E.s.r. studies on oxidation processes in irradiated polyethylene: 2. Diffusion of oxygen into crystalline regions

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The oxidation process in irradiated polyethylene was investigated by means of the e.s.r. method, and diffusion of oxygen molecules into the crystalline region of polyethylene was studied in detail. Computer simulation was carried out in order to determine various parameters of the process including diffusion constant. In the course of the simulation, the crystallite was assumed to have a plate-shaped form and the diffusion constant was considered to be larger at the region near the surface of the crystallite, D_f, and to be smaller at the inner region of the crystallite, D_s. Making these assumptions in the simulation gave a much better result than the assumption based on a sphere-shaped crystallite. D_f/D_s was found to be about 2 for thicker crystallite and it was 4 ~ 5 for thinner crystallite. Diffusion constants at various temperatures were determined, and the order of magnitude of diffusion constants in the crystalline region was found to be 10^{-16} cm^2/sec at about 320K both for thicker and thinner crystallites. The activation energy of diffusion of oxygen in the crystallites was found to be 32 kcal/mol.

INTRODUCTION

The mechanism of the oxidation of polyethylene has been discussed in many studies on thermal oxidation[1,2] and radiolytic oxidation[2–4]. In these oxidation processes, especially in radiolytic oxidation processes at low temperatures, the diffusion of oxygen into polyethylene was considered to play an important role. Michaels and his coworkers[5–8], Giberson[3,9] and Böhm[4] studied the diffusion processes of various gases into polyethylene in detail. However, due to the restrictions of experimental techniques in their studies, only the diffusion constants of oxygen into polyethylene of the order of 10^{-8} cm^2/sec or larger could be measured. However, the diffusion constant of oxygen into the crystalline part of polyethylene must be much smaller. The smaller diffusion constant for the amorphous part of polyethylene can be obtained at lower temperatures and was reported in our previous paper[10] (part 1 of the present article), to be of the order of 10^{-11}–10^{-10} cm^2/sec at 182–201K. In the course of estimating these values, the migration of allylic radicals was assumed to be negligible at the temperatures studied and the reaction kinetics were determined by use of computer simulation of the spectra which changed with the progress of the reaction between allylic radicals and oxygen molecules. Although in previous works, the diffusion of oxygen into the crystalline part of polyethylene has been neglected, it will now be reported that diffusion constants can be obtained by the methods used in ref 10. The application of the e.s.r. technique and computer simulation to the diffusion-controlled reaction mechanism gave an accurate determination of the small diffusion constant into the crystalline part of polyethylene.

EXPERIMENTAL

The sample used in this study was powdered single crystals of high density polyethylene, Sholex 6050. Materials were crystallized from dilute xylene solution (~0.1 wt %) for more than a week at 50°C (PE-50) and at 85°C (PE-85). The crystallinities of the samples determined from density measurements were 82.4% for PE-50 and 87.2% for PE-85. According to small angle X-ray diffraction measurement, the long periods of the lamellae of the crystals were 97 Å for PE-50 and 147 Å for PE-85. The approximate thickness of the inner crystalline region, *l*, and that of the lamellar surface, *d*, can be estimated from the following equation:

$$\rho = \rho_c - (\rho_c - \rho_a) \cdot d/(l + d)$$

where ρ_c, ρ_a and ρ are the densities of the inner crystalline part, amorphous part, and the whole material respectively and $\rho_c = 1.008$, $\rho_a = 0.86$. From this equation and the values of the sample density, ρ, and the long period, the thickness of the crystalline region, *l*, was estimated to be 74 Å for PE-50 and 120 Å for PE-85.

About 150 mg of the powdered crystals grown in solution were put into an e.s.r. sample tube which had two breakable seals. After evacuating for 6 h at 10^{-6} torr, the samples were irradiated *in vacuo* at room temperature using a ^{60}Co source and stored at the same temperature for 2 weeks. The total dosage was 20 Mrad at a dose rate of 0.25 Mrad/h. After storage at room temperature, almost all of the alkyl radicals produced by the irradiation had disappeared and only the allylic free radicals were trapped in the sample. The hydrogen gas produced during the γ-irradiation was

