E.s.r. studies of peroxy radicals in polyethylene: 1. Temperature dependence of spectra and molecular motion of radical sites

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The temperature dependence of the e.s.r. spectrum of the peroxy radicals in polyethylene was successfully observed. Two kinds of radical site were found in the amorphous region of polyethylene, one bearing the radicals corresponding to the usual e.s.r. spectrum of the amorphous pattern as for the usual polymer peroxy radicals, and the other presenting the singlet-like pattern which has never actually been observed. Computer simulation of these spectra was carried out in order to determine the anisotropic g-values as well as the ratios of the amounts of the radicals located at respective radical sites. The temperature dependence of these values made it possible to discuss the difference of the radical sites and the molecular motion of these radical sites. The motion around the chain axis was found to be much more rapid than that around the C—O bond axis in the peroxy raidcals.

INTRODUCTION

The e.s.r. spectra of the peroxy radicals of polyethylene have been studied by only a few authors[1,2], although many investigations[3–5] have been reported for those of the other polymers. Furthermore, the temperature dependence of the e.s.r. spectra of the peroxy radicals have also not been obtained for polyethylene until now. On the other hand, several authors[6,7] have pointed out that the peroxy radicals play an important role in the auto-oxidation of polyethylene. The peroxy radicals of polyethylene have therefore been studied indirectly with other experimental techniques[7].

Though the e.s.r. method has the advantage of direct observation of the free radicals, there have been only a few e.s.r. studies of the peroxy radicals in polyethylene. The peroxy radicals of polyethylene are less stable than those of other polymers[8] and so they have not been measured at room temperature, but those of polytetrafluoroethylene or polypropylene are very stable at the same temperature. The oxygen molecules cannot permeate into the crystalline part of polyethylene as they do in the other polymers. This makes difficult pure trapping of the peroxy radicals in polyethylene. For example, γ-irradiation of polyethylene produces carbon radicals in both the amorphous and crystalline parts; the oxygen molecules react with the carbon radicals mainly in an amorphous part so that the peroxy radicals admixed with the carbon radicals in the crystalline part are only trapped in the last stage. On the other hand, no paper has reported successful trapping of peroxy radicals in polyethylene up to a concentration high enough for investigation of the temperature dependence of their e.s.r. spectra. This paper reports observations of the e.s.r. spectra of peroxy radicals in polyethylene, and discusses the phenomena relating to their temperature dependence.

In this study, the experiments were conducted according to the following properties of the peroxy radicals:

(1) The e.s.r. spectrum of the peroxy radicals behaves differently from that of the carbon radicals at power saturation[1]. At a power of 10 mW, the spectrum of the peroxy radicals is much more enhanced than that of the allylic radicals.

(2) The peroxy radicals are stable at a temperature lower than 241K, at which oxygen molecules are found to permeate into the amorphous part of polyethylene[8].

(3) The peroxy radicals are less stable than the carbon radicals, and allylic radicals are found to be much more stable. The peroxy radicals therefore disappear after storage of the materials at room temperature, and only the spectrum from the allylic radicals can be observed.

In this paper, the physical properties of the sites at which the peroxy radicals are trapped in the polyethylene are mainly discussed according to the studies of the temperature dependence of the spectral shape. This includes studies of the different molecular motion at different kinds of radical site.

EXPERIMENTAL

The samples used in the experiments were powders of linear polyethylene ranging from 20 to 35 mesh, made from resins of Sholex 6050 after refluxing three times in toluene and washing three times in acetone. About 55 mg of the powder was stacked into a Pyrex glass ampoule with two breakable seals. After evacuation for 6 h at 10^{-6} mmHg, the samples were irradiated with ^{60}Co γ-rays at room temperature and stored for a week. The total dosage was about 20 Mrad at a dose rate of 0.25 Mrad/h. After storage, almost all the alkyl radicals vanished and only the allylic radicals were trapped in the sample.

