E.s.r. studies on oxidation processes in irradiated polyethylene: 1. Diffusion of oxygen into amorphous parts at low temperatures

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(Received 4 June 1976)

Oxidation processes in irradiated polyethylene were studied by e.s.r. By utilization of the characteristic feature of power saturation of the e.s.r. spectrum of peroxide radicals, quantitative measurement of the process of the reaction of oxygen with allylic radicals trapped in the amorphous part of the polyethylene were made and the data were analysed based on the diffusion-controlled process theory. Diffusion equations were solved by computer simulation method. Diffusion of the oxygen into the amorphous part of the polyethylene is discussed and diffusion constants at low temperature are estimated. Related values such as the activation energy of the diffusion process and the solubility constant, are also estimated.

INTRODUCTION

In this paper, we study the post-irradiation oxidation of linear polyethylene using the e.s.r. technique; (a) measuring a small number of the peroxy free radicals of the polyethylene in a large number of the carbon radicals quantitatively by means of the e.s.r. method; (b) confirming by computer simulation that the reaction of the oxygen with the allylic radicals is a diffusion-controlled one in the amorphous part of the linear polyethylene at lower temperature; (c) observing the smaller diffusion constant of the oxygen into the amorphous region of the polyethylene at low temperature.

The mechanism of the oxidation of polyethylene has been studied in many investigations of thermal oxidation[1,2] and radiolytic oxidation[2–4]. In these oxidation processes, especially in the processes at low temperatures, i.e. the radiolytic oxidation, the diffusion of the oxygen into polyethylene was considered to be an important mechanism.

All of these studies were, however, made by the application of the optical method. Therefore, quantitative considerations about the oxidation processes were never established in these studies, because the optical method contains an uncertainty in obtaining the quantitative data on the stage of the reaction, and the groups measured in the optical studies are not always the peroxy radicals. Observations and estimates of the peroxy radicals, which are the direct products at a certain stage of the reaction between oxygen and carbon radicals, must present useful data for the consideration of the oxidation processes. However, since we applied the e.s.r. method in order to measure the amount of peroxy radicals, the reaction of the oxygen of the allylic radicals are successfully analysed quantitatively; i.e. the mechanism of the reaction can be confirmed.

The quantitative measurement of the amount of free radicals can be performed by a double integration of the first derivative e.s.r. spectrum of the radicals consisting of only one species. If the radicals consist of more than two components, it is difficult to calculate the amount of one of them. In order to overcome this difficulty, the height of the peak which is not superposed on another spectrum is normally used as the scale of the concentration of the radicals. This method is, however, not advantageous if all the peaks of the spectrum under consideration are not distinguished from that of the superposed spectrum, and the shape of the spectrum changes during the measurement for a considerable length of time. For this reason, the above mentioned method was not applicable to the present study in order to calculate the concentration of the peroxy radicals as the spectrum of the peroxy radicals has no peak that can be distinguished from that of the allylic radicals, and the shape of the allylic radicals' spectrum changes in different trap-site.

Therefore, we adopted the use of the difference of the power saturation behaviour between the peroxy radicals and the carbon radicals reported by Ohnishi and coworkers[5]. By using this method, we could measure the concentration of the peroxy radicals existing with a large number of the allylic radicals in the linear polyethylene. This procedure will be described in detail in a later section.

Concerning the diffusion of the oxygen into polyethylene, Michaels and his coworkers[6,9] and Giberson[3,10] have studied in detail the diffusion processes of several gases into polyethylene and into the irradiated polyethylene. Experimental conditions in their studies restricted the measurements of the small value of the diffusion constant of oxygen into polyethylene, and only the diffusion constants of the order of 10^{-8} cm^2/sec or much larger could be measured. However, diffusion constants of oxygen into the crystalline part of polyethylene must be much smaller, and it is probable that the smaller diffusion constant for the amorphous part can be obtained at lower temperatures. In this respect, application of e.s.r. technique and computer simulation of the diffusion-controlled reaction mechanism gave a much more accurate determination of the smaller diffusion constant at lower temperatures.