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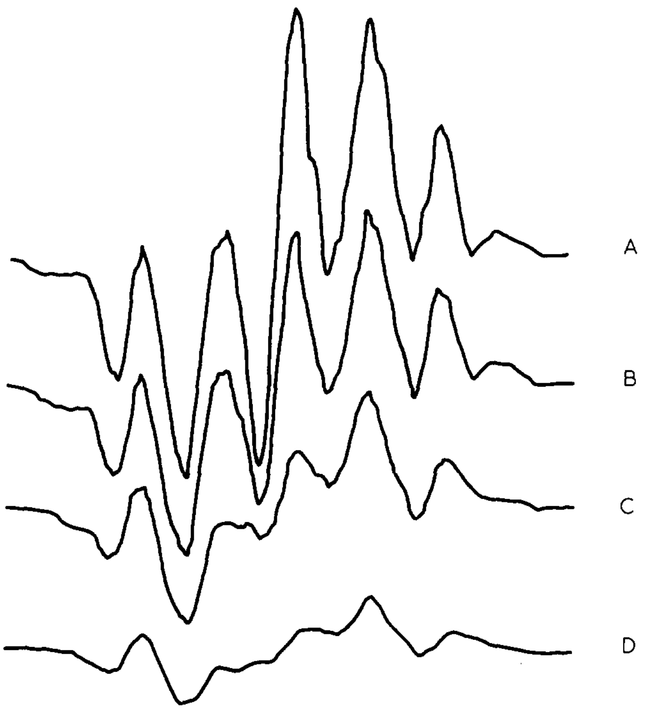

Figure 1 Changes of e.s.r. spectra of allylic radicals in PE-85 observed at 328K after storage for various times at the same temperature; (A) 0 sec. (B) 135 sec. (C) 1000 sec. (D) 3456 sec

evacuated through one of the two breakable seals and the sample tube was sealed off in vacuum again. A tube, attached to the e.s.r. sample tube via another breakable seal, was filled with oxygen or butadiene gas at a known pressure.

The e.s.r. measurements were made using a Jeol ME-3 X-band spectrometer. The signals were recorded by a Jeol spectrum computer, JEC-6. After the samples placed in the e.s.r. cavity reached the desired temperature, the oxygen was introduced from the tube into the e.s.r. ampoule by breaking the seal. E.s.r. signals were recorded at appropriate time intervals. The relative concentrations of the free radicals were obtained by double integrations of the first derivative curves recorded with a electronic computer, HITAC 8400.

EXPERIMENTAL RESULTS

The fraction of the allylic radicals trapped in the amorphous part of the single crystals initially was calculated as follows: after the allytic radicals had been reacted with butadiene gas at 160 torr for 1 h at 306K, the fraction of the residual radicals was 78% for PE-50 and 82% for PE-85. After the allylic radicals had been reacted with oxygen at 200 torr for a few seconds at 291K, the fraction of the residual radicals was 80% for PE-50. Butadiene molecules cannot diffuse into the crystalline part of single crystals but can diffuse into the amorphous part of the materials at 306K. Therefore, all the radicals trapped in the amorphous part of polyethylene materials can react with these butadiene molecules, and only the radicals in the inner crystalline part should remain. Similarly, oxygen molecules cannot diffuse into the crystalline part but can diffuse into the amorphous part[3–10] at low temperature e.g. 291K for a few seconds, and all the radicals trapped in the amorphous part can disappear. The radicals trapped in the inner crystalline part of single crystals might not be influenced by these treatments. Therefore, in both cases, the residual radicals were all allylic radicals trapped in the crystalline part and were not those trapped in the amorphous part of the materials. Thus, the fraction of the radicals in the amorphous part of polyethylene single crystals was estimated to be 22% for PE-50 and 18% for PE-85. In other words, the fractions of the radicals in the crystalline parts were 78% for PE-50 and 82% for PE-85.

Temperature dependence and pressure dependence of the radical decay, due to the reaction of allylic radicals in the crystalline part with oxygen molecules, were studied in order to investigate the diffusion process of oxygen molecules into the crystalline region.

The temperature dependence of the decay of the radicals was observed by the reaction with oxygen at constant pressure of 200 torr at various temperatures both for PE-50 and PE-85. The examples of the changes of e.s.r. spectra are shown in *Figure 1*. Decay curves of all the radicals trapped in solution-grown crystals are illustrated in *Figure 2* for PE-50 and in *Figure 3* for PE-85 together with the theoretical lines obtained.

