Free radicals trapped in polyethylene matrix:
2. Decay in single crystals and diffusion

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The kinetics of the decay of main chain free radicals trapped in polymer matrix in vacuum was investigated. The decay behaviour of alkyl radicals trapped in the lamellar surface of the crystallites of solution grown polyethylene should be different from that of the same radicals trapped in the inner part of the crystallite, and this difference was clearly observed. The analysis of the data of the decay reaction was made, based on three-dimensional diffusion-controlled reaction theory, and reasonable interpretation of the data was made. Alkyl radicals were also observed in an irradiated urea–polyethylene complex and the decay rate of these radicals were very slow in spite of the large mobility. According to these occurrences, it was concluded that the mechanism of three-dimensional diffusion of the free radicals across the chain may occur in the inner part of the crystallites via hydrogen abstraction reactions.

INTRODUCTION

Kinetic studies of the decay of free radicals in irradiated polyethylene have been reported by many authors[1], and the rate constants of the decay reactions at several temperatures were obtained. Nara[2] *et al.* and Kusumoto *et al.*[3] analysed the data of the decay of alkyl radicals, $\sim CH_2-\dot{C}H-CH_2\sim$ in irradiated polyethylene in terms of a second order reaction. Johnson *et al.*[4] interpreted the data in terms of fast and slow first order decay processes on the same material. In the second order reaction, the radical concentration at time t, C, and the initial concentration, C_0, should satisfy the relation $-1/C + 1/C_0 = kt$, where k is a rate constant. On the other hand, in the first order reaction, C and C_0 should satisfy the relation $-\ln C_0/C = kt$. However, the actual experimental results of the decay process did not show either second order reaction or first order reaction at the shorter duration of time of the process. It is possible to say that there are more than two kinds of radicals trapped in the materials under consideration and they behave differently in the decay process with different rate constants, and this gives rise to the deviation from the simple first order or second order processes. In order to clarify this problem, separate observation of the decay process for each of the coexisting species would be helpful. Since we were successful in the separated observation of each of the superposed spectra and in clarifying the trapping regions of respective free radicals as reported in a previous article, much clearer investigations of the decay processes of the free radicals can be anticipated and some of the results will be presented in this article.

Recently, Seguchi *et al.*[5] observed the reaction of the alkyl radicals with oxygen in irradiated polyethylene and explained the kinetics of radical decay by the diffusion theory assuming that the decay rate is controlled by the rate of radical migration in the crystallites. However, it is doubtful whether one can assume that the alkyl radicals react with oxygen only in the lamellar surface, because it is not clear whether the rate of free radical migration or that of oxygen diffusion is faster. On the other hand, Waterman and Dole[6] suggested that alkyl radicals migrate by hydrogen transfer across the polymer chains. In a previous paper[7], we presented a tentative speculation about the radical migration along the chain based on the studies of the radical conversion from $CH_3-\dot{C}H-CH_2-CH_2\sim$ to $CH_3-CH_2-\dot{C}H-CH_2\sim$, and alkyl to allylic radical conversion. Also we tried to extend the same consideration to the decay reactions of the free radicals in the bulk. However, this kind of extension does not seem to be very successful. In the present paper, we will again discuss this problem based on the results obtained in the analysis of the decay reaction of the free radicals. More than ten years ago, Waite[8,9] studied the problem of the kinetics of the diffusion-controlled reaction $A + B \rightarrow AB$ in terms of the pair probability densities of the reacting particle. This theory was applied in the analysis of the data concerning the decay of free radicals.

EXPERIMENTAL

Sample treatment

A high density polyethylene, Sholex 6050 (product of the Showa Electric Industry Co., Ltd) was used in this study. The polyethylene sample was purified by dissolving it in boiling toluene, then it was precipitated by cooling, washed in acetone, and dried in a vacuum oven. A-85 samples were recrystallized from a dilute xylene solution of ~0.1 wt %. After crystallization for more than a week at 85°C, xylene was removed by filtration and the polyethylene was dried in a vacuum oven for a long time.

Sample U was a urea–polyethylene complex which was prepared according to the method of Yokoyama and Monobe[10]; i.e. urea–PE complex was prepared by mixing the xylene solution of polyethylene with urea–n-hexadecane complex at 393K. The urea–polyethylene complex was identified by comparing its d.s.c. curve with that of the urea–n-hexadecane complex. Observation with the scanning electron microscope was also made.

