E.s.r. studies of peroxy radicals in polyethylene: 2. Peroxy radicals in urea – polyethylene complexes

Yasurō Hori, Shigetaka Shimada and Hisatsugu Kashiwabara
Nagoya Institute of Technology, Showa-ku, Nagoya 466, Japan
(Received 25 April 1977)

Temperature dependent e.s.r. spectra of peroxy radicals in urea–polyethylene complex materials (UPEC) were discussed. Peroxy radicals in UPEC were much more stable than in normal polyethylene. Change of anisotropic g-values of the radicals with temperature were investigated and it was found that the g_1-axis, which was assigned to be parallel to the chain axis, seemed to be almost unchanged throughout the temperature range in the present study, but the g_2- and g_3-axes changed drastically. Using these results, it was concluded that the main motion of the radical sites was rotation around the chain axis and this motion was found to be much faster than in normal polyethylene, which we have already studied and which we reported recently. This is a reflection of the properties of the materials studied, i.e. interaction between molecular chains in UPEC must be much weaker than in normal polyethylene because of the presence of the wall of urea molecules in the former.

INTRODUCTION

In the previous paper[1], temperature-dependent e.s.r. spectra of peroxy radicals in normal polyethylene were discussed. In this article the similar but specific case of the urea–polyethylene complex will be described. The e.s.r. spectra of the peroxy raidcals of polyethylene have been studied by only a few authors[2,3], although many investigations[4–6] have been reported for those of other polymers. Temperature-dependent e.s.r. spectra of the peroxy raidcals for polyethylene have not been obtained. On the other hand, several authors[7,8] have pointed out that the peroxy radicals play an important role in the auto-oxidation of polyethylene, and therefore, peroxy radicals were studied indirectly with other experimental techniques[8]. The fact that only very few studies of peroxy radicals in polyethylene have been made using the e.s.r. method probably reflects the following problems: the peroxy radicals of polyethylene are very unstable and the oxygen molecules cannot permeate easily into the crystalline part of polyethylene. Therefore, it is very difficult to obtain sufficient concentration of peroxy radicals in order to observe the temperature dependence of the e.s.r. spectra. Difficulties in e.s.r. studies of the peroxy radicals in polyethylene were considered to be due to the fact that an insufficient concentration of the peroxy radicals was trapped and the superposition of the e.s.r. spectra both of peroxy radicals and carbon radicals gave a very complicated observed spectrum.

Recently we successfully observed the temperature-dependent e.s.r. spectra of peroxy radicals trapped in the amorphous part of polyethylene[1]. These were made by correct usage of power saturation and the results were reported in part 1 of the series. It was concluded that more than two kinds of trap sites existed in the amorphous part, in which different modes of motion were observed, and rotation around the chain axis was found to be the main motion of the peroxy radicals. In the present paper, the peroxy radicals trapped in urea–polyethylene complexes (UPEC) will be discussed. The method of preparing urea–polyethylene crystalline complexes (inclusion compounds or adducts) was reported[9] recently and the structure of the model compound has also been studied extensively[10]. The structure of UPEC is illustrated schematically in *Figure 1*. In UPEC, the polyethylene chain is extended and the distance between the polyethylene chain and the urea wall is larger than that of the nearest neighbour polyethylene chains in the normal polyethylene crystal. We considered this UPEC as a model compound of the crystalline part of polyethylene and also a model of a separated polyethylene molecule. We can expect to have two favourable circumstances for observation of e.s.r. spectra of the peroxy radicals, when the UPEC materials are studied; mainly peroxy radicals are produced in UPEC and the peroxy radicals in UPEC are more stable than in normal polyethylene. Both these circumstances are expected because of the weaker interaction between the molecular chains of polyethylene.

EXPERIMENTAL

The sample used in this study was the complex of urea and polyethylene, and the polyethylene materials used were Sholex 6050. The complex will be called UPEC in the present paper. The complex materials were made by the so-called indirect method[9] which was to replace the hydrocarbon molecules in urea–hexadecane complex with polyethylene molecules. The purity of UPEC was determined by the d.s.c. method and materials with satisfactory purity were selected. These samples were stacked into e.s.r. sample tubes and evacuated to 10^{-6} torr for 6 h. Sealed UPEC were irradiated by γ-rays from a ^{60}Co source at room temperature up to 3 Mrad with the dose rate

