Electron Spin Resonance of Peroxy Radicals in Gamma-irradiated Polytetrafluoroethylene

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Quite a few ESR investigations have been carried out on polytetrafluoroethylene (PTFE) irradiated by gamma- or X-rays.[1-8] When irradiation and measurements have been made in the absence of oxygen, the ESR spectra of PTFE specimens have been found to consist mainly of double quintets, arising from the fluoroalkyl radical, $-CF_2\dot{C}FCF_2-$, produced by the removal of a fluorine atom from the polymer chain. Some measurements of the oriented samples have also been made; they have given information concerning the relation between the polymer structure and the ESR spectra.[7]

The double-quintets signal disappeared, giving an asymmetrical spectrum, when PTFE specimens irradiated in vacuo were aged in air.[3] The kinetics of this reaction was analyzed under the assumptions: $\dot{R}+O_2 \rightleftarrows R\dot{O}_2$, and $[\dot{R}]+[R\dot{O}_2]=[\dot{R}]_0$, where $\dot{R}$ and $R\dot{O}_2$ represent fluoroalkyl radical and its peroxy radical respectively and $[\dot{R}]_0$ was the initial concentration.[9] On the other hand, it has been reported[8] that the ESR spectra of peroxy radicals can be separated into two components. One of them is associated with the peroxy radical derived from the aforesaid fluoroalkyl radical, while the other is ascribed to the peroxy radical originating in the chain scission-type radical.

This paper intends to pretent an examination of the transition process from the spectrum observed in vacuo to the spectrum which is obtained in a specimen aged in air, considering two sorts of peroxy radicals, and also an examination of the stability of these peroxy radicals under heat treatment. The nature of the peroxy radicals will be discussed in the light of data on the orientation dependence of their ESR spectra and the crystalline arrangement of PTFE.

Experimental

All the ESR spectra were measured at a frequency of 24000 Mc./sec. with a superheterodyne-type spectrometer,[10] which displays the first derivative

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1) W. B. Ard, H. Shield and W. Gordy, *J. Chem. Phys.*, **23**, 1727 (1955).

2) H. N. Rexrord and W. Gordy, ibid., **30**, 399 (1959).

3) Yu. D. Tsvetkov, N. N. Boubnov, M. A. Makulskii, Yu. S. Lazurkin and V. V. Voevodskii, *Doklady Akad. Nauk, SSSR*, **122**, 1053 (1958).

4) N. Tamura, *J. Phys. Soc. Japan*, **15**, 943 (1960).

5) Ya. S. Lebedev, Yu. D. Tsvetkov, and V. V. Voevodskii, *Optics and Spectroscopy*, **8**, 426 (1960).

6) N. Tamura, *J. Chem. Phys.*, **37**, 479 (1962).

7) D. W. Ovenall, ibid., **38**, 2448 (1963).

8) T. Matsugashita and K. Shinohara, ibid., **35**, 1652 (1961).

9) Yu. C. Tsvetkov, Ya. S. Lebedev and V. V. Voevodskii, *Vyskomol. Soedinenie*, **1**, 1519 (1959); ibid., **1**, 1634 (1959).

10) This spectrometer was designed and constructed by the Applied Electric Laboratory Co. It consists of an automatic frequency-control unit, two 24V10 klystrons, a klystron power supply, a sweep generator an electromagnet, a magnet power supply, and a field scanning unit.

of the resonance curve. Some spectra were recorded as absorption figures with an integrator. For the determination of the correct line width, proton resonance signals at 36.5 Mc./sec. with 100 kc./sec. side bands were recorded. Small quantities of 1,1-diphenyl-2-picrylhydrazyl (DPPH) were employed as a standard for the g-factor and intensity of spectra.

The specimens of PTFE films and powder were supplied by the Daikin Kogyo Co., Ltd. The film, 0.2 mm. thick, had a density of 2.17, and the degree of crystallinity was estimated to be about 55%.[11] In preparing oriented samples, the film was stretched further by using a screw-jacket elongation apparatus up to 200%. All samples were placed in quartz tubes 3 mm. in o. d. In the case of irradiation in vacuo, the samples were sealed off after evacuation with an oil diffusion pump for 24 hr. The irradiation was carried out with Co-60 gamma rays, the intensity of which was about 10^5 rad./hr. the total dose reached up to about 10^7 rad.

