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A review of experimental studies of the role of free-radicals in polyethylene oxidation

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Abstract.

This paper reviews current understanding of the role of free radicals in the oxidation of polyethylene induced by high-energy irradiation (gamma or e-beam).To evaluate the reactivity, stability and mobility of different macroradicals, their reactions after gamma irradiation of different polyethylenes (LDPE, LLDPE, VLLDPE, HDPE, UHMWPE) are considered. Macroradicals are formed in all phases of PE (crystalline, amorphous and interphase). Their overall determination is possible only if both irradiation and detection are carried out at 100K, or below. At this temperature, the most abundant macroradical formed is the secondary alkyl macroradical (R''°). On gradually raising the temperature, the macroradicals decay with formation of vinylene double bonds and molecular hydrogen. At room temperature, the macroradical concentration is about 4% of the original quantity at 100K for LDPE and around 15% for HDPE. In HDPE and UHMWPE; the macroradicals are mainly present in the crystalline phase and in short times (hours) they migrate to the amorphous phase. In LDPE and LLDPE macroradicals are mainly allylic, present in minimal amounts at the crystalline-amorphous interphase. In the nearly fully amorphous VLDPE no residual macroradicals can be detected at room temperature.

The mobility of R''° is variable and is a function of the mobility of the polymer backbone, slow in the crystalline phase, relatively fast in the amorphous phase. Kinetic stability, or persistence, is often more important than thermodynamic stability in determining radical lifetimes, in particular for radical processes in the solid phase. Alkyl macroradicals react with chain imperfections, additives and oxygen, in a cyclic process involving initiation, propagation and termination reactions. The initiation reactions form macroradicals by cleavage of the C-H bonds of PE, induced by irradiation or by photo- or thermal-scission of peroxides formed during processing of the polymer. Propagation involves the reaction of R''° with vinyl or vinylidene double bonds, with the formation of a new radical, in competition with their reaction with oxygen to form various oxidation products (ketones, hydroperoxides acids, alcohols and esters). It is notable that the formation of ketones does not necessarily require decomposition of the hydroperoxides. In the presence of stabilizing additives, radicals react with the additive (ADH), with the formation of a more kinetically stable radical (AD°), which considerably decreases the propagation rate, but a termination reaction between R''° and AD° may also be envisaged.

It is observed that radiation-induced oxidation has a constant rate during irradiation. Post-irradiation, the oxidation occurs via transfer of the macroradicals from the crystalline phase and the interphase to the amorphous phase, where oxygen is available, and the rate decreases, approaching zero. The occurrence of termination is apparent. Termination must occur through the reaction of two macroradicals. The reaction between two R''° is difficult, due to steric hindrance. The most probable reaction is that between peroxy macroradicals (ROO°), fixed in position on the polymer chain and R''°, which migrate through the polymer bulk. This reaction is difficult to confirm experimentally because of the lack of reliable analytical methods for ROOR species in the presence of ROOH.

The formation reactions of the different oxidation products are reported and the branching reactions occurring in thermal and photo-oxidation are also discussed.

Keywords: radicals, macroradicals , oxidation, polyethylene

Abbreviations

r° (low molecular weight radical free to move in the amorphous polymer phase)
R° (generic alkyl macroradical)
R'OO° (primary peroxy macroradical)
R' (primary substituent carbon groups) R'° (primary macroradical)
R''(secondary substituent carbon groups) R''°(secondary macroradical)
R''' (tertiary substituent carbon groups) R'''°(tertiary macroradical)
R_{all} (allylic substituent carbon groups) $R°_{all}$ (allylic macroradical)
R''OO° (peroxy macroradical bond at secondary substituent groups, fixed on the polymer chain).
PE (generic type of polyethylene)
RT room temperature

Note: This article will make use of notation whereby low molecular weight radicals(r°) and primary (R'°), secondary (R''°) and tertiary (R'''°) macroradicals are defined according to their chemical structure and not according to when they are formed (i.e. primary first, secondary second etc.) as often occurs in the literature on radicals.

1. **Introduction.**

Oxidative degradation of PE under radiochemical initiation has been widely studied for many years, partly because of its technological importance in sterilisation and crosslinking and partly because radiation provides a very convenient way of generating free radicals at controlled rates. This is very difficult to achieve by thermal or photochemical initiation, both of which involve uncontrolled levels of impurities.

It has been accepted for decades that the degradation is a free-radical process but many aspects remain confused, in part because of the low concentrations of radical species which are involved and in part because of the complex morphological effects on radical mobility and the solubility and migration of oxygen and antioxidants. In this review, we summarise results from our work over many years, correlate them with results reported in the literature and highlight the influence of local environment and mobility of radical species. We reconsider the interaction between radicals or macroradicals with the imperfections and chain ends of the polymer, with oxygen and with the stabilizing additives. In the context of oxidation, we suggest the improbability of some reactions, not for thermodynamic reasons but for kinetic reasons related to steric hindrance, and their influence on the stabilization of polyolefins. We take into account different types of PE, from UHMWPE to VLLDPE, which have different morphologies (i.e. different degree of crystallinity and different crystallite sizes). The chain imperfections produced in PE which depend on the polymerization chemistry are vinyl, vinylene and vinylidene double bonds together with short and long-chain branches and are consequently easily identified by UV and FTIR spectroscopy [1–5].

We will consider results obtained using γ–radiation or e-beams at temperatures below 40°C which are similar to the industrial processes of sterilisation and cross-linking. These are compared with results obtained from thermal oxidation in accelerated tests of aging carried out at temperatures below 100°C, and with results obtained using photo-oxidation in accelerated tests of aging. The latter use lamps filtered to exclude wavelengths below 290 nm at up to 60°C, where thermal oxidation is limited, making this comparable to natural photo-oxidation.

This is article is not intended as a comprehensive, non-critical review of the whole of the literature but rather is a summary of the point of view of the authors, based on experimental data and substantiated by reference to the extensive literature.

As stated above, the degradation and stabilization of polyolefins (degradation induced by radiation, thermo- and photo-oxidation, stabilization against thermo- or photo-oxidation, thermal degradation, mechanical degradation,) involves radical and macroradical species [6–24]. In studying the kinetics of these processes, it must be recognised that polyolefins are normally semi-crystalline and contain three solid phases with different characteristics: amorphous, crystalline and an amorphous-crystalline interphase which is formed during the crystallisation of the polymer from the molten state because the polymer is unable to crystallize perfectly due to kinetic and steric restrictions. This last phase, possesses a higher degree of organization with respect to the amorphous phase, but lower than the crystalline [25,26].

The three phases have different chemical and physical characteristics; in particular, different mobility of the polymer chains. Only the very smallest molecules can enter the close-packed crystal phase, whilst some small molecules may be soluble in the fully-amorphous phase but too large to enter the amorphous interlayer separating two crystallites [27]. The segmental mobility of the amorphous component in a semi-crystalline polymer generally differs considerably from that of a fully amorphous polymer, especially above the glass transition temperature, ($T_{g)}$) [28]. The accumulation of chain defects, e.g. chain ends and chain branches, in the amorphous phase during crystallisation, gives the amorphous phase different properties in semi-crystalline polymers from those in fully amorphous material. For example, it was found that at room temperature (RT), the local chain

mobility in the interphase of UHMWPE is two orders of magnitude higher than that in the crystalline phase and three orders of magnitude smaller than in the fully-amorphous phase [29–32]. The crystalline phase contains few, or no, structural flaws, and the permeation of small molecules into a perfect crystal phase is only possible for very small species, such as He and H_2 [25,33–36]. In the amorphous phase the polymer chains can move with rotational and (limited) translational motions as a function of their temperature (above or below Tg). The movement of macroradicals and their reactions will be more facile at temperatures above Tg, compared to those occurring below Tg because the amorphous phase is much more mobile above Tg.

1.1 Kinetic and thermodynamic stability of macroradicals at RT.

In chemistry, a radical (also called a free radical) is a neutral atom, or molecule which possesses an unpaired valence electron. With some exceptions, the unpaired electron makes radicals chemically reactive. In the gas phase, or in solution, free radicals, with their high possibility of movement in all directions, have very short lifetimes, typically less than 10^{-9} s, which corresponds to high thermodynamic and kinetic reactivity [8,9,11,12,24]. Kinetic stability, or persistence, is often more important than thermodynamic stability in determining radical lifetimes. Moreover, we must distinguish between radicals obtained in a solid matrix (crystalline, glassy, or composite) and radicals in liquids or in solution. In solution, the so-called "stable" radicals are stabilized by their chemical structure i.e. by stabilization by electron delocalisation, with half-lives typically of the order of some minutes. In contrast, radicals present in the solid phase, and in particular all polymeric macroradicals formed duringγ- or e-beam irradiation may be trapped in the crystalline phase and be more persistent. Their persistence mainly depends on the steric protection of the unpaired electron, while the transfer rate depends on the dimension of the crystallites and the temperature [37–43].

For example, Carpentieri et al. [1] irradiated a number of PE samples with differing crystalline phase fractions, using e-beam irradiation in nitrogen under identical conditions, and analysed their radical contents by EPR after 30 min storage at RT (Fig 1). The crystalline phases of HDPE and UHMWPE, whose crystallites were bigger than those of LDPE, contained R"° macroradicals. In LDPE, however, only R_{all}° were found, present in the crystalline phase and the interphase as their transfer to the amorphous phase is partially impeded by their stability, for steric reasons, and macroradicals were totally absent in VLLDPE. The radicals in HDPE and UHMWPE took longer to transfer to the amorphous phase than those in LDPE.

