Hindered oscillation and e.s.r. spectra of alkyl free radicals trapped in irradiated polyethylene crystals

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Structures of alkyl radicals trapped in solution grown crystals of polyethylene and urea–polyethylene complex were studied in detail. A twisted configuration of methylene group with angle of 4.6° from the regular *trans–trans* configuration was found for the rigid state configuration of the alkyl radical at 77K. Temperature dependences of hyperfine splitting widths due to the β-protons were observed, and analysed in terms of the hindered oscillation of the β-methylene group. The value of the potential barrier height of hindered oscillation was found to be 900 kcal/mol for polyethylene crystal and 600 kcal/mol for urea–polyethylene complex; indicating that the radical site in urea–polyethylene complex is more mobile than that in polyethylene crystal.

INTRODUCTION

E.s.r. spectra[1–5], decay reactions[6–11] and locations of the alkyl free radical[12,13], $-CH_2-\dot{C}H-CH_2-$, trapped in irradiated polyethylene have been studied by many authors. However, the precise structure of the radical and its mobility are still open for further studies. It is well known that the e.s.r. spectral shape of alkyl radicals in polyethylene changes drastically with temperature and the change was interpreted in terms of the variation in coupling constant[14] due to interaction with the β-proton. On the other hand, the ambiguity originating from the broad linewidth, the anisotropic coupling constant due to interaction with α-proton, and the determinations of the values of coupling constants due to interactions with β-protons result from the complicated analysis of the spectra of alkyl radicals. However, these quantities are the parameters in simulation procedures of the spectra, and the difficulties in identifications of the spectra observed were solved by the use of computer simulation. The broad linewidth is usually an apparent width and this is ascribed to the superposition of two different patterns which correspond to two kinds of alkyl radicals trapped in different regions, i.e. amorphous and crystalline regions. Concerning the locations of different kinds of alkyl free radicals, detailed interpretation has already been presented and the separation of the superposed spectrum was reasonably achieved[13]. In order to observe the spectra of the radicals trapped in the crystalline region, it is helpful to study the materials treated by fuming nitric acid, and these results will be presented later.

Deformed conformation and hindered oscillation of organic free radicals were found by several authors[15–19]. E.s.r. spectra of the radicals were also studied for the complex systems composed of organic compounds and urea molecules[20,21] and the variation of coupling constant due to the β-proton was interpreted in terms of the restricted motion of β-protons around the main chain axis. Molecular chains in polyethylene are usually surrounded by the same molecules of polyethylene. On the other hand, however, each molecular chain in a urea–polyethylene complex is placed in a pore composed of urea molecules. Hence, intermolecular distance and potentials are different in both cases. Therefore, the effect of inter-main chain potential on mobility of alkyl radicals can be clarified by comparing the variations of e.s.r. spectra of the radicals with temperature both for polyethylene crystals and urea–polyethylene complex crystals. In the present article, the structure of alkyl radicals and the relation between the mobility of alkyl radicals and the intermolecular potential will be discussed.

EXPERIMENTAL

Sample preparation

High density polyethylene, Sholex 6050 (product of the Showa Electric Industry Co., Ltd.), was purified by dissolving in boiling toluene, precipitated by cooling, washed in acetone, and dried in the vacuum oven. The purified polyethylene sample was recrystallized in dilute xylene solution of 0.1 wt % for more than a week at 85°C. After crystallization, xylene were removed by filtration and polyethylene was dried in the vacuum oven. 1 g of the sample was also subjected to the fuming nitric acid (100 ml) treatment at 60°C for 196 h. After treatment, the materials were washed with distilled water and then with acetone with a Soxhlet-extractor in order to remove fuming nitric acid and homopolymers. The urea–polyethylene complex (UPEC) was prepared according to the method of Yokoyama and Monobe and the detailed procedure was described in the paper by Yokoyama and Monobe[22] and in our previous paper[11].

Irradiation techniques

All samples were subjected to γ-irradiation by the use of ^{60}Co γ-ray source at liquid nitrogen temperature under a

