

Free radicals trapped in polyethylene matrix:

1. Location of the alkyl radicals in irradiated polyethylene

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(Received 4 June 1976)

Two types of alkyl radicals were found to be trapped in irradiated crystals grown from polyethylene solution. One of them corresponds to the broad sextet pattern of the e.s.r. spectrum and the other corresponds to the sharp sextet pattern. The free radicals attributed to the broad sextet began to disappear at a lower temperature than the temperature at which the free radicals attributed to the sharp sextet disappeared. When butadiene molecules were brought into contact with the specimen, the decay of the free radicals corresponding to the broad sextet was accelerated. When the specimen was subjected to fuming nitric acid treatment, no broad sextet was observed. The mat of the crystals, was aligned so that the *c*-axes of its crystallites were perpendicular to its surface. The broad sextet showed no anisotropy when the angle between the direction of applied magnetic field and that of the *c*-axis of the crystallite was varied. On the other hand, the sharp component of the spectrum showed apparent anisotropy. Consequently, it can be concluded that the broad component comes from the free radicals trapped in the lamellar surface and the sharp component is attributed to the free radicals trapped in the inner part of the crystallite. Hence, the locations of these two types of free radicals have been clarified with much more certainty than before.

INTRODUCTION

Electron spin resonance of irradiated polyethylene has been observed by many authors, and alkyl free radicals, $\sim\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2\sim^1$, allylic free radicals, $\sim\text{CH}=\text{CH}-\dot{\text{C}}\text{H}-\text{CH}_2\sim^2$, and polyenyl free radicals, $\sim(\text{CH}=\text{CH})_n-\dot{\text{C}}\text{H}\sim^3$, have been identified by the analyses of hyperfine splittings due to the interactions between unpaired electrons and protons. The behaviour of free radicals trapped in a polymer matrix has also been investigated by several authors. For example, the mechanisms of the decay reactions^{4,5} and the grafting reactions of the free radicals⁶⁻¹⁰ have been discussed on the basis of hydrogen migration and molecular motion in the matrix. In this paper, detailed studies on the relation between the behaviour of the free radicals and the physical state of the main chain of the polymer are discussed; i.e. the molecular mobility, the molecular orientation, the inter-main-chains potentials etc. In these discussions, it is essential that the trapping regions of free radicals are identified; i.e. in the crystalline phase, in the amorphous phase, or in the intermediate phase. It is known that the alkyl radicals are more reactive than the allylic or polyenyl radicals, therefore, the behaviour of the alkyl radicals can reflect the physical state of the matrix, where the alkyl radicals are trapped, much more clearly than that of allylic radicals or polyenyl radicals. In the first section of this paper, the authors will clarify the locations of the alkyl free radicals in the single crystals of polyethylene, which are composed of an inner crystalline region and the fold surface. This means that we can separate the superposed spectra into the respective patterns corresponding to the free radicals trapped at each region i.e. fold surface or inner crystalline region. These studies are very interesting, because we can study the molecular motion in each of the regions from the temperature

dependences of the respective patterns. Also, it is possible to discuss the local molecular motion around the radical sites in connection with the physical properties of the polymer matrix where the free radicals are trapped.

It is well known that a major part of the e.s.r. spectrum observed at liquid nitrogen temperature is a sextet spectrum corresponding to the alkyl free radicals. In a previous paper⁴ on the study of melt crystallized polyethylene, it was concluded that the alkyl free radicals, which decayed at temperatures ranging from 77 to 204K, had been trapped in the *gauche* conformation and that the amount of the decay in this temperature range was proportional to the amount of amorphous part. On the other hand, conformation of the site of the free radicals which decayed at higher temperature was the *trans* zig-zag form, and the amount of the decay of the radicals was proportional to the crystallinity. However, the location of the free radicals which disappeared at higher temperatures is still not clear; i.e. in the inner crystalline region or lamellar surface. Based on studies on the relation between the radical concentration and the lamellar thickness, Kusumoto *et al.*¹¹ found that alkyl radicals were concentrated at the surface of the crystallite. However, there was no discussion on the e.s.r. spectrum of alkyl free radicals. In this paper, two types of sextet e.s.r. spectra from alkyl free radicals will be discussed in connection with their location.