Irradiation techniques

All samples were subjected to γ-irradiation at liquid nitrogen temperature under a vacuum of 10^{-4} mmHg. The γ-irradiation from ^{60}Co was carried out up to a total dose of 1.1 Mrad at dose rate of 0.22 Mrad/h.

E.s.r. techniques

E.s.r. spectra were recorded with a JEOL ME2 electron spin resonance (X band) spectrometer with 100 kHz field modulation. The variable temperature controller made by JEOL associates was used to control the temperature of the e.s.r. cavity for the kinetic studies. Relative change of the concentration of the alkyl radical was obtained by observing the change in the height of the wing peak of the spectrum of alkyl radical as shown in *Figure 6*. The wing peak is the outermost and weakest peak of the six-line spectrum corresponding to the alkyl radicals, and the e.s.r. signal from coexisting allyl radicals does not overlap with the wing peak considered.

Application and modification of Waite's equation[8,9]

Concerning the diffusion-controlled bimolecular reaction, A + B → AB, Waite presented the following equations for the processes in condensed phase. The general rate equations derived can be simplified as followings:

$$-\frac{\mathrm{d}C_A}{\mathrm{d}\tau'} = -\frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}\tau'} = K(r_0, S, \tau')C_\mathrm{A}C_\mathrm{B} \tag{1}$$

$$\tau' = \frac{D'}{r_0^2}t \tag{2}$$

$$S \approx \exp\frac{(E_{D'} - E^*)}{RT} \tag{3}$$

and

$$K(r_0, S, \tau') = 4\pi r_0^3\left(\frac{S}{S+1}\right)[1 - 2\exp(S+1)^2\tau']$$

$$\times\int_{(S+1)\tau^{\frac{1}{2}}}^{\infty}\frac{\exp(-\alpha^2\mathrm{d})}{\pi^{\frac{1}{2}}}\,\mathrm{d}\alpha \tag{4}$$

where C_A is the concentration of A at time t; C_B is the concentration of B at time t; r_0 is the capture radius; D is the sum of diffusion coefficients of A particles and B particles; E_D is the activation energy of diffusion; E^* is the activation energy of reaction of A and B upon collision; R is the gas constant and T is the temperature.

The above equations can be rewritten for convenience for our studies.

Free radicals are very reactive chemically because they have a localized unpaired electron. Therefore, E^* in the decay reaction of free radicals is very small. On the other hand, the particles trapped in the solid are not mobile and the activation energy of diffusion of free radicals in solid polymer, E_D, is therefore much larger than E^*. Subsequently, when the initial distribution of free radicals at time $t = 0$ is uniform, equation (1) can be simplified as follows:

$$-\frac{\mathrm{d}C_\mathrm{A}}{\pi t} = 4\pi r_0 D'\left(1 + \frac{1}{(\pi\tau')^{1/2}}\right)C_\mathrm{A}C_\mathrm{B} \tag{5}$$

Usually, a polymer matrix which traps free radicals is a multiphase system, i.e. a combination of amorphous and crystalline phases. Therefore, more than two kinds of free radicals species can be observed in a polymer matrix. In order to estimate the concentration of free radicals, which do not disappear at a certain reaction temperature, equation (5) was modified to the following equations. By integrating equation (5) and assuming A = B:

$$\frac{C_\mathrm{A}^0}{C_\mathrm{A}} = 1 + 8\pi r_0 D C_\mathrm{A}^0\left[\frac{1 + (2)^{1/2}r_0}{(\pi D t)^{1/2}}\right]t \tag{6}$$

$$= 1 + A(t)^{1/2} + Bt = 1 + B\left[1 + \frac{A'}{(t)^{1/2}}\right]t \tag{7}$$

where

$$A = 8(2)^{1/2}r_0^2C_\mathrm{A}^0(\pi D)^{1/2} \tag{8a}$$

$$B = 8\pi r_0 D C_\mathrm{A}^0 \tag{8b}$$

C_A^0 is the initial value of $C(t)$, and

$$D = D_\mathrm{A} + D_\mathrm{B} = \frac{D'}{2} \tag{9}$$

Subsequently, the relative concentration and the diffusion constant of free radicals can be obtained from the following equations, respectively:

$$x = \frac{C_\mathrm{A}}{C_\mathrm{A}^0} = \frac{C}{C^0} = \frac{1}{1 + A(t)^{1/2} + Bt} \tag{10}$$

$$D = \frac{2}{\pi}\left(\frac{B}{A}\right)^2 r_0^2 \tag{11}$$

Here, for the case of the two phase system the concentration of the free radicals must be represented as:

$$C = C' + C'', C_0 = C_0' + C_0'' \tag{12}$$

C' and C'' are the concentrations of fast-decaying and slow-decaying (non-vanishing) free radicals, respectively. By the use of this expression, the following equation can be obtained instead of equation (7)

$$\frac{C_0 - C_0'}{C - C''} = \frac{1 - a}{x - a}$$

$$= 1 + B\left[1 + \frac{A'}{(t)^{1/2}}\right]t \tag{13}$$

or

$$x = \frac{1}{B\{1 + [A'/(t)^{1/2}]\}} \, \frac{1-x}{t} + a \qquad (14)$$

where

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

These equations lead to the following points. (a) Equation (7) shows that the inverse concentration tends to become proportional to t when the time t is very large since the quantity $A'/(t)^{1/2}$ is negligible for large t. This means that the reaction behaves like a simple second order reaction for very large t. In most of the papers reporting the decay reaction of the free radicals in polymers, plots of inverse concentration of the radicals against t show the deviation from a linear plot for small values of t, but they show a good linear relation for large t. This behaviour of the plot is just as that represented by equation (7). (b) Equation (7) indicates that a plot of inverse concentration vs. time at large t gives the value of B and plot of inverse concentration vs. $(t)^{1/2}$ at very small t gives the approximate value of A for the case of a one component system. (c) A similar estimation for the more complicated two component system can be made by the application of equations (13) and (14). If we plot x vs. $(1-x)/t$, the value of a in equation (14) can be obtained by extrapolating the curve to $(1-x)/t = 0$. In the case of the one component system, quantity a must vanish. (d) The diffusion constant can be estimated from the values of A and B which are calculated by the method of least squares using an electronic computer if an appropriate value of r_0 is assumed.

RESULTS AND DISCUSSION

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

In a previous paper[12], it was reported that two types of alkyl radicals were trapped in polyethylene single crystals after the irradiation at liquid nitrogen temperature. One of them was termed B radical corresponding to the e.s.r. spectra of a broad sextet, and it was found to be trapped in the lamellar surface and very unstable at temperatures higher than 248K. The other one, the S radical, corresponding to the e.s.r. spectra of a sharp sextet is trapped in the inner crystalline region and decays at a much higher temperature than the B radical. Most of the B radicals disappeared when heat treated at 273K for a long time.

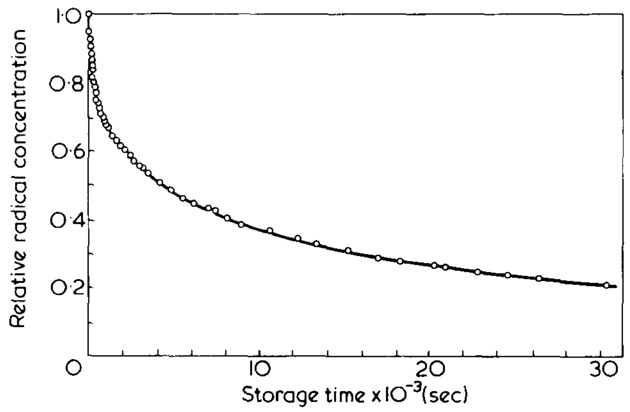

Figure 1 The decay curve of alkyl radicals trapped in irradiated polyethylene single crystals, A-85, at liquid nitrogen temperature after heating to 273K for a long time. Experiments were made at 307K. ———, shows calculated decay curve of equation (7); the constants in equation (7) are: $A = 1.2 \times 10^{-2}$ (sec$^{-1/2}$); $B = 4.5 \times 10^{-5}$ (sec^{-1})

