Peroxy Radical Formation from Plasma-Induced Surface Radicals of Polyethylene As Studied by Electron Spin Resonance[1]

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ABSTRACT: The nature of peroxy radical formation from plasma-induced surface radicals of polyethylene (PE), both low-density polyethylene (LDPE) and high-density polyethylene (HDPE), was studied by electron spin resonance with the aid of systematic computer simulations. It was found that peroxy radical formation varies with the structure of component radicals of plasma-irradiated PE, both LDPE and HDPE: Among three plasma-induced radicals of PE, dangling bond sites (DBS) undergo an instant conversion into the corresponding peroxy radicals in contact with oxygen, while the midchain alkyl radical is of very low reactivity with oxygen in both LDPE and HDPE. Computer simulations disclosed that ESR spectra of peroxy radicals are similar to each other in LDPE and HDPE, both being composed of two types of spectra, a partial *g*-averaging anisotropic spectrum and a nearly isotropic single line spectrum due to different molecular motional freedom at the trapping sites of peroxy radicals.

Introduction

In the preceding paper, we reported the electron spin resonance (ESR) study on plasma-induced low-density polyethylene (LDPE) radicals on its comparison with those of high-density polyethylene (HDPE).[2] The observed ESR spectra of plasma-irradiated LDPE are largely different in pattern from those of HDPE. It was found with the aid of systematic computer simulation that such observed spectra of plasma-irradiated LDPE consist of three kinds of radicals, a midchain alkyl radical (1) (sextet spectrum), a midchain allylic radical (2) (septet spectrum) as discrete radical species, and a large amount of dangling bond sites (DBS) (3) (smeared-out broad line) at the surface cross-linked region. All these component radicals are essentially identical with those of HDPE reported earlier, but thermally stable DBS (3) is a major component radical, instead of a midchain alkyl radical in HDPE, indicating the formation of a highly cross-linked network on the plasma-irradiated LDPE surface.

Peroxy radical formation for the auto-oxidation process has been extensively studied due to the importance of industrial application of a wide variety of γ-irradiated polymers[3] including those of HDPE.[4] All kinds of plasma-irradiated polymers are eventually exposed to air for their practical use, so the studies of the auto-oxidation process are also important for plasma-irradiated polymers.

In this paper, we report the nature of peroxy radical formation as an initial process of auto-oxidation studied by ESR with the aid of systematic computer simulations, from two types of plasma-irradiated PE, both LDPE and HDPE, (1) by its exposure to air (oxygen) immediately after plasma irradiation and (2) by its exposure to air after standing the plasma-irradiated sample for 92 h anaerobically at room temperature, which contains only thermally stable radicals.

Experimental Section

Materials. Plasma-irradiated LDPE obtained in the preceding paper[2] and plasma-irradiated HDPE reported earlier[5] were used for peroxy radical formation.

Peroxy Radical Formation and ESR Spectral Measurement. The peroxy radical formation was performed simply by opening the ampule containing the PE samples plasma-irradiated for a prescribed period of time to introduce air into the ampule. ESR spectra were recorded by a JES-RE1X (JEOL) spectrometer with X-band and 100 kHz field modulation. Since most observed ESR spectra here are those of peroxy radicals mixed with remaining carbon-centered radicals, the power saturation of carbon-centered radicals occurs easily, unlike the peroxy radicals, when a high microwave power is used on the ESR spectral measurement. Thus, from a plot of the square root of the microwave power versus the signal peak height, a power level of 0.04 mW was chosen. The computer simulations of ESR spectra were performed according to the same method as described in the preceding paper.[2]

Results

Observed ESR Spectra of Plasma-Irradiated PE on Exposure to Air at Room Temperature. It is a well-known fact that most polymer radicals produced by high-energy irradiation, including plasma irradiation, are rapidly converted, in contact with oxygen, into the corresponding peroxy radicals, and the ESR spectra can be observed at room temperature in many polymers.[3,4] Figure 1 shows what happened to the ESR spectra when LDPE and HDPE, both plasma-irradiated for 3 min, were exposed to air.

