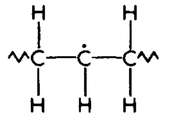
Relation between diffusion controlled decay of radicals and α-relaxation in polyethylene and polyoxymethylene

S. Shimada, Y. Hori and H. Kashiwabara
Nagoya Institute of Technology, Showa-ku, Nagoya 466, *Japan*
(*Received* 4 *July* 1980; *revised* 3 *December* 1980)

Diffusion controlled process theory was applied to the analysis of the data concerning decay reactions of free radicals in irradiated polyethylene and polyoxymethylene in detail. Diffusion constants of free radical sites were estimated from the data of the decay reactions and their time constants were calculated by using Stokes–Einstein relation. These time constants were plotted against the inverse temperature in the relaxation maps, which were arranged by Wada. In the case of polyethylene, the time constants of decay reactions of alkyl radicals trapped in the lamellar surface and the inner part of crystallites were in good agreement with the relaxation times of α'- and α-processes, respectively. However, it was found that the time constants of main chain radicals trapped in polyoxymethylene were closely related to α-relaxation processes. The activation energies of the decay reactions of free radicals were in good agreement with those of the corresponding relaxation processes in both cases. From these results, it was concluded that the decay reactions of the free radicals reflect the molecular motions associated with the respective relaxation processes. Concerning the decay reaction of free radicals in the inner crystallite of polyethylene, effects of lamellar thickness and crystal surface were also studied by using solution grown crystals, which were crystallized at various temperatures, and the fuming nitric acid treated materials. It was found that the diffusion constant of free radical sites and its activation energy were strongly dependent on the lamellar thickness and half-life of free radicals was a function of the amount of the fold surface; i.e., the reaction rate was much depressed as the lamellar thickness was increased and the amount of the fold surface was decreased.

INTRODUCTION

Decay of free radicals trapped in irradiated polymers is one of the interesting subjects with respect to relaxation processes in the solid phase. Many studies in this field have been made for last twenty years[1–6] and decay reactions of the free radicals were considered as a reflection of the molecular motions associated with the relaxation processes in the polymer. However, clear relationship between time constants of the decay reactions and that of molecular motions are still open for further studies. For example, the scheme of the decay reactions were analysed by the model of the simple second order reaction in some cases and by the model of the simple first order reaction in the other cases. However, activation energies and time constants of the decay reactions, estimated by these analyses, were not determined accurately as discussed later. In our previous papers, decay reactions of alkyl radicals,



$$\sim\mathrm{CH_2}-\dot{\mathrm{C}}\mathrm{H}-\mathrm{CH_2}\sim$$

trapped in irradiated polyethylene was successfully interpreted by the application of diffusion controlled process theory[7] and two types of alkyl radicals, which correspond to the broad and sharp sextet patterns of e.s.r. spectra, were found[8] to be trapped in the lamella surface and the inner part of the crystallite, respectively. Mobility and precise structure of alkyl radicals trapped in solution grown crystal and urea-polyethylene complex were also studied in detail[9] and the mobility of alkyl radicals was concluded to be the same as that observed by broad line n.m.r. taking the distribution of relaxation time into consideration[10]. It is interesting that the diffusion constants of two types of free radicals located in the different phases, i.e., the lamella surface and the inner part of the crystallite, can be observed separately and the time constants of the decay reactions of respective types of radicals can be compared with the relaxation times of molecular motion in the respective phases, since the molecular motions of the respective phase can be clarified, separately, by e.s.r. It is also meaningful and important that temperature dependences of the time constants of the decay reactions are estimated by the diffusion controlled process theory and their relation between the relaxation processes of solid polymers are discussed. In this paper, time constants of decay processes at various temperatures in the case of polyethylene and polyoxymethylene will be plotted against the inverse temperature in the relaxation maps of polymers and the relation between decay processes and molecular motions of polymer chains will be discussed in detail.

0032–3861/81/101377–08$02.00

Table 1 Structural constants of polyethylene single crystals

Materials	Long period, L (Å)	Thickness of fold surface, d (Å)	Density (g cm^{-3})	$\frac{d}{l}$	Degree of crystallinity χ_c (%)
Tc-50	97	23	0.9734	0.31	79.3
Tc-65	108	22	0.9778	0.25	82.1
Tc-77	132	25	0.9798	0.23	83.1
Tc-85	147	27	0.9810	0.22	84.1

EXPERIMENTAL

Sample preparation

A high density polyethylene, Sholex 6050 (Product of the Showa Electric Industry Company Ltd.) was purified by the method described in the previous paper[7]. Tc-50, TC-65, Tc-77 and Tc-85 samples were recrystallized from dilute zylene solution (~0.1 wt %) for more than a week at 50°, 65°, 77° and 85°C, respectively. Crystallinities of the materials were determined as shown in *Table 1* by measurement of their densities. A part of Tc-85 samples were also subjected to fuming nitric acid treatment at 60°C. In order to indicate the rule of specification of the materials studied, an example is shown; Tc-85-FNAT-100 means the materials crystallized at 85°C (Tc-85) and subjected to fuming nitric acid treatment at 60°C for 100 h. Fuming nitric acid treatment was carried out by mixing ~1 g of specimen in 100 ml of the acid in a sealed glass tube. After the fuming nitric acid treatment, the materials were washed in distilled water and then in actetone with a Soxhlet-extracter in order to remove fuming nitric acid and low molecular weight compounds. The lamellar thickness of the sample, L, was estimated by small angle X-ray scattering method and the results are tabulated in *Table 1*. Polyoxymethylene (POM), Derlin 5000 (product of the E.I. du Pond de Nemours Company), was also used for this study.

Irradiation

All samples were subjected to ^{60}Co γ-irradiation at liquid nitrogen temperature under a vacuum of 10^{-4} Torr up to the total dose of 1.1 ~ 3.5 Mrad with a dose rate of 0.22 Mrad h^{-1}.

E.s.r. observation

E.s.r. spectra were recorded with a JEOL ME-2 electron spin resonance spectrometer (X-band) with 100 KHz field modulation. The variable temperature controller made by JEOL Associates was used in order to control the temperature of e.s.r. cavity for the kinetic studies.