Results and Discussion

The ESR Spectrum of Peroxy Radicals in Powder.—The dominating feature of the ESR spectrum in the powder sample irradiated and measured in vacuo is the double quintets. This spectrum shows a slight asymmetry, as a result of the g-anisotropy. This appears more clearly in the present K-band measurement than in the reported X-band spectra.[1-4]

Upon exposure of the sample to oxygen, the double quintets disappear rapidly and new resonance lines build up. This new spectrum gives an appearance of the superposition of two components, one symmetric and the other asymmetric, as may be seen in Fig. 1. Matsugashita and Shinohara obtained the symmetrical signal and the asymmetrical signal, which disappear upon the re-evacuation of the oxygenated sample, at 250°C and 150°C respectively.[8] In the present case, no treatment is required to resolve them. The intensity of the symmetrical component, I_s, is obtained under the assumption that the line shape is Lorentzian. By subtracting I_s from the total intensity, the intensity of the asymmetrical component, I_a, is obtained. If the sample is irradiated in the presence of air, the intensity ratio of the symmetrical component, I_s/I_a, increases by a factor of two.

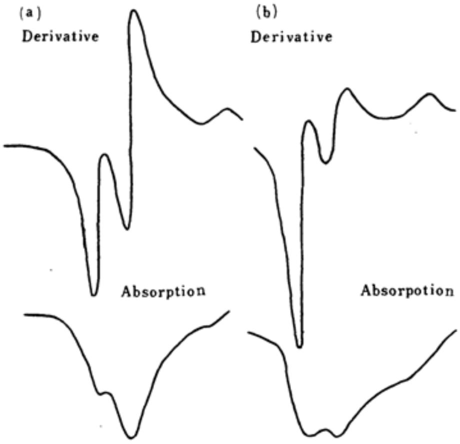

Fig. 1. ESR spectra of peroxy radicals in PTFE powders, (a) irradiated and observed in air, (b) irradiated in vacuo and observed in air.

The Transition Process.—In order to examine the transition process from the spectrum in vacuo to that of oxygenated sample, a small quantity of oxygen is introduced, with a velocity of 10^{-3} cc./min. (reduced to 1 atm.), into a sample tube containing about 30 mg. of PTFE powder irradiated in vacuo. The variation of the spectrum with time is shown in Fig. 2. A decrease in the double quintets accompanies the increase in the asymmetrical component. The intensity of each component in the double quintets, I_{dq}, is expressed by:

$$I_{dq}=I^{\circ}_{dq}\exp(-\lambda t) \quad (1)$$

where I°_{dq} is the initial intensity of each component of the double quintets, t is the time in minutes, and λ is a constant (0.035/min. in the present case). The intensity of the asymmetrical component in the oxygenated spectrum, I_p, is given by:

$$I_p=I_p^{\infty}\{1-\exp(-\lambda t)\} \quad (2)$$

where I_p^{∞} is the intensity of the asymmetrical component after equilibrium, and λ is the same constant in Eq. 1. The initial intensity

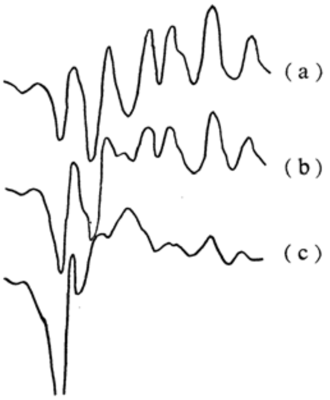

Fig. 2. Changes in shape of ESR spectrum in PTFE powder, upon exposure of oxygen.
(a) Before admission of oxygen
(b) Some 5 min. after admission of oxygen
(c) Some 15 min. after admission of oxygen

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[11] P. E. Thomas, J. F. Lontl, C. A. Sperati and J. L. McPherson, *SPE Journal*, June, 89 (1956).

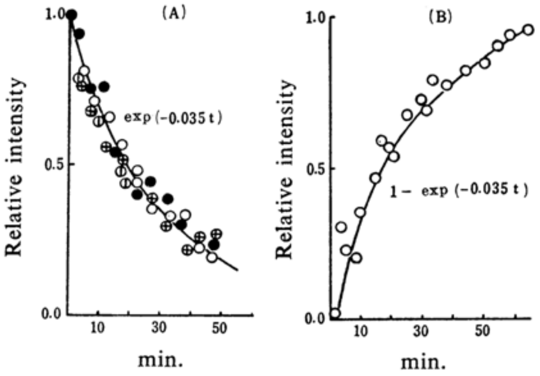

Fig. 3. Intensity variation of ESR spectrum in irradiated PTFE powder, as a function of time after exposure of air, (A) relative intensity of each component of double quintets, (B) relative intensity of an asymmetrical signal of peroxy radicals.