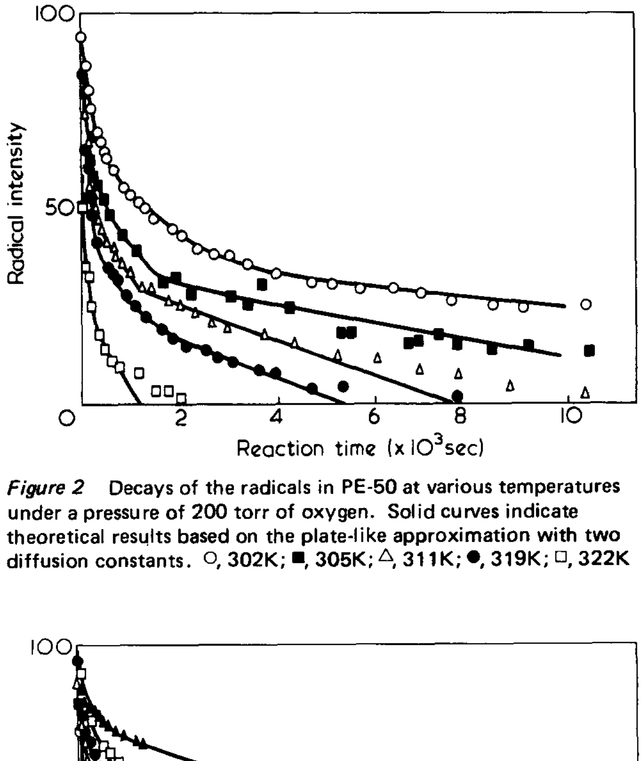

Figure 2 Decays of the radicals in PE-50 at various temperatures under a pressure of 200 torr of oxygen. Solid curves indicate theoretical results based on the plate-like approximation with two diffusion constants. ○, 302K; ■, 305K; △, 311K; ●, 319K; □, 322K

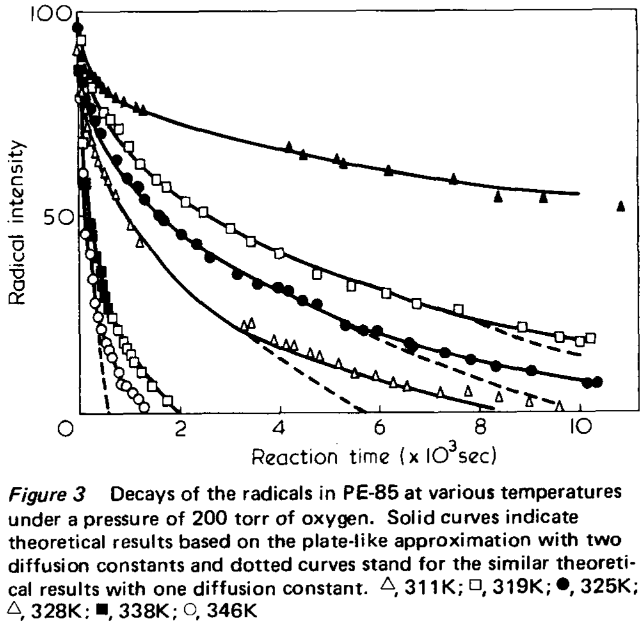

Figure 3 Decays of the radicals in PE-85 at various temperatures under a pressure of 200 torr of oxygen. Solid curves indicate theoretical results based on the plate-like approximation with two diffusion constants and dotted curves stand for the similar theoretical results with one diffusion constant. △, 311K; □, 319K; ●, 325K; △, 328K; ■, 338K; ○, 346K

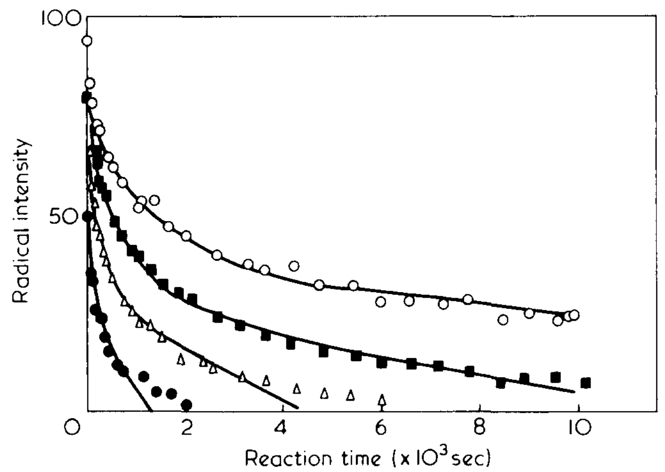

Figure 4 Decays of the radicals in PE-50 under various pressures of oxygen at various temperatures. Solid curves indicate theoretical results based on the plate-like approximation with two different constants. ○, 200 torr 322K; ■, 100 torr 321K; △, 50 torr 321K; ●, 10 torr 321K

The pressure dependence of the decay of the radical was observed for the reactions with oxygen molecules at various pressures at 321K for PE-50. Decay curves of the reactions are illustrated in *Figure 4* together with theoretical curves.