The hydrogen gas produced during the γ-irradiation was evacuated through a breakable seal; then the sample tube was heated to eliminate the colour centres in the glass. The e.s.r. measurements were carried out with a JEOL ME-3 X-band spectrometer. The temperature of the e.s.r. observation was well controlled by nitrogen gas flow. The micro-

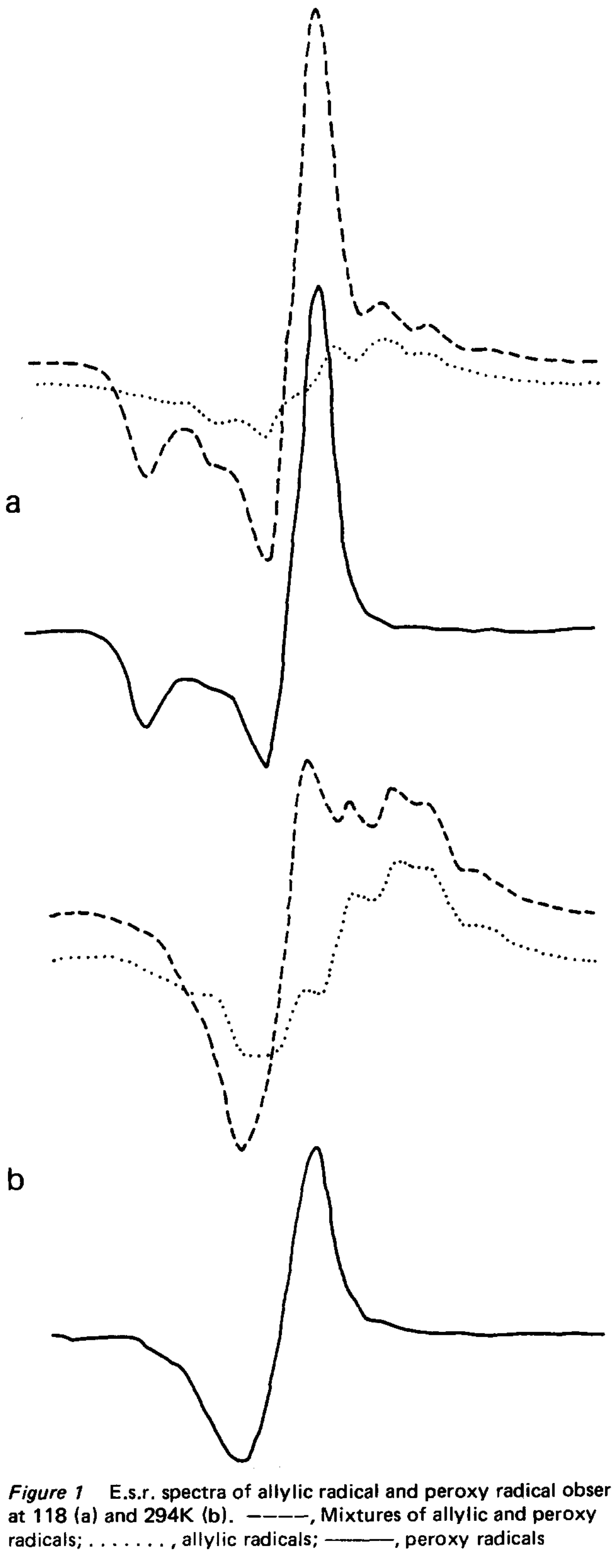

Figure 1 E.s.r. spectra of allylic radical and peroxy radical observed at 118 (a) and 294K (b). ———, Mixtures of allylic and peroxy radicals; . . . . , allylic radicals; ———, peroxy radicals

wave power was kept at 10 mW throughout the measurements. The signal of diphenyl-picryl-hydrazyl (DPPH) was used as a standard for the *g*-value, and taken as 2.0036. The magnetic field sweep was calibrated with known splitting constants of Mn^{2+}. The signals were recorded in a JEOL JEC-6 spectrum computer. The oxygen was introduced into the ampoule through a breakable seal. The volume of the introduced oxygen was 20 cm^3 and the pressure was 0.5 mmHg. The peroxy radicals were produced by reaction of the oxygen with the allylic radicals for 75 min at 241K. After reaction, all the oxygen molecules introduced were completely expended. The number of oxygen molecules introduced was approximately equal to that of the radicals in the amorphous phase and about half the total radicals. The spectra of the mixture of peroxy and allylic radicals were recorded at temperatures from 118 to 294K. After storing for 2 h at room temperature, the peroxy radicals disappeared. At this stage, only the spectra from the allylic radicals were observed over the same temperature range. The spectral patterns of the peroxy radicals at the various temperatures were obtained by subtractions of the spectra of the allylic radicals from the superposed spectra for the corresponding temperatures. The spectrum of the peroxy radicals at 77K was obtained by the same method using a liquid nitrogen Dewar vessel.