ANALYSIS PROCEDURE

Application of Waite's equation[11,12] to the decay reaction of the free radicals in condensed phase and a convenient modification of the equations were discussed in detail previously[7] and the following equations were derived.

$$\frac{C_A^\circ}{C_A}=1+8\pi r_0 DC_A^\circ\left[1+\frac{(2)^{1/2}r_0}{(\pi Dt)^{1/2}}\right]t \tag{1}$$

$$=1+A(t)^{1/2}+Bt=1+B\left[1+\frac{A'}{t^{1/2}}\right]t \qquad (A'B=A) \tag{2}$$

$$A=8(2)^{1/2}r_0^2 C_A^\circ(\pi D)^{1/2} \tag{3}$$

$$B=8\pi r_0 DC_A^\circ \tag{4}$$

Here, C_A is the concentration of free radicals at time t, C_A° is the initial value of the radical concentration, r_0 is the capture radius, and D is the half value of diffusion constant of free radicals. Subsequently, the relative concentration and the diffusion constant of free radicals can be obtained from the following equations, respectively.

$$X=\frac{C_A}{C_A^\circ}=\frac{C}{C_0}=\frac{1}{1+A(t)^{1/2}+Bt} \tag{5}$$

$$D=\frac{2}{\pi}\left(\frac{B}{A}\right)^2 r_0^2 \tag{6}$$

In the case of two phase system, the concentration of the free radicals must be represented by equation (7).

$$C=C'+C'' \quad , \quad C_0=C_0'+C_0'' \tag{7}$$

where C' and C'' are the concentrations of fast-decaying and slow-decaying (non-vanishing) free radicals, respectively. By use of these expressions, the following equation can be obtained instead of equation (2).

$$\frac{C_0-C_0''}{C-C_0''}=\frac{1-a}{x-a}=1+B\left[1+\frac{A'}{(t)^{1/2}}\right]t \qquad (A'B=A) \tag{8}$$

or

$$x=\frac{1}{B\left[\left\{1+\frac{A'}{(t)^{1/2}}\right\}\right]}\frac{1-x}{t}+a \tag{9}$$

where $a=\frac{C_0''}{C_0}$.

When the value of t is large, the values of $1/B[1+A'/(t)^{1/2}]$ and $(1-x)/t$ are nearly equal to $1/B$ and 0, respectively. Therefore, when x is plotted against $(1-x)/t$, the value of a in equation (9) can be obtained by extrapolating the curve to $(1-x)/t=0$. In our previous paper[7], equation (9) was applied to the analysis of the decay reactions of alkyl radicals trapped in two phase system composed of lamella surface and inner part of crystallite. Here, it is assumed that alkyl radicals react within the respective regions and then the decay of alkyl radicals trapped in the lamella surface was observed at low temperatures at which those in the inner part of crystallite did not vanish. From the plots of x vs. $(1-x)/t$ at the low temperatures, the value of a (the amounts of alkyl radicals trapped in the lamella surface) was determined to be 0.39. However, the quantity a was obtained to be 0 in the case of the study of decay of alkyl radicals trapped in the inner part of crystallite at higher temperatures. The latter at higher temperatures was considered to be one component system. Equation (9) can also be applied to the decay reactions of two different kinds of free radical species trapped even in a one phase system, if one of them is non-vanishing. This is the case of polyoxymethylene which will be discussed in the next section.

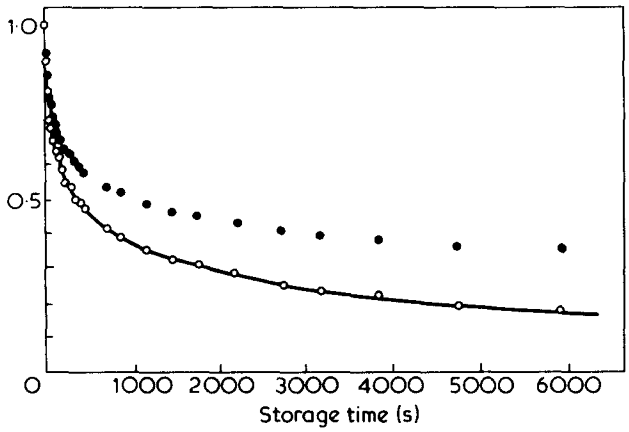
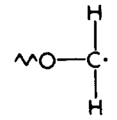


Figure 1 **Decay curve of free radicals trapped in irradiated polyoxymethylene at 354K after heating at room temperature for extended time period: ●, irradiation at 77K; ○, show the reduced amount of decay obtained after subtracting the amount of non vanishing radicals; ——; shows calculated decay curve with A = 5.0 x 10^{-2} ($s^{-1/2}$) and B = 1.6 x 10^{-4} (s)**

RESULTS AND DISCUSSION

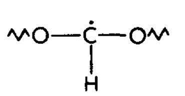
Decay of free radicals trapped in polyoxymethylene

It is well known that scission type radicals



$$\sim O-\overset{H}{\underset{H}{\dot{C}}}$$

and chain type radicals,



$$\sim O-\underset{H}{\dot{C}}-O\sim$$

are produced in γ-irradiated polyoxymethylene[13]. The e.s.r. pattern of the chain type radicals shows a well known doublet pattern attributed to hyperfine splitting due to one α-proton. Triplet like spectrum, caused by the scission type radicals, vanished by warming at room temperature after γ-irradiation at liquid nitrogen temperature and the stable doublet spectrum remained. *Figure 1* shows the variation of the intensity of this doublet spectrum with storage time at 354K. Similar experiments were made at several heating temperatures higher than room temperature. For these data,

$$x \sim \frac{(1-x)}{t}$$

plots of equation (9) were made in order to estimate the value of a (the relative amounts of non reacting free radical species). The extrapolations of experimental curves at various temperatures to

