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Electron Spin Resonance Studies of γ-Irradiated Cellulose. II. Free Radicals in Accessible Regions to Water in Cellulose I and Cellulose II

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Synopsis

The types of free radicals produced in the water-accessible regions of cellulose I and cellulose II fibers by γ-irradiation in nitrogen atmosphere at room temperature were studied by ESR spectroscopy. The ESR spectra of the irradiated cellulose I and II change by contacting the fibers with water, and after immersion in water the spectral shape depends on the orientation of the fiber axes to the magnetic field. These spectra are probably related to the free radicals generated in the highly ordered regions inaccessible to water in irradiated cellulosic fibers. The ESR spectrum of free radicals generated in decrystallized cellulose after irradiation consists of a singlet and a doublet. When the ESR spectra of free radicals formed in the highly ordered regions of cellulose I and II and the singlet and the doublet are combined in adequate ratio, the constructed spectra are similar to those of the radicals scavenged by water in the irradiated cellulose I and II fibers. From these facts, the spectra due to the free radicals in the water-accessible regions in irradiated cellulose I and II are considered to consist of the singlet and the doublet formed by free radicals in the typical amorphous regions and the spectra of other types of radicals generated in the semicrystalline regions.

INTRODUCTION

Many papers have reported the electron spin resonance (ESR) study of γ-irradiated cellulose.[1-8] However, the radical species and radical-trapping regions in γ-irradiated cellulose have not been elucidated sufficiently. In the previous paper,[9] in order to clarify such characteristics, we prepared decrystallized cellulosic fibers from cellulose I and II and studied the ESR spectra obtained after γ-irradiation. The ESR spectrum observed at room temperature consists of a narrow singlet and a doublet. The singlet spectrum is attributed to alkoxyl radical formed by rupture of glycosidic linkage at the C 1 or C 4 position, and the doublet spectrum is ascribed to radical formed by hydrogen abstraction from the C 1 position of the glucose unit.

Further ESR studies on trapped free radicals in γ-irradiated cellulose I and cellulose II are reported here. Experimental conditions for scavenging selectively some of the free radicals with water were such as to resolve the spectra of the irradiated free radical species in regions accessible to water. Orientation of irradiated cellulosic fibers in the magnetic field and the ESR

spectrum of γ-irradiated decrystallized cellulose also proved useful for resolving the ESR spectra of free radicals generated in the regions accessible to water in irradiated celluloses.

EXPERIMENTAL

Materials

Scoured cotton cellulose (cellulose I) of Mexican variety and commercial polynosic-type viscose rayon (cellulose II) fibers were purified by extracting with hot ethanol–benzene (1/1 volume ratio) for 24 hr. Decrystallized cellulosic fibers were prepared by saponifying secondary cellulose acetate fibers prepared from cellulose I and II in absolute ethanol with sodium hydroxide.[9] Recrystallized cellulosic fibers were prepared by treating the decrystallized cellulose in boiling water for 1 hr.

Methods

Cellulose I and II fibers were combed, so that their axes were mutually parallel, and then dried under vacuum for 24 hr at 50°C by using a dry-box. The samples were sealed in glass tubes under nitrogen atmosphere at room temperature and irradiated with ^{60}Co γ-rays at an exposure rate of 1.0×10^6 R/hr for 1 hr at room temperature. The irradiated fibers were led into quartz tubes under nitrogen atmosphere at room temperature in the dry-box for ESR measurement. In order to investigate the effects of orientation on the spectra, the well-aligned fibers were cut under nitrogen atmosphere at room temperature and then led into quartz tubes so that the fiber axes were perpendicular to the tube axes.

ESR spectra were taken with a JES-ME ESR spectrometer with 100 kHz modulation. The microwave power used was 1 mW, and under these conditions no saturation effect was observed.