EXPERIMENTAL

Samples used in this study were powders of linear polyethylene ranging from 50 to 100 mesh, and were made from resins of Sholex 6050 after refluxing three times in

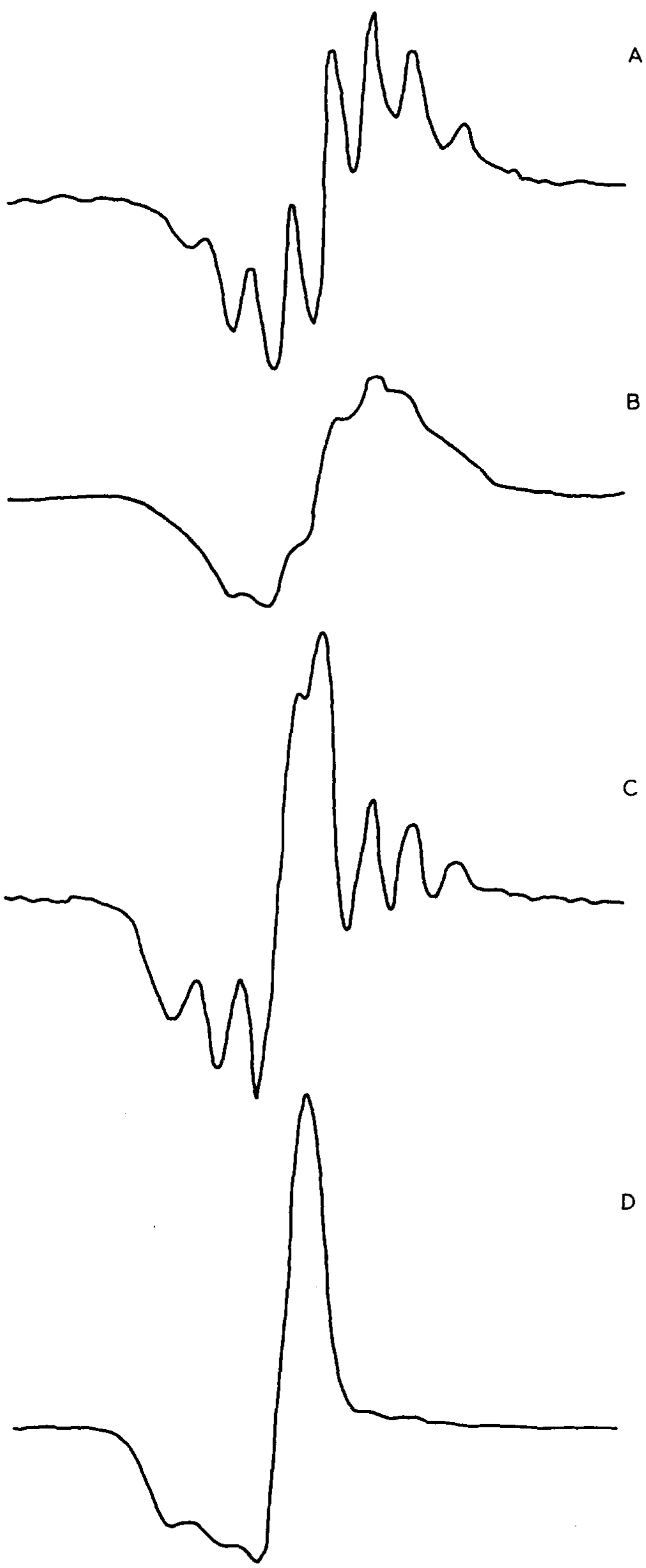

Figure 1 Changes of the e.s.r. spectra due to the applied microwave powers and duration of the reaction of oxygen with free radicals. A, 0.1 mW, $t = 0$; B, 10 mW, $t = 0$; C, 0.1 mW, $t = 4$ h; D, 10 mW, $t = 4$ h

toluene and washing three times in acetone. The powder consists of blocks of sizes ranging from 20 to 50 μm in diameter, and the amorphous volume fraction of this powder determined from density measurements was 24%.

About 50 mg of the powder were put into a Pyrex glass ampoule with two breakable seals. After evacuating for 6 h at 10^{-6} Torr, the samples were irradiated with ^{60}Co γ-rays at room temperature and stored for a week. After storage, almost all of the alkyl radicals disappeared and only the allylic radicals were trapped in the sample. The total dosage was ~20 Mrad at a dose rate of 0.25 Mrad/h. The hydrogen gas produced during the γ-irradiation was evacuated through a breakable seal. The sample tube was heated to eliminate the colour centres in the glass. A tube with a breakable seal, separated from the sample tube for e.s.r. observation, was filled with oxygen at a known pressure.

The e.s.r. measurements were made using a JEOL ME-3 X-band spectrometer. The amount of nitrogen gas flowing from the Dewar-vessel of liquid nitrogen and the heater current along the guide tube of the flowing nitrogen gas were well controlled for the setting of the temperature of e.s.r. observation. The microwave power was kept at 10 mW throughout the measurements. The signals were recorded by a JEOL spectrum computer, Model JEC-6.