RESULTS

Figure 1 shows the spectra of the mixture of peroxy radicals (LOO·) and allylic radicals (L·), and those of L· only, observed at 118 and 294K. The spectra of LOO· (solid line) were obtained by subtraction of those of L· (dotted line) from those of the mixture (broken line). The spectra of the LOO· observed at the various temperatures are illustrated in *Figure 2*. These spectra of the peroxy radicals produced by the reaction of oxygen with allylic radicals in the amorphous region of polyethylene were not similar to those of peroxy radicals in the other polymers or the low molecular weight compounds of hydrocarbons. The spectra comprised two components. One, which we will call the A-radical, was similar

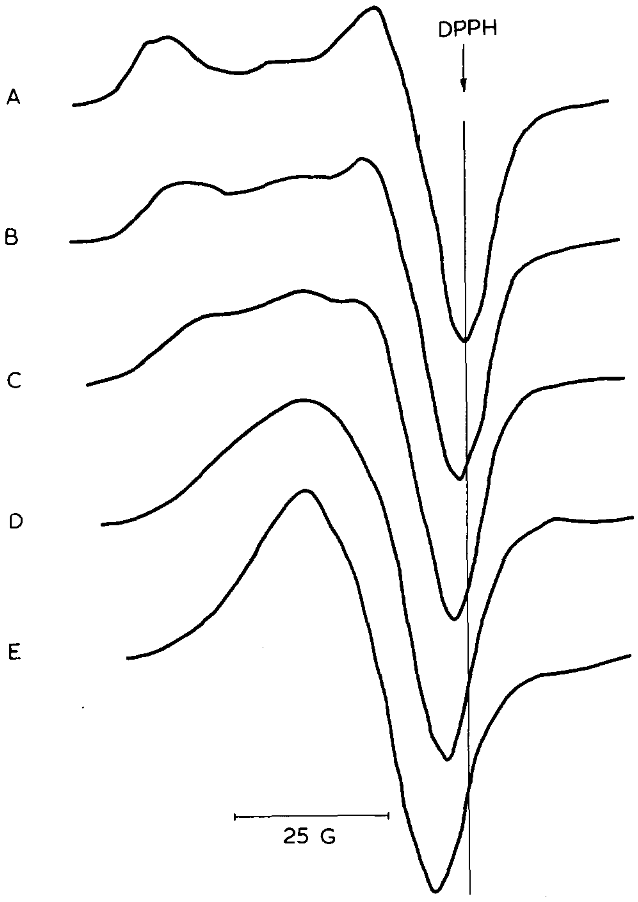

Figure 2 E.s.r. spectra of peroxy radicals in polyethylene obtained at various temperatures. The arrow indicates the position of the spectrum of DPPH, *g* = 2.0036. Temperatures of observation: A, 118K; B, 168K; C, 207K; D, 257K; E, 294K

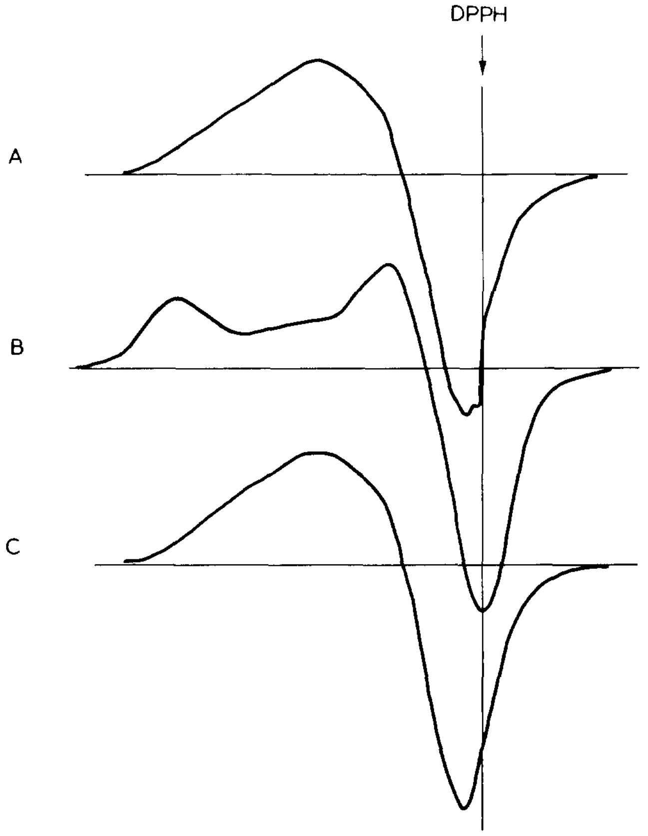

Figure 3 Reversible change of the e.s.r. spectra of peroxy radicals at the following temperatures: A, 241K; B, 18K; C, 245K

to the amorphous patterns of the other polymer peroxy radicals; the other, the B-radical, was a broad singlet-like pattern. Both showed anisotropic g-values. *Figure 2* shows the change of the e.s.r. spectra with temperature, and it can be seen that all the spectra are superpositions of the A- and B-radical spectra at every temperature, but the ratio of the intensity of B-radicals to that of A-radicals increases with increasing temperature. A-radicals can be assigned to the peroxy radicals by virtue of our experimental conditions, and the similarity of the spectra to those of the other well-known peroxy radicals.