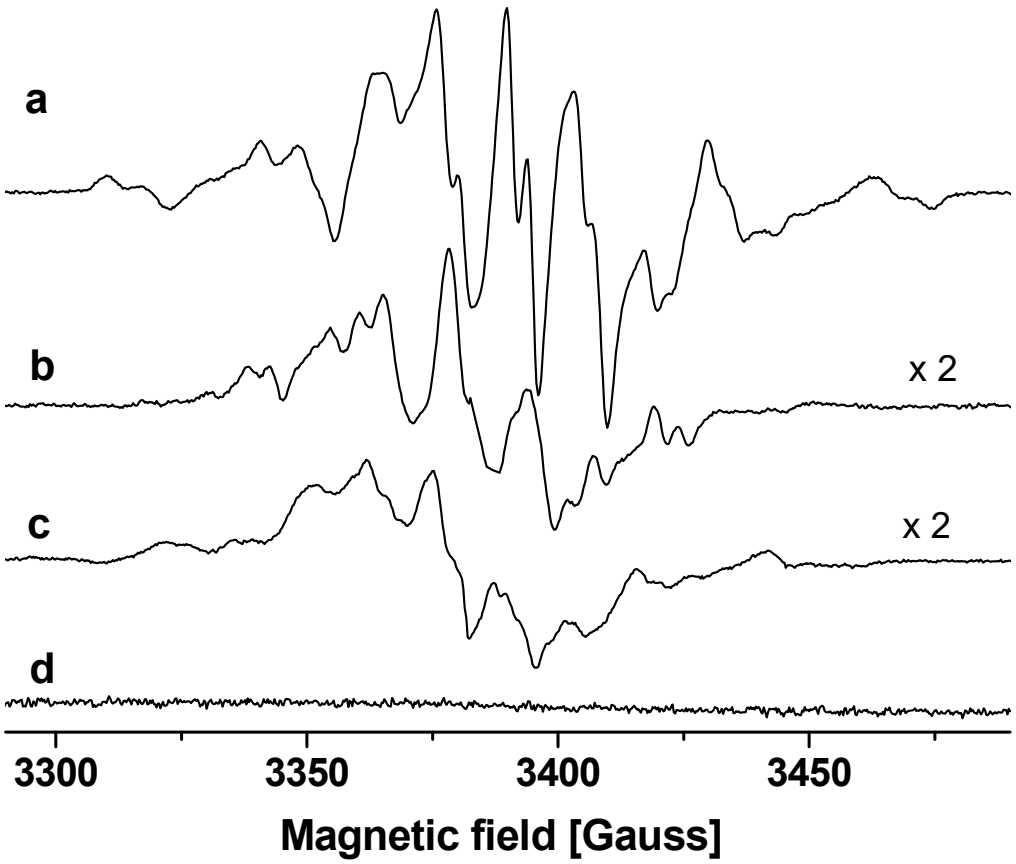


Fig 1. EPR signals of different polyethylenes irradiated with e-beam at 60 kGy at RT: a) UHMWPE and HDPE, 30 min after e-beam irradiation; b) UHMWPE and HDPE, 24 h after e-beam irradiation; c) LDPE and LLDPE, 30 min after e-beam irradiation; d) VLLDPE, 30 min after e-beam irradiation. In order to compare intensities, a multiplying factor was applied. Reprinted with permission from [1].

1.2 Stability of macroradicals – effect of temperature.

The γ-irradiation of HDPE (50% crystallinity) to 30 kGy at 77K produces 50 mmol/l of alkyl macroradicals[37,38], with formation of H_2 and vinylene double bonds [44,45]. On gradually raising the temperature, the macroradicals decay, with peaks in decay rate in the vicinity of the relaxation temperatures of PE (120K, 180-190K, and 230-240K) whose magnitude depends on the chain structure and crystallinity of the sample [37]. At RT the macroradical concentration is about 4% (2 mmol/l) of the original quantity at 100K for LDPE and around 15% for HDPE as reported in fig 2.. In essentially the same temperature ranges low-temperature irradiated PE samples also emit light, the so-called radiothermoluminescence, attributed to recombination of electron-cation pairs produced during irradiation[46]. Both observations imply the onset of molecular motions, through the exact nature of the motions at each temperature is still controversial.

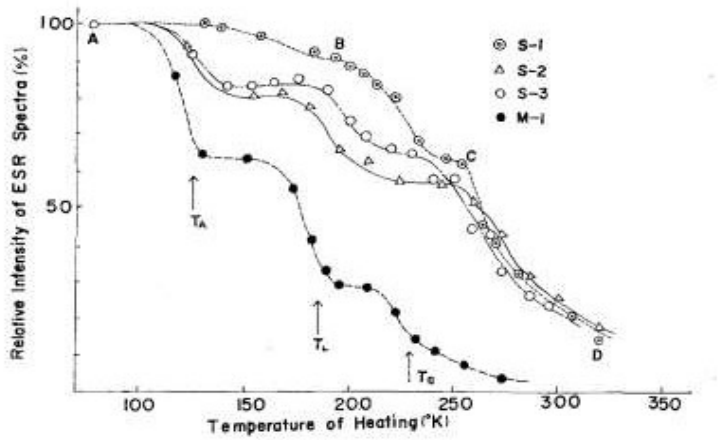


Fig 2. Decay curves for the free radicals produced in the same HDPE with different level of crystallinity (S-1,89,%, S-2, 84%, S-3, 68%)and LDPE (M1 50%) irradiated in liquid nitrogen under vacuum at 10^{-4} mm Hg. T_A (120K) , T_l(180K), T_b(220 K) are relaxation temperatures of PE [32]. Reproduced with permission from [37] .

1.3 Mobility and migration of macroradicals .

An obvious condition for any bimolecular reaction is that the reacting species must meet, i.e. reach a separation distance at which they can interact, a distance of the order of a few angstroms. The probability of collision is related to the mobility and the dimensions of the reactants; the probability of reaction depends upon the activation energy and steric hindrance to reaction [47,48]. In the gas phase, diffusion is rapid, collisions are frequent and the duration of a collision is very short, so that collision frequencies are much higher than reaction rates except for the most reactive species.

In contrast, reactions in a solid polymer are much more likely to be diffusion controlled since the movement of macroradicals, small molecules and low MW radicals is very much slower than in the gas phase, and the duration of encounters much longer. Thus in PE, and polyolefins in general, the mobility of the species involved is limited, and this may lead to unusual consequences in the kinetics of degradation [22,49–51].

The amorphous phase of a semi-crystalline polymer above Tg has considerable local mobility through rotational motions of sections of polymer chains, but long-range mobility is restricted by the fact that the chain is “pinned” by the crystalline material. The energy difference between *t* and *g* conformers in the amorphous part of crystalline PE is around 6 kJ mol^{-1} , only slightly higher than the value for n-butane (about 5 kJ mol^{-1}) [52]. That suggests that although crystallinity restricts bulk motion, the amorphous part is locally very mobile. The amorphous and interphase regions also contain chain imperfections (end-groups, branches, other groups that have formed during the polymerization reaction or induced during degradation, for example by interaction with photons or electrons) which are attached to the polymer chain but rejected by the growing crystalline phase during crystallisation. Such groups have the possibility of rotational movement, but little translational freedom, so that they are substantially fixed in position.

Oxygen and any additives added during processing, are able to migrate in the amorphous phase, but are usually insoluble in the crystal phase, from which they are excluded. Their migration is controlled by the diffusion coefficient (D). For a spherical particle moving in a uniform viscous fluid, D depends on the temperature, the viscosity of the fluid and the size of the particles according to the Stokes-Einstein relation. The diffusion of small molecule penetrants in the various phases of PE and other polymers has been reviewed by Hedenqvist and Gedde [27].

Small radicals (H° and OH°) can move easily in the amorphous polymer and, because of their high reactivity and the high local concentration of CH bonds, they react quickly with the polymer by abstraction of an H atom to form an alkyl macroradical and H_2 or H_2O. Thus H°, OH° and R''° are the species with highest mobility in PE that play a key role in the degradation and oxidation phenomena.

Whilst it is easy enough to visualise molecular motions in amorphous and interphase regions well above Tg, which allow radicals to interact in pairs, it is harder to understand how macroradicals which are formed in the crystalline phase are also able to decay, an observation which implies some long-range mobility. This issue was much discussed in the 1960s when it was generally assumed that the crystal phase of PE is immobile. One suggestion to explain the mobility of radicals apparently trapped in a crystal is that secondary alkyl macroradicals produced in the crystalline phase may migrate as R"° [1,43] along a polymer chain, or between chains, by a repeating inter- or intra-molecular H-transfer mechanism, eventually decaying in the amorphous phase. For R"° in PE the possibility of migration of macroradical sites by transfer ("hopping") of hydrogen is discussed in the literature [6,38,40,41].

Dole reported that after irradiation of HDPE by γ–rays, the elimination of the H_2 formed and successive treatment with D_2, HD is formed and suggested that "the exchange probably involves the hydrogen atoms closest to the free radicals or on the nearest neighbour sites, and provides a new mechanism for free radical migration" [6,35] This observation shows that H_2 can act as a transfer agent, perhaps not hugely surprising given its mobility in the crystal phase and the fact that the reaction is close to thermoneutral. However. it does not prove that H-migration can occur in the general case where H_2 is absent.

Sohma also reports [40] "There is experimental evidence to indicate that free radicals are produced uniformly in a polymer in the primary stage of γ-irradiation and decay preferentially in the amorphous regions. […] These facts require that free radicals in polymer matrices migrate from the original site (crystalline phase) to the amorphous phase. […] A molecular mechanism for radical migration was demonstrated via the analysis of the changes in the ESR spectrum of PE. An unpaired electron migrates in a polymer matrix just like the elastic collision of molecules in a gas phase until it is stabilised or reacts." It should be emphasised that the migration of alkyl radicals by H-transfer in a polymer at RT can only be significant if the local concentration of O_2 is low enough, since reaction of a C-centred radical with O_2 is expected to be at least 10^2 times faster than H-migration.

The occurrence of the H-migration reaction has been extensively discussed, particularly by Russian authors, and its occurrence mainly inferred from kinetic arguments [49–51]. If it occurs, H-migration between nominally identical sites appears to be entirely a property of polymer radicals. 1,2- and 1,3- H-atom shifts in small alkyl radicals are unknown [53] because of ring strain energy in the cyclic transition state [54,55]. Intramolecular shifts, such as 1,6-H-atom transfer, are known but are facile only at high temperatures and for exothermic processes such as the conversion of primary to secondary radicals [56]. For example, Lehrle and Pattenden [57] suggested that 1,6-transfer is at least an order of magnitude faster than any other process. In agreement with these conclusions, Dole considers secondary macroradical transfer between two neighbouring molecules to be more likely than migration along the chain [58]. This hypothesis has been confirmed by calculation [59].

The transfer of radicals has been described using the hopping effect[60]. The possible contribution of the quantum tunnelling effect to alkyl radicals rearrangements has been discussed [61]. The effect of the transfer of an electron has also been observed between two metalloproteins [62]. It has also been possible to identify transfers over distances of the order of 25nm, despite the fact that they are very quick as they occurred in water dispersions.

It has been suggested that R"° take around ten hours to travel across the typical 25 nm dimensions of UHMWPE crystallites [1]. It is not easy to interpret H-migration in terms of a bulk diffusion coefficients because it is not a random walk process. However, Shimada et al. [63] modelled migration as a diffusion-controlled process and quote a value of $D = 3 \times 10^{-21}$ cm^2 s^{-1} at 307K for diffusion of radicals from the inner crystal phase of PE to the amorphous interface.

As an alternative hypothesis we can also ask just how much mobility there really is in PE at 298K. There is a lot of indirect evidence, most of which was not available when the H-migration reaction was invoked. Thus, Hendra et al. [64,65], and others [66] showed that HDPE can be quenched by very rapid cooling to give a state which is amorphous as judged by IR, Raman and x-ray methods. That material is mobile enough to form "proper" crystals at temperatures as low as 170K (-100ºC) and will crystallise completely at 220K (-50ºC) or so. That implies easy long-range molecular motion. Perhaps more importantly there is a lot of evidence from NMR relaxation studies to show that the crystallites in PE, even UHMWPE are not rigidly locked, but that chains can and do, diffuse through the crystal. There are many reports, but the work of Spiess et al. [67], is relevant and is confirmed by e.g. Klein et al. [68,69]. The process essentially involves a rotation of 180º in the chain and a corresponding "jump" translation through the crystal. It is directly connected with the ability of PE to be ultra-drawn. Even at RT the polymer can be extended, often to draw ratios of 20 or more, at finite strain rates, which implies that there is considerable mobility of chains through the crystal. Hu and Schmidt-Rohr [70] relate this to the ease with which polymer chains can slip through crystallites around the α-relaxation temperature to allow reorientation to take place.

