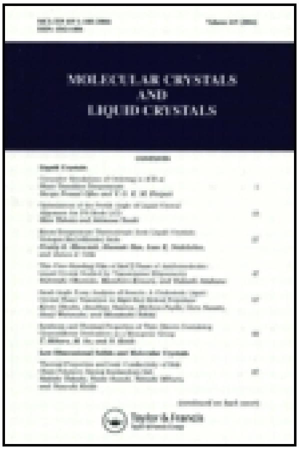

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Time Dependent Reactivity in the Post Irradiation Oxidation of Polypropylene

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KINETIC MODELLING OF SOLID STATE REACTIONS: TIME DEPENDENT REACTIVITY IN THE POST IRRADIATION OXIDATION OF POLYPROPYLENE.

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Abstract A kinetic model for the radiation induced oxidation of isotactic polypropylene film (38μ thick) has been developed which allows determination of the concentration profiles, rate constants and diffusion coefficients. The match with the experimental data is consistent with a distribution of reactivity that changesduring the course of the reaction giving rise to time dependent rate constants according to the Plonka's equation ($k=k_0t^{(\alpha-1)}$).This equation can be rationalized within the framework of the random walk models under the assumption of temporal, geometric or energetic disorder. The origin and the characteristics of the reactivity distribution have been investigated by an ESR spectroscopy study of the degree of order and the molecular dynamics of the intermediate peroxy radicals.

Keywords: Dispersive kinetics, Kinetic modeling, Structure-reactivity relationships, Peroxy radicals, Electron spin resonance, Polypropylene

INTRODUCTION

The simulation of oxidation processes in solid polymers is important from a practical point of view since it suggests the possibility of predicting the lifetime of the materials and of optimizing the use of stabilizers and other additives. Furthermore, it is a challenging effort for fundamental research since it requires the investigation of the peculiar effects arising from the solid state, in particular the dispersive kinetics reflecting distributions of reactivities and their origin, the role of molecular dynamics and the influence of the structure and morphology of the matrix. Pursuant to previous investigations (1,2,3,4), in this paper we give a description of the radiation induced oxidation of isotactic polypropylene based on a more complete set of experimental data and a more adequate treatment of the time dependent reactivity.

EXPERIMENTAL

Polypropylene with 97.5% isotacticity, from Montedison, was cast at 200 °C into bioriented films of 38 μ thickness. The films were sealed under high vacuum in quartz tubes and submitted to gamma radiation at 77 K to a total dose of 5 Mrad. After the irradiation the samples were kept at room temperature for 15-20 minutes. This procedure enabled us to obtain a relatively uniform population of initiating radicals since the radiation dose was enough to reduce spur concentration effects. The ESR spectra recorded after the annealing were consistent with the presence of only a single species, namely the macroalkyl radical formally arising from the cleavage of the tertiary C-H bond:

$$-CH_2\dot{C}(CH_3)-$$

The reaction was initiated at room temperature by admitting oxygen at a pressure of about 200 torr. During the oxidation the following experimental measurements were made: the oxygen uptake with a gas volumetric apparatus using silicon oil as manometric fluid; the yield of hydroperoxides by spectrophotometric determination of the I^{3-} ions (5); the decay of initiating radicals, and the build up and decay of peroxy radicals by ESR spectroscopy.

The reaction was followed during several months up to a decay of more than 90% of the maximum concentration of peroxyradicals. The experimental data are collected in Figs. 1-2 and presented together with the computed results for the sake of comparison.