$$\frac{(1-x)}{t}=0$$

gave us the value of a, 0.21, as shown in *Figure 2*. Though the stable radical species giving the value a could not be identified, it seems to correspond to the radicals of antioxidant reagent mixed in the polyoxymethylene. However, the relative amounts of these radical species was determined to be 0.21 by the above analysis. In order to study the decay reaction in only the one component system, we can make the plot of the variation concerning the value, $(C-C_0'')$, in equation (8). *Figure 1* shows an example for the decay at 354K. Open circles in *Figure 1* shows this plot, which indicates the true amount of the chain radicals, $\sim O\dot{C}HO\sim$, vs. the storage time. If the value of a was not reduced from the total concentration, determinations of A and B in equation (2) was not possible. Filled circles in *Figure 1* show the total concentrations. The results obtained at various heating temperatures are shown in *Figure 3*. The time constants of the decay reactions were found to be strongly dependent on the heating temperature. Constants A and B in equation (2) were determined from the curves in *Figure 3* by the same method as mentioned previously[7]. The experiments of decay reaction were carried out until the reduced relative concentration, $(C-C_0'')$, approached ~15%. Solid lines in *Figure 3* show the calculated curves corresponding to the values of A and B tabulated in *Table 2*. These simulated curves based on diffusion controlled reaction theory are in good agreement with the experimental data and make a good interpretation for the decay rection of free radicals trapped in solid polyoxymethylene.

Relation of diffusion constant of free radicals to time constant of molecular motion in polyoxymethylene

Three dimensional migration of free radicals trapped in the polyoxymethylene was considered in the previous section and diffusion-controlled theory was successfully

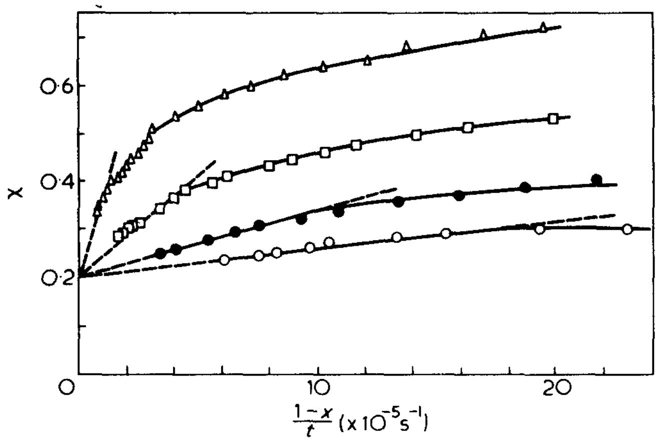


Figure 2 Relative concentration of free radicals: value of $(1-x)/t$ at various temperatures: △, 343.5K; □, 349.0K; ●, 354.0K; ○, 364.0K

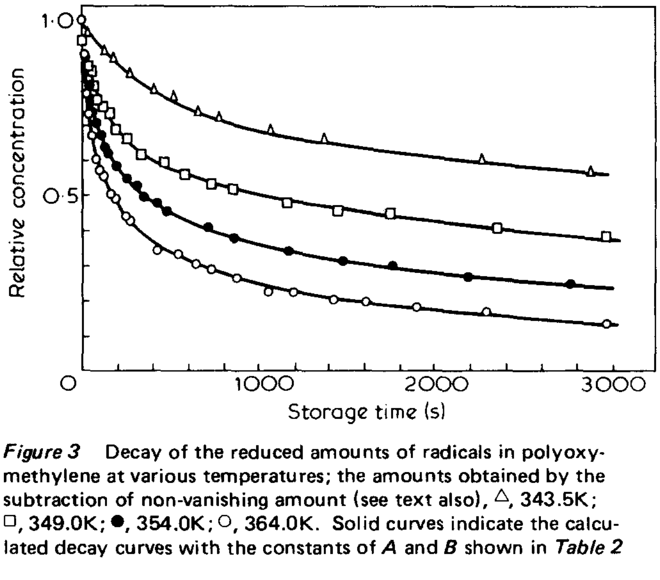


Figure 3 Decay of the reduced amounts of radicals in polyoxymethylene at various temperatures; the amounts obtained by the subtraction of non-vanishing amount (see text also), △, 343.5K; □, 349.0K; ●, 354.0K; ○, 364.0K. Solid curves indicate the calculated decay curves with the constants of A and B shown in *Table 2*

Table 2 Values of *A, B* and *D* for radical decay in polyoxymethylene

Temperature (K)	A ($s^{-1/2}$)	B (s^{-1})	D ($cm^2\ s^{-1}$)
343.5	1.4×10^{-2}	8.0×10^{-6}	4.6×10^{-23}
349.0	2.8×10^{-2}	4.0×10^{-5}	2.7×10^{-22}
354.0	5.0×10^{-2}	1.6×10^{-4}	1.3×10^{-21}
364.0	6.5×10^{-2}	9.0×10^{-4}	2.5×10^{-20}

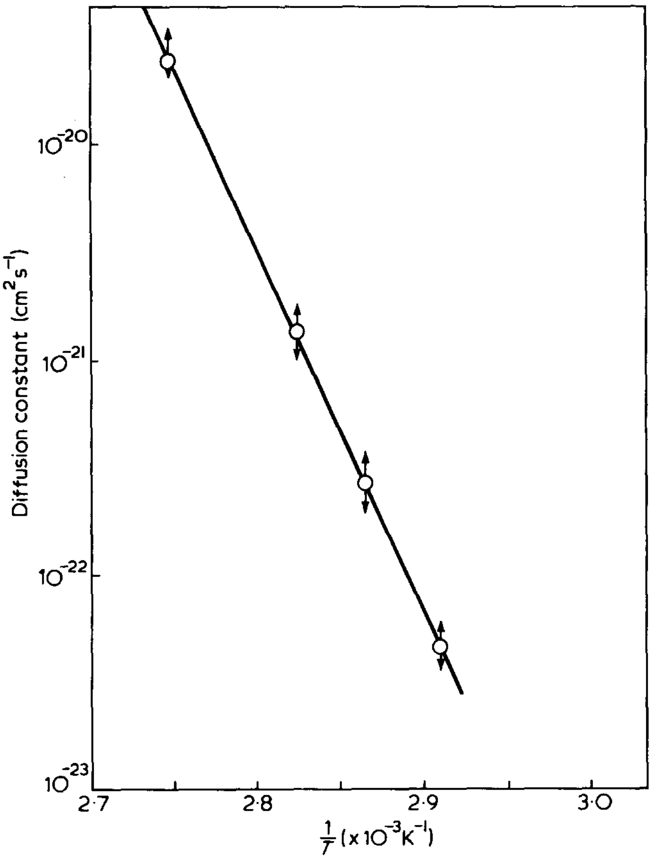


Figure 4 Diffusion constant of free radicals trapped in polyoxymethylene vs. inverse temperature