It is again not easy to interpret these chain diffusions in terms of bulk diffusion coefficients because it is not a random walk process. However, Spiess quotes an effective D value of 10^{-16} m^2 s^{-1} (10^{-12} cm^2 s^{-1}) at 360K, corresponding to a chain displacement along the crystal axis of about 10 nm in 100 s (or 250 s to cross the 25 nm crystal size discussed earlier). They quote E_a as 105 kJ mol^{-1}. That would give $D = 7 \times 10^{-20}$ cm^2 s^{-1} at 298K, which gives a figure of about 40 hrs to cross a crystal. These numbers are very comparable to those quoted for H-migration models. Given all the assumptions one could conclude that physical migration of radical centres from the crystal phase to the amorphous would be fast enough to account for radical decay without invoking C-H transfer. It is hard to see how one could experimentally distinguish H-migration from simple chain diffusion. At this stage it seems that all we can sensibly conclude is that free-radicals do indeed migrate in the crystal phase of PE, by one (or perhaps both) of the proposed mechanisms.

2. Cyclic radical reactions in polymer oxidation.

The oxidative degradation of a polymer involves cyclic radical chain reactions, classified as:

- Initiation, which produces small radicals, (r°) and °OH, or alkyl (R°) or alkoxide macroradicals (RO°), which react with the PE to give R"°. The formation of radicals takes place by homolytic breakage of a bond. This may be induced by exposure of the polymer to high-energy photons, x-rays, electrons or mechanical stress. Less energy is involved in interaction with solar UV radiation or heat, both of which involve cleavage of weak bonds, typically in impurity centres. Depending on the type of energy supplied, the process may be defined as mechanical, thermal or photochemical degradation or radiation-induced degradation. In the presence of oxygen the processes are defined as thermal, mechanochemical or photo-oxidation or as oxidation induced by high-energy radiation;
- Propagation, in which R"°, can react with the polymer chains, the chain imperfections and the oxygen that they meet in their movement in the polymer, forming in one or two steps, a neutral macromolecule and a new R° which continues the propagation;
- Kinetic chain branching. If oxidation occurs at low enough temperatures the primary products, ROOH, ketones etc. may be stable, in which case the overall oxidation reaction is kinetically a linear chain process. However, it is often the case that oxidation products are unstable in the conditions of exposure and decompose to form new free radicals. Examples include thermal and photo-decomposition of ROOH, and photolysis of ketones. In kinetic terms these are kinetic chain

branching reactions and their occurrence is responsible for the auto-accelerative behaviour typical of thermal and photo-oxidation;

- Termination, which involves the elimination of two radical species with formation of a neutral product, sufficiently stable that it does not re-initiate. In the presence of a chain-breaking antioxidant it may also involve elimination of a radical in a transfer reaction to form a new radical which is too stable to re-initiate the chain and decays by some other mechanism.

2.1 Initiation: production of alkyl macroradicals through interaction with high-energy radiation

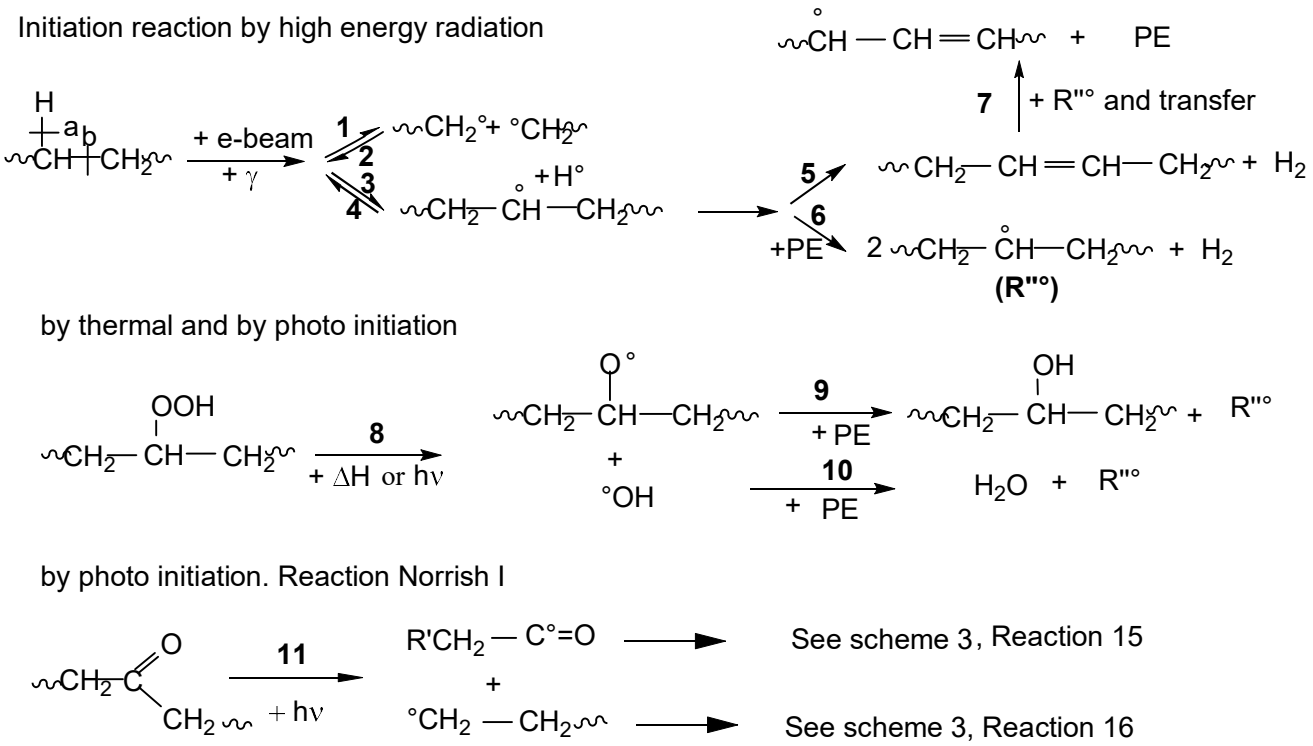
The first interaction between a polymer and high-energy photons or electrons is similar, but in both cases interactions will produce new electrons with similar energy, for which subsequent interactions with the PE are equal and form the same products [6,8,12–14,17,19,21,23,24].

The homolytic cleavage of C-C or C-H bonds is endothermic: the initiation rate is a function not of the physical state of the polymer but of the amount of energy supplied to the chemical bonds. High-energy photons i.e., γ rays, x-rays or electrons (e-beam) possess an energy more than three orders of magnitude higher than the chemical bonds. They penetrate into the amorphous phase, interphase and the crystal and all the bonds are cleavable, producing radicals.

γ-rays may penetrate throughout the polymer mass up to several metres, depending on the characteristics of the material, and the dose rate normally used in industrial sterilisation is some kGy/h. To achieve significant changes in the polymer, doses of the order of 25 kGy are needed, the dose that is used for the sterilization of polymeric materials [71,72]. This thus requires irradiation times of several hours. During γ-irradiation, the rate of formation of radicals is generally constant [5,73–77]. By working at temperatures slightly above RT, it is possible to study the overall process of initiation, propagation and termination of the degradation. Mallègol [74] asserts that "γ-irradiation is a valuable method for triggering oxidation because it is very controlled, the radical formation rate being constant during irradiation and ending immediately after irradiation stops […]"
In contrast, electrons can penetrate from a few mm to a few cm in PE, as a function of their energy. They are typically produced with a very high dose rate of the order of 5-10 kGy/s and, therefore, for a dose of 25 kGy, the irradiation times are a few seconds. Thus e-beam technology allows one to achieve the required irradiation dose in a few seconds, to stop the irradiation, and thus stop the production of macroradicals. Subsequently, if working at RT, where the thermally-formed products are stable and the reactions in the amorphous phase are complete [77], it is possible to study the transfer of R''° from the crystalline to the amorphous phase, and the termination of the oxidation cycle [1,43]. Commercial irradiations are typically carried out at or near room temperature. As we have indicated elsewhere, irradiation at much lower temperatures is a convenient way to accumulate higher radical concentrations in laboratory conditions. Even if irradiation is carried out in air, the (limited) oxygen content of the polymer will be destroyed very early on at the sorts of doses, dose rates and sample thicknesses typical of industrial practice.

The interaction of γ-photons or electrons with PE through a complex energy transfer process [13,14,23,24,78] leads to the cleavage of C-C bonds and C-H (cleavage a and b in scheme 1) in all three phases of the PE, with the formation of two primary macroradicals R'° (scheme 1, reaction 1) or a hydrogen atom, H° and a secondary macroradical (R"°) (scheme 1, reaction 3), with the simultaneous formation of trans-vinylene double bonds and H_2 [78], that is, with a termination reaction (Scheme 1 reaction 5). The remaining macroradicals move in PE. (Scheme 1, reaction 6)

The H° radical formed during γ or e-beam treatment has dimensions of the order of angstroms – thus giving high possibility of movement. In particular H° can move in all the phases in which the polymer chains are organized, with a rapid transfer reaction and transformation into H_2 by abstraction of an H-atom from a polymer chain (time less than 10^{-5} s) and the formation of R"°. (Scheme 1 reaction 5).



Scheme 1: Initiation reaction by irradiation, and by thermal and photo-initiation.

2.2 Initiation: production of alkyl macroradicals in thermal oxidative processes in accelerated testing.

In thermal oxidation in typical accelerated testing conditions, it is generally considered that initiation is due to the formation of radicals by homolytic cleavage of the weak –O-OH links of hydroperoxy groups formed in the amorphous phase during the processing of the polymer [18–21], with the formation of alkoxy macroradicals (RO°) and hydroxyl (OH°). Ketones, esters and acids are formed, in addition to alcohols and water, in the thermal or photo-decomposition of ROOH[3–5,79].

The OH° radical is among the more reactive radicals, with a size of the order of angstroms, also with a high possibility of movement between the polymer chains, at least in the amorphous phase. OH° radicals react rapidly with the polymer, abstracting an H atom with formation of water and R"°, the same macroradical that is obtained in irradiation (scheme 1, reaction 9). Thus, R"° also arise as a secondary product of thermal initiation (scheme 1 reactions 8,10). Thermal oxidation is often studied in accelerated tests at 80°C or above, temperatures at which alkyl hydroperoxides decompose at significant rates with a kinetic branching effect.

