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Molecular Weights and Molecular Weight Distributions of Irradiated Cellulose Fibers by Gel Permeation Chromatography

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Synopsis

Radiation degradation of cellulose fibers was investigated by gel permeation chromatography (GPC). Scoured cotton of Mexican variety (cellulose I), Polynosic rayon (cellulose II), and their microcrystalline celluloses obtained by hydrolysis of the original fibers were irradiated by Co-60 γ-rays under vacuum or humid conditions. The irradiated samples were then nitrated under nondegradative conditions. The molecular weights and molecular weight distributions were measured by GPC using tetrahydrofran as solvent. The relationship between molecular weight and elution count was obtained with cellulose trinitrate standards fractionated by preparative GPC. The degree of polymerization of the fibers decreased with increasing irradiation dose, but their microcrystalline celluloses were only slightly degraded by irradiation, especially in microcrystalline cellulose from cellulose I. Degradation of the fibers irradiated under humid conditions was less than that irradiated under vacuum. It was found that the G-values for main-chain scission for the irradiated cellulose I, cellulose II, microcrystalline cellulose I, and microcrystalline cellulose II were 2.8, 2.9, less than 1, and 2.9, respectively, but the G-value for main-chain scission for the irradiated cellulose II was increased to 11.2 at irradiation doses above 3 Mrad. Consequently, it is inferred that cellulose molecules in the amorphous regions are degraded more readily, and the well-aligned molecules in crystalline regions are not as easily degraded by irradiation.

INTRODUCTION

Many investigations have been available since Seaman[1] initially reported that the viscosity of the cellulose decreased by ionizing radiation. Among them, Charlesby[2] proposed a degradation equation from the number-average molecular weight by viscosity measurement with the following assumptions: degradation occurs by random fracture of the main chain, the number of fracture is proportional to the irradiation dose and independent of initial molecular weight (assumed to be high). Recently, Sakurada[3] reported that the number of scission of chemical bonds of cellulose molecule by irradiation was practically independent of the degree of polymerization and microstructure of the initial cellulose fiber. All of these results were obtained by viscosity measurement of the cellulose, and little information has been reported about

the relationship between radiation degradation behavior and the microstructure of the cellulose.

In recent years, much progress has been achieved on the measurement of molecular weight distribution by gel permeation chromatography. Segal[4] reported that the molecular weight of the cellulose obtained by GPC using polystyrene as a standard showed a much higher value than that obtained by viscometry. But Meyerhoff[5] pointed out that good agreement was observed between GPC and viscometry by using the fractionated cellulose trinitrates (CTN) as a standard for the GPC calibration. These facts suggest that the elution behavior of the GPC for different polymers cannot be dealt with on the basis of unit chain length alone. Furthermore, molecular weight distributions of cellulose have been reported by Muller[6] and Huang,[7] and good agreement was obtained between GPC data and viscometry data. Ueno[8] reported that narrow cut fractions of CTN could not be obtained by conventional fractionation methods.

In this paper, the molecular weights and molecular weight distributions of the irradiated cellulose I and II fibers and their microcrystalline celluloses are determined by GPC whose columns were calibrated by fractionated cellulose trinitrates. G-values for main chain scission of the irradiated samples and the relationship between degradation behavior and microstructure of the cellulose are also discussed.

EXPERIMENTAL

Material

Two types of cellulose fibers, scoured cotton of Mexican variety (cellulose I) and Polynosic rayon (cellulose II), were used. These fibers were used after extraction with a 50:50 mixture of benzene–ethanol in Soxhlet apparatus for 48 hr and then dried under vacuum at 50°C.

In order to compare difference of degradation behavior in crystalline and amorphous regions by gamma-ray irradiation, microscrystalline celluloses were prepared from celluloses I and II by treating them with 2.4N hydrochloric acid for 1 hr at 100°C. After hydrolysis, the residues were washed with distilled water to remove residual acid.