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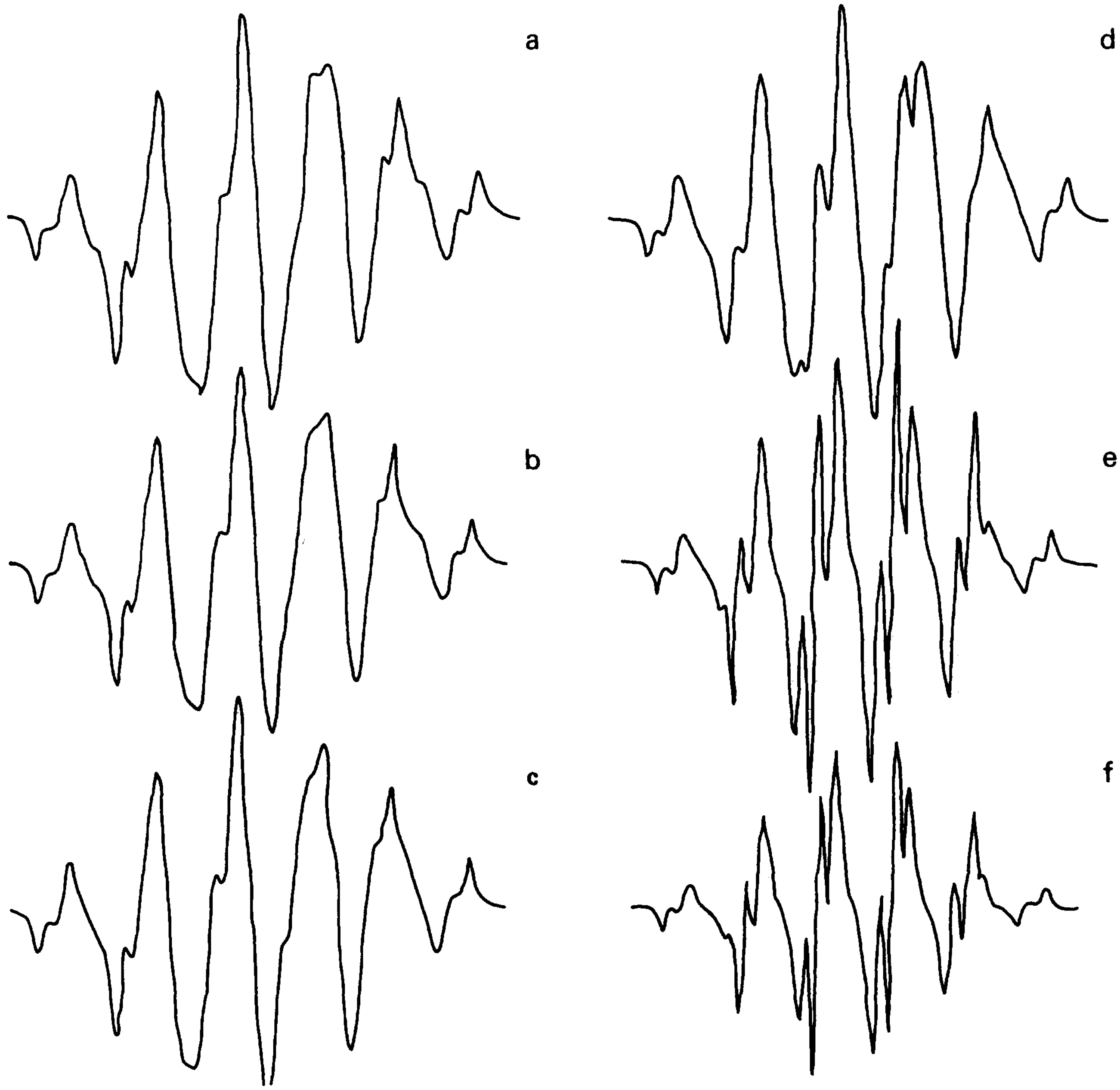

Figure 1 E.s.r. spectra of alkyl radicals trapped in polyethylene crystals in UPEC. (a) 108K; (b) 158K; (c) 195K; (d) 243K; (e) 321K; (f) 386K

vacuum of 10^{-4} torr up to a total dose of 3.0 Mrad at the dose rate of 0.22 Mrad/h.

E.s.r. measurements

E.s.r. spectra was recorded with JEOL ME3 electron spin resonance spectrometer (X band) with 100 kHz field modulation. The JEOL temperature controller was used to control the temperature of observation.

RESULTS AND DISCUSSION

Variation of e.s.r. spectra of alkyl radicals trapped in UPEC

Figure 1 shows the change of e.s.r. spectra of free radicals produced in irradiated UPEC with temperature of observation. The patterns do not show the e.s.r. spectrum of all the species. When an e.s.r. spectrum was observed immediately after γ irradiation, a superposed spectrum composed of singlet and sextet was obtained. However, the singlet pattern disappeared after the heat treatment at room temperature and the intensity of sextet, which is shown in *Figure 1* increased. The spectrum in *Figure 1a* is similar to the sextet, which has already been observed by many researchers for γ irradiated polyethylene solids. This sextet spectrum is assigned to that of alkyl free radicals, $\sim CH_2-CH-CH_2\sim$, based on the analyses of hyperfine splittings caused by the interactions between the unpaired electron and protons. The alkyl free radicals trapped in UPEC crystals are very stable and could be observed even at 400K. As indicated in *Figure 1*, the e.s.r. spectra of alkyl free radicals change remarkably when the observation temperature is about 243K and the sharper spectra are observed at temperatures higher than 243K, e.g. the linewidth of the spectrum in *Figure 1e* is very narrow. We could not observe such a sharp spectrum in the case of γ irradiated polyethylene matrix. It is thought that the change of the e.s.r. spectra in *Figure 1* originates from the decrease of the linewidth, the averaging out of the anisotropy of the coupling constant due to the α-proton and the variation of coupling constant due to β protons.