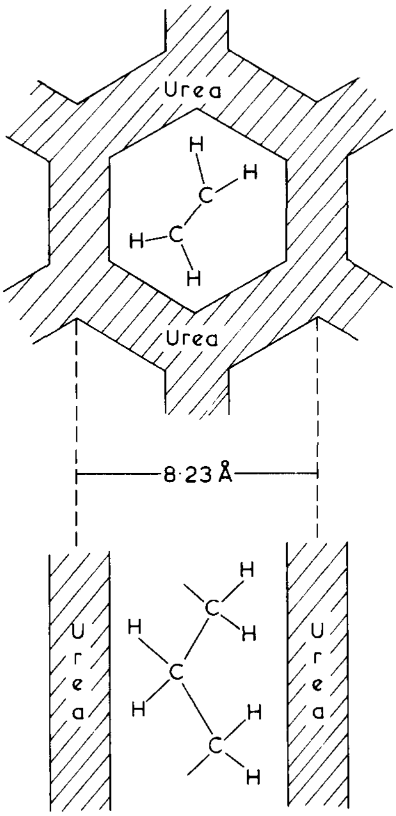

Figure 1 Schematic illustration of the structure of the urea–polyethylene complex (UPEC)

of 0.25 Mrad/h. Only the alkyl radicals were produced in UPEC and they were stable at room temperature[11]. No signal from radicals in urea materials was observed. Oxygen molecules at a pressure of 150 torr were introduced into ampoules of the irradiated UPEC and the peroxy radicals were produced by the reaction of these alkyl radicals with oxygen molecules for 45 h at room temperature. We were successful in converting all of the alkyl radicals of polyethylene to peroxy radicals, and these peroxy radicals in UPEC were stable even at room temperature. This was a different case from that of normal polyethylene[1,12]. Because of the stability of the peroxy radicals in UPEC, and the easier permeation of oxygen molecules through them, we could convert all alkyl radicals to peroxy radicals and hence sufficient concentration of peroxy radicals for e.s.r. observation was obtained.

The e.s.r. measurements were made using a Jeol ME-3X spectrometer (x-band), and the temperature setting for measurement of the temperature dependence of the spectra was performed by controlling the amount and the temperature of flowing nitrogen gas. The microwave power was kept at 0.1 mW. The signal of diphenyl-picryl-hydrazyl (DPPH) was used as a standard for g-values, and the g-value of DPPH was taken as 2.0036. Magnetic field sweep was calibrated with known splitting constants of Mn^{2+}. The signals were recorded by a Jeol spectrum computer, Model JEC-6. The spectra were observed at 77K and at various temperatures ranging from 113 to 390K.

RESULTS

E.s.r. spectra observed at various temperatures are shown in *Figures 2* and *3*, and these spectra show that peroxy radicals in UPEC are much more stable than those in the normal polyethylene, i.e., the peroxy radicals in normal polyethylene were unstable even at 241K, but those in UPEC were observed to be stable at 336K as shown in *Figure 2*. The e.s.r. spectrum observed at 354K in this Figure also indicates a superposition of the spectra of peroxy and alkyl radicals, and this means that some of the peroxy radicals in UPEC convert into alkyl radicals at this temperature. The e.s.r. spectrum observed at 390K is that of alkyl radicals only. Of course, the spectrum of pure alkyl radicals was observed below 390K when the materials trapping peroxy radicals were stored for a long time at a temperature above 354K. To the best of our knowledge, no observation of the conversion of peroxy radicals to alkyl radicals in polyethylene has been reported. According to the results of the present study, it can be said that this conversion of the peroxy radicals into alkyl radicals was caused by the hydrogen abstraction reaction of peroxy radicals with methylene groups in polyethylene. Although the hydrogen abstraction reaction must have an important role in the auto-oxidation process in the polymer, no direct observation of the reaction has been reported by means of e.s.r. method. Clearly, more careful investigations and subsidiary experimental results are necessary in order to confirm the abstraction reaction, and we are preparing another paper in this respect. In the present paper, however, the temperature dependence of the spectra of the peroxy radicals in UPEC will be discussed.