Irradiated cellulose samples were nitrated under nondegradative conditions as described by Alexander and Mitchel.[6]

Gamma-Ray Irradiation

Cellulose I, cellulose II, and microarystalline celluloses obtained from celluloses I and II were irradiated by Co-60 γ-rays at a dose rate of 1×10^6 rad/hr. Irradiations were carried out at room temperature under vacuum and humid conditions (20% and 65% R.H.).

GPC Measurement

In order to calibrate the analytical-scale GPC columns, cellulose trinitrates obtained by nitration of the original cellulose I and cellulose II were fractionated by preparative GPC. Tetrahydrofuran was used as solvent for cellulose

trinitrates, and 2% solution were prepared for the fractionation. The GPC was equipped with 4-ft columns with 1-in. diameter in series, having pore sizes of 3×10^3, 3×10^4, 10^5, and 10^6 Å. The flow rate was 12.3 ml/min, the injection time and collecting intervals were 6 min, respectively. The number-average molecular weight of each fraction was determined by a Hewlett-Packard Model 502 high-speed membrane osmometer.

A Waters Associates Model 200-type GPC was used for the determination of the molecular weight distributions of the irradiated samples. The five columns were packed with porous polystyrene gels having pore sizes of 10^2, 10^3, 10^4, 10^5, and 5×10^6 Å, respectively. Calibration of the columns was carried out with fractionated CTN of known molecular weight; 2% solutions of the irradiated samples in THF were injected by an automatic injection system with six cells, and the instrument was operated at a flow rate of 1 ml/min. Fractionation and analysis were carried out at room temperature.

RESULTS AND DISCUSSION

Calibration of the GPC

Figure 1 shows the differential molecular weight distributions of cellulose trinitrate fractions and nitrated cellobiose. It is clear that each fraction has a fairly narrow molecular weight distribution. The values of $\bar{M}_w/\bar{M}_n$ calculated from the GPC chromatograms are in the range of 1.1 to 2.0.

Figure 2 shows calibration curves for cellulose; line 1 is obtained by monodispersed polystyrene as a standard, and line 2 is obtained by fractionated CTN as a standard. As shown in Figure 2, the calibration curve 1 using polystyrene standard lies considerably above the line 2; the tendency of deviation between calibration curves 1 and 2 is remarkable in the high molecular weight region. That is, cellulose trinitrates were eluted at a lower elution count during the GPC separation process than polystyrene. Similar results were re-

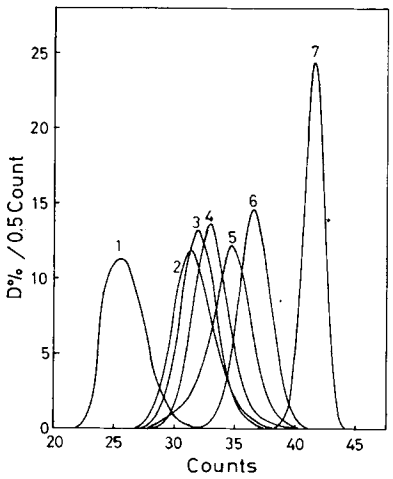

Fig. 1. GPC chromatograms of selected fractions of cellulose trinitrate obtained from cellulose I and cellobiose: (1) original cellulose I; (2–6) fractionated cellulose trinitrate from cellulose I; (7) nitrated cellobiose.

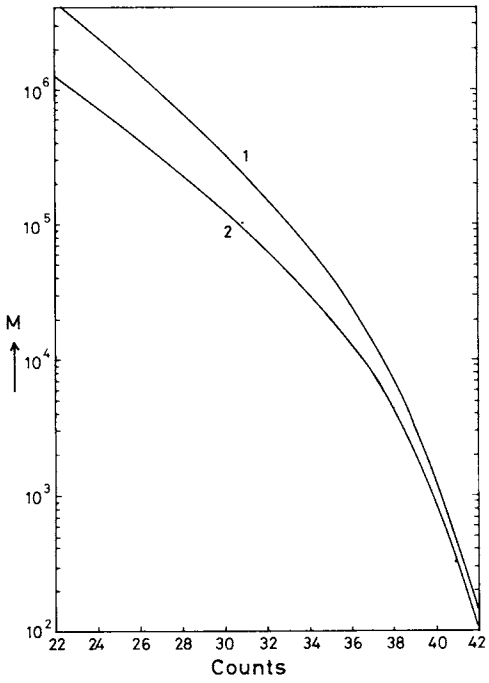

Fig. 2. Relation between elution counts and molecular weight of cellulose: (1) molecular weight of cellulose calculated from polystyrene standards; (2) molecular weight of the cellulose calculated from cellulose trinitrate standards.

