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Electron Spin Resonance Study of the Special Features of Plasma-Induced Radicals and Their Corresponding Peroxy Radicals in Polytetrafluoroethylene

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ABSTRACT: Plasma-induced polytetrafluoroethylene (PTFE) radicals were first studied by electron spin resonance (ESR). The room temperature ESR spectrum of plasma-irradiated powdered PTFE consists of three kinds of spectral components: double quintet (3.2 and 8.7 mT) as a major spectrum, a triplet (1.4 mT) with broad lateral peaks due to hyperfine anisotropy, and smeared-out broad line. The double quintet and triplet were assigned to the mid-chain radical, $-CF_2-\dot{C}F-CF_2-$, and the end-chain radical, $-CF_2\dot{C}F_2$, respectively. 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 at the cross-linked portion. It has also been shown that the effect of plasma irradiation on radical formation of PTFE was much smaller than on hydrocarbon polymers due to the much larger dissociation energy of the C–F bond over that of the C–H bond (e.g. PTFE; $k = 4.3 \times 10^{12}$ spin cm^{-2} min^{-1}, polyethylene (PE); $k = 1.9 \times 10^{14}$ spin cm^{-2} min^{-1} for initial rate of radical formation at 40 W). When the plasma-irradiated PTFE was exposed to air, peroxy radicals were rapidly formed. They were markedly stable for a long period of time at room temperature due to the absence of hydrogens in PTFE which could undergo chain termination reactions through the hydroperoxide. It was difficult to isolate completely each of the component radicals formed because of the presence of durable dangling-bond sites. Thus, in view of the fact that the ESR spectra of the γ-irradiated PTFE are superficially similar to that of plasma-irradiated PTFE, we suggest that the study of molecular motion by use of a peroxy radical probe in PTFE should take into account the effect of the cross-linkings.

Introduction

Electron spin resonance (ESR) spectra of free radicals of polytetrafluoroethylene (PTFE) (commercially known as Teflon) produced by X-ray irradiation were first reported in 1955.[1] Since then a number of ESR studies of radiation-induced PTFE radicals have been reported.[2-8] This reflects, in part, interest in the high degree of technical importance of PTFE. It has been shown that the room temperature ESR spectra of γ-irradiated PTFE consist mainly of an isotropic double quintet (I) with hyperfine splitting constants (HSC) of ca. 2.5 and 9.0 mT as a major component spectrum, accompanied by a small amount of triplet (II) with HSC of 1.4 mT.[3-8] Several authors have also reported the presence of a "smeared-out" broad line (III) in the spectra of γ-irradiated PTFE.[3,4] The double quintet (I) was assigned to the mid-chain radical, $-CF_2-\dot{C}F-CF_2-$ (**1**), produced by elimination of a fluorine atom from the polymer chain. The triplet (II) was first assigned to an oxygen-centered radical, $-CF_2-\dot{O}$.[4,5] It is now firmly established, however, that the triplet spectrum (II) is only the central component lines of a "triplet of triplets", arising from the end-chain radical, $-CF_2-\dot{C}F_2$ (**2**), and the two β-fluorine atoms are responsible for the observed hyperfine splitting.[7] This was further substantiated by the fact that the end-chain radical (**2**) of PTFE is also produced by mechanical fracture under anaerobic conditions.[9] The characterization of the smeared-out broad line (III), however, has been left out of this account.

The ESR study on the nature of peroxy radicals derived from irradiated PTFE has been more intensively carried out[10-23] and has shown them to be effective probes for elucidating molecular motion in solids by incomplete averaging of *g* anisotropy in both peroxy radicals, the mid-chain peroxy radical (**1P**) and the end-chain peroxy radicals (**2P**),[14,15,20-23] each of which was produced by temperature annealing of irradiated PTFE followed by air exposure (**1P**) and the ensuing photochemical reactions of **1P** followed by air exposure (**2P**), respectively.[7,8] However, the detailed ESR study of PTFE radicals and the kinetics for their formation coupled with computer simulations has not yet been reported, to our knowledge.

