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Energy transfer in polymers submitted to ionizing radiation: a review

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Abstract

As a result of the energy deposition of ionizing radiation in organic polymers and in organic compounds in general, excited and ionized species are formed. The latter can readily react with emitted electrons to form excited species that will eventually lead to macromolecular defects and gas emission - their counterpart. Charges from ionized species and excitations can also be transferred, and trapped, far from their creation sites before leading to defects creation. In dense materials submitted to irradiation, excitations, charge transfer or mass transport from one molecule to the other has been proven to happen since the early 1930's in organic molecules mixtures and the 1950's in polymers. Radical stemming from the evolution of the excited molecules, which results either from direct energy deposition by the radiations or from the electron-hole recombination, can also migrate before being trapped or reacting, on a site far from its creation site. Radical, excitation, electron and hole transfers are gathered in the generic term of energy transfer. In this review is presented an overview on the research performed in this field. We evaluate the influence of different parameters that can alter the efficiency of energy transfer: these can be related to the polymer composition (chemical structure of the molecules composing the monomers or the additives inserted in the bulk) or to the irradiation characteristics (radiation type among ionizing radiations, dose and temperature for example). To get rid of the complexity brought by the polymer structure and the existence of different levels of organization, polymers are sometimes modelled by molecules, either pure or as mixtures. To take this into account, some studies on energy transfer in molecule mixtures are also presented.

Keywords

Radiolysis; ionizing radiation / matter interaction; organic materials; polymers; energy transfer

Highlights

- Energy transfer along with their underlying mechanisms are defined
- Evidences of these energy transfer in organic molecules and polymers are given
- Irradiation parameters influence is evaluated

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Introduction

When submitted to ionizing radiations, organic compounds and polymers are modified. Radiolysis is initiated by the primary species (excitations, electrons and holes) created from the energy deposited in the matter during its interactions with the radiation. In the absence of groups or molecules able to stabilize either the holes or the electrons, the ions and electrons formed during the ionization process will recombine very rapidly and revert to excitations. The further evolution of these primary species leads to the formation of radicals, from which stems, in a large fraction, the chemistry in organic compounds and polymers submitted to radiations. This evolution of the primary species can take place on or very close to their creation sites or take place after they have migrated in the medium. This stands also for radicals. As organic mixtures and polymers can hardly be considered as isolated molecules, the migration of excitations, electrons, holes and radicals between molecules or chains, during the irradiation process, is expected (Burton and Lipsky, 1957; Charlesby, 1960; Rabek, 1996; Reichmanis et al., 1993). The migration of these unstable species, followed by their trapping, is gathered hereafter under the generic term of energy transfer. The molecules on which the energy is trapped are called hereafter energy sinks or acceptors[†]. Their stability after the energy trapping is an important parameter in the behaviour of the material under ionizing radiation, as their evolution defines the type of defects created, their creation efficiency and their localization.

In the dense media that are the subject of this review, the studies of energy transfer under ionizing radiation were first performed using small molecules in the liquid state, either pure or as mixtures (Manion and Burton, 1952; Norrish and Bamford, 1937; Schoepfle and Fellows, 1931); they are still studied as surrogates for polymers (Tilquin, 1991). The evidence of energy transfer in polymers under ionizing radiation were shown about two decades after they were first evidenced in small molecules (Alexander and Charlesby, 1955; Gardner and Harper, 1965; Witt, 1959). Most of the early studies aimed at modulating the radiation-induced behavior of polymers either by inserting molecules accelerating their degradation (Witt, 1959) or by adding molecules less sensitive than the polymer thereby increasing its radiation-stability (Slivinskas and Guillet, 1974).

Researches concerning energy transfer or their consequences, in polymers submitted to ionizing radiation, have continued since those first evidences and remain relevant in different fields. Research areas concern polymer stabilization or basic studies and are meant to improve the understanding of the mechanisms involved in the dose effect, the chemical structure influence being the most common topic of these studies (Ferry et al., 2016b; Seguchi, 2001; Ventura et al., 2016).

The aim of this review is to present, in a non-exhaustive way, the studies performed for improving the understanding of energy transfers in polymers submitted to ionizing radiations. As said in the beginning of this section, the term energy transfer gathers, electrons, holes, radicals and excitation transfers. We further separate them into species transfers and excitation transfers. After a brief presentation of species transfers and the conditions in which they occur, we will present the processes involved in excitation transfers, both in molecule mixtures and in polymers. We will continue by presenting first the influence of the material composition (mixture of molecules, physical mixtures of polymers and/or copolymers, be they random, block or grafted) and second the influence of irradiation parameters (such as the dose or the irradiation temperature) on energy transfer.

[†] An energy sink is a molecule or a chemical group in a molecule that is able to easily capture excitations, electrons, holes or radicals transferred from another component of the system.

Although a great number of studies on energy transfer in polymers under radiation were performed during the photolysis of polymers under long-wavelength UV (Guillet et al., 1991; Ng and Guillet, 1978), and aside from their potential interest in understanding excitation transfers, they are not taken into account herein as we focus on energy transfer occurring under ionizing radiations. The particular reason of this lays on the fact that, under long-wavelength UV only chromophores absorbing particular wavelengths are excited whereas the energy deposited by ionizing radiations is high enough to excite and/or ionize any molecule or atom of the target.

1. Definitions and mechanisms

The term “energy transfer” encompasses various forms of transfers: mass transport (radicals and ions) (Seguchi et al., 1991; Shimada et al., 1981), pure charge transfer (electrons and holes) (Hirsch and Martin, 1972; Tabata, 1991) and electronic excitation transfer (Grigoriev and Trakhtenberg, 1996; Rabek, 1996). In polymers above their glass transition (T_g), *i.e.* at temperatures above which long range molecular mobility and thus radicals’ migration in the amorphous phase is effective, it appears difficult to distinguish pure charge transfer from mass transport as the species transferred may be charged (Ferry et al., 2016a; Ranby and Rabek, 1977). Therefore, in the following, except when they can be discriminated, that is when the temperature at which the polymer is irradiated stands well below its T_g , pure charge transfer and mass transport will be considered as a whole and named species transfer.

