Nature of Plasma-Induced Surface Radicals of Powdered Polyethylene Studied by Electron Spin Resonance

Masayuki Kuzuya,* Junji Niwa, and Hideki Ito

Laboratory of Pharmaceutical Physical Chemistry, Gifu Pharmaceutical University, 5-6-1, Mitahora-Higashi, Gifu 502, Japan

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ABSTRACT: Plasma-induced polyethylene (PE) radicals were studied in detail by electron spin resonance (ESR). The room temperature ESR spectrum of plasma-irradiated PE exhibits an apparent sextet spectrum, which is virtually identical with that of γ-irradiated PE at 77 K. It was found with the aid of systematic computer simulations, however, that the room temperature ESR spectrum consists of three kinds of spectral components: a sextet spectrum (I) as a major spectrum, a septet spectrum (II), and a smeared-out broad line (III). The sextet and septet spectra were assigned to the midchain alkyl radical, $-CH_2\dot{C}HCH_2-$, and the allylic radical, $-CH_2\dot{C}HCH{=}CHCH_2-$, respectively, as in the case of those in γ-irradiated PE. The smeared-out broad line, thought to be an intermediate level of conversion to a broad single line, was assigned to an immobilized dangling-bond site (DBS) at the surface cross-linked region, not to a polyenyl radical, $-CH_2\dot{C}H(CH{=}CH)_nCH_2-$, as in most studies of γ-irradiated PE. This indicates that studies of temperature-dependent ESR spectra of peroxy radical probe as a direct evidence of the molecular motion of a linear PE chain should be carefully discussed. The observation of a well-defined sextet spectrum of plasma-irradiated PE at room temperature can be ascribed to the fact that the radical formation of PE has been achieved with a brief plasma irradiation using the sample which is completely unsaturated bond-free. Thus, the nature of radical formation of PE was found to be reflected by the presence or absence of unsaturated bonds in the virgin sample in a very sensitive manner.

Introduction

Polyethylene (PE) is one of the most well-investigated polymers concerning radicals generated by high-energy radiation such as X-ray and γ-ray irradiation. A number of electron spin resonance (ESR) studies of radiation-induced radicals of PE, both high-density PE[1] and low-density PE,[2] have been reported. This reflects, in part, interest in the high degree of technical importance of PE.

The effect of ultraviolet light on polymers is also of practical importance, e.g., for the outdoor stability of plastics, elastomers, and fibers. Thus, UV-induced radical formation in PE has also been extensively studied.[3]

It is known that a midchain alkyl radical, $-CH_2\dot{C}HCH_2-$, is formed in irradiated PE at 77 K as a primary product.[1,2] The ESR spectrum of the midchain alkyl radical consists of six hyperfine structure lines (sextet) with a total width of ca. 16.2 mT. When the temperature is raised to room temperature, the sextet spectrum is converted to seven hyperfine structure lines (septet), assigned to an allylic radical, $-CH_2\dot{C}HCH{=}CHCH_2-$. Thus, γ-irradiation and UV irradiation of PE at room temperature afford only an allylic radical. On comparatively large doses, polyenyl radicals (dienyl, trienyl, tetraenyl, etc.), $-CH_2\dot{C}H(CH{=}CH)_nCH_2-$, are believed to be formed also in PE. Polyenyl radicals are usually obtained with different polyene chain lengths. When the radiation dose is increased, the number of polyenyl radicals with large values of *n* also increases. The ESR spectra of these polyenyl radicals are known to be a broad single line. It is also known that the allylic radical undergoes UV-induced photorearrangements to give different types of alkyl radicals such as $-CH{=}CHCH_2\dot{C}HCH_2-$ or $CH_3\dot{C}HCH_2-$, depending on the UV irradiation conditions.[4] It should be noted, however, that several authors have described a significant extent of cross-linking on γ-irradiation even at 77 K.[1c,e,i,j]