After the desired temperature of the samples placed in the e.s.r. cavity was achieved, the oxygen molecules were introduced into the e.s.r. sample tube by breaking the seal. The e.s.r. signals were recorded at appropriate time intervals. The signal intensity was obtained by a double integration of the recorded first derviative signals.

RESULTS

When the peroxy radicals form a minor fraction, observation of the e.s.r. spectrum with power saturated condition is an advantage for measuring the spectrum from peroxy radicals. Though this was already mentioned in a previous paper, this advantage can be seen in *Figure 1*. In *Figure 1*, A and B are the e.s.r. patterns of the allylic radicals with microwave power of 0.1 mW and 10 mW respectively, and C and D are the superpositions of the spectra from allylic radicals and peroxy radicals with the microwave power of 0.1 mW and 10 mW, respectively. Both C and D are the spectra observed 4 h after the introduction of oxygen. Therefore, the number of the total spins must be constant for patterns A, C and B, D, but the D pattern emphasizes the peroxy radicals. This emphasis of the change from the allylic radicals to the peroxy radicals with power of 10 mW can be shown more clearly by the values of double integration of the e.s.r. spectra. The change of the integral values are as follows: $S_A = 225916, S_C = 260095$ (for 0.1 mW) and $S_B = 211308, S_D = 459940$ (for 10 mW). As mentioned above, the small quantity of the peroxy radicals in a large number of the allylic radicals trapped in the polyethylene must be calculated by using the change of the integration values of the e.s.r. signals with the power saturated condition.

The change of the integral values, $S_t - S_0$, in proportion to the quantity of the peroxy radicals will now be discussed. Verification of this estimation can be shown based on the following reasonable assumptions: (a) the values of the double integration of e.s.r. signals of different radicals is proportional to the concentration of the respective radicals at every microwave power; (b) the peroxy radical is produced from the allylic radical in the ratio of one to one and does not disappear. At $t = 0$, the concentration of the allylic radicals is C_0 and the integral value of the e.s.r. signals is AC_0. At $t = t_1$, the concentrations are C_{t_1} for the allylic radicals and $C_0 - C_{t_1}$ for the peroxy radicals, and the integral values are AC_{t_1} and $B(C_0 - C_{t_1})$, respectively; so $S_{t_1} = AC_{t_1} + BC_0 - BC_{t_1}$. In the same manner, S_{t_2} =

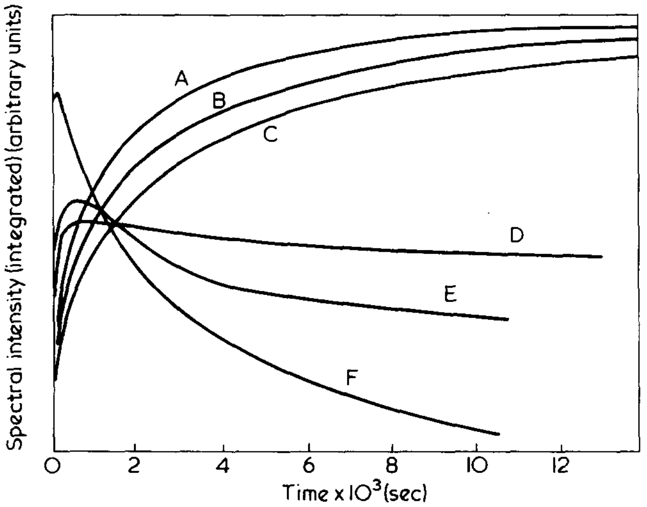

Figure 2 Changes of the spectral intensities with reaction time at various temperatures when 10 mW microwave power was applied: A, 198K; B, 190K; C, 182K; D, 213K; E, 227K; F, 241K

$AC_{t_2}+BC_0-BC_{t_2}$ at $t=t_2$. Finally, the following equation is obtained:

$$(S_{t_1}-S_0)/(S_{t_2}-S_0)=\{(AC_{t_1}+BC_0-BC_{t_1})-AC_0\}/\{(AC_{t_2}+BC_0-BC_{t_2})-AC_0\}$$

$$=(A-B)(C_{t_1}-C_0)/(A-B)(C_{t_2}-C_0)$$

$$=(C_0-C_{t_1})/(C_0-C_{t_2})$$

Therefore, (S_t-S_0) is proportional to the concentration of the peroxy radicals, (C_0-C_t). But the value of (S_t-S_0) cannot be linear with the concentration of the peroxy radicals at higher temperatures because the second assumption mentioned above does not hold at higher temperatures.

