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A mechanism of photo-oxidative destruction for polyethylene polymers in the presence of ferrocene derivative additives

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The effect of ferrocene additive concentrations on the stability of polyethylene polymers under atmospheric ageing and ultraviolet irradiation is reported. At concentrations under *ca* 5×10^{-3} mol kg^{-1} polymer the ferrocene compound is shown to diminish polymer resistance to light, whereas above this concentration such a compound stabilizes the polymeric matrix. Another purpose of the work is to look into the photo-oxidative destruction of polyethylene doped with ferrocene compound by using an EPR technique. A mechanism of photo-oxidative destruction of polyethylene polymers in the presence of ferrocene compounds is proposed.

Keywords: Polyethylene polymers, photo-oxidative destruction, ferrocene compounds

1. INTRODUCTION

Transition-metal compounds, and particularly ferrocene derivatives, are known to be very effective stabilizers of photo-oxidative destruction of polyethylene polymers.[1-3] On the other hand, in low concentrations ferrocene derivatives have been shown to cause the accelerated photodegradation of a polymeric matrix.[4,5] In this context it is only natural to pose a problem concerning the possible dual function of such derivatives in these processes and the associated mechanism. Therefore the main purpose of this work is to study the effect of the ferrocene compound concentration on polymer photo-oxidation and its mechanism.

2. RESULTS AND DISCUSSION

2.1 The effect of ferrocene additive concentration on polyethylene polymer stability

A number of polyethylene polymers such as low-density and high-density polyethylene (LDPE and HDPE, respectively) were studied under atmospheric aging and ultraviolet radiation conditions (in the latter case from a high-pressure mercury-vapour lamp) in test chambers. Various ferrocene compound derivatives were added to the polymers (1×10^{-3}–2×10^{-2} mol kg^{-1} polymer).

The degree of polymer oxidation was estimated from the optical density of the stretching vibration band for the carbonyl groups (D_{1720}), relative elongation (ε) and dielectric loss tangent ($\tan\delta$).

Figure 1a shows the characteristic dependence of the number of carbonyl groups in the polymer, linearly related to D, the optical density of the stretching bond for the carbonyl group $D = M_{\mathrm{CO}}(\%)$ in Fig. 1(a), on ferrocene additive concentration in LDPE. It is evident, for example, that for 2,2-diferrocenylpropane (DFP) this dependence is different, in that in the region between 0 and 5×10^{-3} mol kg^{-1} the ferrocene compound decreases the polymer light resistance. Contrary to this, at higher concentrations (over 5×10^{-3} mol kg^{-1}) the ferrocene derivative acts as a polymeric matrix stabilizer. It should be noted that the effect of stabilization shows up, primarily, in enhancing the life of the polymers as compared with that for the non-inhibited samples. Although the introduction of substituents affects the additive effectiveness, particularly in that it brings about a change in the position of the peaks (see Fig. 1), the general type of dependence remains unaltered. Note also that the

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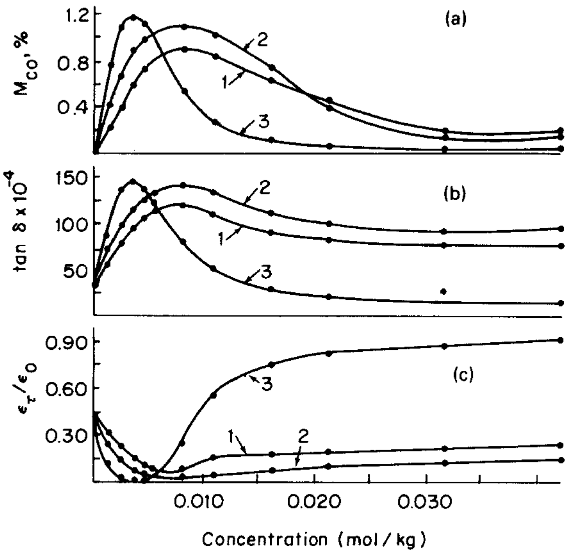

Figure 1 Concentration (M_{CO}, %) of the carbonyl groups (A), dielectric loss tangent (B) and change in the relative LDPE elongation (C) versus additive concentration after a three-month atmospheric aging. 1, Ferrocene; 2, 1,1′-diethylferrocene; 3, 2,2-diferrocenylpropane. [M_{CO}, % = D (text).]

physico-mechanical (ε) and dielectric ($\tan\delta$) characteristics show a dependence on ferrocene derivative concentration (Figs 1b, 1c), the position of the extremes being similar.