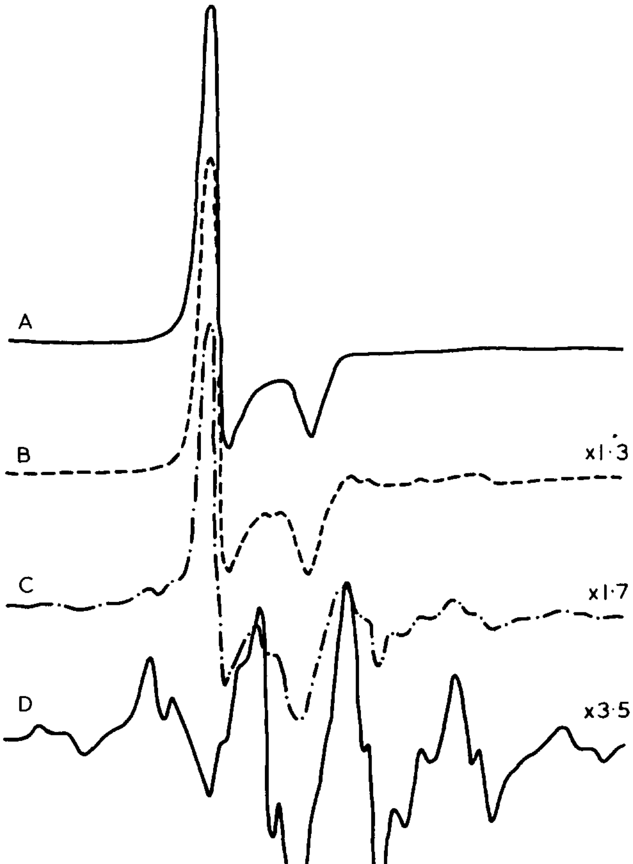

Figure 2 Stability of peroxy radicals in UPEC. Spectrometer gains relative to the case of the pattern for 336K are shown at the right hand sides of the respective patterns. A, 336K; B, 354K; C, 372K; D, 390K

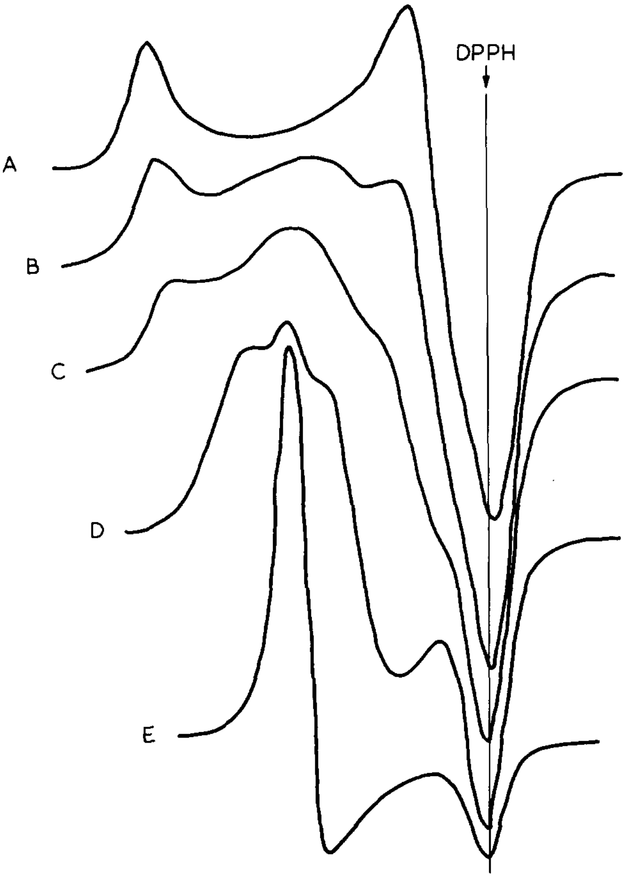

Figure 3 E.s.r. spectra of peroxy radical in UPEC observed at various temperatures. A, 142K; B, 187K; C, 212K; D, 261K; E, 290K

Figure 3 indicates the temperature dependence of the spectra. The variation of the spectra illustrated in the same Figure was completely reversible at temperatures below 336K. It can easily be said that all spectra in *Figure 3* are superpositions of more than two components. *Figure 3a* and *3e* look like a single component, but careful analysis by computer simulation indicates that these two spectra are not one component spectra. Also the same spectra, *Figure 3a* and *3e*, show the remarkable inversion of the g-values, and this problem will be discussed in connection with *Figure 6* later.

In comparison with the case of normal polyethylene which were reported in our previous paper[1], the following characteristics of e.s.r. spectra of peroxy radicals in UPEC were found:

(a) peroxy radicals in UPEC are stable up to 336K, but those in normal polyethylene are not stable even at 241K;

(b) spectra for UPEC show remarkable inversion of g-values;

(c) spectra of both for UPEC and normal polyethylene are composed of more than two components, but the circumstances are different between these two cases.

Detailed analysis of the spectra of computer simulation is discussed below.