1.1. Species transfer

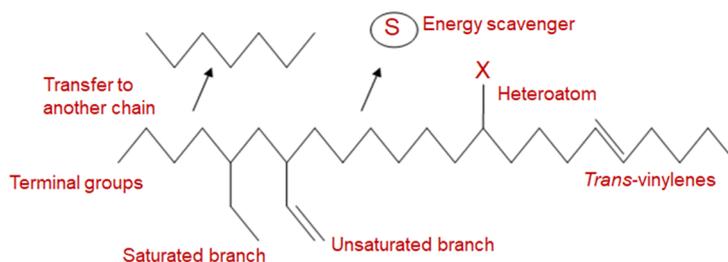
Charge transfer in polymers were first evidenced through the measure of radiation-induced conductivity (Hirsch and Martin, 1972). They are regulated both by the transport and the trapping processes. Transport may occur through the hopping mechanism, resonant charge transfer or tunneling (Partridge, 1972). For charge transfer to occur, the effective separation of the radiation-induced electron and hole is mandatory. As a consequence, in simple polyolefins with neither heteroatom nor conjugated bonds, the radiation-induced electrons and holes are tightly bound and revert readily to excitation so that charge transfer is hardly observed. To the contrary, provided one of the created charges (the hole or the electron) can be stabilized on a given site in the polymer (in the presence of an electrophilic or a nucleophilic center), charge transfer is observed. Net charge transfer was mostly studied in presence of aromatic molecules inserted in the polymer bulk - pyridine in most cases - or in the polymer chain (Zhang and Thomas, 1996). Besides, charge transport was shown to be very efficient, even at temperatures as low as 77 K (Thomas, 2007).

Charges can also be transferred as protons through the hopping or through the tunneling mechanism. The same processes can be observed for proton radicals (Waterman and Dole, 1971; Willard, 1987).

1.2. Excitation transfer

Under ionizing radiation, excitation transfer is the most discussed types for the two following reasons. Firstly, the hole and the electron tend, at one point of the polymer evolution, to revert to a polymer excited state and secondly, as the deposited energy is well over the molecule ionization energy, the charged molecules created are likely excited (Bouffard et al., 1995; Kinchin and Pease, 1955).

In the course of the process, the electronic excitation is transferred from an excited state of the donor (D) to the ground state of the acceptor (A). As exemplified in Scheme 1, this acceptor can be a scavenger (S), a heteroatom (X), an unsaturated bond or a terminal group; located on the same chain or on another chain or blended in the polymer bulk.

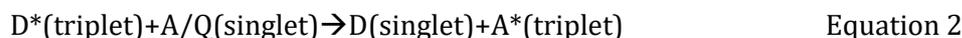


Scheme 1. Schematization of possible energy transfer routes in polymers under ionizing rays. Redrawn from Brede *et al.* (Brede *et al.*, 1996).

The electronic excitation can be transferred in the polymer either through radiative processes or through non-radiative processes. Radiative processes are not taken into account here as this review is interested in the chemical transformations induced by energy deposition and in the radiation-induced behavior mastery through the insertion of specific groups. Non-radiative excitation transfer can take place along three main processes:

- The exchange-resonant (or Dexter process),
- The induction-resonant (or Förster process),
- The molecular exciton process.

The first two processes imply reduced distances between the donor (D) in an excited state and the acceptor (A) in its ground state. Both processes are of the resonant type and each of them has its specificity (Grigoriev and Trakhtenberg, 1996). Based on the Wigner's rule (Terenin and Ermolaev, 1956), the spin multiplicity is conserved during the resonant processes. The exchange process can proceed through singlet-singlet (Equation 1) or triplet-triplet (Equation 2 - Q represents a quencher) transfers (Porter and Wright, 1959; Terenin and Ermolaev, 1956). In the latter case, the energy level of molecule A is necessarily lower than that of molecule D in the triplet state. Concerning the induction-resonant process, it preferentially takes place through singlet-singlet interactions, that is through Equation 1 (Förster, 1959).



The exchange-resonant process or Dexter process, proceeds through the exchange of an electron between a non-bonding excited orbital of the excited molecule of the donor and the ground bonding orbital of the acceptor. For this reaction to happen, a positive overlapping of the orbitals of the acceptor and the donor should be effective. This process is as efficient as the distance between D and A is small and as a strong interaction in the electron clouds is possible. Its efficiency decreases exponentially with the distance between the molecules (Dexter, 1953) and the maximal interaction distance is comprised between 10 and 20 Å; depending on the experimental conditions. For instance, for small molecules in non-viscous solvents at room temperature, the maximum distance of interaction is calculated to be lower or equal to 15 Å (Turro, 1977).

The ***induction-resonant process*** is also known as the Förster energy transfer process. This mechanism is based on coulombic interactions between the electrons of the donor in its excited state and those of the acceptor in its ground-state. This process is considered as a dipole-dipole interaction and occurs on longer ranges than the Dexter process. However, for the transfer to occur through the Förster process, the donor emission spectrum and the acceptor absorption spectrum should overlap. Transitions will thus proceed between dissimilar molecules in an intermolecular mode in non-isolated molecules systems, or in an interchains mode in polymers (Levitsky et al., 1999; Rose et al., 2007).

Dipole-dipole interactions can take place either between single molecule dipoles, higher multipoles or vibrational-induced dipoles. These weak interactions more often take place from the lowest vibration level of the D* molecule and the process is efficient in D*/A couples where both the quantum yield of emission of D* and the absorption of the acceptor A (*i.e.* high extinction coefficient, ϵ) are important and in presence of a strong coupling factor. In the absence of molecular diffusion, the transfer efficiency decreases with the distance between molecule D* and A, through a $1/r^6$ function. The maximal distance of transfer is included in the 50-100 Å range for an extinction coefficient of A of about 10^5 . This range will be lower for A molecules with lower ϵ values and may become inexistent for ϵ below one (Turro, 1977). As for the Dexter process, in presence of multiple molecules, the energy can migrate from one molecule to another.

The molecular exciton process implies long distance migration and the subsequent trapping of the molecular exciton on an acceptor. As reported by Partridge (Partridge, 1972), molecular excitons were defined by Kasha as “neutral excitation particles consisting of travelling electron-positive hole pairs that are bound together roughly within the confines of a single molecule or molecular units”. For the molecular exciton transfer mechanism to take place, the energy of molecular interactions must be high enough and the excitation relaxation time should be higher than the time necessary for the transfer itself. The minimum molecular energy is said to be of about 10^{-2} eV (Grigoriev and Trakhtenberg, 1996). The efficiency of these transfer is a composite of their migration and their trapping rate on a given acceptor.

According to Partridge, the trapping process entices coulombic interactions stronger than those prevailing in the Förster process and which can happen from any vibrational state of the lowest level of the exciton band (Partridge, 1972). However, according to Grigoriev and Trakhtenberg (Grigoriev and Trakhtenberg, 1996), the trapping can also occur through exchange interactions. Therefore, instead of using the $1/r^6$ law, the use of the absolute black sphere model is more accurate to define the transfer efficiency of an exciton to an acceptor. A given exciton will thus be captured only if it is at a distance lower than the capture radius. This radius was shown to be relatively small: around four ethylene fragments in polyethylene containing *trans*-vinylene groups as acceptors (Ventura et al., 2016).

