RESULTS AND DISCUSSION

Functional groups present in low density polyethylene at the end of a mild processing operation (10 min at 165°C) are shown typically in Table 1 together with the groups present after u.v. degradation.

TABLE 1
FUNCTIONAL GROUPS IDENTIFIED IN TYPICAL LDPE FILM BEFORE AND AFTER U.V. IRRADIATION

Functional group	ν (cm^{-1})	Absorbance	
		Unirradiated	Irradiated (1500 h)
RCOCH_3	1725 ± 1	0.005	—
RCOR'	1720 ± 1	—	0.815
—OH	~3400	0.015	0.067
—COOH	1710–13 1185	—	0.929
$\begin{array}{l} \text{R} \\ \diagdown \\ \text{C} = \text{CH}_2 \\ \diagup \\ \text{R}' \end{array}$	887 ± 1	0.045	—
$\text{RCH} = \text{CH}_2$	909	0.006	0.268
$\text{RCH} = \text{CHR}'$	1645 ± 1	0.013	0.083
—CHO	1735	—	0.929
—COOR	1748	—	0.698
$\begin{array}{l} \text{O} \\ \parallel \\ \text{—C} \\ \diagdown \\ \text{OOH (R)} \end{array}$	1785	—	0.333

The most significant changes are in the carbonyl region ($1700\text{--}1785\text{ cm}^{-1}$) and in the unsaturation region, particularly at 887 cm^{-1} due to the rapid decrease of vinylidene and at 909 cm^{-1} due to the increase of vinyl. The disappearance of vinylidene cannot be followed to completion since, in the later stages of degradation, the 887 cm^{-1} absorption is observed only as a shoulder on the 909 cm^{-1} absorption. However, the peak height can be measured reproducibly until the intensity has been reduced to 25 per cent of the initial value.

Vinylidene (887 cm^{-1}) initially present in a mildly processed sample decays rapidly on u.v. irradiation and this precedes the formation of significant amounts of carbonyl (see Fig. 1). This suggests that vinylidene decay must be in some way associated with the photo-initiation step. The formation of vinyl 909 cm^{-1} which is present to a much smaller extent in the processed polymer also parallels carbonyl formation and appears to be consequent upon it. This is the expected sequence of events if vinyl is formed by Norrish II breakdown of carbonyl. The formation of aldehyde (1735 cm^{-1}) and carboxylic acid (1185 cm^{-1}) are almost certainly a consequence of Norrish I photolysis of carbonyl. These results support the previous conclusion (Hutson & Scott, 1972 & 1974) that once significant amounts of carbonyl are present in the polymer either as a result of thermal oxidation or by u.v. catalysed

oxidation then they are involved in the photodegradation process. However, the rapid disappearance of vinylidene suggests that other photo-oxidative reactions involve this group and that this process precedes carbonyl formation.