SIMULATION

The computer simulation was performed in order to obtain several spectral parameters and this method confirmed the coexistence of more than two kinds of radical sites. It was assumed that there were two groups of peroxy radicals and the extents of the averaging of anisotropic g-values were different for respective groups. One group, which is in slower motion, is called the A-radical and the other is called the B-radical. Therefore averaging of the g-values of B-radicals was much more perfect than for A-radicals. Distribution of correlation times attributed to molecular motions of respective radical sites should be taken into consideration in the estimation of apparent linewidths. In other words, the linewidths used in this simulation can be larger than the intrinsic linewidths. Based on the assumptions mentioned above, anisotropic g-values, g_1, g_2, g_3 ($g_1 < g_2 < g_3$ for A-radical) and g_1', g_2', g_3' ($g_1' < g_2' < g_3'$ for B-radical), the ratio of the amount of B-radicals to A-radicals ([B]/[A]), and linewidths were determined by the computer simulation. Linewidths were assumed to vary linearly with the inversion of g-value. The method of simulation was the same as that described in the previous article (ref 1).

The best fit simulated spectra and the experimental spectra are shown in *Figure 4*. As shown in *Figure 4*, the agreement between the simulated spectra and the observed spectra is very good and also it indicates that the classification of the radicals into A- and B-radicals was a good approximation. For reference, the spectra simulated from one component are shown in *Figure 5* for the cases in which the observed spectra may be regarded as one component. But the agreement was not good, and at these temperatures there are more than two kinds of peroxy radicals.

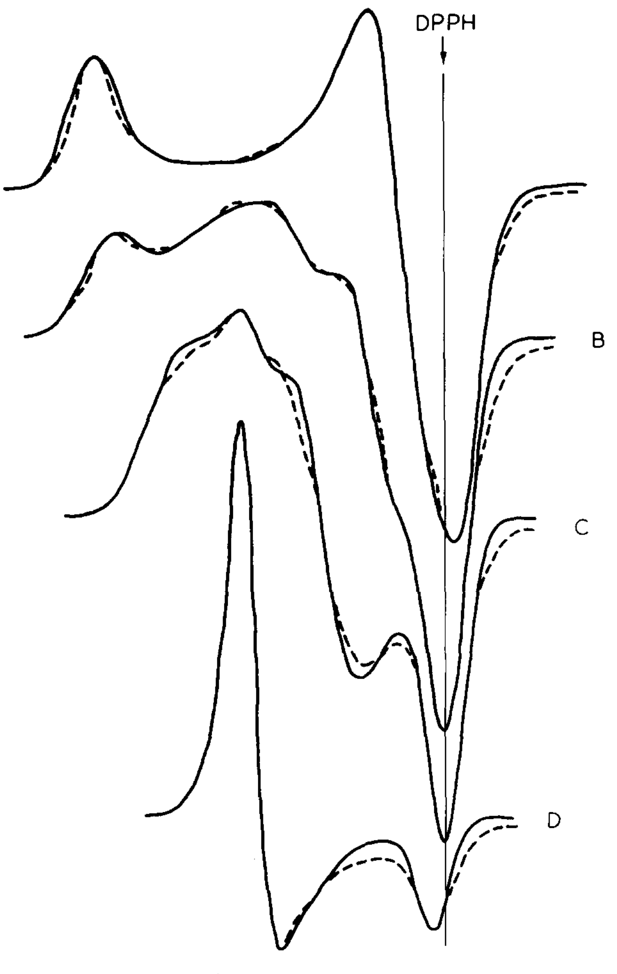

Figure 4 Examples of spectrum simulations: ——— simulation; – – – – observed. A, 113K; B, 200K; C, 249K; D, 326K

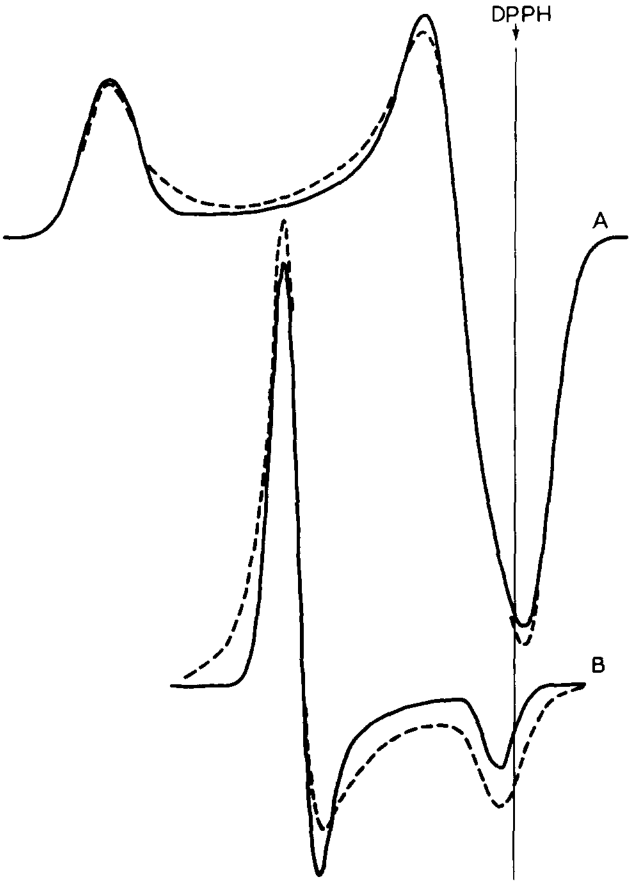

Figure 5 Example of simulation assuming one component pattern. A, 113K; B, 326K; ———, simulation; — — — —, observed