On the other hand, plasma irradiation can provide a different phase of study of polymer radicals. One of the characteristics of plasma irradiation is the effective energy transfer to solid surface to create free radicals on a variety of polymer surfaces.[24]

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 polymerizations, and incorporation of functional groups. All these techniques are referred to as plasma treatment, which has been rapidly developing since the 1970s.[24] Thus, there is a growing body of literature concerned with the plasma treatment of a variety of polymers, several of which involve fluorine-containing polymers. Yasuda et al. have found in an XPS study that a considerable amount of fluorine is eliminated from the PTFE surface.[25] Hirotsu et al. have also reported that the effect of plasma exposure on the changes of the surface properties of several perfluorinated polymers with respect to some experimental factors, and the resulting surface properties as well as the plasma susceptibility were also discussed.[26]

However, despite the fact that the surface reactions are initiated by the radicals produced by plasma irradiation, none of the papers dealt with the detailed ESR studies on the characterization of such plasma-induced surface radicals and their kinetics in any polymer including fluorine-containing polymers. We believe that the study of the nature of plasma-induced polymer radicals and their formation is of fundamental significance for the full understanding of the nature of plasma treatment. Thus,

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we have recently reported a detailed ESR study on plasma-induced polystyrene[27] and polymethacrylate radicals[28-30] as representative examples of cross-linkable and degradable polymers upon radiation influence.

One of the advantages of plasma irradiation over other types of irradiation used in the study of polymer radicals is that radical formation can be achieved with a brief plasma duration by simple experimental apparatus such as those we have devised.[27-30] 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 radical formation.

In this paper, we report for the first time a detailed ESR study coupled with systematic computer simulations of plasma-induced PTFE radicals and their corresponding peroxy radicals.

Experimental Section

Materials. Powdered polytetrafluoroethylene (PTFE) is commercially available (Mitsui Fluorochemicals, Ltd., Japan) and was screened with a 200-mesh sieve. The powdered PTFE thus obtained was used for plasma irradiation after it was dried at 60 °C in vacuo for 3 days. The mean particle size was measured in 4% NH_4SCN-MEK (methyl ethyl ketone) by a Coulter counter (Model TA-2, Coulter Electronics Inc.), and the specific surface area was determined: 1.30×10^4 μm^2 for PTFE and 0.27×10^4 μm^2 for PE.

Plasma Irradiation and ESR Spectral Measurements. Powdered PTFE (50 mg) was placed in a specially designed ampule (30 mm i.d., 100 mm long) connected with 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 with agitation of samples by a radio frequency discharge of inductive coupling at 13.56 MHz with a prescribed power and duration. After the plasma irradiation, the ampule was inverted and the ESR spectral measurements were performed while turning the ampule upside down. The procedure is essentially the same as that reported earlier.[29]

The ESR spectral intensity was determined by double integration. The radical concentration (spin number cm^{-2}) was calculated from the spectral intensities with the aid of calibration lines which were obtained from the spectral intensity of a 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 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 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 PC9801RA). The simulated spectra were obtained by iteratively fitting spectroscopic parameters (g value, line width at half height (HV), hyperfine splitting constant (HSC), and relative peak intensity) with observed spectra digitized via A/D converter according to a nonlinear least-squares method.[27,29] For simulated spectra of peroxy radicals and end-chain radicals, the simulation programs were fabricated so as to include the effect of an anisotropy of g factor and HSC on the line shape according to Kneubühl's equation[31] and Cochran's equation,[32] respectively.

Results and Discussion

ESR Spectra of Plasma-Induced PTFE Radicals. The progressive changes of ESR spectra of plasma-irradiated powdered PTFE with various plasma durations are shown in Figure 1a.

It is seen that the spectral intensity increases as the plasma duration increases, but the spectral pattern remained nearly unchanged.