RESULTS AND DISCUSSION

Effects of Water

The ESR spectrum of irradiated cellulose I oriented perpendicular to the magnetic field is shown in Figure 1a. The spectrum of cellulose II (Fig. 1b) is similar in shape to that of Figure 1a. From the hyperfine splitting on either side of the major line and the discontinuity of each spectrum, these spectra are attributed to more than two types of radicals, as has been suggested.[1–6]

When the irradiated cellulose I and II were immersed in water for 1 hr at room temperature, the ESR spectra (Fig. 1) changed to those shown in Figure 2. When the fiber axes were perpendicular to the magnetic field, the remaining free radicals generated three lines in cellulose I (Fig. 2a) and five lines in cellulose II (Fig. 2b). These spectra are the same as those reported by Arthur et al.[6] About 82% of the initial concentration of free

radicals in cellulose I and about 93% in cellulose II are scavenged by water. Obviously, most of the free radicals in irradiated celluloses are trapped in the water-accessible or less ordered regions of the cellulosic fibers. The spectra of free radicals scavenged by water in irradiated cellulose I and cellulose II are shown in Figures 3a and 3b, respectively, which were constructed by subtracting the spectra in Figure 2 from those in Figure 1. These spectra are similar in shape to the original spectra (Fig. 1). Presumably, the free radicals generated in the water-accessible regions in the irradiated celluloses contain some amount of free radicals which give three lines for cellulose I and five lines for cellulose II, in addition to the major component of free radicals which are probably present in the amorphous parts of the irradiated cellulose.

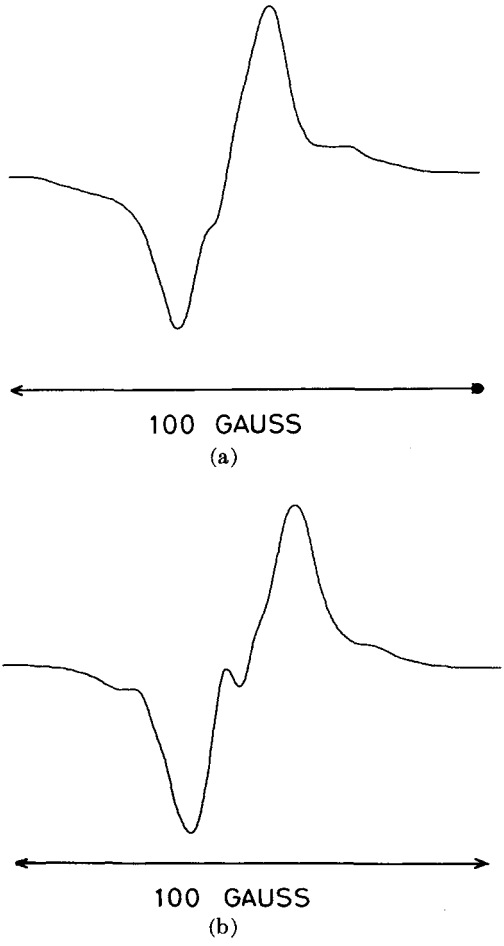

Fig. 1. ESR spectra of free radicals in cellulosic fibers irradiated in dry nitrogen atmosphere. Fibers are oriented perpendicular to magnetic field: (a) cellulose I; (b) cellulose II.

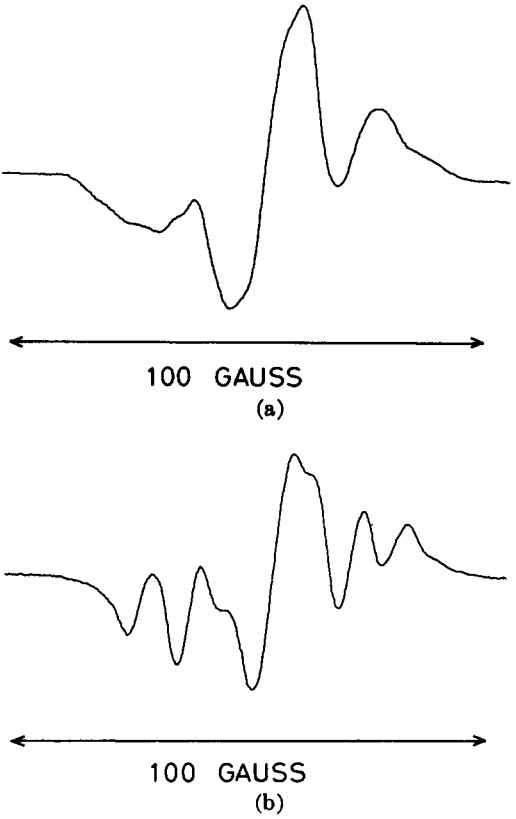

Fig. 2. ESR spectra of free radicals remaining in irradiated cellulosic fibers after contact with water for 1 hr at room temperature. Fibers are oriented perpendicular to magnetic field: (a) cellulose I; (b) cellulose II.