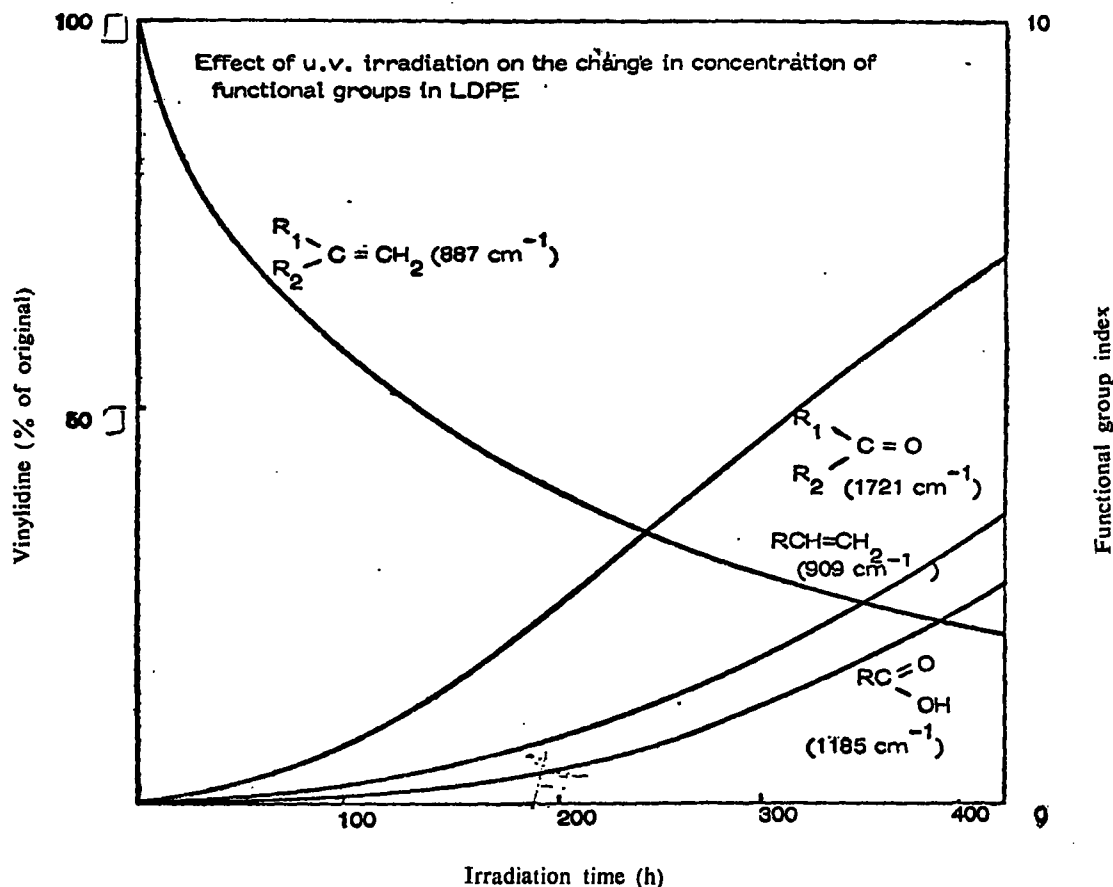


Fig. 1. Effect of u.v. irradiation on the change in concentration of functional groups in LDPE

Samples of polyethylene processed in the presence of air were examined for hydroperoxide by the method of Bocek modified as described in the experimental section. Fig. 2 shows the results and also the associated changes in vinylidene and carbonyl during the processing operation. Hydroperoxide could not be accurately determined by this technique before 20 min or after 40 min processing. It reached a very sharp maximum at about 30 min and samples stored at room temperature were found to have the same hydroperoxide concentration after several weeks. It is clear that hydroperoxide formation precedes carbonyl formation when the polymer is processed in the presence of air and that under mild processing conditions, where changes in the u.v. lifetime of the polymer are greatest, hydroperoxide and vinylidene must both be involved in the photo-initiation process. This accords with the auto-accelerating nature of the carbonyl formation during the initial stages of both thermal and photooxidation and confirms the essential similarity of the two processes.

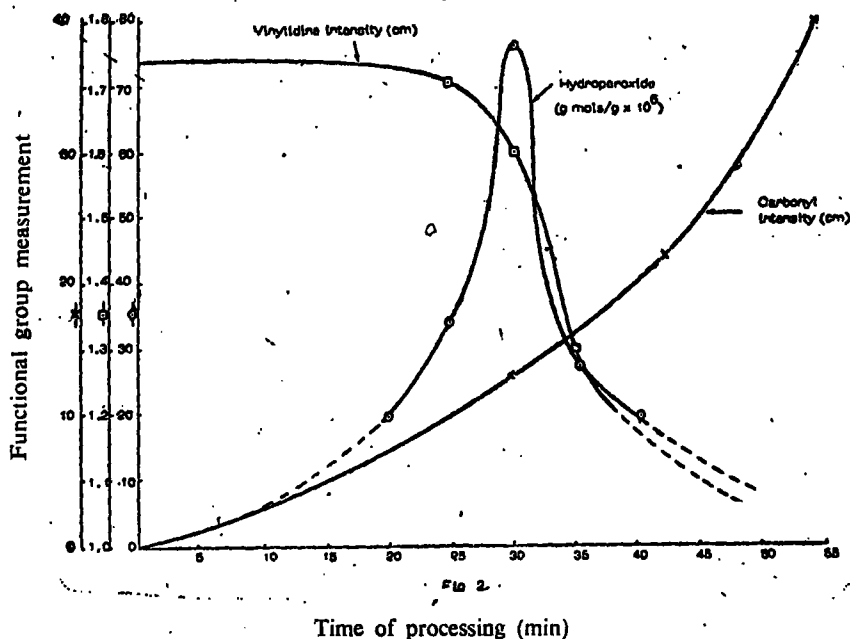


Fig. 2. Change in functional group concentrations during processing of LDPE

From Fig. 2 it is clear that the disappearance of vinylidene during processing is related to the formation of hydroperoxide and indeed, the hydroperoxide concentration curve appears to be a slightly displaced differential of the vinylidene concentration curve. This is the behaviour expected if the rate of disappearance of vinylidene is directly related to the hydroperoxide concentration.

Figs. 3 and 4 relate the change in carbonyl and vinylidene concentration, respectively, on u.v. irradiation to the processing conditions and to carbonyl initially present in the processed polymer. Films prepared from the polymers produced in the series of experiments reported in Fig. 2 were irradiated and the carbonyl indices was measured at intervals. For samples containing hydroperoxide and vinylidene, there was a sharp increase in carbonyl formation due to the above photo-oxidation which destroys, both vinylidene and hydroperoxide. More extensively oxidized samples have a lower peroxide and vinylidene content but a higher initial concentration of ketonic carbonyl (1721 cm^{-1}). This photolyses rapidly by a Norrish type II process and is followed by a slower growth of secondary carbonyl compounds, notably carboxylic acid, peracid and aldehyde. Ketonic carbonyl cannot be detected in the later stages of photo-oxidation.