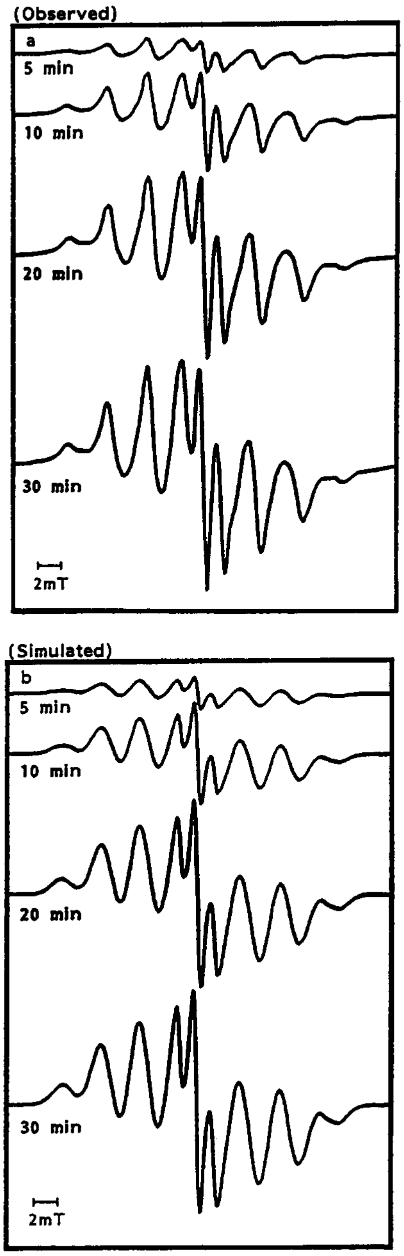

Figure 1. Observed (a) and simulated ESR spectra (b) of Ar plasma irradiated PTFE powders with various duration.

We note that, although the ESR spectra of plasma-irradiated PTFE are rather complicated, the main spectral features are similar, but not identical, to those of γ-irradiated PTFE, and the spectra persisted unchanged for a long period of time on standing at room temperature under anaerobic conditions.

We have already performed a number of plasma irradiations on a wide variety of polymers including hydrocarbons such as high-density polyethylene (PE), and the details will be reported later in a separate paper. The special features of PTFE radicals, however, may be best described by its comparison with that of PE. Thus, part of the results of PE are also briefly presented here for comparison.

Figure 2 shows the progressive changes of total radical concentrations of plasma-irradiated PTFE together with those of PE.

It is seen that the nature of radical formation in PTFE is very different from that of PE, and it is very clear that the effect of plasma irradiation on PTFE is much smaller than that of PE. The ratio between PTFE and PE in the

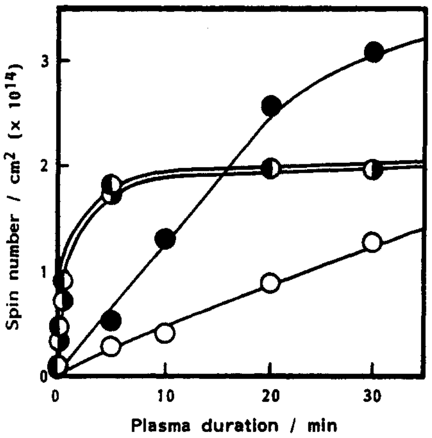

Figure 2. Progressive changes in total spin concentration per unit surface area of Ar plasma irradiated PTFE and PE powders determined by double integration: (●) PTFE (80 W); (○) (40 W); (◐) PE (40 W); and (◑) PE (20 W).

initial rate of radical formation per unit surface area was ca. 1:50 ($k = 4.3 \times 10^{12}$ spin cm^{-2} min^{-1} for PTFE and $k = 1.9 \times 10^{14}$ spin cm^{-2} min^{-1} for PE at 40 W). Thus, PTFE requires more than several minutes of plasma duration to produce a detectable amount of radicals. This is in sharp contrast to the fact that even less than several seconds of plasma duration on a variety of non-fluorine-containing organic polymers as well as PE gave enough radicals to be detected by conventional ESR measurements. This result apparently stems from the larger dissociation energy of the C–F bond compared to the C–H bond.

Simulated Spectra. Since these observed spectra are outlines of multicomponent spectra, one can make kinetic analyses only after the spectral components have been elucidated. Thus, we have systematically conducted the computer simulations of the spectral changes in an interrelated manner. The corresponding simulated spectra are shown in Figure 1b.