Assignment of the B-radicals does not seem to be so simple, but the following facts were observed. The spectral change with temperature is just reversible, as indicated in *Figure 3*. This reversibility cannot be explained unless the B-radicals are peroxy radicals, because the conversion equilibrium between the peroxy radicals and the other radicals cannot be maintained at all stages with various temperatures under our experimental conditions. The B-radicals can therefore be assigned to peroxy radicals with a different site from that of the A-radicals. Different kinds of radical site reasonably show different modes of molecular motion, and examples of this have already been found for other polymers[5,9]. However, the situation in the present study is slightly different, and is discussed in detail later.

SIMULATION

The computer simulation was carried out in order to obtain several spectral parameters and to confirm the coexistence of two kinds of radical, A-radicals and B-radicals. The quantities determined were anisotropic g-values, g_1, g_2, g_3 ($g_1 < g_2 < g_3$ for the A-radical) and g_1', g_2', g_3' ($g_1' < g_2' < g_3'$ for the B-radical), the ratio of the amount of B-radical to that of A-radical ([B]/[A]), and line widths. Line widths were assumed to vary linearly with the inversion of g-value. Since it was a reasonable assumption that the observed radicals have completely random orientation, g-values could be computed from the following equation choosing the 30 000 sets of (θ,ϕ) in a solid angle of $\pi/2$:

$$g = (g_1{}^2\sin^2\theta\sin^2\phi + g_2{}^2\sin^2\theta\cos^2\phi + g_3{}^2\cos^2\theta)^{1/2}$$

In this equation, g_1, g_2 and g_3 were taken as parameters of the simulation. These computed g-values and the g-value of DPPH were used to construct the spectrum at 0.1 Gauss interval – (1Gauss = 10^{-4} T). The spectra were multiplied with the line shape functions. The simulated spectra were determined for the A-radicals and B-radicals, and the two spectra were added in the assumed ratio. Finally, this spectrum was differentiated and normalized. Examples of the simulated spectra of A-radicals, B-radicals, and the mixture of A- and B-radicals are illustrated in *Figure 4*, and the best fitted spectra to the experimental spectra of 118 and 195K are shown in *Figure 5* as examples. As shown, the simulated

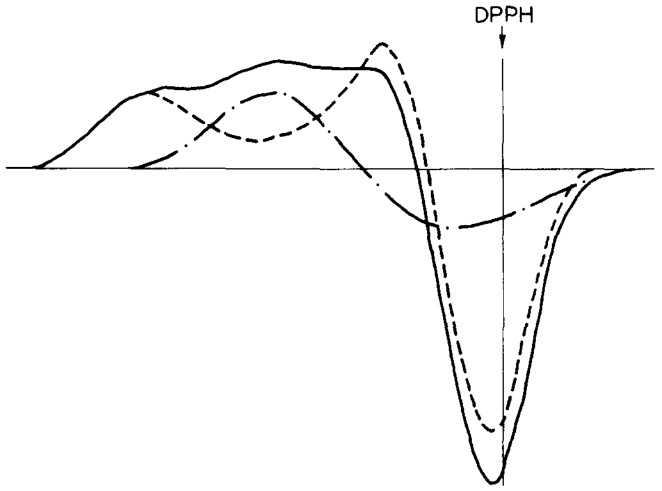

Figure 4 An example of the simulated spectrum of peroxy radicals with superposition of two kinds of spectra