It is seen that the spectrum of LDPE has quickly changed to an unsymmetrical spectral pattern, which is representatively characterized by a sharpening of the central line. The spectral pattern continues to change on standing in air with a decrease in the spectral intensity, and the well-defined sextet-type spectrum was obtained more than 30 min later, which is apparently similar to that of HDPE. The simulated spectra shown as dotted lines in Figure 1 disclosed that the change in the spectral pattern in LDPE is caused by a rapid formation and slow dissipation of the peroxy radicals, which has a larger *g* value than carbon-centered radicals (vide infra).

The result is in sharp contrast to the nature of spectral changes in HDPE. Exposure of a well-defined

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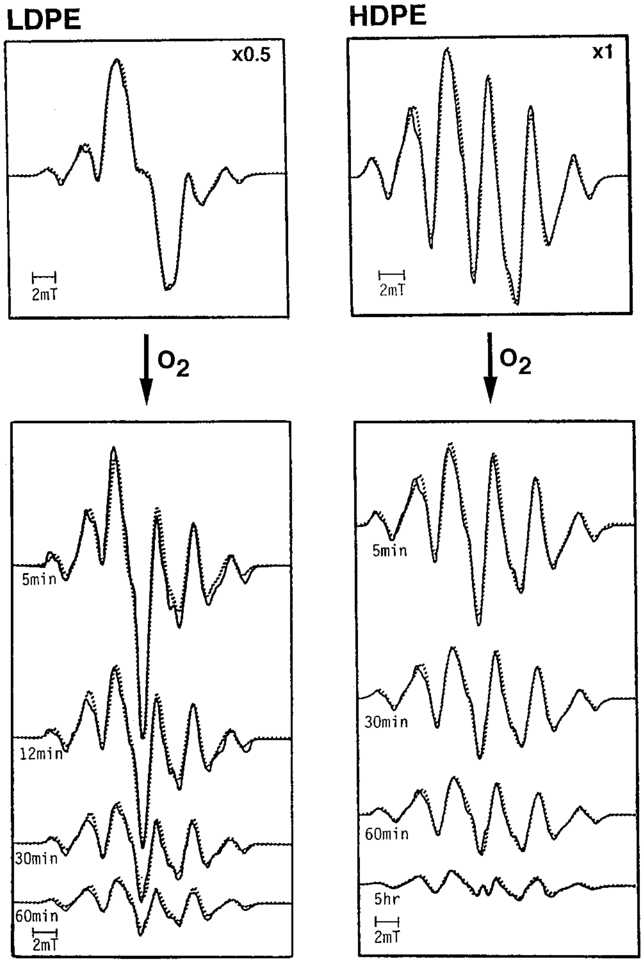

Figure 1. Progressive ESR spectral changes on exposure to air of LDPE and HDPE plasma-irradiated for 3 min, respectively, together with the simulated spectra shown as dotted lines.