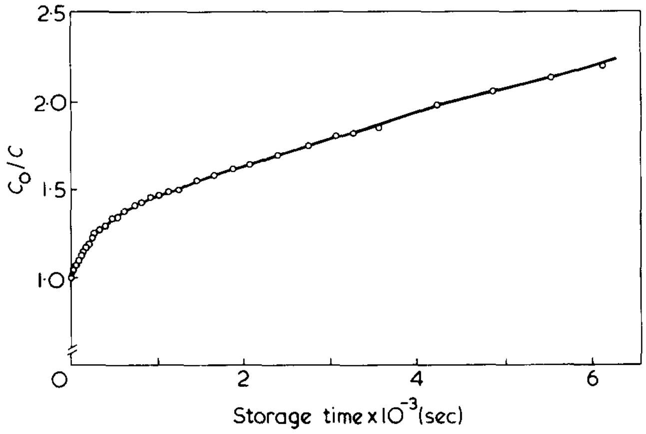

Figure 2 Inverse concentration of alkyl radicals vs. duration of time of storage at 307K

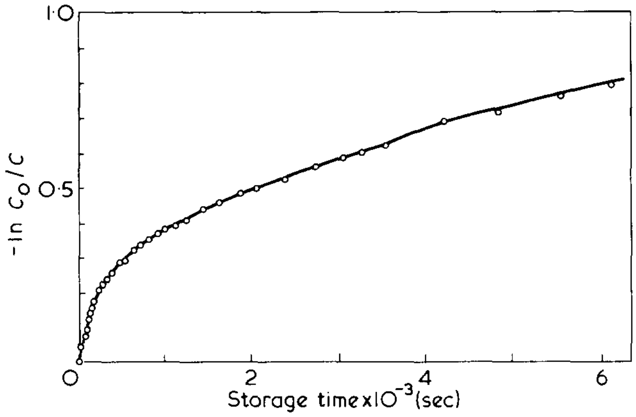

Figure 3 Logarithm of inverse concentration of alkyl radicals vs. duration of time of storage at 307K

Figure 1 shows the decay curve of S radicals at 303K obtained by the following procedure. The sample was heated up to 273K for 1 h after the irradiation at liquid nitrogen temperature. Next, the sample tube was inserted into the e.s.r. cavity, maintained at a temperature of 307K and the heights of the outermost and weakest peak of the sextet spectrum were recorded at appropriate time intervals. From these peak heights, the percentage concentrations of S radicals against that observed before heat treatment at 307K were obtained.

In *Figure 1*, zero-time is the time at which the e.s.r. measurement started. From these data, the inverse concentration can be plotted against time as shown in *Figure 2*. The data show the obvious deviation from the linear plot and indicate also that the rate constant of the second order reaction is time dependent. This character is reflected in equation (7). The slope, 8.5×10^{-5} at large t in *Figure 2* is considered to be an approximate value of B. *Figure 3* shows the plot of the logarithms of the relative concentration vs. time. Because the plotted points deviate from a straight line for a shorter duration of time, the kinetics of

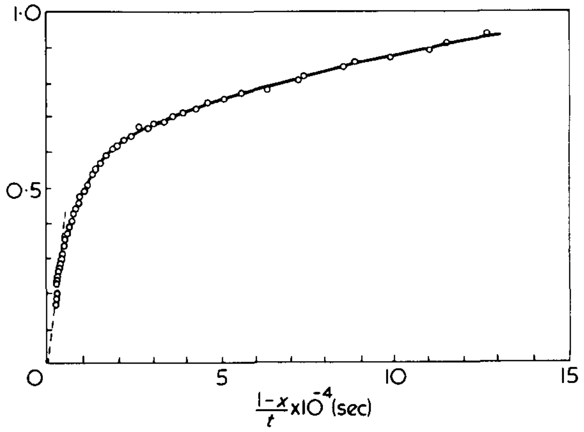

Figure 4 The relative concentration of alkyl radicals vs. value of $(1-x)/t$ at 307K