ported by Meyerhoff[5] and Huang.[7] Huang pointed out that the deviation observed in the calibration curves may be caused by the relative stiffness of the cellulose trinitrate chains because of the glucosidic linkages and the steric hindrance to rotation.

Chromatogram Analysis

GPC chromatograms of cellulose I and cellulose II irradiated under vacuum are shown in Figure 3 and 4, respectively. From Figure 3, it is clear that peak count of the molecular weight distribution curve shifts noticeably to the lower molecular weight side with increasing irradiation dose, and the shape of the distribution curve gradually changes from narrow to broad. Similar results were also reported by Huang[7] for the irradiated wood pulp.

It can be seen from Figure 4 that the molecular weight distribution curve of cellulose II, having initially broad distribution, changes to narrow distibution containing two peaks in the GPC profiles with increasing irradiation dose. The appearance of the second peak in the chromatograms of the irradiated cellulose II with increasing irradiation dose is not clearly explained, but it suggests that cellulose II shows different degradation behavior under irradiation because it is structurally different from cellulose I.

The change of the values of $\bar{M}_w/\bar{M}_n$ together with the molecular weights for these samples calculated from the chromatograms of Figures 3 and 4 are summarized in Tables I and II. From Table I, it is seen that the molecular weight of the irradiated cellulose I decreased remarkably, but the value of

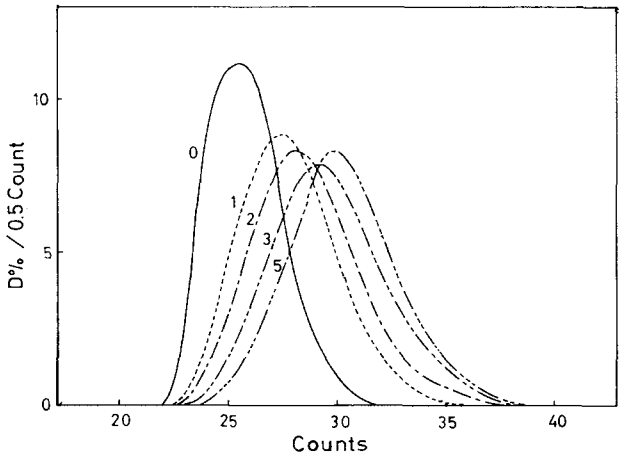

Fig. 3. Molecular weight distributions of irradiated cellulose I: (0) original cellulose I sample (Mexico cotton); (1–5) cellulose I samples irradiated by Co-60 γ-rays from 1 to 5 Mrad (under vacuum).

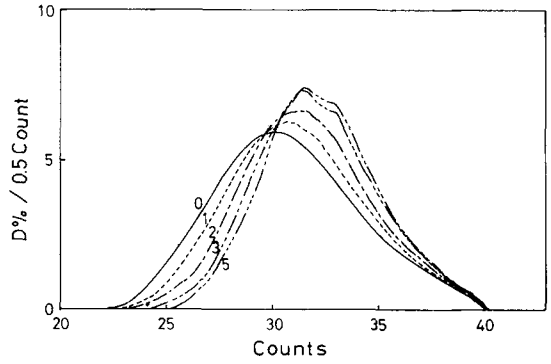

Fig. 4. Molecular weight distributions of irradiated cellulose II: (0) original cellulose II sample (Polynosic rayon); (1–5) cellulose II samples irradiated by Co-60 γ-rays from 1 to 5 Mrad (under vacuum).