EXPERIMENTAL

Sample preparation

A high density polyethylene, Sholex 6050 (product of the Showa Electric Industry Co., Ltd), was used for this

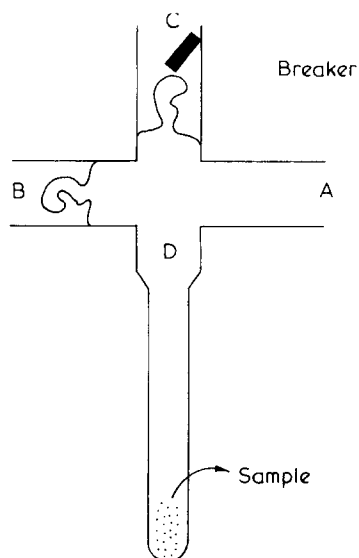


Figure 1 A glass tube system used for study of the decay reaction in butadiene atmosphere

study. The sample was purified by dissolving it in boiling toluene, precipitating it by cooling, washing in acetone, and drying in a vacuum oven. Several preparative treatments were carried out in the following ways: A-65 and A-85 samples were recrystallized from dilute xylene solution (~ 0.1 wt %) for more than a week at 65°C and 85°C , respectively. After the crystallization, xylene was removed by filtration. The density of the sample was determined at 0.9810 by floating the powdered specimens in a glass tube in which toluene and monochlorobenzene were mixed with a density gradient. The lamellar thickness of the sample was estimated to be 147 Å by small-angle X-ray scattering. Some of the A-85 samples were also subjected to fuming nitric acid treatment at 60°C for 10 h and others were treated for 196 h. The former were called N-10 and the latter N-196. Fuming nitric acid treatment was carried out by mixing ~ 1 g of specimen per 1000 ml of acid in a sealed glass tube. After the fuming nitric acid treatment, the materials were washed in distilled water and then in acetone with a Soxhlet-extractor in order to remove fuming nitric acid and homopolymer. Sample M was recrystallized from very dilute xylene solution (~ 0.025 wt %) for more than 48 h at 71°C in a vessel with a glass filter. In order to align the *c*-axes of single crystals, to the surface of the mat of crystallites, xylene was removed by slow filtration using a water jet-pump. All samples were dried in a vacuum oven and then inserted into the tube for e.s.r. observation. Thus, A and N were powdered materials and M was a plate-shaped material with the surface perpendicular to the *c*-axis of the crystallites.

Irradiation techniques

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

E.s.r. observation

E.s.r. spectra were recorded with a JEOL ME-2 spectrometer (X-band) with field modulation of 100 kHz. On-line spectrum computer JEOL EC-6 was connected to the spectrometer, and the 8 data were punched out on the paper tape by an A-D convertor. The double integration of the

first derivative curves was carried out by the electronic computer HITAC 8400. In this way, the relative concentration of free radicals was computed. Subtractions of the spectra were conducted in the spectrum computer and the analogue curves of the subtracted patterns were also obtained through the A-D convertor. The decay reaction of free radicals in an atmosphere of butadiene was also studied. Figure 1 shows the assembly used for the study of the decay reaction in butadiene atmosphere. Firstly, the sample sealed in the tube was irradiated with γ -rays after degassing through A. Then, the gas produced by γ -irradiation was evacuated through B and sealed again. Finally, the glass tube containing the purified butadiene was connected at C using a vacuum line equipment and butadiene molecules were introduced into D by a breakable seal.

RESULTS AND DISCUSSION

Separation of two types of the alkyl free radicals

Figure 2 shows e.s.r. spectra of free radicals produced in irradiated polyethylene A-85. The first three patterns in this Figure are the observed patterns, and they are the sextet spectra corresponding to the alkyl free radicals,