It can be seen from Figure 1b that the observed spectral features have been satisfactorily reproduced by the present simulations. Figure 3 shows the representative spectral components of the simulated spectra.

Thus, the simulated spectra consist principally of three kinds of spectra: an isotropic double quintet (I) as a major component spectrum, a triplet of triplets (a triplet with broad lateral peaks) (II), and a smeared-out broad line (III). The best simulated spectra were obtained when Gaussian and Lorentzian functions were used for I and II, respectively. An outline of a smeared-out broad line of III was approximated by a summation of five Gaussian curves, including a small amount of a single line at the central part (ca. 2–3% in intensity).

The ESR spectroscopic parameters for a representative selection of component spectra, I, II, and III, in simulated spectra are as follows: $g = 2.0045$; $a_\alpha = 8.55$ (1F), $a_\beta = 3.15$ (4F), and $a_\gamma = 0.32$ (4F) mT for I; $g = 2.0053$; $a_{\alpha1} = 6.90$, $a_{\alpha2} = 8.10$, $a_{\alpha3} = 10.5$ (2F), and $a_\beta = 1.43$ (2F) mT for II; and $g =$ ca. 2.0051 for III.

The double quintet (I) and the triplet of triplets spectrum (II) can be unambiguously assigned to the mid-chain radical (**1**) and the end-chain radical (**2**), respectively. The spectral feature of **2** is apparently caused by α-fluorine hyperfine anisotropy with quasi-axial symmetry due to free rotation of carbon–carbon bond.

It is difficult to obtain direct evidence (e.g. examination of insoluble surface layer formation) for the formation of the cross-linked portion of plasma-irradiated PTFE, unlike non-fluorine-containing polymers, because of intrinsic insolubility and general intractability of untreated PTFE. Schonhorn and Hansen have shown, however, that plasma irradiation on PTFE also caused a sizable amount of CASING, similar to the case of various other polymers, on the basis of the enhanced adhesive joint strength.[33] Thus, the smeared-out broad line spectrum (III) can be ascribed to the outline of multicomponent spectra derived from dangling-bond sites (DBS) (structureless radical) (**3**), at the cross-linked surface, which should incorporate a variety of chemical structures including conjugated and nonconjugated radical centers. The small single line peak with a small peak-to-peak width (ΔH_{msl}) at the central part of III should belong to the radical center which has essentially no neighboring fluorine atom capable of coupling with the free radical electron. The same type of single line with a relatively small value of ΔH_{msl} in tertiary carbon-centered DBS is well known to be observed in amorphous carbon and diamond thin films formed by plasma polymerizations.[34,35]

The formation of DBS in several other polymers, including radiation-induced degradable polymers, has also been reported[27–30] and seems to be a common feature in plasma-irradiated polymers.

It should be mentioned, however, that the ESR spectra of most plasma-induced DBS exhibit only an isotropic broad single line. We believe that the large value of HSC intrinsic to a fluorine nucleus as well as the vast difference in HSC between α-fluorine and β-fluorine (ca. 7.5–9.0 mT for α-fluorine and ca. 1.5–2.5 mT for β-fluorine coupling[36]) is responsible for the poorly defined hyperfine splitting with unequal spacings observed in the present DBS (**3**), and such lines may be due to an intermediate level of conversion to a broad single line.

The presence of this kind of DBS was further confirmed by the following experimental fact: Since heating the plasma-irradiated PTFE at 300 °C for 10 min caused nearly complete dissipation of two component radicals, **1** and **2**, and incomplete dissipation of DBS (**3**), an attempt has been made to create a larger amount of cross-linked surface by alternately repeating plasma irradiation (80 W, 30 min) and heat treatment (at 300 °C for 10 min) several times. The spectrum finally obtained is shown in Figure 4.

In fact, the initially observed contour of the ESR spectrum of plasma-irradiated PTFE has been considerably distorted with a considerable decrease in the total spectral intensity after thus repetition (12 times) as a result of accumulation of surface cross-linked portion.