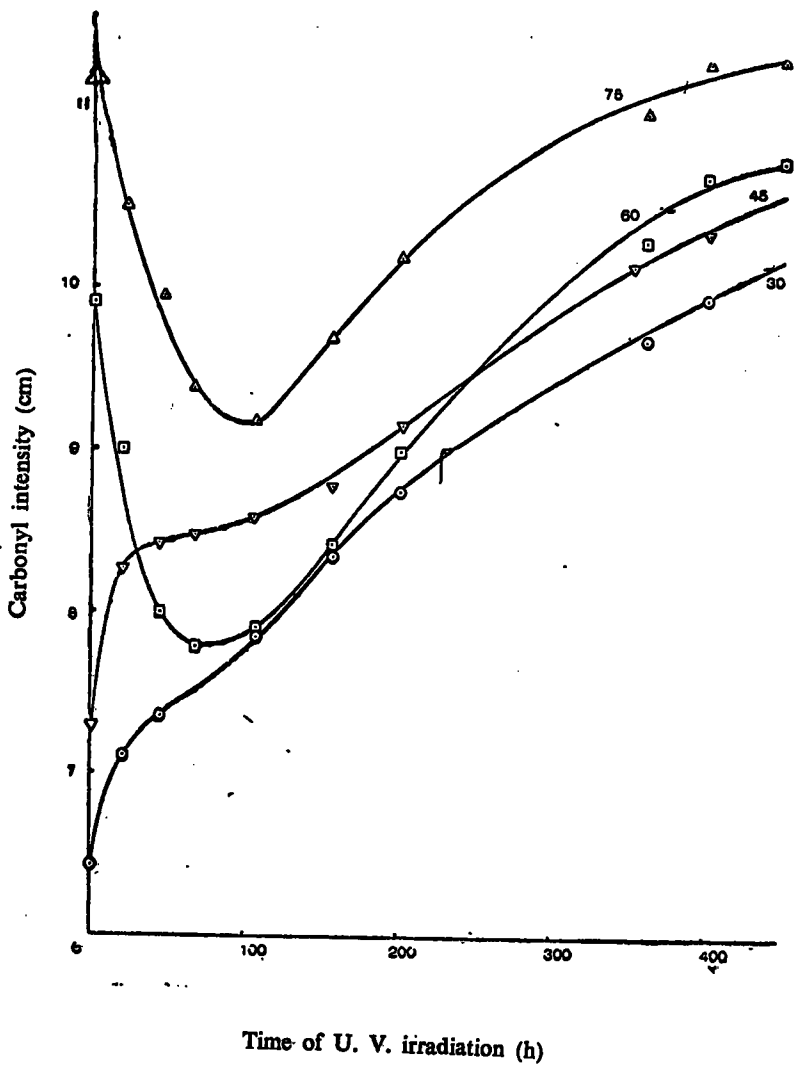


Fig. 3. Change in carbonyl intensity in LDPE on irradiation (numbers on curves indicate time of processing in min)

