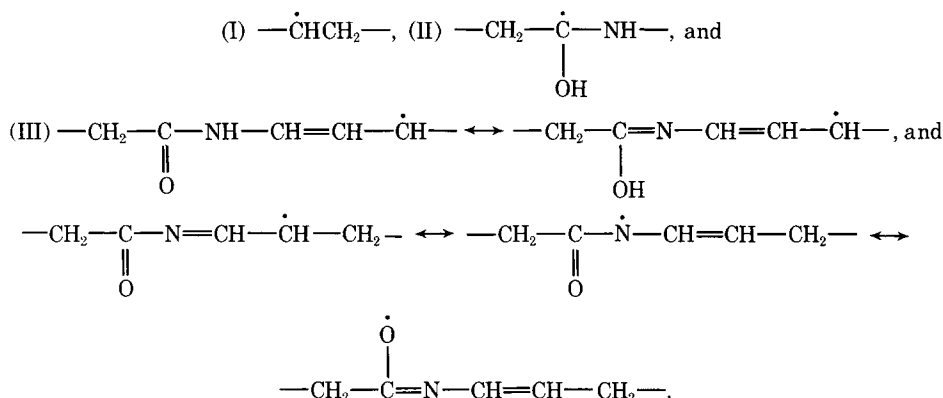


Electron Spin Resonance Study of γ -Irradiated Nylon 6

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Synopsis

The free radicals trapped in oriented nylon 6 filaments after γ -irradiation under vacuum at room temperature were studied by ESR spectroscopy. The ESR spectrum measured after irradiation gradually changed to a broad singlet spectrum with decrease in the intensity. The ESR spectrum consisted of radicals with different orientation effects with respect to the outer magnetic field, and saturation effects in reference to microwave power. The simulation of the ESR spectrum from a Gaussian function gave a better fit to the observed spectrum than the calculation from a Lorentzian function. From the resolution of the spectrum from a Gaussian function, the observed spectrum is generated from three kinds of radicals:



The relative radical concentration for the first, second, and third radical is about 75%, 6%, and 19% of the total radical concentration, respectively. With regard to the stability of the radicals, the third radical shows a comparatively long lifetime. The first and second radicals show almost identical lifetime, and their concentrations reduce to about 40% of the initial value during the 2 days at room temperature.

INTRODUCTION

Abraham and Whiffen¹ detected the presence of free radicals in γ -irradiated polyamide by ESR. Many workers²⁻⁵ have since discussed the radical species and characters in irradiated polyamide. Recently, a least-squares approximation method by a computer has been used for the analysis of the ESR spectrum.⁶⁻⁸ The radical with an α -proton and two β -protons $\text{---}\dot{\text{C}}\text{HCH}_2\text{---}$ has been recognized as dominant for γ -irradiated polyamides at room temperature.

However, two kinds of proposals have been given for the radical sites. One

was a radical generated by hydrogen abstraction from the carbon contiguous to amide nitrogen^{2-4,7,8} $\text{—CONH}\dot{\text{C}}\text{HCH}_2\text{—}$. The second was a radical formed on the carbon adjacent to carbonyl group⁵ $\text{—CH}_2\dot{\text{C}}\text{HCONH—}$. Other kinds of radicals in irradiated polyamides have also been proposed. Shinohara and Ballantine² have proposed a radical with a conjugated system including the amide group for a stable broad singlet spectrum. Graves and Ormerod⁴ have reported the analogous radical as Shinohara and Ballantine.² Kashiwagi³ has suggested a biradical resulting from a C—C main chain scission as another kind of radical. Szöcs et al.⁷ have assigned radicals in the form of $\text{—CH}_2\dot{\text{C}}\text{HCH=CHCONH—}$, and $\text{—CH}_2\dot{\text{C}}(\text{OH})\text{NHCH}_2\text{—}$ to an unresolved spectrum and a triplet spectrum, respectively.

In this paper, characters of the radicals trapped in γ -irradiated nylon 6 filaments are studied by ESR spectroscopy, and the ESR spectrum is resolved into each component by a computer. The radical species and their positions are discussed based on the computation.