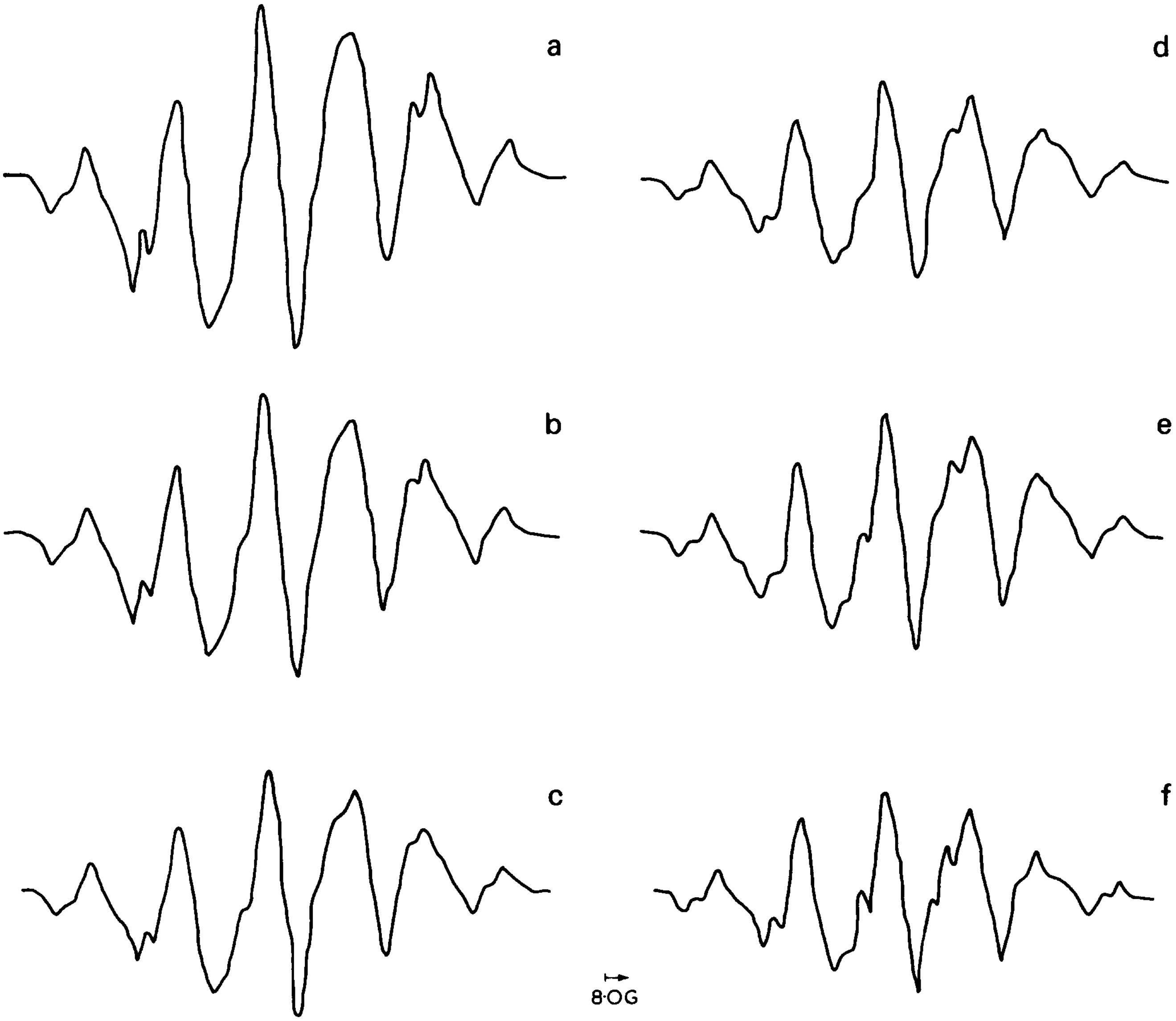

Figure 2 E.s.r. spectra of alkyl radicals trapped in solution grown crystals of polyethylene. (a) 114K; (b) 164K; (c) 179K; (d) 242K; (e) 319K; (f) 359K

Comparison of calculated and observed spectra

In order to elucidate the structure and the mobility of alkyl radicals, it is necessary to determine the exact values of the linewidths and coupling constant due to the α proton and β protons. Based on the variation of these parameters with temperature of observation, detailed information about the local molecular motion of free radical sites can be obtained. For this purpose, the spectrum simulation was made in the following way.

(a) The small splitting of the wing peak of sextet spectrum was assumed to reflect the anisotropy of coupling constant due to the α proton; in other words, the pattern is the so-called amorphous pattern[23]. Therefore, we could estimate the rough values of A_1, A_2, A_3 (principal values of coupling constant due to α proton) and the linewidth from the line shape of the wing peak.