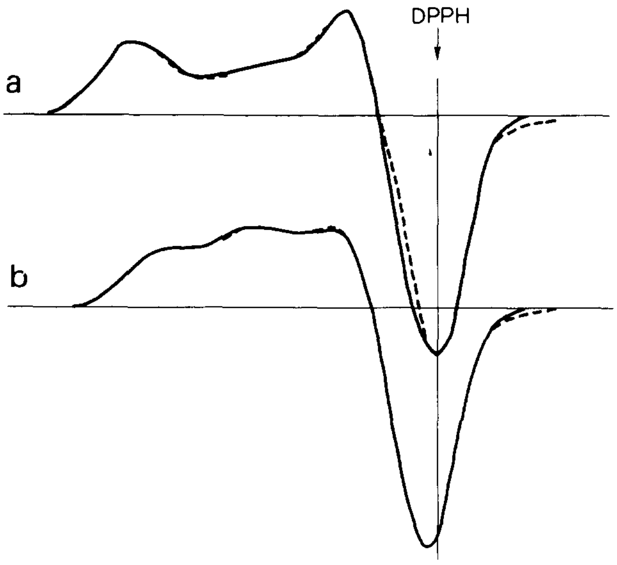

Figure 5 Comparisons of the simulated spectra and observed spectra of peroxy radicals at 118K (a) and 195K (b) (———, simulated patterns; — — —, observed patterns)

Table 1 Spectroscopic parameters at various temperatures (quantities without parentheses for A-radical and quantities in parentheses for B-radicals)

Temperature (K)	$g_1(g_1{}')$	$g_1(g_2{}')$	$g_3(g_3{}')$	Mean value	ΔH_1	ΔH_3	[B]/[A]
77	2.0024 (———)	2.0092 (———)	2.0366 (———)	2.0161 (———)	7.0 (——)	10.5 (——)	
118	2.0030 (2.0025)	2.0096 (2.0157)	2.0358 (2.0250)	2.0161 (2.0144)	8.0 (15.0)	10.5 (11.0)	0.12
135	2.0034 (2.0026)	2.0096 (2.0152)	2.0353 (2.0247)	2.0161 (2.0142)	8.0 (15.0)	10.5 (11.0)	0.17
152	2.0035 (2.0027)	2.0097 (2.0150)	2.0349 (2.0243)	2.0160 (2.0140)	8.0 (15.0)	11.0 (12.0)	0.22
168	2.0038 (2.0030)	2.0098 (2.0147)	2.0343 (2.0243)	2.0160 (2.0140)	8.0 (15.0)	11.5 (12.5)	0.30
183	2.0040 (2.0040)	2.0097 (2.0146)	2.0337 (2.0236)	2.0158 (2.0141)	8.0 (16.0)	11.5 (13.0)	0.36
195	2.0042 (2.0042)	2.0099 (2.0149)	2.0331 (2.0236)	2.0157 (2.0142)	8.0 (15.0)	11.5 (12.0)	0.40
207	2.0046 (2.0046)	2.0102 (2.0146)	2.0329 (2.0232)	2.0159 (2.0141)	8.0 (16.0)	12.0 (13.0)	0.50
220	2.0048 (2.0048)	2.0101 (2.0146)	2.0322 (2.0227)	2.0157 (2.0140)	8.0 (16.5)	12.0 (14.0)	0.60
233	2.0051 (2.0051)	2.0104 (2.0146)	2.0323 (2.0227)	2.0159 (2.0141)	8.0 (16.5)	12.0 (14.0)	0.73
245	2.0051 (2.0051)	2.0106 (2.0146)	2.0312 (2.0222)	2.0156 (2.0140)	8.0 (16.0)	13.0 (14.0)	0.72
257	2.0055 (2.0055)	2.0107 (2.0148)	2.0305 (2.0215)	2.0156 (2.0139)	8.0 (15.5)	13.0 (14.0)	0.82
269	2.0060 (2.0060)	2.0114 (2.0154)	2.0302 (2.0214)	2.0159 (2.0143)	8.0 (15.5)	13.0 (14.0)	0.89
278	2.0063 (2.0063)	2.0114 (2.0152)	2.0302 (2.0216)	2.0160 (2.0144)	8.0 (15.5)	13.0 (14.0)	1.17
287	2.0064 (2.0064)	2.0114 (2.0154)	2.0302 (2.0209)	2.0160 (2.0142)	8.0 (15.5)	13.0 (14.0)	1.50
294	2.0066 (2.0066)	2.0119 (2.0152)	2.0288 (2.0212)	2.0158 (2.0143)	8.0 (15.5)	13.0 (13.5)	1.40

spectra were in good agreement with the observed spectra. From these simulations, g_1, g_2, g_3 (for A-radical), $g_1{}', g_2{}', g_3{}'$ (for B-radical), ΔH_1 (at H_1), ΔH_3 (at H_3) (for A-radical), $\Delta H_1{}'$, $\Delta H_3{}'$ (for B-radical), and [B]/[A] were determined at various temperatures; these values are listed in *Table 1* and the g-values are illustrated in *Figure 6*. For the A-radicals, the maximum errors of g-value, line width and ratio are 0.0003, 0.5 Gauss and 10% respectively, but those of the B-radicals are much larger. The constancy of the mean of the g-values shows that the simulation is satisfactory.