EXPERIMENTAL

Materials

Nylon 6 filaments produced by Toray Co., Ltd. were used in this study. The filaments were washed with distilled water several times and extracted with hot benzene for 24 h. After extraction, the filaments were rinsed with methanol and washed with distilled water prior to air-drying. The viscosity-average molecular weight of nylon 6 measured in 85% formic acid⁹ was 1.9×10^4 , and the degree of crystallinity of the sample determined by X-ray diffraction¹⁰ was 40.6%. After the purified filaments were arranged mutually parallel and cut to about 5 mm in length, the well-aligned filaments were stacked in a quartz tube. The sample was evacuated for 24 h and sealed off at 10^{-5} mm Hg before γ -ray irradiation.

ESR Measurement

The sample was irradiated by ^{60}Co γ -rays with an exposure rate of 1.0×10^6 R/h for 1 h at room temperature. The ESR measurements were made using a JES-ME ESR spectrometer with 100-kHz modulation at room temperature. The microwave power was changed from 0.1 mW to 51.2 mW to observe the saturation effects. In order to study the radical anisotropy, the ESR measurements were conducted at various filament orientations with respect to the outer magnetic field. The relative radical concentration of the irradiated sample was determined by the double integration method using strong pitch as standard sample.

Resolution of ESR Spectrum

The ESR spectrum was evaluated by simulation of the experimental spectrum using a HITAC 8800/8700 (OS-7) at the Tokyo University Computer Center. The computer program was written using the least-squares approximation method for the first derivatives of Gaussian (y_G') and Lorentzian (y_L') line

shapes⁶:

$$y_G' = -2 \sum_{i=1}^r \frac{y_{\max,i}}{a_i^2} \sum_{p=0}^{l_i-1} \sum_{q=0}^{m_i-1} \sum_{s=0}^{n_i-1} \binom{l_i-1}{p} \binom{m_i-1}{q} \binom{n_i-1}{s} \\ \times \left[x - x_{0,i} + \left(\frac{l_i-1}{2} - p \right) A_i + \left(\frac{m_i-1}{2} - q \right) B_i + \left(\frac{n_i-1}{2} - s \right) C_i \right] \\ \times \exp \left\{ - \left[x - x_{0,i} + \left(\frac{l_i-1}{2} - p \right) A_i + \left(\frac{m_i-1}{2} - q \right) B_i \right. \right. \\ \left. \left. + \left(\frac{n_i-1}{2} - s \right) C_i \right]^2 / (a_i)^2 \right\} \quad (1)$$

and

$$y_L' = -2 \sum_{i=1}^r a_i^2 y_{\max,i} \sum_{p=0}^{l_i-1} \sum_{q=0}^{m_i-1} \sum_{s=0}^{n_i-1} \binom{l_i-1}{p} \binom{m_i-1}{q} \binom{n_i-1}{s} \\ \times \left[x - x_{0,i} + \left(\frac{l_i-1}{2} - p \right) A_i + \left(\frac{m_i-1}{2} - q \right) B_i + \left(\frac{n_i-1}{2} - s \right) C_i \right] / \\ \left\{ a_i^2 + \left[x - x_{0,i} + \left(\frac{l_i-1}{2} - p \right) A_i + \left(\frac{m_i-1}{2} - q \right) B_i + \left(\frac{n_i-1}{2} - s \right) C_i \right]^2 \right\} \quad (2)$$

where r is the number of free radical species, i is the radical index ($i = 1, 2, \dots, r$), a_i is the line width, $y_{\max,i}$ is the peak height of absorption line, and l_i , m_i , and n_i are numbers of lines resulting from the first, second, and third splittings, respectively. A_i , B_i , and C_i are hyperfine splitting constants for the first, second, and third splittings, respectively, and x_0 is center of the spectrum of the free radical species i .

RESULTS AND DISCUSSION

Saturation Behavior

After 3 h from the γ -irradiation, the ESR measurements were conducted at various microwave powers to study the influence of the trapped radicals. The change of the spectra measured at various microwave powers are shown in Figures 1(a) and 1(b) for the parallel and perpendicular orientations with respect to the outer magnetic field, respectively. Under parallel orientation with respect to the magnetic field, each spectrum measured up to 0.8 mW showed almost the same four-line pattern independent of the change of the microwave power. However, in the range of the microwave power of more than 0.8 mW, the ratio of the absorption of the outside peak to the central part of the spectrum was gradually decreased with an increase in the microwave power. The overall width of the spectrum was slightly narrowed at microwave powers of more than 3.2 mW. Such tendencies were more clearly found under the perpendicular orientation [Fig. 1(b)]. If only one kind of radical species exists in the irradiated nylon 6, the intensity of each peak in the spectrum should be uniformly broadened because of the saturation effect with an increase in the microwave power. Therefore, the saturation behavior found in the ESR spectrum is attributed to overlapping of different saturation behaviors due to different kinds of radical

