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ESR Study of γ-Irradiated Silk : Effect of Oxygen

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Synopsis. The ESR spectra of silk γ-irradiated in a vacuum showed a doublet at room temperature and at -196 °C. The doublet turns to a singlet at $g=2.006$ by admission of O_2. This is explained in terms of the formation of peroxide radicals.

ESR spectra of γ-irradiated proteins and polypeptides have been reported, the effect of O_2 being examined.[1,2] It is well-known that γ-irradiated polytetrafluoroethylene and polypropylene react with O_2 and form peroxide radicals.[3,4]

We report herewith on the ESR spectra of γ-irradiated silk and the effect of O_2.

Experimental

Raw silk, Japanese race Dōei×Kōhaku (spring 1974), was used. Silk fibroin was prepared by degumming with a 0.5% solution of Marseilles soap and rinsed thoroughly with Na_2CO_3 solution and deionized water. Oily matters were then extracted with ethyl ether with a Soxlet extractor.

Gamma-irradiation was carried out at a dose rate *ca.* 5×10^4 R/hr for 17—30 hr. ESR spectra were recorded at the X-band on a Japan Electron Optics Model JES-3BS.X spectrometer with 100 KHz field modulation.

Results and Discussion

The ESR spectrum of the silk fibroin, γ-irradiated in a vacuum at room temperature for 2 days and measured at room temperature, is shown in Fig. 1. It consists of a strong doublet and a weak background absorption. From the fact that about 50% amino-acid-residues are glycine, the doublet is thought to be attributed to

$$-NH-CO-\dot{C}H-NH-CO-$$

radicals formed at α-carbons of polymer main chains.[1,5]

The doublet turned to a singlet (Fig. 2-A) when the spectrum was measured one day after the admission of O_2 into the sample tube. The intensity of the singlet became only a few percent of that of the doublet. Thus most of the radicals were destroyed by O_2.

The spectrum became asymmetric at -196 °C due to an axially symmetric g-tensor. The values $g_\parallel=2.034$ and $g_\perp=2.002$ were calculated from the position of the peaks (Fig. 2-B). However, some uncertainty remains in the determination of the $g_\parallel$ value because of the weakness and broadness of the $g_\parallel$ peak. The values are almost equal to those of the peroxide radicals formed by the reaction of γ-irradiated polytetrafluoroethylene and polypropylene with O_2.[3,4] The results suggest that the peroxide radicals

$$-NH-CO-\underset{\displaystyle O-O\cdot}{CH}-NH-CO-$$

Fig. 1. ESR spectrum of γ-irradiated silk, measured at room temperature.

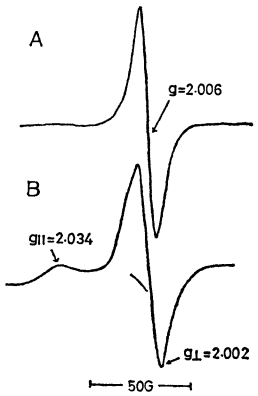

Fig. 2. ESR spectra of the peroxide radicals formed in γ-irradiated silk, measured at room temperature (A) and at -196 °C (B).

are formed in silk. Their molecular motion is considerably free at room temperature since it shows a singlet spectrum.

The doublet spectrum of γ-irradiated polyglycine does not turn to a singlet[1] in contrast to the above result. The difference is explained by assuming that the rate of the diffusion of O_2 into the solid is smaller than that of the decomposition of the peroxide radicals.[1] The glycine residues in silk are thought to exist in a coarse structure.

The ESR spectrum of silk γ-irradiated at -196 °C in the presence of O_2 showed no absorption due to the peroxide radicals when it was measured at -196 °C. However, when the temperature of the sample was elevated to -86 °C for a day, the formation of the radicals was observed. Thus the peroxide radicals are not formed at -196 °C.

The spectra of the raw silk did not differ from those of the silk fibroin.

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