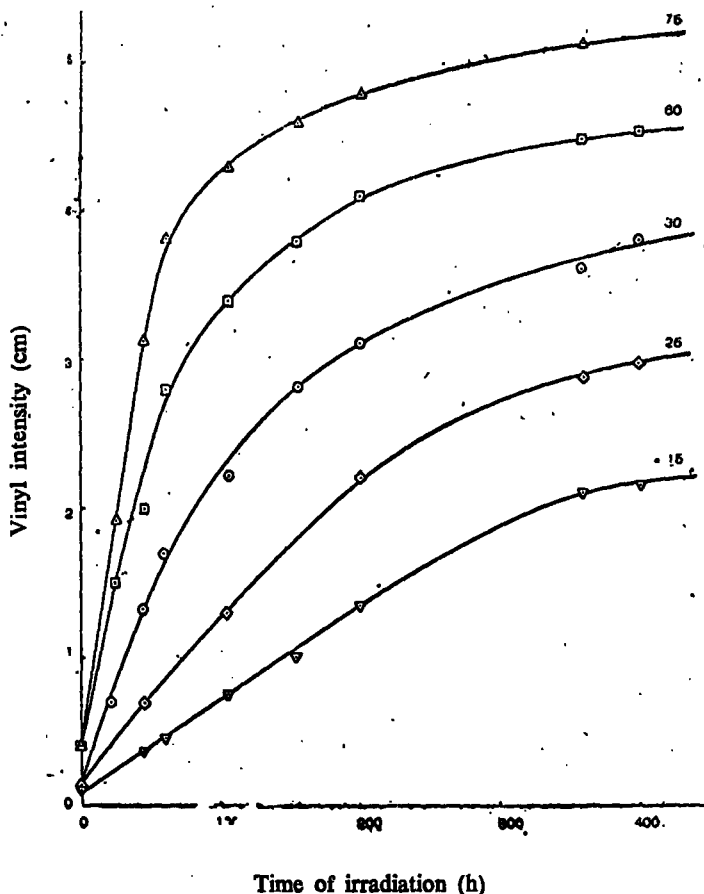


Fig. 4. Change in vinyl group concentration in LDPE on uv irradiation (figures on curves indicates time in min)

The fact that the more lightly oxidized polymers exhibit a sharp pro-oxidant effect whereas the heavily oxidized polymers undergo photolysis is of great significance and indicates that hydroperoxide initiation of vinylidene oxidation is much more important than activation of carbonyl in commercial plastics. A commercial processing operation would normally be of shorter duration than that involved in the present studies and would involve lower oxygen contact than the experiments described, although at the higher temperatures used the induction period to hydroperoxide formation would be shorter (Hutson & Scott, 1972 & 1974). It follows that antioxidants which destroy peroxides or in some other way inhibit the oxidative chain reaction are likely to be much more effective in commercial polymers than agents which quench excited states of photoactivated carbonyl, although this may be significant at advanced degrees of photo-oxidation. The significance of these results for the mechanism of u.v. stabilization has been discussed elsewhere (Rana-weera & Scott, 1974).

The results serve to explain the puzzling reversal of the change in mechanical properties of LDPE observed during photo-oxidation. This is exemplified by an initial increase followed by a decrease in elongation at break (Scott, 1973), a decrease followed by an increase in melt flow index and a decrease followed by an increase of dynamic modulus (Amin & Scott, 1974). A study of dynamic modulus decrease

carried out under the conditions described in the present paper has shown (Amin & Scott, 1974) that this occurs during the first 30 - 50 h after which reversal occurs due to the supervention of chain scission. This is the same period during which rapid oxidation of the polymer occurs (Fig. 3) and vinylidene disappears rapidly. An insoluble cross-linked gel is also formed during this period (Gan & Scott).

The following sequence of chemical reaction is proposed to account for the main features of the photo degradation process.

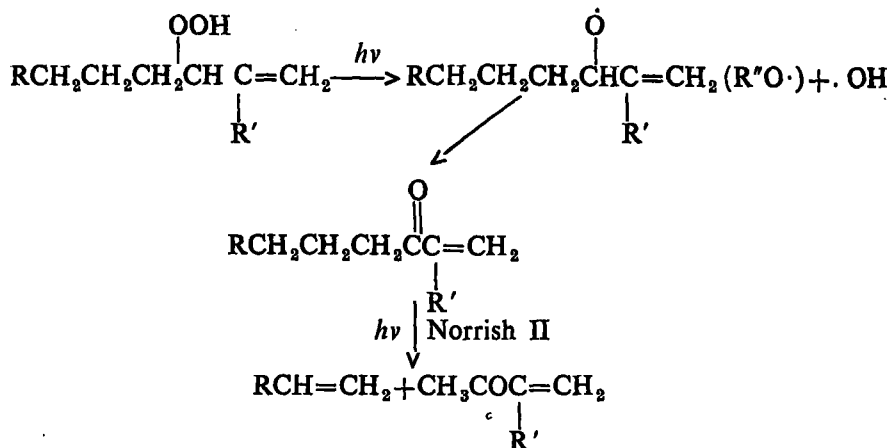
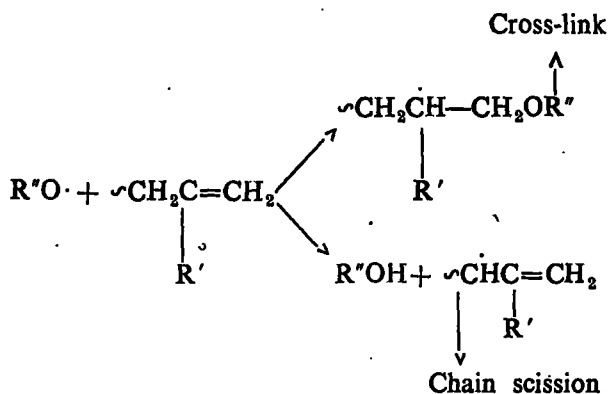


Photo-initiation occurs by further reactions of the primary alkoxy and hydroxyl radicals, and cross-linking through vinyl addition competes with chain scission through allylic hydroperoxide breakdown (Scott, 1965).



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