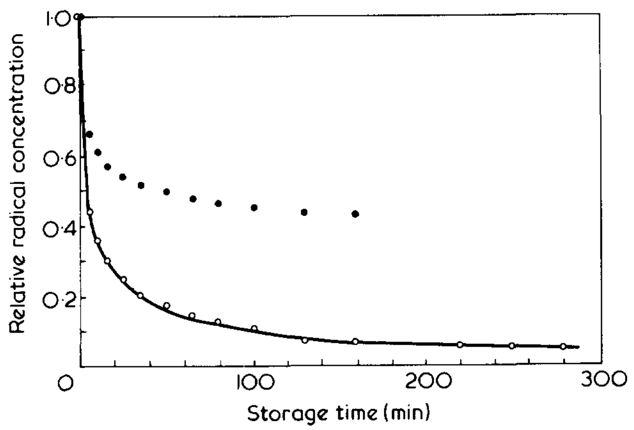

Figure 5 The decay curve of alkyl radicals trapped in irradiated polyethylene single crystals A-85 at 269K after heating at 195K for a long time. Irradiation was made at 77K and e.s.r. observations were made at 77K. ○, Show the reduced amount of decay obtained after subtracting the amount of non-vanishing radicals. ———, shows calculated decay curve with $A = 4 \times 10^{-2}$ $(\text{sec}^{-1/2})$ and $B = 1 \times 10^{-3}$ (sec^{-1})

decay of S radicals cannot be explained by the treatment of the first order reaction. A plot of $(1-x)/E$ vs. x is shown in *Figure 4*. By extrapolation of the curve to $(1-x)/t = 0$, the value of 'a' is nearly equal to zero in this system. Subsequently, equation (10) can actually be applied to the estimation of A and B because of this negligible value of a. The solid line in *Figure 1* shows the calculated decay curve obtained by the method of least squares using an electronic computer. Consequently, the values of A and B are found to be 1.2×10^{-2} and 4.5×10^{-5}, respectively. This simulated curve is in good agreement with data based on diffusion-controlled reaction theory and makes for improved interpretation of the decay reaction of the free radicals trapped in solid polymer. For simplicity, the capture radius r_0 was assumed to be 1.5 Å which is the carbon–carbon bond length. This assumption of the capture radius should be reasonable for the rough estimation of the diffusion constant, and the diffusion constant of the radical decay process was estimated to be 1.1×10^{-21} cm^2/sec according to equation (11).

Decay of free radicals trapped in the lamellar surface of the crystallites of polyethylene

No decay of S radicals was observed between 248 and 275K. Consequently, the decay reaction of B radicals between the corresponding temperatures can be analysed by equation (14) which can be applied to the interpretation of the reaction in the case of the two component system. *Figure 5* shows the decay curve which was obtained by the following procedure. First, the e.s.r. spectrum was observed at liquid nitrogen temperature after heat treatment at 195K for a long time (~3 h) in order to get rid of the unstable free radicals. The spectrum is shown in *Figure 6*. Next, the sample was warmed up to 265K and stored at the same temperature for 5 min, then cooled down to liquid nitrogen temperature when the e.s.r. spectrum was observed again. The same heat treatment was repeated with increasing heat treatment time. Relative percentage intensities of the spectra observed after the respective heatings were obtained against the intensity of the spectrum observed after the heat treatment at 195K (spectrum shown in *Figure 6*, curve A). *Figure 7* shows the plots of $(1-x)/t$ vs. x from the data of the decay reactions observed at several temperatures. By extrapolation of the curve to $(1-x)/t = 0$, the value of a was found to be about 0.39 in all cases. This means that the percentages of the amounts of B radicals and S radicals are 61 and 39, respectively. Assuming that no diffusion of radicals occurs between the different phases, the decay of the free radicals trapped in the lamellar surface, B radicals, can be studied by applying equation (13); i.e. a in equation (13) is the amount of S radicals in this case. According to equation (13) and the value of a obtained from *Figure 7*, plot of $(x-0.39)/0.61$ against t is better for the study of B radicals and this is shown in *Figure 5*, where the solid line shows the calculated