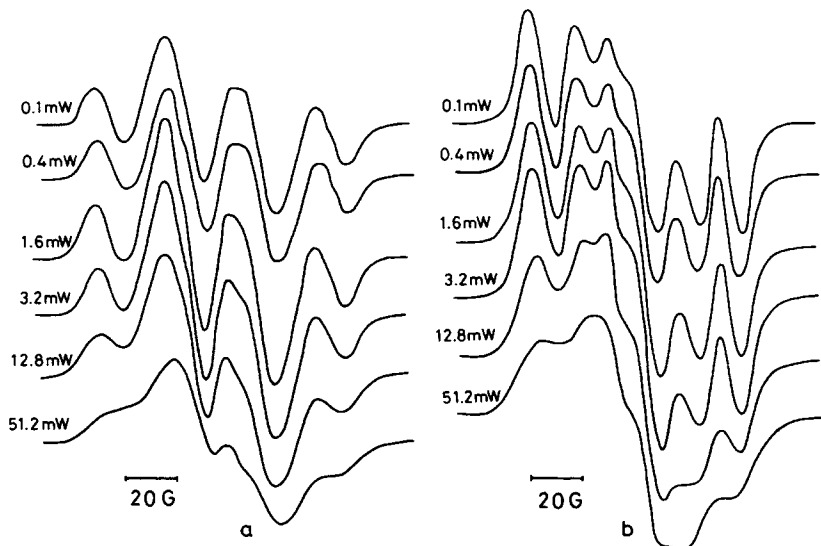


Fig. 1. ESR spectra of γ -irradiated nylon 6 filaments at various microwave powers. (a) Filament axes are parallel to outer magnetic field. (b) Filament axes are perpendicular to outer magnetic field.

species. One is the radical with apparent four-line spectrum at the parallel orientation or six-line spectrum in the case of the perpendicular orientation, and is easily saturated at low microwave power.

Effects of Orientation

The ESR measurements were conducted after 3 h from the irradiation at 0.4-mW microwave power to eliminate the saturation effects. The ESR spectra of irradiated nylon 6 filaments at various angles between the filament axes and the outer magnetic field are shown in Figure 2. The spectrum measured at 0° , namely the filament axes are parallel with respect to the magnetic field, and showed four-lines in appearance. The shape of the spectrum gradually varied with increase in the angle, and a six-line spectrum with incompletely resolved hyperfine structure was observed at 90° . The overall width of the spectra decreased with increase in the angle. The remarkable orientation effects on the spectra are attributed to the interaction of a free radical with an α -proton. Therefore, there is a radical with an α -proton in irradiated nylon 6 filaments. However, the existence of other kinds of radicals may be expected in the irradiated sample, because the spectrum is not symmetrical at each angle.

Effects of Storage Time

The influence of the storage time at room temperature was studied. The measurement was conducted with 0.4-mW microwave power at room temperature for the parallel and perpendicular orientations with respect to the magnetic field. The sample after the measurement was kept in a dark place at room temperature to eliminate change in the radical from light during storage. The changes in the spectra with storage time for the parallel and perpendicular or-

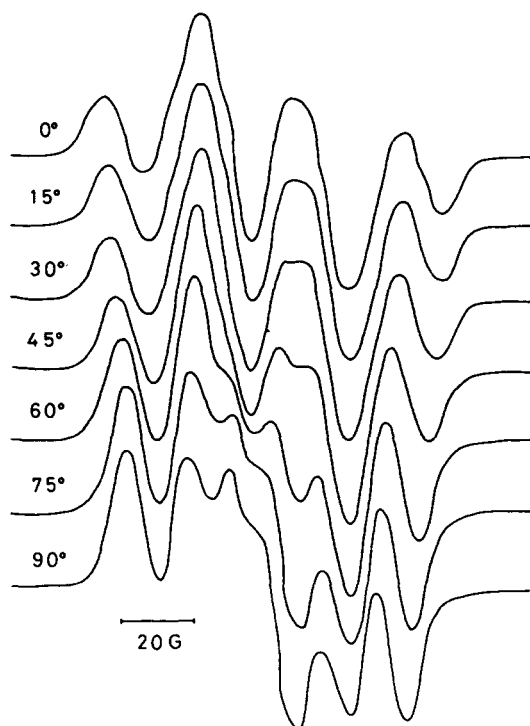


Fig. 2. ESR spectra of γ -irradiated nylon 6 filaments for various orientation of the specimen in outer magnetic field.