DISCUSSION

In the light of this simulation, we can say that the experimental e.s.r. spectra of the peroxy radicals are a mixture of two kinds of spectra corresponding to two different radical species, at all observed temperatures. Both are peroxy radicals, but the molecular motions of the radical sites are different. Hence these molecular motions will be discussed in fuller detail. As seen in *Table 1* and *Figure 6*, the smallest g-values for the A- and B-radicals, g_1 and $g_1{}'$, are equal or nearly equal at all temperatures, but the larger g-values for A-radicals (g_2 and g_3) are different from the corresponding values for B-radicals ($g_2{}'$ and $g_3{}'$); g_2 is smaller than $g_2{}'$, but g_3 is larger than $g_3{}'$. These facts indicate that the motional averaging between $g_2{}'$ and $g_3{}'$ in B-radicals is different from that in A-radicals at the same temperature. In other words, the molecular motion of the B-radical sites around the g_1 axis is more rapid than that of the A-radicals at every temperature. Since both A-radicals and B-radicals are peroxy radicals produced from allylic radicals in polyethylene, and the sites of both radicals are located in the amorphous region of linear polyethylene, these differences in molecular motion might be a reflection of the difference of the surrounding matrix, perhaps the difference of the near region around the radicals. To confirm the above discussions, the logarithm

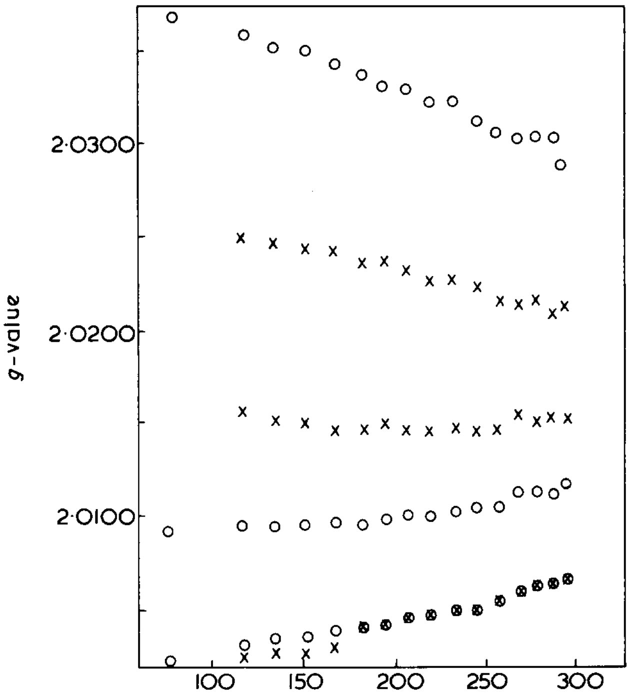

Figure 6 Anistropic g-values at various temperatures; O, A-radical; X, B-radical

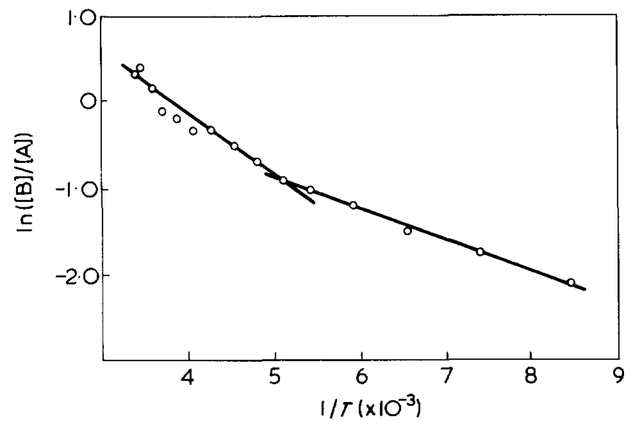

Figure 7 Relation between logarithm of the ratio of the radical amounts and inverse temperatures

of [B]/[A] *versus* the inverse of temperature has been plotted in *Figure 7*.