From these simulations, g_1, g_2, g_3 (for A-radical), g_1', g_2', g_3' (for B-radical), ΔH_1 (linewidth 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 for various temperatures and they are tabulated in *Table 1* in which the mean values of g-values are also shown. Temperature dependences of g-values for the cases of UPEC and normal polyethylene are also shown in *Figure 6*. The fact that the mean values of the g-values at different temperatures are almost constant and both mean values for A- and B-radicals are equal indicate that our simulations are good enough. For most cases, the maximum errors in g-values, linewidths and the ratio are 0.0003, 0.5 Gauss and 10%, respectively. But the errors are much larger for B-radicals at low temperature and for A-radicals at high temperature.

DISCUSSION

According to the simulation mentioned in the previous section, it can be said that the experimental e.s.r. spectra of the peroxy radicals produced by the reaction of oxygen with the alkyl radicals in UPEC are a mixture of two spectra corresponding to two different radical species, A- and B-radicals, at all temperatures; i.e., both A-radicals and B-radicals are the peroxy radicals, but the molecular motions of the respective radical sites are different. Change of g-values with temperature are illustrated in *Figure 6a* for the case of UPEC and in *Figure 6b* for the case of normal polyethylene. As seen in *Table 1* and *Figure 6*, the smallest g-values of A- and B-radicals, g_1 and g_1', are equal at every temperature, but the larger g-values for A-radicals (g_2 and g_3) are different from the corresponding quantities for B-radicals (g_2' and g_3'); i.e., g_2 is smaller than g_2', but g_3 is larger than g_3' at all temperatures. These facts indicate that the motional averaging between g_2' and g_3' in B-radicals is