orientations are shown in Figures 3(a) and 3(b), respectively. Under parallel orientation with reference to the magnetic field, the apparent four-line spectrum measured after 3 h from the irradiation gradually changed to an almost singlet spectrum with decrease in the overall width as the storage time increased. For perpendicular orientation, the initial unresolved six-line spectrum varied to the apparent singlet in a similar manner as the case of the parallel orientation. The shapes of the spectra after storage for more than 16 days were almost the same, regardless of the filament orientations with respect to the outer magnetic field. The relationship between the time of storage and the normalized radical concentration calculated for the perpendicular orientation is shown in Figure 4. The radical concentration decreased considerably during the storage for the first 3 days, and then decreased gradually. The same relationship was obtained for the parallel orientation with reference to the magnetic field. Therefore, there are at least two kinds of radical species with different lifetimes in irradiated nylon 6; one is the radical with an α -proton, and the other might be the radical without anisotropy in the ESR spectrum. The former is a dominant radical, and a large amount of the radical disappears in the early stage of the storage. However, for the latter, it is difficult to estimate the radical species and their characters from the shape of the spectrum, because the broad singlet spectrum is not symmetrical even after 27 days from the γ -irradiation. Details on the radical species generated in irradiated nylon 6 filaments will be discussed later using a computer.

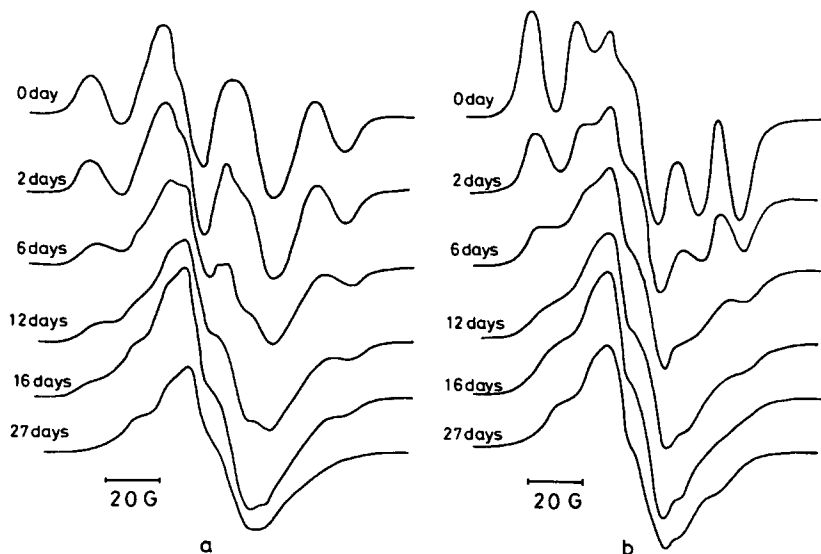


Fig. 3. ESR spectra of γ -irradiated nylon 6 filaments measured after storage at room temperature. (a) Filament axes are parallel to outer magnetic field. (b) Filament axes are perpendicular to outer magnetic field.

Resolution of ESR Spectrum

Assuming that three kinds of radical species exist in irradiated nylon 6 filaments, we tried the resolution of the ESR spectrum measured at 0.4-mW microwave power using a computer. Since the spectrum calculated by a Gaussian function fits the experimental spectrum measured at the parallel orientation with respect to the outer magnetic field more accurately than the spectrum by a Lorentzian function, the simulation of the ESR spectrum was conducted using the Gaussian function. The experimental and the best-fitting calculated spectra for the parallel and perpendicular orientations with reference to the magnetic field are shown in Figures 5(a), 5(b), and 6(a), 6(b), respectively. The calculated spectra were determined under the following combinations: $l_1 = 2, m_1 = 2, n_1 = 2, l_2 = 2, m_2 = 2, n_2 = 1, l_3 = 1, m_3 = 1, n_3 = 1$, respectively. The results of the parameters used in the simulation of the spectra are given in Table I. The mean square residue (s^2) of the parallel orientation was not equal to that of the