When the fiber axes of the samples are aligned parallel to the magnetic field, the ESR spectra generated by free radicals remaining after immersion in water show five lines for both cellulose I and II, as shown in Figure 4, though some differences in the spectral shapes are observed in their spectra. These spectra differ distinctly from those obtained with the fibers aligned perpendicular to the magnetic field (Fig. 2).

Since the ESR spectra of the cellulosic fibers obtained after immersion in water depend on the angle between fiber axes and the magnetic field, the remaining free radicals are trapped in highly ordered regions inaccessible to water. The difference of the spectral shape between cellulose I and cellulose II may be due to differences in their crystal lattices.

ESR Spectra of Decrystallized and Recrystallized Celluloses

In the previous paper,[9] it was found that the ESR spectrum of the γ-irradiated decrystallized cellulosic fibers is composed of a singlet and a doublet. Those spectra are shown in Figures 5 and 6.

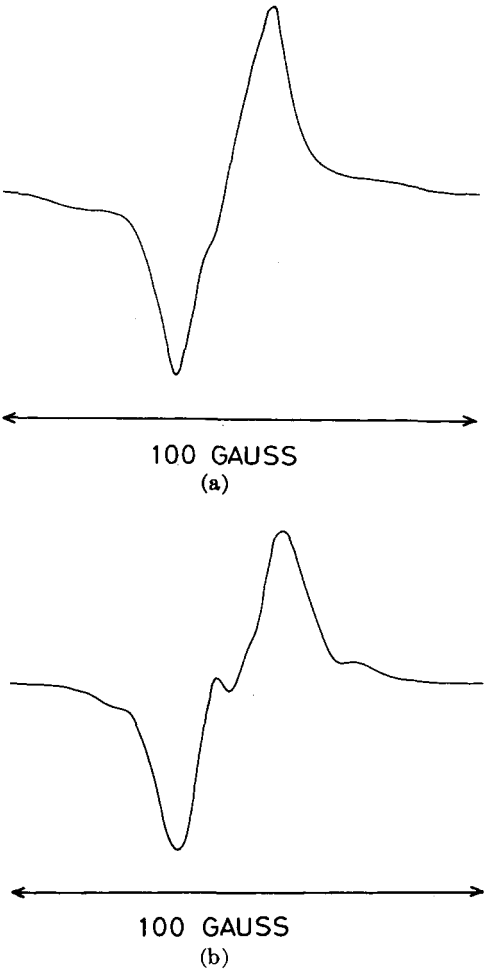

Fig. 3. ESR spectra of free radicals scavenged by water at room temperature in irradiated cellulose, Fig. 1 minus Fig. 2: (a) cellulose I; (b) cellulose II.

The recrystallized fibers of decrystallized cellulose I or II were investigated. X-Ray diffraction study shows that both the recrystallized cellulose I and II have almost the same structure as the initial cellulose II and give 45% crystallinity with somewhat less orientation than the original cellulose I and II. The free radicals generated in the recrystallized cellulosic fibers aligned perpendicular to the magnetic field after irradiation in dry nitrogen at room temperature give the ESR spectra shown in Figure 7. It was found that the spectrum for the recrystallized cellulose I is almost the same as that of the recrystallized cellulose II. They are similar in shape to the spectrum shown in Figure 1b for the initial irradiated cellulose II before decrystallization, but somewhat different from the spectrum for cellulose I. However, the spectrum for the recrystallized cellulosic fibers differs much