Examples of the results observed at various temperatures are shown in *Figure 2*, where the values of S_t are plotted against time after the introduction of the oxygen i.e. the reaction time. *Figure 2* shows that the peroxy radicals produced by the reaction of oxygen with the allylic radicals decay above 213K. We used the data at 182, 190 and 198K at an oxygen pressure of 41 Torr, and 201K at 222 Torr in the following analysis. The concentration of the peroxy radicals, values of (S_t-S_0), were normalized at about 10 000 sec for the data at 182, 190 and 198K and at 610 sec for those at 201K, and are shown together with the theoretical curves in *Figure 3*.

SIMULATION

As mentioned in the Introduction, the analysis of the oxidation process was satisfactorily made based on the diffusion-controlled mechanism. The equations for the diffusion-controlled reaction are as follows:

$$\frac{\partial[\mathrm{O}_2]}{\partial t}=\Sigma_i D_i\frac{\partial^2[\mathrm{O}_2]}{\partial x_i^2}-k[\mathrm{L}\cdot][\mathrm{O}_2] \qquad (1)$$

$$\frac{\partial[\mathrm{L}\cdot]}{\partial t}=-k[\mathrm{L}\cdot][\mathrm{O}_2] \qquad (2)$$

where D is the diffusion constant of oxygen, k is the reaction rate constant, and $[\mathrm{O}_2]$ and $[\mathrm{L}\cdot]$ are the concentrations of oxygen and the allylic radicals, respectively. It is shown in these equations that the allylic free radicals are immobile and the peroxy radicals do not disappear. Since it is difficult to solve these equations analytically, we used the method of digital simulation. In this simulation, the following boundary conditions and assumptions are taken into consideration. (a) The distribution of the allylic radicals is homogeneous in polyethylene and the concentration of the oxygen is zero at $t=0$; (b) all of the blocks of the samples are spheres with the same radius; (c) Fick's law is valid for small volume; (d) the diffusion constants have no anisotropy and do not change before and after the production of the peroxy radicals.

Under these conditions, the following simulation procedure was made. The sphere was divided into a number of shells, N, which have the same thickness Δr. Equations derived from equations (1) and (2) can be expressed as:

$$A(I,t+\Delta t)=A(I,t)+\frac{D\Delta t}{\Delta rV(I)}\{S(I-1)[A(I-1,t)-A(I,t)]-S(I)[A(I,t)-A(I+1,t)]\}-kA(I,t)B(I,t) \qquad (3)$$

and

$$B(I,t+\Delta t)=B(I,t)-kA(I,t)B(I,t) \qquad (4)$$

where $A(I,t)$ and $B(I,t)$ are the concentrations of oxygen and the allylic radicals, respectively, in the Ith shell at time t, $V(I)$ and $S(I)$ are the volume and the surface area of the Ith shell. The boundary conditions are (a) $A(I,0)=0$ and $B(I,0)=B_0$; (b) $A(0,t)=A_0$ and $A(N,t)=A(N+1,t)$. We used N and A_0/B_0 as the parameters and fixed $D\Delta t/\Delta r$ at 0.45, Δt at 1.0 sec and used the largest value of k under the condition that $B(I,t)$ has no negative value at any time and in any shell.

The best fitted curves to the experimental data were determined and illustrated in *Figure 3*. The simulated curves are in good agreement with the experimental data. The values of N and A_0/B_0 obtained from these best fitted simulations are given in *Table 1*. The diffusion constant in

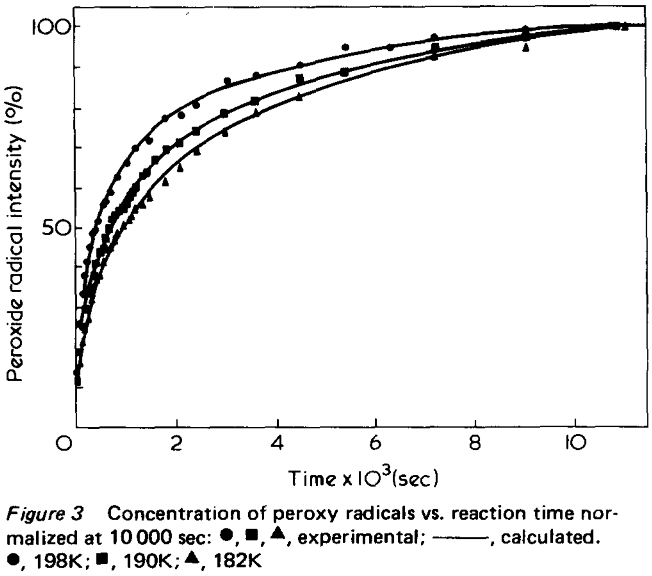

Figure 3 Concentration of peroxy radicals vs. reaction time normalized at 10 000 sec: ●, ■, ▲, experimental; ——, calculated. ●, 198K; ■, 190K; ▲, 182K