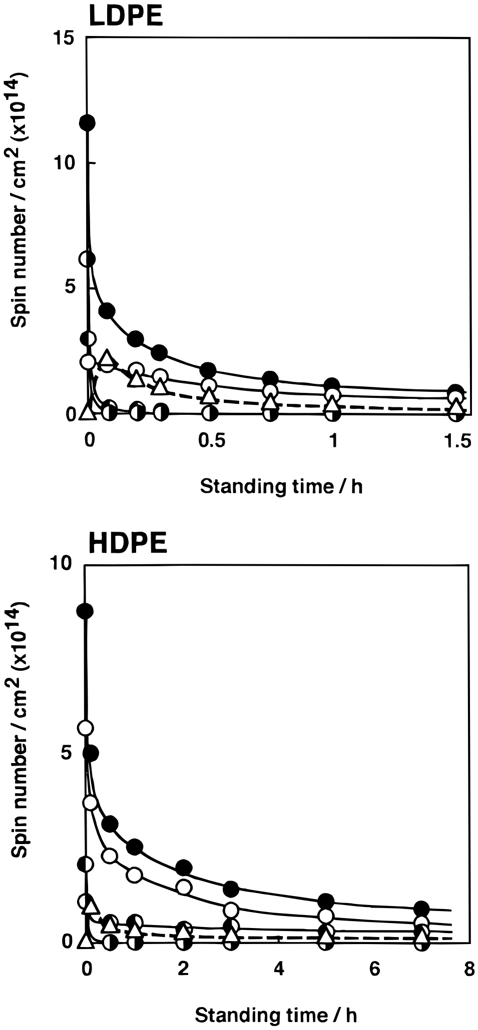

Figure 2. Simulated progressive changes in component spectra on standing in air of LDPE and HDPE plasma-irradiated for 3 min, respectively. Key: (●) total; (○) sextet; (◐) septet; (◑) DBS; (△) spectrum of peroxy radical.

sextet-type spectrum of HDPE to air at room temperature does not show a significant change in spectral pattern but appears to show only the decrease in the spectral intensity. The computer simulations of these progressive changes, however, have clearly shown the presence of a small amount of peroxy radicals.

Figure 2 shows the progressive changes of the component spectra of LDPE and HDPE as a function of standing time in air for the simulated spectra shown in Figure 1. It can be seen that all the component spectra, I, II, and III, in LDPE decay in intensity on exposure to air, but among these, II and III quite rapidly disappeared. Likewise, the component spectrum (III) in HDPE almost instantly disappeared, but the spectrum (II) in HDPE behaved differently from that in LDPE, which decays only gradually with standing time. The rate of decay of the sextet spectrum (I) of LDPE is similar to that of HDPE (I_{1h}/I_0 = ca. 0.34 for LDPE and ca. 0.32 for HDPE). On the other hand, the formation of peroxy radical (dashed lines in Figure 2) shows a maximum in intensity at a very early stage (several minutes later) and then decreases gradually with prolongation of standing time in air in both PE, which could undergo the chain termination reactions through the hydroperoxide consuming several moles of oxygen.

Further, it was deduced from Figure 2 that the ratio of peroxy radical quantity against a total amount of radicals in HDPE is only ca. 16% at the stage showing a maximum amount of peroxy radical formation, while it is ca. 54% in LDPE. Thus, it became clear that only a slight change in spectral pattern on exposure of plasma-irradiated HDPE to air is caused by peroxy radical formation in a much lower ratio and is almost concealed from its clear observation in the spectra.

Figure 3 shows the peroxy radical spectra in the simulated spectra shown in Figure 1. It is apparent that both spectral features in LDPE and HDPE change gradually with time, indicating that the spectra are composed of more than two components due to the difference in the molecular motion of the radical located, and can be deconvoluted into two kinds of representative component spectra shown as two types of dotted lines in both LDPE and HDPE: One spectrum (1P) has been shown to be of a partial *g*-averaging spectral pattern (fine dotted line), which is a typical spectral pattern of powdered peroxy radicals, and the other (2P) gave a nearly isotropic single line with nearly complete averaging of *g* anisotropy (rough dotted line) due to a random molecular motion at the site of peroxy radical formation (vide infra). A set of anisotropic *g* values deduced from the simulated spectra are listed in Table 1.