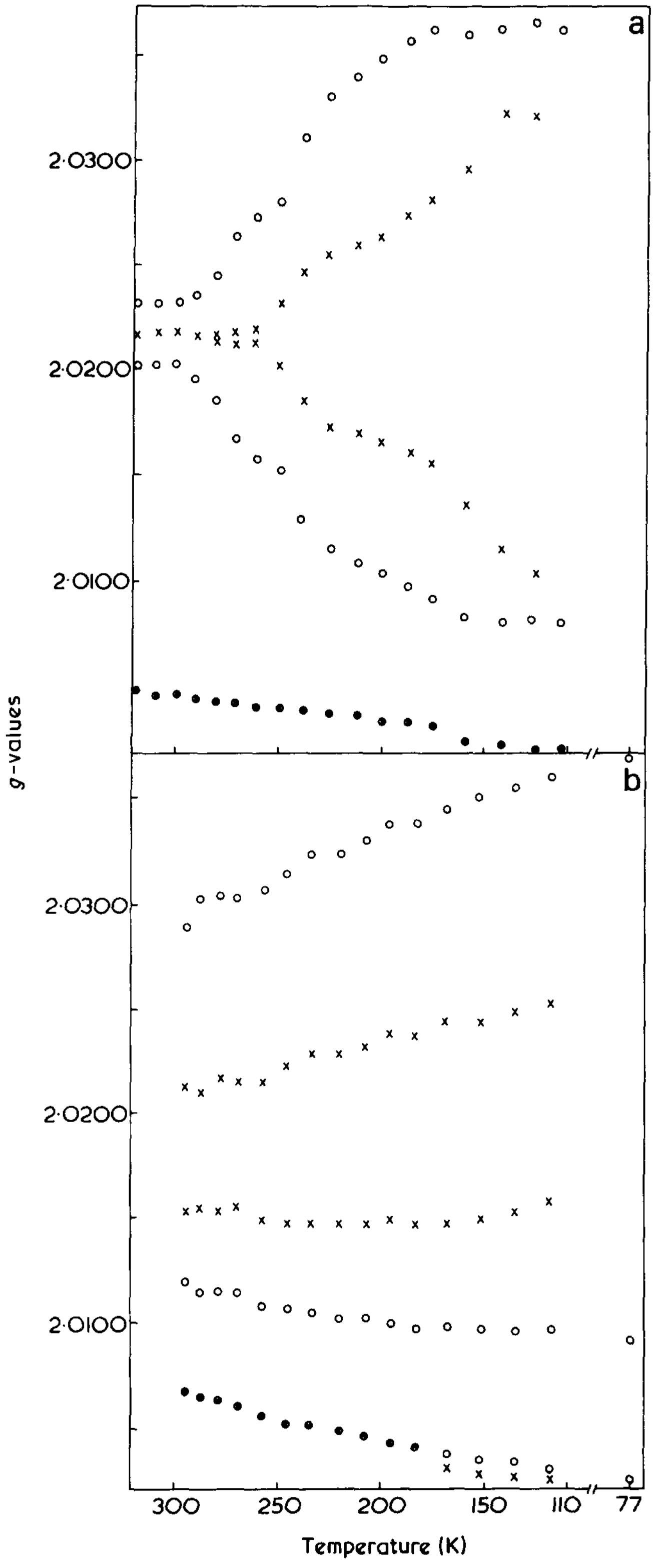

Figure 6 Change of g-values with temperature. (a) Case of UPEC; (b) Case of normal polyethylene

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

T	g_1 (g_1')	g_2 (g_2')	g_3 (g_3')	mean value	ΔH_1 ($\Delta H_1'$)	ΔH_3 ($\Delta H_3'$)	[B]/[A]
77	2.0022	2.0081	2.0366	2.0156	6.0	6.5	0.10
	(2.0022)	(2.0105)	(2.0343)	(2.0157)	(8.5)	(10.0)	
113	2.0024	2.0081	2.0364	2.0156	6.0	6.5	0.20
	(2.0024)	(2.0105)	(2.0343)	(2.0157)	(8.5)	(10.0)	
126	2.0025	2.0082	2.0363	2.0157	6.0	6.5	0.20
	(2.0025)	(2.0110)	(2.0340)	(2.0158)	(8.5)	(12.0)	
142	2.0027	2.0083	2.0362	2.0157	6.0	6.5	0.25
	(2.0027)	(2.0120)	(2.0330)	(2.0159)	(8.0)	(12.0)	
159	2.0028	2.0085	2.0360	2.0158	6.0	6.5	0.35
	(2.0028)	(2.0130)	(2.0310)	(2.0156)	(7.0)	(13.0)	
176	2.0032	2.0093	2.0360	2.0162	6.0	7.0	0.45
	(2.0032)	(2.0155)	(2.0280)	(2.0156)	(5.0)	(15.0)	
187	2.0033	2.0097	2.0355	2.0162	6.0	7.5	0.6
	(2.0033)	(2.0160)	(2.0273)	(2.0155)	(5.0)	(14.0)	
200	2.0035	2.0104	2.0347	2.0162	6.0	7.5	0.8
	(2.0035)	(2.0165)	(2.0264)	(2.0155)	(5.0)	(13.0)	
212	2.0036	2.0109	2.0339	2.0161	6.0	7.5	0.9
	(2.0036)	(2.0169)	(2.0259)	(2.0155)	(5.0)	(12.0)	
225	2.0037	2.0116	2.0330	2.0161	6.0	7.5	1.0
	(2.0037)	(2.0172)	(2.0255)	(2.0155)	(5.0)	(12.0)	
238	2.0039	2.0129	2.0310	2.0159	6.0	9.5	0.8
	(2.0039)	(2.0185)	(2.0245)	(2.0156)	(5.0)	(12.0)	
249	2.0040	2.0152	2.0280	2.0157	5.5	10.0	0.085
	(2.0040)	(2.0202)	(2.0230)	(2.0157)	(5.0)	(5.0)	
261	2.0041	2.0158	2.0273	2.0157	5.0	8.5	0.1
	(2.0041)	(2.0213)	(2.0218)	(2.0157)	(5.0)	(5.0)	
271	2.0042	2.0167	2.0263	2.0157	5.0	7.0	0.1
	(2.0042)	(2.0212)	(2.0218)	(2.0157)	(4.5)	(4.5)	
280	2.0043	2.0185	2.0245	2.0158	5.0	7.5	0.6
	(2.0043)	(2.0214)	(2.0216)	(2.0158)	(4.0)	(4.0)	
290	2.0044	2.0195	2.0235	2.0158	5.0	7.5	0.6
	(2.0044)	(2.0215)	(2.0215)	(2.0158)	(3.5)	(3.5)	
299	2.0045	2.0202	2.0232	2.0160	5.0	7.5	0.6
	(2.0045)	(2.0217)	(2.0217)	(2.0160)	(3.5)	(3.5)	
309	2.0045	2.0205	2.0225	2.0158	5.0	7.5	0.6
	(2.0045)	(2.0215)	(2.0215)	(2.0158)	(3.5)	(3.5)	
318	2.0047	2.0205	2.0225	2.0159	5.0	7.5	0.6
	(2.0047)	(2.0215)	(2.0215)	(2.0159)	(3.5)	(3.5)	
326	2.0048	2.0204	2.0224	2.0159	5.0	7.5	0.6
	(2.0048)	(2.0214)	(2.0214)	(2.0159)	(3.5)	(3.5)	
336	2.0049	2.0203	2.0223	2.0158	5.0	7.5	0.6
	(2.0049)	(2.0213)	(2.0213)	(2.0158)	(3.5)	(3.5)	
344	2.0050	2.0202	2.0222	2.0158	5.0	7.5	0.6
	(2.0050)	(2.0212)	(2.0212)	(2.0158)	(3.5)	(3.5)	
354	2.0050	2.0201	2.0221	2.0157	5.0	7.5	0.6
	(2.0050)	(2.0211)	(2.0211)	(2.0157)	(3.5)	(3.5)	
363	2.0052	2.0202	2.0222	2.0159	5.0	7.5	0.6
	(2.0052)	(2.0212)	(2.0212)	(2.0159)	(3.5)	(3.5)	
372	2.0055	2.0201	2.0221	2.0159	5.0	7.5	0.6
	(2.0052)	(2.0211)	(2.0211)	(2.0159)	(3.5)	(3.5)	