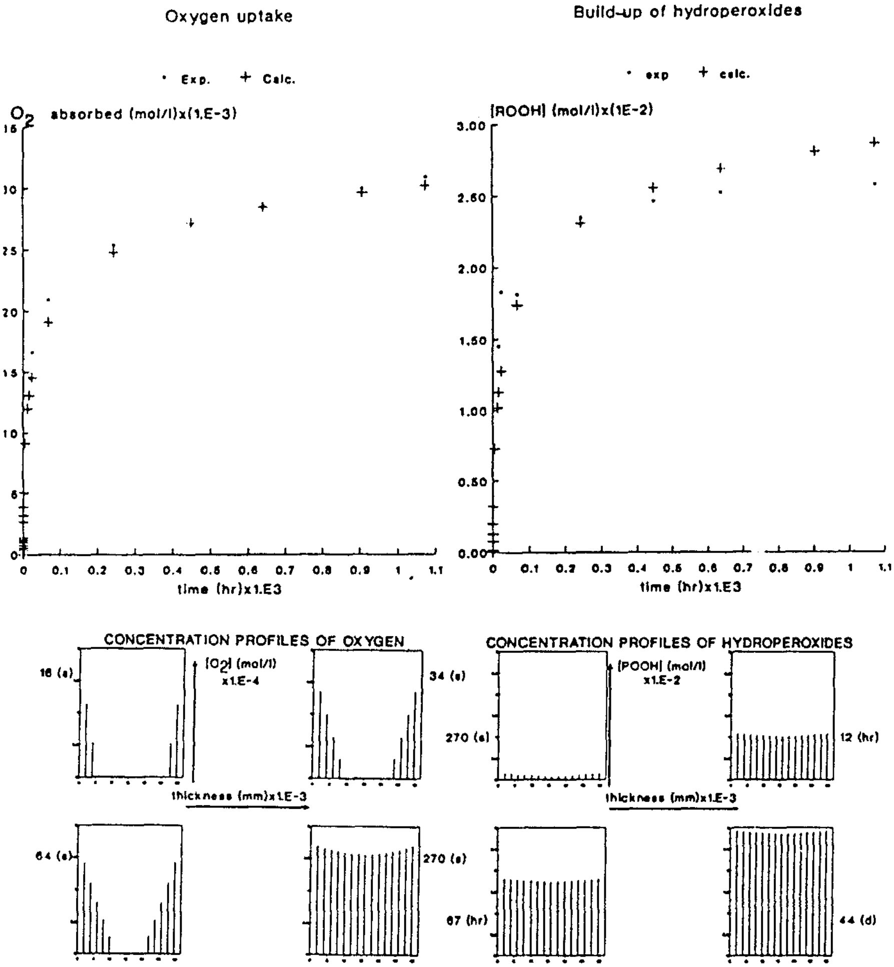

FIGURE 1 Post-irradiation oxidation of isotactic polypropylene films of 38μ thickness: experimental and calculated kinetics of the hydroperoxides and oxygen uptake .