It can be considered that the presence of two kinds of spectra of peroxy radicals is due to the difference in the polymer surface morphology at the site of the peroxy

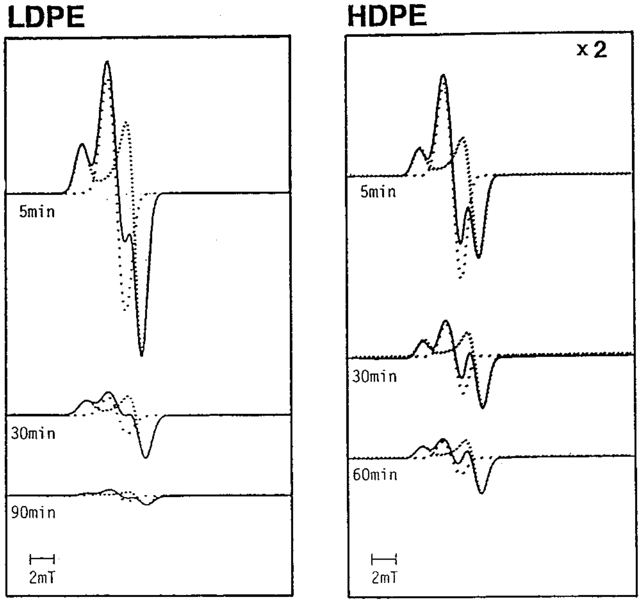

Figure 3. Progressive ESR spectral changes of peroxy radical with two-component spectra deduced from the simulated spectra on exposure to air of LDPE and HDPE plasma-irradiated for 3 min.

Table 1. ESR Spectral Data for Peroxy Radicals in Simulated Spectra of LDPE and HDPE

		1p	2p
LDPE	$\bar{g}$	2.0145	2.0171
	g_1	2.0030	2.0120
	g_2	2.0074	2.0169
	g_3	2.0332	2.0224
HDPE	$\bar{g}$	2.0144	2.0176
	g_1	2.0030	2.0128
	g_2	2.0070	2.0167
	g_3	2.0334	2.0229

[a] Values of HSC are given in mT.

radical formation. As shown in Figure 4, although a larger amount of 1P were formed than 2P, the progressive changes in the spectral intensity of two types of peroxy radicals indicated that 2P decays with a higher rate than 1P due to more rigorous molecular motion, thus changing gradually the spectral pattern with time.

All these results strongly indicated that a midchain alkyl radical of the sextet spectrum (I) is of much lower reactivity with oxygen, and the formation of peroxy radicals stems mainly from a smeared-out broad line (III) (DBS) and then a septet spectrum (II) (midchain allylic radical) in both cases.

We have also examined the peroxy radical formation of both LDPE and HDPE plasma-irradiated for 3 min followed by standing for 92 h in anaerobic conditions and then exposed to air, since such a sample of LDPE does not contain a sextet spectrum (I), and that of HDPE contains a sextet spectrum (I) only to a negligible extent, although the total radical quantity is significantly reduced, as reported in the preceding paper.[2]

The ESR spectral changes on exposure to air of both LDPE and HDPE thus obtained are shown in Figure 5, together with the simulated spectra shown as dotted lines. It is seen that the broad single line spectrum of LDPE was quickly converted into a new spectrum that appeared at lower magnetic field with a significant decrease in intensity and continued to decrese in intensity, whose spectral pattern is roughly similar to those shown in Figure 3. In fact, on the basis of the simulated progressive changes of the component spectra shown in Figure 6, it is clear that the spectra of LDPE consist of only the corresponding peroxy radicals. On the other hand, the spectral features on exposure of HDPE to air (Figure 5) have been considerably distorted with a significant decrease in intensity and with appearance of a part of peaks for a septet spectrum (II). In fact, it is seen from Figure 6 that only a smeared-out broad line (III) of DBS in HDPE rapidly disappeared to convert into the peroxy radicals, and the septet spectrum (II) slowly decreased in intensity. Thus, these results parallel the view of the difference in reactivity of the component radical with oxygen in the case of fresh plasma-irradiated PE stated above.