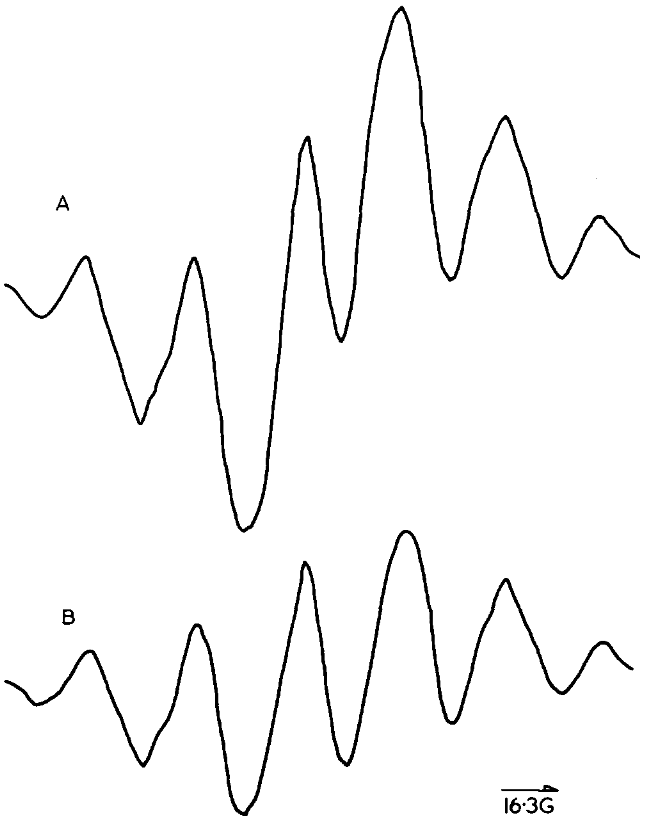

Figure 6 E.s.r. spectra of irradiated polyethylene single crystals. Observation was made at liquid nitrogen temperature after irradiation at the same temperature. A, observed after heating up to 195K for a long time; B, spectrum after heat treatment at 269K for 280 min

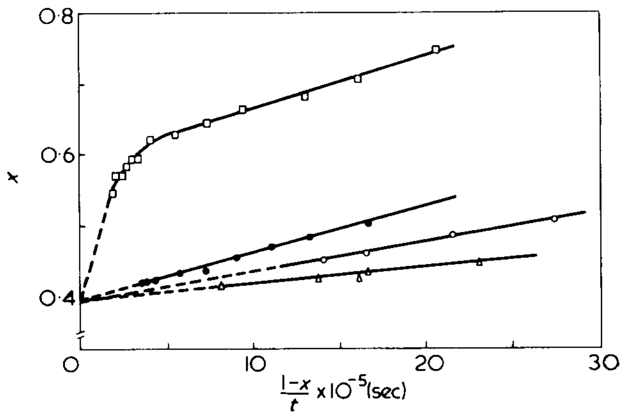

Figure 7 The relative concentration of alkyl radicals vs. value of $(1-x)/t$ at various temperatures: □, –23.0°; ●, –8.0°; ○, –3.0°; △, –1.5°C. E.s.r. measurements were made at 77K

values of the B radicals for the case where the constants A and B are 4×10^{-2} sec$^{-1/2}$ and 1×10^{-3} sec^{-1}, respectively. The good agreement between the calculated and experimental values suggests that the decay reaction of alkyl radicals in the lamellar surface is a diffusion-controlled process. The diffusion constant of free radicals in this case was estimated to be 9×10^{-22} cm^2/sec. The value of the diffusion constant of free radicals can be considered to be reflected in the mobility of polymer matrix where the free radicals are trapped. Subsequently, we can discuss the molecular motion of polymer chain by observing the decay reaction of free radicals. Since the semicrystalline polymer consists of multiphases, i.e. the amorphous, the lamellar surface and the inner crystalline, we can estimate molecular mobilities in the respective regions, separately, by the analysis of the decay reactions of free radicals mentioned previously. These estimations and the more detailed discussions including the data at various temperatures will appear in a forthcoming publication.

Decay of alkyl radicals trapped in urea–polyethylene complex

Three-dimensional migration of the free radicals trapped in the crystalline region was considered in a previous section, and diffusion-controlled theory was shown to be a good interpretation for the decay reaction of the free radicals. Concerning this problem the behaviour of the free radicals trapped in urea–polyethylene complex was studied.

Before going on to the presentation of the experimental results, a problem in the migration process will be reconsidered briefly. We have the following question: whether the migration of the free radicals is intramolecular or intermolecular? The former mechanism means equation (15), migration along the chain, and the latter, equation (16), migration across the chain.

$$-CH_2-\dot{C}H-CH_2-CH_2- \longrightarrow -CH_2-CH_2-\dot{C}H-CH_2- \tag{15}$$

$$\begin{array}{ccc} -CH_2-\dot{C}H-CH_2- & & -CH_2-CH_2-CH_2- \\ & \longrightarrow & \\ -CH_2-CH_2-CH_2- & & -CH_2-\dot{C}H-CH_2- \end{array} \tag{16}$$

If only the migration along the chain occurs, three-dimensional considerations cannot be applied, at least, for the decay process in the crystalline phase. On the other