The molecular exciton migration can proceed through diffusion, through intermolecular transfer or through intramolecular transfer. In the situation where the molecular mobility is impeded, without being frozen, as in polymers above their T_g , the excitation energy can migrate along a given chain or between two chains, from D* to A, either in presence of delocalized electrons in the said chains or in pure σ -bond chains through σ -bond molecular exciton migration. The σ bond exciton model, initially proposed by Raymond and Simpson (Raymonda and Simpson, 1967) for small alkanes, was extended to polymers by Partridge (Partridge, 1970b, c). To sum up, the excitations created through direct interaction between ionizing radiation and the polyolefin (the excitations stemming for ion-electron recombination are not accounted for in this model) are parted in two categories. The first is dissociative and is located on C-H pairs and is non-transferable and thus not quenchable. The second is non dissociative and can be

transferred on long distances (up to 1500 Å in a perfect polyethylene), mainly along the chain through C-C bonds and less frequently between chains. For this second type, the migration happens until the excitation is trapped by a molecule with an excitation energy comprised between 7.5 and 9.5 eV or when it reaches end-chains, where C-C and C-H excitations are mixed. Although the σ -bond exciton theory focused on excitation trapping in defects covalently bound to the polymer chain, excitation transfer to foreign molecules inserted in the polymer bulk are worth considering and have been used as additives for decades for polymers stabilization.

As a summary, it can be concluded from the excitation transfer processes presented above, that the Dexter process will be intramolecular whereas the Förster and the exciton transfer processes would happen either in an intramolecular (intrachain in polymers) or in an intermolecular (interchains in polymers) mode.

2. Influence of the material composition

The transfer process involved in liquids or in polymers, its rate and its efficiency will depend on:

- The system composition, *i.e.* the chemical and the electronic structures of molecules,
- The donor and acceptor environments,
- The donor and acceptor mobility in the system,
- The distance between the donor and the acceptor, *i.e.* their concentration in liquids in the case of small molecules or in polymers acting as a solvent.

Small molecules have been used since pioneering works to assess the polymers behavior under ionizing radiation (Avivi and Weinreb, 1957; Ferry, 2008; Ferry et al., 2013; Miller et al., 1956; Tilquin, 1991). Therefore, as long as it is kept in mind that some process characteristics such as the rate and the efficiency may change with the molecule length and mobility, presenting the studies dealing with energy transfer in small molecules in the present review is aimed for a better comprehension of these processes in polymers.

2.1. Organic molecules

Energy transfer can take place either inside a given molecule (intramolecular) or between different molecules (intermolecular). From a practical point of view, most studies on energy transfer in organic molecules are related to the intermolecular route as they focused on the stabilisation of a saturated molecule in presence of unsaturated molecules, aromatic or not. Aromatic molecules were initially the most studied ones as they were meant to stabilise the otherwise highly radiation-sensitive aliphatic molecules. One of the most studied couple is cyclohexane/benzene: benzene stabilizes cyclohexane even at very low aromatic moiety concentrations (Foldiak et al., 1992; Freeman, 1960; LaVerne and Dowling-Medley, 2015; Manion and Burton, 1952; Schoepfle and Fellows, 1931; Stone and Dyne, 1962). In most of the studies related to the cyclohexane/benzene systems, energy transfer was assessed through the quantification of gas emission, mainly hydrogen. Unfortunately, this gas can come either from cyclohexane or from benzene and does not really give information on the fate of each molecule. As hydrogen emission comes preferentially from the cyclohexane moiety, it was generally surmised that the reduction in hydrogen emission, more important than what is expected from the mixture law, is coherent with energy transfer from cyclohexane to benzene, thus reducing cyclohexane dissociation (Foldiak et al., 1992; Freeman, 1960; LaVerne and Dowling-Medley, 2015; Manion and Burton, 1952; Schoepfle and Fellows, 1931; Stone and Dyne, 1962). Most of

these early studies resulted in the conclusion that the cyclohexane was stabilized by benzene with no effect on the benzene; the absence of effect being explained by an energy release under the form of heat by double bonds delocalization in the benzene molecule. This mechanism was named the sponge-type protection mechanism (Chapiro, 1988; Dole and Williams, 1959).

Only few studies interested in specific defects created in both molecules concluded in an increase in the creation of radiation-induced defects specific to benzene. For instance, Manion and Burton (Manion and Burton, 1952) showed that the radiation chemical yield of acetylene, a gas specifically released from benzene in cyclohexane/benzene mixtures, increases more than what is expected by the law of averages when benzene concentration decreases in the liquid mixtures. This aromatic sensitization was later confirmed by Ferry *et al.* (Ferry, 2008; Ferry *et al.*, 2012, 2013) who evaluated, at 11 K and using Fourier transform infrared spectroscopy (FTIR), the initial destruction of benzene molecules, the creation of new defects in benzene molecules and the creation of defects specific to cyclohexane, as a function of the benzene fraction. It appeared from these studies that conversely from the pioneering studies stating the harmless thermal dissipation of energy in benzene, this aromatic molecule protects the cyclohexane moiety at its expense. Within the same idea, energy transfer was studied in conditions where the donor and the acceptor are part of the same molecule, in an attempt to assess the relative efficiency of intramolecular and intermolecular transfer. This was for instance performed in phenylcyclohexane irradiated using X-rays and γ -rays (LaVerne and Dowling-Medley, 2015; Ohnishi *et al.*, 1962; Schoepfle and Fellows, 1931; Zeman and Heusinger, 1966). Comparisons between hydrogen emission and the creation of the benzene-ring specific defects between phenylcyclohexane and a 50/50 cyclohexane/benzene mixture showed that intermolecular and intramolecular transfer in these liquids are equally effective; whatever the irradiation nature (LaVerne and Dowling-Medley, 2015).