On the other hand, plasma irradiation can provide a different phase of study for polymer radicals. One of the characteristics of plasma irradiation is the effective energy transfer to a solid surface to create stable free radicals on a variety of polymer surfaces.[5] Plasma-induced surface radicals thus formed permit reactions for surface modifications in several different ways such as CASING (cross-linking by activated species of inert gas), surface graft and/or block copolymerizations, and incorporation of functional groups. All these techniques are referred to as plasma treatment.[5]

Although the importance of these surface radicals has often been emphasized to understand the nature of plasma treatment, detailed studies on the characterization of such plasma-induced surface radicals and the kinetics for the radical formation have not been worked out. Thus, we have undertaken plasma irradiation studies of a variety of polymers, both synthetic and natural, to explore the molecular mechanism of plasma treatment; the radicals formed were studied by ESR, coupled with systematic computer simulations, temperature annealing, the corresponding mechanoradical formation, and theoretical considerations based on molecular orbital calculations. Results for several polymers have already been reported.[6,7]

One of the advantages of plasma irradiation over other types of radiation for the study of polymer radicals is that the radical formation can be achieved with a brief plasma duration by a simple experimental apparatus such as those we have devised.[6] This method makes it possible not only to study the polymer radicals without a significant change of polymer morphology but also to follow readily the ESR kinetics for the radical formation, so that we can carry out systematic computer simulations with a higher credibility.

Although a number of papers have dealt with the nature of plasma treatment of PE for surface modifications,[8] plasma-induced PE radicals have not yet been studied.

We report the first detailed account of plasma-induced PE radicals studied by ESR coupled with systematic computer simulations. We also discuss the special features of plasma-induced PE radicals in comparison with those produced by high-energy irradiations.

Experimental Section

Materials. PE (high density) is commercially available, but all commercially available PE shows the presence of unsaturated

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bonds (vinylene, carbonyl groups, etc.) by FT-IR spectral measurements. Therefore, PE was purified by dissolving it (2 g) in hot xylene (50 mL, 100 °C) and then precipitating it in a large excess of methanol (1 L). The precipitated PE was collected by filtration and dried in vacuo at 60 °C for 3 days. This procedure was repeated at least twice until disappearance of unsaturated bonds was confirmed by FT-IR spectral measurement. The PE thus obtained was screened with a 200-mesh sieve. The mean particle size was measured in 4% NH$_4$SCN–MEK (methyl ethyl ketone) by a Coulter counter (Model TA-2, Coulter Electronics Inc.), from which the specific surface area was determined: 0.27 ($\mu m^2 \times 10^4$). The X-ray powder diffraction pattern measurement (Rigaku RAD-1C) indicated ca. 85–90% crystallinity of the PE surface, deduced from a comparison of the integrated peak area of the crystalline peak and the halo pattern area of the amorphous regions. The degree of crystallinity remained unchanged before and after plasma irradiation within the limits of detection by X-ray powder diffraction pattern measurement.

Plasma Irradiation and ESR Spectral Measurement. The unsaturated bond-free PE powder (20 mg) was placed in a specially-designed ampule (30-mm i.d., 100 mm long) connected with a capillary tube (2-mm i.d.) at the uppermost part of the ampule, and the ampule was filled with argon gas and sealed (0.5 Torr). Then the plasma state of argon was sustained during agitation of the samples by a radio-frequency discharge of inductive coupling at 13.56 MHz with a prescribed power and duration. The ESR spectral measurements were performed while turning the ampule upside down at appropriate intervals. The procedure is essentially the same as that reported earlier.[6]

The experimental design for plasma irradiation in a flow system of argon gas is essentially the same as that for the plasma polymerization experiment reported previously.[9]

The ESR spectral intensity was determined by double integration. The radical concentration (spin numbers/cm^2) was calculated from the spectral intensities with the aid of calibration lines obtained from the spectral intensity of a poly(methyl methacrylate) (PMMA) powdered sample impregnated with DPPH. Measurements of g values were made relative to the fourth signal from the lower magnetic field (g = 1.981) of Mn^{2+} in magnesium oxide (MgO). ESR spectra were recorded by a JES-RE1X (JEOL) spectrometer with X-band and 100-kHz field modulation. Care was taken to ensure that no saturation occurred and that the line shape was not distorted by an excessive modulation amplitude. 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.