much more perfect than that in A-radicals at the same temperature. In other words, the molecular motion of the sites of B-radicals around the g_1-axis is much more rapid than that of A-radicals at every temperature. These differences in molecular motions between A- and B-radicals must be caused by the difference of the trap sites of the respective peroxy radicals, since both A- and B-radicals are chemically identical.

Perhaps B-radicals are trapped near the end of the pore of the urea crystal and A-radicals trapped in the inner portion. UPEC have a structure such that the straight chain of the polyethylene molecule is enclosed in the pore of the urea crystal, and the peroxy radicals are randomly trapped on the polyethylene chain. Therefore, we can say that the radicals trapped near the end of the chain can move more rapidly than those in the inside at every temperature.

As in the case of normal polyethylene, the ratio of concentrations of the respective radicals, [B]/[A], was estimated for various temperatures. However, no regular change of [B]/[A] with temperature was seen for the present case. This can be explained as follows: intrinsically, consideration of the distribution of correlation times of A- and B-radical sites is necessary. In the case of normal polyethylene, this distribution could be well replaced by two groups, B- and A-radicals, and a kind of well-regulated change of [B]/[A] with temperature was seen. In the case of UPEC, however, distribution of the correlation times must be much more continuous than the former case, and therefore, fractionation into two groups, B and A, is certainly not enough. This may be the cause of a not well-regulated change of [B]/[A] with temperature in the case of UPEC, and relation between [B]/[A] and temperature for UPEC must be of less physical meaning than that for normal polyethylene. However, fractionation into B- and A-radicals is still a convenient way for consideration of the molecular motion of radical sites. With respect to these problems, it is worthwhile to discuss the

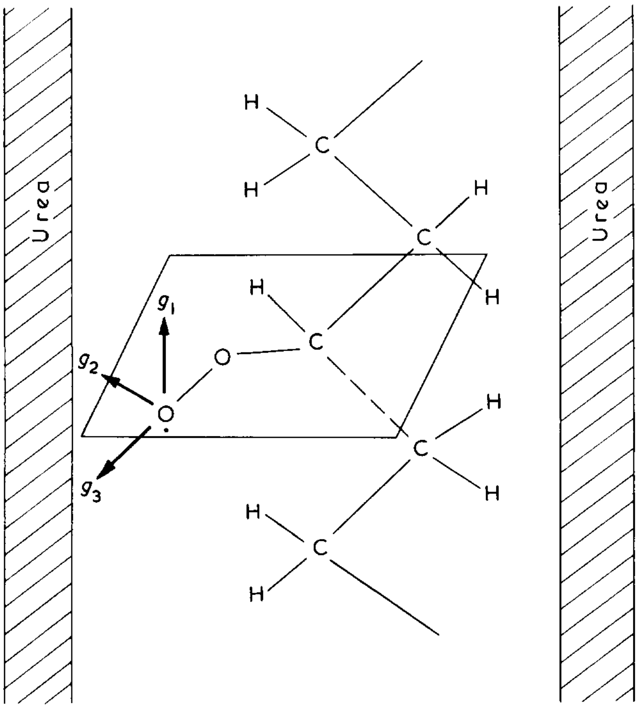

Figure 7 Schematic illustration of peroxy radicals in UPEC

motions which are the causes of averaging of the anisotropic g-values of the peroxy radicals.