The progressive changes of the ratio of component spectra on these treatments were deduced from the respective simulated spectra, and the result is shown in Figure 5.

It is seen that the ratio of DBS (**3**) to the total spectral intensity gradually increased (up to ca. 60%) with decrease in that of **1**, reinforcing clearly the formation of DBS. We emphasize here that the distorted spectrum (Figure 4) cannot be obtained from plasma irradiation of PTFE after only heat treatment of native PTFE at 300 °C for 5 h.

ESR Kinetics. The progressive changes of the component spectral intensities of plasma-induced PTFE radicals deduced from the simulated spectra are shown in Figure 6.

It is seen that the intensities of all component spectra increase almost linearly at initial stages of plasma duration (k_1:k_2:k_3 = 8.6:1.0:5.6), but the spectral intensities of I and III tend to level off at longer plasma duration. One of the noteworthy features evidenced here may be the formation of much larger amount of DBS (**3**) than that of the end-

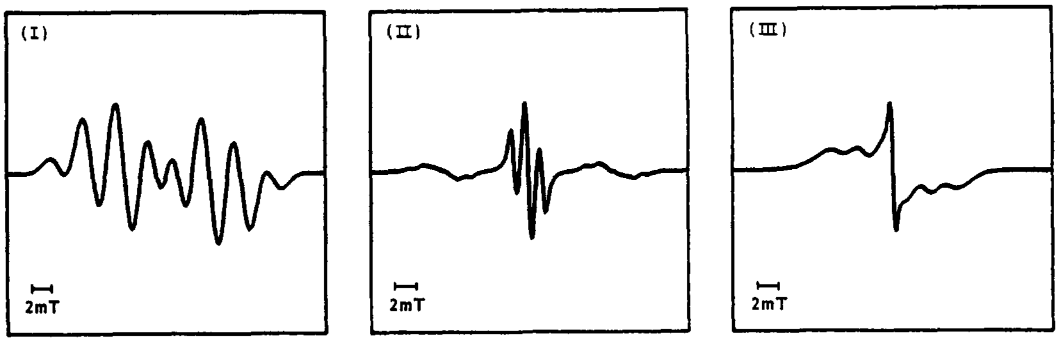

Figure 3. Representative spectral features for three component spectra in simulated spectra.

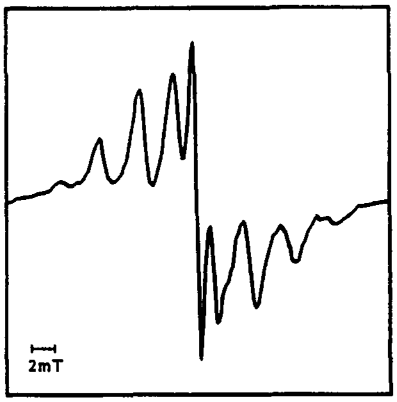

Figure 4. Observed ESR spectrum of Ar plasma irradiated sample of PTFE obtained after alternating plasma irradiation (80 W, 30 min) and temperature annealing (300 °C, 10 min) 12 times.

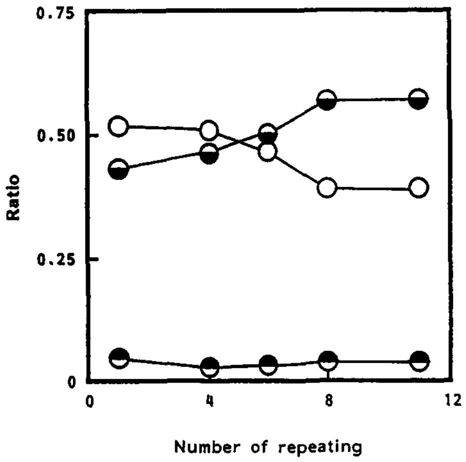

Figure 5. Progressive changes in the relative ratio of the spectral components of plasma-induced PTFE radicals on the alternating plasma irradiation and temperature annealing deduced from simulated spectra: (○) double quintet; (◓) triplet of triplets; (◒) DBS.

chain radical (2). We believe this is the first detailed spectral analysis of PTFE radicals and of the nature of progressive changes of its formation produced by any kind of radiation method.