Computer Simulation of ESR Spectra. The computer simulations were performed using a 32-bit microcomputer (NEC PC9801FA). The simulated spectra were obtained from Gaussian functions by iteratively fitting spectroscopic parameters (g value, line width at half-height (HV), hyperfine splitting constant (HSC), and relative peak intensity) with the observed spectra digitized through an A/D converter according to a nonlinear least squares method.[6c] The simulation programs were fabricated so as to include the effect of g-factor anisotropy and/or α-hydrogen anisotropy on the line shape of the powder spectra according to Kneubühl's equation and Cochran's equation, respectively.[10]

To assist the simulation procedure, we have also fabricated a program for obtaining the difference spectrum by subtracting one observed spectrum from another.

Results

Observed Room Temperature ESR Spectra of Plasma-Irradiated PE. The progressive changes of the room temperature ESR spectra of plasma-irradiated powdered PE with various plasma durations are shown in Figure 1, together with the corresponding simulated spectra.

It is seen that even less than several seconds of plasma irradiation is long enough to detect the radicals formed. The room temperature ESR spectrum of plasma-induced radicals of PE shows a well-defined sextet spectrum, but not with a binomial intensity distribution. It is apparent that the spectral intensity increases as the plasma duration increases, but the sextet spectral pattern has gradually changed, especially characterized by a lowering of the peak height of the fourth line from the left relative to that of the third line.

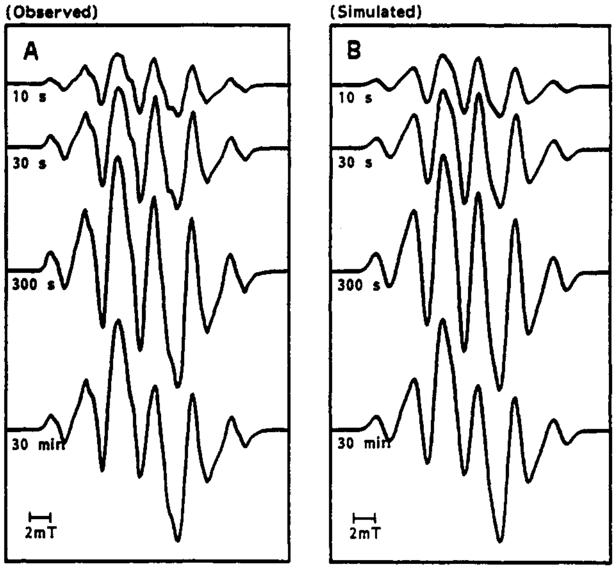


Figure 1. Observed and simulated ESR spectra of Ar-plasma-irradiated PE powder for various durations.

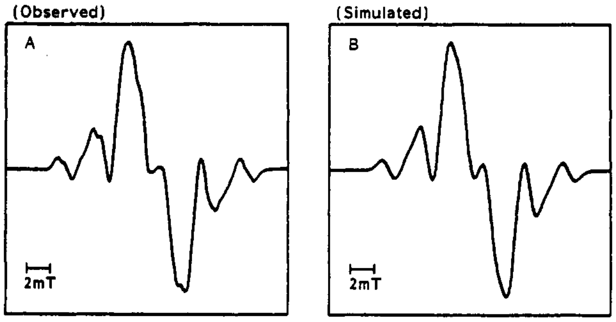


Figure 2. Observed and simulated ESR spectra of 2-h Ar-plasma-irradiated PE powder in a flow system. The simulated spectrum consists of a sextet (I), a septet (II), and a smeared-out broad line (III) with the ratio of 32:33:35.