The structure of the peroxy radical in the pore of the urea is illustrated schematically in *Figure 7*. Because the peroxy radicals of the low molecular weight hydrocarbons and the other polymers have the g_3-principal axis along the O–O bond direction, it is reasonable to assign the g_3-axis of the peroxy radical of polyethylene as the direction parallel to O–O bond as illustrated. In the same way, one of the g_1 or g_2-axes must be in the direction perpendicular to the C–O–O plane, and the other axis is perpendicular to both of the other two. It was concluded that the C–O–O plane is perpendicular to the chain direction and the g_1-axis is parallel to the chain axis as illustrated in *Figure 7* for the following reasons: two kinds of main motions of the peroxy radical can be considered in the case of polymeric chain molecule, one of them is the rotation around the C–O bond axis and the other is the rotation or vibration around the chain axis. But three dimensional random motion is forbidden with the wall of urea. All g-values, g_1, g_2, g_3, will be averaged if the rotation around the C–O bond axis occurs, or if the rotation around the chain axis occurs when the C–O–O plane is not perpendicular to the chain. But the experimental results indicate that only the averaging between g_2 and g_3 occurs, and the value of g_1 hardly changes as illustrated in *Figure 6a*. Therefore, the rotation around the C–O bond is not a main motion of the peroxy radical and the C–O–O plane is perpendicular to the chain. Thus it can be said that the almost unchanged axis, the g_1-axis, must be parallel to the chain axis, and a main effect of motional averaging among the anisotropic g-values is the averaging between g_2 and g_3 caused by rotation around the chain axis. In other words, rotation around C–O bond axis and three dimensional motion play no important roles.

Comparison of the changes of these g_1-values with temperature for the case of UPEC and normal polyethylene is interesting. As mentioned previously, g_1 for UPEC seems to be almost unchanged, but the same quantity for normal polyethylene shows much larger temperature dependence as shown in *Figure 6b*. This must be a reflection of the situation when three dimensional motion of peroxy radicals is slightly allowed in normal polyethylene. Comparison of *Figure 6a* and *Figure 6b* indicates that changes of g_2 and g_3 in UPEC are larger than those in normal polyethylene. This is a reflection of much more perfect motional averaging between g_2 and g_3 in UPEC than in normal polyethylene and this may be caused by the facts that the intermolecular interaction of the polyethylene chain in UPEC is weaker than that in normal polyethylene and, therefore, the rotation around the chain in UPEC is faster than in normal polyethylene.

The difference between the stability of the peroxy radicals in UPEC and in normal polyethylene is probably a reflection of following circumstances: the intramolecular abstraction of hydrogen by the peroxy radical is difficult because the rotation around the C–O bond is not a main motion of the peroxy radical; the intermolecular abstraction is easier in normal polyethylene than in UPEC because of the difference of the intermolecular distance.

ACKNOWLEDGEMENTS

The present study was partly supported by the Scientific Research Expenditure of The Ministry of Education in Japan, Grant No. 075237 and 843022. The authors are grateful to Mr Somsak who has improved the language of the manuscript.

REFERENCES

1 Hori, Y., Shimada, S. and Kashiwabara, H. *Polymer* 1977, **18**, 567
2 Ohnishi, S., Sugimoto, S. and Nitta, I. *J. Polym. Sci. (A)* 1963, **1**, 605
3 Davis, L. A., Pampillo, C. A. and Chiang, T. C. *J. Polym. Sci. (A–2)* 1973, **11**, 841
4 Matsugashita, T. and Shinohara, K. *J. Chem. Phys.* 1961, **35**, 1952
5 Chien, J. C. W. and Boss, C. R. *J. Am. Chem. Soc.* 1967, **89**, 571
6 Iwasaki, M. and Sakai, Y. *J. Polym. Sci. (A–2)* 1968, **6**, 265
7 Baum, B. *J. Appl. Polym. Sci.* 1959, **2**, 281
8 Luongo, J. P. *J. Polym. Sci.* 1960, **42**, 139
9 Monobe, K. and Yokoyama, F. *J. Macromol. Sci. (B)* 1973, **8**, 277
10 Smith, A. E. *Acta Crystallagr.* 1952, **5**, 224
11 Shimada, S., Hori, Y. and Kashiwabara, H. *Polymer* 1977, **18**, 25
12 Hori, Y., Shimada, S. and Kashiwabara, H. *Polymer* 1977, **18**, 151