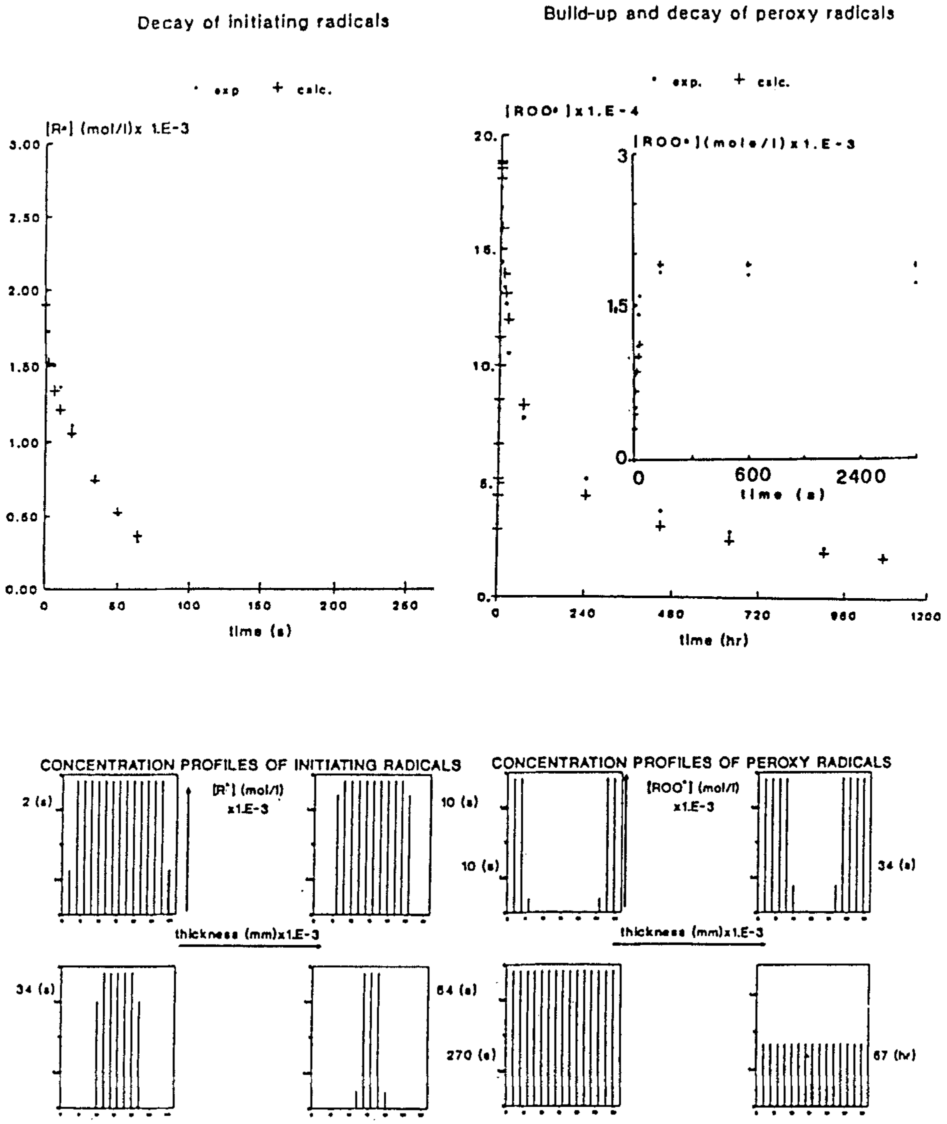

FIGURE 2 Post irradiation oxidation of isotactic polypropylene films of 38 μ thickness: experimental and calculated kinetics of the initiating and peroxy radicals.

Kinetic Model

The kinetic model was based on the set of elementary reactions shown in Table 1.

The material balance at the end of the reaction shows that more than 80% of the oxygen absorbed is converted to hydroperoxides. This was confirmed by IR measurements which showed no appreciable increase in the carbonyl and OH bands. As a consequence, reactions 4,7,8 have been considered to be of negligible importance under the experimental conditions employed, and their rate constants have been kept equal to zero in the fitting procedure.

These reactions are expected to become important in the in source oxidation and in the post-irradiation oxidation at higher temperature.

TABLE 1 Reaction scheme and rate constants derived from the kinetic model through a best fit procedure.

	Reactions	*Kinetic Constants* ($L.M^{-1}sec^{-1}$)
1	$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}$	10^7
2	$RO_2^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$	$3.x10^{-2} \rightarrow 4.4x10^{-6}$ *
3	$RO_2^{\cdot} + RO_2^{\cdot} \longrightarrow ROOR + O_2$	$2.x10^{-2} \rightarrow 3.3x10^{-4}$ *
4	$RO_2^{\cdot} + RO_2^{\cdot} \longrightarrow 2RO^{\cdot} + O_2$	
5	$RO_2^{\cdot} + R^{\cdot} \longrightarrow ROOR$	$7.5x10^{-3} \rightarrow 1.2x10^{-4}$ *
6	$R^{\cdot} + R^{\cdot} \longrightarrow RR$	$6x10^{-3} \rightarrow 9.8x10^{-5}$ *
7	$RO^{\cdot} + RH \longrightarrow ROH + R^{\cdot}$	
8	$RO^{\cdot} \longrightarrow RR'{=}O + R^{\cdot}$	
	Diffusion	
O_2	D (cm^2/sec)	$2.x10^{-7}$ *
$R^{\cdot}$	" "	$< 5.x10^{-17}$
$RO_2^{\cdot}$	" "	$< 5.x10^{-17}$

for k_2, k_4, k_5, k_6 $k = k_o t^{(\alpha-1)}$ $0 < \alpha \leq 1$

* = rate constants and diffusion constant of O_2 used as fitting parameters.