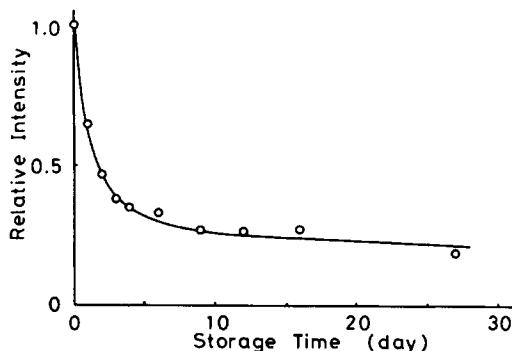


Fig. 4. Decay of radical intensity at room temperature. Measurements carried out at perpendicular orientation with respect to outer magnetic field.

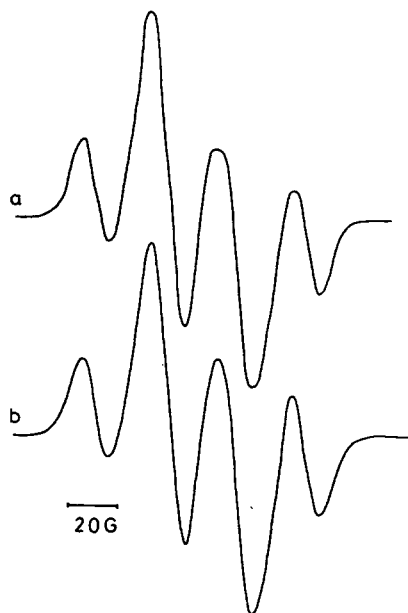


Fig. 5. ESR spectra of γ -irradiated nylon 6 filaments measured at room temperature. Filament axes are parallel to outer magnetic field. (a) Experimental spectrum. (b) Calculated spectrum.

perpendicular orientation. The difference might be due to: (i) the errors in reading the experimental spectrum, (ii) the experimental errors in ESR spectrometer, (iii) the possibility of linear combination of Gaussian and Lorentzian

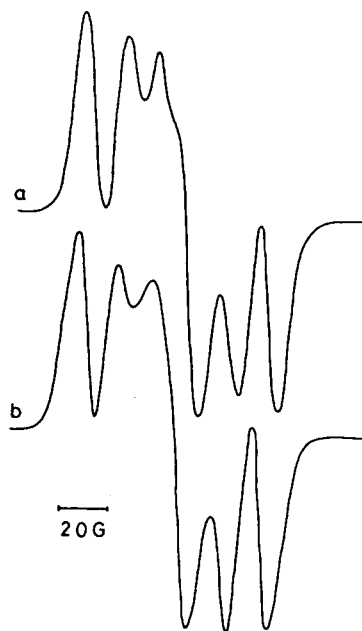


Fig. 6. ESR spectra of γ -irradiated nylon 6 filaments measured at room temperature. Filament axes are perpendicular to outer magnetic field. (a) Experimental spectrum. (b) Calculated spectrum.

TABLE I
Magnetic Parameters of Free Radicals in γ -Irradiated Nylon 6 Filaments for the Day of Irradiation

Sample	i	l_i	m_i	n_i	x_0 (G)	y_{\max} (arbitrary unit)	a_i (G)	A_i (G)	B_i (G)	C_i (G)	s^2 (arbitrary unit)
Parallel	1	2	2	2	3245.4	403.1	9.5	26.8	23.8	33.3	15.4
	2	2	2	1	3243.1	90.7	6.0	23.3	33.8	—	
	3	1	1	1	3245.1	586.1	24.2	—	—	—	
Perpendicular	1	2	2	2	3245.5	913.1	8.3	14.4	22.7	32.5	23.3
	2	2	2	1	3244.6	216.5	5.8	16.8	30.7	—	
	3	1	1	1	3244.1	852.9	17.7	—	—	—	

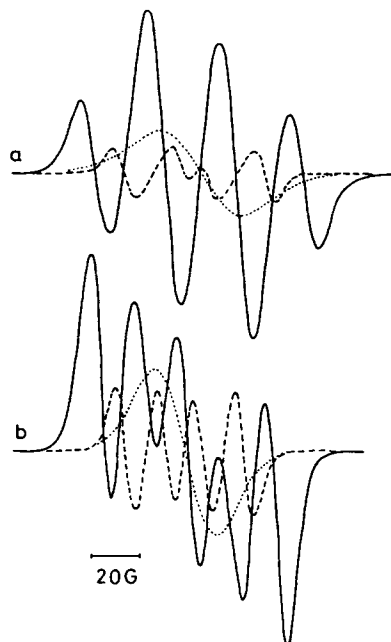


Fig. 7. Components of the calculated ESR spectra. (—) $i = 1$; (---) $i = 2$; (.....) $i = 3$. (a) Filament axes are parallel to magnetic field. (b) Filament axes are perpendicular to magnetic field.

