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Trapped and transient radicals observed in ethylene–propylene–diene terpolymers

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Abstract

Radicals formed by irradiation by high energy electron in ethylene–propylene–hexadiene terpolymer (EP–HD) have been studied using electron spin resonance (ESR). Two methods were used to analyse the different radicals formed by irradiation: firstly, classical low temperature irradiations were carried out, secondly, rapid quenching in liquid nitrogen of the material after high dose rate irradiation.

The feasibility and the efficiency of the latter method to observe short-lived radicals have been demonstrated. This type of experiment provides unique information concerning the rate of production and the rate of reaction of radicals.

Keywords: EPDM; ESR; Radical

1. Introduction

Ionising radiations induce in organic materials excitation and ionisation, which give formation of radicals. The identification of the primary radicals is of relevant importance for understanding the basic mechanism that lead to radiation damage. Electron spin resonance spectroscopy (ESR) is a powerful technique to detect the radicals produced by irradiation. In material containing low mobility zones such as crystallites, a fraction of the radicals formed by radiation can be trapped in these regions. These long life species can be observed at room temperature for a long time. To study more reactive radicals, irradiation at low temperature (for example 77 K), is generally used [1]. Annealing experiments have been also carried out to study the reaction of primary radicals.

Formation of radicals in polyethylene or polypropylene by high energy radiation has been the subject of a large number of ESR studies. Nevertheless a few studies concerning investigations of radicals in copolymers or terpolymers of ethylene and propylene have been reported. Faucitano et al. [2] studied in different terpolymers of ethylene–propylene–diene the reaction of primary radicals with termonomer units and identified new type of allyl radicals. They concluded that the dominant mechanism of reaction is double bond addition for ethylene–propylene–1-isopropylidendicyclopentadiene terpolymer (EP–IPCDP), ethylene–propylene–tricyclico-5.2.1.0$^{2.6}$-deca-2.5.8-triene terpolymer (EP–DDCP), and hydrogen abstraction for ethylene–propylene–5-ethylidene-2-norbordene terpolymer (EP–ENB). Geissler et al. [3] analysed cross-linking, double bond consumption and radical formation induced by radiation in ethylene–propylene copolymers (EPM) and ethylene–propylene–diene terpolymers (EPDM). Based on their results, a mechanism for radiation induced cross-linking in EPDM was proposed. Singh et al. [4] determined the structure of peroxyl radicals generated by UV light at low temperature with a combination of ESR and FTIR coupled with derivatisation reactions. Composition and crystallinity effects were studied by O'Donnel and Whittaker [5]. They compared radiolytic yields of polymers containing different fractions of crystallinity and concluded that the chemical changes occur preferentially at crystalline surfaces and defects. Baccaro et al. [6] investigated

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the ESR spectra of a commercial ethylene–propylene rubber. They identified several different types of radicals. In air, they observed the formation of nitroxide radicals attributed to the presence of antioxidant. Post-irradiation evolutions of radicals were also investigated in order to clarify their role in the degradation process [7].

The first aim of the present work is to clarify the identification of primary radicals formed in ethylene–propylene–hexadiene terpolymer (EP–HD) and to investigate their reactions with diene groups. In another part, some irradiations of EP–HD terpolymer in presence of oxygen have also been carried out in order to identify the relatively short-lived radicals responsible for the chemical evolution of the material at room temperature and to test the oxidation models and their assumptions. Mainly, we tried to verify if the steady state conditions are satisfied and we investigated the dose rate dependence of the peroxy radical concentration.

2. Experimental

2.1. Materials

The material was provided by Dupont de Nemours with trade name NORDEL 2722. It is an ethylene–propylene–1,5-hexadiene terpolymer. The mass ratios determined by NMR are 75.3%, 18.6% and 6.1%, respectively [8]. The thermograms reveal a broad melting endotherm, with a maximum at 46 °C. This low melting temperature indicates the presence of small size crystallites (~10 nm) [9]. Using standard value for polyethylene, the degree of crystallinity is estimated at 20%. The material was used without purification. Yet FTIR spectrum reveals the presence of a small amount of phenol stabilizer.

For comparison, an ethylene–propylene copolymer (EPM) supplied by Exxon (Vistalon 703) was studied, the nominal molar composition was 72.5% ethylene and 27.5% propylene.

The films were prepared by compression moulding (120 °C, 4 tons, 3 mn). Film thickness was varied from 20 to 500 μm.

2.2. Irradiation

Irradiations were performed using a 2.5 MeV Van de Graaff accelerator (LSI, Palaiseau, France).

For low temperature irradiations, samples were placed in a liquid hydrogen cryostat. After irradiation, the samples were rapidly transferred in a liquid nitrogen Dewar. It was verified that during the transfer, sample temperature did not exceed 100 K.

EP–HD films were irradiated at room temperature under different atmospheres (oxygen and helium) and with different dose rates between 30 and 1600 Gy/s. The temperature of the sample was monitored using a thermocouple. No warming was detected even for the highest dose rate. After irradiation, the films were stored under liquid nitrogen. For ESR measurements, the samples were transferred into a quartz tube using a liquid nitrogen bath and some skill.