In the formulation of the model, the film of thickness L was ideally divided into a number, n, of layers of thickness $h = L/n$; then, by assuming a monodirectional diffusion along the direction x perpendicular to the film surface and constant diffusion coefficients, a set of diffusion-reaction differential equations were derived for the concentration variables in each layer using Fick's second law. By applying the discretization formula to the second order derivatives, a first order ODE system was obtained and was integrated by numerical methods. The discretization formula has a definite physical meaning since it represents the balance of the fluxes in each layer, each flux being represented by a linear equation of the type

$$F_i = k_i C_i$$

where $k_i = D_i/h^2$ (Table 2).

TABLE 2 Diffusion-reaction equations for the post irradiation oxidation of isotactic polypropylene

$$\frac{\partial C_1}{\partial t} = D_1 \cdot \frac{\partial^2 C_1}{\partial x^2} + f_1(C) \qquad \frac{\partial C_4}{\partial t} = D_4 \cdot \frac{\partial^2 C_4}{\partial x^2} + f_4(C)$$

$$\frac{\partial C_2}{\partial t} = D_2 \cdot \frac{\partial^2 C_2}{\partial x^2} + f_2(C) \qquad \frac{\partial C_5}{\partial t} = D_5 \cdot \frac{\partial^2 C_5}{\partial x^2} + f_5(C)$$

$$\frac{\partial C_3}{\partial t} = D_3 \cdot \frac{\partial^2 C_3}{\partial x^2} + f_3(C)$$

$C = [C_1, C_2, C_3, C_4, C_5]$ $\quad f_i(C) = \Sigma_i k_i C_i$. = reaction terms

$C_1 = [R^\cdot]$ $\quad C_2 = [RO_2{}^\cdot]$ $\quad C_3 = [RO^\cdot]$ $\quad C_4 = [O_2]$ $\quad C_5 = [ROOH]$

$$D_i \frac{\partial^2 C_i}{\partial x^2} = \frac{D_i}{h^2} \left\{ C_i(x+h) + C_i(x-h) - 2C_i(x) \right\}$$

Here, $h = l/n$, l = thickness of the film, n = number of layers

$k = k_o\, t^{(\alpha-1)}$

Because of the rapidity of the first stage of the oxidation (reactions 1,2 in the scheme) the system of differential equation is higly stiff and the numerical integration had to be performed by a stiff method developed by Gear (6).

Gear's method is a variable order and step size multistep implicit method based on the backward difference formulas. At each step the algorithm generates a non-linear system of equations, which is solved by the generalized Newton method. The procedure inherent in the kinetic modelling implies that initially the number of layers be determined to achieve constancy of the results. In the present case a number, $n < 9$, was necessary. Successively, best fit calculations with respect to the experimental data were done using a least squares method based on the Levemberg-Marquandt algorithm (7). The rate constants of reactions 2,3,5,6 and the diffusion coefficient of oxygen were used as fitting parameters (asterisked in Tab.1). The rate constant of reaction 1 was assigned a fixed value in the range reported in the literature (8). The diffusion coefficients for the intermediate radicals, which could not be determined because of the lack of experimental concentration gradient data, were assigned values estimated from the Smolouchowski equation relating diffusion constants and decay rate constants (9)

$$D = k_c \cdot 1000/4\pi R N_a$$

RESULTS

The reaction shows two distinct stages: the first stage is accomplished in about 200 seconds and is characterized by a relatively fast diffusion of oxygen through the layers with a sharp boundary surface and the build up of strong concentration gradients for the macroalkyl and peroxy radicals (Figs. 1,2). The second stage is much slower and is under the kinetic control of the hydroperoxidative cycle based on reactions 1 and 2. As a consequence, (see the concentration profiles of the hydroperoxides in Fig.1), most of the oxidation takes place in a situation of uniform oxygen concentration throughout the layers.