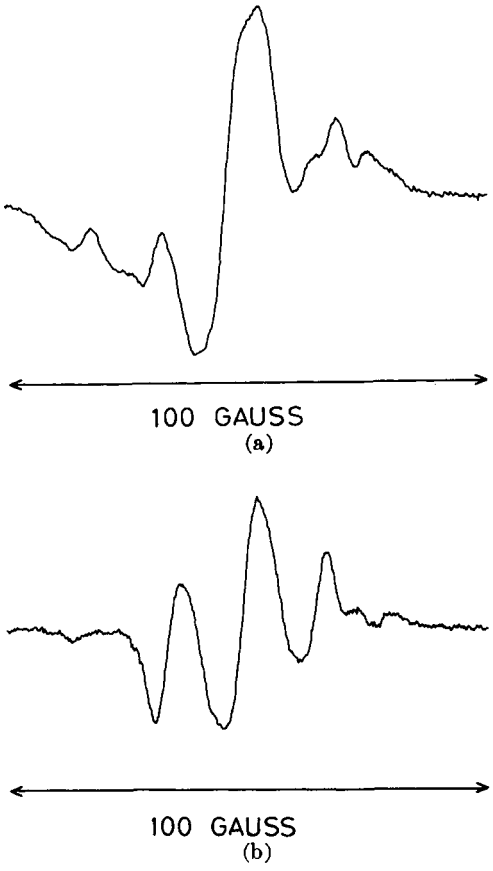

Fig. 4. ESR spectra of free radicals remaining in irradiated cellulosic fibers after contact with water for 1 hr at room temperature. Fibers are oriented parallel to magnetic field: (a) cellulose I; (b) cellulose II.

from the apparent singlet spectrum for the decrystallized cellulosic fibers after irradiation, as reported in the previous paper.[9] When the recrystallized irradiated cellulosic fibers were immersed in water for 1 hr at room temperature, the remaining free radicals which are not scavenged by water give the same ESR spectra as in the initial irradiated cellulose II which received the same treatment. From these facts, it is concluded that the ESR spectrum of free radicals generated in the regions accessible to water in the irradiated cellulosic fibers consists of a singlet and a doublet, which derive from free radicals formed in the typical amorphous regions, and the spectra for other types of radicals.

ESR Spectra of Regions Accessible to Water in Cellulose I and II

Generally, water diffuses not only into the typical amorphous regions, but also into the semicrystalline regions in which the cellulose molecules are less

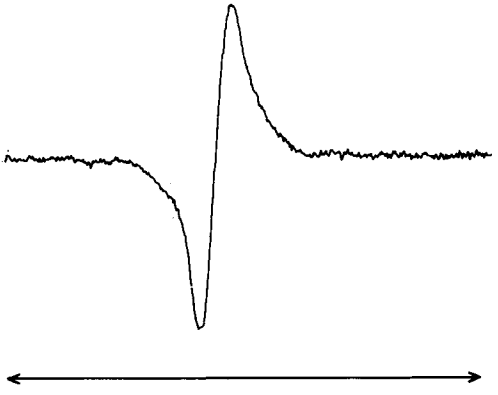

Fig. 5. ESR spectrum of free radicals in decrystallized cellulose after irradiation and contact with moist nitrogen for a few days at room temperature.

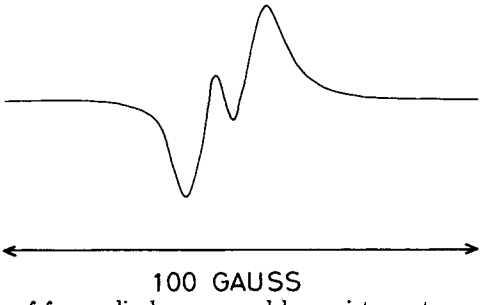

Fig. 6. ESR spectrum of free radicals scavenged by moisture at room temperature in decrystallized cellulose.

oriented than in the typical crystalline regions. Therefore, the spectra of the free radicals formed in the semicrystalline regions are probably attributable to the free radicals trapped in the decrystallized cellulose or typical amorphous regions, which give the singlet (Fig. 5) and the doublet (Fig. 6), and to the free radicals in the water-inaccessible regions or the typical crystalline regions, which give the spectra shown in Figures 2 and 4.

Thus, the ESR spectra shown in Figure 8 were constructed from Figures 2a, 4a, 5, and 6 for cellulose I fibers, and from Figures 2b, 4b, 5, and 6 for cellulose II fibers. These spectra are similar to those shown in Figure 3. The relative spectral intensity of each component for the construction of the spectra in Figure 8 is shown in Table I. Obviously, the spectra generated by free radicals in the amorphous regions accessible to water in irradiated cellulose I and II consist of a singlet and a doublet attributable to the free radicals in the typical amorphous regions, and other components, attributable to the free radicals formed in the crystalline regions. The spectra of free radicals formed in the water-accessible regions consist mainly of the doublet.