$\bar{M}_w/\bar{M}_n$ of the cellulose I increased with increasing irradiation dose. From Table II, it appears that the molecular weight of the irradiated cellulose II also decreased and the value of $\bar{M}_w/\bar{M}_n$ of the cellulose II decreased with increasing irradiation dose.

TABLE I
Weight-Average and Number-Average Molecular Weights of Irradiated Cellulose I (Mexico Cotton)

Dose, Mrad[a]	$\bar{M}_w \times 10^5$	$\bar{D}_{pw}$	$\bar{M}_n \times 10^5$	$\bar{D}_{pn}$	$\bar{M}_w/\bar{M}_n$
0	5.29	3265	4.19	2590	1.26
1	3.12	1900	1.89	1200	1.65
2	2.54	1570	1.34	830	1.90
3	1.93	1190	0.93	575	2.07
4	1.52	940	0.74	460	2.06
5	1.55	960	0.71	440	2.18

[a] Irradiated under vacuum at room temperature.

TABLE II
Weight-Average and Number-Average Molecular Weights of Irradiated Cellulose II (Polynosic Rayon)

Dose, Mrad[a]	$\bar{M}_w \times 10^5$	$\bar{D}_{pw}$	$\bar{M}_n \times 10^4$	$\bar{D}_{pn}$	$\bar{M}_w/\bar{M}_n$
0	1.55	960	2.61	160	5.94
1	1.25	772	2.43	150	5.14
2	1.00	620	2.15	130	4.65
3	0.97	600	2.23	140	4.35
4	0.71	435	1.71	105	4.12
5	0.63	390	1.45	90	4.36

[a] Irradiated under vacuum at room temperature.

Calculation of the Probability of Main Chain Scission

The effect of irradiation dose on the degrees of polymerization of celluloses I and II irradiated under vacuum and humid conditions with 20% and 65% R.H. are shown in Figures 5 and 6, respectively. As shown in Figure 5, steep decreases in both weight- and number-average degrees of polymerization of cellulose I with increasing irradiation dose are observed. A decrease in degree of polymerization of celluloses I and II irradiated under 65% R.H. is somewhat smaller than that of the samples irradiated under vacuum or 20% R.H. This is explainable by the fact that radicals generated by irradiation which may produce main-chain scission recombine easily in the humid conditions, because the cellulose molecule may be more flexible and possible to make a molecular motion in humid conditions. This fact is proved by the ESR studies of irradiated cellulose in humid conditions reported by Florin et

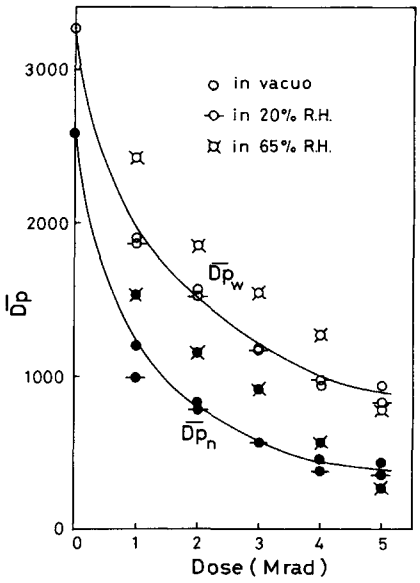

Fig. 5. Relation between degree of polymerization and absorbed dose of irradiated cellulose I under various conditions.

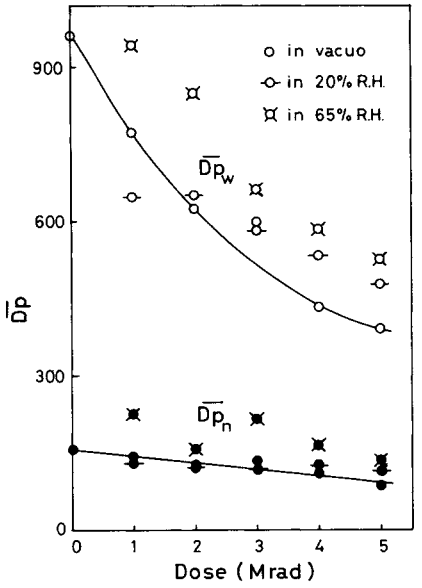

Fig. 6. Relation between degree of polymerization and absorbed dose of irradiated cellulose II under various conditions.

al.[9] and Dilli et al.[10] From Figure 6, the number-average molecular weight of the irradiated cellulose II decreases more gradually with increasing irradiation dose than that of cellulose I.