Time Dependency of the Rate Constants

A most important inference stemming from the kinetic model is that the rate constants are predicted to be time dependent according to the equation originally proposed by Plonka to account for numerous experimental data in condensed media and predicted by the same author to be of general validity in solid state kinetics (10,11,12)

$$k = k_o t^{(\alpha-1)} \qquad 0<\alpha\leq 1 \qquad 1)$$

A rationalization of the physical meaning of this equation can be based on the following arguments (11): the time dependency of the rate constants is the consequence of a distribution of reactivity that changes during the course of the reaction when the relaxation of the matrix is slow compared to the process. Considering a first order process as an example, if the matrix relaxation is fast with respect to the process, the distribution expressed in terms of lifetimes would not change with the time and the kinetics would be described by an average time independent rate constant described by the equation :

$$<1/\tau> = f(\tau,0)(1/\tau)d\tau$$

On the other hand if the rate of relaxation is slow, the distribution of reactivity will change with the time according to the equation

$$f(\tau,t)= f(\tau,0)\exp(-t/\tau) \qquad 2)$$

As a consequence there will be a more rapid depletion of the more reactive species and the decay will be multiexponential:

$$C/C_o = \int_0^\infty f(\tau,0)\exp(-t/\tau)d\tau = \exp-(t/\tau)^\alpha \qquad 3)$$

By definition, the equation $\exp(-t/\tau)^\alpha$ is an approximation of the Laplace trasform of the distribution $f(\tau,0)$. Furthermore, it corresponds to the analytical solution of first order kinetics provided that a time dependence of the life times is assumed according to equation 1 with $1/\tau_0 = k_0 = B/\alpha$. It follows from these observations that there is the possibility of recovering the distribution $\psi f(\tau, t)$ through the inverse Laplace transform of $\exp-(t/\tau)^{\alpha}$. Unfortunately there does not seem to be a closed form analytical solution for this equation. Only approximate solutions have been obtained by saddle point calculations by Majumdar (13). The time dependency of the reactivity expressed by equation 1 may be justified within the framework of the random walk model by assuming a continuous distribution of residence times of the species at the sites of the matrix. This is expressed by the equation $\psi(t) = t^{-(\alpha-1)}$ (14, 15), from which the number of distinct sites visited at the time t, $N(t) = t^{\alpha}$, is obtained. By introducing N(t) in the equation expressing the reaction rate constant:

$$k = b dN(t)/dt$$

where b is the volume of each site, the equation 1 is obtained. Similar derivations of the equation 1 can also be based on assumptions that the distribution of reactivity is generated by a distribution of activation energies for site to site jumping (energetic disorder) (14) or from a distribution of reaction distances (spatial disorder) (14).

Time Dependent Reactivity and Degree of Order at the Reaction Sites

Most of the oxidation seems to occur in regions characterized by low degree of order ('amorphous phase'). This is inferred from the fact that the ESR spectra of the macroalkyl radicals and peroxyradicals, which are obtained by photolysis of hydroperoxides at the end of the oxidation according to the scheme:

$$-CH_2C(OOH)(CH_3)- \xrightarrow{h\nu} -CH(CH_3)-\dot{C}H_2 \xrightarrow{O_2} -CH(CH_3)CH_2OO^{\cdot}$$

$$-CH(CH_3)\dot{C}H_2 \longrightarrow -CH_2\dot{C}(CH_3)CH_2- \xrightarrow{O_2} -CH_2C(OO^{\cdot})(CH_3)CH_2-$$

show only a limited, though detectable, anisotropy (16). A closer look at the problem of the morphology of the reaction sites can be obtained by following the changes in the ESR spectra of the residual peroxyradicals as a function of the orientation of the film and the reaction time. A significant dependence of the spectra on the angle between the main stretch direction and the magnetic field can be detected from the start (Fig.3). This becomes more and more evident with the progress of the reaction.