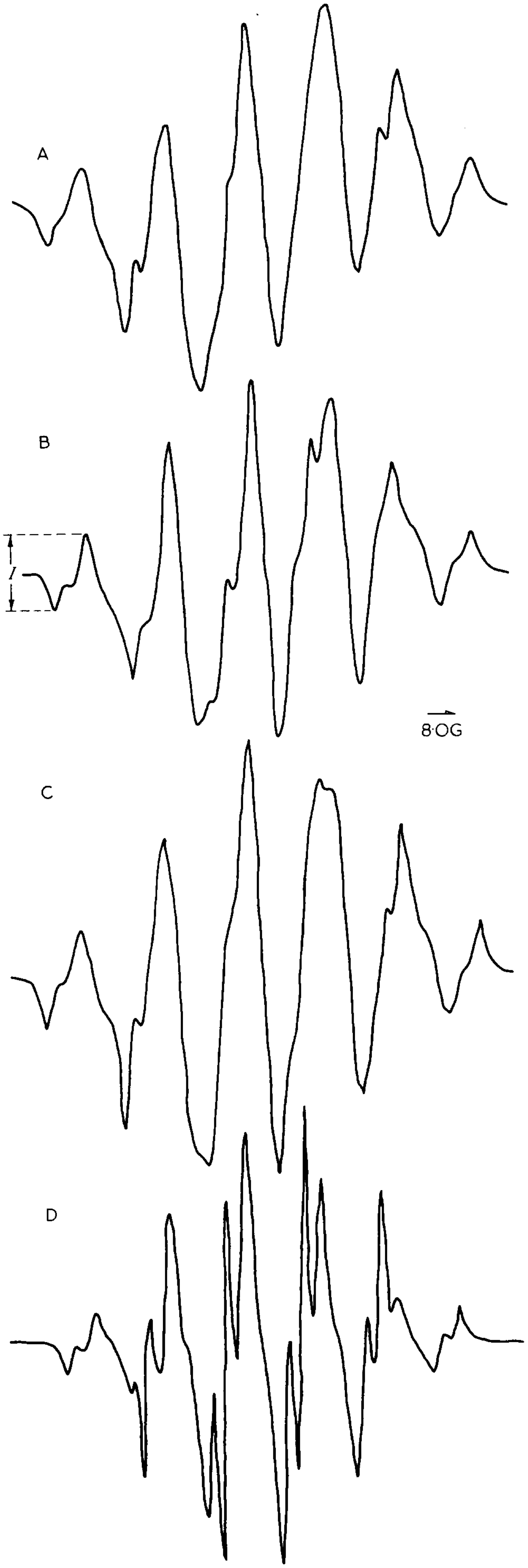

Figure 8 E.s.r. spectra of alkyl radical produced in polyethylene single crystals (A, B) and urea polyethylene complex (C, D). A, 77K; B, 280K; C, 77K; D, 289K

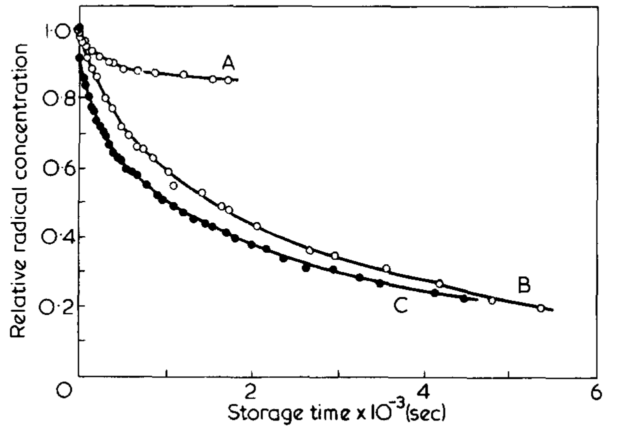

Figure 9 The decay curves of alkyl radicals in irradiated urea–polyethylene complex and that of polyethylene single crystal. A, 380K; B, 411K; C, 327K. ○, Relative concentration of free radicals in urea–PE complex; ●, relative concentration of free radicals in solution grown PE single crystals