2.3 Initiation: production of alkyl macroradicals in photo oxidative processes in accelerated test and natural process.

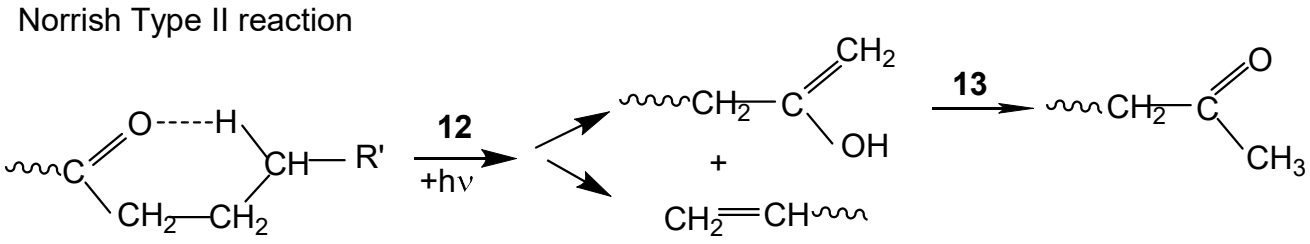
Photo-accelerated oxidation is generally conducted at temperatures lower than 60°C where the rate of thermal oxidation is low compared to the induced photo-oxidation, so as to separate photo-induced reactions from purely thermal contributions [5,80]. Oxidation induced by high-energy radiation begins upon the interaction of a photon or an electron with the polymer itself, matter which is uniformly distributed across the sample. In contrast, the start of photo-oxidation requires the presence of chromophores, typically hydroperoxides and ketones, which are formed during the polymer production and whose distribution may not be homogeneous, meaning that oxidation may also not be uniformly distributed. In particular, rejection of impurity groups by the

growing crystal front during crystallisation implies that photo-initiation, like its thermal equivalent is confined to the amorphous or interphase regions.

Under the conditions used in the study of photo-oxidation, it is difficult to study the initiation alone as it is not separable from the propagation and chain branching, since the hydroperoxides and ketones formed during processing and by chain propagation are photochemically unstable under the irradiation conditions used for photo-oxidation studies. Furthermore, in contrast with radiation-induced reactions, the radicals involved in typical photo-oxidations are produced only in the amorphous phase where they react immediately with the species present and therefore their concentrations remains low and they are generally undetectable by EPR spectroscopy [1,24].

ROOH groups partially decompose in the same way as in the thermal oxidation process shown in scheme 1 (reactions 8-10) to produce acids and esters [79], while ketones proceed according to the Norrish I reaction forming macroradicals R'° and acyl macroradicals (scheme 1 reaction 13). Both are kinetic chain branching reactions, meaning that thermal and photo-oxidation reactions are typically auto-accelerated.

The other photo-reaction of ketones (Norrish II, scheme 2) does not lead to the formation of macroradicals, but of methyl ketones, meaning that it is not a radical initiation reaction, but a photo-decomposition. However, it does cause chain scission, which may be important if the polymer contains significant concentrations of C=O groups.



Scheme 2. Norrish II reaction

2.4 Reaction and decay of alkyl macroradicals

Macroradicals, whether formed by irradiation, by reaction of OH° or RO° radicals with PE, or by transfer of H°, may be alkyl (primary, secondary or tertiary) or allyl macroradicals. The rate of their formation is a function of the concentration of the groups present in the polymeric chain (CH_3, CH_2 and CH), the energy of the bond that is broken, and steric hindrance. In the case of PE, they are substantially of the type R"° because of the large excess of CH_2 groups compared to $CH_3$and CH.

The primary R'° expected from simple cleavage of C-C bonds in PE have been detected only at low temperature during γ-irradiation of PE or during mechanochemical degradation and in the synthesis of LDPE [24,81]. After irradiation of PE no increase in methyl groups is detected. There are no detectable reaction products from disproportionation of two primary radical species. The only possible reaction is thus termination by coupling of two macroradicals with re-formation of a C-C bond (Scheme 1 Reaction 2) [78], probably due to the steric hindrance of the cage effect arising from the low mobility of the chain ends compared to the high reactivity of two radicals formed in close proximity.

Tertiary alkyl macroradicals were recently detected in PE [82,83] and are kinetically stable at room temperature due to steric hindrance to subsequent abstraction of H. Their formation may be due to transfer of H from a R"° to a tertiary carbon, already

present in the original polymer in the amorphous or interphase due to branches (short or long) on the chain, or they may be formed, with the consumption of vinyl double bonds, in the so-called “type Y” crosslinking reaction (scheme 3, reaction 15, 16).

Allyl macroradicals are formed by intra- or intermolecular H-transfer from R”° to a vinylene double bond, originally present in the polymer and/or produced during irradiation (Scheme 1 reaction 7) [1]. They are not detected after irradiation of amorphous PE [1]. It must therefore be assumed that they are formed in the crystalline or interphase regions. This leads us to assume that reactions 5 and 7 of scheme 1 all occur in the crystal phase of PE, but allyl radicals are stabilised by steric hindrance in the crystalline and/or interphase regions. The allyl radical is so stable that in a highly crystalline sample the PE must be heated to 90° when the crystallites start to melt for the allyl decay rate to become significant [84,85].

It must be noted that the alkyl macroradicals present after irradiation at liquid nitrogen temperature are detectable both in the amorphous phase and the crystalline phase only at 77K, whereas at RT they are detectable only in the crystalline phase after quite short times of irradiation [1].

In conclusion, the alkyl macroradicals initially formed during irradiation of PE are substantially secondary. They are detectable at RT if present in the crystalline phase and in the amorphous phase if produced and detected at low temperatures. In the amorphous phase they are very reactive and have very short lifetimes, less than 10^{-3} s at RT. The R’’’° and R_{all}°, not present after irradiation in LDPE, LLDPE or VLLDPE, are probably formed mainly in the interphase during the migration of R’’° from the crystalline phase to the amorphous phase [1].

2.5 Formation, reaction and decay of oxygenated macroradicals (ROO° and RO°)

Oxygen is able to migrate in the amorphous phase of PE, but is insoluble in the fully-formed PE crystal, meaning that it is excluded from the crystalline phase [33]. However, no information about the presence of oxygen in the interphase is currently available

Peroxy macroradicals in PE are mainly secondary, formed through the reaction between alkyl macroradicals and the oxygen present in the amorphous phase (Scheme 7, reaction 30). Reaction of oxygen with alkyl radicals in the gas phase is encounter controlled, with zero activation energy, driven by the exothermicity of formation of the more-stable peroxy radical, which is of the order of -150 $kJmol^{-1}$ for simple alky radicals [86–88].It is similarly encounter controlled in solution and it is generally accepted that there is no reason to assume any difference in the restricted mobility of an amorphous polymer above Tg. The reaction is an equilibrium but it is well to the product side at temperatures below around 600 K, except for C-centred radicals with high resonance stabilisation [89]. When a thick sample is irradiated in nitrogen or vacuum then exposed to air, the reaction of alkyl radicals with oxygen is controlled by diffusion of oxygen into the polymer, in competition with other reactions of the alkyl radicals, which are present at concentrations very much higher than would be expected in thermally initiated reactions.

Peroxide radicals in PE are not easy to identify by EPR spectroscopy [90,91]. At RT, they have a half-life of around 10 min [74,92]. Their spectra overlap with those of polyenyl radicals, and the two can be easily confused [74,93]. Carlsson et al. [94] showed that ROO° radicals formed on γ-irradiation of HDPE at temperatures below 200K, where they are stable, are exclusively secondary. Reactions with ^{17}O have demonstrated that the species present during irradiation is generally not the polyenyl macroradical [93]. EPR, UV and FTIR analyses of samples allow the species that are actually present to be identified as ROO° [2,5,92–94].

ROO° radicals are generally stable when produced and stored at 77K. Upon heating, they are generally believed to react by abstracting an H-atom to form ROOH + R"° during the propagation cycle (Scheme 7 reaction 34). Some ROO• radicals are stable in HDPE and UHMWPE for longer times, in spite of the large concentration of available hydrogen atoms. Their stability may be attributable to steric hindrance and not thermodynamic stability. As long as there is sufficient oxygen available, this reaction will regenerate the ROO° radical on a different C-atom as the R"° produced will react again with oxygen.

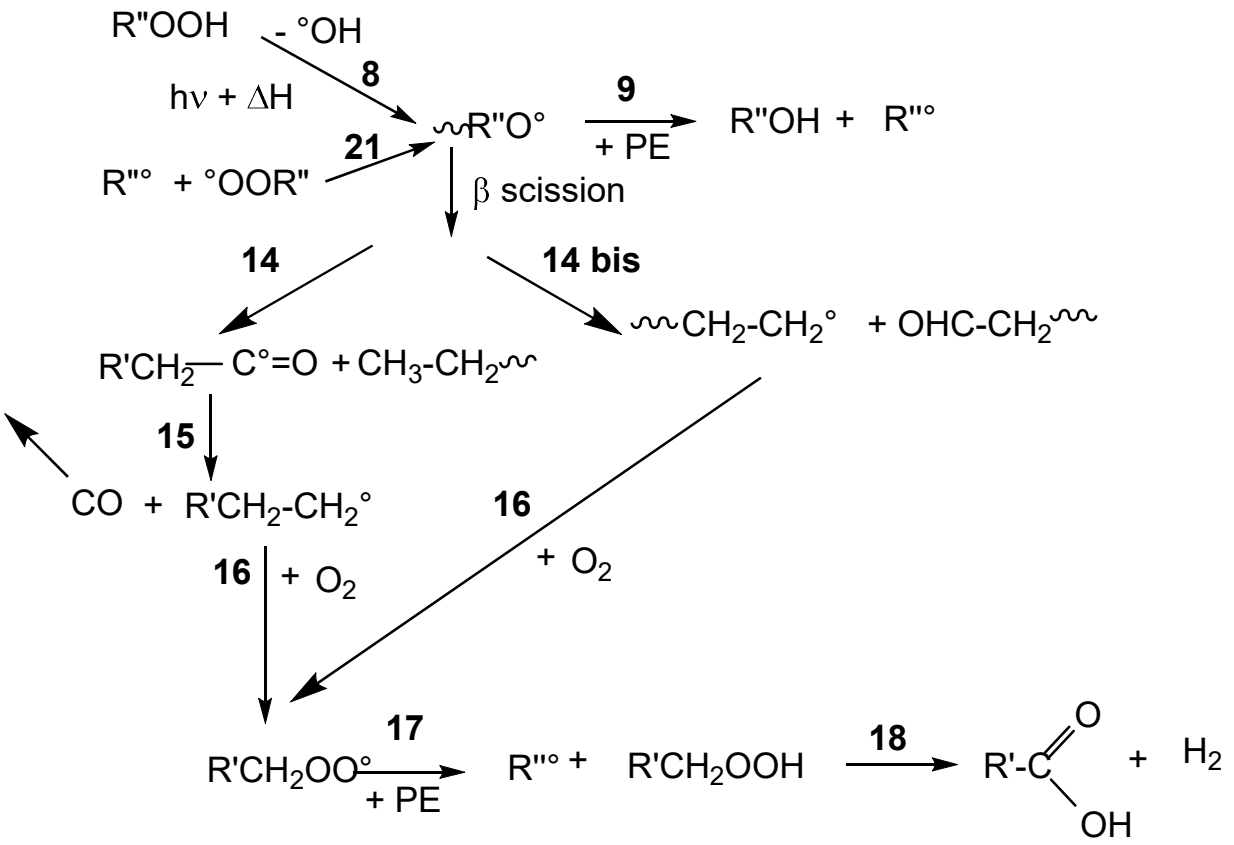
In contrast to the oxygen addition reaction, H-abstraction has a significant activation energy (typically of the order of 50-60 kJ mol^{-1}) [90,95]. This makes the second stage of the propagation cycle slow in saturated polymers such as PE or PP. The selectivity of the H-abstraction, and hence the distribution of OOH groups, has been a subject of discussion, though it is generally recognised that they are present both as isolated OOH groups and as H-bonded associated pairs or clusters, clearly distinguishable in their IR spectra. Whilst many authors have assumed essentially random abstraction, others have assumed more localised reaction. It has been suggested that ROOH production might involve intramolecular abstraction via a cyclic transition state, as described by Chien for PE [96], to produce localised clusters of OOH groups. Gugumus [97] considers that isolated OOH groups formed in PE at temperatures of 80 ºC and above may be partly sterically isolated and partly the result of an equilibrium between free and associated groups, with the distribution becoming more random as the temperature is raised into the melting range. In contrast, it has recently been suggested, based on theoretical calculations of free-energy changes [95], that the conventionally assumed ability of R"° radicals to abstract H-atoms from e.g. the normal -CH_2- groups in PE may be so thermodynamically disfavoured as not to occur, ROOH groups being formed only by H-abstraction from structural defects present in the polymer, or as a result of oxidation chemistry.