SIMULATION

The decay of the radicals trapped in single crystals of polyethylene by the reaction with oxygen could be separated into two stages. The first stage is the decay of the radicals trapped in the amorphous part and the second is that of the radicals trapped in the crystalline part. The following procedures were carried out.

Decay of the radicals trapped in the amorphous part

The processes of decay of radicals in the amorphous part seemed to consist of the following three steps.

(1) Diffusion of oxygen molecules into the amorphous part of solution grown materials of polyethylene. This diffusion of oxygen was very rapid at the temperatures[3–10] in the present study.

(2) Reaction of these oxygen molecules with allylic radicals trapped in the amorphous part followed by the production of peroxy radicals. The rate constant of this reaction is believed to be very large.

(3) Vanishing of the peroxy radicals. The decay of the peroxy radicals seemed to be slower than step 1 and step 2.

Considering the conditions of these three steps, we approximated the decay of the radicals in the amorphous part of solution-grown materials by equation (1) representing a single component exponential decay starting at $t = 0$,

$$[\mathrm{R}\cdot]_a = [\mathrm{L}\cdot]_a^0 \exp(-q_a t) \qquad (1)$$

where $[\mathrm{R}\cdot]_a$ and $[\mathrm{L}\cdot]_a^0$ are the concentrations of all the radicals trapped in the amorphous part at time t and of the allylic radicals in the amorphous part at $t = 0$, respectively, and q_a is the decay constant of all the radicals in the amorphous part. The initial stage of the decay of radicals trapped in whole polyethylene could be explained by equation (1). This fact may indicate that the decay process of the peroxy radicals is the first order decomposition or that step 1 and step 2 influence the rate of the radical decay and consequently equation (1) is apparently applicable to the present case. But it is not our intention to determine in this paper which is the actual case, since decay of peroxy radicals will be reported in a forthcoming paper.

Decay of radicals trapped in the inner crystalline part

The processes of decay of the radicals trapped in the crystalline region of solution-grown materials were very different from those of the decay of the radicals in the amorphous part. The decay of the radicals in the crystalline region was controlled mainly by the diffusion of oxygen molecules into the crystalline part. Equations for the decay process based on the diffusion-controlled mechanism are as follows:

$$\partial[\mathrm{O_2}]/\partial t = \Sigma_i D_i \partial^2[\mathrm{O_2}]/\partial X_i^2 - k[\mathrm{L}\cdot]_c[\mathrm{O_2}] \qquad (2)$$

$$\partial[\mathrm{L}\cdot]_c/\partial t = -k[\mathrm{L}\cdot]_c[\mathrm{O_2}] \qquad (3)$$

$$\partial[\mathrm{LOO}\cdot]_c/\partial t = k[\mathrm{L}\cdot]_c[\mathrm{O_2}] - q_c[\mathrm{LOO}\cdot]_c \qquad (4)$$

$$[\mathrm{R}\cdot]_c = [\mathrm{L}\cdot]_c + [\mathrm{LOO}\cdot]_c \qquad (5)$$

where $[\mathrm{O_2}]$, $[\mathrm{L}\cdot]_c$, $[\mathrm{LOO}\cdot]_c$ and $[\mathrm{R}\cdot]_c$ are the concentrations of oxygen, allylic radicals, peroxy radicals in the crystalline region, respectively, and D is the diffusion constant of oxygen into the crystalline part, k is the rate constant of the reaction and q_c is the decay constant of peroxy radicals in the crystalline region. In these equations, it is assumed that the peroxy radicals decay by a first order reaction scheme and do not produce any stable radicals, and that the allylic radicals are immobile. Since it is difficult to solve these equations analytically, we used a method of digital simulation in which the following boundary conditions and assumptions were made: (a) at $t = 0$, the distribution of the allylic radicals was homogeneous in the crystalline region and the concentration of oxygen and hence of the peroxy radicals was zero; (b) Fick's law was valid for small volume; (c) the diffusion constants had no anisotropies and did not change the production of the peroxy radicals.