The relationship between the reciprocal of number-average molecular weight and irradiation dose is expressed by the following equation derived from Charlesby's[2] assumption of the random chain scission,

$$1/\bar{M}_{rn} = 1/\bar{M}_{0n} + \dot{r}R/w \tag{1}$$

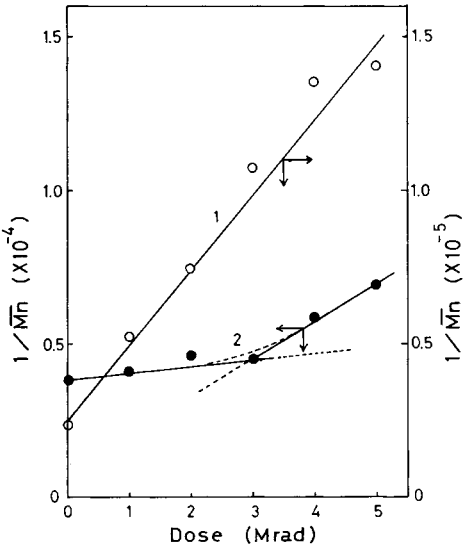

Fig. 7. Relation between reciprocal of number-average molecular weights of celluloses I and II and absorbed dose: (1) irradiated cellulose I; (2) irradiated cellulose II.

TABLE III
Molecular Weights of Irradiated Microcrystalline Celluloses Obtained from Celluloses I and II

Sample	Dose, Mrad[a]	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
Microcrystalline cellulose I (from cellulose I)	0	5.13×10^4	1.88×10^4	2.73
	1	5.43	1.88	2.89
	2	6.75	2.30	2.94
	3	4.96	1.94	2.56
	4	4.98	1.71	2.91
	5	4.46	1.81	2.46
Microcrystalline cellulose II (from cellulose II)	0	8.32×10^3	4.11×10^3	2.02
	1	8.34	4.21	1.98
	2	8.10	4.00	2.03
	3	8.00	3.90	2.05
	4	7.89	3.92	2.01
	5	7.86	3.99	1.97

[a] Irradiated under vacuum at room temperature.

where $\bar{M}_{0n}$ and $\bar{M}_{rn}$ are the number average molecular weights of the initial and irradiated samples, respectively; R is the unit absorbed dose; $\dot{r}$ is the probability of main-chain scission per unit of absorbed dose; and w is the molecular weight of the unit structure of the polymer. Figure 7 shows the relation between the reciprocal of number-average molecular weight for celluloses I and II and the absorbed dose.

Whereas the value of $1/\bar{M}_n$ for irradiated cellulose I increases linearly with increase in irradiation dose, the linear relation is not observed in the case of irradiated cellulose II. If the assumption basis for eq. (1) is valid, it must be considered that the probability of the main-chain scission for irradiated cellulose II changes along with increase in irradiation dose. Besides, the profiles of GPC chromatograms for irradiated cellulose II are changed more, and the minor peak appears more clearly with increasing irradiation dose as com-

TABLE IV
Probability of Main-Chain Scission ($\dot{r}$) and G-Value for Main-Chain Scission of Irradiated Celluloses[a]

Cellulose	Probability of scission $\dot{r}$, no./Rad	G-value for scission
Mexico cotton	4.4×10^{-10}	2.8
Polynosic rayon	4.5×10^{-10} [b]	2.9
	1.8×10^{-9} [c]	11.2
Microcrystalline cellulose I	1.3×10^{-10}	<1
Microcrystalline cellulose II	4.5×10^{-10}	2.9

[a] Irradiated under vacuum at room temperature.
[b] Probability of main-chain scission for cellulose II at irradiation dose below 3 Mrad.
[c] Probability of main-chain scission for cellulose II at irradiation dose above 3 Mrad.

pared with cellulose I. Therefore, it can be assumed that degradation of the cellulose II molecule by γ-ray irradiation, being accelerated with increasing irradiation dose, may be caused by the change in microstructure brought about by main chain scission caused by irradiation. These results also suggest that radiation degradation of cellulose is related to the difference in the microstructures of the celluloses.