2.2 Oxygen absorption kinetics in the dark and under UV irradiation

The catalytic effects for transition-metal compounds in chain degenerated/branched process oxidation of saturated hydrocarbons and polyethylene polymers are known to be associated with the influence of complexes on dark initiation reactions, i.e. catalysis of hydroperoxide decomposition.[6] On the other hand, data exist indicating that ferrocene and its homologues are capable of acting as self-oxidation photocatalysts for organic compounds through activation of the oxygen molecule.[7] The problem of the effect of various ferrocene derivatives on hydroperoxide decomposition has not been studied in much detail.

Therefore the purpose of this work is to look at the effect of various derivatives of this kind on the rate of the t-butyl hydroperoxide (TBHP) decomposition reaction. The resulting data are presented in Table 1. Ferrocene (FcH) derivatives were found to initiate the TBHP decomposition, the rate of the process being correlated with the value of the redox potentials for the corresponding ferrocene derivatives in that the lower the potential, the higher the decomposition rate. This is accompanied by one-electron oxidation of the organometallic compound (Eqn [1]):

$$\mathrm{FcH} + \text{t-BuOOH} \rightarrow \mathrm{FcH}^{+\cdot} + \mathrm{OH}^- + \text{t-BuO}^\cdot \quad [1]$$

Then we correlated the rate of oxygen absorption by the polymeric samples doped with ferrocene derivatives in the dark and under UV irradiation. The corresponding kinetic curves are shown in Fig. 2. It is evident that in the presence of ferrocene derivatives the absorption rate is higher than that in the undoped ones. The presence of long induction periods in the dark processes may indicate that the ferrocene derivatives do affect the process of hydroperoxide decomposition via the preliminary build-up which generates a need for such a period. Note that the modified samples require a shorter induction period as compared with that for the catalyst-free ones (curves 2 and 1, respectively). This suggests that the appearance of induction periods cannot be attributed to ferrocene derivative decomposition and the effects of decomposition product catalysis.

Starting with the data obtained, the thermo-oxidative destruction can be discussed in terms of the classical degenerate/branched model. In this

Table 1 The influence of ferrocene compounds on t-butyl hydroperoxide (TBHP) decompositon[a]

Compound	Initial concentration (mol dm^{-3})	Final concentration (mol dm^{-3})	Quantity of TBHP decomposed (% mass)
—	0	0	0
Ferrocene	0.0100	0.0071	65.1
1,1′-Diethyl ferrocene	0.0100	0.0064	72.5
1,1′-Diethyl ferrocene	0.0010	0.0005	40.1
1,1′-Diethyl ferrocene	0.0050	0.0020	67.7
1,1′-Diethyl ferrocene	0.0100	0.0048	76.5
1,1′-Diethyl ferrocene	0.0200	0.0072	95.1

[a] Time, 10 min; solvent, cyclohexane/argon. See Barnard, D and Wong, K C, *Anal. Chim. Acta*, 1976, 84: 355.