Under these conditions, the following simulation procedure was adopted for diffusion of oxygen molecules into plate-shaped crystallites. The plate was divided into a number of thinner plates, $2N$, having the same thickness, Δr.

The following equations were derived from equations (2)–(5):

$$\mathrm{A}(I, t+\Delta t) = \mathrm{A}(I,t) + (D\Delta t/\Delta r)\mathrm{V}(I)\mathrm{S}(I-1) \times$$
$$[\mathrm{A}(I-1,t) - \mathrm{A}(I,t)] - \mathrm{S}(I)[\mathrm{A}(I,t) - \mathrm{A}(I+1,t)] -$$
$$- k\mathrm{A}(I,t)\mathrm{B}(I,t) \qquad (6)$$

$$\mathrm{B}(I, t+\Delta t) = \mathrm{B}(I,t) - k\mathrm{A}(I,t)\mathrm{B}(I,t) \qquad (7)$$

$$\mathrm{C}(I, t+\Delta t) = k\mathrm{A}(I,t)\mathrm{B}(I,t) + \mathrm{C}(I,t)\exp(-q_c\Delta t) \qquad (8)$$

$$\mathrm{F}(I, t+\Delta t) = \mathrm{B}(I, t+\Delta t) + \mathrm{C}(I, t+\Delta t) \qquad (9)$$

where $\mathrm{A}(I,t)$, $\mathrm{B}(I,t)$, $\mathrm{C}(I,t)$ and $\mathrm{F}(I,t)$ are the concentrations of oxygen, allylic radicals, peroxy radicals and the total radicals, respectively, in the I-th plate at time t. $\mathrm{V}(I)$ and $\mathrm{S}(I)$ are the volume and the surface area of the I-th plate. The boundary conditons are as follows: (i) $\mathrm{A}(I,0) = 0$, $\mathrm{C}(I,0) = 0$ and $\mathrm{B}(I,0) = \mathrm{B_0}$; (ii) $\mathrm{A}(0,t) = \mathrm{A_0}$ and $\mathrm{A}(N,t) = \mathrm{A}(N+1,t)$. N, $\mathrm{A_0}/\mathrm{B_0}$ and q_c were the varying parameters.

$D\Delta t/\Delta r$ was fixed at 0.45 and Δt was fixed at 1.0 sec. The largest value of k was used under the condition that $B(I, t)$ has no negative values at any time and in any plate. According to the method mentioned above, the relative concentration of the total radicals trapped in solution-grown crystals of polyethylene was computed. This can be expressed by equation (10), in which $[L\cdot]_a^0$ and $[L\cdot]_c^0$ are the relative initial concentrations of the radicals in the amorphous and crystalline parts, respectively.

$$[R\cdot](t) = [L\cdot]_a^0 \exp(-q_a t) + [L\cdot]_c^0 \{\Sigma_I F(I, t)V(I)\} \quad (10)$$

The best fitted curves to the experimental data were determined and illustrated in *Figure 3* for the case of PE-85. The broken lines in the same Figure are the simulation curves based on the plate-like approximation and it is seen that the plate-like approximation does not seem to be in good agreement with the experimental points for large t. It may be that the diffusion constant of oxygen into the polyethylene crystallite is not constant throughout the whole region of the crystallite but varies according to the place of diffusion, i.e. in the region near the surface, having diffusion constant D_f, and in the inner part of the crystallite having diffusion constant D_s and where $D_f > D_s$. By means of simulation with these two diffusion constants for the plate-like approximation, the best fitted curves to the experimental data were determined and illustrated in *Figures 2, 3* and *4*, in which the solid lines are the simulated curves with two diffusion constants, D_f and D_s. These simulated curves are in good agreement with the experimental data. We also made simulations assuming sphere-like crystallites to compare with the plate-like approximation but with only one diffusion constant. The results for PE-85 are illustrated in *Figure 5* and appear to be in good agreement with experimental data, but we could not obtain good simulated curves for PE-50 using the sphere-like approximation.