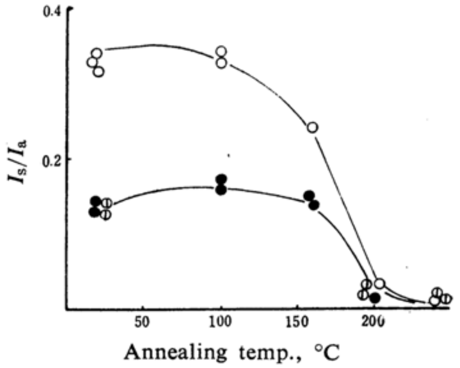

Fig. 4. Effect of anneal temperature on the intensity ratio of a symmetrical component to an asymmetrical one, I_s/I_a, in ESR spectrum of PTFE peroxy radicals.

	Irrad.	Anneal.
○	in air	in air
●	in vac.	in air
⦶	in vac.	in vac.

of the double quintets agrees with the final intensity of the asymmetrical component.

These results accord with those of Tsvetkov, Lebedev and Voevodskii,[9] though the present experiment was carried out with samples smaller in size and at lower oxygen pressures. The experiment shows only that the fluoroalkyl radical is converted into the peroxy radical, $-CF_2CF(\dot{O}O)CF_2-$ which gives the asymmetrical component of the ESR spectrum in air, but it does not bring out information about the symmetrical component.

The Thermal Stability of Peroxy Radicals.—The intensity ratio of the symmetrical component to the asymmetrical component changes upon heat treatment. In the experiment, three groups of PTFE powder were used: (1) irradiated and heated in air, (2) irradiated and heated in vacuo before aging in air, and (3) irradiated in vacuo and heated in air. The change in I_s/I_a when it is heated for 30 min. at various temperatures is shown in Fig. 4. It is evident that the radical which gives the symmetrical component is unstable at temperatures above 150°C; the I_s/I_a ratio decreases rapidly at an annealing temperature of 150°C, though the I_a intensity does not change greatly until 250°C.

It has bee reported[12] that one of the peaks of the mechanical loss tangent of crystalline PTFE exists near 130°C in the dynamical measurement at 1 c./sec. This shows the presence of a configurational transition of the material in this temperature region.[13] The decomposition of the radical species which give a symmetrical spectrum must be related to this transition. From the symmetrical profile, this "heat sensitive radical" must be trapped in the region where the motional freedom of the polymer, for example, vibrational or rotational motion, is large and local order does not exist. The "heat sensitive radical" does not seem to come from the fluoroalkyl radical which gives the double quintets signal, but from radicals of a different type, for example, the type with "carbon-carbon bond" breakage. The scission of the main chain destroys the local order and gives much more motional freedom. The situation holds even after aging in air, so that the peroxy radical derived from the scission-type radical shows a symmetrical spectrum. As the temperature rises beyond 130°C, the chain motion increases and the radicals trapped at the ends of the chains disappear as a result of recombination and decomposition. This estimate accords substantially with that of Matsugashita and Shinohara.

The asymmetrical spectrum, on the contrary, holds even above about 250°C. It must originate from the fluoroalkyl radical trapped in PTFE crystallite.

The Anisotropy of the *g* Factor in an Oriented Sample.—Further investigation of the asymmetric component has been undertarken from the point of view of the angular dependence of its *g* factor. The ESR spectrum of peroxy radicals in oriented films can be resolved into two singlets when the axis of the molecular chain is along the orientation axis. One has a stronger intensity than the other.

The resonance field position of the strong signal changes as a function of the angle between the orientation axis and the external magnetic field; the *g* factor shows a maximum

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12) K. H. Illers and E. Jenckel, *Kolloid-Z.*, **160**, 97 (1958).

13) Y. Wada, *J. Phys. Soc. Japan*, **16**, 1226 (1961).

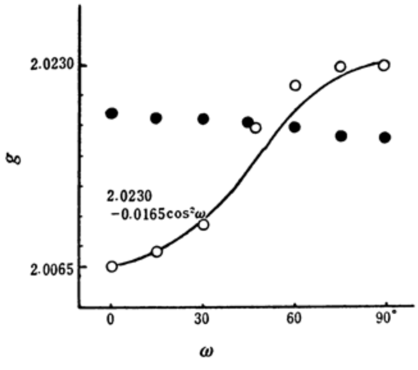

Fig. 5. Variation of g factor of ESR in oriented PTFE films irradiated and observed in air, as a function of the orientation of the sample in the magnetic field.
○ Stronger signal
● Weaker signal