functions for the observed spectrum, and (iv) the contribution of other kinds of radical species in the irradiated nylon 6 filaments. The components of the spectra computed from the parameters in Table I are given in Figures 7(a) and 7(b) for the parallel and perpendicular orientations. At the parallel orientation, the calculated spectrum was composed of two kinds of four-line resonances with different line width, and a singlet resonance. On the other hand, the spectrum for the perpendicular orientation consisted of a five-line, a four-line, and a singlet resonance.

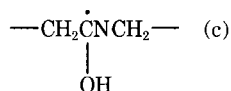
Assignment of Radical Sites

As noted from the simulation of the ESR spectrum by a computer, the observed spectrum was composed of three kinds of resonances, one with $l_1 = 2$, $m_1 = 2$, $n_1 = 2$ and others with $l_2 = 2$, $m_2 = 2$, $n_2 = 1$, and $l_3 = 1$, $m_3 = 1$, $n_3 = 1$. The first spectrum [Figs. 7(a), 7(b)] with $l_1 = 2$, $m_1 = 2$, and $n_1 = 2$ showed the obvious anisotropy on the angle between the filament axes and the outer magnetic field. The anisotropy of the spectrum might result from the contribution of the α -proton.³ The hyperfine splitting constant A_1 was 26.8 G and 14.4 G for the parallel and perpendicular orientations, respectively. The hyperfine splitting constants due to the α -proton which were calculated by Kashiwagi³ were 25.8 G and 14.2 G for the parallel and perpendicular orientations, respectively. These values were in good agreement with the values found by our computation. Therefore, the first splitting constant A_1 is due to the α -proton. On the contrary, the hyperfine splitting constants B_1 and C_1 did not vary remarkably regardless of the change of the filament orientation with respect to the magnetic field. Therefore, the hyperfine splitting constants B_1 and C_1 are due to the β -protons.

Heller and McConnell¹¹ have reported the relationship between the hyperfine splitting constant of the β -proton [$a_H(\theta)$] and the projected angle (θ) as follows,

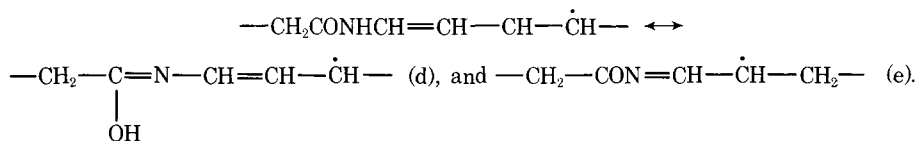
$$a_H(\theta) = \rho_\alpha K \cos^2\theta$$