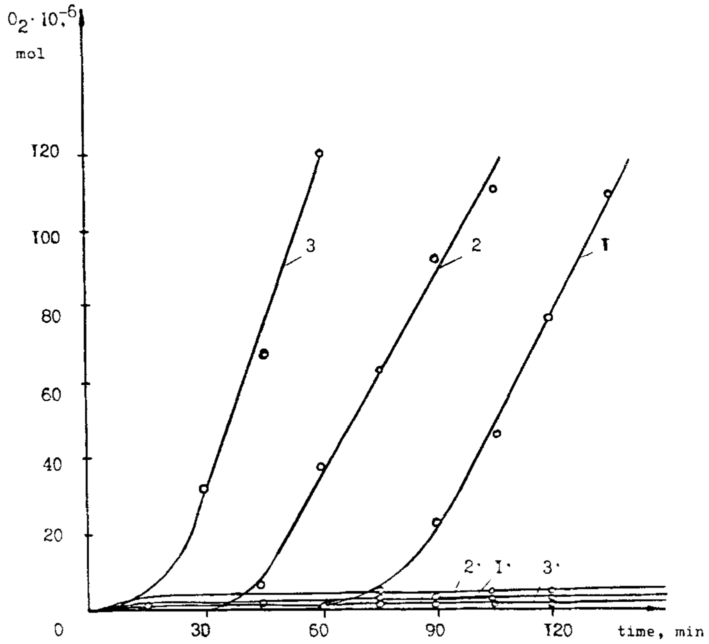

Figure 2 Kinetics of oxygen absorption by HDPE under UV irradiation (a DRSH-1000 lamp; $T = 293$ K; curves 1', 2', 3') and LDPE on thermo-oxidation ($T = 433$ K; $P = 300$ GPa; curves 1, 2, 3) DFP additive contents (mol kg^{-1}): 1 and 1', 0; 2 and 2', 0.001; 3 and 3', 0.01.

case the role of the derivatives consists in the initiation of hydroperoxide decomposition according to Eqn [1].

However, the processes of oxygen absorption by the polymeric samples under irradiation are distinguished by the rapid growth and absence of the induction period (see Fig. 2). This difference can be naturally linked to the participation of the ferrocene derivatives in the process of primary initiation. Thus the role of ferrocene derivatives in the process of photo-oxidative destruction cannot be reduced to the hydroperoxide decomposition alone.

2.3 EPR studies of photo-oxidative polyethylene destruction

The exposure of HDPE films to the entire visible range of a spherical mercury-vapour lamp gives rise to free radicals whose spectra are presented in Fig. 3. The EPR spectrum of the HDPE sample irradiated at 77 K is composed of eight hyperfine split lines with $\Delta H \simeq 22.5$G (Fig. 3, curve *1*).[8] Irradiation in air at 315 K involves the formation of short-lived radicals whose spectrum is formed by superposition of the alkyl and peroxide radicals (Fig. 3, curve *2*).

The addition of ferrocene and its derivatives to the polymer does not affect the form of the EPR spectra but greatly decelerates the process of

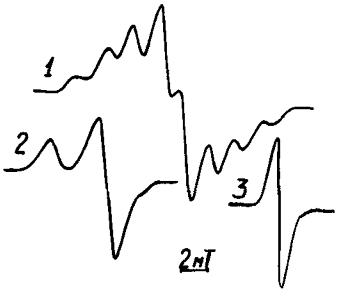

Figure 3 EPR spectra of the UV-irradiated HDPE (1, 2) and UV-irradiated HDPE with 0.010 mol kg^{-1} DEFP additive (3): curve 1, irradiation in air at 77 K; curves 2, 3, irradiation in air at 315 K. λ, 236–340 nm; *I*, 10^{17} quanta $cm^2 s^{-1}$. The spectra were recorded at 77 K.

Table 2 Quantum yield of free-radical formation reaction in the photolysis of HDPE and its compositions with ferrocene compounds[a]

Concentrations of the additive (mol kg^{-1})	Quantum yield, $\varphi_{R\cdot}$ (quanta cm^{-2} s^{-1})		
	Ferrocene	1,1′-Diethyl-ferrocene	DEFP
0	2.3×10^{-3}	2.3×10^{-3}	2.3×10^{-3}
0.001	7.0×10^{-4}	6.5×10^{-4}	3.7×10^{-4}
0.003	5.7×10^{-4}	2.8×10^{-4}	1.6×10^{-4}
0.005	4.8×10^{-4}	2.5×10^{-4}	1.2×10^{-4}
0.010	4.0×10^{-4}	2.3×10^{-4}	0.6×10^{-4}
0.020	3.7×10^{-4}	1.8×10^{-4}	0.3×10^{-4}