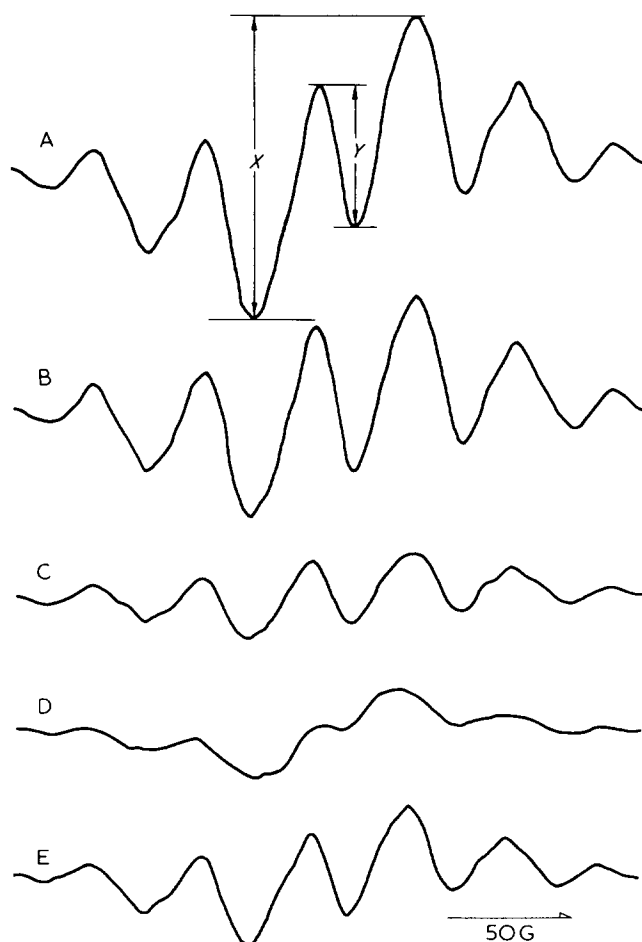


Figure 2 E.s.r. spectra of irradiated polyethylene A-85. Observation was made at liquid nitrogen temperature after irradiation at the same temperature, sharpness = X/Y . A, Spectrum after heat treatment at 245K for 10 min; B, spectrum after heat treatment at 277K for 10 min; C, spectrum after heat treatment at 317K for 10 min; D, spectrum obtained by subtracting B from A; E, spectrum obtained by subtracting C from B