We note that the main spectral features of PE, especially for the sample plasma-irradiated for 300 s, are very similar to the low-temperature (77 K) ESR spectra of γ-irradiated PE with a comparatively large dose;[1,2] also, the ESR spectral measurement at low temperature (−130 °C) of plasma-irradiated PE (300 s) did not show any appreciable change in spectral pattern except for natural enhancement of the peak intensity (due to changes in Boltzmann's distribution).

Further plasma duration resulted in weakening of the discharge glow under the present plasma operational conditions, apparently caused by an increase in gas pressure in the ampule reactor due to an evolved gas (vide infra). Finally, sustaining the plasma state became difficult (ca. 1 h). Thus, we also conducted plasma irradiation in a flow system to study further spectral changes.

Figure 2 shows the ESR spectrum of PE plasma-irradiated for 2 h under an argon flow system (ca. 0.5 Torr with a flow rate of ca. 50 mL/min). It can be seen that the spectral features have been considerably distorted (compared with the spectrum shown in Figure 1) characterized by an increase in the peak intensity of the central lines, although the spectra with shorter plasma duration were essentially identical with those in a closed system as shown in Figure 1.

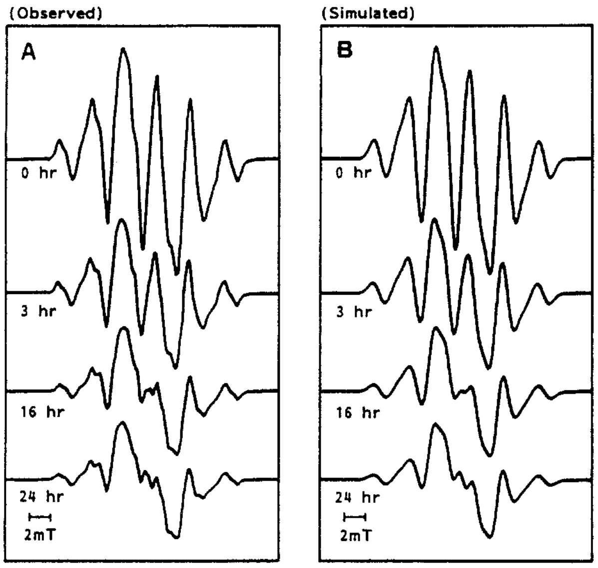


Figure 3. Progressive ESR spectral changes on standing at room temperature of PE powder plasma-irradiated for 3 min together with the corresponding simulated spectra.

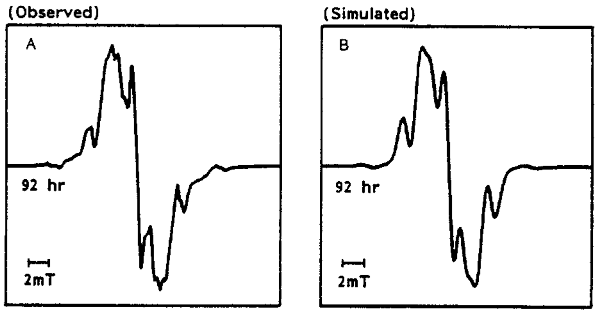


Figure 4. Observed and simulated ESR spectra after standing for 92 h at room temperature of PE powder plasma-irradiated for 3 min.

ESR Spectral Changes on Standing at Room Temperature. Figure 3 shows a series of ESR spectra of a sample plasma-irradiated for 3 min on standing at room temperature together with the corresponding simulated spectra. It is seen that the spectral pattern has gradually changed with a decrease in the total spectral intensity, but in a different manner from those in the course of plasma irradiation. On standing at room temperature for 92 h, the spectrum shown in Figure 4 was finally obtained. After that, the spectral pattern persisted unchanged on further standing. This indicates that the ESR spectrum observed in plasma-irradiated PE is from overlapping spectra of more than one component spectrum derived from stable and less-stable radicals.