Table 1
Irradiation conditions

Material	Dose rate (Gy/s)	Dose range (kGy)	Temperature (K)	Atmosphere
EP–HD	~1600	100	20	–
EPM	~1600	100	20	–
EP–HD	~1600	50–1000	300	He
EP–HD	~1600	100–500	300	O_2
EP–HD	~81	25–500	300	O_2
EP–HD	~27	10–100	300	O_2

Irradiations' conditions are listed in Table 1.

For ESR experiments, a special device was developed to quench the samples at a fixed time after irradiation. The films were fixed on a sample holder maintained by an electromagnet. The power cut of the electromagnet results in the falling of the sample holder into a liquid nitrogen Dewar set underneath. The duration of the fall was estimated to be 0.25 s. In practice the measurement of the concentration of the radicals immediately after irradiation was very disperse. To avoid this problem, the samples were quenched for 1 s or more after irradiation.

During the irradiation, the current that goes through the sample was monitored. The conversion of the fluence in dose was done using the results of dosimetry calculations carried out with the PENELOPE simulation code [10].

The *G*-value for radicals, $G(R^{\circ})$ was estimated from the concentration of radicals $[R^{\circ}]$ given in mol/kg,

$$G(R\bullet) = \frac{[R\bullet]}{D} \qquad (1)$$

$D =$ dose given in Gy or J/kg. The unit of G is mol/J.

2.3. ESR spectroscopy

ESR spectra were recorded at the X-band (9.4 GHz) on a Bruker ER-200D ESR spectrometer equipped with a nitrogen flow cryostat. The cryostat temperature was usually set at 120 K. We calculated the radical concentration from a sample of known diphenyl picryl hydrazine (DPPH) (Aldrich) concentration.

2.4. Simulation

The electron spin resonance parameters were determined by means of an automated simulation programs using the Levenberg–Marquardt method. For all the spectra Gaussian line shapes were assumed.

The hyperfine anisotropy of the H_{α}-proton was not considered explicitly in the simulations. Yet we verified that the shape of the spectra is governed by the broadening induced by the different orientations of the H_{β}-protons and almost insensitive to the hyperfine anisotropy.

3. Results and discussion

3.1. Irradiation at low temperature

Radiation degradation of polymers involved radical intermediates, which can be observed by ESR spectroscopy. The yield of radicals formed at low temperature measures the extent of radical reactions involved in irradiation at higher temperature and can be compared with the *G*-values observed for chemical changes.

The ESR spectra of the EP–HD and EPM copolymers after irradiation at 20 K and storage at 77 K are shown in Fig. 1. They are similar to the spectra of polyethylene of low crystallinity irradiated at 77 K [11]. Yet the features of this spectrum are less pronounced, a six-line spectra characteristic of secondary alkyl radicals (I) formed on the polyethylene chains can be observed.

$$-CH_2-C{\bullet}H-CH_2- \qquad \text{(I)}$$

In fact the spectrum does not correspond to the spectrum of a pure secondary radicals but certainly includes a minor fraction of tertiary radicals. Radicals arising directly from the termonomers are also likely to be formed. Nevertheless the spectra are similar and equivalent to the spectra reported previously for EPM copolymers and different EPDM terpolymers [2]. This result implies that the same alkyl radicals are formed as major products during irradiation. The majority of radicals detected come likely from ethylene–propylene units rather from the unsaturated groups. The $G(R\bullet)$ values of 2.3 and 2.1×10^{-7} mol/J were obtained for EP–HD and EPM, respectively. These results are very close to the $G(R\bullet)$ reported by O'Donnel et al. [5] and are smaller than the data published for polyethylene or polypropylene. In fact these values represent a low estimation of the total yield of radicals. Yet studies of radiolysis of polymers at temperature inferior to that of liquid nitrogen have demonstrated that radical concentration decreased upon annealing at 77 K. For polyethylene irradiated at 4.2 K and annealed at 77 K, the total number of radicals decreased by 18% [12]. If we suppose that this last result applied to our EP–HD copolymer, the $G(R\bullet)$ is now estimated to be 3×10^{-7} mol/J which is almost equal to the *G*-value for hydrogen production [13,14]. This is in contradictory with the following assumed mechanism that predicts $G(R\bullet) = 2G(H_2)$:

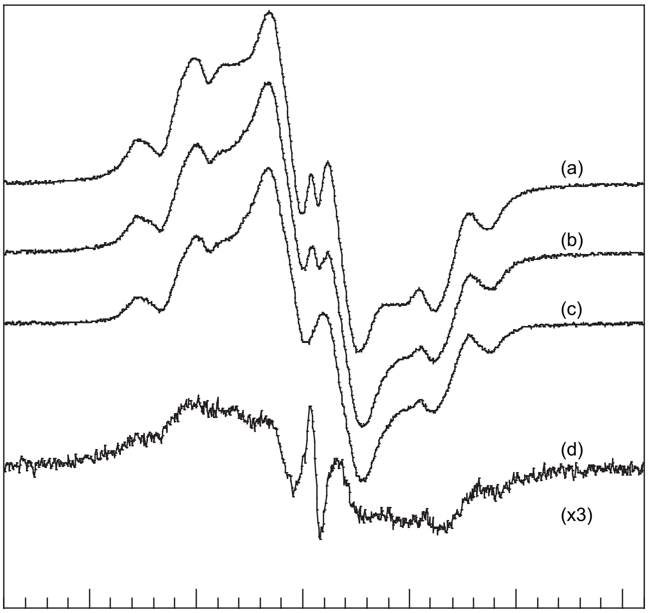

Fig. 1. ESR spectra of EPM (a) and EP–HD (b) after electron irradiation at 20 K; (c) represents the ESR spectra of electron irradiation EP–HD after annealing at 170 K; (d) corresponds to the difference between (b) and (c). All the spectra were recorded at 120 K.