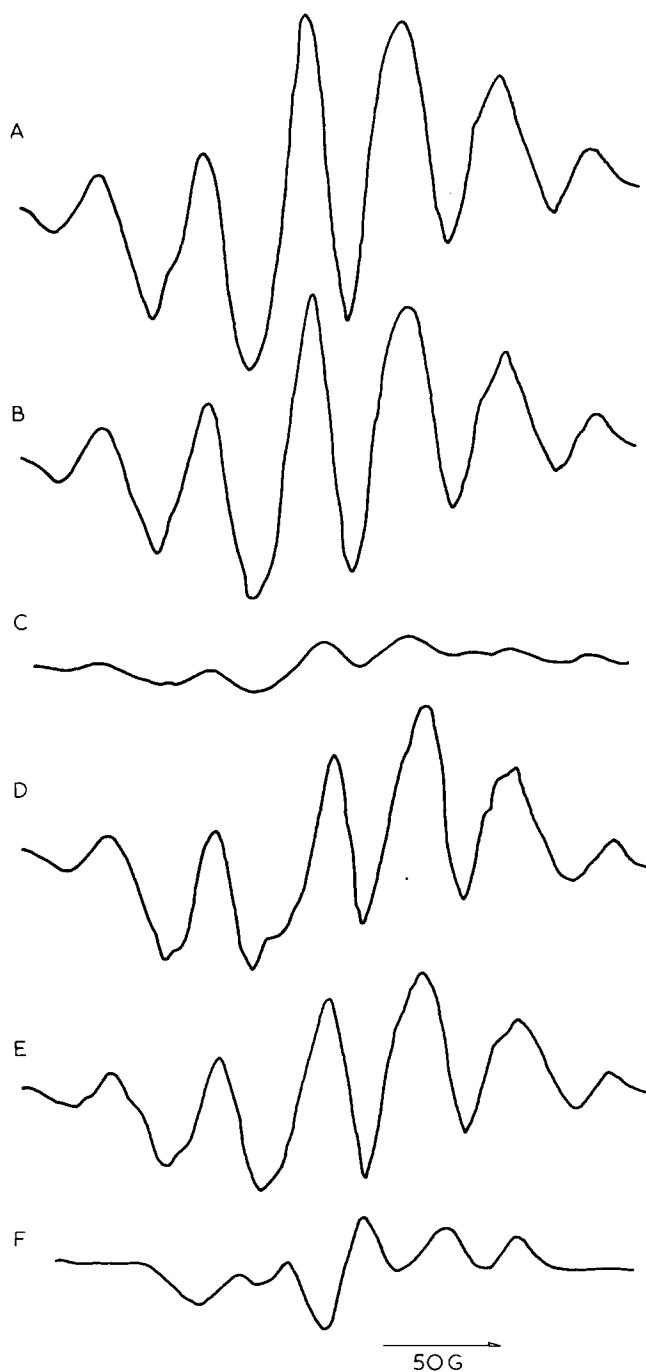


Figure 3 E.s.r. spectra of irradiated polyethylene N-10 and N-196. Observation was made at liquid nitrogen temperature after irradiation at the same temperature. A, Spectrum of N-10 after heat treatment at 244K for 10 min; B, spectrum of N-10 after heat treatment at 276K for 10 min; C, spectrum obtained by subtracting B from A; D, spectrum of N-196 after heat treatment at 245K for 10 min; E, spectrum of N-196 after heat treatment at 277K for 10 min; F, spectrum obtained by subtracting E from D

$\sim\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2\sim$. The drastic change of e.s.r. spectra was also observed during the heat treatment. The reason for this change must be that many kinds of free radical species and structural isomers are present before heat treatment, and these kinds of complications would be removed by heat treatment. The unstable free radicals disappear at lower temperatures, and more stable radicals are still observed after heat treatment. Complications due to the structural isomers means that e.s.r. spectra of the free radi-

cals appear different depending on the steric configurations of the radical sites. Therefore, if the steric configurations of the radical sites are not uniform, the spectrum observed before heat treatment appears to be a rather diffuse spectrum due to the superposition of the different kinds of the patterns. However, the free radicals trapped in the mobile site disappear after the heat treatment and the spectrum observed after heat treatment appears different from that observed before heat treatment. The spectrum of these free radicals can be obtained by the subtraction of the spectrum observed after the heat treatment from that observed before the treatment. Curves D and E in *Figure 2* show the spectra of the free radicals in sample A-85 which disappeared during heating at temperatures ranging from 245 to 277K and at temperatures ranging 277 to 317K, respectively. All of the patterns in *Figure 2* were observed at liquid nitrogen temperature. Based on the characters of the patterns, both D and E in *Figure 2* can be said to correspond to the alkyl free radicals but it is interesting to note that two types of the patterns correspond to the same alkyl radicals; i.e. D shows a very broad sextet and E shows a rather sharp sextet, and, therefore, we can say that two types of free radicals of the same chemical structure, $\sim\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2\sim$, can be observed separately. For the sake of convenience, we have called the free radicals attributed to the broad sextet B radicals and those to the sharp sextet S radicals, respectively. We can consider several reasons for the fact that two types of alkyl radicals give rise to different e.s.r. spectra. One reason is that the difference in the spectra corresponds to the difference in line width magnitude which comes from the quantum relaxation times T_1 and T_2 and also depends on the mobility of the polymer matrix and the radical concentration. The other reason is that the difference in spectra is caused by the variation of the molecular conformation^{12,13}; i.e. Heller and McConnell¹⁴ showed that the hyperfine splitting $\Delta H_{\beta i}$ due to the i -th proton of the neighbouring methylene group was determined by $\Delta H_{\beta i} = k\rho \cos^2 \theta_i$, where k and ρ are a constant and spin density, respectively, and θ_i is the projected angle between the $\text{C}_{\beta i}-\text{H}_{\beta i}$ bond and the π -electron axis in the plane perpendicular to the direction of $\text{C}_{\alpha i}-\text{C}_{\beta i}$ bond. The larger the fluctuation of θ_i , the larger is the apparent line width of the observed spectrum. In either case it can be said that e.s.r. spectra of alkyl radicals depend on their trap-sites, i.e. the inner crystalline region or the lamellar surface. Therefore, it is an important and interesting problem to clarify the trap-sites of alkyl radicals. The same experimental results were also obtained for sample A-65.