Simulated Spectra. The simulations of powdered PE radicals produced by γ-irradiation have been intensively studied. Anisotropic effects of α-hydrogen[1f] as well as temperature-dependent β-hydrogen coupling constants in terms of a twisted configuration and the exchange of two β-hydrogens due to the hindered oscillation around the C_α–C_β bond have also been studied.[1p,w] Furthermore, an attempt has been made to simulate the spectra under the consideration of the difference in the lamellar surface and inner crystalline region.[1x] No simulated spectrum showing a complete fit, however, has yet been obtained, as far as we are aware. It has also been reported that α-hydrogen anisotropic interaction in powdered PE radicals is small even at low temperature because of the motional narrowing.[1p]

We also have attempted to simulate the spectra of plasma-irradiated PE and include the effects of the anisotropic interaction of α-hydrogen. The result, however, was not much different from the present simulated spectra. Such an effect was easily blurred due to broadening of the width of the individual peak. So, we decided to simulate the present spectra using only isotropic lines for simplicity. We believe that systematic simulations using isotropic lines can provide a sufficiently fundamental insight into the nature of radicals formed in PE.

The corresponding simulated spectra are shown in Figures 1B–4B, respectively. It can be seen that all the observed spectral features have been satisfactorily reproduced by the present simulations. Figure 5 shows representative component spectra of the simulated spectra.

The simulated spectra consist principally of three kinds of component spectra: a sextet spectrum (I), a septet spectrum (II), and a smeared-out broad line (III), thought to be intermediate-level conversion to a broad single line. All these simulated spectra were obtained from the same component spectra but with different ratios.

The ESR spectroscopic parameters for a representative selection of the component spectra, I, II, and III, in the simulated spectra are as follows: $g = 2.0037$, $H_\alpha = 2.19$ mT (1 H), and $H_\beta = 3.22$ mT (4 H) for the sextet and $g = 2.0037$, $H_\alpha = 1.77$ mT (2 H), $H_\alpha' = 0.58$ mT (1 H), and $H_\beta = 1.82$ mT (4 H) for the septet. An outline of a smeared-out broad line (III) ($g = 2.0036$) was approximated by a single broad line ($\Sigma H = 9.38$ mT) with a small amount of a triplet of doublets (2.30 and 1.39 mT).

Note that this smeared-out broad line has converted to a single broad line spectrum with approximately the same value of total line width in the simulated spectrum (Figure 2) in PE plasma-irradiated for 2 h in a flow system.

Figure 6 shows the progressive changes of the three component spectral intensities in the simulated spectra in the course of plasma irradiation (Figure 6A) and on standing at room temperature (Figure 6B).

It is seen from Figure 6A that the spectral intensity, due to components II and III parabolically increases as plasma duration increases, while the sextet spectral intensity shows a maximum at the irradiation for ca. 10 min and then begins to decrease. This captures the essential reason for the changes in the observed spectral pattern in the course of plasma irradiation (see Figure 1).

On the other hand, it is seen from Figure 6B that only the sextet component spectrum gradually decreases in intensity, while the other two spectral intensities remain nearly unchanged, demonstrating that the decrease in the total spectral intensity is caused only by instability of the sextet spectrum. The decay of the sextet spectrum was found to follow a diffusion-controlled kinetics, as in many cases of γ-irradiation.[11] Thus, the simulated spectrum shown in Figure 4B consisted of only two component spectra, II and III.

Structural Assignments of Radicals and Their Reactions. In the studies of γ-irradiated PE, the sextet spectrum (I) and septet spectrum (II) have already been assigned to the mid-chain alkyl radical (1) and the allylic radical (2), respectively.[1,2] The smeared-out broad line (within 30-min irradiation) and/or single broad line (with longer plasma irradiation) apparently corresponds to polyenyl radicals previously assigned in the studies of PE with high-energy irradiation. However, on the basis of the rationale given later, we are strongly inclined to consider that the smeared-out (or single) broad line spectrum should be assigned to immobilized dangling bond sites (DBS) (3) at the surface cross-linked portion (vide infra).