applied to the decay reaction of free radicals. It is important to discuss the relation of diffusion constants of free radicals to the time constant of polymer molecular motion in view of mechanism of the chemical reaction in the solid state. Diffusion constants can be expressed as in equation (6),

$$D = \frac{2}{\pi}\left(\frac{B}{A}\right)^2 r_0^2$$

according to the definition of A and B. Since r_0 means a capture radius with which reactants recombine immediately, r_0 was assumed to be 1.43 Å (bond length of carbon and oxygen) in order to make an approximate estimation of diffusion constant. Diffusion constants of free radicals at various temperatures estimated by equation (6) are tabulated in *Table 2* and its temperature dependence is illustrated in *Figure 4*.

However, the following consideration was also made: In our present discussion, 'diffusion' does not mean mass translation but the migration of the radical site. Migration of the radical site requires the inter-exchange of the sites of an unpaired electron and a proton. This naturally requires a distortion of the back bone chain of the trapping matrix. Therefore, a distorted region' must move with the proceeding of the radical migration. The distorted region can correspond to the free volume in Stokes–Einstein relation[14]

$$D = KT/3\pi a_0{}^* y \qquad (10)$$

where K is gas constant, T is absolute temperature, $a_0{}^*$ means radius of free volume and y stands for viscosity determined from relaxation time, τ, and Young's modulus, E, by equation (11).

$$y = \tau \cdot E \qquad (11)$$

To get the order of magnitude of the relaxation time, it was assumed that the time constant of migration of free radicals was almost the same as the relaxation time of polymer molecular motion. Therefore, the relaxational frequency of polymer molecular motion, f, is estimated from the diffusion constant of free radicals by the following equation.

$$f = \frac{1}{\tau} = \frac{3\pi a_0{}^* D \cdot E}{KT} \qquad (12)$$

$a_0{}^*$ was estimated to be 18.4 Å from the known values of lattice constants of polyoxymethylene and $E = 1 \times 10^{10}$ dyne cm^{-2} [15]. The relaxational frequencies calculated by use of equation (12) and the values of D represented in *Table 2* were plotted in a relaxation map of polyoxymethylene, which was arranged by Wada as shown in *Figure 5*[15]. In this figure, the results obtained in the

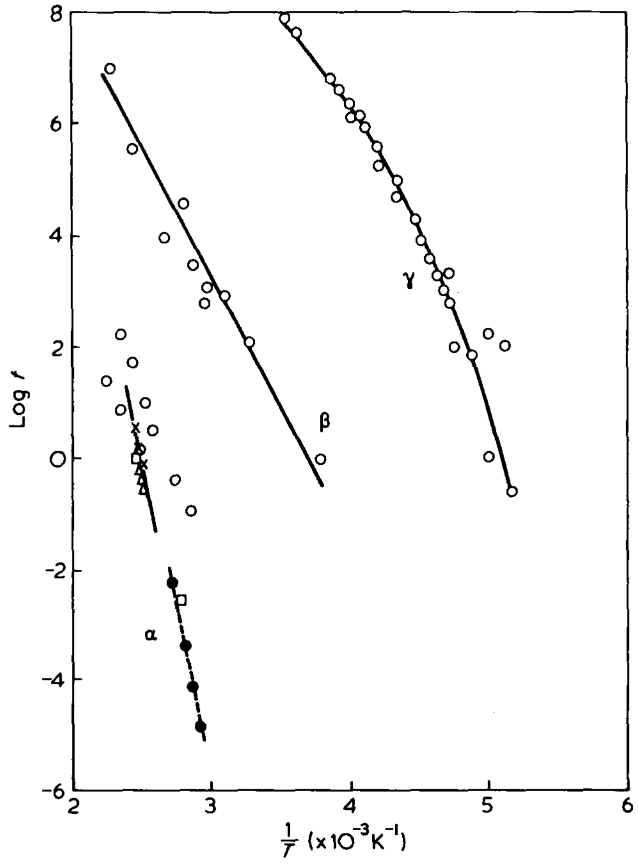


Figure 5 Relaxation map of polyoxymethylene: ○, Wada map; x, □, △, dielectric data (Morita); ●, decay reaction of free radical

Table 3 Values of *A, B* and *D* for radical decay in the lamellar surface of polyethylene

Temperature (K)	A (s$^{-1/2}$)	B (s^{-1})	D (cm^2 s^{-1})
265.0	4×10^{-2}	1.0×10^{-3}	9.5×10^{-20}
270.0	4×10^{-2}	1.7×10^{-3}	2.7×10^{-19}
274.5	4×10^{-2}	3.4×10^{-3}	1.1×10^{-18}