Free radicals are trapped in the solution grown crystals of polyethylene irradiated after removing the lamellar surface by the fuming nitric acid treatment. *Figure 3* shows the e.s.r. spectra obtained for the case of the sample subjected to the fuming nitric acid treatment. In this case, the same heat treatments were also made as in the case for *Figure 2*. It is well known that a selective oxidizing effect can be expected by the fuming nitric acid treatment. Only the molecules in the lamellar surface would be attacked by the fuming nitric acid at the first stage of the treatment, therefore, only the inner crystalline molecules would remain when all surface molecules are removed after the prolonged treatment. No e.s.r. spectrum corresponding to B radicals was observed for sample N-196 which was etched for a long time as shown in *Figure 3* (curve F). The residual e.s.r. spectrum corresponding to S radicals is shown in *Figure 3* (curve E). However, the e.s.r. spectrum of B radicals was observed in the sample N-10 which was treated for only a short time,

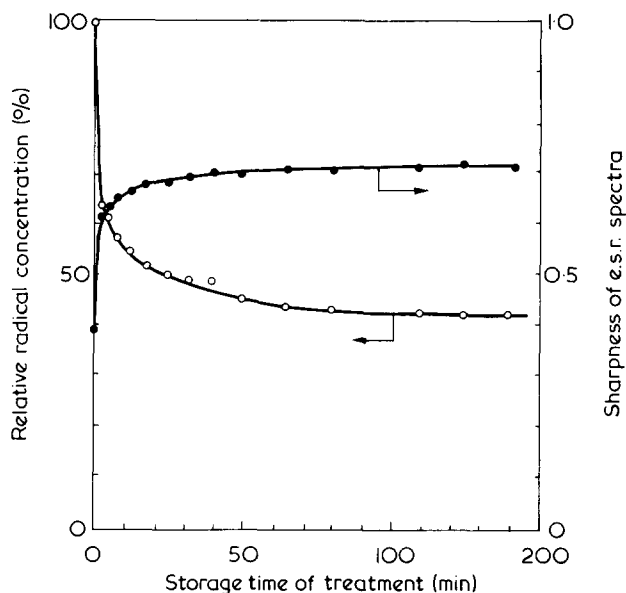


Figure 4 The decay curve (○) of alkyl radicals produced in irradiated polyethylene A-85 at 265 K and the sharpness (●) of e.s.r. spectra of the correspondence

and where the fold parts were considered to still be remaining as Keller *et al.*^{16,17} had concluded by g.p.c. study. The spectrum in Figure 3 (curve F) is unsymmetrical and its peak positions are quite different from those of B and S radicals. This difference could be due to the free radicals related with nitrogen and oxygen atoms, which were introduced when the oxidation at fold surface was carried out by fuming nitric acid. Based on these facts, it can be said that B and S radicals are trapped in the lamellar surface and the inner crystalline region, respectively.

Decay of alkyl radicals at 265K

Figure 4 shows the decay of the free radicals at 265K. Before observing the decay reaction at this temperature, the sample was stored at 195K for 3 h in order to remove the unstable free radicals. It was then cooled down to liquid nitrogen temperature and the e.s.r. spectrum was observed at this temperature. After storing the sample at 265K for 5 min, the e.s.r. spectrum was observed at liquid nitrogen temperature again. Similar storages of the sample at 265K were repeated for various lengths of time and e.s.r. spectra were observed at liquid nitrogen temperature after each storage of the sample at 265K. Percentage intensities of each of the spectral intensities observed were obtained assuming that the intensity at first observation was taken to be 100. Relative radical concentration was asymptotic to ~40% after a long period of the heat treatment. The e.s.r. spectrum after heat treatment over a long period became similar to the spectrum shown in Figure 2 (curve B). Sharpness of the spectrum defined in Figure 2 can be considered to be a measure of the magnitude of the apparent line width and the variation of this quantity with time of storage at 265K is also shown in Figure 4. The sharpness increases with the length of heat treatment and its variation indicates a saturation behaviour in contrast with variation of the radical concentration. These facts show that B radicals are more unstable than S radicals and the amount of B radicals is ~60%.

The approximate thickness of the inner crystalline region, l , and that of the lamellar surface, d , can be estimated from the equations:

$$\rho = \rho_c - (\rho_c - \rho_a) \frac{d}{l+d}, \rho_c = 1.008, \rho_a = 0.86$$

where ρ , ρ_c and ρ_a are the density of the sample, the density of inner crystalline part and the density of amorphous part, respectively. Since the lamellar thickness, L , obtained by small-angle X-ray scattering equals $l+d$, d and l can also be estimated. In the present case, d and l were approximately determined as 27 and 120 Å, respectively. Assuming these values, k_a/k_c was estimated to be 7 from the amounts of B and S radicals, where k_a and k_c are the radical concentrations in the inner crystalline region and in the lamellar surface region, respectively. On the other hand, if d and l were assumed to be 5 and 142 Å in the case of a sharp folded structure following Kusumoto *et al.*¹¹ k_a/k_c was estimated to be 43. In either case, it was reasonable to assume that the alkyl free radicals are concentrated at the lamellar surface in the case of solution grown single crystals as Kusumoto *et al.* concluded.