Apart from alkane (mostly cyclohexane)/benzene mixtures, various other mixtures of alkane and molecules containing energy sinks (unsaturated bonds - conjugated or not - or heteroatoms) were studied, showing efficient energy transfer from the alkanes to these molecules. As an example, in the nuclear power industry, many processes bring together organic molecules and radionuclides: in these studies too, intermolecular as well as intramolecular energy transfer have been evidenced. Solvent extraction is used in the spent fuel reprocessing step: in the PUREX process[‡], the extracting molecule, tributylphosphate (TBP) is used along with dodecane - or an equivalent - as diluent and both are irradiated. The gas emission, mainly hydrogen and methane, was found to show a clear deviation to the law of averages, evidencing energy transfer between TBP and the alkane used as solvent (Holland *et al.*, 1978). Stearates, used as lubricants either in the nuclear fuel manufacturing or in the waste package conditioning, mainly undergo decarboxylation: the preponderant degradation mechanism of fatty acids under irradiation (Jones, 1971; Williams, 1962). This was later attributed to energy transfer from their aliphatic segment to their carboxylate function (Gracia *et al.*, 2018; Lebeau *et al.*, 2015; Lebeau *et al.*, 2017), irrespective of the associated cation and of the irradiation atmosphere.

Organic molecules are of high interest to evaluate the polymers behavior under ionizing radiation, as they are less complex systems (Foldiak, 1981). However, as Tilquin already pointed out from the middle of the 80's (Tilquin, 1991), differences in the molecular scales have to be accounted for. Indeed, studies on models can reveal mechanisms not yet envisaged and avoid definite statements without sufficient evidences. Moreover, chain-ends (Soebianto *et al.*, 1992a; Soebianto *et al.*, 1993; Soebianto *et al.*, 1992b) and differences in physical properties between

[‡] PUREX: The PUREX chemical process (acronym for Plutonium and Uranium Refining by EXtraction) is a method for reprocessing nuclear spent fuel.

organic molecules and polymers should not be forgotten. Hence, only general tendencies can be drawn. By comparing linear polyethylene and one of its oligomer - the octacosane, Miller *et al.* (Miller et al., 1956) evidenced that with low chain-ends concentrations, *i.e.* in the polymer, gas emitted was almost only composed of hydrogen whereas with high chain-ends concentrations, *i.e.* in oligomers and/or in polymers with a high number of side chains, the ratio of hydrocarbons is highly increased. It was latter shown that C-C bonds at end-chains have a different reactivity (Partridge, 1970c): their scission probability is roughly seven times higher than that of in-chain C-C bonds, due to excitation energy trapping on these particular bonds and very rapid excitation transfer between in-chain C-C bonds (see σ -bond model in section 1.2). This difference in the scission probability at the chain-ends compared to the inner carbon-carbon bonds was later confirmed by Seguchi *et al.* (Seguchi et al., 1988), who showed that in the crystalline phase, chain scission proceed at the crystallite surfaces - only one or two carbon atoms depending on the crystalline lattice - and that, either in the amorphous or in the crystalline phase, inner bonds present a low scission probability. That means that, to understand thoroughly energy transfer mechanisms in polymers real polymers, even idealized ones, have to be studied.

2.2. Pure polymers

The early literature on energy transfer in polymers dealt with polymers containing conjugated bonds (Alexander and Charlesby, 1955; Dole and Williams, 1959). Energy transfer studies were performed in physical mixtures of homopolymers, in copolymers, and in homopolymers containing groups or bonds different from those constituting the repeating units, either in their backbone or as side chains that were inserted intentionally or resulting from the polymerization process.

Due to the quite reduced mobility of molecules in polymers, the optimized mixing of the units in the materials is of primary importance for energy transfer to effectively occur. Early studies with physical mixtures (blends in the solid state) of polymers tended to show either an absence or a very low efficiency of interchains energy transfer between macromolecules. As an example, radiation-induced crosslinking was shown to perfectly follow the mixture law in polybutadiene/polystyrene mixtures (Witt, 1959), evidencing an absence of energy transfer. In the same way, by studying polyethylene/polybutadiene mixtures, Dole and Williams (Dole and Williams, 1959) concluded on a very low efficiency of energy transfer from polyethylene to polybutadiene. However, as intermolecular transfer was shown not only to exist in small molecules but also to be efficient since very low acceptor concentrations, it can be surmised that the absence of intermolecular energy transfer in physical mixtures of polymers are due to an imperfect miscibility of the systems as proposed by Dole and Williams (Dole and Williams, 1959). Indeed, if a phase segregation exists, distances between acceptors and donors can become greater than the maximum migration length of 150 nm estimated from the σ -bond exciton model (Partridge, 1970b). Moreover, more recent studies using the black sphere model evidenced even smaller distances of energy transfer (Ferry, 2008; Seguchi, 2001; Ventura et al., 2016).

In copolymers, energy transfer is effective but their efficiency is a function of the copolymer type. Energy transfer efficiencies in block copolymers are close to those in physical mixtures (Basheer and Dole, 1984). This is also related to phase segregation because in this type of polymers, depending on the ratio between the two monomers, the distances between donors and acceptors may become very large compared to the optimal transfer radius. In the case of grafted polymers, energy transfer efficiency is expected to rank between the ones in physical mixtures of polymers and those in random copolymers. This hypothesis has been experimentally

confirmed for example in ethylene/styrene polymers: the styrene moiety efficiency in reducing the radiation damage in the aliphatic moiety in poly(ethylene-*g*-styrene) is higher than it is in polyethylene/polystyrene mixtures (Gardner and Harper, 1965) but is lower than the one observed in random copolymers (Mal'tseva et al., 1976). As a matter of fact, all sinks are heterogeneously located in the polymers; therefore, the concentration in these acceptors actually involved in the energy transfer is much lower than the real concentration of sinks in the polymer.

To understand energy transfer mechanisms under irradiation, random copolymers were by far the most studied materials. Can be cited poly(styrene-*co*-butadiene) (Basheer and Dole, 1984), poly(isobutylene-*co*-styrene) (Alexander and Charlesby, 1955), poly(ethylene-*co*-styrene) (Ferry et al., 2013; Ferry et al., 2019; Mal'tseva et al., 1976) or copolymers of ethylene and carbon monoxide (Slivinskas and Guillet, 1974) and polyethylene containing C=C double bonds (Dole et al., 1958; Miller et al., 1956; Seguchi, 2001; Ventura et al., 2016) or ester bonds (Ferry et al., 2014) as energy sinks. Comparing all these studies shows that the nature of the energy sink is very important, but that for a given energy sink, its position and configuration are also of great importance. The comparison of hydrogen release in ethylene-based polymers containing ester bonds showed a higher efficiency in energy transfer when the ester groups were located on the backbone, compared to when they were located on the side chains, whatever their concentration in the polymer (Ferry et al., 2014). This is in concordance with the work of Slivinskas and Guillet (Slivinskas and Guillet, 1974), who stated that energy deposited along a given polymer chain by the interaction with secondary electrons migrates principally along this chain, with few transfers between chains. However, focusing on excitation energy transfer, Dole *et al.* (Dole et al., 1958) supported the conclusions of Avivi and Weinreb (Avivi and Weinreb, 1957) who deduced that intermolecular transfer is more effective than intramolecular one.