(b) We assumed that the anisotropies of coupling constant due to β protons, ΔH_{β_1}, ΔH_{β_2}, $\Delta H_{\beta'_1}$, $\Delta H_{\beta'_2}$ were negligible and $\Delta H_{\beta_1} = \Delta H_{\beta'_1}$, $\Delta H_{\beta_2} = \Delta H_{\beta'_2}$. (This assumption implies that the structure of alkyl radicals are symmetric.) Concerning the two methylene groups, the rough value of $2(\Delta H_{\beta_1} + \Delta H_{\beta_2})$ was estimated from the magnitude of the whole spread of the pattern.

(c) Finally, we were able to obtain the theoretical spectra. By using values of spectral parameters described in the previous part, we could obtain the theoretical spectra assuming that each of the components was of Gaussian lineshape. Several theoretical spectra were calculated by gradually changing the values of spectral parameters. These spectra were recorded on an $X-Y$ plotter and compared with observed spectra in order to get the best fit. *Figure 3* shows examples of calculated spectra with various values of splitting widths due to β-protons. *Figure 3* indicates a remarkable change in the calculated patterns when ΔH_{β_1} and ΔH_{β_2} change slightly, provided $\Delta H_{\beta_1} + \Delta H_{\beta_2} =$ constant. In *Figure 3*, one of experimental spectra is also shown and the calculated spectrum (c) seems to be the best fit with respect to the whole lineshape and peak positions. By this method, spectral parameters of the spectra observed at various temperatures can be determined. In the present study, variations of linewidth and principal values of hyperfine tensor originating from interaction with the α proton were found to be small. Varia-