Decay of B and S radicals in butadiene atmosphere

It is well known that free radicals produced in irradiated polyethylene react with butadiene monomer and initiate the graft copolymerization in the amorphous phase. In the present study, only the effect of butadiene molecules on the decay reactions of B and S radicals is discussed. Since the butadiene molecules cannot be considered to diffuse into the inner part of the crystallites, they can make mobile or catalyse chemically the free radicals located only in the fold surface. In either case, behaviour of B radicals in butadiene atmosphere will be different from their behaviour in vacuum. The experimental facts concerning this behaviour can also present information concerning the location of alkyl free radicals. Figure 5 shows the influence of butadiene molecules on the decay reaction

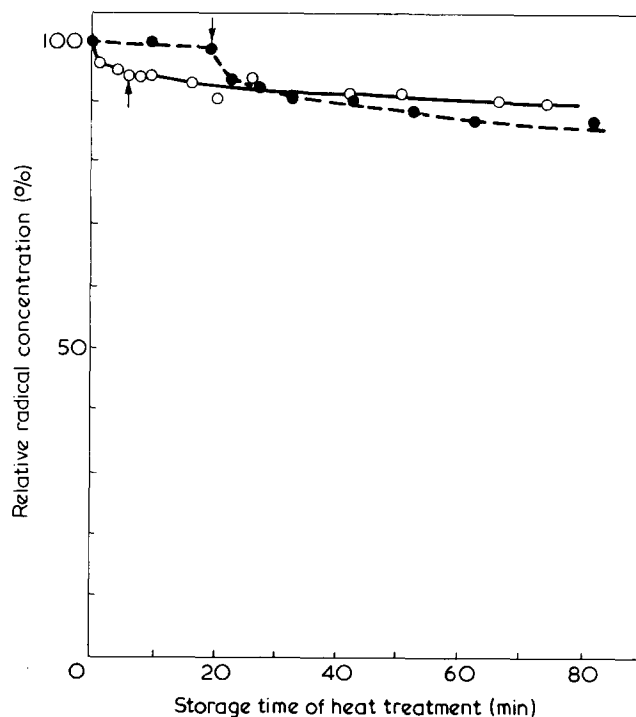


Figure 5 The decay curves of B (●, 315K) and S (○, 223K) radicals in butadiene atmosphere. Arrows show the time when butadiene gas is introduced