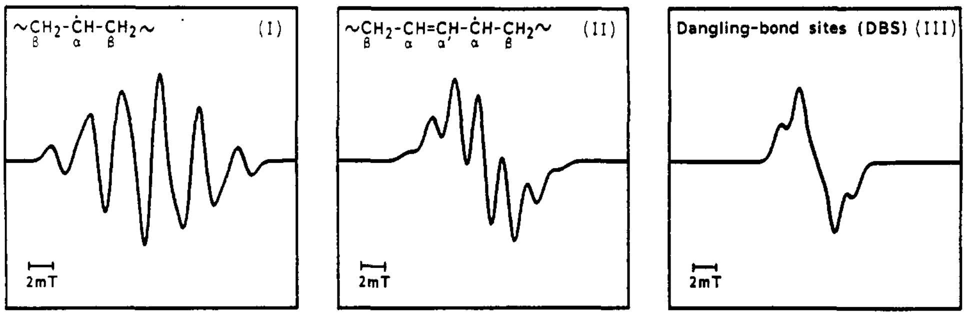


Figure 5. Representative spectral features for the three component spectra I, II, and III in the simulated spectra.

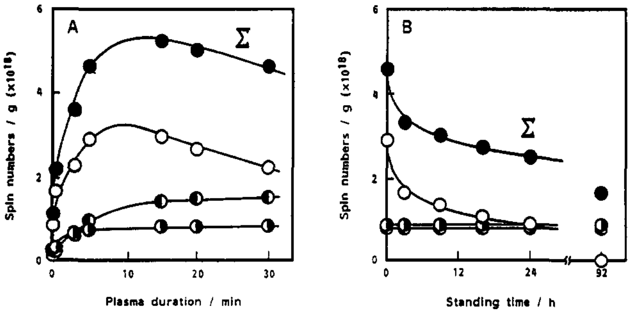


Figure 6. Simulated progressive changes in component spectra in Ar-plasma-irradiated PE powder: (A) on plasma duration; (B) on standing at room temperature [(●) total; (○) sextet; (◐) septet; (◑) DBS].

Discussion

Comparison of Observed Sextet Spectrum between Plasma Irradiation and γ-Irradiation. The representative sextet ESR spectrum of PE γ-irradiated at low temperature (77 K) has been assigned to a single midchain alkyl radical.[1o] The spectral features are nearly identical with that of 30-min plasma-irradiated PE, including the relative peak height of the fourth line to the third line (Figure 1).

In plasma-irradiated PE, however, well-defined sextet spectra have been observed even at room temperature, and the systematic computer simulation disclosed that such observed sextet spectra consisted of three components. Thus, the component sextet spectral feature in the simulated spectrum is different in detail from the observed sextet spectrum, which is characterized by the larger peak height of the fourth line compared with that of the third line, although the component septet spectrum in the simulated spectrum is nearly identical with the observed septet spectrum of γ-irradiated PE (30-Mrad irradiation followed by heating at 50 °C).[1u]

There exists an example for such a type of room temperature sextet spectra of γ-irradiated PE, when solution-grown polycrystalline PE was used.[1p] We believe that the difference stems from the presence or absence of vinylene bonds in virgin PE used for γ-irradiation.

Likewise, the observation of well-defined sextet spectra of plasma-irradiated PE at room temperature may be ascribed to the fact that the radical formation in PE can be achieved with a brief plasma irradiation using the sample which is completely unsaturated bond-free. In fact, the room temperature ESR spectrum shown in Figure 7 was obtained on only 3-min plasma irradiation of commercial PE (unpurified) (the ratio of component spectra I, II, and III was ca. 43:30:27 based on the simulated spectrum),[12] which is nearly identical with those obtained by room temperature γ-irradiation, as well as that of 30-min plasma-irradiated PE (Figure 1).