[a] $\lambda = 236$–340 nm; $I = 1.5 \times 10^{17}$ quanta cm^{-2} s^{-1}; $T = 77$ K; in air.

signal build-up in these spectra. On UV irradiation of the ferrocene and its derivatives the radicals are not detected at either 300 or 77 K. The dependence of the quantum yield of the radical formation reactions ($\varphi_{R\cdot}$) at 77 K on the concentration of the ferrocene additives, 1,1′-diethylferrocene and 2,2-bis(1,1′-diethylferrocenyl)propane, in polyethylene is shown in Table 2.

It is evident that the quantum yield decreases markedly with additive content, the highest effectiveness being displayed by 2,2-bis(1,1′-diethylferrocenyl)propane (DEFP) in that at concentrations of 0.020 mol kg^{-1} the yield, as compared with that for the HDPE containing no additive, decreases by *ca* two orders of magnitude.

However, the quantum yield found at 77 K in the kinetically stable conditions of the free radicals does not indicate that the initiation rate is typical of elevated temperatures (*ca* 300 K) in the presence of oxygen. Therefore this study deals with radical build-up directly under photo-oxidation conditions which are undoubtedly of practical interest. For this purpose the samples were irradiated with short (second-duration) focused light flashes from the spherical mercury-vapour lamp in air at 315 K, then rapidly cooled by immersion in liquid nitrogen and their EPR spectrum was recorded. The experimental data for radical build-up in the HDPE and HDPE + DEFP are presented in Fig. 4.

It can be seen in this figure that the effect of the DEFP additives on the initiation rate is anomalous as compared with that at low temperatures and agrees with the data of Section 2.1 above. At 77 K the DEFP additive only inhibits the process of radical formation whereas in the case of photo-oxidation at 315 K in air (depending on concentration) it displays both stabilizing and sensitizing properties. In small concentrations (under 0.003 mol kg^{-1}) it increases the rate of radical build-up, the quantum yield rising by *ca* two-fold compared with that for HDPE containing no additives. At concentrations of 0.010 mol kg^{-1} DEFP sharply decelerates the process of radical formation and the $\varphi_{R\cdot}$ value drops by nearly one order of magnitude. The kinetic data obtained by the above procedure allows us to determine the free-radical concentration in the quasi-stationary conditions (curves *2* and *3*, Fig. 4) and, hence, to estimate the termination rate constant for two HDPE + DEFP compositions. For HDPE with 0.010 mol kg^{-1} DEFP the rate constant is $K_{\text{term}} \geqslant 6 \times 10^{-18}$ cm^3 s^{-1} whereas for the same substance with 0.003 mol kg^{-1} DEFP, $K_{\text{term}} \geqslant 1 \times 10^{-19}$ cm^3 s^{-1}, i.e. the termination rate constants for the two cases differ by a factor of 60 or so.

One more interesting and important fact should be mentioned concerning the effect of the DEFP additive on the type of radicals appearing in the HDPE. Usually in the presence of mobile oxygen, polymer irradiation is accompanied not only by radicals build-up but also by their oxidation, and the EPR spectra represent the superposed signals of alkyl and peroxide radicals. The concentration of the latter can be readily determined

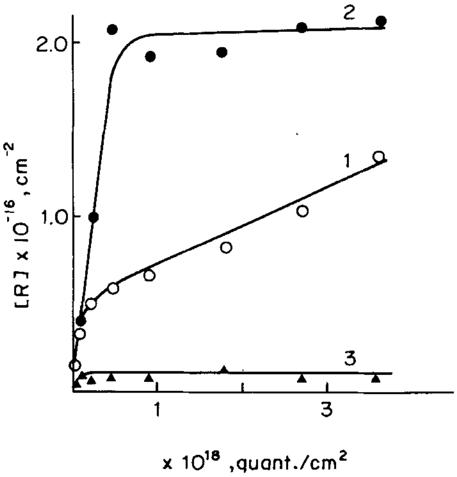

Figure 4 Kinetics of free-radical build-up in HDPE and its DEFP composition under UV irradiation of the samples in air at 315 K: *1*, HDPE; *2*, HDPE + 0.003 mol kg^{-1} DEFP; *3*, HDPE + 0.010 mol kg^{-1}DEFP (λ, 236–340 nm; *I*, 6×10^{16} quanta cm^{-2} s^{-1}; sample thickness, 2 mm; area irradiated, *ca* 0.5 cm^2).