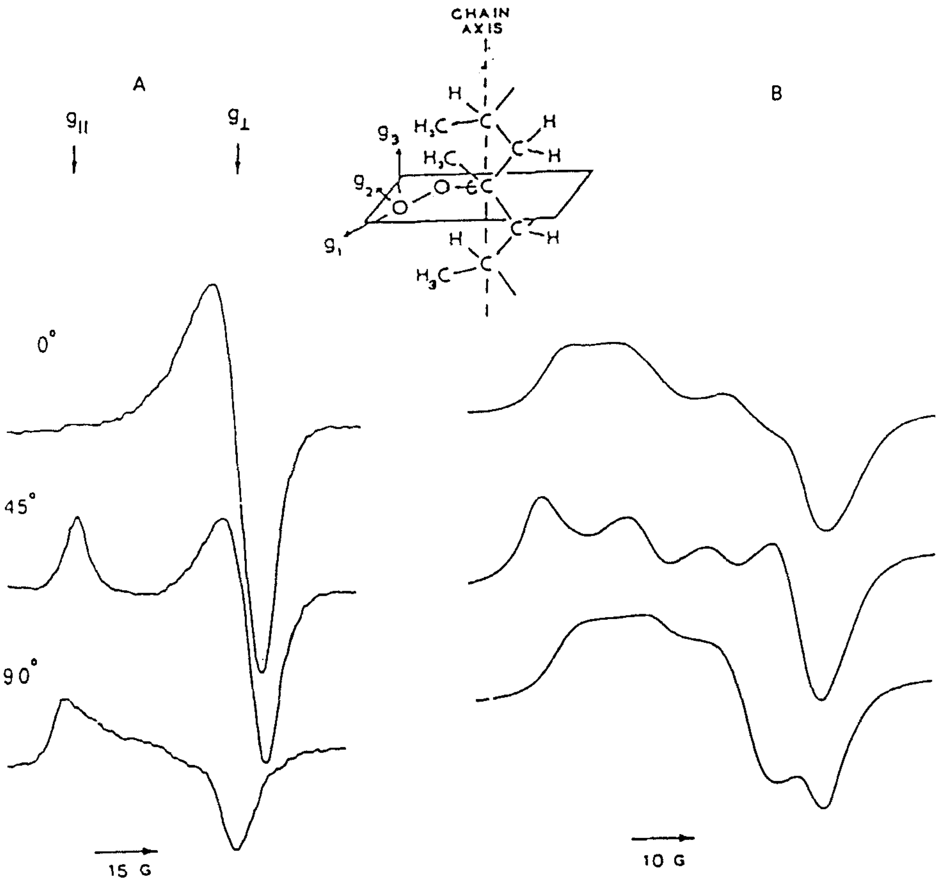

FIGURE 3 Post-irradiation oxidation of isotactic polypropylene: dependence of the peroxy radicals ESR spectra on the orientation of the magnetic field with respect to the main stretching direction of the films. Sequence A is recorded after about 150 days and sequence B soon after the admission of oxygen.

As a consequence of this trend, at the end of the reaction the residual fraction of peroxy radicals (less than 5% of the initial amount) shows ESR behaviour consistent with the trapping in 'crystalline' type regions with the polymer chains aligned along the main stretching direction and the COO planes of the radicals oriented perpendicularly to the chain axis (Fig.3). This situation causes the ESR spectrum to appear as a singlet at g = 2.00 or as a random pattern depending whether the field is perpendicular or parallel to the chain axis respectively (Fig.3) (17). The picture stemming from these observations is that the peroxyradicals experience a range of degrees of order from amorphous to crystalline, and that the average order of the residual reaction sites is enhanced with increasing the reaction time. This latter effect and the connection with the observed time dependency of the rate constants implies that the decay rate of the peroxyradicals as well as the overall oxidation rate are faster the lower the degree of order at the sites.

Time Dependent Reactivity and Molecular Dynamics of the Reacting Species.

Another approach to a direct insight into the reactivity distribution in the oxidation process can be based on line shape analysis of the ESR spectra of the peroxyradicals performed according to the modified Bloch formalism (17,18,19). This method enables information to be obtained on the nature and frequencies of the molecular motions that modulate the g tensor anisotropy of the peroxyradicals during the course of the reaction. The experimental and computed spectra reported in Fig.4, which show the similarity of line shape changes induced by the temperature and reaction time, lead to the conclusion that a progressive decrease of the average mobility of the surviving peroxyradicals takes place during the reaction. This effect is a consequence of a faster depletion of the more mobile (more reactive) species and of the progressive trapping of the surviving species in sites with higher trapping efficiency.