As it was the case for organic molecules under radiolysis, only very few studies were interested in the fate of the energy sinks after energy trapping, although this is of a major importance on the further evolution of the system. As a matter of fact, the fate of the energy sink is subjected to its chemical structure and depends on the intermediary species formed. The sink under study can act either towards an increased stability or towards an increased degradation of the polymer under ionizing radiation. Aromatic rings have long been supposed to release the trapped excitation by the well-known sponge-effect (Chapiro, 1988); that is without being damaged (see section 2.1). However, it was relatively recently evidenced that the radiation protection effect conferred to the aliphatic moiety by the aromatic one happens at the expense of the aromatic moiety (Ferry et al., 2012). In their early studies, Dole and Williams (Dole and Williams, 1959) evidenced in ethylene/butadiene physical mixtures that the protection of polyethylene is performed at the expense of the polybutadiene moiety. Decades later, by using *ab initio* molecular dynamics, Ceresoli *et al.* (Ceresoli et al., 2005; Ceresoli et al., 2004) showed that excited C=C bonds, C=O bonds and HO-C=O groups evolve through different mechanisms after the exciton trapping. In the time span of the calculation (10 ps maximum) and under the assumptions used for the calculation, the exciton is deeply trapped on the ketone function, this ketone bond acquiring the characteristics of a single bond. *Trans*-vinylene groups experience radiationless electron-hole (e-h) recombination and the carboxyl groups undergo a dissociative non-radiative e-h recombination leading to CO₂ release. Depending on the de-excitation route of a given energy sink and its position in the polymer chain, the sink influence on the radiation behaviour of a given polymer can be defect-dependant and sometimes opposite between defects. One of the first studies acknowledging these seemingly opposite evolutions was presented by Slivinskas and Guillet (Slivinskas and Guillet, 1974) when comparing the effect of ketone on hydrogen emission and crosslinking on copolymers of ethylene and carbon monoxide.

2.3. Polymers and their stabilizers

Polymers are rarely perfect and are rarely used pure: various molecules acting as antioxidants, antirads or plasticizers are usually added to improve their properties and/or stability under usage. Those molecules are, in most cases, hindered amines or phenols (Audouin et al., 2012), and apart from their action as antioxidants to limit the oxidation chain reaction, they can also act as energy sinks thanks to the benzene ring.

Various authors (Brede et al., 1989; Soebianto et al., 1995; Wüdrich, 1974) have evaluated the efficiency of different aromatic molecules on the energy transfer as a function of the number of the aromatic rings, their concentration and their resonance for condensed polycyclic molecules. The radiation protection efficiency increases with the aromatic ring concentration (Soebianto et al., 1995) and with the resonance of the additive - thus the lowering of its lowest energy excited singlet state (Wüdrich, 1974). This result shows that in these systems, energy transfer occur mainly *via* excitation transfer, although charge and radical transfer, which is less efficient, may also take place. Using pulse radiolysis, Brede *et al.* (Brede et al., 1989) showed that in presence of phenols the main three protection reaction paths are: (i) excitation transfer along the polymer chain leading to the dissociative trapping with the additive, (ii) electron attachment to the additive and the subsequent formation of the corresponding radical by neutralization, and (iii) reaction of the polymer macroradical with the stabilizer.

As already pointed in the section dealing with pure polymers (section 2.2), because of the limited excitation migration distances, energy transfer implying additives can only be fully efficient in conditions of a perfect dispersion in the polymer matrix (Wüdrich, 1974). In regards to antioxidant, as they can be inserted only in the amorphous phase, solely this phase should be taken into account when considering their action under radiation (Seguchi et al., 2012).

3. Influence of the irradiation parameters

3.1. Influence of the dose

When a fully aliphatic polyolefin with no heteroatom is irradiated under low linear energy transfer (LET) radiation (γ , β or X-rays) the main radiation-induced defects are crosslinking or chain scissions depending on the presence or not of ternary and quaternary carbon atoms (Miller et al., 1954), C=C double bonds under inert atmosphere and C=O double bonds under oxidative atmosphere (Cambon, 2001; Ferry et al., 2016a; Ferry et al., 2020). The counterpart of these macromolecular defects (*i.e.* defects created in the polymer chain) formation is gas emission. The gas mostly emitted from polyethylene irradiated under vacuum is hydrogen, the concentration in small hydrocarbons increasing with the side chains in the polymer. Most of these macromolecular defects can act as energy scavengers and doing so interfere with the defect accumulation pattern when increasing the dose. The evolution of defect creation with the dose depends on the defect considered. In polyethylene, the *trans*-vinylene concentration increases with increasing dose then levels off. Minor unsaturated groups as vinyls or *trans-trans*-dienes follow the same pattern. Hydrogen radiation chemical yield decreases with increasing dose since very low doses and then levels off at high doses. The evolution pattern of H₂ emission as a function of the dose was first assigned by Seguchi (Seguchi, 2001) to energy transfer to radiation-induced C=C defects bonds acting as energy sinks. According to this author, one radiation-induced C=C bond protects by energy transfer about 800 -CH₂- methylene units, which corresponds to a sphere of 1.6 nm around the defect. This result assumes an equivalent

efficiency between intrachain transfer and interchains energy migration. This study was completed by Ventura *et al.* (Ventura et al., 2016) through the comparison, during irradiation under helium atmosphere, of pure polyethylene irradiated up to 10 MGy and of tailored polyethylenes containing variable concentrations in *trans*-vinylene bonds located in the main chain, at doses inferior to 100 kGy. These authors confirmed that the evolution of hydrogen emission (as well as *trans*-vinylenes, *trans-trans*-dienes and vinyls) as a function of the dose is due to efficient energy transfer towards *trans*-vinylenes and the subsequent trapping. However, the volume of protection they proposed (Ventura et al., 2016) is far lower than the one indicated by Seguchi (Seguchi, 2001): it was calculated to be only about 130 -CH₂- methylene units, which corresponds to a sphere of *ca.* 4 monomer units radius.

Under oxidative atmosphere, the main defects that accumulate in aliphatic simple polyolefins are C=O bonds, which are very efficient energy sinks. In a polyethylene irradiated under oxidative atmosphere, these defects will concentrate in the polymer as the dose increases, leading to the radiation-stabilization of the unmodified polymeric chains. As a consequence and as already introduced just above, hydrogen radiation chemical yield - for instance - decreases when the dose increases (Ferry et al., 2016b).