Assuming that the amounts of A-radical and B-radical are in thermal equilibrium, the enthalpy difference between the A-radical and the B-radical was determined from *Figure 7*, and it was found to be 722 cal/mol below 195K and 1404 cal/mol above 195K. The value for the range below 195K, 722 cal/mol, was very close to the enthalpy difference between the *trans*- and *gauche*-conformation in the amorphous part of polyethylene[11]. According to the preceding discussions, the B-radical seemed to be produced from the A-radical by changing from *trans*-conformation to *gauche*-conformation of the methylene group existing near the radicals. The larger value of the enthalpy difference obtained for the temperature range above the bending point in *Figure 7*, 1404 cal/mol, might be a reflection of the large scale motion related with the crystallization process which was observed by Hendra *et al.*[12]. It could also be said that the slight abnormality of the plots around 245K in the same Figure might be a reflection of the glass–rubber transition.

For the A-radicals, the molecular motion could be discussed, assuming that the g-values at 77K are the rigid-state g-values. Kneubühl[13] derived the following equation for averaging the anisotropic g-values due to three-dimensional Brownian motion:

$$\langle g^2\rangle_{av} = [s + (g_1^2 - s)\Gamma]\sin^2\beta\sin^2\gamma$$

$$+ [s + (g_2^2 - s)\Gamma]\sin^2\beta\cos^2\gamma + [s + (g_3^2 - s)\Gamma]\cos^2\beta$$

$$s = (g_1^2 + g_2^2 + g_3^2)/3$$

$$\Gamma = (2/\pi)\tan^{-1}(\tau/T_2)$$

However, for two-dimensional random motion around two axes or for motion with more than one relaxation time, the equation for averaging anisotropic g-values has not been derived until now. Our experimental data showed two relaxation times, as illustrated in *Figure 8*. This shows the relation between τ and $1/T$, in which τ was calculated from Kneubühl's equation and experimentally determined values of g_1 and g_3 for A-radicals. T_2 was calculated from ΔH according to the approximate equation $T_2 = [1/\Delta H\,(\text{Gauss})] \times 1.428 \times 10^{-7}$ sec for Gaussian shape. The two values estimated from g_1 and g_3 were clearly different and the difference was larger than the experimental error, especially at higher temperatures; i.e. the relaxation time estimated from g_3 was shorter than that from g_1. Although the two values of relaxation time calculated from Kneubühl's equation were not completely correct, it could be said at least that the motion of A-radicals might have two relaxation times, and the g_3-axis moved more rapidly than the g_1-axis. A schematic structure of the peroxy radical is illustrated in *Figure 9*. Because the peroxy radicals of the low molecular weight molecules and the other polymers had the g_3-principal axis along the O–O bond direction, it was reasonable to assume that the g_3-axis of the peroxy radical of polyethylene has a direction parallel to the O–O bond as illustrated. In the same way, one of the g_1 or g_2 axis is in the direction normal to the C–O–O plane,

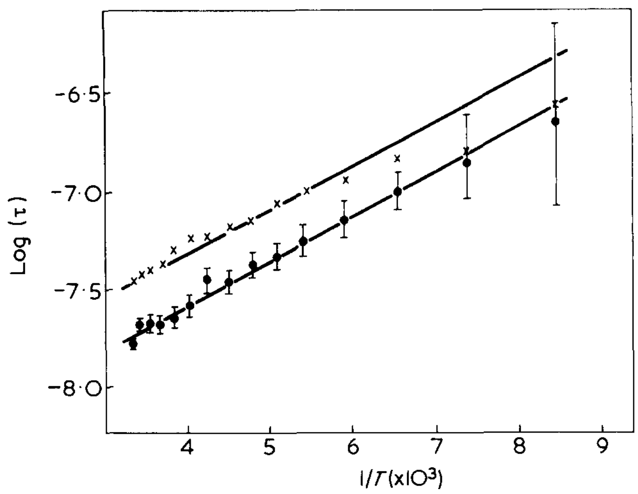

Figure 8 Relation between logarithm of the relaxation times and inverse temperatures: X, relaxation times calculated from g_1; ●, from g_3