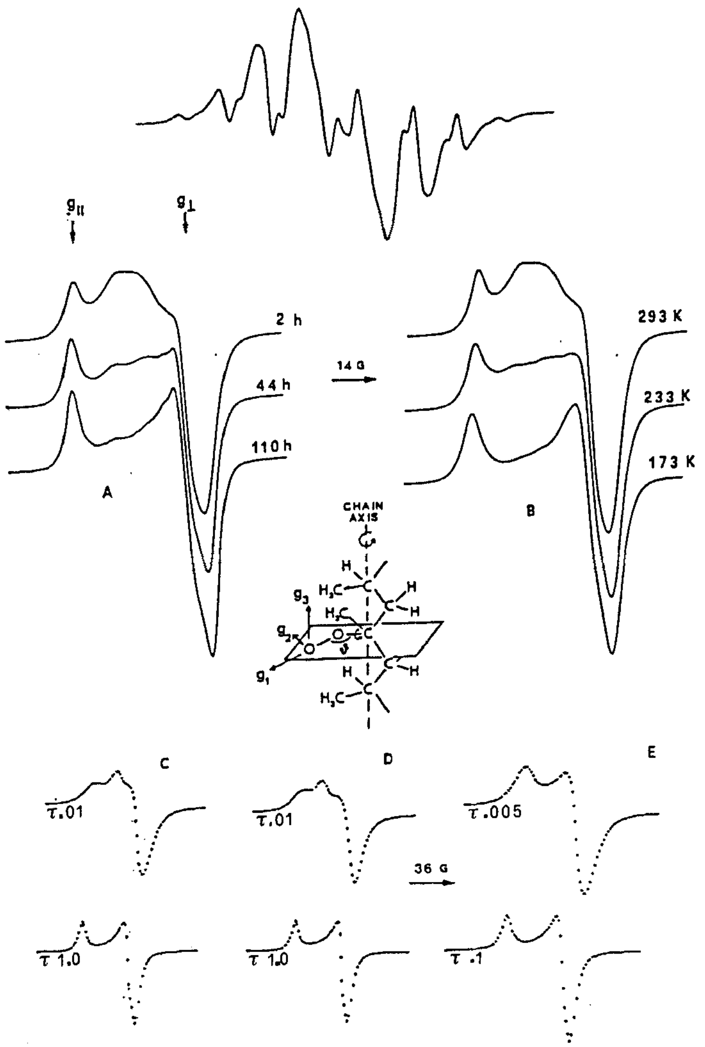

FIGURE 4 Post-irradiation oxidation of isotactic polypropylene: effect of reaction time (sequence A) and of the temperature (sequence B) on the line shape of the peroxyradicals ESR spectra. The top spectrum is that of the initiating macroalkyl radicals before the admission of oxygen. C, D, E, are the computer simulations based, respectively, on the motional models of cubic jump, rotation about the chain axis, rotation about the C-O bond (COO angle = 104°). The correlation times are in microseconds.

In the initial stage of the reaction, motions of greater amplitude are allowed such as 'cubic jump' (interconversion of the principal values of the g tensor by rotation about a body diagonal of a cube) and rotation about the chain axis. These motions give rise to characteristic extra features between the $g_\perp$ and $g_\parallel$ field positions. In the latter stage, only the rotation about the C-O bond is possible at a progressively decreasing rate. The progressive slowing down of the rotation about the C-O bond is made evident by the correlated lineshape changes in the peroxy radical spectrum, which consists of an increase of the distance between the peaks at $g_\perp$ and $g_{//}$ (Fig.4). The molecular dynamics of the peroxy radicals correlate nicely with the change of their degree of alignment as well as with the observed change of reactivity. These effects can be regarded as direct evidence of the dispersion of the reacting species at a variety trapping sites where they experience different constraints exercised by the matrix, the mobility being higher the lower the degree of order. This in turn gives rise to a distribution of residence times and activation energies for site to site jumping which are the origin of the observed time-dependent reactivity. The molecular dynamics study also affords evidence of the motion of peroxy radicals throughout the matrix, which may occur by a relay mechanism based on free valence migration combined with diffusion (20). A most challenging perspective in this type of investigation is represented by the possibility of finding quantitative correlations between the parameters of molecular motion and reaction rate constants. These correlations would allow reactivity distributions to be predicted by molecular dynamics experiments, which can be performed with a variety of powerful spectroscopic techniques.

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