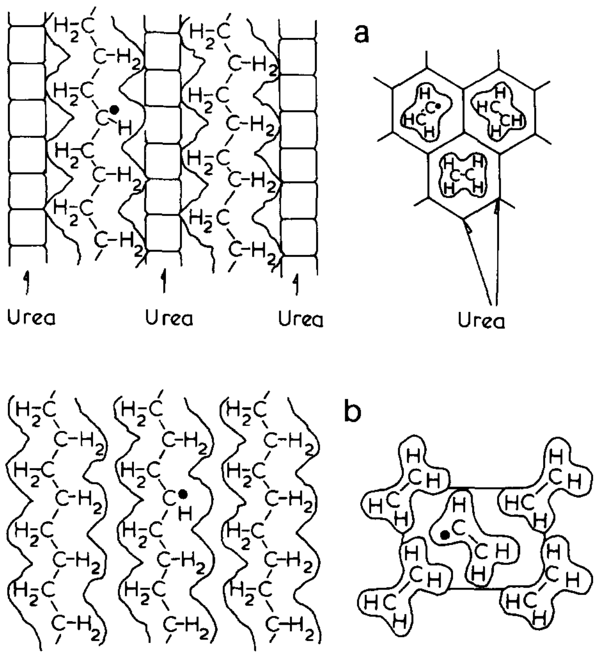

Figure 10 Schematic model of (a) urea–polyethylene complex structure and (b) polyethylene single crystals

hand, however, even if the migration takes place only through the intermolecular hydrogen abstration, equation (16), migration along the chain will be possible through a certain set of two-step processes of equation (16); chain A → chain B → chain A. Of course, a mixed process of inter- and intra-molecular migrations is also possible, and this leads naturally to a three-dimensional diffusion aspect.

An answer to the question mentioned above will be given from the following study of the free radicals trapped in urea–polyethylene complex. *Figure 8* shows e.s.r. spectra observed at 77K and at room temperature (observations were made in the winter season), and it shows also the difference between the spectra of the alkyl radicals trapped in urea–polyethylene complex and that in solution grown crystals of polyethylene. Fortunately since no spectrum due to the free radicals of urea molecules was superposed, the behaviour of the free radical trapped in polymer main chain of the urea–polyethylene complex can be clearly studied. *Figure 8* indicates that the spectra for urea–polyethylene complex is very different from that for solution grown crystals when the observation is made at room temperature; line width and total spread of the spectrum of the former is smaller than that of the latter. This shows that the radical site in urea–polyethylene complex is more mobile than that in the solution grown crystals. Of course, narrower line width is partly due to the weaker dipole–dipole interaction in the urea–polyethylene complex. Temperature dependence of e.s.r. spectra of alkyl radicals can be interpreted on the basis of the hindered oscillation of polyethylene molecules around the molecular *c*-axis. These problems will also be discussed in a forthcoming publication.

In addition to the difference of the spectra shown in *Figure 8*, the difference between the decay behaviours of alkyl radicals trapped in the complex and solution grown crystals was also observed. *Figure 9* shows the decay processes of the free radicals. Decay reactions were observed at the temperatures described in the Figure. From *Figure 9*, it can be said that the free radicals in the complex have a very long lifetime at 380K ($\sim$100°C higher than room temperature), and the decay rate in the complex at 411K is the same order as that in solution grown crystals at 327K. Thus, the decay reaction of the radicals in urea–polyethylene complex was found to be very slow. *Figure 10* illustrates a scheme of the probable orientation in the solution grown crystals (*Figure 10b*) and that in the urea–polyethylene complex (*Figure 10a*). In the urea–polyethylene crystals the molecules of polyethylene are wholly surrounded by the urea molecules, and, therefore, interchain migration of alkyl radicals is inhibited. If the radical migration along the chain is a main process of the decay reaction of the alkyl radical, a remarkable decay of the radicals in the complex must be observed because of the high mobility character of the polyethylene in the complex as mentioned previously in connection with the characteristics of the e.s.r. spectrum shown in *Figure 8*.

The experimental fact shows, however, this is not the case. This means that free radical migration along the chains hardly occurs at room temperature in urea–polyethylene complex. Therefore, it can be considered that the rate of radical migration along the chain is very small in the solution grown crystals of polyethylene where the molecular mobility is lower than in the complex. On the other hand, the decay of free radicals in the solution grown crystals was observed at 307 and 327K as shown in *Figures 2* and *9*. This decay should originate from free radical migration across the chains. From these facts, it can be concluded that the rate of free radical migration across the chain is much faster than that along the chains in polyethylene crystals.

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