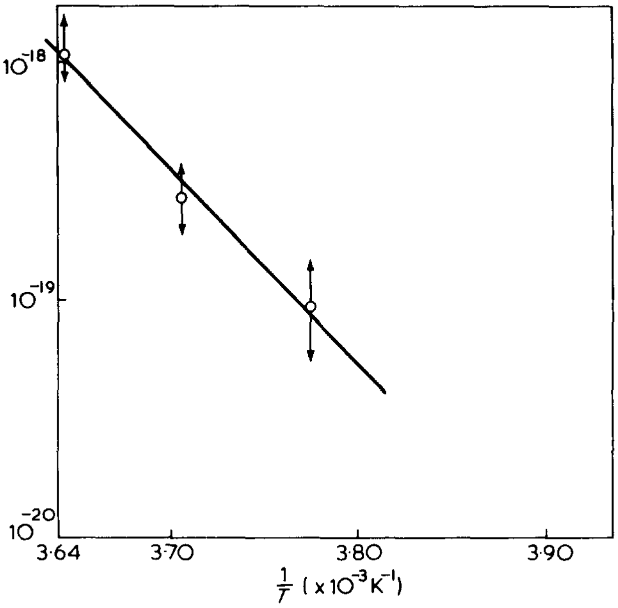


Figure 6 Diffusion constant of alkyl radicals trapped in the lamellar surface of polyethylene single crystals vs. inverse temperature

dielectric relaxation study by Morita and Hideshima[16] were also shown. The time constants of the decay reaction of free radicals are in good agreement with those of α-relaxation process of polyoxymethylene. The activation energy of the diffusion process of the free radicals was found to be ~60 kcal mol^{-1} from *Figure 5*. The order of magnitude of this value is in good agreement with 40 kcal mol^{-1} of the α-relaxation process obtained by the dielectric study[16]. From these results, it was concluded that the decay reaction of free radicals trapped in polyoxymethylene at high temperature region, 343–364K, must be a reflection of the molecular motion in the crystalline part associated with α-relaxation process of polyoxymethylene

Decay of alkyl radicals trapped in the lamella surface of polyethylene crystals

Decay reactions of two types of alkyl radicals trapped in polyethylene single crystals were reported in detail in the previous paper[7]. *B* radicals, which were trapped in the lamella surface of crystallites, decayed at low temperature ranging from 240 to 280K. However, *S* radicals, which were trapped in the inner part of the crystallites, disappeared at temperatures higher than room temperature. The relative amount of *B* radicals was estimated to be 0.39 by applying equation (9). The plot of amount of *B* radicals vs. storage time were made (*Figure 5* in reference 7) and then constants of *A* and *B* in equations (3) and (4) were determined by the method mentioned previously. The diffusion constants of *B* radicals at various temperatures were also calculated from equation (6) on the assumption of $r_0 = 1.54$ Å (C–C bond length) and tabulated in *Table 3*. Their temperature dependence is shown in *Figure 6*. The relaxational frequencies of decay reactions were calculated by use of equation (11) and were plotted in a relaxation map of polyethylene, which was arranged also by Wada[15,17], as shown in *Figure 7*. In this case, a_0* was assumed to be 5 Å from the well known values of lattice constants of polyethylene and $E = 2 \times 10^{10}$ dyne cm^{-2} was applied[15]. The order of magnitude of the relaxational frequencies estimated from the decay reaction of *B* radicals seems to be similar with that of α′-relaxation process and its activation energy agrees with that of α′-relaxation process. However, it is known that the α′-relaxation process is related to molecular motion associated with the lamella surface of crystallites. From these results, it can be said that the decay behaviour of *B* radicals at low temperature ranging from 240 to 280K is a reflection of a so called α′-relaxation process.

Decay of free radicals trapped in the inner crystalline region of polyethylene single crystals

Most of the *B* radicals disappeared under extended heat treatment at 273K. After this treatment, decay reactions of *S* radicals, which were trapped in the inner part of crystallites, were observed. In this case, the equation of the diffusion controlled decay for one component system was applied since the quantity *a* in equation (9) vanished. Constants *A* and *B* and diffusion constants were determined by the same method mentioned in the previous section. These values obtained in the case of Tc-85 samples were tabulated in *Table 4* and temperature dependence of diffusion constant is shown in *Figure 8*. The relaxation frequencies as shown by the filled circles in *Figure 7* were also estimated from equation (11) by use of the same values of a_0* and *E* for polyethylene mentioned in the previous sub-section. From this figure, it can safely be said that the plots of the time constants obtained from the data of the decay reaction are on the extrapolation of the line of the time constants corresponding to the α-relaxation process. Furthermore, the activation energy of

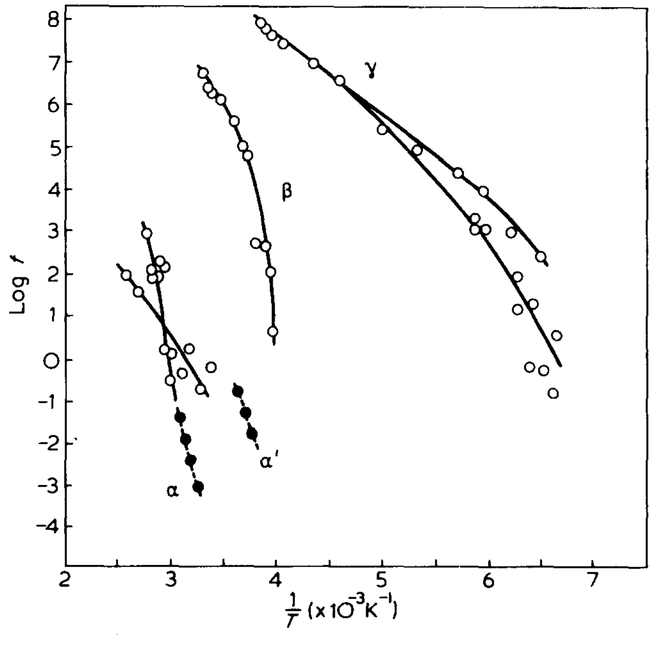


Figure 7 A relaxation map of polyethylene: ○, Wada map; ●, decay reaction of free radical

Table 4 Values of *A*, *B* and *D* for radical decay in the inner part of crystallites

Temperature (K)	A ($s^{-1/2}$)	B (s^{-1})	D ($cm^2\ s^{-1}$)
307	1.1×10^{-2}	6.0×10^{-5}	3.0×10^{-21}
314	1.2×10^{-2}	1.3×10^{-4}	1.2×10^{-20}
319	0.9×10^{-2}	1.7×10^{-4}	3.6×10^{-20}
327	1.4×10^{-2}	6.0×10^{-4}	1.8×10^{-19}