Corresponding Peroxy Radical Formation and Its Reactions. There exist abundant examples that when the free radicals produced in polymers are in contact with oxygen, the corresponding peroxy radicals are formed. In fact, it has been shown that the present PTFE radicals were quite rapidly reacted with oxygen to give the corresponding peroxy radicals, and the room temperature ESR spectrum is shown in Figure 7.

One of the special features of the PTFE peroxy radical formation distinct from those of other plasma-irradiated polymers is that the peroxy radicals of PTFE are extremely stable for a long period of time at room temperature. The ESR spectral intensity, therefore, is nearly the same as that of the original plasma-induced PTFE radicals, whereas, in most other polymers, such an intensity decreases to 30–40% of the original polymer radicals even immediately after exposure to air, except for polyacrylamide (PAAM)[30] and polymethacrylamide (PMAAM),[37] having strong interpolymer hydrogen-bonding networks. The stability of PTFE peroxy radicals can be ascribed to the absence of any abstractable hydrogen in PTFE to undergo the chain termination reactions leading to stable diamagnetic molecules through the hydroperoxide.

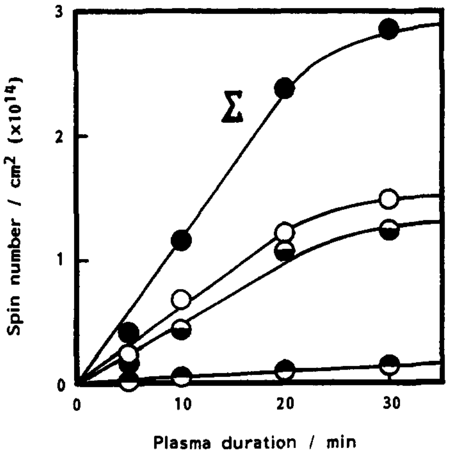

Figure 6. Simulated progressive changes in component spectra of Ar plasma irradiated PTFE: (●) total; (○) double quintet; (◓) triplet of triplets; and (◒) DBS.

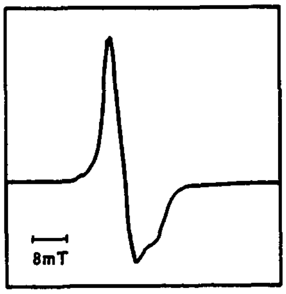

Figure 7. Observed ESR spectrum of the peroxy radical obtained by exposure of plasma-irradiated PTFE to air.

The anisotropic line shape of ESR spectrum of the peroxy radicals in Figure 7 appears to be an outline of multicomponent spectra due to the presence of three types of radicals, mid-chain radical (1), end-chain radical (2), and DBS (3), in plasma-irradiated PTFE. An attempt has been made to observe the ESR spectrum of the peroxy radical derived from each component radical.

It has been well documented as stated briefly in the Introduction section that the ESR spectra of the double