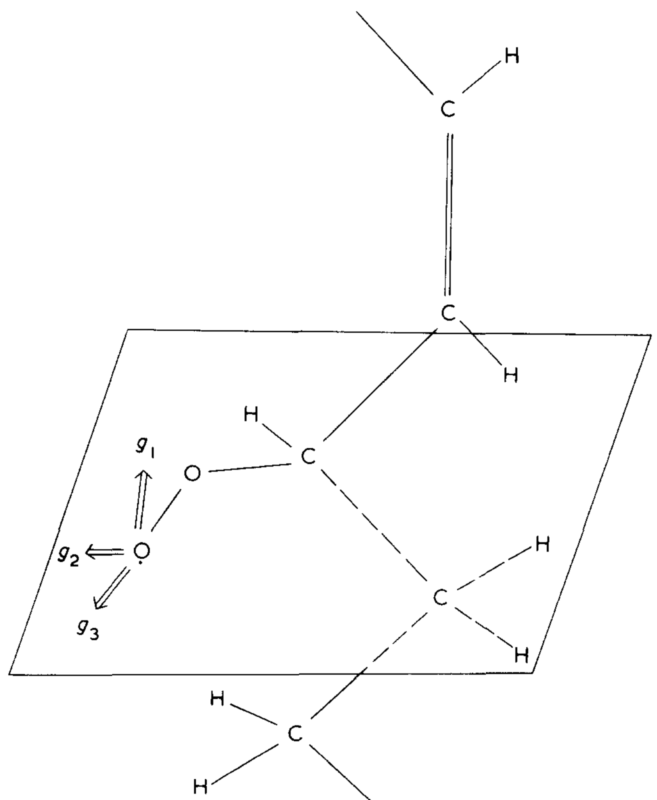

Figure 9 Schematic illustration of the structure of peroxy radicals from allylic radicals

and the other axis is perpendicular to both the other two axes. It could be concluded that the C–O–O plane was perpendicular to the chain direction and the g_1-axis was parallel to the chain illustrated in *Figure 9* for the following reasons. Two kinds of main motion of the peroxy radicals could be considered in the polymeric chain molecule, rotation around the C–O bond axis and rotation or vibration around the chain axis. When rotation around the C–O bond axis occurs, all g-values, g_1, g_2 and g_3, are averaged with the same relaxation time. For rotation around the chain axis, averaging between g_2 and g_3 can only occur when the direction of the g_1-axis is along the chain axis. Then the assumption that the C–O–O plane is perpendicular to the chain axis and the g_1-axis is parallel to the same axis can provide a satisfactory explanation of the two facts mentioned in the previous part of this paper; i.e. the average between g_2' and g_3' of the B-radical was more perfect than that of the A-radical and the relaxation time estimated from g_3-values was different from that estimated from g_1-values. The facts that the B-radicals were in more rapid motion around the g_1-axis than the normal peroxy radicals in polyethylene, and the relaxation time calculated from g_3-values is shorter than that from g_1-values in normal peroxy radicals, indicate that the rotation or vibration around the chain axis was faster than the rotation around the C–O bond axis, and a similar phenomenon was found for the other polymers' peroxy radicals^5.

In the previous calculations, the mean values of g-value for the B-radicals appeared to be different from those of the A-radicals and ΔH_1 of the B-radicals was abnormally larger. Those results were caused by our procedure in that we treated the B-radicals as one component, although they were mixtures of different averaging g-values component.

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REFERENCES

1 Ohnishi, S., Sugimoto, S. and Nitta, I. *J. Polym. Sci. (A)* 1963, **1**, 605
2 Davis, L. A., Pampillo, C. A. and Chiang, T. C. *J. Polym. Sci. (A-2)* 1973, **11**, 841
3 Matsugashita, T. and Shinohara, K. *J. Chem. Phys.* 1961, **35**, 1652
4 Chien, J. C. W. and Boss, C. R. *J. Am. Chem. Soc.* 1967, **89**, 571
5 Iwasaki, M. and Sakai, Y. *J. Polym. Sci.* 1968, **6**, 265
6 Baum, B. *J. Appl. Polym. Sci.* 1959, **2**, 281
7 Luongo, J. P. *J. Polym. Sci.* 1960, **42**, 139
8 Hori, Y., Shimada, S. and Kashiwabara, H. *Polymer* 1977, **18**, 151
9 Eda, B., Nunome, K. and Iwasaki, M. *J. Polym. Sci. (Polym. Lett. Edn)* 1969, **7**, 91
10 Goldman, S. A., Bruno, G. V., Polnaszek, C. F. and Freed, J. H. *J. Chem. Phys.* 1972, **56**, 716
11 Nielsen, J. R. and Holland, R. F. *J. Mol. Spectrosc.* 1960, **4**, 488
12 Hendra, P. J., Jobic, H. P. and Holland-Morts, K. *J. Polym. Sci. (Polym. Lett. Edn)* 1975, **13**, 365
13 Kneubühl, F. K. *J. Chem. Phys.* 1960, **33**, 1074