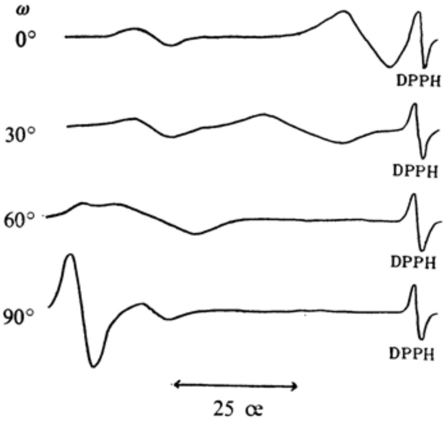

Fig. 5a. Change of the ESR spectrum with the angle, ω, between the orientation of PTFE films and the magnetic field.

value of 2.0230 when the magnetic field is perpendicular to the orientation axis, and it reaches a minimum value of 2.0065 when the magnetic field is parallel to the orientation axis, as may be seen in Fig. 5. The weak signal hardly changes its field position throughout the angle variation. Its g factor, 2.018, agrees with the value obtained from the symmetrical component in the powder spectrum. It becomes evident that the weak signal gives nearly the same profile in both oriented films and powder, while the strong signal appears asymmetric in powder because of its g anisotropy.

The Origin of the *g* Anisotropy—One can consider the origin of the g anisotropy in the oriented sample to be as follows. The fluoroalkyl radical to which the oxygen molecule is attached forms the peroxy radical, $-CF_2CF(\dot{O}O)CF_2-$. To the first approximation it is assumed that the local order of original PTFE does not change markedly during the desertion of the fluorine atom and the insertion of the oxygen molecule. The crystal structure of PTFE is pseudo-hexagonal at room temperature,14) and its C–C chain has a torsion whose period is 6.5 carbon atoms along the crystal c axis (see Fig. 6). Now, we suppose that the oxygen molecule in the defect of the fluorine atom forms a C–O–O bond perpendicular to the crystal c axis. The unpaired electron localized on the oxygen atom has an axially symmetrical distribution around the C–O–O axis. We choose three Cartesian coordinates, (x, y, z), (ξ, η, ζ), and (x', y', z'), connected with each other by the Eulerian angles shown in Fig. 7, where the system x', y', z' is connected with the system (ξ, η, ζ) by three angles, θ, φ and ψ, and where ω is an angle between the ζ axis and the z axis. In these systems we assume that the crystal c

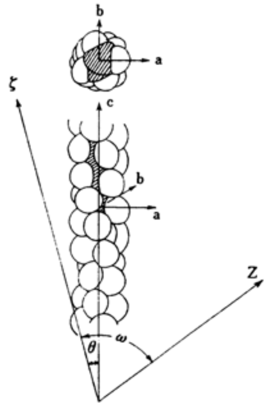

Fig. 6. The crystal structure of polytetrafluoroethylene.
▨ C atom ○ F atom

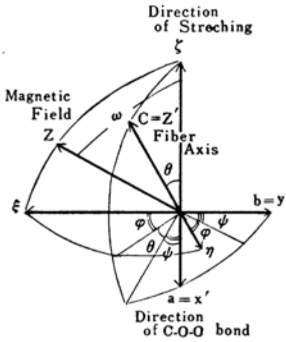

Fig. 7. The relation among three Cartesian coordinate systems, xyz, $\xi\eta\zeta$, and $x'y'z'$.

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14) I. Nitta, "X-sen Kessyogaku," Maruzen, Tokyo (1961).

axis of PTFE is along the z′ axis, and that the x′ axis is approximately in the direction of the C–O–O bond, which is the symmetrical axis of the unpaired electron density. The ζ axis is taken as in the direction of the orientation axis, while the z axis is in the direction of the external magnetic field. Then, the rotation of the ζ axis in the z−x plane about the y axis is expressed only by the angle ω.