Table 3 Quantum yields for the photoinitiation and photo-oxidation of HDPE and its DEFP compositions under UV radiation

Additive concentration (mol kg^{-1})	Quantum yield (quanta cm^{-2} s^{-1})		
	$\varphi_{R^{\cdot}}$	φ_{O_2}	φ_{gas}
0	0.03	0.04	0.11
0.003	0.05	0.10	0.22
0.010	0.006	0.06	0.01

[a] $\lambda \geq 236$ nm; $T = 315$ K; $P_{O_2} = 150$ Torr.

from a characteristic low-field peak of the asymmetric $RO_2^{\cdot}$ singlet. In the irradiation of polymer samples in which DEFP displays sensitizing properties, as in the case when an additive-free HDPE is irradiated, the EPR signal of the resulting radicals is composed of the superposed $R^{\cdot}$ and $RO_2^{\cdot}$ spectra (Fig. 3, curve *2*). In this case the $RO_2^{\cdot}$ fraction in such a composition from the very onset of irradiation will be *ca* 80% and this concentration will remain unchanged on further irradiation. In the irradiation of an HDPE containing 0.010 mol kg^{-1} DEFP the EPR spectrum is composed of a narrow low-intensity singlet (*ca* 11 G) whereas the peroxide radical spectrum is absent altogether (Fig. 3, curve *3*). It can be assumed that the narrow signal belongs to the O_2^- superoxide ion.

Hence, the high concentrations (over 0.010 mol kg^{-1}) of the DEFP additives in HDPE inhibit the formation of peroxide alkyl radicals and act as effective inhibitiors of radical reactions. They decrease the rate of initiation (the $\varphi_{R^{\cdot}}$ value drops by *ca* one order of magnitude as compared with that when no additive is used), increase the radical mortality rate (the reaction rate constant exceeds the K_{term} value by more than one order of magnitude for the HDPE + 0.003 mol kg^{-1} DEFP system) and suppress the formation of peroxide radicals.

We now discuss the behaviour of the DEFP additives in the photo-oxidation of HDPE. The quantum yields of initiation and photo-oxidation (from the oxygen absorption φ_{O_2} and evolution of the gaseous destruction products φ_{gas}) for the HDPE and two of its DEFP compositions are listed in Table 3.

The photo-oxidation rate is controlled by the quantum yield of the initiation reaction and, as can be seen from Fig. 5, the highest rate of initiation (Table 3) is matched with that of photo-oxidation (for the HDPE + 0.003 mol kg^{-1} DEFP composition). However, the most interesting system is that in which the DEFP behaves like a stabilizer (HDPE + 0.010 mol kg^{-1} DEFP). At a small $\varphi_{R^{\cdot}}$ value (*ca* 0.006) the φ_{O_2} value at the initial stage of the process is virtually coincident with that for the additive-free HDPE; however, the gaseous oxidation products are evolved in a minimum quantum yield (*ca* 0.01). As mentioned above, no peroxide radicals in the EPR spectra of these systems are recorded. Their absence (or low concentrations) may be responsible for a minimum quantum yield of the volatile oxidation products which are mainly formed during $RO_2^{\cdot}$ destruction. Thus the stabilizing effect of the DEFP additive on the process of HDPE photo-oxidation shows up in the inhibition of peroxide radical formation and, consequently, a lower rate of appearance of the gaseous oxidation products (Fig. 5).