where ρ_α is the spin density on the α carbon, K is a proportionality constant, and θ is the angle between the carbon p_π orbital on the α carbon and the C_β — H_β bond, both projected to a plane perpendicular to the C_α — H_β bond. If the two β -protons are equivalent with respect to the unpaired π electron on the carbon, the hyperfine splitting constants B_1 and C_1 should show the same values in each orientation. However, since an obvious difference was found between B_1 and C_1 for each filament orientation with respect to the magnetic field, it is difficult to regard two β -protons as equivalent. Nylon 6¹²⁻¹⁴ shows dynamic mechanical loss maxima at about 90°C, -40°C, and -120°C. These have been termed the α , β , and γ relaxations, respectively. The α relaxation originates with the rupture of interchain hydrogen bonding, and is ascribed to the motions of long-chain segments in the amorphous regions of the polymer. The β relaxation originates with motions of both nonhydrogen bonded polar groups and polymer-water complex units. The γ relaxation is associated with the onset of cooperative movement of methylene groups between amide linkages in the amorphous regions. The motions reflecting the β relaxation might be inhibited in our study, because the nylon filaments were well dried before γ -irradiation. According to the above information, the two β -protons adjacent to the first radical species show nonequivalent values, although the ESR measurements were conducted at room temperature. Tiño and Szöcs⁸ have reported similar values for the β -protons on oriented nylon 6 filaments. From the above distributions, the first radical species with $l_1 = 2$, $m_1 = 2$, and $n_1 = 2$ is in the form of $-\dot{C}HCH_2-$, which is either (a) $-\text{CONH}\dot{C}HCH_2-$ or (b) $-\text{NHCO}\dot{C}HCH_2-$ in irradiated nylon 6. However, it is difficult to exactly determine the position of the radical site. In the case of the second radical species with $l_2 = 2$, $m_2 = 2$, and $n_2 = 1$, the calculated spectrum showed four lines with a slightly different shape for both orientations. The hyperfine splitting constant A_2 of the parallel orientation differed from that of the perpendicular orientation (Table I), but the hyperfine splitting constant B_2 showed an almost equal value for both orientations. The difference found in the calculated spectrum might be due to the variation of the hyperfine splitting constant A_2 . However, the value of A_2 was fairly removed from the hyperfine splitting constant of the α -proton calculated by Kashiwagi³ for both filament orientations with respect to the magnetic field. The disagreement of A_2 found in both orientations might be attributed to the calculation errors because of the fewer numbers of radicals [Figs. 7(a), 7(b)]. Therefore, both hyperfine splitting constants A_2 and B_2 might be due to nonequivalent β -protons adjacent to the radical. The second radical species with $l_2 = 2$, $m_2 = 2$, and $n_2 = 1$ is assigned to the radical site

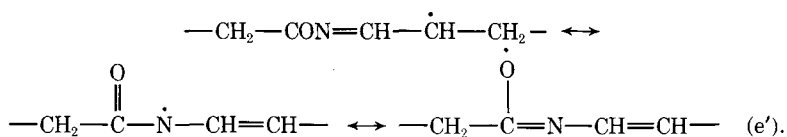


The same radical site was proposed by Szöcs et al.⁷ The radical species has thermal stability at 120°C. However, the second radical species in this study

does not have thermal stability. Details concerning such a difference are not understood, but it is probably due to the conditions of ESR measurement. In the case of the third radical species with $l_3 = 1$, $m_3 = 1$, and $n_3 = 1$, it showed a broad singlet resonance for both orientations. The line width (a_3) of each singlet resonance was much larger than that of other radicals. Therefore, the singlet is due to the radical with unresolved hyperfine structure. Similar broad singlet spectra have been observed in irradiated polyamides.^{2,4} Shinohara and Balantine² assigned the broad singlet to the radicals with conjugated structure;



Graves and Ormerod⁴ suggested an analogous conjugated system with an unpaired electron in the (e) form;



The inability to detect any hyperfine structure results from the extension of the spin distribution over the conjugated system. A similar explanation exists for the broad singlet spectrum of highly irradiated polyethylene¹⁵ and many other

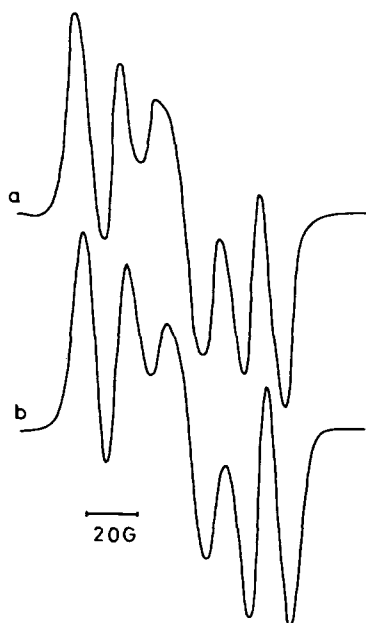


Fig. 8. ESR spectra of extinguished free radicals during storage for 2 days at room temperature. Filament axes are perpendicular to magnetic field. (a) Experimental spectrum. (b) Calculated spectrum.

TABLE II
Magnetic Parameters of Free Radicals in γ -Irradiated Nylon 6 Filaments for the Day of Irradiation and Extinguished Radicals during Storage for 2 Days at Room Temperature

Sample	i	l_i	m_i	n_i	x_0 (G)	y_{\max} (arbitrary unit)	a_i (G)	A_i (G)	B_i (G)	C_i (G)	s^2 (arbitrary unit)	Radical concentration (%)	Corrected ^a radical concentration (%)
Original radicals	1	2	2	2	3245.5	913.1	8.3	14.4	22.7	32.5	—	74.9	74.9
	2	2	2	1	3244.6	216.5	5.8	16.8	30.7	—	23.3	6.3	6.3
	3	1	1	1	3244.1	852.9	17.7	—	—	—	—	18.8	18.8
Extinguished radicals	1	2	2	2	3245.8	911.8	8.1	14.4	22.8	32.6	—	85.6	46.2
	2	2	2	1	3244.9	199.9	5.8	17.3	30.3	—	16.9	6.7	3.6
	3	1	1	1	3245.5	317.4	17.0	—	—	—	—	7.7	4.2

^a Value converted to total concentration of original radicals.