$$RH \rightarrow R\bullet + H\bullet$$

$$H\bullet + RH \rightarrow R\bullet + H_2$$

This result could suggest that the recombination of H-atoms is efficient at moderate temperature:

$$H\bullet + H\bullet \rightarrow H_2$$

We propose another explanation that calls into question the use of low temperature measurements to estimate the total radical yield. The absence of trapped hydrogen atoms at low temperature demonstrated by ESR [15] is attributed to capacity of thermal hydrogen atom to abstract hydrogen even at very low temperature by quantum tunneling. The new radical is created in the vicinity of the parent alkyl radical. The formation of close-paired radicals was identified by ESR [16]. Then we suppose that low temperature irradiation exacerbates the inhomogeneous repartition of radicals and promotes recombination or dismutation. Besides Mélot et al. [17] showed that in polyethylene irradiated with high energy ions the formation of *trans*-vinylene groups is very efficient even at low temperature (8 K). Finally the following material balance is valid:

$$G(R\bullet) = 2G(H_2) - 2G(X) - 2G(t\text{-vinylene})$$

where $G(X)$ and $G(t\text{-vinylene})$ are the *G*-values for the formation crosslinks and *trans*-vinylene groups, respectively.

A sharp singlet centred at 2.0022 and of linewidth 0.3 mT is also observed immediately after irradiation, but its intensity decays even at nitrogen liquid temperature. It disappears completely above 150 K. This spectrum was observed in different polyolefins and was attributed to electron trapped by defects in the crystalline regions of the polymer (see for example Ref. [18]).

Annealing at temperature inferior to glass transition (for example 170 K, see Fig. 1) causes a reduction of the total intensity of the ESR spectra. The subtraction of the spectra before and after annealing reveals the disappearing of a broad signal while the intensity of the six lines remains approximately the same. This signal is attributed to radicals' clusters formed during irradiation at low temperature. The large broadening of the signal is a consequence of the elevated local concentration of radicals inside the clusters. This explanation is supported by the work done by Nuome et al. [12] that studied using microwave power saturation the local concentration of radicals in polyethylene irradiated at low temperature (1.5, 4.2 and 77 K). The results suggest that the local concentration is considerably higher in samples irradiated at very low temperature. After annealing or irradiation at 77 K, the local concentration decreased due to the expansion of the initial spurs but remains relatively high [11].

On warming to room temperature, alkyl radicals could react, some recombine and a fraction react with the unsaturated groups yielding new radicals. At 290 K, the ESR spectrum of irradiated EP–HD consists of a quartet of nearly equally spaced lines with a hyperfine splitting of 1.3–1.4 mT (Fig. 2). A careful examination of the spectra reveals the presence of two satellite lines. In fact the quartet is a sextet. This spectrum is not observed in EPM material. So it attributes to the radical formed by reaction of alkyl radicals with the hexadiene side groups. Moreover the small splitting suggests a delocalized radical, presumably of allyl type. The choice is directed to the following species

$$-\mathrm{HC}-\mathrm{C{\bullet}H}-\mathrm{CH}{=}\mathrm{CH}-\mathrm{CH_3} \qquad \text{(II)}$$

$$-\mathrm{HC}-\mathrm{CH_2}-\mathrm{CH}{=}\mathrm{CH}-\mathrm{C{\bullet}H_2} \qquad \text{(III)}$$

It is well known that the proton in the centre of the allyl triad does not contribute to the hyperfine structure because of its small coupling. The sextet spectrum is characteristic of radicals in interaction with five equivalent protons. So it is attributed to radical (III). The equivalence of the protons is certainly due to analysis temperature (290 K) where chain oscillations are sufficient to average the positions of the H_β-protons.