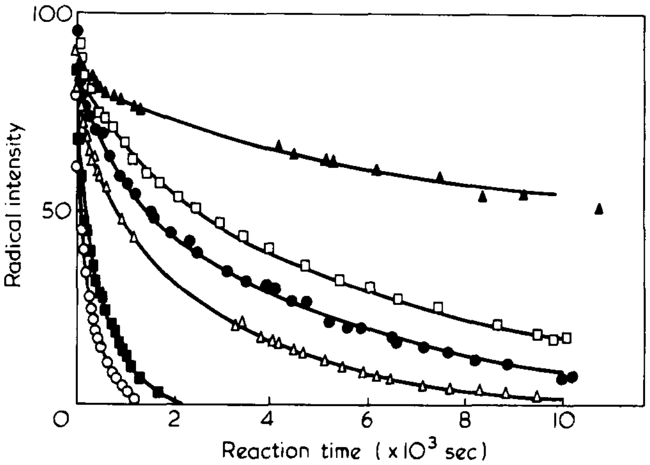

Figure 5 Decays of the radicals in PE-85 under a pressure of 200 torr of oxygen at various temperatures. Solid curves indicate theoretical results based on the sphere-like approximation. ▲, 311K; □, 319K; ●, 325K; △, 328K; ■, 338K; ○, 346K

The values of N and A_0/B_0 and the other parameters corresponding to these best fitted simulations are given in *Table 1*. The diffusion constant in real space can be expressed as $D = 0.45 \times (R/N)^2$, where R is the half-width of the plate or the radius of the sphere. We estimated that R was 37 Å for PE-50 and 60 Å for PE-85 from the thickness of the crystallite. The diffusion constants estimated from these values are also shown in *Table 1*. The solubility constant can be calculated using the ratio (A_0/B_0) and G value of allylic radicals in polyethylene (0.3).

DISCUSSION

The good agreement between experimental data and simulated curves shown in *Figures 2–5* means that the reaction of oxygen with the allylic radicals in the crystalline region of linear polyethylene is a diffusion controlled process and that the conditions used in our analysis were quite appropriate.

Table 1 Diffusion constants

Temperature (K)	P_{O_2} (torr)	N	A_0/B_0	D_f (D_s) (cm²/sec)	Fraction of the region with D_s
(a) For PE-50 by the plate-like approximation					
302	200	30	0.1	6.9×10^{-17} (3.2×10^{-17})	0.44
305	200	20	0.1	1.5×10^{-16} (3.4×10^{-17})	0.40
311	200	16	0.1	2.4×10^{-16} (6.4×10^{-17})	0.38
319	200	13	0.1	3.6×10^{-16} (8.1×10^{-17})	0.31
322	200	6	0.1	1.7×10^{-15} (3.8×10^{-16})	0.33
321	100	7	0.04	1.3×10^{-15} (2.8×10^{-16})	0.42
321	50	7	0.015	1.3×10^{-15} (2.8×10^{-16})	0.36
321	10	7	0.006	1.3×10^{-15} (2.8×10^{-16})	0.36
(b) For PE-85 by the plate-like approximation					
311	200	79	0.1	2.6×10^{-17} (————)	–
319	200	35	0.1	1.3×10^{-16} (7.3×10^{-17})	0.25
325	200	29	0.1	1.9×10^{-16} (1.1×10^{-16})	0.24
328	200	22	0.1	3.3×10^{-16} (1.5×10^{-16})	0.23
338	200	10	0.1	1.6×10^{-15} (7.2×10^{-16})	0.30
346	200	7	0.1	3.3×10^{-15} (1.1×10^{-15})	0.29
(c) For PE-85 by the sphere-like approximation					
311	200	220	0.1	3.3×10^{-18}	
319	200	82	0.1	2.4×10^{-17}	
325	200	68	0.1	3.5×10^{-17}	
328	200	52	0.1	5.9×10^{-17}	
338	200	24	0.1	2.8×10^{-16}	
346	200	19	0.1	4.5×10^{-16}	