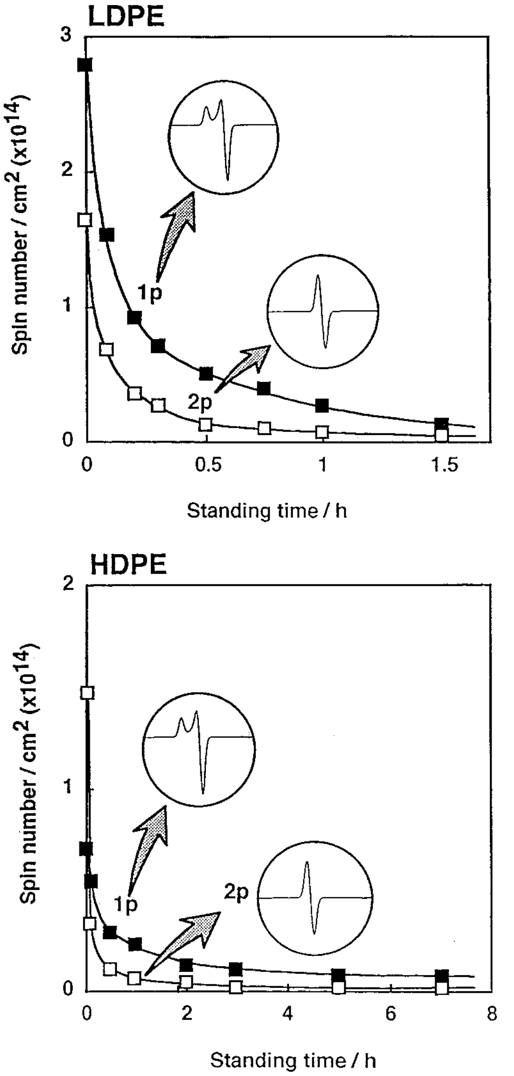

Figure 4. Simulated progressive changes in the spectral intensity of peroxy radicals, 1p and 2p. Plots at zero standing time were estimated from the extrapolation by line-fitting.

Discussion

Comparison in the Nature of Peroxy Radical Formation between Plasma-Irradiated LDPE and HDPE. It is a well-known fact that peroxy radical formation of HDPE occurs mostly at the amorphous region due to the high capability of oxygen diffusion. In fact, the rate of oxygen diffusion into the crystalline region was reported to be about one-tenth relative to that to amorphous region.[4b,d,g] Thus, the difference in the nature of radical formation between LDPE and

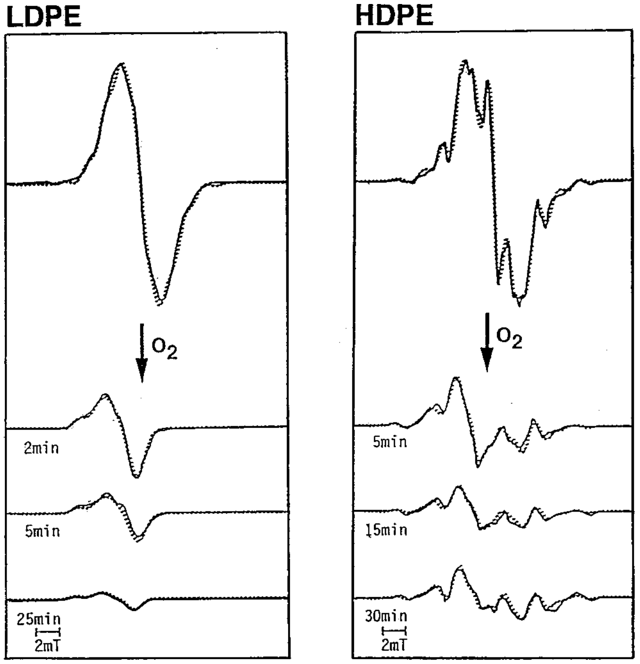

Figure 5. Progressive ESR spectral changes on exposure to air of LDPE and HDPE plasma-irradiated for 3 min followed by standing for 92 h together with the simulated spectra shown as dotted lines.