Whatever the details of their origin and distribution, it is clear that ROOH is one of the most important products in the oxidation of PE [2–5]. Because of the presence of both isolated and associated groups, the decomposition of ROOH in polyolefins, as in solution, is not a simple unimolecular reaction but consists of at least two clearly resolvable processes, attributed to the unimolecular decomposition of isolated peroxides and the bimolecular decomposition of associated pairs [77,96]. The decomposition is not induced by radicals [96].

The other oxygenated radical involved in oxidation is the alkoxy, R"O° macroradical. Like the ROO° radicals, the alkoxy radical is attached to the polymer chain and can only move with the chain, or by transfer of the radical activity to another site via chemical reaction. Alkoxy radicals can be formed via three different mechanisms:

- by thermal decomposition of hydroperoxides at the beginning of thermal oxidation (Scheme 1 reaction 8)
- in the interaction between a peroxide macroradical R"OO° and an alkyl radical, R"° with formation of 2R"O° (Scheme 7 reaction 31)[60,98]
- in photo-oxidation by the Norrish I excitation of a ketone (scheme 1 reaction 11).

β scission alkoxy macroradicals



Scheme 3: Reactions of the alkoxy radical

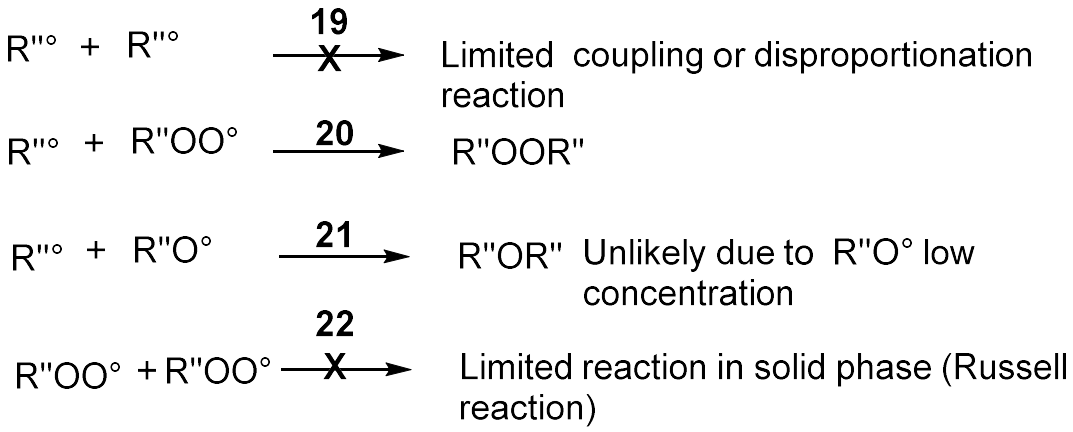
Literature studies demonstrate [60,99] that the alkoxy radical can undergo β-scission forming a primary alkyl radical or an acyl radical, which may lose CO (Scheme 3, reactions14-16), a product which is found during the irradiation of PE in the presence of oxygen in the polymer. This reaction is in competition with H-atom abstraction to form alcohols. (scheme 3 reaction 9). Reaction 14 in scheme 3 causes cleavage of the polymer chain. The activation energy of the reaction is only 24-50 kJ mol^{-1}, surmountable at RT and much less than the energy of the C-C bonds (347 kJ mol^{-1}) in the polymer chain. CO and primary alkyl macroradicals are formed in photo oxidation by the Norrish I (scheme 1 reaction11). For peroxy and alkoxy macroradicals, which are linked to the polymer chain, there is no possibility of migration via simple H-transfer, as hypothesised for the alkyl radicals, and their mobility is restricted to the local mobility of the polymer chain segments.

3. Termination reaction in oxidation.

When oxidation is induced by e-beam or γ-irradiation at temperatures and times low enough for ROOH decomposition to make an insignificant contribution to radical generation, the initiation reaction, i.e. the production of R"'°, ceases as soon as irradiation stops. After post-irradiation oxidation, induced by macroradicals migrating from the crystalline phase, oxidation, as measured by formation of non-volatile products at RT, ceases in times of some hours, implying the expected termination reactions [78]. Oxidation of PE induced by γ–ray irradiation was found to have a constant rate; as the initiation rate is constant, it follows that the termination rate during irradiation is also constant.

Radical termination requires the interaction of two macroradicals to produce non-radical products(s). The main macroradicals present in oxidation are R''°, R"OO° . The concentration of R"C°=O is significantly lower due to its fast decomposition (scheme 3, reaction 15). R"O° and R''OO° are fixed on the polymer chain and they can also abstract H° from a polymer chain, forming alcohol or hydroperoxides, with formation of a new R"° which continues the propagation reaction (scheme 1 reaction 9 and scheme 7 reaction 34).

The possible termination reactions are reported in Scheme 4.



Scheme 4. Termination reactions

The reaction (scheme 4 reaction 19) allows the elimination of two alkyl radicals via their combination, with formation of a saturated product, or via disproportionation to give two non-radical products of which one is saturated and the other unsaturated, as may occur in termination of a polymerization reaction in solution. There are a number of results that show that secondary alkyl radicals in HDPE are stable for more than 15 hours after irradiation with γ–rays [98] and e-beam in inert atmospheres, whereas they decay rapidly in the presence of O_2 (Figure 3) [98]. ^{13}C solid state NMR analyses of PE show that early-stage cross-linking is only of the Y-type, i.e. reactions with vinyl and vinylidene double bonds in the amorphous phase, and not of the H-type, i.e. via the coupling of two macroradicals R"° [20,100–103]. This implies that the R"° formed are not able to react with each other during irradiation at RT. The coupling reaction between R"°, leading to their elimination, is therefore not feasible, at least for a radical population formed in this way. ^{13}C solid state NMR analyses of γ–irradiated LLDPE clearly show resonances from H-links, though in this case the polymer was irradiated to a very much higher (8 MGy) dose [104].

There is abundant evidence that the termination reaction in thermal oxidation [Scheme 4 reaction 22] of low MW materials under oxygen-saturated conditions is predominantly the Russell reaction between two peroxy radicals via an unstable tetroxide [105–107] with the production of a ketone an alcohol and oxygen. Aside from kinetic evidence, the expected formation of singlet oxygen can be detected both indirectly [104] and from its luminescence emission [105] in oxidation of low MW materials. This situation is general for oxidation of saturated hydrocarbons in solution because the overall reaction rate is relatively slow, so that oxygen saturation conditions are maintained, and the rate of H-abstraction by ROO° radicals is low. For more reactive substrates this may not be true. For example, Bateman and Morris [108] showed that all three termination reactions (scheme 4, reactions 19, 20, 22) are involved, as a function of the O_2 pressure, in oxidation of 2,6-dimethylhepta-2,5-diene, because the rate of H-abstraction by ROO° radicals is rapid due to stabilisation of the resulting R° radical, so that the R° radical is present in high enough concentrations to participate in termination. They find that Reaction 19 in scheme 4 is possible in solution but not in the solid phase at low O_2 pressure, up to 5mm Hg[108]The same situation can arise in melt processing of a polyolefin, where R° radicals are formed by mechanochemical scission and oxygen is largely excluded. Reaction 20 in scheme 4 is easier at higher pressures, above 100 mm Hg, and the Russell reaction (Scheme 4 reaction 22) is more likely in the presence of pure oxygen. As

we discuss below, the situation can also arise in radiation-induced oxidation, where initiation rates are high and oxygen depletion can be significant.

A number of authors have suggested that the relative immobility and stability of peroxy radicals in polyolefins disfavours the bimolecular Russell termination in the solid state at RT [74,91,109–111]. Termination might also occur between the peroxy radical, fixed on the polymer chain, and the sec-alkyl macroradical, which can migrate through the polymer, with formation of dialkyl peroxides

The results shown in fig 3 suggest the reaction between the R"° and R"OO° as described in the scheme 4, for the termination reaction 20 [98]. This reaction is not kinetically inhibited and it is thermodynamically feasible, provided that the oxygen concentration is low enough.