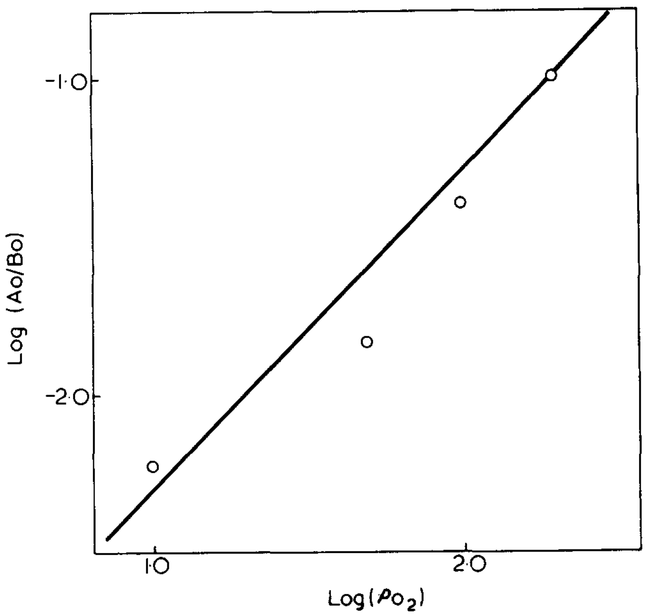

Figure 6 Relation between (A_0/B_0) and the pressures of oxygen, P_{O_2}

Trapping sites of allylic radicals

Kashiwabara[11] reviewed several studies concerning the location of the allylic radicals in irradiated polyethylene at an earlier stage of research in the field of e.s.r. studies of polymers, and he concluded that the allylic radicals were trapped in the pseudo-crystalline region in polyethylene. Seguchi and Tamura[12] also concluded that the allylic radicals were trapped in the surface region of crystallite as a result of study on the reaction between the allylic radicals and various monomers. Our interpretations of the location of allylic radicals differ from those obtained from earlier research in that we suggest that the allylic radicals produced by γ-irradiation are trapped uniformly in polyethylene. This interpretation explains the following:

(A) most of the allylic radicals survived after contact with butadiene gas;

(B) the relative concentration of the allylic radicals trapped in the crystalline part is nearly equal to the crystallinity, i.e. 82.4% (crystallinity) and 78% (concentration of radicals) for PE-50 and 87.2% and 82% for PE-85.

(C) the e.s.r. spectra of the observed allylic radicals (see *Figure 1*) were much sharper than those shown in ref 12, where it was reported that the sharp component of e.s.r. spectra came from the radicals trapped at the inner part of crystallite.

The phase 'the region near the surface' does not mean the folding region of the crystallite otherwise an inconsistency appears: a portion of the radicals contributing to the reaction with fast diffusion constant, D_f, might correspond to the radicals trapped on the folding part of the crystallite. If this is the case for our study, the diffusion constant in the surface region can be calculated to be 6.6×10^{-18} cm^2/sec and that in the inner part of the crystallite becomes 7.7×10^{-16} cm^2/sec for PE-85 at 319K, provided that the thickness of the surface region is 10 Å. In other words, if the allylic radicals are trapped mainly in the surface of polyethylene crystallites, the diffusion of the oxygen molecules into the surface region is less than into the inner part by a factor of 100. Therefore, this argument must be rejected since it seems that the radicals under consideration are trapped almost uniformly.

Structure of a single crystal of polyethylene

Single crystals of polyethylene consist of lamella-like crystallites with thickness of about 100 Å and width of a few microns with the molecular chains oriented perpendicular to the surface of the lamellae. Recently, Yoda *et al.*[13] reported that the mean size of crystallites of polyethylene single crystals was estimated to be about 250 Å based on X-ray diffraction studies. Seguchi and Tamura[14] reported that the decay of alkyl radicals due to the reaction with oxygen could be explained more exactly by the approximation of sphere-like crystallites than by the plate-like approximation, reflecting the presence of many defects in the single crystals. In our case,the approximation of a simple plate-like crystallite was not an adequate explanation of the experimental data, but the sphere-like approximation gave good fitted curves only for the case of PE-85. However, it does not seem that the defects in polyethylene single crystals are so large that the oxygen molecules can diffuse into these defects as fast as into the amorphous parts. Therefore, the good results were obtained for PE-85 by the sphere-like approximation by chance because this approximation could not give any good result for PE-50 in spite of the larger defects in PE-50 than in PE-85. On the other hand, all the results for PE-85 and PE-50 under the various pressures were nicely simulated by plate-like approximation which included two diffusion constants, the larger diffusion constant at the surface region of crystallite and the smaller one at the inner part of the crystallite. According to these facts, it seems that the crystallites should better be regarded as plates when the diffusion of oxygen into the crystalline parts is considered.