For the purpose of comparing the difference between the degradation behavior of crystalline and amorphous regions in irradiated celluloses I and II, microcrystalline celluloses prepared from celluloses I and II were irradiated under vacuum and humid conditions at 20% and 65% R.H. Table III shows the effects of irradiation dose on molecular weights and molecular weight distributions of microcrystalline celluloses I (MC-I) and II (MC-II) irradiated under vacuum. The molecular weights of the irradiated microcrystalline celluloses decrease slightly with irradiation dose, especially in the samples from cellulose I. The values of $\bar{M}_w/\bar{M}_n$ for MC-I and MC-II are almost constant against irradiation dose. The second peak in the chromatograms does not appear for the microcrystalline celluloses irradiated up to 5 Mrad, even in the case of MC-II.

Humidity has hardly any effect on the molecular weights of irradiated MC-I and MC-II, because the moisture cannot penetrate into the microcrystals. Such results differ remarkably from these for celluloses I and II, both of which include amorphous and semicrystalline regions (which is the intermediate region of crystalline and amorphous regions), as shown in Figures 3 and 4. Sakurada[11] reported that cellulose fibers, irradiated in aqueous solution of pyrogallol, showed little decrease in strength because the radicals generated by irradiation were scavenged by pyrogallol and did not cause main-chain scission. But in this case, water cannot penetrate into the microcrystal of the cellulose, so the pyrogallol can scavenge radicals generated only in amorphous and semicrystalline regions.

Table IV shows the probability of main-chain scission ($\dot{r}$) calculated by

$$G = 0.97 \times 10^6 \dot{r}/w \tag{2}$$

where notations are the same as in eq. (1). The G-value for the main-chain scission of the irradiated cellulose I is 2.8, compared to less than 1 for MC-I. This result suggests that the main-chain scission of cellulose I by irradiation is generated in a region other than in the well-aligned region, while in cellulose II, the G-value for main-chain scission caused by irradiation doses beyond 3 Mrad is four times larger than that found below 3 Mrad.

The G-value for main-chain scission of the irradiated MC-II is larger than that of the MC-I. But this value is almost the same as that of the irradiated cellulose I and cellulose II in the initial stage, both of which include amorphous and semicrystalline regions. It is considered that the amorphous regions of both celluloses I and II show almost same behavior against radiation degradation. From these fact, the difference between the degradation behavior of celluloses I and II is attributable to the difference in microstructure of the celluloses, especially in the semicrystalline regions. Even in the crystalline region, cellulose II has a rather loose or disordered structure compared to cellulose I.

The minor peak appearing in the chromatograms of GPC for the irradiated

cellulose II (Fig. 4) may be caused by chain degradation occurring mainly in semicrystalline regions other than crystalline or amorphous regions. This fact also suggests that cellulose II contains a larger amount of semicrystalline region than cellulose I, and the radicals which may produce main-chain scission of the cellulose are generally generated more readily in the semicrystalline region. Therefore, at higher doses, comparatively high radical concentrations in the semicrystalline regions of cellulose II are transferred to other molecules to produce main-chain scission.

The present result seems to be different from the previous result by Sakurada et al. This difference is mainly due to the method of molecular weight measurement. The number-average molecular weight derived from the viscometric data is only valid if the molecular weight distribution is assumed to be the most probable distribution.

The present result obtained by GPC clearly indicated that the molecular weight distribution changes with irradiation dose and type of cellulose. It is also concluded that the degradation behavior can be discussed in detail with molecular weight distribution in addition to the average molecular weight.

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