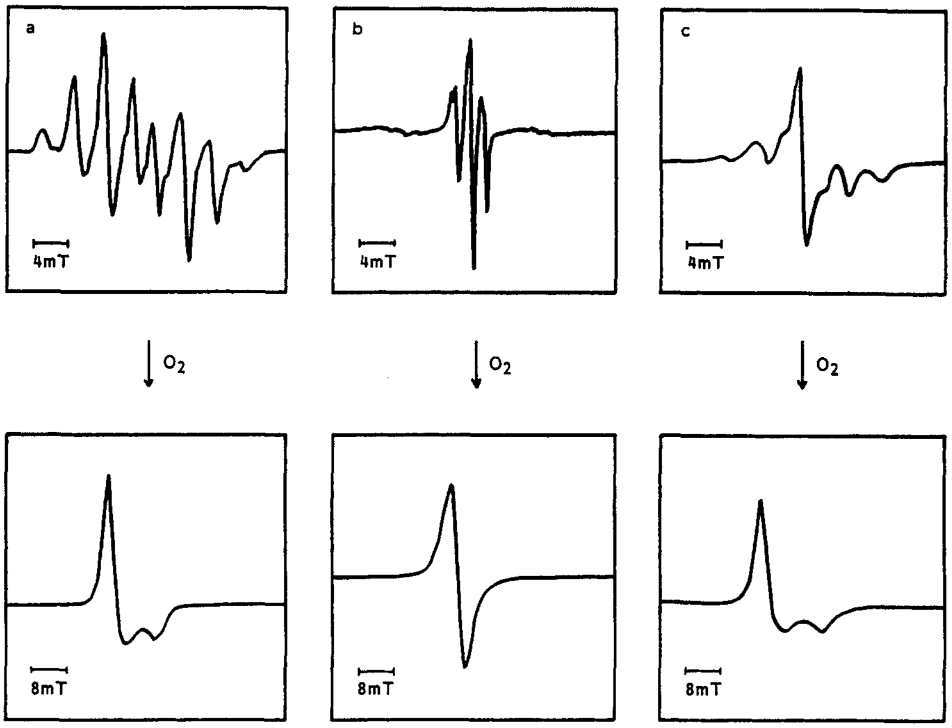

Figure 8. ESR spectra observed with each component radicals of plasma-irradiated PTFE obtained respectively by following the procedure described in the text, and the corresponding peroxy radicals on the exposure to air: (a) for I, (b) for II, and (c) for III.

quintet of mid-chain radical (1) and its corresponding peroxy radical (**1P**) have been obtained by temperature annealing of γ-irradiated PTFE at 200–250 °C followed by oxygen exposure, although the total spectral intensity decreases to a considerable extent on such a heat treatment. And UV irradiation of **1P** with a high-pressure mercury lamp at room temperature have produced the end-chain radical (2), which further gives the corresponding peroxy radical (**2P**) on exposure to air.[7,8] In fact, following the above-mentioned procedure on plasma-irradiated PTFE, the similar results were also obtained as shown in Figure 8.

It is seen that the room temperature ESR spectra of the two peroxy radicals, **1P** and **2P**, derived from the radicals, 1 and 2, are different from each other, although both peroxy radicals exhibited the ESR spectra almost identical to each other at 77 K as in the case of those from γ-irradiated PTFE. The spectrum of **1P** has been shown to be of a partial g averaging spectral pattern due to a chain–axis rotational motion, although incomplete (g_1 = 2.0061, g_2 = 2.0227, g_3 = 2.0231), and that of **2P** gave an isotropic single line with complete averaging of g anisotropy due to the random molecular motion (g_{iso} = 2.0166).

However, one may question as to the fate of DBS on the temperature annealing and/or the peroxy radicals derived from the DBS, which have never been discussed before. In fact, although the gross feature of double quintet spectrum (I) shown in Figure 8a is superficially similar to the simulated spectrum shown in Figure 3, the computer simulation clearly indicated that a large amount of smeared-out broad line of DBS (**3**) (ca. 68% of total intensity) are superimposed in the spectrum shown in Figure 8a.

In order to gain further insight into this point, the plasma-irradiated PTFE sample was heated at 300 °C for 10 min, the ESR spectrum of which shows a small amount of smeared-out broad line of DBS (Figure 8c), and then exposed to air.

It is seen that the ESR spectral feature of the resulting peroxy radical is similar to that of **1P** with incomplete g averaging, (g_1 = 2.0022, g_2 = 2.0230, g_3 = 2.0237), but it should be assigned to the peroxy radical derived from DBS **3P**. **3P** was also shown to be photolabile to give a triplet spectrum similar to the central part of a triplet of triplets, (II), of end-chain radical (**2**). This fact indicates that the spectrum of **3P** derived from DBS (**3**) is easy to escape detection in the ESR spectra of PTFE peroxy radicals, **1P** and **2P**, and the ESR spectrum thought to be a single peroxy radical, **1P** or **2P**, may also contain **3P** as a spectral component.

Our results seem very significant in connection with the study of the molecular motion of PTFE using the peroxy radical probe obtained from γ-irradiated PTFE.