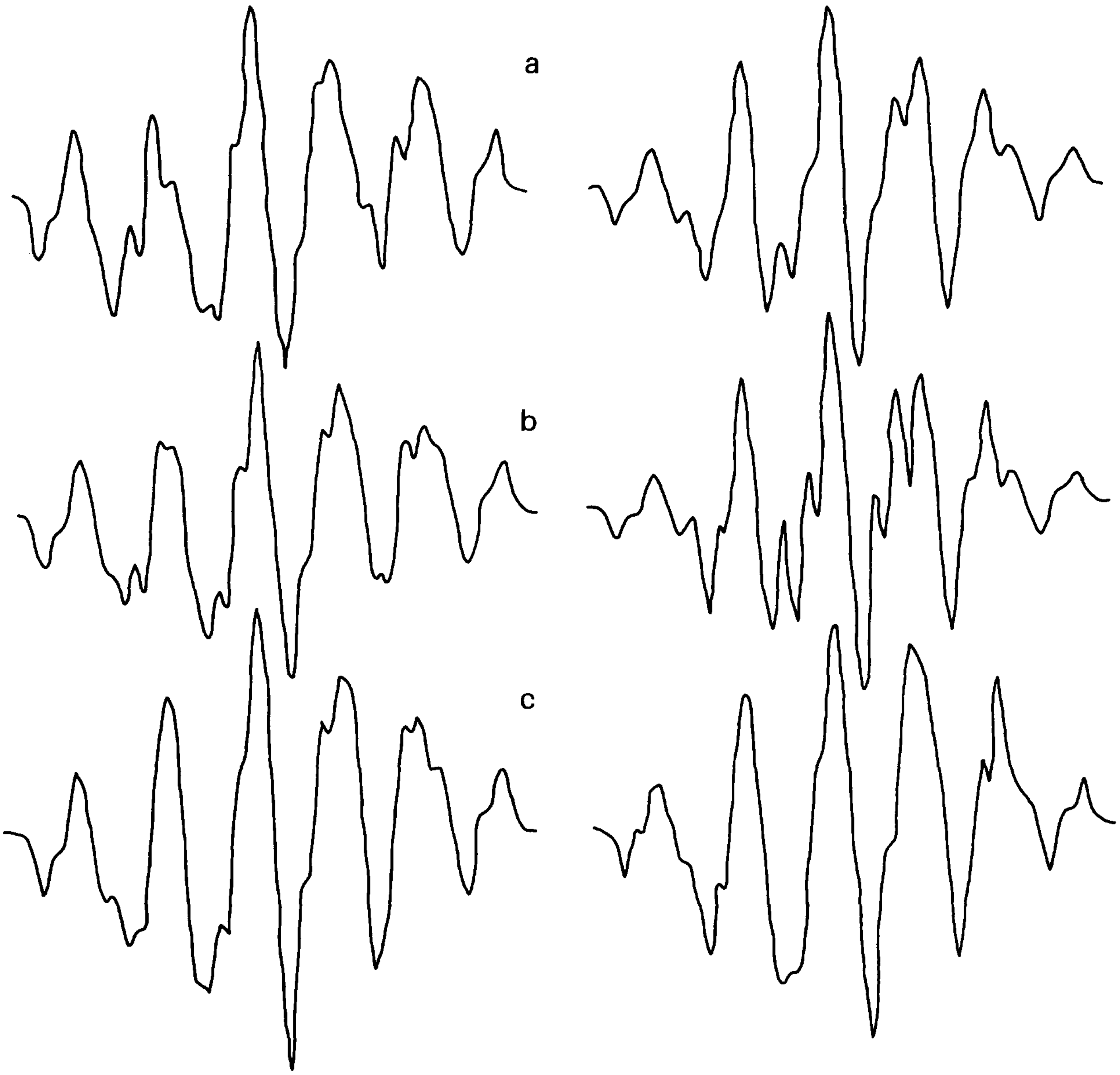

Figure 3 Comparison of the experimental e.s.r. spectra of alkyl radicals observed at 107K in the case of UPEC with the calculated spectra. B1 and B2 stand for the β-proton coupling constant (gauss). (a) B1 = 29.0, B2 = 38.5; (b) B1 = 30.0, B2 = 37.5; (c) B1 = 30.8, B2 = 36.7; (d) B1 = 32.0, B2 = 35.5; (e) B1 = 33.7, B2 = 33.7; (f) experimental. (a)–(e) calculated spectra

tions of ΔH_{β_1} and ΔH_{β_2} with temperature of observation are plotted in *Figure 4*, and will be discussed later.

Structure of alkyl free radicals in UPEC

It is well known that the configuration of the free radical site can be clarified by exact estimation of the values of hyperfine splitting due to β-protons. Heller and McConell[24] found that the hyperfine splitting due to β protons of the neighbouring methylene group, ΔH_{β_i}, could be determined by the following equation

$$\Delta H_{\beta_i} = K\rho\cos^2\theta_i = B\cos^2\theta_i \qquad (1)$$

where K is a constant, ρ the spin density, and θ_i is the projected angle between the $C_\beta - H_{\beta_i}$ bond and the π-electron axis in the plane perpendicular to the direction of the $C_\alpha - C_\beta$ bond. This situation is illustrated in *Figure 5*. Previously, the analysis of the sextet spectrum corresponding to the alkyl radical of polyethylene was based on the assumption that $\theta_1 = \theta_2 = 30°$[5]; i.e. a symmetric structure for the alkyl radicals was assumed. It is clearly shown in *Figures 3* and *4* that the value of ΔH_{β_1} is not equal to that of ΔH_{β_2} at low temperature. Therefore, the alkyl radicals are considered to have a structure deformed from the symmetric position at low temperature. Assuming that the molecular motion of the alkyl radicals at 77K is frozen, the deformed angles are calculated from the values of ΔH_{β_1} and ΔH_{β_2} at 77K. These values are expressed with $\Delta H_{\beta_{10}}$ and $\Delta H_{\beta_{20}}$, respectively. If ΔH_{β_1} and ΔH_{β_2}, determined from the simulated spectra, are substituted into the equation (1), the following relations may be obtained:

$$\Delta H_{\beta_{10}} = 31.0 = B\cos^2\theta_{10} \qquad (2)$$

$$\Delta H_{\beta_{20}} = 37.4 = B\cos^2\theta_{20} \qquad (3)$$

where θ_{10} and θ_{20} are the angles defined in equation (1) for the frozen state. Since the β methylene group is in the regular tetrahedral arrangement, equation (4) is satisfied:

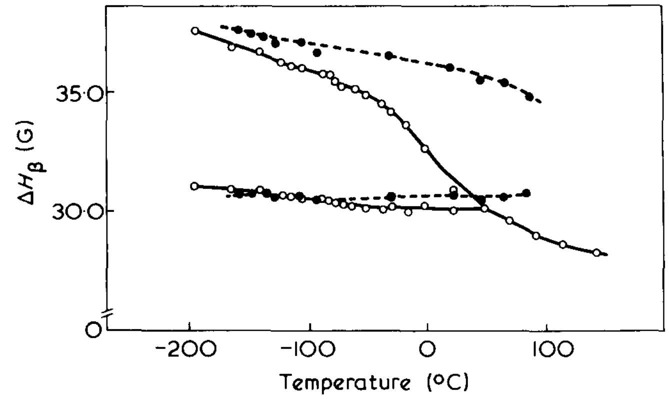

Figure 4 The variation of the value of ΔH_β with the observation temperature. ○, UPEC; ●, solution grown crystals of polyethylene