Solubility constant

The relation between A_0/B_0 and the pressure of oxygen is illustrated in *Figure 6*. The ratio of A_0/B_0 was roughly linear to the pressures of oxygen, and Henry's Law holds in these cases. The solubility constant was calculated to be 0.035 cm^3 (STP)/cm^3 atm using the ratio (A_0/B_0), the G value of the allylic radicals in polyethylene (0.3), the crystallinity and the concentration of allylic radicals trapped in the crystalline region. We had reported that the value in the amorphous parts was 0.095 cm^3 (STP)/cm^3 atm at 182K and also their temperature dependence[10]. The solubility constants of oxygen in the crystalline parts were smaller than that in the amorphous parts for irradiated polyethylene and both of them were larger than those for non-irradiated polyethylene. We considered that the irradiation effects are reflected in the larger solubility constants in irradiated polyethylene and that the difference of morphology is reflected in the difference between the solubility constants in the crystalline and in the amorphous regions. In this work, we neglected the temperature dependence of the solubility constants of oxygen in order to simplify the simulation.

Diffusion constant

The diffusion constants estimated from these simulations are tabulated in *Table 1* and they are also shown in *Figure 7*. The activation energy of the diffusion of oxygen molecules into the crystalline region of linear polyethylene is calculated and it was found to be about 32 kcal/mol. This value is much larger than the values in amorphous parts which were reported in the papers by Michaels and Bixler[7] for the non-irradiated polyethylene at similar temperatures, (8.8 kcal/mol) and this value is larger than the diffusion constant reported by us[10] for the irradiated polyethylene at lower temperatures also (12 kcal/mol). It is quite reasonable

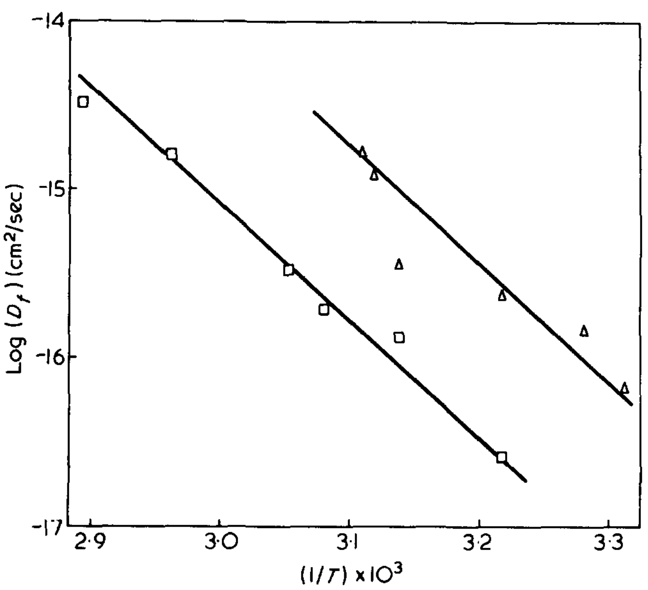

Figure 7 Diffusion constants in the crystalline region. △, PE-50; □, PE-85

that the activation energy into the crystalline region should be greater than those into the amorphous part. The values of 10^{-15}–10^{-17} cm^2/sec were obtained as the actual values of diffusion constants in the crystalline region of irradiated polyethylene at temperatures ranging from 302K to 346K using the plate-like approximation (see *Table 1*). These values are very small compared with those in the amorphous regions of both irradiated and non-irradiated polyethylenes.

The rate of diffusion at the region near the surface is faster than that in inner part, but the difference is small. The fraction of the region corresponding to D_s is not large. These facts indicate that the molecular motion in the region near the surface is faster than that in the inner part of the crystallite, but the difference in the schemes of molecular motion in different regions is not large.

The differences between diffusion constants in PE-85 and in PE-50 at the same temperatures were caused by the differences of perfection of single crystals and of molecular motions of chains. The diffusion constants in PE-50 were larger than those in PE-85. These results are consistent with the fact that the crystallites of PE-85 are said to be more perfect than those of PE-50 and it can be said that the molecular motions in crystallites of PE-50 are more rapid than those of PE-85 because of the difference of the thickness of lamellae.

Such a very small diffusion constant could be obtained firstly by use of the e.s.r. technique and the computer simulation in the present work. The diffusion of oxygen in the crystalline region maybe neglected when the diffusion in the amorphous part is considered under the condition of lower oxygen pressure. However, the diffusion of oxygen into the crystalline region must be taken into account when the phenomena in the crystallite under an oxygen atmosphere is studied.

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