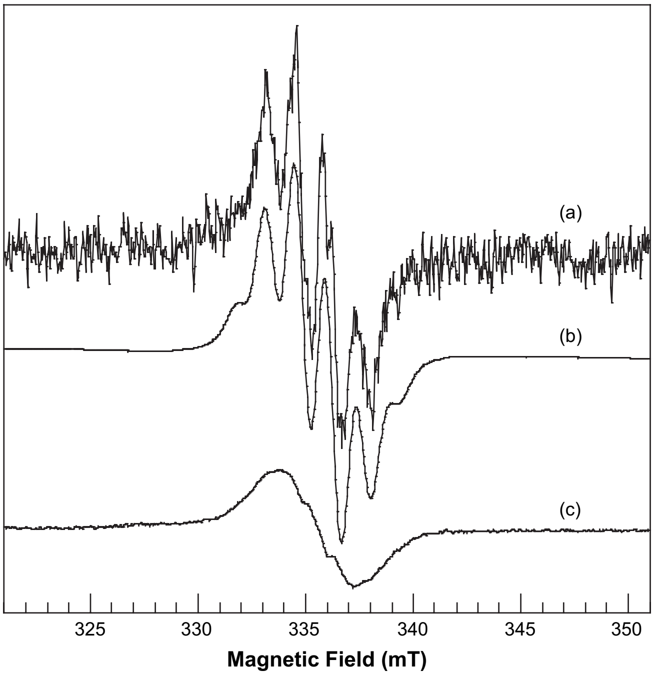

Fig. 2. ESR spectra of electron irradiated EP–HD recorded at 290 K (a) and after annealing 45 min at 300 K (c). The simulated spectrum (b) corresponds to the composite of two species with the following parameters: allyl (38%) $g = 2.0034$; $a_{H_\alpha} = 1.355, 1.355, 1.355$; $a_{H_\beta} = 1.355, 1.355$; $\Delta H_{pp} = 0.99$ mT; polyenyl (62%) $g = 2.0034$; $\Delta H_{pp} = 3.8$ mT.

The formation of allyl radicals (IV) by the reaction of alkyl radicals with *trans*-vinylene was studied in polyethylene by Waterman et al. The shape of ESR spectrum of the allyl radical depends upon the temperature. At high temperature, it appears as a septet with a hyperfine splitting constant of 2.1 mT [19].

$$-\mathrm{CH_2}-\mathrm{C{\bullet}H}-\mathrm{CH}{=}\mathrm{CH}-\mathrm{CH_2}- \qquad \text{(IV)}$$

No evidence of this signal was found. This result is not surprising because in EP–HD, even at 1 MGy, the concentration of hexadiene group remains much higher than that of the concentration of *trans*-vinylene.

When the material is conserved at 300 K under nitrogen atmosphere, the sextet disappears and a singlet remains (see Fig. 2). It centred at $g = (2.0032 \pm 5) \times 10^{-4}$, the shape is clearly Gaussian and the peak-to-peak linewidth is 4.0–4.1 mT. This signal could be attributed to polyenyl radicals (V).

$$-\mathrm{C{\bullet}H}-(\mathrm{CH}{=}\mathrm{CH})_n- \qquad \text{(V)}$$

To our knowledge, this is the first report of the formation of this type of radicals after an irradiation of 50 kGy. Generally the presence of polyenyl radicals is reported for dose of several MGy [20]. It was shown that the delocalisation of the electron associated with the polyenyl produces a singlet with a linewidth that converges towards 1.7 mT with increasing doses. In irradiated polypropylene at moderate dose (1 MGy), a broad spectrum is observed having a peak-to-peak linewidth of ~3.9 mT [21]. Moreover, in polyethylene, Bodily and Dole [22] demonstrated that allyl radicals and obviously higher polyenyl radicals or polyene groups are not primary products of irradiation but require the presence of a conjugated diene groups to be formed. Rather surprisingly our results demonstrate that, in EP–HD, polyenyl radical concentration initially grows linearly with the dose and that the growth rate decreases with the dose. This decrease can be correlated to the destruction of hexadiene groups by irradiation [15]. Then we assume that these radicals could be formed either directly from the hexadiene groups or by the reaction of an allyl radical (III) with hexadiene groups. Finally, by analogy with the results reported in irradiated polypropylene, it is assumed that the singlet is the superposition of the signals of different kinds of conjugated diene radicals.

Finally we suppose that the spectrum recorded at 290 K is a mixture of the signals attributed to allyl and polyenyl radicals. The simulation is shown in Fig. 2 and the parameters are summarized in the caption.

3.2. Anaerobic irradiations at room temperature

In order to identify the intermediate radicals some irradiations under helium atmosphere at room temperature were performed. After irradiation, the samples were quenched in liquid nitrogen. After an irradiation dose of 50 kGy, the spectrum is composed of a composite pattern: the main component is the sextet attributed to alkyl radicals (I), superimposed on this signal, a spectrum with a smaller splitting that is attributed to the spectra of the radicals (III).

