Effects of High Energy Ionizing Radiation on Crystallinities of Cellulose II, III and IV

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(Received July 24, 1961)

Several reports of the effects of ionizing radiation on cellulose I[1] are known. In this communication, the effects of ionizing radiation on the crystalline regions of cellulose II, III and IV were reported.

We used viscose rayon as cellulose II. Cellulose III was prepared by treatments of the cellulose II in liquid ammonia at about $-78°C$ for four hours, and the ammonia was removed above 0°C, and then the sample was dried at room temperature. Cellulose IV was made from cellulose II by treatments in glycerin at 260~265°C for one hour, then glycerin was washed off with ethanol and then the sample was dried in vacuo.

The samples were wrapped with aluminum foil and irradiated, cooling at about $-78°C$ with dry ice, by electron beam from a van de Graaff till total dosages were attained to 10^7, 5×10^7, 10^8 and 3×10^8 rad.

The crystallinities of the samples were determined by acid hydrolysis method and also by X-ray diffraction method, estimating the crystallinity by the ratio of crystalline diffraction areas to total diffraction areas (Hermans method[2]).

1) R. E. Glegg and Z. I. Kertesz, *J. Polymer Sci.*, **26**, 289 (1957); F. A. Blouin and J. C. Arthur, *Text. Res. J.*, **28**, 198 (1958); Y. Shinohara and H. Tanzawa, High Polymer Chemistry Meeting of Japan, November, 1958.

2) P. H. Hermans and A. Weiding, *J. Polymer Sci.*, **4**, 135 (1949).

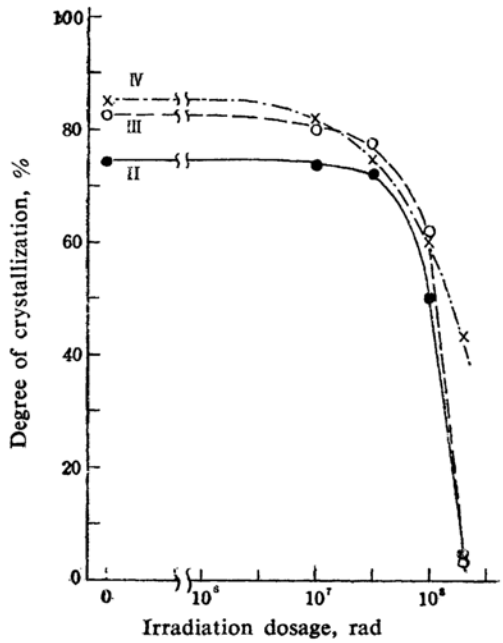

Fig. 1. The relationship between irradiation dosage and crystallinities by acid hydrolysis of celluloses.

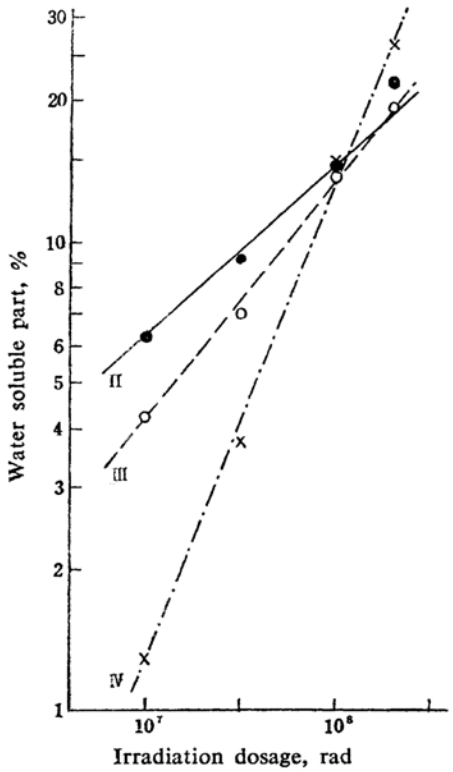

Fig. 2. The relationship between irradiation dosage and water soluble parts of celluloses.

The relationship between dosage and crystallinties by acid hydrolysis of celluloses is shown in Fig. 1. By the irradiation up to 5×10^7 rad, the decrease of crystalline regions is not observed for all celluloses. But by the irradiation of above 5×10^7 rad, in all types of celluloses remarkable lowering of crystallinities was observed.

The relationship between dosage and crystallinities by X-ray diffraction method is illustrated in Table I. There are not remarkable differences between X-ray diffractive crystallinities of unirradiated samples and those of samples irradiated with $10^7\sim3\times10^8$ rad.

Thus, the crystallinities of these celluloses are quite different depending on the measuring methods. The reason is explained as follows; large crystallites in the samples are degraded into small ones by the irradiation, but total crystalline areas determined by X-ray diffraction almost do not change. However, the velocity of acid hydrolysis becomes much greater as the crystallites are smaller.

TABLE I

Radiation Dose (rad)	Crystallinities by X-ray diffraction method, %		
	Cellulose II	Cellulose III	Cellulose IV
Unirradiated	62.9	73.5	62.7
10^7	62.0	78.1	63.2
5×10^7	62.2	65.0	64.2
10^8	61.7	65·8	59.9
3×10^8	61.7	62.5	59.0

In Fig. 2, plots of water-soluble parts of celluloses versus dosage are shown. For each cellulose, the water soluble part increases rapidly by irradiation of above 10^8 rad. Saeman et al.[3] reported that almost all parts of cotton linter become water soluble by 5×10^8 roentgen of Cathode ray in the Resonant-Transformer. From these results it is clear that cellulose is degraded to lower molecular weight substance by $3\sim5\times10^8$ rad.

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3) J. F. Saeman, M. A. Millett and E. J. Lawton, *Ind. Eng. Chem.*, **44**, 2848 (1952).