Structural Assignment of Broad Single-Line Spectrum. There seems to exist some paradox in the structural assignment of the single broad line spectrum. Some authors assigned it to linear polyenyl radicals of the polymer main chain, while other authors have considered it to be dangling-bond sites (DBS) at the cross-linked portion.[1c,e,i,j] The assignment to the polyenyl radicals, at least in part, was supported by the UV spectral measurements of γ-irradiated PE, associated with the changes in the total width of the broad single line ESR spectra.[3a,13]

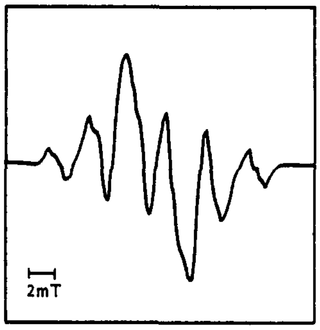


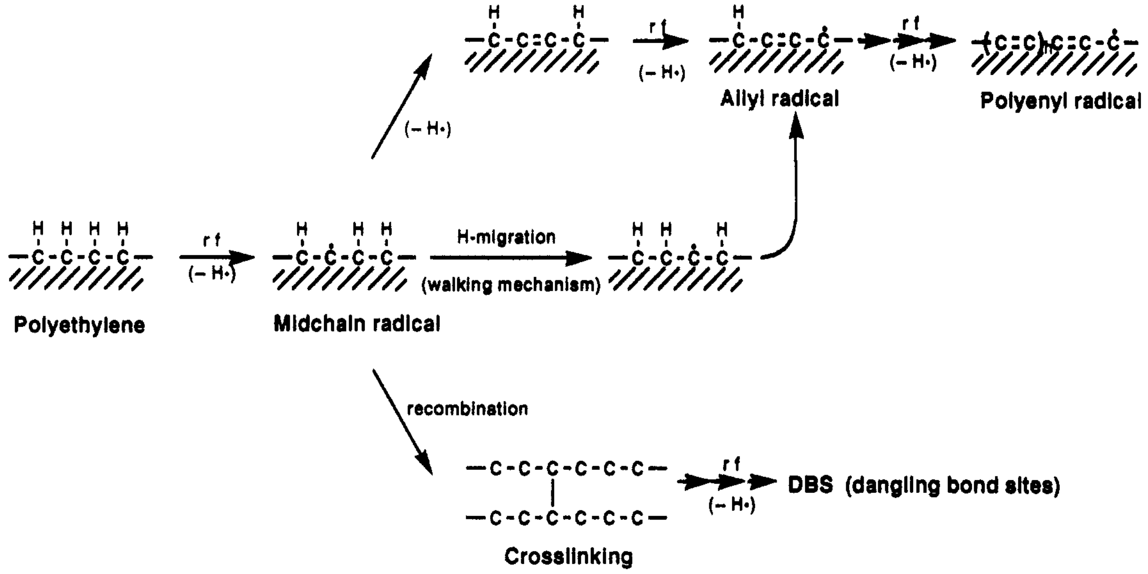
Figure 7. Observed ESR spectra of commercial PE powder Ar-plasma-irradiated for 3 min.

However, in light of the results of a series of studies on plasma-induced radicals of several kinds of synthetic polymers reported previously,[6,7] the smeared-out broad line spectrum and/or a broad single-line spectrum should be assigned to immobilized DBS at the surface cross-linked network as in the case of other polymers, which incorporates a variety of chemical structures including conjugated and nonconjugated radical centers, and are of no discrete structure. This is further substantiated by the fact that the initially observed contour of the ESR spectrum of 300-s plasma-irradiated PE (Figure 1) has been largely distorted toward the single broad line spectrum in pattern by alternatively repeating plasma irradiation (40 W, 10 min) and heat treatment (at ca. 100 °C, 20 min) (four times) as a result of accumulation of surface cross-linked region.