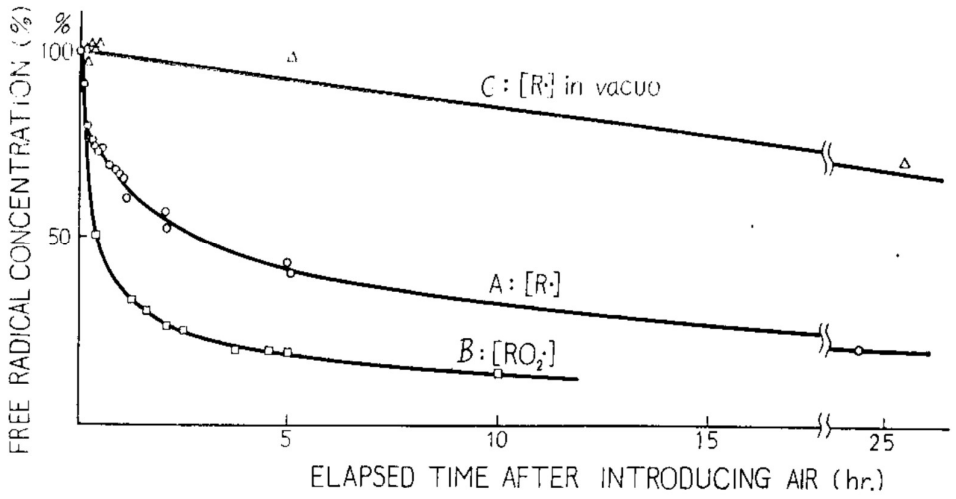


Figure3: decay after breaking vacuum of the free radical in HDPE electron beam-irradiated at - 78°C at 10 kGy and then stored at RT for 2 h. (A) measured at 1 mW, corresponds to the decay of R"°; (B) measured at 1 mW corresponds to the decay of R"OO°; (C) measured at 1 mW. shows decay of the R"° in vacuum. Reproduced with permission from [98]

An analytical method for the determination of peroxides has been reported in the literature [112]. However it is important to note that Carlsson wrote that “as yet there is not truly reliable analytical method to detect the low level of dialkyl peroxides expected from polyolefin oxidation” [74]. This is especially true given the need for analysis of low concentrations of ROOR in the presence of ROOH. Some confirmation of possibility that the formation of dialkyl peroxides may occur is given by kinetic modelling studies of sample thickness and oxygen pressure effects on oxidation which show better fits if the P ° + PO_2° reaction is included [113]

PE that has been irradiated with γ -rays in air can display a significant concentration of peroxides [73].The thermal decomposition of peroxides is complex and does not always produce radicals [114]. It was reported that the decomposition of peroxides can lead to the formation of esters via a non-radical mechanism [115]. Since esters are thermally stable this reaction will reduce the rate of initiation under conditions where hydroperoxide decomposition to radicals is concurrent [78,115].

4. Propagation reactions

Propagation is the key reaction of the cyclic radical process, in which the R"° react with the chain imperfections, with oxygen and with the additives present in the polymer, forming in one step a saturated molecule or, in two steps, ROOH and another radical species able to react further

The concentrations of the species that can be found in the amorphous phase of various types of PE are reported in Table 1 [1]. Where oxidation is initiated by radiation, the received irradiation dose generally depends on the instrument used, but can be calculated from the concentration of vinylene species formed during irradiation [116,117]. The concentration of macroradicals formed at -190°C is reported in [2,37] for HDPE and, considering that at RT only 4% of radicals produced in HDPE are still present it has a value of about 2 mmol per 30 kGy of irradiation.

Table 1: Concentration ranges in mmol l^{-1} of the various species present in various PE types.

Species	-CH=CH_2 Vinyl [34]	>C=CH_2Vinylidene [34]	-CH=CH- Vinylene [34]	O_2 [64]	Radical formation at RT [27]	CH_2 in PE amorphous phase for 50% crystallinity
Conc. mmol/l	3 - 30	0 - 25	4-5 mmol l^{-1}/30 kGy	>5 Function of crystallinity.	2 mmol l^{-1} / 30 kGy	$34x10^3$

The solubility of O_2 in polyethylene has been reported to be around 0.1-1 mmol/l, as derived from permeability and diffusion measurements [33,118,119]. The concentrations of ROOH have recently been determined, after reaction with NO, from spectroscopic measurements of the inside of orthopaedic prostheses that had been irradiated with differing doses of γ–rays in O_2 saturated conditions. They were found to be constant. in the centre of the prosthetic component [120,121]. It can be supposed that all of the oxygen present in the amorphous phase of UHMWPE reacted with the R"° present, that it terminated the oxidation through the reaction scheme 4 reaction 20 and that it is present in at least the same concentration as the oxidised products (bound and free ROOH and ketones); 5 mmol/kg.

The possible, competing propagation reactions are as follows:

R"° + (double bonds in the chain) → crosslink + new radical (scheme 5 reaction 23,)

R"° + O_2→ oxidation products + free radical (scheme 7 reactions 29, 30)

R"° + ADH → R"H + AD° (scheme 5 reaction 26)

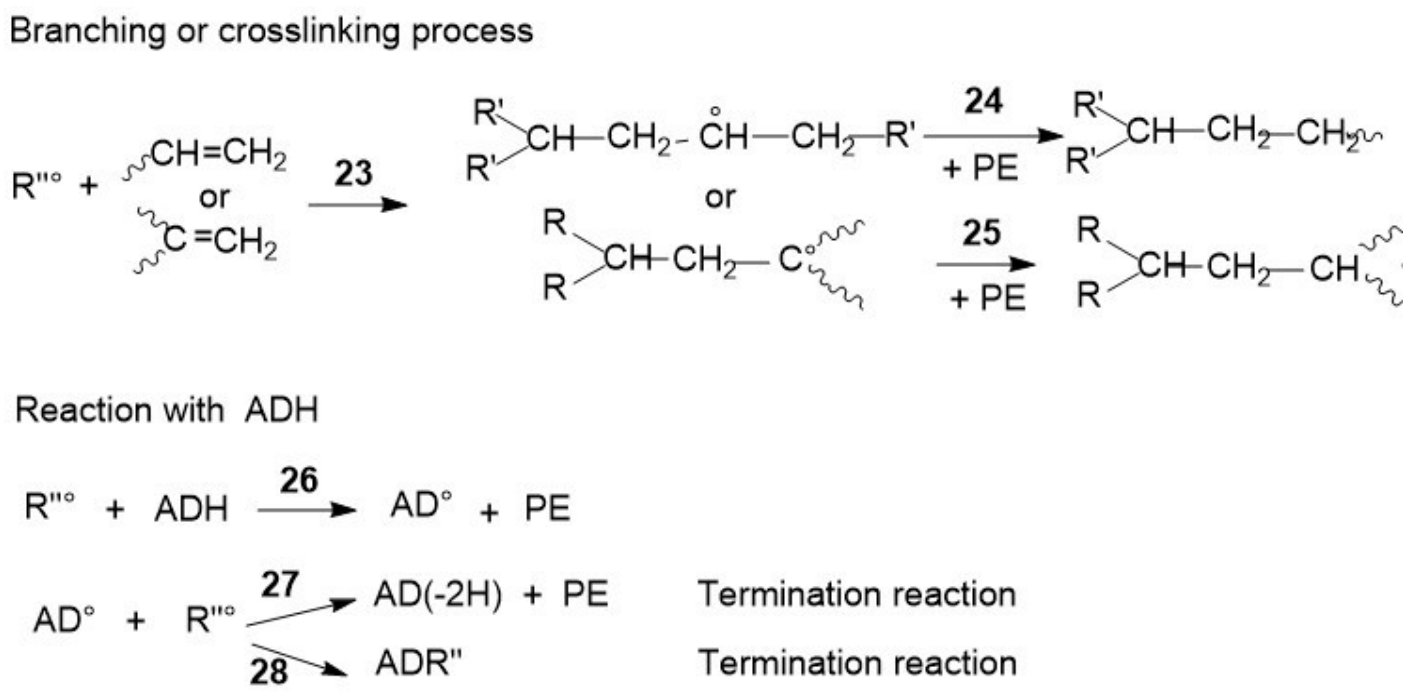
The rates of these steps can be described as:

$V_1 = k_{23}$ [R"°] [vinyl and vinyldene double bonds]

$V_2 = k_{29}$ (or k_{30}) [R"°] [O_2]

$V_3 = k_{26}$ [R"°] [ADH]

Reactions scheme 5 reaction 23, scheme 7 reaction 29 and 30 are exothermic, feasible from a thermodynamic point of view. Reaction 26 is an H-atom abstraction. It is a process which occurs rapidly at RT and is thermodynamically feasible [95]. However, it is only a propagation reaction, if the AD° radical is able to reinitiate R"° formation – otherwise it is a termination (or retardation), particularly if AD° can react again with R"° as in the reaction scheme 5 reaction 27 and 28.



Scheme 5: Branching, crosslinking and additive reactions.

4.1 **Propagation reaction with chain imperfections, vinyl, vinylidene and vinylene double bonds. Branching and crosslinking reaction.**

When UHMWPE is irradiated, the vinyl double bonds, fixed on the polymer chain in the amorphous phase, monosubstituted and not sterically hindered, immediately decrease in number, via an addition reaction, with branching or crosslink formation which depends on the initial PE chain length, on the number of double bonds and the irradiation dose. (Scheme 5 reaction 23) [44,45]. The reaction, similar to polymerization by addition to a double bond, is exothermic. The same reaction can take place with lower efficiency even with the 1,1-substituted vinylidene double bonds, albeit that they are partially sterically hindered However it is prevented for steric reasons for the 1,2-disubstituted vinylene double bonds which are formed during irradiation [122].

During irradiation it is possible to detect the decrease of the double bonds and a corresponding increase in branching until the vinyl double bonds are completely consumed. Therefore, the crosslinking density is a function of the concentration of double bonds and of the irradiation dose. Additives with at least two vinyl double bonds on the same molecule can be used to promote crosslinking [102,103].

4..2. Influence of stabilizing additives on chain propagation

Generally speaking, stabilizing additives are chosen to be molecules which contain easily abstractable H-atoms and produce AD° radicals which are too stable to reinitiate. As mentioned above, the possibility of reaction between two species is related to their encounter, which in the case of the interaction among the macroradicals present, R "° and ROO ° with ADH, depends on their ability to move.

As previously seen, R"° have the possibility of moving in the polymer mass. ROO° radicals are bound to the polymer chain and their mobility is limited to that of the polymer chains. In this situation, the most probable reaction for ROO° is the abstraction of a H atom from a neighbouring polymeric chain, with formation of R"°; and of a hydroperoxide (Scheme 7 reaction 30).

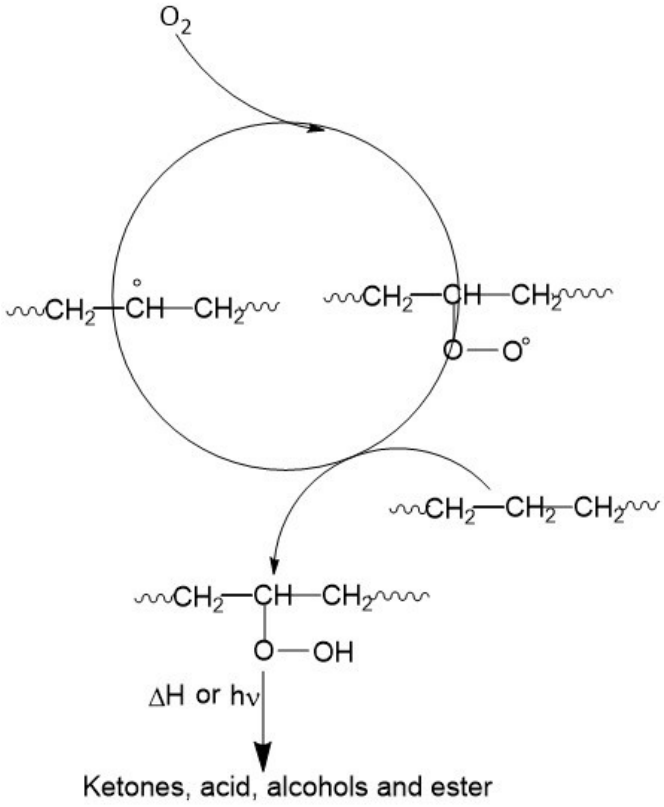
The mobility of additives (ADH) in the polymer mass is related to their diffusion coefficient (D), hence to their molecular mass. D is at least one order of magnitude smaller than that of oxygen [120].

