# Saccharide Radicals Induced by UV Irradiation at Room Temperature

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## Synopsis

The stability of saccharide radicals induced by UV irradiation at room temperature and the ability to initiate polymerization of acrylamide were investigated. UV light of $220 < \lambda < 300$ nm was proved to form saccharide radicals effectively at room temperature. ESR signal intensity of the irradiated saccharide was in the order of sucrose > methyl-$\alpha$-$D$-glucopyranoside $\gg$ cellobiose > $D$-xylose > $D$-glucose $\approx$ $D$-fructose. The saccharide radicals were fairly stable at room temperature, however, the markedly declined in amount as the samples were brought to their own melting points or allowed contact with water. When an aqueous solution of acrylamide was added to the irradiated saccharide, polymerization was initiated and the conversion increased with an increasing amount of the preirradiated saccharide. Regarding the kind of saccharide, the conversion decreased in the following order: sucrose > methyl-$\alpha$-$D$-glucopyranoside > cellobiose > $D$-glucose, which indicated a good agreement with the magnitude of ESR signal intensity.

## INTRODUCTION

In a previous paper[1] on ESR studies of sugars UV irradiated at 77°K, we observed that the formation of radicals on cellobiose is easier than on $D$-glucose, for which light shorter than 300 nm is requested. On the other hand, several ESR studies[2–8] of $\gamma$-ray irradiated saccharides have been reported. Kuri et al.[4,9] observed that radicals formed on poly(vinyl alcohol) and some saccharides are fairly stable at an ambient temperature, and are not damaged by gases such as oxygen, nitrogen monoxide, and hydrogen sulfide.

We also observed that some radicals formed on cellulose[10] and poly(vinyl alcohol) fibers[11] with the use of UV light at room temperature are considerably stable at the same temperature and exhibit an ability to initiate graft copolymerization of methyl methacrylate. Since almost the same phenomena were observed for various saccharides, it seems to be very significant to examine the characteristics of the saccharide radicals in more detail for the purpose of discussing the active species of irradiated cellulose.

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## EXPERIMENTAL

### Sample

D-glucose, D-xylose, D-fructose, methyl-α-D-glucopyranoside, maltose, cel-
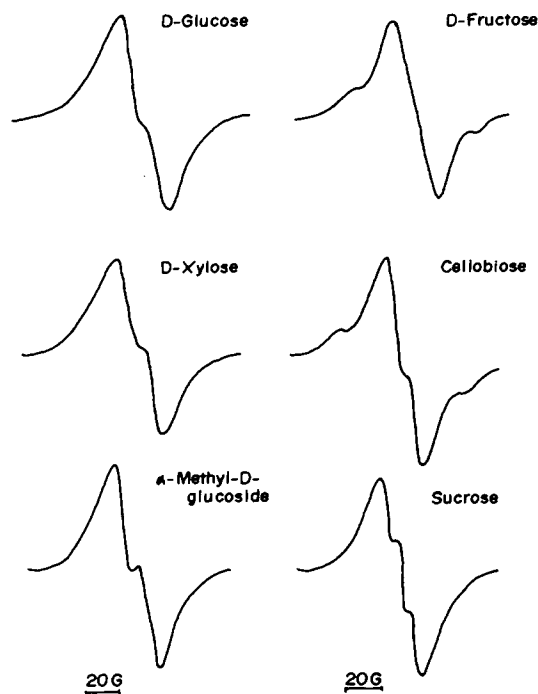lobiose, and sucrose were used as saccharide samples. These were reagent grade



Fig. 1. ESR spectra of saccharide induced by UV irradiation at room temperature. Time; 60
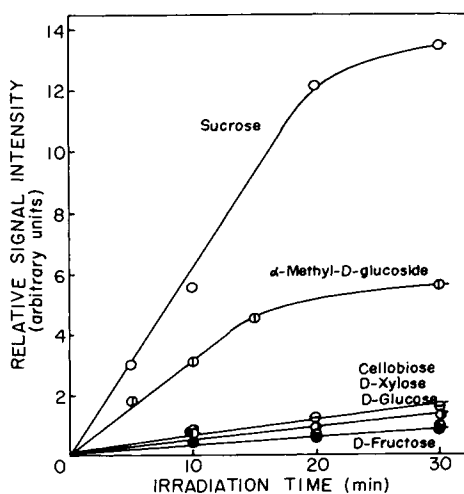min; recording; room temperature.