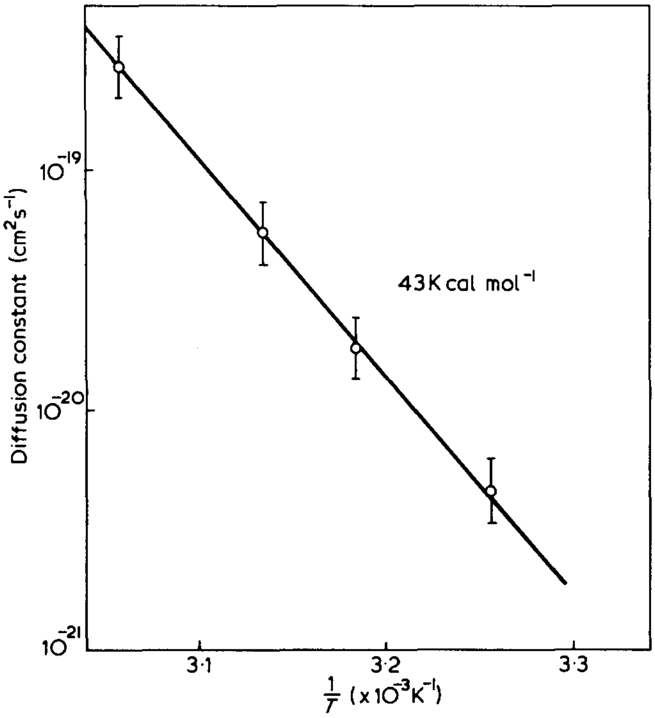


Figure 8 Diffusion constant of alkyl radical trapped in the inner part of crystallites for Tc-86 sample vs. inverse temperature

decay process was found to be 43 kcal mol^{-1} from the plot in *Figure 8*. This value is in close agreement with the activation energy of α-relaxation process, 46 kcal mol^{-1}, which was obtained in the case of solution grown crystals by Takayanagi *et al.*[18,19]. This good agreement of the values of the activation energies obtained independently in both studies must be a confirmation of our interpretation that the decay of free radicals reflects the molecular motion of the matrix polymer. Kusumoto *et al.*[4] estimated the smaller activation energies of the radical decay reaction than that obtained in the present study. They observed the variation of radical intensities for the shorter storage time less than 1 h and analysed in terms of a simple second order kinetics,

$$\frac{C_A^{\circ}}{C_A} = 1 + Bt$$

Hence, the procedures in their estimations were to neglect the second terms in equation (2) and to overestimate the rate constants or diffusion constants at lower temperature; i.e., since they assumed the simple second order reaction scheme, the term

$$B\left[1 + \frac{A'}{(t)^{1/2}}\right]$$

in equation (2) was replaced by B, which is proportional to the diffusion constant, D (see equation (4)). This is to say that they did not consider that B is actually a time dependent quantity. However, the value of

$$B\left[1 + \frac{A'}{(t)^{1/2}}\right]$$

is nearly equal to B at a higher temperature or after long duration of the reaction, since the value of A' becomes small

$$\left(\text{remember the relations; } A' = \frac{A}{B} \propto \sqrt{\frac{1}{D}}\right)$$

Therefore, the activation energies in their studies were found to be smaller than the true values.

The same experiments as that for Tc-85 sample were made for the other various samples in order to study the dependence of diffusion constants on the lamella thickness. *Figure 9* shows the temperature dependences of the diffusion constants for the polyethylene materials crystallized in the dilute xylene solutions at various temperatures. Both the absolute value of diffusion constant and its activation energy were found to be dependent on lamella thickness. The activation energy of the decay reaction of free radicals increased with the increasing lamella thickness for solution crystallized samples and fuming nitric acid treated samples as shown in *Figure 10*. This phenomenon was comparable with the results obtained by Kusumoto *et al.*[4], who compared them with the results of viscoelastic measurements. The absolute values of the activation energies estimated in the present paper are in good agreement with the viscoelastic data. Also, it is

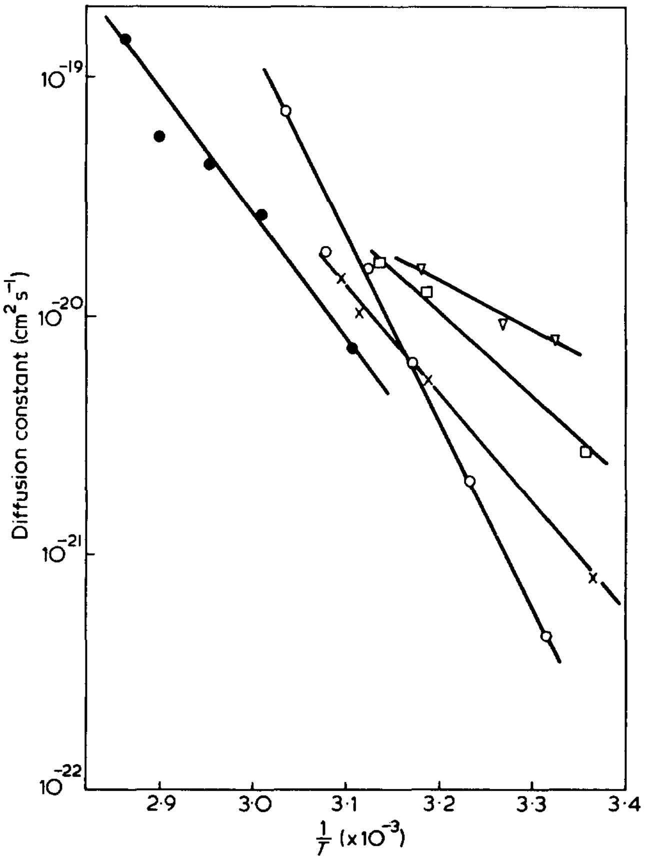


Figure 9 Diffusion constant of alkyl radicals trapped in the inner part of crystallites for various samples vs. inverse temperature: △, Tc-50; □, Tc-65; x, Tc-77; ○, Tc-85; ●, Tc-85-FNAT, 196