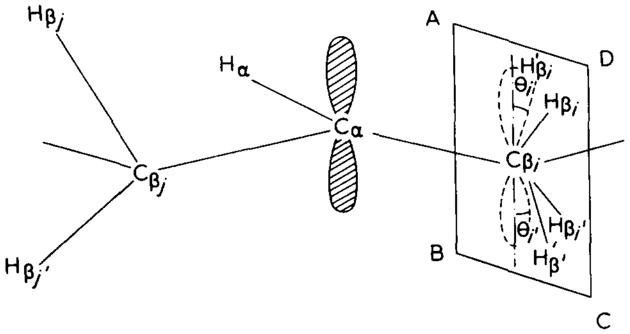

Figure 5 Steric configuration of the alkyl free radicals (plane ABCD ⊥ direction of C_α–C_β bond). Broken lines and primes indicate the projection of the corresponding items on the plane ABCD

$$\theta_{10} + \theta_{20} = 60° \qquad (4)$$

Equations (2), (3) and (4) lead to equation (5)

$$\cos^2\theta_{10}/\cos^2(60° - \theta_{10}) = 0.8288 \qquad (5)$$

and give the following relations:

$$\theta_{10} = 25.4° \qquad (6)$$

$$\theta_{20} = 34.6° \qquad (7)$$

$$B = 45.8 \text{ Gauss} \qquad (8)$$

By the same procedure, the following relations (with prime) can also be obtained for the configuration of the β methylene group on the other side of the unpaired electron:

$$\theta'_{10} = 25.4 \qquad (9)$$

$$\theta'_{20} = 34.6 \qquad (10)$$

As a result, it is concluded that the structure of the alkyl radicals trapped in urea–polyethylene complex is a deformed one with deformation angle of 4.6°. This slightly deformed structure was previously ignored in the analysis of the e.s.r. spectra.

Hindered oscillation of the alkyl radicals trapped in UPEC

Figure 6 shows the observed and calculated e.s.r. spectra of UPEC crystals at 321K. From the simulation of this spectrum, ΔH_{β_1} and ΔH_{β_2} were each found to have a value of 30 gauss. By substituting this value into equation (1), the following relation can be obtained:

$$\theta_1 = \theta_2 \text{ and } B = 40.0 \text{ (gauss)} \qquad (11)$$

However, the validity of the assumption that molecules are frozen, used in obtaining equation (11), fails in the case of higher temperature. As indicated in the patterns of *Figure 1* the decrease of the linewidth and the averaging out of the anisotropy of coupling constant due to α proton are shown in the spectra observed at higher temperatures. These phenomena are a reflection of the molecular motion at the free radical sites. In addition, the change of the value of B should be less probable. The temperature change of the coupling constant due to β proton shown in *Figure 4* is interpreted in terms of the exchange of two β proton due to the hindered oscillation around the C_α–C_β bond. Two deformed conformations which are the mirror images of each other were considered to be stable at low temperature as discussed above. These deformed conformations were designed with the schematic potential energy curve of the alkyl radical as illustrated in *Figure 7*. However, at higher temperatures, rapid exchange between two sites takes place and eventually the values of the coupling constant due to β proton must be averaged out into a single value for each conformation. Several authors interpreted the change of the coupling constant due to β proton in terms of the large torsional displacement of only one conformational methylene group. For example, Adrian[25] *et al.* explained the difference of the coupling constant due to β proton of the end radical, $\cdot CH_2$–$CH_2\sim$, for n-propyl and n-butyl radicals by comparing the amplitude of a harmonic torsional oscillation of only one conformational radical. The structure of the main chain alkyl radical, $\sim CH_2$–CH–$CH_2\sim$, mirror images, which intersect the C_α–H_β bond and are perpendicular to the plane of the main chain in contrast to the case of the end radical. Therefore, it is reasonable to consider

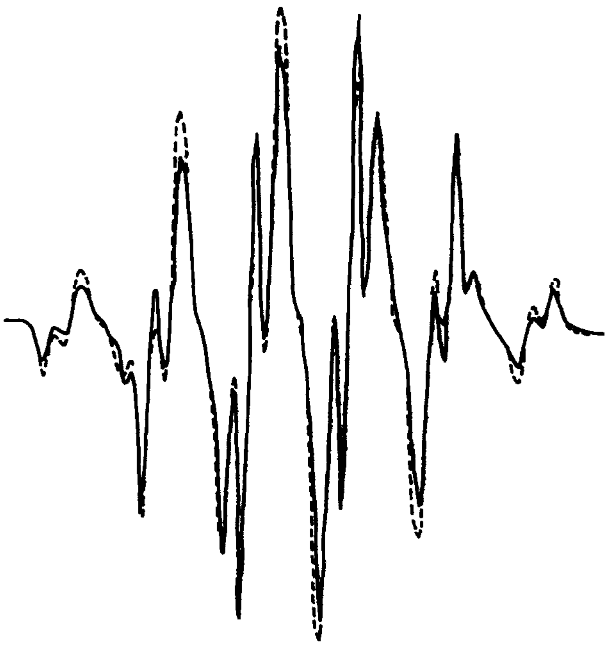

Figure 6 Comparison of the e.s.r. spectra observed at 321K with the simulated spectra in the case of UPEC