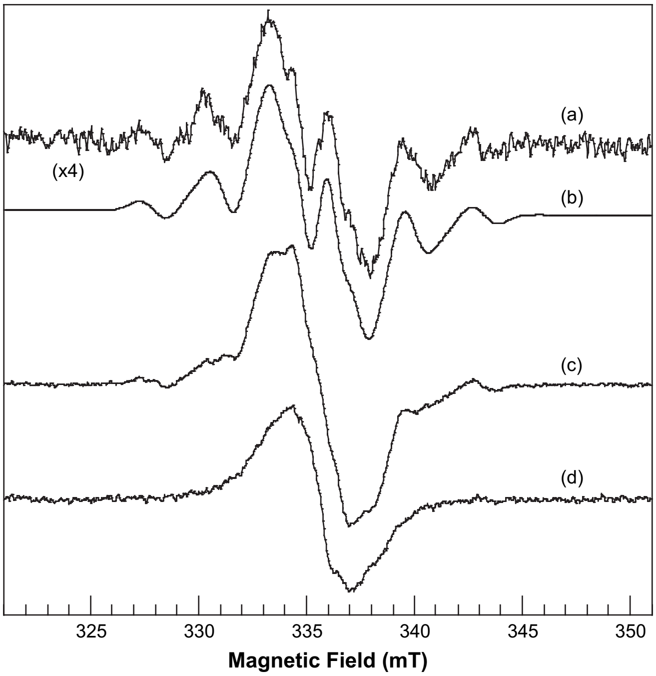

Fig. 3. ESR spectra of electron irradiated EP–HD at 300 K recorded and 120 K at 50 kGy (a) and 500 kGy (c), respectively. (d) Corresponds to the difference between (a) and (c). The simulated spectrum (b) corresponds to the composite of three species with the following parameters: alkyl (33%) $g = 2.0034$; $a_{H_\alpha} = 32.7$; $a_{H_\beta} = 2.19, 2.19, 2.19, 2.19$; $\Delta H_{pp} = 13.3$ mT; allyl (11%) $g = 2.0034$; $a_{H_\alpha} = 1.30, 1.30, 1.30$; $a_{H_\beta} = 1.07, 1.07$; $\Delta H_{pp} = 0.99$ mT; polyenyl (56%) $g = 2.0034$; $\Delta H_{pp} = 3.8$ mT.

The increase of the dose led to the increase in intensity and to change in spectra which become less structured. The spectrum of EP–HD irradiated at 500 kGy under helium at room temperature is shown in Fig. 3. The difference between the spectra of EP–HD irradiated at 500 kGy and the spectra of EP–HD irradiated at 50 kGy reveals a singlet spectrum. The g-value and the linewidth are analogous to the parameters of the signal observed after annealing experiments (see Section 3.3). Finally above 50 kGy, the new spectral features can be interpreted as the accumulation with the dose of conjugated polyene radicals.

Simulations show that the mixture of the signals of radicals (I), (II) and (V) can account satisfactory for the observed signal (see Fig. 3). At 50 kGy, the relative intensity of alkyl, allyl and polyenyl radicals are 33%, 11% and 56%, respectively.

The kinetics curves of the concentrations of the different species versus dose are shown in Fig. 4. It appears that the steady state is rapidly achieved for alkyl and allyl radicals. On the other hand, polyenyl radicals accumulate inside the matrix. The formation yield of polyenyl radicals is 0.05×10^{-7} mol/J approximately.

3.3. Destruction of polyenyl radicals under oxygen

Annealing measurements showed that the conjugated polyene radicals are very stable at 300 K under nitrogen atmosphere. Nevertheless when the film is exposed to air, these radicals react very rapidly with oxygen. This effect can be used to estimate the diffusion coefficients of oxygen in the irradiated materials. The length and width of the samples are supposed to be larger when compared to the thickness, then, the relative variation of the primary radical concentrations is given by the following expression [23]:

$$\frac{C}{C_0} = \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(-(2n+1)^2\pi^2 Dt/4L^2\right)$$

where L is the thickness; D, the diffusion coefficient, C_0 and C, the concentration of primary radicals at time 0 and t, respectively. For EP–HD irradiated at 50 kGy, the diffusion coefficient is estimated to be comprised between 1 and 3×10^{-6} cm^2/s. This value is close to the published data [24].

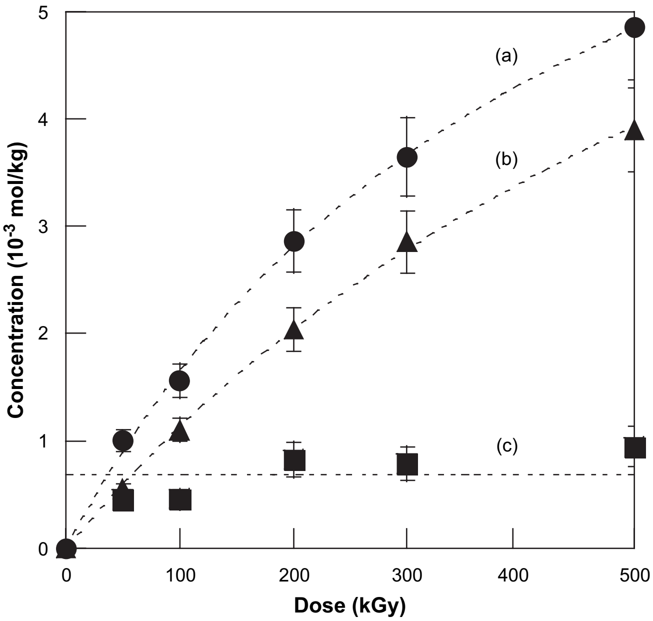

Fig. 4. Evolution of the radical concentrations with the dose: (a) total concentration, (b) polyenyl radicals concentration, and (c) alkyl + allyl radicals concentration.