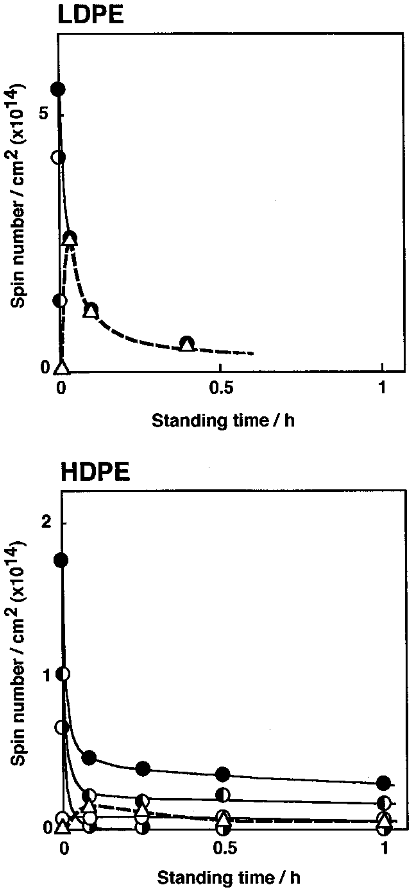

Figure 6. Simulated progressive changes in component spectra on standing in air of LDPE and HDPE plasma-irradiated for 3 min followed by standing for 92 h at room temperature. Key: (●) total; (○) sextet; (◐) septet; (◑) DBS; (△) spectrum of peroxy radical.

HDPE can be rationalized in terms of the fact that a large amount of DBS was formed at the amorphous surface cross-linked layer of plasma-irradiated LDPE and was very sensitive to oxygen, whereas the midchain alkyl radicals were mainly formed in plasma-irradiated HDPE and unimportant in the formation of peroxy radical, since most of such radicals are located in the crystalline region. Part of midchain allylic radicals is considered to be located in the crystalline region especially in the case of HDPE. In fact, as was shown in Figure 2, part of the septet spectra (II) as well as the sextet spectrum (I) remained even after standing for a long period of time in air and, thus, must be located in the crystalline regions.

A similar propensity has also been observed in other polymers. For example, the ESR spectral studies on a series of plasma-irradiated carbohydrates clearly demonstrated that plasma-induced radicals of amorphous polycarbohydrates such as ethylcellulose and (hydroxyethyl)cellulose disappeared instantly in contact with air,[6] whereas plasma-induced radicals formed in totally crystalline monocarbohydrates such as glucose and *myo*-inositol were quite stable in dry air for a long period of time at room temperature.[7] For these reasons, the ESR spectra of peroxy radicals (Figure 3) were similar in pattern for LDPE and HDPE, and a much smaller amount of peroxy radicals was formed in HDPE than in LDPE, although the ESR spectra of plasma-induced radicals (Figure 1) are quite different in pattern from each other.

The ESR spectrum of peroxy radicals does not give any information on the original radical structures due to the absence of any hyperfine splitting constants, although it does give the information of molecular motion where the peroxy radicals are located. It is difficult for PE, therefore, to elucidate the spectral feature of peroxy radicals derived from each of the three original carbon-centered radicals, unlike the case of plasma-irraidated poly(tetrafluoroethylene) (PTFE) where three component radicals formed were experimentally separated so that the ESR spectrum of each peroxy radical was delineated.[8] However, the present result in PE can be most reasonably explained by invoking that 1P could be formed from DBS (a major component in LDPE) and 2P was formed from the other radicals, 1 and 2, since much larger amounts of 1P were present than 2P in the case of LDPE (Figure 4). Therefore, it can be considered that a typical partial *g*-averaging spectral pattern of powdered peroxy radical such as 1P is due to the fact that the molecular motional freedom at the cross-linked layer where DBS is located is highly restricted, and a nearly isotropic single line spectrum such as 2P is due to the random molecular motion including the C−O bond rotation at the site of trapped peroxy radicals (Figure 7).