It should be pointed out that a paradox of this situation consists in the fact that the HDPE samples with a high content of DEFP (0.010 mol kg^{-1}) are distinguished by a lowered quantum yield of the alkyl radicals (as compared with that of the additive-free species), on the one hand, and a more vigorous oxygen absorption with no appearance of $RO_2^{\cdot}$ on the other. This

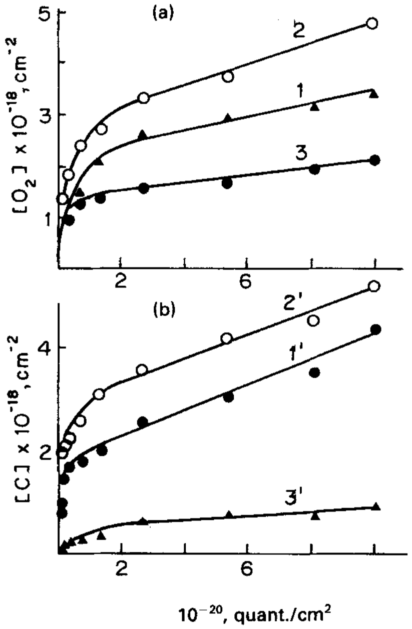

Figure 5 Kinetics of oxygen absorption (a) and evolution of volatile oxidation products (b) on the photo-oxidation of HDPE (*1*, *1'*) and its DEFP compositions in concentrations (mol kg^{-1}) of 0.003 (*2*, *2'*) and 0.01 (*3*, *3'*). P_{O_2}, 150 Torr; λ, 236–340 nm; $I = 1.5 \times 10^{17}$ quanta cm^{-2} s^{-1}; $T = 315$ K.

leads to an unexpected situation when despite a lower yield of the gaseous oxidation products and the general inhibition, the oxidation chain length ($l = \varphi_{O_2}/\varphi_{R^\cdot}$) increases as compared with that when both the additive-free HDPE and the same species with a low content of the same additive ($0.003\ \mathrm{mol\ kg^{-1}}$) are used. All this suggests that the principles observed cannot be interpreted in terms of the classical degenerate/branched chain photo-oxidation mechanism.

It could be appropriate to attempt to relate these principles to the photoabsorption effects of the ferrocene derivatives resulting in the shielding and, hence, protection of the polymeric matrix. In fact, both DEFP and 1,1′-diethylferrocene (like any other ferrocene derivatives) absorb in the region between 200 and 400 nm. In this case an accelerated polymer decomposition observed in the addition of small additive concentrations ($10^{-3}\ \mathrm{mol\ kg^{-1}}$) could be associated with the catalysis of this process by the decomposition products. However, such an interpretation contradicts data on the increased φ_{O_2} value at small additive concentrations and its decrease at high concentrations.

3. MECHANISM OF PHOTO-OXIDATIVE POLYETHYLENE POLYMER DESTRUCTION IN THE PRESENCE OF FERROCENE DERIVATIVES

One of the most important premises of the model proposed in this work is the assumption of the mechanism by which ferrocene derivative complexes are formed in the polymeric matrices. This assumption is based on the known data concerning the ability of these derivatives to give oxygen-containing complexes.[9]

Due to the fact that the fixed oxygen concentration in the non-polar HDPE-type is equal to *ca* $10^{-2}\ \mathrm{mol\ kg^{-1}}$,[10] it can be assumed that the whole of the ferrocene or its major portion is bound to such complexes (Eqn [2]):

$$\mathrm{FcH} + \mathrm{O_2} \rightleftharpoons \mathrm{FcH \cdot O_2} \qquad [2]$$

As has been shown earlier, the irradiation of these complexes results in the photoinduced transfer of an electron to give a ferricinium cation and superoxide ion (Eqn [3]):[11]

$$\mathrm{FcH \cdot O_2} \xrightarrow{h\nu} \mathrm{FcH^{+\cdot}} \ldots \mathrm{O_2^{-\cdot}} \qquad [3]$$

At small ferrocene concentrations the superoxide ion has time to undergo a reaction in a cage to provide for a fairly high initiation rate at a relatively short chain length ($l \simeq 2$, Table 3). Thus in this case the process occurs by an ordinary oxidation mechanism at a higher photoinitiation rate. It is quite probable that this process involves a singlet oxygen, too (Eqn [4]):

$$\mathrm{FcH^{+\cdot}} + \mathrm{O_2^{-\cdot}} \rightarrow {}^1\mathrm{O_2} + \mathrm{FcH} \qquad [4]$$