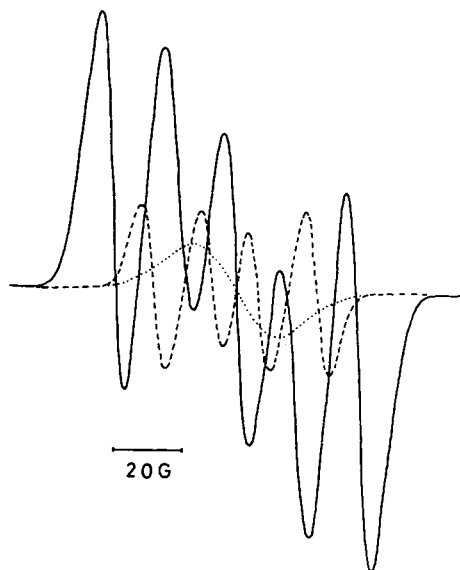


Fig. 9. Components of the calculated ESR spectrum for extinguished free radicals during storage for 2 days at room temperature. Filaments axes are perpendicular to magnetic field. (—) $i = 1$; (---) $i = 2$; (···) $i = 3$.

polymers¹⁶ with a carbon backbone. The third radical species can be assigned to the radical sites (d) and (e') with a conjugated system.

Stability of Radical

The spectrum measured after storage at room temperature for 2 days was subtracted from the spectrum after 3 h from γ -irradiation on the sample oriented perpendicular to the magnetic field [Fig. 8(a)]. The apparent five-line spectrum is due to the extinguished radicals during the storage, but it is not completely symmetrical. The best-fitting calculated spectrum by a Gaussian function is shown in Figure 8(b), and the parameters used in the simulation are given in Table II together with the results of the day of γ -irradiation. The mean square residue (s^2) of the extinguished radicals was less than the case of the day of γ -irradiation. For the radical species with $l_1 = 2$, $m_1 = 2$, and $n_1 = 2$ in the extinguished radicals, all of the parameters were in good agreement with those of the first radical species in the day of γ -irradiation. Therefore, the first radical species in the extinguished radicals is the same as the first radical found in the day of γ -irradiation. The same elucidation can serve the second and third radical species, because the parameters were similar as compared with those of the day of γ -irradiation, except for the value of $y_{\max,3}$. The components of the spectrum due to the extinguished radicals are given in Figure 9. The shape of each resonance is identical to the corresponding resonance in the day of γ -irradiation, but the intensity of the resonance for the third radical is much less than that for the day of γ -irradiation. The relative radical concentration for each component was determined by the double integration method on the original and extinguished radicals, and the results based on each total radical concentration are given in Table II. The first radical species amounts to a great part of the total

radical concentration in both cases. The second radical species shows similar values. However, the value of the third radical species in the extinguished radicals is smaller than that in the original radicals. These results suggest that the lifetimes of the radical species are not equivalent to each other. On the other hand, the total radical concentration generated in the γ -irradiated nylon 6 was reduced to about 46% of the initial concentration after storage for 2 days at room temperature. The total radical concentration of the extinguished radicals is almost 54% of the original radical concentration. The concentration of each radical species in the extinguished radicals is converted to the percentage of the total radical concentration of the original radical (Table II). The concentration of the first and second radical species in the extinguished radicals are ca. 60% of the initial values, respectively. In contrast, the intensity of the third radical species in the extinguished radicals is only about 20% of the original values. Therefore, the first and second radical species have shorter lifetimes than the third radical species, and the third radical is relatively stable at room temperature. This kind of stable radical is attributed to the broad stable singlet for the double bond generated in polyamide as suggested by Shinohara and Ballantine² and Graves and Ormerod.⁴

The γ -ray irradiation work associated with this study was conducted in the irradiation facility of the Japan Atomic Energy Research Institute at Takasaki.

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