Fig. 2. Radical formation on saccharides by UV irradiation at room temperature.

of commercial origin and were used in the crystalline state for experiments. Acrylamide was recrystallized from benzene and used for polymerization.

## Measurement of ESR Spectra

A quartz glass tube (5 mm diameter) filled with the saccharide sample and flushed with nitrogen was exposed to the radiation from a Toshiba high-pressure mercury lamp H400-P (400 W) at room temperature (or 77°K). An ESR measurement was made at room temperature (or 77°K) with a Japan Electron Optics Laboratory JES-ME-X instrument. The resonance spectrum was observed with the $x$ band and 100 Kcps field modulation.

## Polymerization of Acrylamide

A quartz glass tube containing a given amount of saccharide sample was irradiated with light at room temperature under nitrogen for 60 min. Then, 10 ml of 20% aqueous solution of acrylamide was injected into the system. Polymerization was carried out by keeping the system at 30°C for 60 min without further irradiation. Saccharide samples dissolved perfectly in an aqueous so-
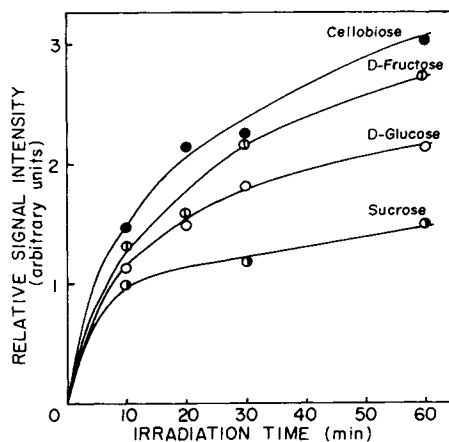
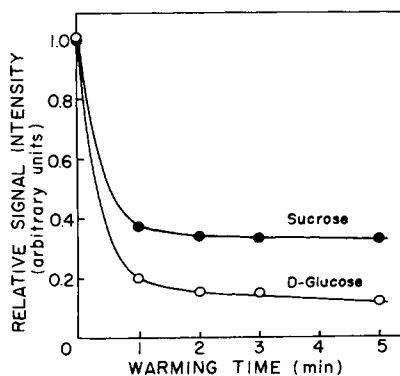Fig. 3. Radical formation on saccharides by UV irradiation at 77°K.

Fig. 4. Effect of warming on saccharide radicals induced by UV irradiation at 77°K. Warming: room temperature.

lution of acrylamide, making the system quite homogeneous. After polymerization, the solution was poured into excess methanol to deposit polyacrylamide. The polymer was separated, washed with methanol, and dried under reduced pressure, then weighted to calculate the conversion.

## RESULTS AND DISCUSSION

### Formation of Radical

No radical formation was observed in the system irradiated with light longer than 300 nm. However, the saccharide radicals were found in the system using a light longer than 220 nm, for which the ESR spectra are shown in Figure 1. The linewidth and $g$ value of the central maximum peak were 22–24 G and 2.003 in common to each spectrum, respectively. Besides the main absorption, the spectra were noted to involve the other weak absorptions at the center or satellite, depending upon the kind of saccharide. Because of such complexity of the lines, it is inferred that the spectra of saccharides induced by the irradiation at room temperature are constructed of several kinds of radicals.