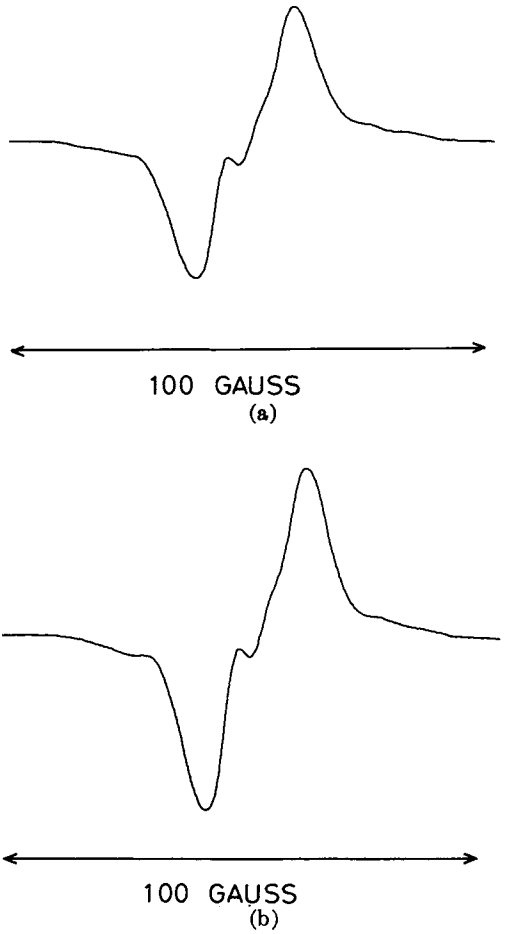

Fig. 7. ESR spectra of free radicals in recrystallized cellulosic fibers irradiated in dry nitrogen atmosphere: (a) recrystallized cellulose I; (b) recrystallized cellulose II.

TABLE I
Relative Spectral Intensity of Each Component in Construction of Spectra in Figure 8

Varieties	Ratio of radical concentration			
	Singlet (Fig. 5)	Doublet (Fig. 6)	Perpendicular (Fig. 2)	Parallel (Fig. 4)
Cellulose I	11	51	24	14
Cellulose II	14	61	16	9

The singlet and the doublet spectra of free radicals formed in the typical amorphous regions are the same as the spectra of free radicals formed in decrystallized cellulose after irradiation. Therefore, the singlet spectrum is mainly generated by alkoxyl radical formed by the rupture of glycosidic linkage at the C 1 or C 4 position, and the doublet spectrum is attributed to

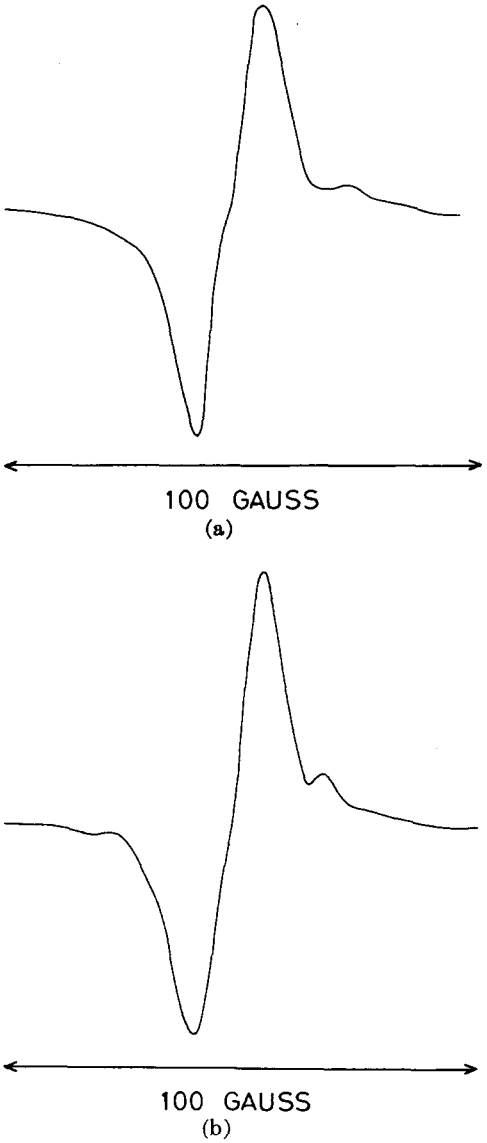

Fig. 8. ESR spectra constructed from Figs. 2, 4, 5, and 6: (a) cellulose I; (b) cellulose II.

the radical formed by hydrogen abstraction from the C 1 position of the glucose unit.

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