3.4. Irradiations at room temperature in oxygen atmosphere

In this study high dose rate irradiations under oxygen atmosphere were used. Therefore precautions have to be taken to avoid oxygen diffusion-limited oxidation. Thin films of 20 μm thickness were employed. Two different observations confirmed that the oxidation of the samples was homogeneous. Firstly the ESR spectra of 20 μm films irradiated under oxygen did not reveal the presence of radicals observed after irradiation under anaerobic atmosphere. This absence proofs that all the radicals have react with oxygen. Secondly, the critical oxidation thickness l was determined using a thick sample irradiated at high dose rate under oxygen. In these conditions, the ESR signal of this sample is the superimposition of the spectra of anaerobic radicals and of a new signal that is attributed to peroxy radicals. To estimate l, we suppose that the sample is composed of a non-oxidised core where the formation of radicals is equivalent to irradiation under helium and two oxidised layers of thickness l. Then the intensity of the non-oxidised radicals is proportional to $L-2l$. In our case, a 440 ± 10 µm film was irradiated at 1600 Gy/s and l is estimated to be 25 ± 5 µm. This result confirms that the oxidation of irradiated films (~20 µm thick) is homogenous even for the highest dose rate.

The oxidation scheme used as first approximation for the oxidation mechanism is shown below [25].

$$\mathrm{RH}\xrightarrow{R_\mathrm{i}}\mathrm{R}\bullet$$

$$\mathrm{R}\bullet+\mathrm{O_2}\xrightarrow{k_2}\mathrm{RO_2^{\bullet}}$$

$$\mathrm{RO_2^{\bullet}}+\mathrm{RH}\xrightarrow{k_3}\mathrm{RO_2H}+\mathrm{R}^{\bullet}$$

$$\mathrm{R}\bullet+\mathrm{R}\bullet\xrightarrow{k_4}\text{products}$$

$$\mathrm{R}\bullet+\mathrm{RO_2^{\bullet}}\xrightarrow{k_5}\text{products}$$

$$\mathrm{RO_2^{\bullet}}+\mathrm{RO_2^{\bullet}}\xrightarrow{k_6}\text{products}$$

R_i represents the initiation rate. It is proportional to the radicals yield and to the dose rate.

For most oxidation of polymers the termination process corresponds to a complex expression depending of the type of peroxy radicals involved. Indeed in liquid phase, it was shown that bimolecular reaction of tertiary peroxy radicals occurs by the following reaction sequence:

$$\mathrm{RO_2^{\bullet}}+\mathrm{RO_2^{\bullet}}\xrightarrow{k_6'}\mathrm{ROOOOR}\rightarrow2\mathrm{RO}\bullet+\mathrm{O_2}$$

$$\mathrm{RO}\bullet\rightarrow\,>\!\mathrm{C{=}O}+\mathrm{R}\bullet$$

For secondary peroxy radicals, Russel's mechanism that involves the decomposition of a tetraoxide in which a hydrogen atom is transferred to give ketone, alcohol and oxygen is favoured. Finally in the following we will simplify and use only an average rate constant (noted K_6).

Generally, the above kinetic scheme was applied to the oxidation of polymers using a steady state analysis. The following conditions are supposed:

$$\frac{\mathrm{d}[\mathrm{R}^{\bullet}]}{\mathrm{d}t}=0\quad\text{and}\quad\frac{\mathrm{d}[\mathrm{RO_2^{\bullet}}]}{\mathrm{d}t}=0$$

Moreover the predominant termination is the bimolecular reaction of peroxy radicals in excess of oxygen.

Then the expression of the steady state concentration of peroxy radicals is as follows:

$$[\mathrm{RO_2^{\bullet}}]^{\infty}=\sqrt{\frac{R_\mathrm{i}}{2K_6}}\tag{2}$$

The steady state concentration depends on the square root of R_i, and therefore, on the square root of the dose rate d.

The time t_S or dose D_S to reach the saturation concentration of $\mathrm{RO_2}\bullet$ is approximately equal to the following:

$$t_\mathrm{S}=\frac{D_\mathrm{S}}{d}\sim\frac{[\mathrm{RO_2^{\bullet}}]^{\infty}}{R_\mathrm{i}}=\sqrt{\frac{1}{2R_\mathrm{i}K_6}}\tag{3}$$

In applying the oxidation kinetic scheme to the very inhomogeneous situation characteristic to ionising radiation, some precaution has to be taken. Indeed to calculate the initiation rate only radicals that escape their originating spur and terminate bimolecularly with radicals formed in a different spur has to be taken into account. A new parameter is needed: f that represents the fraction of escape radicals from the spur. Then,

$$R_\mathrm{i}\approx fG(\mathrm{R}^{\bullet})d.\tag{4}$$

In the following part, we tried to verify the prediction of the oxidation model by analysing and quantifying the radicals formed in presence of oxygen.

The ESR spectrum observed in irradiated EP–HD under oxygen is an anisotropic singlet typical of peroxide radicals with partially hindered rotation. At 150 K, $g_\mathrm{x}=g_\mathrm{y}=2.004\pm6\times10^{-4}$ and $\mathrm{g_z}=2.034\pm6\times10^{-4}$. These values are very close to those reported in polyethylene, polytetrafluoroethylene, polyvinylidene fluoride or polypropylene [1]. During warming to 300 K, variations of the line shape of the ESR spectra are observed. The motional analysis of the ESR spectra seems incompatible with an assignment to end chain type peroxy radical [26]. Finally radicals are secondary or tertiary peroxy.

Fig. 5 presents the variation of the concentration of peroxy radicals 1 s after the end of the irradiation with the dose up to 500 kGy for different dose rates. For a given dose rate, whatever the dose is, this concentration is almost constant within the experimental dispersion. Even for the lowest dose (10 kGy) at 28 Gy/s the steady state conditions are satisfied.