Trans-vinylenes formed under inert atmosphere and carbonyl groups formed under oxidative atmosphere are obviously not the only defects formed when polyethylene is irradiated. To evaluate the efficiency of the other defects in the energy transfer processes, pure polyethylene was irradiated at high doses and polyethylene containing chemically inserted C=C or C=O bonds irradiated at doses inferior to 100 kGy were compared (Ferry et al., 2016b; Ventura et al., 2016). These studies showed that, even though C=C and C=O bonds are the most effective energy sinks, energy trapping on other defects should be accounted for when their lower efficiency can be counterbalanced by their concentration. As an example, Ventura *et al.* (Ventura et al., 2016) have estimated that one crosslink - a defect formed under inert atmosphere - is able to protect *ca.* 60 -CH₂- methylene units. This is less than half the efficiency of *trans*-vinylene bonds but at very high doses when tertiary carbons concentration become important, their action becomes visible.

3.2. Influence of the irradiation type

As already indicated, long-wavelength UV irradiation is beyond the scope of this review; solely ionizing radiation are discussed here, *i.e.* γ -rays, e-beams and ion beam irradiations. The basic processes induced by swift heavy ion (SHI) irradiations are identical to those initiated by γ -rays or electron beams: ionization and excitation. The main difference comes from the spatial structure of energy deposition, which is profoundly heterogeneous for SHI. As a matter of fact during SHI energy is deposited in a cylinder around the ion path: the latent track. Most of the primary excitations and ionizations occur in a track core of a few nanometers created during the initial ion/electron interactions and the resulting secondary electrons of low energies. High-energy electrons emitted during ion/polymer interactions induce ionizations/excitations at larger distances from the ion trajectory, in the so-called track penumbra (Gervais and Bouffard, 1994; Ngonu-Ravache et al., 2015; Waligórski et al., 1986). This radial energy deposition pattern induces a radial distribution of the deposited dose. SHI irradiations are characterized by high linear energy transfer (LET) values, which means that energy locally deposited by SHI within the track is huge and thus induces specific damage processes that involve complex molecular rearrangements and collective atoms motion. The question is to know how these specific features interplay with energy transfer in polymers. Besides, modulating the LET can be of great help in a better understanding of the energy transfer mechanisms; especially in the bulk.

The use of swift heavy ion (SHI) irradiations in the study of organic molecule mixtures and polymers is relatively recent (Balanzat et al., 1994). In these organic materials when submitted to SHI, energy transfer does exist as long as fragmentation is impeded, that is as long as the LET remains below the LET threshold for fragmentation that is equal to $20 \text{ MeV}\cdot\text{mg}^{-1}\cdot\text{cm}^2$ (Ferry et al., 2020; LaVerne and Dowling-Medley, 2015; Ventura et al., 2016). However, the efficiency of these transfers varies somewhat between low LET irradiations (γ -rays, e-beam) and SHI: energy transfer is favoured in conditions of moderate excitation and ionization densities. This behaviour is generally assigned to the very high excitation and ionizing density in the core that induces important recombination. This leads to two features. First, the non-scavengeable energy fraction is slightly but noticeably more important at high LET than at low LET (Ventura et al., 2016). Second, all radiation-induced defects are located in highly concentrated defects domains, *i.e.* the tracks. As energy transfer occur on small distances, the number of them really intervening in energy trapping is lower than those created. As a consequence, at the same defect concentration, the increase in the protection of the unmodified backbone with increasing dose is less rapid under SHI than under γ -rays or e-beam irradiations.

The dependence of energy trapping efficiency with the LET was further studied by Furtak-Wrona *et al.* (Furtak-Wrona et al., 2019) for C=C and C=O bonds either located on the backbone or on side-chains. The energy transfer efficiency decreases with increasing LET but this decrease in efficiency is more rapid for C=C located on side-chains. Concerning C=O of the ketone type located on the backbone, no LET dependence is observed when considering their action on hydrogen emission. However, it was observed that carbon monoxide release, stemming from ketone destruction via Norrish-like type I mechanism, decreases with increasing LET. This implies that energy and radical transfers on these functions are less effective under SHI irradiations. This result is a clear indication of the dependence of the energy transfer on the defect nature in conditions of high LET irradiations; as already observed under γ -rays (Slivinskis and Guillet, 1974). It has already been indicated that at low LET, under vacuum, *trans*-vinylene concentration in polyethylene increases with increasing dose until it saturates. The same trend is observed under SHI irradiations but the concentration at saturation is higher. However, this conclusion is no more true for defects like vinyl bonds, which formation requires high excitation and ionization densities (Ferry et al., 2019).

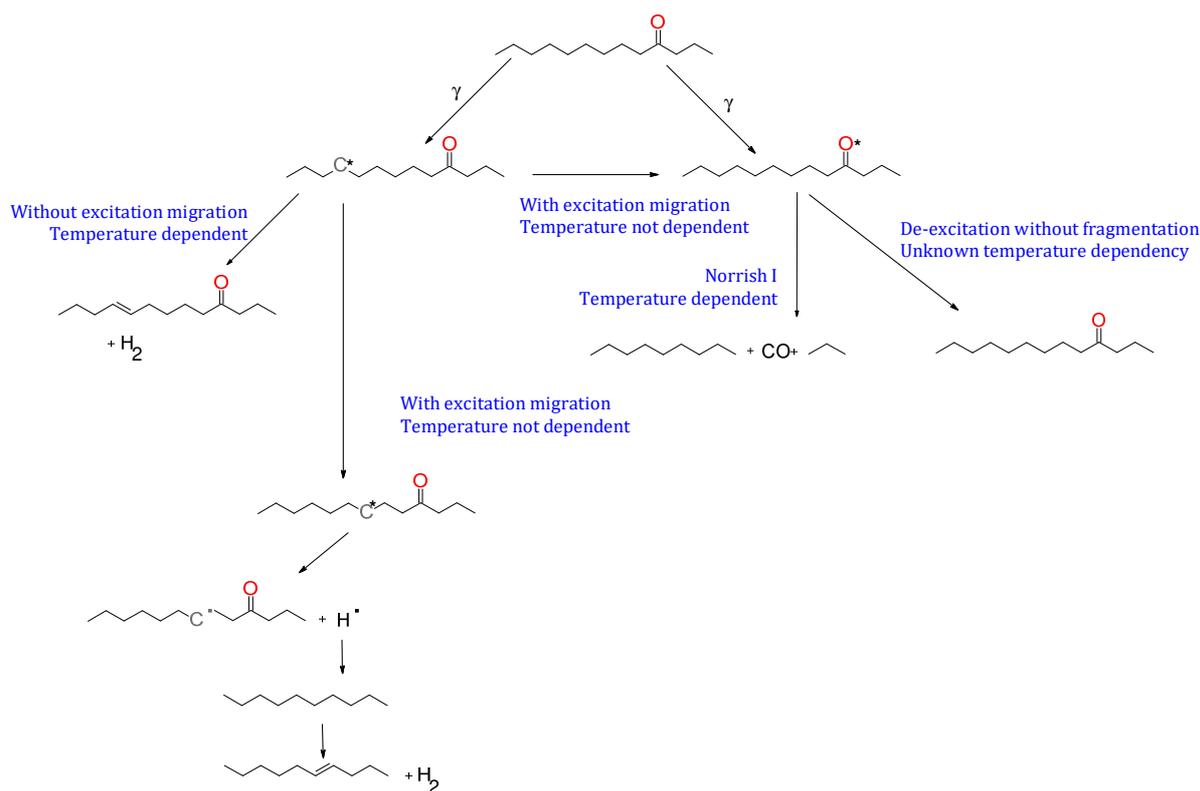
The difference in the radiation protection efficiency observed under inert atmosphere was also ascertained under oxidative conditions (Ferry et al., 2016b): when considering hydrogen emission, energy transfer efficiency is lower under SHI than under γ -rays irradiation. This stems first from the heterogeneous energy deposition structure of SHI and second from dose rate effects. As a matter of fact, dose rates employed for γ -rays and SHI irradiations were not of the same order of magnitude in this work and this has a clear influence on the concentration in oxidized defects (Decker and Mayo, 1973): the higher the dose rate, the lower the oxidized defects concentration.