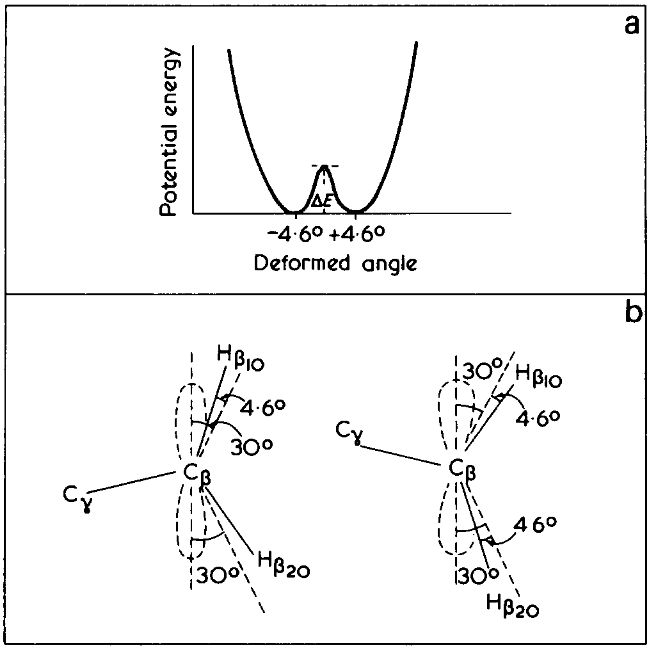

Figure 7 (a) Schematic potential energy curve of the alkyl free radical for hindered oscillation around the C_α–C_β bond. (b) Two stable conformations which are the mirror images of each other

two deformed conformations which are the mirror images of each other and the double minimum potential of the main chain alkyl radical as illustrated in *Figure 7*. The gross approximate values of coupling constant due to the β proton can be expressed in the following equation:

$$\Delta H_{\beta_1} = \langle \Delta H_{\beta_{10}} \rangle\,[1 - \exp(-\Delta E/RT)] + \langle \Delta H_a \rangle \exp(-\Delta E/RT) \qquad (12)$$

The factor $[1 - \exp(-\Delta E/RT)]$ represents the probability of the free radical site oscillating below the barrier and the factor $\exp(-\Delta E/RT)$ represents the probability of the free radical site oscillating above the barrier, where ΔE is the potential barrier and $\langle\,\rangle$ denotes the average over the torsional oscillation.

Taking an average below the barrier based on the assumption of harmonic oscillation, the following relations can be derived:

$$\langle \Delta H_{\beta_{10}} \rangle = B\langle \cos^2\theta_1 \rangle = B\langle \cos^2(\theta_{10} + \Delta\theta) \rangle$$
$$= B[\cos^2\theta_{10}\langle \cos^2\theta \rangle + \sin^2\theta_{10}\,\{1 - \langle \cos^2\Delta\theta \rangle\}\,] \qquad (13)$$

where θ_{10} is the equilibrium angle and $\Delta\theta$ is the displacement due to torsion. As discussed in the previous section, θ_{10} was found to be 25.4°C and $\Delta\theta$ to be 4.6°C, which is the maximum displacement. When these values are substituted into equation (13), the following values can be obtained:

$$[\langle \Delta H_{\beta_1} \rangle = 37.2\ \text{(gauss)}\,] \approx [\Delta H_{\beta_{10}} = 37.4\ \text{(gauss)}] \qquad (14)$$

On the other hand, the average value above the barrier, $\langle \Delta H_a \rangle$, can be estimated as following:

$$\langle \Delta H_a \rangle = B\langle \cos^2\theta \rangle$$
$$= B[\cos^2 30^\circ \langle \cos^2\Delta\theta' \rangle + \sin^2 30^\circ (1 - \langle \cos^2\Delta\theta' \rangle)] \qquad (15)$$

In equation (15), $\Delta\theta'$ can be more than twice that of $\Delta\theta$ as interpreted for the model illustrated in *Figure 7*. The value of $\langle \Delta H_a \rangle$ estimated by equation (15) can be less than $B\cos^2 30^\circ$ when $\Delta\theta'$ is not zero, and it is a decreasing function with increasing $\Delta\theta'$. This means that $\langle \Delta H_a \rangle$ is decreasing with increasing temperature because the amplitude of torsional oscillation, $\Delta\theta'$, increases with increasing temperature. According to the same procedure, the equation for the other β-proton is:

$$\Delta H_{\beta_2} = \langle \Delta H_{\beta_{20}} \rangle\,[1 - \exp(-\Delta E/RT)] + \langle \Delta H_a \rangle \exp(-\Delta E/RT) \qquad (16)$$

Thus the following relations can be obtained when the temperature is very low, i.e. $\Delta E \gg RT$:

$$\Delta H_{\beta_1} = \langle \Delta H_{\beta_{10}} \rangle \approx \Delta H_{\beta_{10}}$$
$$\Delta H_{\beta_2} = \langle \Delta H_{\beta_{20}} \rangle \approx \Delta H_{\beta_{20}} \qquad (17)$$

On the other hand, when the temperature is very high, $\Delta E \ll RT$, equation (18) can be expected:

$$\Delta H_{\beta_1} = \Delta H_{\beta_2} = \langle \Delta H_a \rangle \qquad (18)$$

As discussed previously, $\langle \Delta H_a \rangle$ is decreasing with increasing temperature. Thus ΔH_{β_1} and ΔH_{β_2} take the same value at the temperature satisfying equation (18) and the splitting due to the β-proton decreases with rising temperature. This circumstance is clearly reflected in the observed data shown in *Figure 4*.