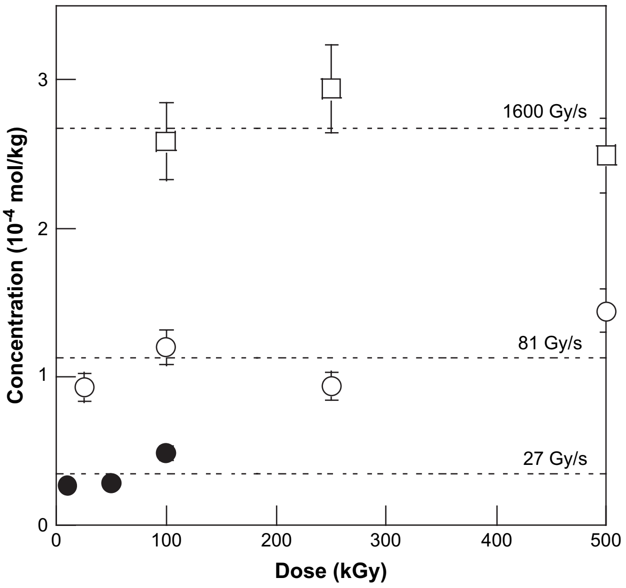

Fig. 5. Evolution of the peroxy radical concentration with the dose at different dose rates.

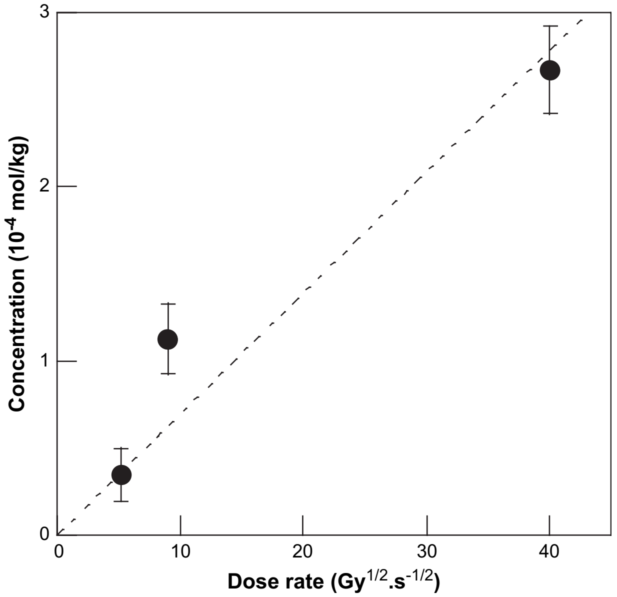

Fig. 6. Evolution of stationary peroxy radical concentration with the dose rate.

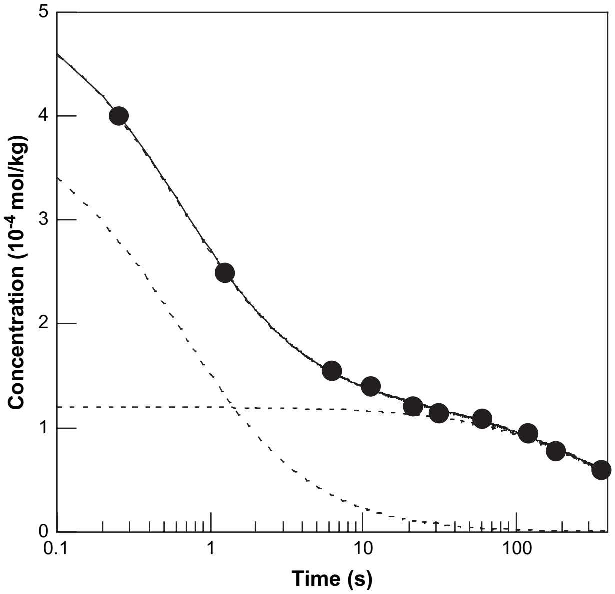

Fig. 7. Kinetics of peroxy radical concentration decay in EP–HD at room temperature. Solid line represents the calculation by Eq. (5) and dashed lines the two different contributions.

Using Eq. (3), we conclude that for dose rates d inferior to 28 Gy/s the steady state conditions are reached for dose inferior to $10/\sqrt{d}$ kGy[1]. Finally we concluded that even at low dose rates the hypothesis of steady state conditions is always fulfilled.

In Fig. 6, the $RO_2\bullet$ concentration is plotted as a function of the dose rate. The relation obtained is of the form $[RO_2\bullet] = kd^x$, where the exponent x is very close to 0.5. This result is in accord with the standard oxidation kinetic analysis presented previously (see Eq. (2)).