Klemchuk [123] reports the transformation of some additives present in PP, after γ–irradiation in the presence of air. In the presence of a stabilizing additive (ADH), R"° react with ADH with formation of a stable or permanent radical of the additive (AD°) (Scheme 5 reaction 26). Phenolic chain-breaking antioxidants, such as Vitamin E, can react with the R"° produced by γ or e-beam irradiation, as reported in the literature, both in the presence and in the absence of oxygen. (Scheme 5 reaction 26) [124,125]. In an inert environment, the disappearance of vitamin E is slightly more effective than in air. This decrease can be related to the termination reaction due to the presence of oxygen (Scheme 4 Reaction 20) [125].

If the reaction product is unable to initiate further oxidation, then there is a decrease of the concentrations of all radical species, with the effect of permanent stabilization. Which radicals are captured depends on the relative population of R"° and ROO° species. Radicals may react further with the AD° radical depending on their structure. Coupling may be possible if there is no steric hindrance (Scheme 5, reaction 28), or there may be abstraction of a second H-atom from the additive molecule [78] (Scheme 5 reaction 27). Whilst it is generally assumed that reactions with ROO° are dominant, reactions with R’’° radicals are also possible [78,125–127]. In some cases, depending on the Vit E concentration and irradiation dose, AD° and AD-2H can react with the R’’° and bond permanently to the polymer as a result of the termination reaction [127,128].

4.3 Propagation reaction with oxygen: oxidation.

Bolland [129]studied the oxidation of hydrocarbons in solution at the end of the 1940s and, since then, it has been common to apply this study to the oxidation of polymers. Oxidation, according to Bolland, is described in scheme 6. Essentially, it is believed that the primary products are the hydroperoxides which then decompose, leading to the formation of all other oxidized products and to branching of the kinetic chain with consequent auto-acceleration of oxidation. As described earlier, this argument presumes that oxidation takes place under conditions where hydroperoxides are sufficiently unstable to decompose at finite rates. This may not be entirely valid for oxidation in the condensed phase of PE at low temperatures particularly for oxidation induced by γ– or e-beam irradiation.



Scheme 6. Bolland Cycle

The oxidation behaviour of products formed during γ-irradiation of LLDPE in air [5,73], after γ–irradiation of HDPE in post irradiation oxidation [73–76] and after e-beam irradiation of several PEs [16,17,38,67,118] has been studied. In all the cases the processes were conducted at temperatures below 40°C, at which temperature the hydroperoxides are thermally stable [79,96].

In those studies [5,73–76,120,121], the rate of formation of all species during ongoing irradiation was found to be proportional to the absorbed dose of γ-rays, thus to the amount of macroradicals produced. It follows that, as expected under those conditions, all the oxidized species are produced in proportion to [R"°] and not to [ROOH].

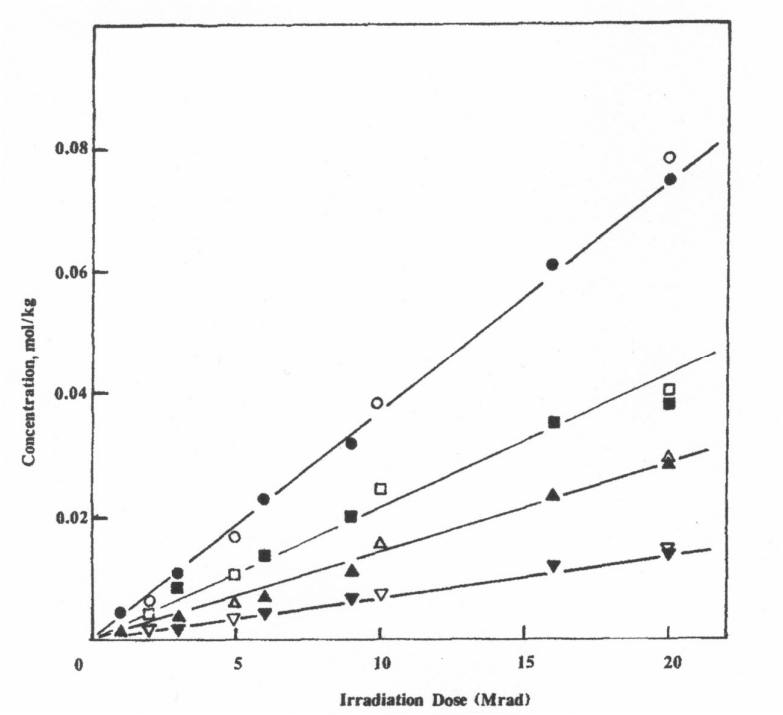
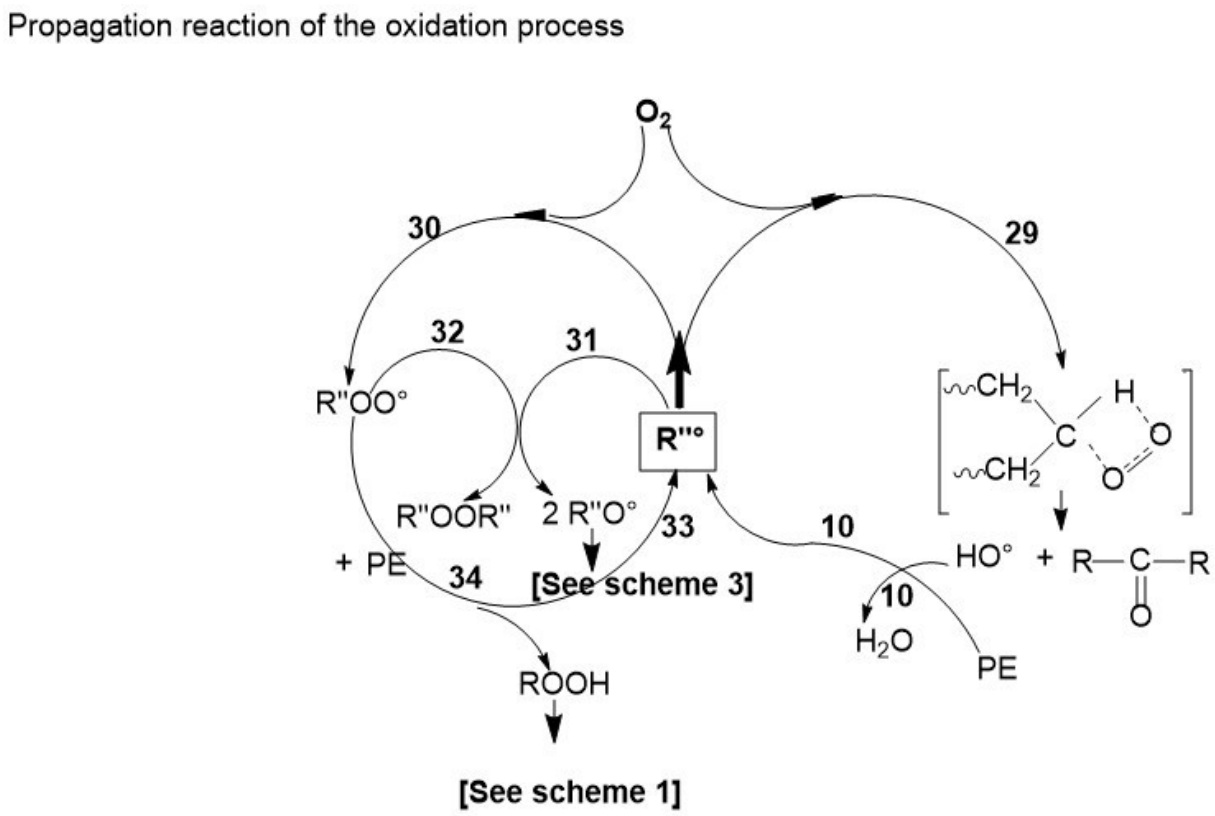


Figure 4: Oxidation products from theγ-initiated oxidation of PE films. Closed symbols HDPE; open symbols LLDPE: ● Ketone; ▲ carboxylic acid; ■ secondary hydroperoxide; ▼secondary alcohol. Reproduced with permission from [111].

In post e-beam irradiation oxidation of UHMWPE [77], the rate of formation of the products after irradiation ceased was always proportional to [R"°] but, since there is no on-going initiation, only the transfer of R"° from the crystalline phase, their formation rate reduced over time, while maintaining the same relationship between species, as termination was ongoing.

Oxygen has a measurable mobility in the polymeric mass through simple diffusion [33,118]. In the amorphous phase and possibly in the interphase, encounter between the oxygen and the polymeric macroradical (R°) occurs due to the oxygen mobility and the mobility of the R"° (scheme 7 reaction 29 and 30). All the reactions are exothermic and there are no limitations of steric hindrance, the oxygen being of minimal size.



Scheme 7. The propagation reactions between oxygen and secondary macroalkyl radicals.

Once locally consumed, oxygen penetrates from the air present outside the polymer and this process is controlled by diffusion. If oxygen is consumed faster than it can migrate, then the O_2 concentration will vary according to the distance from the external surface in contact with oxygen. For this reason, oxidation is often non-uniform [120,121].

The reported oxidation products in the two conditions, γ and e-beam irradiation are the same with slight variations in their concentrations: unbound and bound hydroperoxides, ketones, and to a lesser extent acids, alcohols and esters [1,5] and the volatile products (H_2O, H_2,CO, CO_2) [81,130]. These products appear to be the same as for thermal oxidation and photo-oxidation (in the latter case, apart from the products which are formed by Norrish I and II reactions) conducted at temperatures above 60°C [5].

In contrast to the work of Bolland [129], all of the oxidation products may be formed without decomposition of hydroperoxides, solely by reaction between the R"° and the oxygen and subsequent decomposition of the radical products, which occurs even at RT.

5. Critical products in the oxidation process.

R"° reacts at RT in the presence of O_2 and forms all oxidation products without any activation energy problems. The activation energy is exceeded at RT, but it is likely that some products will form at different rates, because the activation energies are not the same for all reactions, meaning that the ratios between the various species will depend on the oxidation reaction temperature.

5.1 Ketone.

Reaction 29 in scheme 7 shows the formation of ketones from the reaction between R"° and oxygen with the formation of an OH° radical which immediately forms a molecule of water and a R"° upon reaction with PE. It has been proven that the ketones and water form in equimolar amounts [131].