3.3. Influence of irradiation temperature

As already introduced, energy transfer can proceed through species transfer or electronic excitation transfer. These are difficult to discriminate when polymers are irradiated above their glass transition temperature. Therefore, lowering the irradiation temperature well below the T_g , in conditions where molecular motion is hindered and mass transport is generally considered as frozen or almost frozen, enables to discard mass transport and study solely excitation and charge transfers. Except for the very first study (Charlesby and Davison, 1957), all the experiments interested in the influence of the irradiation temperature on polymer evolution

under γ -rays, from 77 K to room temperature, concluded on the combination of excitation and radical transfers in the ethylene moiety stabilization in presence of various energy sinks (Dole et al., 1958; Mal'tseva et al., 1976; Partridge, 1970c; Salih et al., 2007). A similar conclusion was driven under SHI irradiation of cyclohexane/benzene mixtures or in ethylene/styrene copolymers, for all of the radiation-induced defects except those, such as vinyl groups, which formation is LET dependent (Ferry et al., 2013; Ferry et al., 2019). As a matter of fact, vinyl groups are created in the track core and their creation yield increases with increasing LET (Balanzat et al., 1994; Sun et al., 2002). At low temperatures (11K), no influence of the benzene moiety is observed in the creation of vinyl groups whereas the formation of *trans*-vinylenes and *trans-trans*-dienes is reduced (Ferry et al., 2013; Ferry et al., 2019). On the basis of this thorough study, the authors concluded that in the track core, excitation transfer is inefficient but radical migration, when thermally allowed, is effective for energy transfer. In the penumbra both types of transfers are efficient.

In the high temperature range - that is from the glass transition temperature to the degradation temperature-, long range molecular motions are enhanced and some polymers can even be in the molten state. In these conditions too, except for one of the first studies on polyethylene irradiated at room temperature and at 120°C, which led to the conclusion that there is no effect of the irradiation temperature in this temperature range (Kang et al., 1967), all studies performed on this polymer showed an increase in energy transfer efficiency with increasing irradiation temperature, at least up to 300°C (Dole and Williams, 1959; Ferry et al., 2016a; Furtak-Wrona et al., 2019). This increase in energy transfer with increasing temperature was assigned to an increase in radical migration enabled by a higher molecular mobility when the temperature rises above its T_g - of 105°C in the case of poly(methyl methacrylate), the polymer irradiated in this study - (Wündrich, 1974). Within the same idea, charge and excitation transfers that were absent at room temperature in polyethylene/polybutadiene physical mixtures due to phase segregation become effective at 142°C in the molten state thanks to the increase in molecular motion and thus to the subsequent increase in the frequency of random collisions (Dole and Williams, 1959). The dependence of energy transfer efficiency with the irradiation temperature can be defect-dependant. Recently, an analysis of the influence of the irradiation temperature on the behavior of C=O and C=C containing polyethylenes evidenced that only part of the energy transfer is temperature dependent (Furtak-Wrona et al., 2019). These conclusions, which are in agreement with those of previous studies (Brede et al., 1989; Miyazaki et al., 1980; Wündrich, 1974), are summarized on Scheme 2, in a non-exhaustive way, for one type of polyethylene containing C=O groups in the main chain.



Scheme 2. Non-exhaustive scheme of temperature dependency of radicals and excitation transfers in a methylene-based polymer (Furtak-Wrona et al., 2019).

Conclusion

Energy transfer can occur through excitation, radical, ion or charge migration followed by trapping on a "defect" in the polymer, called the energy sink. These transfers that take place between a donor and an acceptor group were first evidenced in the early 30's (Schoepfle and Fellows, 1931), first defined and theorized in the 50's for excitation transfers (Dexter, 1953; Förster, 1959) and completed in early 70's for charge transfers (Hirsch and Martin, 1972). The first pieces of knowledge on this topic were acquired through molecular mixtures, most of them composed of alkanes and aromatic molecules. From these first evaluations, both intramolecular and intermolecular transfers were evidenced to be roughly equally efficient in energy transfers under low LET irradiations (Schoepfle and Fellows, 1931), and this remains true under high LET irradiations such as SHI irradiations (LaVerne and Dowling-Medley, 2015).

Two decades after the aforementioned first works on molecular mixtures, energy transfer studies were extended to polymers: first using polymer mixtures (Witt, 1959), then using copolymers (Basheer and Dole, 1984; Gardner and Harper, 1965; Mal'tseva et al., 1976). As it was the case for molecular mixtures, most acceptors contained aromatic groups. Except for the case of physical mixtures made of immiscible polymers, energy transfer does take place in polymers; either in the interchains or the intrachain mode. However, to the contrary of molecular mixtures in which both modes were assessed equally efficient, the consensus in polymers agreed in the greater efficiency of the intrachain mode compared to the interchains one. The latest was first discarded, on the basis of theoretical works on the exciton model by

Partridge (Partridge, 1970a), who supposed that exciton transfer is far more efficient along the polymer chain.