Table 1 Diffusion constants and solubility constants

Temperature (K)	P_{O_2} (Torr)	N	A_0/B_0	D (cm^2/sec)	Solubility constants [cm^3 (STP)/ cm^3 atm]
182	41	200	0.16	2.5×10^{-11}	0.095
190	41	100	0.20	1.0×10^{-10}	0.120
198	41	55	0.25	3.3×10^{-10}	0.145
201	222	40	1.5	6.3×10^{-10}	0.165

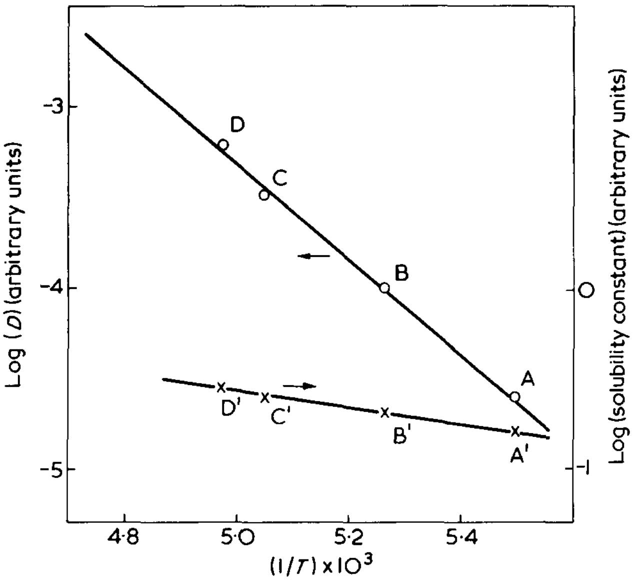

Figure 4 Diffusion constants and solubility constants of oxygen into the amorphous part of polyethylene

real space is expressed as $D = 0.45 \times (R/N)^2$, where R is the radius of the spherites. We assumed that R is 15 μm because the block size of the sample ranges from 20 to 50 μm. The diffusion constants estimated from these values are also given in *Table 1*. The solubility constant can be calculated using the ratio (A_0/B_0), G value of the allylic radicals in the amorphous part of polyethylene (0.3) and the weight fraction of the amorphous part (0.22) and these values shown in *Table 1*.

DISCUSSION

The good agreement between the experimental data and the simulated curves shown in *Figure 3* indicates that the reaction of oxygen with the allylic radicals in the amorphous region of the linear polyethylene at low temperature is a diffusion-controlled process and it can also be said that the conditions used in our analysis are adequate.

The logarithms of both the diffusion constants and the solubility constants obtained with the simulation are plotted against the inverse temperature in *Figure 4*. In this Figure, the data of points D and D' were observed from the experiment with an oxygen pressure of 222 Torr and the other points were from that of 41 Torr. The fact that all of the data obtained from the measurements at different temperatures under different pressures give a single straight line indicates that our analysis is very suitable.

The activation energy of the diffusion of the oxygen molecule into the amorphous region of the linear polyethylene is calculated to be 12.0 kcal/mol from *Figure 4*. This value is slightly greater than that at higher temperature in the non-irradiated polyethylene obtained by Michaels and Bixler[8] (8.8 kcal/mol). This small difference may be caused by the irradiation effect and the fact that the temperature range studied in the present article is different from that in the paper of Michaels and Bixler. The value of activation energy, 12 kcal/mol, is very close to the value of the same quantity obtained in a recent study on the oxygen diffusion into low density polyethylene by Tochin *et al.*[11]. For the absolute values of the diffusion constants, the value obtained by the extrapolation of the data in ref 8 is 1.3×10^{-11} cm^2/sec at 182K, and our result is 2.5×10^{-11} cm^2/sec. We can say that the agreement of these values is satisfactory for the present approximate estimation.

Concerning the solubility constants, the apparent heat of solution for the oxygen into the irradiated linear polyethylene at low temperature was found to be 2.1 kcal/mol from *Figure 4*, and the absolute value was calculated as 0.095 cm^3 (STP)/cm^3 atm at 182K. The values at 25°C are said to be −0.4 kcal/mol and 0.018 cm^3 atm[7]. These differences, especially in the case of absolute values, are important when the irradiation effect is taken into consideration. In general, the solubility constant is affected more strongly by the irradiation than the diffusion constant. The conclusion that the solubility constant in our analysis is larger than the corresponding quantity in the case of non-irradiated polyethylene is consistent with the above consideration.

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