In order to estimate activation energy or barrier height which appeared in equations (12) and (16), the following procedure was used. Subtraction of equation (16) from equation (12) led to the relation:

$$1 - (\Delta H_{\beta_1} - \Delta H_{\beta_2})/(\langle \Delta H_{\beta_{10}} \rangle - \langle \Delta H_{\beta_{20}} \rangle)$$
$$= \exp(-\Delta E/RT) \qquad (19)$$

The left hand side of equation (19) is denoted by X. X is temperature dependent and can be estimated experimentally in the rigid state if, $\langle \Delta H_{\beta_{10}} \rangle - \langle \Delta H_{\beta_{20}} \rangle$ is taken to be the same as the value of $\{\Delta H_{\beta_{10}} - \Delta H_{\beta_{20}}\}$. The temperature dependence of X shown in *Figure 8*, shows that deviation from a linear plot appears at temperatures higher than 200K. This may be caused by the variation of $\{\langle \Delta H_{\beta_{10}} \rangle -$

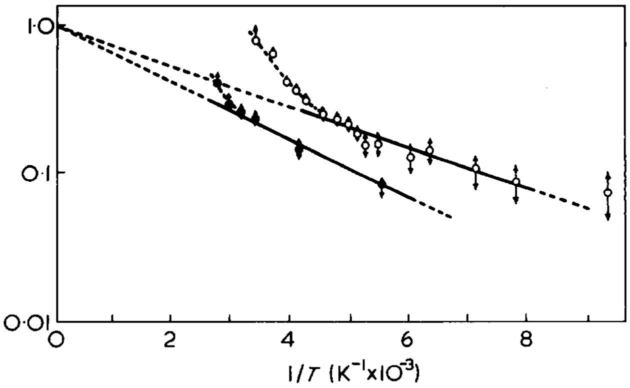

Figure 8 Value of X vs. inverse of observation temperature. ○, UPEC; ●, solution grown crystals of polyethylene

$\langle \Delta H_{\beta 20} \rangle\}$ due to the departure from the harmonic oscillation at higher temperatures. (At lower temperatures, $\{ \langle \Delta H_{\beta 10} \rangle - \langle \Delta H_{\beta 20} \rangle \}$ can be considered to be less dependent on temperature and it was taken to be the value at rigid lattice as mentioned above.) From the slope of straight line in the low temperature range in *Figure 8* the value of ΔE was found to be 600 cal/mol.

Structure and hindered oscillation of alkyl radicals trapped in solution grown crystals of polyethylene

Six spectra of alkyl radicals trapped in solution grown crystals of polyethylene are shown in *Figure 2.* Materials used in this observation were subjected to fuming nitric acid treatment after crystallization from dilute xylene solution. These spectra were observed over almost the same temperature range as that in *Figure 1.* The spectra observed at lower temperatures are similar for both of the solution grown crystal and the urea–polyethylene crystal. However, the situation is not the same for the spectra observed at higher temperatures. For example, the spectra in *Figures 2a–2e* are strikingly dissimilar from *Figures 1a–1e* with respect to linewidth, overall splitting and whole line shape. Similar simulations as in the case of UPEC were made for solution grown polyethylene and $\Delta H_{\beta 1}$ and $\Delta H_{\beta 2}$ are plotted against temperature of observation as shown in *Figure 4* (●). Gradual variations of $\Delta H_{\beta 1}$ and $\Delta H_{\beta 2}$ can also be interpreted in terms of hindered oscillation of the β methylene group around the axis of the C_α–C_β bond as discussed previously for the radicals trapped in UPEC. However, it is clear that the temperature, at which $\Delta H_{\beta 1}$ and $\Delta H_{\beta 2}$ become equal does not occur in the temperature range under present study, and variations of $\Delta H_{\beta 1}$ and $\Delta H_{\beta 2}$ seem to shift to higher temperature than for UPEC. The quantity X defined by equation (16) plotted against $1/T$ for radicals in solution grown crystals [*Figure 8*, (●)] also indicates shift to higher temperature than those for UPEC. These results show that alkyl radicals trapped in solution grown crystal are less mobile than the radicals in UPEC. The potential barrier in equation (12) was found to be 900 cal/mol for solution grown crystal, and this is also a reflection of the lower mobility of the radicals in the same materials. This interpretation seems reasonable since intermolecular chain interaction can be larger in solution grown crystals that in UPEC due to the shorter interchain distance in the former.

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