The common drawback of all these early studies is that, except for the endeavour of Manion and Burton (Manion and Burton, 1952), the fate of the acceptor after energy trapping was never taken into consideration. This is certainly due to the fact that hydrogen emission from aromatic being quite reduced, its emission in polymers mixtures and copolymers was considered essentially to stem from the aliphatic polymer and thus served as the tracer to evaluate the polymer stability. In polymers containing aromatic moieties, it has generally been accepted - without much experimental validation - that the protection happens through a sponge-type protection mechanism (Chapiro, 1988); the energy absorbed in the benzene ring being released under the form of heat through double bonds delocalization.

At the end of the 80's and early 90's, the number of research studies on the topic of energy transfers has considerably decreased, probably because of the difficulty to go deeper in that topic. At that point, energy transfer was proven to efficiently take place in polymers in presence of various chemical groups acting as (Farhataziz and Rodgers, 1987; Tabata, 1991; Zhang and Thomas, 1996): (i) excitation sinks (carbonyls, alkenes, or aromatic cycles), (ii) electron scavengers (polar groups, chlorinated molecules or polycyclic molecules), and (iii) hole scavengers (heteroaromatic molecules with low ionization potential such as pyrene, their hydrogenated counterpart such as transdecalin or highly substituted carbons). Energy transfer to these sinks and charge scavengers increases the heterogeneity of defect creation or localization in polymers. As a matter of fact, depending on the stability of the sink after energy trapping, reactions may be initiated leading to defect and favoring what Reichmanis called the spatial specificity of chemical reactions or Tabata considered as the heterogeneous nature of radiation effects (Reichmanis et al., 1993).

Moreover, radical transfers were shown to be effective at temperatures just above the polymer glass transition temperature (Ranby and Rabek, 1977). Charge transfers in presence of bulky fused rings were shown effective at temperatures as low as 77K in polystyrene (Zhang and Thomas, 1996), a temperature well below the T_g of this polymer. Finally, excitation transfers were shown to remain efficient whatever the irradiation temperature (Ferry et al., 2013).

At the beginning of the 2000's the topic regained some interest thanks to the development of new tools and methodologies, which allowed, among other things, differentiating the fate of each moiety in aliphatic-aromatic systems. These new tools encompass the modulation of the irradiation and acquisition temperatures, with on-line characterization of macromolecular defects. Thanks to these new developments, it was for instance proven that under SHI, below the fragmentation LET threshold, energy transfer is effective solely outside the track core (Ferry et al., 2019) and that interchains transfers are as efficient as the intrachain ones (Ferry et al., 2013). Actually, recent works realized by Ahn *et al.* (Ahn et al., 2020) on alkyl radical propagation in pure polyethylene tend to show the predominance of interchains over intrachain transfers.

Over the past twenty years, two commonly admitted energy transfer patterns were proven incorrect. First, contrarily to the generally admitted sponge-type radiation protection mechanism and as it was hypothesized by Manion and Burton (Manion and Burton, 1952), the protection of the donor group is shown to happen at the expense of the acceptor; be it the benzene ring (Ferry et al., 2012). Second, in contradiction with the exciton model proposed by Partridge (Partridge, 1970a), interchains transfers are at least as efficient as intrachain transfers. Because of this, energy transfer distances are more reduced than hypothesized from the σ -bond model. Therefore, the radiation protection of a given sink can be considered as

circumscribed in a restricted volume around the sink and the radiation protection efficiency can be modelled using a black sphere model of reduced volume (Ferry, 2008; Seguchi, 2001; Ventura et al., 2016). Yet, inside the protection sphere, part of the energy is transferred, through excitation, from the bulk polymer to the energy sink (Ventura et al., 2016).

Transfer's efficiency depends on the energy sink under consideration, its stability after energy trapping, and its concentration in the polymer (Ceresoli et al., 2005; Ceresoli et al., 2004). These patterns can be used first to deliberate on the radiation-stability of a given polymer, based on the groups forming its monomer and second to have an idea of its behavior as a function of the dose. In fact, some of the defects created under irradiation are energy sinks (alkenes C=C, crosslinks and alkynes under inert environment; carbonyl containing groups or alcohol under oxidative atmosphere). Therefore, the dose effect can be summed up as an energy sink concentration effect, which itself depends on the irradiation conditions (Ferry et al., 2016b). These energy sinks, acting through different mechanisms are created concurrently. How do these energy sinks interact in terms of radiation protection or in terms of transfer mechanisms is an open question: do they act synergistically or do they act antagonistically? To understand and quantify interaction between energy sinks, two communities should be associated: the polymer synthesis community and the community studying polymer under ionizing radiation. The first to synthesize tailored polymers with the given defect(s) at the given concentrations and positions and the second to propose these polymers' designs according to the aim of the study and to evaluate how they evolve under irradiation, as a function of the dose, at different temperatures.

Almost all the studies above were performed under inert atmosphere or under vacuum, which includes the influence of the temperature on energy transfers and thus on the stability of polymers was studied under vacuum. However, as polymers are irradiated in presence of oxygen and at various temperatures in their conditions of use, it appears important to assess how energy transfer is modified under these conditions. To the best of our knowledge, few studies have questioned how the presence of oxygen in the irradiation environment modifies energy transfer in the polymer. As a matter of fact, the generally accepted radio-oxidation mechanism is the one of Bolland and Gee (Bolland and Gee, 1946). This mechanism is an oxidation chain reaction, which starts with the reaction between the oxygen molecule and the carbon-centered radical. What is to be questioned here is what happens prior to the carbon-centered radicals' formation?

Indeed, oxygen is known to be a strong electron scavenger and this can potentially modify energy migration in the polymer under irradiation. Using alkane molecules as polymer models, Soebianto *et al.* (Soebianto et al., 1996) showed that, under γ -rays, excitation and charge transfers are effective under oxidative conditions, in presence of fused phenyl cycles. However, when the phenyl ring was associated to an alkyl moiety, as in tetralin for instance, this moiety was subjected to oxidation. These results are interesting, but complementary and systematic studies are required. Studies coupling the oxidative atmosphere with the most influent parameters (temperature and nature of irradiation) will afterwards have to be performed.

Associating new set-ups for on-line analysis at various temperatures, the design and tailoring of specific polymers and the study of the influence of the environment (oxygen pressure) in the study of energy transfer in polymers submitted to ionizing radiation on both gas emission and macromolecular defects should pave the way to modeling polymer ageing under ionizing radiations.

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