At higher additive concentrations when the average intermolecular distances between the organometallic compounds reduce to $\leqslant 10$ Å (1nm), there appears a possibility for realizing the exchange diffusion mechanism for the ferricinium cation–$\mathrm{O_2^{-\cdot}}$ pair[12] (Eqn [5]):

$$\mathrm{FcH/O_2} \ldots \mathrm{FcH/O_2} \ldots \mathrm{FcH^{+\cdot}/O_2^{-\cdot}}$$
$$\rightleftharpoons \mathrm{FcH^{+\cdot}/O_2^{-\cdot}} \ldots \mathrm{FcH/O_2} \ldots \mathrm{FcH/O_2} \qquad [5]$$

As in the case of low concentrations, one can observe the generation of $\mathrm{O_2^{-\cdot}}$ which is likely to be responsible for the above described narrow singlet, but here the electron exchange reaction [5] is possible. The exchange diffusion will lead to the superoxide ion being brought out beyond the polymer sample to the polar phase on its surface without first reacting in the cage. On the other hand, the oxygen absorption rate in this process should not be lower than that in the pure HDPE. This is a kind of oxygen photoreduction with a ferrocene derivative and 'circulation' of the oxygen through the polymer sample. Therefore the apparent chain length will increase as compared with that of the samples, in which the concentration of such a derivative is low ($l = \varphi_{O_2}/\varphi_{R^\cdot} \simeq 10$) (Table 3).

Concerning the behaviour of the radical pair being brought onto the surface, it will either convert to hydrogen peroxide in the presence of water or ferrocene and ${}^1\mathrm{O_2}$ will be generated under the effect of a harder irradiation component.[13]

To confirm the possibility of hydrogen peroxide formation in these cases, we studied the decane/water model system being oxidized with oxygen in the presence of 1,1′-diethylferrocene. Using a 500 W filament lamp we found that a build-up of hydrogen peroxide in the water phase (peroxidase test, citrate–phosphate buffer, 480 nm) takes place.

The model disclosed permits not only the interpretation of the above descrived concentration anomalies but it is free of the inconsistencies typical of the photoabsorption and photodestruction mechanisms.

4. EXPERIMENTAL

The studies were made with commercially available HDPE and LDPE. Used as additives were ferrocene, 1,1'-diethylferrocene, 2,2-diferrocenylpropane (DFP) and 2,2-bis(1,1'-diethylferrocenyl)propane (DEFP) in 1×10^{-3}–2×10^{-2} mol kg^{-1} of polymer. The ferrocene additives were introduced into the polymer by mixing ether solutions with powdered polymer and then, after removal of the solvent, films were prepared by pressing at 155 °C in argon. The ferrocene was purified by sublimation whereas 1,1'-diethylferrocene and DEFP were purified by in-vacuo distillation (the polyethylene used is 110–120 °C).

The samples were photoirradiated in liquid nitrogen at 77 K in a closed manometric system, as well as in air and under oxygen atmosphere ($P_{O_2} = 150$ Torr) at 300 K. A high-pressure mercury-vapour discharge lamp was used as a source of UV radiation $\lambda = 236$–340 nm, luminous flux intensity $= 6 \times 10^{16}$–1.5×10^{17} quanta cm^{-2} s^{-1}). The EPR spectra were recorded with a spectrometer at a microwave field power of *ca* 10^{-4} W. Photo-oxidation of the HDPE and its compositions with DEFP was studied by means of the oxygen absorption rate and data on the evolution of the gaseous oxidation products as the samples were irradiated in a closed manometric system.

The quantum yields of the radical formation reactions and photo-oxidation of the samples were determined on an assumption of full active light absorption by the samples 2 mm thick (the sample thickness was selected experimentally and the active light band at $\lambda = 236$–340 nm determined from the radical formation reaction in a low-temperature HDPE photolysis).

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