The formation of a highly cross-linked network on the polymer surface by plasma irradiation can be considered to be a kind of plasma polymerization[14] starting from solid organic materials. In fact, a considerable amount of insoluble material is also formed on plasma-irradiated PE with a comparatively longer duration as a result of changes of the polymer surface to a highly cross-linked network containing a larger quantity of higher alkyl radicals. This leads to a decrease in the peak-to-peak width of the broad single line in the ESR spectra of the DBS and accounts also for the changes in the UV spectra.

Furthermore, it is a well-known fact that plasma-polymerized thin films contain a large amount of trapped free radicals[14] which have been considered not to be discrete organic free radicals but to be immobilized DBS in the highly cross-linked network.[15] The ESR spectra of these centers show a broad single line similar to those shown in γ-irradiated polymers.[6,7,9,14]

Scheme I



Nature of Plasma-Induced PE Radicals. We can summarize the formation of plasma-induced PE radicals according to Scheme I. Plasma irradiation causes hydrogen atom elimination to produce midchain alkyl radicals, as in the case of γ-irradiation. There seem to be three available pathway for the alkyl radicals.

First, a β-hydrogen may be eliminated to give a vinylene group in the polymer main chain. The formation of a vinylene group facilitates a hydrogen atom elimination at the vicinal position of the vinylene group, resulting in the formation of stable allylic radicals, and finally polyenyl radicals in a formal sense. The second channel is a hydrogen migration. This continues to occur until the resulting radical migrates to the vicinal position of the vinylene group ending up with the formation of allylic radical. The third channel is radical–radical coupling and/or the reaction of the radical with unsaturated bonds (from a vinylene group to polyenyl groups) to lead to the formation of the cross-linked portion.[16] Repetition of all the above reactions produces the highly cross-linked network at the polymer surface containing the immobilized DBS at the polymer surface.

Reaction with Oxygen at Room Temperature. It is a well-known fact that most polymer radicals produced by high-energy irradiation,[17] including plasma irradiation,[6,7] are rapidly converted, in contact with oxygen, into the corresponding peroxy radicals, and the ESR spectra can be observed at room temperature.

However, exposure of plasma-irradiated PE to air at room temperature did not give the ESR spectra of peroxy radicals, unlike most other polymers, but the ESR spectra did show only the decrease in the spectral intensity due to instability of the peroxy radical formed, which undergoes a rapid chain termination reaction through the hydroperoxide, consuming several moles of oxygens.[18] This implies that various oxygen-derived functional groups to the PE surface are readily incorporated from a single center and then lead to very high efficiency of the plasma-induced surface modifications, such as introduction of surface wettability.

Conclusion

The conclusions drawn from the present study can be summarized as follows: It was found that even less than several seconds of plasma duration is long enough to produce a detectable amount of surface radicals of PE, and well-defined sextet spectra were observed even at room temperature on plasma-irradiated PE, which are superficially similar to those by high-energy irradiation. The result is of interest since the sextet spectra of γ-irradiated PE have been observed only at low temperature (77 K) in most cases.

The observation of well-defined sextet spectra of plasma-irradiated PE at room temperature can be ascribed to the fact that the radical formation of PE can be achieved with a brief plasma irradiation using a sample which is completely unsaturated bond-free. Thus, the nature of radical formation of PE was found to be affected by the presence or absence of unsaturated bonds in the virgin sample in a very sensitive manner.

The systematic computer simulation disclosed that such observed sextet spectra consist of three kinds of radicals, midchain alkyl radical, allylic radical as discrete radical species, and a considerable amount of DBS at the cross-linked portion.

On the basis of the fact that γ-irradiated PE has shown ESR spectra similar to that of plasma-irradiated PE, it can be reasonably assumed that DBS had also been produced in γ-irradiated PE. This indicates that studies of temperature-dependent ESR spectra of peroxy probe in γ-irradiated PE as a direct evidence of the molecular motion of the linear PE chain should be carefully discussed.

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