Based on investigations of paper chromatography[1] and determination of re-
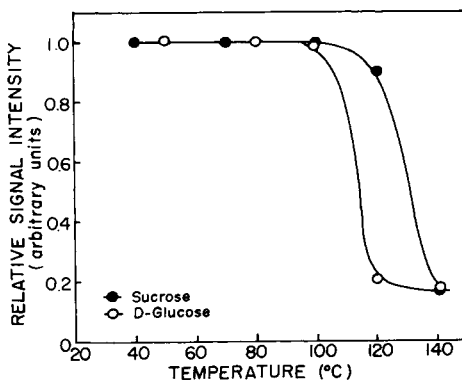


Fig. 5. Effect of warming on saccharide radicals induced by UV irradiation at room temperature. Warming; 30 min.
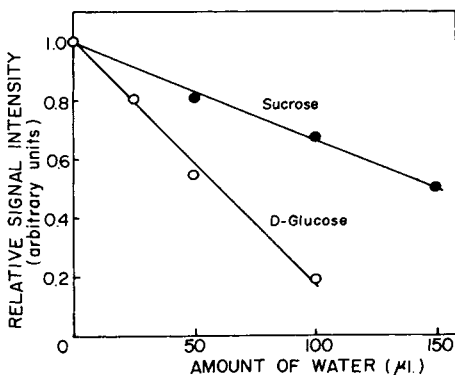


Fig. 6. Decay of saccharide radicals due to water. Radical formation; room temperature, 60 min. ESR recording; 77°K.
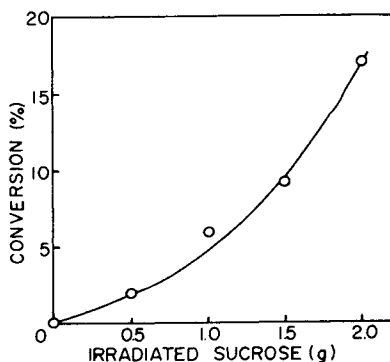
Fig. 7. Polymerization of acrylamide initiated by preirradiated sucrose. Preirradiation; room temperature, 60 min, nitrogen atmosphere. Polymerization; 30°C, 60 min, aqueous medium.
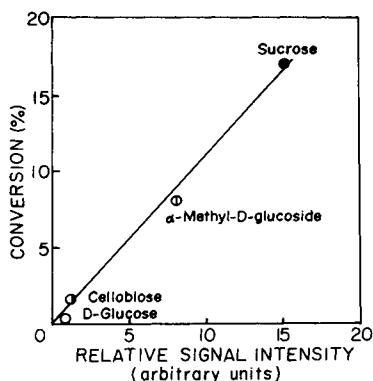


Fig. 8. Relationship between monomer conversion and ESR signal intensity in polymerization of acrylamide using various preirradiated saccharides. Preirradiation; room temperature, 60 min, nitrogen atmosphere, quartz glass system. ESR recording; room temperature. Polymerization; 30°C, 60 min, irradiated saccharide, 2.0 g.

ducing power[12,13] of an aqueous solution of saccharide irradiated at room temperature, we observed that a light shorter than 300 nm contributes to decomposing the reducing groups and to cleaving the glycosidic bonds in the saccharide molecule. Accordingly, in the system of the present study, almost the same kind of decomposition of saccharides seems to proceed under irradiation.

Figure 2 shows the effect of irradiation time on relative signal intensity. The intensity increased with the time or irradiation, while no change in the spectrum shape was shown for each sample. The intensity decreased in the following order: sucrose > methyl-$\alpha$-$D$-glucopyranoside $\gg$ cellobiose > $D$-xylose > $D$-glucose $\approx$ $D$-fructose, showing a higher intensity level of nonreducing saccharides as compared to that of reducing ones. A weaker intensity was observed for the system irradiated in an air atmosphere.

Figure 3 shows results of the irradiation of 77°K. Irradiation and ESR measurements were made using a Dewar flask containing liquid nitrogen. At 77°K, contrary to room temperature, higher signal intensities were observed for reducing saccharides, cellobiose, $D$-fructose, and $D$-glucose than that of nonreducing saccharide, sucrose. Figure 4 shows the results of warming at room temperature. $D$-glucose and sucrose were irradiated at 77°K for 20 and 60 min, respectively, signal intensities of which were almost alike as shown in Figure 3.