A number of ESR studies of peroxy radical formed by temperature annealing of γ-irradiated PTFE as the molecular motion probe have been reported by many authors invoking two kinds of peroxy radicals, mid-chain peroxy radical (**1P**) and end-chain peroxy radical (**2P**),[14,15,20-23] obtained from the procedure as described above, despite the fact that several authors have reported the presence of the smeared-out broad line in γ-irradiated PTFE, indicating the occurrence of cross-linking.[3,4] Furthermore, the ESR observation including temperature dependence 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 native linear PTFE main chain. In fact, the reported activation energies of molecular motions of PTFE considerably varies with authors.[15,21] We are strongly inclined to consider that the difference in the extent of formation of cross-linked portion, due to the difference in the conditions of temperature annealing as well as radiation dose, is responsible for the observed difference.

One of the interesting and noteworthy reactions exhibited by PTFE peroxy radicals may involve the photoconversion of **1P** to **2**, which is also related to the radiation-induced degradability of PTFE, while the radical **2P** was found to be inactive on UV irradiation.[7,8]

We have performed the INDO/S-CI excited-state calculations to discriminate the difference in the photoreactivity between **1P** and **2P**, using $CF_3–CF_2–CF(O\dot{O})–CF_2–CF_3$ and $CF_3–CF_2–CF_2O\dot{O}$ as model compounds for PTFE peroxy radicals. Although we defer to present the details, the computed CI states (configuration interaction) responsible for the excited doublet states in the transition energy of UV region have clearly shown the great propensity of the carbon–carbon bond scission at the β-position to the peroxy radical of **1P** leading to the formation of end-chain radical (**2**), whereas that of **2P** did not show the similar tendency in the nature of such an electronic structure of the excited state, in accord with the experimental fact.

Conclusion

The findings gained from the present investigation can be summarized as follows: it is evident that PTFE requires a much longer plasma duration to produce a detectable amount of surface radicals than other hydrocarbon polymers such as PE. Computer simulations disclosed that the room temperature ESR spectra of plasma-irradiated PTFE consist of three kinds of radicals, **1** and **2**, as discrete radical species, and a considerable amount of DBS (**3**) at the cross-linked portion. However, it was difficult to obtain a completely single component spectrum of each radical, although the gross features of the spectra are superficially similar to the corresponding spectrum of a single radical as in the case of those of γ-irradiation.

When plasma-irradiated PTFE was exposed to air, all the plasma-induced radicals were rapidly converted to peroxy radicals to show the ESR spectrum of a mixture of the three peroxy radicals. In view of the fact that the gross features of the observed ESR spectra of plasma-irradiated PTFE are similar to those observed by γ-irradiation, it can be reasonably assumed that DBS had also been produced in γ-irradiated PTFE. This indicates that the studies of temperature-dependent ESR spectra of peroxy probe as a direct evidence of the molecular motion of linear PTFE chain should be carefully discussed.

Peroxy radicals of hydrocarbon polymers dissipate, consuming several moles of oxygen during the course of complex chain termination reactions through the hydroperoxide. This implies incorporation of various oxygen-derived functional groups to the polymer surface from a single radical center and then leads to very high efficiency of the plasma-induced surface modifications, such as introduction of surface wettability. On the other hand, PTFE peroxy radicals do not readily undergo chain termination reactions, due to the lack of abstractable hydrogen so they are extremely stable at room temperature. The low efficiency of plasma treatment of PTFE, therefore, must be discussed from the absence of such chain termination reactions, which can be considered to be the essential reason for the XPS result of lower efficiency of oxygen atom incorporation to PTFE surface reported by Yasuda.[25] The similar trend has also been observed with surface properties of plasma-treated PTFE on the basis of the contact angles and the critical surface tensions.[26]

Thus, the present results suggest that although one may be able to make an efficient surface graft polymerization for improvement of PTFE surface properties, so long as higher plasma power with longer plasma duration is employed to generate a larger amount of surface radical centers, it may be difficult to introduce high surface wettability to the plasma-irradiated PTFE surface through the reaction with oxygen to such a compatible extent as those on other hydrocarbon polymers due to the above-mentioned intrinsic nature of PTFE peroxy radicals.

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