If the principal values of the g tensor are g_1, g_2, and g_3, the g factor can be written as follows:

$$g^2=g_1{}^2\alpha^2+g_2{}^2\beta^2+g_3{}^2\gamma^2 \tag{3}$$

where α, β, and γ are the direction cosines of the external magnetic field with respect to the principal axis system. We can assume that g_1 is the g factor along the x′ axis, and that g_2 $(=g_3)$ is perpendicular to it. The direction cosines in Eq. 3 may be calculated easily using the above assumption. The defects of the fluorine atom are distributed at random about the crystal c axis, so that the angles φ and ψ have no definite values. Therefore, we must caluculate the average values of $\alpha^2, \beta^2, \gamma^2$ with respect to the equally-probable distribution of φ and ψ.

$$\langle\alpha^2\rangle, \langle\beta^2\rangle=\frac{1}{4}\{(1+\cos^2\theta)+(1-3\cos^2\theta)\cos^2\omega\}$$
$$\langle\gamma^2\rangle=\frac{1}{2}\{(1-\cos^2\theta)-(1-3\cos^2\theta)\cos^2\omega\} \tag{4}$$

Then,

$$g^2=\frac{1}{4}[\{(g_1{}^2+3g_2{}^2)+(g_1{}^2-g_2{}^2)\cos^2\theta\}$$
$$+\{(g_1{}^2-g_2{}^2)+3(g_2{}^2-g_1{}^2)\cos^2\theta\}\cos^2\omega] \tag{5}$$

For the purpose of comparing the calculated results with the experimental data, it is convenient to introduce the new parameters $g_\parallel$ and $g_\perp$; $g_\parallel$ is the component of g along the crystal c axis, while $g_\perp$ is perpendicular to it: $g_{11}=g_2$, $g_\perp=\sqrt{(g_1{}^2+g_2{}^2)/2}$.

$$g^2=\frac{1}{2}[\{(g_\perp{}^2+g_\parallel{}^2)+(g_\perp{}^2-g_\parallel{}^2)\cos^2\theta\}$$
$$+\{(g_\perp{}^3-g_\parallel{}^2)+3(g_\parallel{}^2-g_\perp{}^2)\cos^2\theta\}\cos^2\omega] \tag{6}$$

Equation 6 shows the axial symmetry of g around the orientation axis. If $\theta=0$, Eq. 6 becomes

$$g^2=g_\perp{}^2+(g_\parallel{}^2-g_\perp{}^2)\cos^2\omega \tag{7}$$

and as a simple approximation; $g\fallingdotseq g_\perp-\Delta g\cos^2\omega$, where $\Delta g=g_\perp-g_\parallel\langle\langle g_\perp, g_\parallel$.

The results shown in Fig. 5 show this axially symmetrical property of the g factor. The deviation of the experimental data from the curve, $g=2.0230-0.0165\cos^2\omega$, suggests the presence of distribution in θ. The values of g_1 and g_2 are estimated as 2.037 and 2.0065 respectively.

If the local order of PTFE does not exist, the average values of $\langle\alpha^2\rangle$, $\langle\beta^2\rangle$, and $\langle\gamma^2\rangle$ in Eq. 4 become 1/3, and the value of the g factor is 2.017, which is in good agreement with the value obtained from the symmetrical component of the ESR spectrum in air.

The spectrum of the powder sample, taken off the symmetrical component, must be composed of the sum of randomly-oriented radicals. It shows a fairly good agreement with the curve obtained from the calculations under the assumptions[15,16] of axial symmetry, a Lorentzian line shape and the random orientation of the crystallites, as Fig. 8 shows.

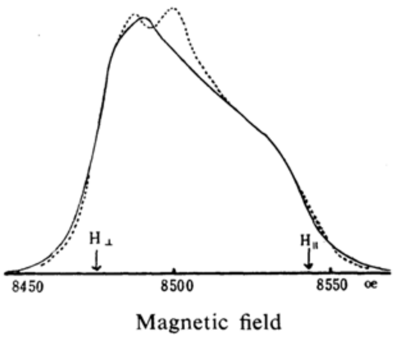

Fig. 8. ESR absorption curve of peroxy radicals in irradiated PTFE powder. Calculated curve obtained from the observed values in oriented sample; $g_\parallel=2.0065$, $g_\perp=2.0230$, and $b=10$ œ. (b: half width at half power.)
—— Calculated ------ Experimental

Summary

In the oriented sample of irradiated PTFE, the ESR spectrum of peroxy radicals consists of two singlets. One of them has an angular dependent g factor: $g=2.0230-0.0165\cos^2\omega$, where ω is an angle between the orientation of the PTFE crystal and the direction of the magnetic field applied. This spectrum shows an asymmetrical profile in a powder sample. It has been interpreted in the light of the crystalline arrangement of PTFE. Additional peroxy radical, which gives an angle-independent ESR signal, is unstable at temperatures above 150°C.

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[15] A. K. Chirkov and A. A. Kokin, *J. Exptl. Theoret. Phys. SSSR*, **39**, 1381 (1961).

[16] J. A. Ibers and J. D. Swalen, *Phys. Rev.*, **127**, 1941 (1962).

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