The intensities were observed to reduce sharply after warming at room temperature for 1 min. However, the amounts of radicals remaining on both samples were not the same. A larger amount of radicals was observed for sucrose than for $D$-glucose after warming.

It is sure that two types of radicals are recorded for samples irradiated at 77°K, one is unstable and the other is stable toward warming. Stable radicals may be considerably measured in the irradiated system at room temperature, resulting in a higher intensity for sucrose than for $D$-glucose, namely, the activity of reducing saccharide for photochemical reaction seems essentially to be higher than that of nonreducing saccharide, which leads to an easier formation of radicals for the former as shown in Figure 3.

## Decay of Radical

Figure 5 shows the change in the spectrum of saccharide samples irradiated at room temperature followed by the warming at each temperature for 30 min. No remarkable changes in intensity and in shape of irradiated $D$-glucose and sucrose were shown by warmings up to 100°C, indicating a large stability of radicals formed at room temperature. However, a marked reduction of the intensities was shown when the irradiated $D$-glucose and sucrose samples were warmed at 120° and 140°C, respectively. The melting point of the saccharides seems to relate to the decay phenomena of the spectrum. The melting point of sucrose is somewhat higher than that of $D$-glucose, which shows a good correspondence to the relatively higher decay temperature.

Figure 6 shows the effect of water on the radical decay. The signal intensity of the irradiated saccharides decreased linearly with the amount of water added to the samples. Thus, the saccharide radicals induced by UV irradiation at room temperature were found to decay as the crystalline state of saccharide samples destroyed by means of heat and/or water.

Ueda et al.[4] reported that the radicals formed on γ-ray irradiated saccharides are not damaged at ambient temperature in the solid state by gases, oxygen, nitrogen monoxide, and hydrogen sulfide, and such phenomena was explained by the difficulty of penetration of gases into the network structure of saccharide constructed of hydrogen bonds. They concluded that the saccharide radicals are stabilized by hydrogen bonds. It is natural to consider that the crystalline state of saccharides is easily affected by melting or water addition. Therefore, the stability of radicals in the irradiated saccharide in the present study seems to be influenced by such factors.

## Polymerization of Acrylamide

Polymerizations of various vinyl monomers were examined using a sucrose sample irradiated beforehand for 60 min at room temperature. No polymerization occured in each system using sucrose without or with preirradiation in a hard glass tube ($\lambda > 300$ nm). However, the polymerization of acrylamide was initiated by using sucrose preirradiated in a quartz glass tube ($\lambda > 220$ nm) under nitrogen atmosphere. The conversion increased as increasing the amount of irradiated sucrose employed, which is shown in Figure 7. This fact seems to support that the radicals induced on sucrose by UV irradiation at room temperature closely relate to the initiation of polymerization. For polymerizations

of acrylic acid, $N$-vinyl-2-pyrrolidone, acrylonitrile, and methyl methacrylate, the irradiated sucrose was almost inactive.

Figure 8 shows the relationship between conversion and ESR signal intensity for polymerization of acrylamide using various preirradiated saccharides. Most preirradiated saccharides other than sucrose were found to initiate the polymerization. The higher the signal intensity of the saccharide sample, the higher the conversion was obtained, and the order was as follows; sucrose > methyl-$\alpha$-$D$-glucopyranoside > cellobiose > $D$-glucose. A straight line relationship was given between the two irrespective of the kind of saccharide. It is conceivable from these that the common radicals to various saccharides perhaps contribute to the polymerization of acrylamide.

Finally, it was concluded that saccharide radicals induced by UV irradiation at room temperature have an ability to initiate the polymerization of acrylamide and decline in the amount as the crystalline state of the sample is destructed by means of heat and/or water.

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