Concerning the Use of Peroxy Radicals for the Molecular Motion Probe in the Polymer Main Chain. A number of ESR studies of peroxy radicals formed by exposure to air of γ-irradiated HDPE and PTFE as the effective molecular motional probe due to incomplete averaging of *g* anisotropy in peroxy radicals have been reported by many authors.[11]

The temperature-dependent ESR spectra of peroxy radicals formed from γ-irradiated HDPE were interpreted as a superposition of two chemically identical radicals, both being peroxy radicals located in the amorphous region, trapped, however, at different locations and with different motional freedoms considering a rotation about the polymer chain axis, parallel to the

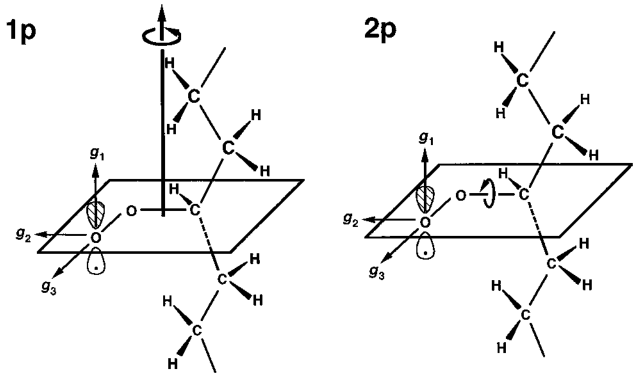

Figure 7. Illustration for orientation of the O−O group of PE peroxy radicals and the principal direction of the **g** tensor (g_1; perpendicular to the COO plane, g_3; direction of the O−O bond). The COO group lies in the plane perpendicular to the polymer main chain axis.

direction of g_1, as illustrated in Figure 7,[9] although Kevan et al. proposed to explain such temperature-dependent spectra by invoking one radical with jumping between equivalent sites.[9] These interpretations are, however, valid on the basis of the assumption that a single radical was present without a change of a significant polymer morphology during the course of the radical formation. The ESR observation, including temperature-dependent spectra of the peroxy probe is blind to nonradical species such as the part of the structure that resulted from cross-linkings. Nevertheless, such studies have been cited as direct evidence for the molecular motion of the native linear HDPE main chain.

On the basis of the fact that γ-irradiated PE, in both HDPE and LDPE, has shown ESR spectra similar to that of plasma-irradiated PE, we are strongly inclined to consider that three kinds of radicals including DBS had also been produced in γ-irradiated PE. The DBS formed at the intra- and intersegmental cross-linked layer, however, cannot undergo the chain axis rotation, giving peroxy radicals with the ESR spectrum similar to that of 1P. Thus, studies in γ-irradiated PE as direct evidence of the molecular motion of the linear PE chain should be carefully discussed, and we believe that the temperature-dependent spectra of peroxy radicals derived from γ-irradiated PE may also be explained in terms of a rationalization similar to those reported herein.

Conclusion

The conclusions drawn from the present study can be summarized as follows: Exposure to air of plasma-irradiated LDPE showed an instant change in the spectral pattern due to the formation of a larger amount of peroxy radical, while HDPE showed only the decrease in the spectral intensity. This was rationalized in terms of the fact that thermally stable DBS (3) (a smeared broad line), which is a major component radical in LDPE, is very susceptible to oxygen, and the thermally less stable midchain alkyl radical (1) (a sextet spectrum), which is a major component radical in HDPE, is much less reactive to oxygen in both LDPE and HDPE, since such radicals are present mainly in the crystalline region.

We believe this is the first detailed ESR spectral analysis and its progressive changes of peroxy radicals freshly formed from irradiated PE, LDPE and HDPE, in any kind of radiation method.