Reliable data on the rate of destruction of peroxy radicals are essential in order to model the oxidation of solid polymers. The constant k_6 was evaluated at high temperature using the stationary concentration of peroxy radicals (see for example Ref. [27]). Roginski and Miller [28] used a method of non-stationary kinetics analogous to flash photolysis to measure k_6 and determine the kinetic law of radical decay in isotactic polypropylene. In their experiments peroxy radicals were generated at moderate temperature (20–110 °C) directly in the ESR cavity by illuminating with UV light a preoxidized polymer. In our case, peroxy radical population was formed by electron irradiation at high dose rate and the decay of these radicals was recorded at different times after the end of the irradiation. The change in the peroxy concentration is shown in Fig. 7. This decay is decomposed in two stages: an initial rapid region attributed to radicals of high mobility formed in the amorphous zone and a long time region associated with low mobility radicals maybe trapped at the interface of the crystallites or stable radicals formed by reaction with primary chemical groups induced by irradiation.

Investigations at 50 °C which is above the melting temperature of the crystallites have been carried out. No radicals can be detected when the material is irradiated at 50 °C. This result indicates that firstly the life time of radicals in the amorphous phase decreases with temperature and at 50 °C, it is too short for our quenching apparatus, secondly long lived radicals are certainly no more trapped inside or in the vicinity of the crystallites.

The decay of peroxy radicals can not be fitted satisfactory by a diffusion-limited bimolecular model [29]. It follows a bimolecular law at short and long times. So the data are fitted using the following composite formula:

$$[RO_2^\bullet] = \frac{[RO_2^\bullet]_1^\infty}{1+2K_6^{(1)}[RO_2^\bullet]_1^\infty t} + \frac{[RO_2^\bullet]_2^\infty}{1+2K_6^{(2)}[RO_2^\bullet]_2^\infty t} \qquad (5)$$

The parameters of the least-squares fitting are:

$$[RO_2^\bullet]_1^\infty = 3.9 \times 10^{-4}\ \mathrm{mol\ kg^{-1}}$$

$$K_6^{(1)} = 2050\ \mathrm{mol^{-1}\ kg\ s^{-1}}$$

$$[RO_2^\bullet]_2^\infty = 1.2 \times 10^{-4}\ \mathrm{mol\ kg^{-1}}$$

$$K_6^{(2)} = 11.8\ \mathrm{mol^{-1}\ kg\ s^{-1}}$$

In the following the numerical values are discussed.

We suppose that $[RO_2^\bullet]_1^\infty$ represents the steady state concentration in the amorphous phase.

Then the values of $fG(R^\cdot)$ for short-lived radicals can be evaluated by Eqs. (2) and (4) as follows:

$$fG(R\bullet) = 2K_6([RO_2^\bullet]_1^\infty)^2/d$$

Finally,

$$fG_1(R\bullet) \approx 3.9 \times 10^{-7}\ \mathrm{mol/J}$$

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[1] For example, at 1 kGy/h, D_S £ 1.9 kGy.

This value is superior to the yield determined using low temperature irradiation. It confirms that very low temperature irradiation underestimate the formation rate of radicals.

The minimal fraction of escaped radicals *f* can be estimated supposing $G(\mathrm{R}\bullet) \leq 2G(\mathrm{H_2})$ and using the *G*-value determined by Dély et al. [14] ($G(\mathrm{H_2}) = 3.2 \times 10^{-7}$ mol/J), then $f \geq 0.65$. This result suggests that the majority of the radicals escaped from the spur at room temperature. This is in contradiction with the results of Niki et al. [27] who estimated that at 45 °C in polypropylene only 16% of all the radicals $\mathrm{RO_2}\bullet$ formed escaped the spurs.

In view of the restriction in mobility in condensed phase state and to the entanglements of chains in the matrix, the termination constant $K_6^{(1)}$ corresponding to the amorphous phase of EP–HD materials is rather high. Then, as Roginski and Miller [28] has pointed out, that the kinetics of macroradicals decay can only be interpreted using some relay mechanisms such chain transfer to low molecular impurity, dissociation of $\mathrm{RO_2}\bullet$…

The experimental $K_6^{(1)}$ constant can also be compared to the values determined by Roginski and Miller in isotactic polypropylene [28]. The highest value estimated in polypropylene corresponds to $[\mathrm{ROOH}] = 0$ and is about $500\ \mathrm{mol^{-1}\,kg\,s^{-1}}$ at 25 °C. But this value can be considerably higher in presence of plasticizers such as aromatic solvents or in presence of low molecular chain transfer agent such as cumyl hydroperoxide [28]. Finally to interpret the experimental $K_6^{(1)}$ value, we suppose either large scale motions of macromolecules in the amorphous phase are more efficient in low crystallinity EP–HD materials than in crystalline polypropylene or EP–HD materials contain more low molecular products that behave as radical transfer agents and increase the recombination rate of radicals.

4. Conclusions

The results of this work have some practical consequences.

The total radical yields determined from low temperature irradiation are not reliable because low temperature increases the cage effect of the proton that favours radicals' recombination.

In polymers, the kinetics of the reaction are rather slow because of the solid effect. Then, in presence of oxygen, it is possible to observe transient radicals like peroxy radicals. It was shown that the stationary conditions are verified even at high dose rate. In conditions of irradiation predominance the stationary conditions hypothesis is reliable. In accordance with the standard oxidation scheme, the stationary peroxy concentration is proportional to the square root of the dose rate. Time dependent measurements after irradiation permit to estimate the bimolecular recombination constant and the yield of escaped radicals.

The peroxide macroradicals decay follows a composite relation that suggests the presence of two different kinds of radicals with very different reactivity or mobility.

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