Depending on the temperature, ketones can also originate from hydroperoxide decomposition, via a "closed" process, which does not create new radicals and thus does not accelerate oxidation [5,74–78]. Furthermore, since the process takes place without further chain scissions, it does not induce any variation of the molecular mass and only minimum changes of the mechanical properties of the PE.

5.2 Hydroperoxides.

The R"° reacts with oxygen to form the peroxy radical, which in turn abstracts a H atom from a methylene to give a hydroperoxide (R''OOH) and R''°. The R"OOH are present as free and bound hydroperoxides. Then, if more oxygen is available, a second hydroperoxide may be formed, close to the first one, giving bound hydroperoxides. In contrast, if the initial alkyl macroradical migrates through the polymer before reaction with oxygen, the formation of a free hydroperoxide occurs. The concentration ratio of hydrogen-bonded and non-hydrogen-bonded hydroperoxides is constant in post-irradiation oxidation induced by e-beam irradiation [77]; therefore it does not depend on the alkyl macroradical concentration or on the irradiation dose. The half-life for decomposition of hydroperoxides during thermal degradation of PE in the solid state at 120°C is of the order of 30 min [77,79,96].

5.3 Carboxylic Acid (RCOOH)

Acids are produced by a mechanism which has not yet been conclusively elucidated [99,132,133]. In the oxidation of PE, the trends of their formation appear to be similar to those reported for ketones and hydroperoxides. Acid formation must involve the cleavage of the polymer chain. Direct splitting of C-C bonds of the polymer chain at RT is very unlikely, the bond energy of C-C bonds being at least 320 kJ/mol for the weakest link, the C-C alpha to a double bond. It is thus necessary to propose the breaking of a C-C bond in some species in which the bond energy is lower. Some reactions for formation of the acids are postulated in the literature [99,133]. In photo-oxidation, acids are the most important product [99]. Photo-oxidation also involves Norrish I photo-reactions, the latter leading to the formation of an alkoxy radical (Scheme 1 reaction 11). The formation of a primary macroalkyl radical, as seen previously (Scheme 3 reactions 15, 16 and 17), can be caused by the decomposition of an alkoxy macroradical. Oxidation of the primary macroradical and subsequent primary hydroperoxide decomposition can then lead to the formation of acid as previously suggested [99,132].

5.4 Sec-alcohol (R_2CHOH)

Alcohols can be formed via H-abstraction from the polymer chain by an alkoxy radical (Scheme 3, reaction 9), which competes with the β-scission reaction. (Scheme 3, Reaction 14). Their presence can be determined by FTIR after their transformation into nitrites by reaction with NO [3,4]. They are always found in oxidation processes, at low concentration.

5.5 Ester.

Ester and lactone formation occurs during oxidative degradation, although the precise mechanism is also not completely clear. These species can also be formed during mechanical degradation, e.g. during microtoming of thin films from PE rods. Costa et al. have shown that esters can be formed by the decomposition of macroalkyl peroxides formed during cutting, in a process which does not produce macroradicals [78,115].

6. 1 Oxidation during the post-irradiation period.

In the case of post-irradiation oxidation of PE, that is, after irradiation ceases, the rate of initiation V_I due to the irradiation is zero in the amorphous phase, i.e. macroradicals are no longer produced by irradiation. However, macroradicals (R"°, R_{all}° and R"'°) present in the crystalline/interphase can be transferred into the amorphous phase at a rate which is a function of the dimensions of the crystallites. R"° then reacts with O_2 and produces new R"° and oxidised products including ROO°. The termination reaction is therefore possible.

6.2 Comparison of oxidation induced by gamma irradiation, thermal and photo-oxidation

The oxidation products that form in the amorphous phase during reactions induced by γ-irradiation are the same as those formed in thermal oxidation and exist in very similar concentration ratios [49, 100]. Any differences may be due to different reaction temperatures. It can be supposed that the propagation processes are the same for both oxidation types. Carlsson [5] states that the oxidation products from the thermal oxidation derive from a reaction between alkyl radicals and O_2 and cites Mayo as evidence [73].

The literature reports three articles [5,134,135], which use two LLDPEs, co-polymerised with hexene and photo-oxidised with two different accelerated tests (Sepap 12-24 MPC and Weather-Ometer 2500 W) and a single photo-oxidised sample in natural conditions in Salerno, Italy. The FTIR spectra of the oxidation products are very similar which leads to the conclusion that the processes in nature and in the accelerated tests are the same and also similar to the thermal and γ-ray induced processes [5].
The propagation of the oxidation cycle is the same whether the cycle is initiated by radiation or the thermal or photolytic decomposition of hydroperoxides [5,77]. Working at different temperatures can lead to minor variations in the composition of oxidation products, in particular, in photo-degradation, due to the Norrish 1 and 2 reactions.

7. Conclusions.

It is generally accepted that hydrogen atoms, alkoxy and hydroxy radicals formed in a polymer at RT are highly reactive, very rapidly converting to R"° by H-abstraction (or β-scission in the case of the alkoxy radical). The two significant radical types are thus R"° and RO_2° and their concentration balance determines the relative rates of the two kinetic chain propagation reactions:

$$R"° + O_2 \rightarrow [R"OO°] \rightarrow \text{ketones, acids, esters}$$
$$R"OO° + RH \rightarrow R"° + ROOH \rightarrow \text{further decomposition}$$

The first reaction is essentially encounter controlled, with an activation energy in solution close to zero. In the more restricted environment of a polymer, one might expect a higher E_a but it is hard to envisage its being larger that the value for diffusion of oxygen in the bulk polymer, which is of the order of 40 kJ mol^{-1} [95], and it is likely to be locally very much lower at least in oxygen-saturated conditions. In contrast, the second reaction is usually very much less facile, since R"OO° radicals are much more stable than R"°, and has a significantly higher activation energy since it involves cleavage of a C-H bond. It is thus reasonable to expect that as long as there is a high enough [O_2], R"OO° radicals should be the dominant species.

Most discussions of oxidation are concerned with the technologically important conditions of long-term thermal or photo-ageing, where polymer lifetimes may well be in the order of years or even decades. Materials generally undergo accelerated tests in order to have information about the efficiency of an additive in a short time period. PEs tested under real conditions produce the same

trends and the same oxidation products as those that undergo accelerated tests [111,112].The mechanisms of initiation in these conditions are very little understood but it is widely assumed that they involve the thermal decomposition of hydroperoxide traces and the photochemical decomposition of hydroperoxides and ketones left in the polymer as a result of processing.

Since hydroperoxide and ketone concentrations in newly-processed polymers are immeasurably small, the initial rates of initiation, whether photochemical or thermal, are extremely low and radical concentrations of whatever type are sub-micromolar, the radicals all being located in amorphous regions since ROOH and ketone groups must be rejected by the crystal growth fronts during crystallisation. Indeed, radical concentrations in "normally" oxidising polymers are too low to be detectable by EPR spectroscopy. Given that saturation oxygen concentrations are millimolar, it is to be expected that R° species will rapidly convert to R"OO° and oxidation products as long as there is no significant diffusion limitation.

The thermal and photochemical instability of ROOH and the photochemical instability of ketones leads to kinetic chain branching and reactions of the R'O° radical lead to chain scission which is linked to the production of acids, while methyl ketones are produced by photo-oxidation, which is the critical process in controlling mechanical properties and hence failure. There is a great deal of accumulated evidence in support of this model, in particular the products of reaction of hindered phenols in oxidising polymers are usually dominated by oxidation products derived from R"O_2° radicals, whereas stabilisers designed to react efficiently with R° radicals are most effective under oxygen-deficient conditions

The situation in radiation-induced oxidation, typical of radiation sterilisation and crosslinking, is somewhat different. Radiation-induced oxidation is carried out at low (near RT) temperatures. As the temperature is lowered, all other things being equal, the rate of reaction of R"° with O_2 will not slow very much whereas the rate of conversion of R"OO° back to R° species should slow much more due to its higher E_a. This would suggest that R"OO° radicals should be even more favoured as the temperature is lowered. However, R° are produced in very high concentrations; even allowing for the loss of 95% of radicals before oxygen exposure, [R°] is 4-5 orders of magnitude greater than in more common conditions. At the same time, at low temperatures, hydroperoxides are stable at least in the timescales usually studied. It is perhaps not surprising then that some differences in chemistry are observed. Of course, the situation may be different at very low dose rates and over very long timescales, where hydroperoxide decomposition and radiation-induced generation of radicals can compete [136]

In radiation-induced oxidation of PE, secondary alkyl macroradicals formed in the crystalline phase during irradiation can move into the interphase and/or the amorphous phase although it is not clear whether this movement is due to chain diffusion, H-transfer migration or a combination of the two. During this process they can react with vinylidene double bonds and form allyl macroradicals in the crystalline phase which are stable for a long time due to resonance stability and steric hindrance. In the amorphous phase, alkyl macroradicals, whether migrating from the crystalline regions or formed by radiation, (or by photo- or thermal decomposition of hydroperoxides and ketones) may encounter reactive imperfections in the chains, particularly double bonds, reactive molecules, which take part in propagation reactions leading to branching or crosslinking and formation of new polymer radicals. They may also react with oxygen in the conventional propagation reactions. Oxygen is consumed, while oxidised products and hydroperoxides are produced along with new alkyl macroradicals. The consumed oxygen can be replaced by diffusion from outside. This process is linked to sample thickness and to oxygen diffusion in the polymer. As discussed earlier, the balance of ROO° and R° species is determined by the oxygen concentration at any particular point.
The nature and concentration of C=C bonds in PE's of different types is also very important in processing. Under the high temperature, shear, and oxygen deficiency conditions of typical processing, alkyl radicals are again expected to be the dominant species (although, being produced by shear-induced scission, they are predominantly primary radicals), and their reactions with

different types of C=C bond determines whether the polymer undergoes scission or chain extension during melt processing [137–139]

Typical stabilizing additives of the H-acceptor type react with both alkyl and alkyl peroxy radicals, the balance depending on the stabiliser structure and the relative concentrations of R"OO° and R° species. In an effective stabiliser the initial AD° product is too stable to reinitiate the oxidation cycle though it usually reacts with a further radical in a termination step.

Additives and imperfections are consumed by their interaction with radicals. New products from processing additives may react further with alkyl macroradicals and possibly oxygen already present in the polymer mass.

Whether oxidation is carried out under conditions where hydroperoxide products are stable or not, similar oxidation products are formed. At low temperatures they can be formed without the necessity of decomposition of hydroperoxides to form radicals, as generally reported in the literature.

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Schemes

Scheme 1. Initiation of the high energy induced oxidation process. Induced by both thermal and photo- energies.
Scheme 2.Norrish II reaction.
Scheme 3.β scission process of alkoxy radicals.
Scheme 4Termination reaction for the oxidation process.
Scheme 5 Branching and termination reactions in the presence of additives.
Scheme 6 Bolland cycle.
Scheme7 Oxidation process.