The result reported herein also reinforced our conclusion on HDPE by reconsidering the conclusion on γ-irradiated PE discussed in a previous paper.[5]

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References and Notes

(1) Part of this work was presented at the Symposium of Plasmas and Polymers; ACS National Meeting, San Francisco, CA, 1997. Kuzuya, M.; Kondo, S.; Sugito, M. *Polym. Prepr.* **1997**, *38* (1), 1049.
(2) Kuzuya, M.; Yamashiro, T.; Kondo, S.; Sugito, M.; Mouri, M. *Macromolecules* **1998**, *31*, 3225.
(3) (a) Siegel, S.; Hedgpeth, H. *J. Chem. Phys.* **1967**, *46*, 3904. (b) Kuznetsov, A. N.; Radtsig, V. A. *Chem. Phys. Lett.* **1972**, *17*, 377. (c) Che, M.; Tench, A. J. *J. Polym. Sci., Lett. Ed.* **1975**, *13*, 345. (d) Hori, Y.; Aoyama, S.; Kashiwabara, H. *J. Chem. Phys.* **1981**, *75*, 1582. (e) Shimada, S.; Hori, Y.; Kashiwabara, H. *Polymer* **1981**, *22*, 1377. (f) Shimada, S.; Kotake, A.; Hori, Y.; Kashiwabara, H. *Macromolecules* **1984**, *17*, 1104. (g) Reuben, J.; Mahlman, B. H. *J. Phys. Chem.* **1984**, *88*, 4904. (h) Carlsson, D. J.; Dobbin, C. J. B.; Wiles, D. M. *Macromolecules* **1985**, *18*, 2092.
(4) (a) Seguchi, T.; Tamura, N. *J. Phys. Chem.* **1973**, *77*, 40. (b) Shimada, S.; Kashiwabara, H. *Polym. J.* **1974**, *6*, 448. (c) Hori, Y.; Shimada, S.; Kashiwabara, H. *Polymer* **1977**, *18*, 151. (d) Hori, Y.; Shimada, S.; Kashiwabara, H. *Polymer* **1977**, *18*, 1143. (e) Hori, Y.; Fukunaga, Z.; Shimada, S.; Kashiwabara, H. *Polymer* **1979**, *20*, 181. (f) Hori, H.; Shimada, S.; Kashiwabara, H. *Polymer* **1979**, *20*, 406. (g) Kashiwabara, H.; Hori, Y. *Radiat. Phys. Chem.* **1981**, *18*, 1061. (h) Hikmet, R.; Keller, A. *Radiat. Phys. Chem.* **1987**, *29*, 15. (i) Carlsson, D. J.; Chmela, S.; Lacoste, J. *Macromolecules* **1990**, *23*, 4934.
(5) Kuzuya, M.; Niwa, J.; Ito, H. *Macromolecules* **1993**, *26*, 1990.
(6) (a) Kuzuya, M.; Morisaki, K.; Niwa, J.; Yamauchi, Y.; Xu, K. *J. Phys. Chem.* **1994**, *98*, 11301. (b) Kuzuya, M.; Yamauchi, Y. Niwa, J.; Kondo, S.; Sakai, Y. *Chem. Pharm. Bull.* **1995**, *43*, 2037.
(7) Kuzuya, M.; Noda, N.; Kondo, S.; Washino, K.; Noguchi. A. *J. Am. Chem. Soc.* **1992**, *114*, 6505.
(8) Kuzuya, M.; Ito, H.; Kondo, S.; Noda, N.; Noguchi, A. *Macromolecules* **1991**, *24*, 6612.
(9) (a) Hori, Y.; Shimada, S.; Kashiwabara, H. *Polymer* **1977**, *18*, 567. (b) Schlick, S.; Kevan, L. *J. Phys. Chem.* **1979**, *83*, 3424. (c) Schlick, S.; Kevan, L. *J. Am. Chem. Soc.* **1980**, *102*, 4622. (d) Kitahara, T.; Shimada, S.; Kashiwabara, H. *Polymer* **1980**, *21*, 1299. (e) Suryanarayana, D.; Kevan, L. *J. Phys. Chem.* **1982**, *86*, 2042.

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