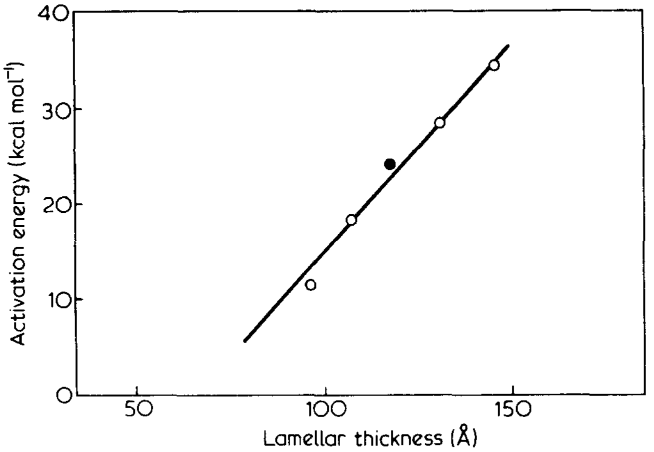


Figure 10 The activation energy of diffusion constant (*D*) vs. lamellar thickness (*L*): ○, Tc-50, Tc-65, Tc-77, Tc-85; ●, Tc-85-FNAT, 196

reasonable to think that the α-relaxation process plays a predominant role in reaction of radicals trapped in the inner crystalline region.

Mechanism of decay reaction of free radicals trapped in polyethylene single crystals

In our previous papers[7,9], it was found that polyethylene molecules were much more mobile in the urea–polyethylene complex than polyethylene molecules in solution grown crystals, but the decay rate of alkyl radical trapped in the urea–polyethylene complex was slower than that in the solution grown crystals. From these facts, it was concluded that the rate of alkyl radical migration across the chain is much faster than that along the chain in polyehtylene crystals[7]. In this section, effects of fold surface to the decay of radicals will be discussed. *Figure 11* shows the results of decay reactions at 42°C under various conditions. Plot 2 and plot 3 in *Figure 11* show the effect of surface area of the lamellar crystallite on the decay reaction of the alkyl radicals. Plot 2 is the decay of the radicals in fuming nitric acid treated materials (Tc-85-FNAT, 196; see Experimental section) and it shows slow decay of the radicals compared with the case of grown materials, plot 3. A plausible interpretation is that the lamellar surface has a strong effect on the molecular motion in the crystallite and it enhances the radical migrations in the inner part of the crystallite followed by the rapid decay of the radicals reflected in plot 3. Other evidence confirming the above interpretation was obtained, which was that the rate of radical migration in the materials subjected to the fuming nitric acid treatment was as follows: (1) The decay of the radicals in Tc-85-FNAT, 196 were slow when the butadiene monomers were also introduced to the system. Butadiene is a large molecule and it cannot diffuse into the inner part of the crystallite. Plot 1 in *Figure 11* shows this circumstance. This fact is reflecting that the radicals trapped in the inner part of the crystallite hardly migrated to the surface area to react with butadiene monomers. Since Tc-85-FNAT, 196 has no radicals trapped in the folded surface, there is no need to take into account the reaction of the radicals in the surface area with butadiene molecules.

(2) The reaction of oxygen molecules and the alkyl radical trapped in Tc-85-FNAT, 196 were studied. The decay of the radicals in Tc-85-FNAT, 196 in the air was shown to be extremely rapid as indicated by plot 4 in *Figure 11*. This reflects the fact that the decay of the radicals under the presence of oxygen molecules was caused by the reaction of the radicals with oxygen molecules, which diffused into the crystallite, and little radical migration to surface from inner crystallite occurred. The above interpretation is supported by the following fact: Plots 5 and 6 in *Figure 11* are the results of reactions of the allylic radicals in polyethylene without FNAT with oxygen. Plot 6 shows the decay of the allylic radicals in polyethylene without FNAT when the material was contacted with oxygen molecules. Usually, allylic radicals are trapped both in folded surface and inner part of the crystallite. However, the amount of the allylic radicals trapped in the folded surface can be estimated from the reacted amount of the allylic radicals with butadiene, and plot 5 in *Figure 11* shows the decay of the allylic radicals caused by the reaction with oxygen when the amount of the allylic radicals in surface area is discounted. Plot 5 and plot 4 are very similar. Therefore, it can be said that the decay behaviour of the alkyl radicals trapped in the inner part of the crystallite is almost the same as the decay behaviour of the allylic radicals which must be very stable due to unsaturation structure and must not migrate in the crystallite. This is further evidence of the fact that alkyl radicals in Tc-85-FNAT, 196 hardly migrate in the crystallite.

Based on the results mentioned above, it can be said that the folded surface of the crystallite has an important effect on the molecular motion in the inner part of the crystallite, molecular motion associated with the α-relaxation process, and therefore, it has strong effect to the migration of the radicals trapped in the inner part of the crystallite.

Concerning the effect of the folded surface of the crystallite to the migration of the radicals, half lives of the radicals trapped in the inner part of the crystallite were observed for the various materials as shown in *Figure 12*. The relative amount of lamellar surface, d/l, was estimated in the following equations. Thickness of amorphous part including the lamellar surface, d, thickness of the inner crystalline part, l, and degree of the crystallinity, χ_c, were

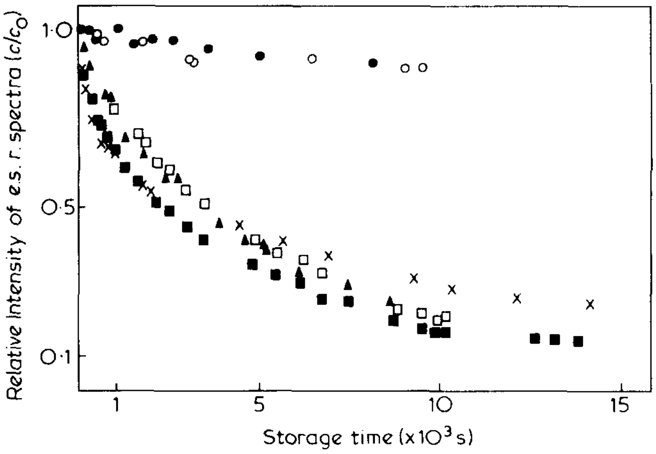


Figure 11 Decay curve of free radicals trapped in various samples of polyethylene at 315K. Plot 1, ●, Tc-85-FNAT, 196 with butadiene; plot 2, ○, Tc-85-FNAT, 196 in vacuum; plot 3, x, Tc-85 in vacuum; plot 4, ▲, Tc-85-FNAT, 196 in air; plot 5, □, Tc-85, allyl radicals with oxygen gas, reduced plot; plot 6, ■, Tc-85, allyl radicals with oxygen gas