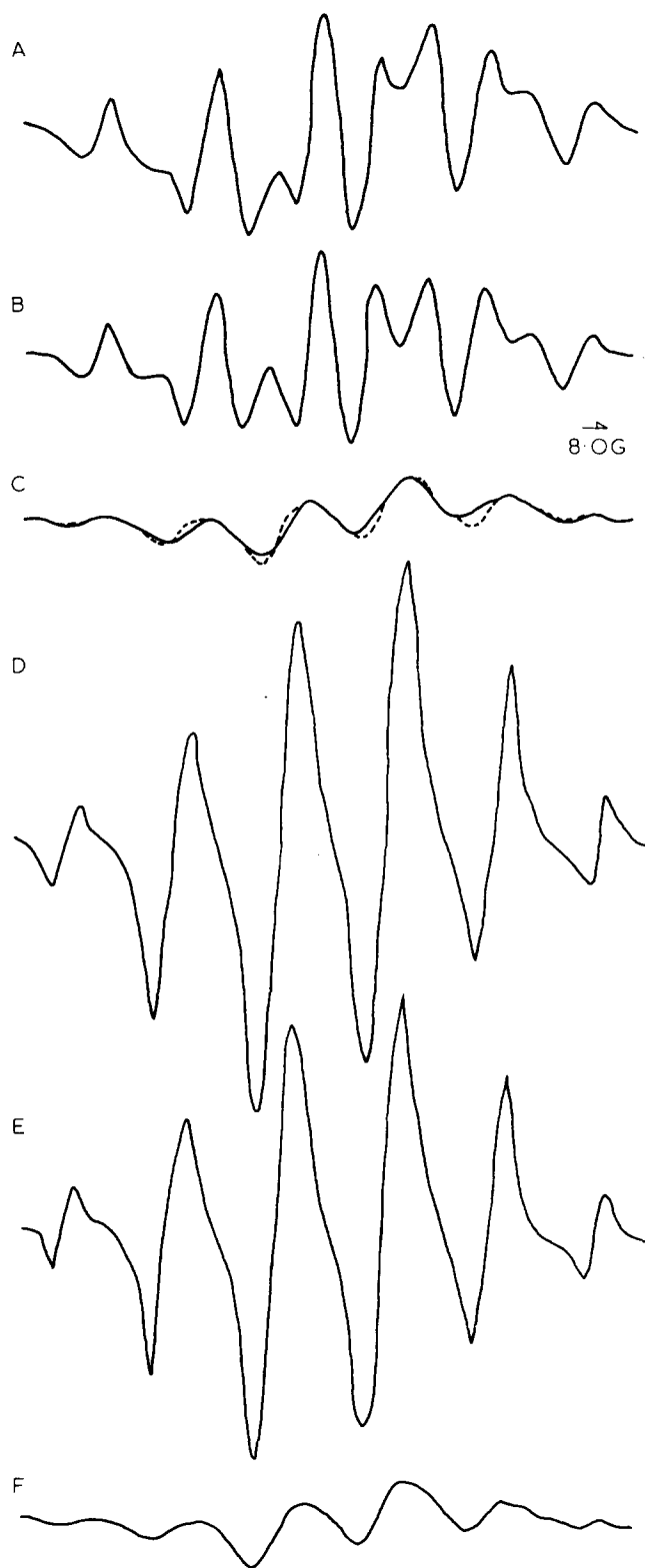


Figure 6 E.s.r. spectra of free radicals produced in irradiated polyethylene M. Observation was made at 122K after irradiation at liquid nitrogen temperature. A, B, C, Spectra at $\psi = 90^\circ$; D, E, F, spectra at $\psi = 0^\circ$; ψ represents the angle between the applied magnetic field and the direction of the *c*-axis of the crystals. — — —, corresponds to F. A, D, Spectra after heat treatment at 243K for 10 min; B, E, spectra after heat treatment at 279K for 10 min; C, spectra obtained by subtracting B from A; F, spectrum obtained by subtracting E from D

of alkyl radicals. The decay curve depicted in *Figure 5* was obtained by the same procedure as in *Figure 4*. The arrows indicate the time at which butadiene molecules were intro-

duced. It can safely be said that the decay of the free radicals was accelerated by the introduction of the butadiene molecules. This means that B radicals disappeared during this procedure but little influence of butadiene molecules on the decay of radicals was observed as depicted in *Figure 5* (curve B).

Anisotropy of e.s.r. spectra of B and S radicals

It is well known that^{18,19} anisotropic e.s.r. spectra are observed for the mat of solution grown crystals, where the *c*-axes of the chain are aligned perpendicular to the plane of the mat. This anisotropy originates from dipole-dipole interaction between electron and α -proton. In our experiment, the direction of the sample tube was set parallel to the plane of the mat. Sextet and ten line were observed in the case of $\psi = 0^\circ$ and $\psi = 90^\circ$, respectively, as shown in *Figures 6A* and *6D*, where ψ is the angle between the external magnetic field and the direction of the *c*-axis of the molecule. *Figure 6C* and *6F* show e.s.r. spectra of B radicals obtained by the same procedure as that in the case of *Figure 2*. It is noteworthy that no anisotropy in the e.s.r. spectra of B radicals was observed, but the spectra of S radicals show remarkable anisotropy. The analysis of this anisotropy was carried out in detail by Shimada *et al.*¹⁹. It can be considered that the directions of *c*-axes of the main chains are at random in the fold surface and the effect of the dipole-dipole interaction between electron and α -proton is cancelled out in the case of B radicals which are trapped in the fold surface. However, the main chains of the molecules in the inner part of the crystallite are perpendicular to the plane of the mat and the magnitude of hyperfine splitting due to α -proton varies with ψ approximately from 18 to 33 Gauss.

Thus it can be concluded that the locations of B and S radicals are in the fold surface and the inner crystalline region, respectively. Consequently, it is possible to label the spins on the inner crystalline region and the lamellar surface separately by the γ -irradiation methods and to observe molecular motions in each of these two regions independently. An example of this kind of investigation will appear in a forthcoming paper.

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