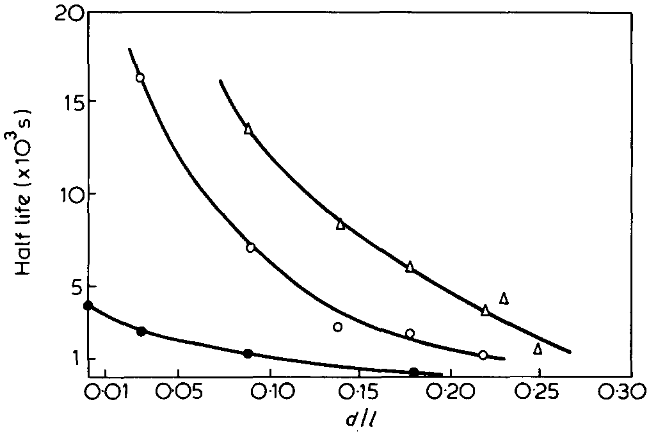


Figure 12 Half life of alkyl radicals trapped in the inner part of crystallites vs. *d/l*. △, 41°C; ○, 52°C; ●, 72°C

Table 5 Structural constants of fuming nitric acid treated samples

Materials	Reduction of long period ΔL (Å)	Thickness of fold surface d (Å)	$\frac{d}{l}$
Tc-85-FNAT, 10	5	22	0.18
Tc-85-FNAT, 25	10	17	0.14
Tc-85-FNAT, 50	16	11	0.09
Tc-85-FNAT, 100	23	4	0.03
Tc-85-FNAT, 196	28		

estimated according to the known relations,

$$\frac{1}{\rho}=\frac{\chi_c}{\rho_c}+\frac{1-\chi_c}{\rho_a} \tag{13}$$

$$\rho=\rho_c-(\rho_c-\rho_a)\frac{d}{L} \tag{14}$$

$$L=l+d \tag{15}$$

where L is the length of the long period. The estimated values of d, d/l and χ_c were presented in *Table 1*. In the estimations, $\rho_a=0.86$ g cm^{-3} and $\rho_c=1.008$ g cm^{-3} were adopted. *Table 5* shows structural constants of the materials subjected to fuming nitric acid treatment at 60°C after the crystallization at 85°C. ΔL in *Table 5* is the reduction of the long period by fuming nitric acid treatment obtained from the paper by Blundell *et al.*[21]. From these values, d and d/l were calculated. *Figure 12* shows variation of the half lives of the radicals with d/l, and it indicates that half life of free radicals becomes shorter with increasing d/l. This fact indicates that the decay behaviours of alkyl radicals are dependent on the amount of the lamellar surface of the crystallite. However, it was found that molecular motion of the α-relaxation process reflected the decay reaction of alkyl radicals in the inner part of crystallite as discussed in the previous section. From these considerations, it can be said that the character of molecular motion at the inner part of crystallite must also be dependent on the amount of lamellar surface. In other words, motion in the lamellar surface must affect the molecular motion in the inner part of the crystallite.

ACKNOWLEDGEMENTS

The authors are grateful for Mr Y. Itoh for his assistance in obtaining the data described in the last subsection. Financial support of Ministry of Education by Grant-in-Aid for Science Research is gratefully acknowledged.

REFERENCES

1 Lawton, E. J., Balwit, J. S. and Powell, R. S. *J. Chem. Phys.* 1960, **33**, 395
2 Cracco, F., Arvia, A. J. and Dole, M. *J. Chem. Phys.* 1962, **37**, 2449
3 Nara, S., Shimada, S., Kashiwabara, H. and Sohma, J. *J. Polym. Sci. A-2* 1968, **6**, 1435
4 Kusumoto, N., Yamaoka, T. and Takayanagi, M. *J. Polym. Sci.* 1971, **9**, 1173
5 Seguchi, T. and Tamura, N. *J. Phys. Chem.* 1973, **77**, 40
6 Shimada, S. and Kashiwabara, H. *Polym. J.* 1974, **6**, 448
7 Shimada, S., Maeda, M., Hori, Y. and Kashiwabara, H. *Polymer* 1977, **18**, 25
8 Shimada, S., Hori, Y. and Kashiwabara, H. *Polymer* 1977, **18**, 19
9 Shimada, S., Hori, Y. and Kashiwabara, H. *Polymer* 1978, **19**, 763
10 Shimada, S., Tanigawa, T. and Kashiwabara, H., paper presented at 17th ESR Symposium, Kyoto, 1978
11 Waite, T. R. *J. Chem. Phys.* 1960, **32**, 21
12 Waite, T. R. *Phys. Rev.* 1957, **107**, 463
13 Yoshida, H. and Ranby, B. *J. Polym. Sci. A* 1965, **3**, 2289
14 Saito, N. *Polym. Phys.* Shokabo Book Co., Tokyo, 1967
15 Wada, Y., Physical Properties of Solid High Polymers, Baifukan Book Co., Tokyo, 1971 (in Japanese)
16 Morita, Y., Thesis for Master's degree, The University of Hokkaido, Japan (1968)
17 Wada, Y. *J. Phys. Soc. Jpn.* 1961, **16**, 1226
18 Takayanagi, M. and Matsuo, T. *J. Macromol. Sci.* 1967, **B1**, 407
19 Kajiyama, S., Okada, T. and Takayanagi, M., Abstracts 21st Polymer Symposium 773, Osaka (1972)
20 Hori, Y., Fukunaga, Z., Shimada, S. and Kashiwabara, H. *Polymer* 1972, **20**, 181
21 Blundell, D. J., Keller, A. and Connor, T. M. *J. Polym. Sci. A-2* 1967, **5**, 991