Effects of Cobalt-60 Gamma Radiation on Poly (vinyl alcohol).
I. Effects of Gamma Radiation on Solid Poly (vinyl alcohol) Films

By

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Solid films of the fractionated and unfractionated poly (vinyl alcohol) were cobalt-60 gamma irradiated both in the presence and absence of oxygen. The methods used to study the change in properties of the irradiated samples include intrinsic viscosity, swelling, solubility and density measurements. The changes of structure and the mechanism of reaction by the gamma radiation were quantitatively discussed in connection with the change in the molecular weight distribution. In our experimental condition of up to $5 \times 10^7 r$ radiation dose, neither gel formation nor any difference dependent on the condition whether in the presence or the absence of oxygen was found. From the results obtained, we conclude that in the solid film, poly (vinyl alcohol) is dominantly degraded by random main-chain fracture throughout the crystalline and amorphous regions, although a small amount of endlinking may occur in the amorphous regions. Assuming the random main-chain fracture, the probability of a given main-chain bond being fractuated was estimated and it was found that the rate of degradation was propotional to the number of bond which was not fractured. The energy dissipation per chain fracture calculated was 38.7 e.v.

Introduction

When polymers are irradiated with high energy radiation, it is known[1] that they may be linked, the main-chains may be degraded, or side groups may be degraded, according to the kind of polymers. Poly (vinyl alcohol) is interesting from the point of view that it can belong[1,2] to either type of changes according to the conditions of irradiation. In Japan, following the preliminary works made by Okamura and Motoyama[3], experiments have been conducted with this material by Shinohara, Matsumoto and others[4,5] and by Chitani and Matsumoto[6]. We also started our work almost at the same time with them. Although there are some recent works published of the research made by Alexander and Charlesby[7] and Berkowitch and Charlesby[8], little has so far yet been known about the effect of the irradiation on poly (vinyl alcohol).

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The following report, in which the change of molecular weight distribution, that of polymer structure and the reaction mechanism are quantitatively discussed, is based upon the measurements of the intrinsic viscosity, the degree of swelling, the solubility and the density of the γ-irradiated poly(vinyl alcohol) solid films. Fractionated PVA and unfractionated PVA of known mole weight distribution were γ-irradiated in air and in vacuo, in the range of radiation dose of $1 \times 10^6 \sim 5 \times 10^7 r$.

Experimental

a. Preparation of Samples: The fractionated PVA is used. The PVA is fractionated with acetone from the water solution, and its degree of polymerization is 1540. The unfractionated PVA has the distribution of degrees of polymerization as shown by curve F in Fig. 4, and its viscosity average degree of polymerization is 1090. They contain no acetic acid residue. Both were cast on the glass plates from 1% aqueous solutions at room temperature. Water was fully removed by drying in vacuo at room temperature until constant weight was achieved. Each about 0.08 mm film obtained is restored in a desiccator containing P_2O_5.

b. γ-ray irradiation: Films were cut into strips of 1.5×5 cm and each about 1g of them was put into a glass tube of about 15 cm length and 1.5 cm in diameter, and one series of which was sealed in air at atmospheric pressure and the other was sealed in vacuo after repeating evacuation in nitrogen atmosphere.

The γ-rays from a 200 curie cobalt-60 source were employed in the positions where the dose rates were $6.8 \times 10^4 r$/hr and $1.7 \times 10^4 r$/hr.

The conditions of γ-irradiation and the decrease in weight in irradiated samples were shown in Table I.

Table I. Condition of irradiation, and decrease in weight
after irradiation on poly (vinyl alcohol) films.

Atmos-phere	Fractionated PVA ($P=1540$)				Unfractionated PVA ($P=1090$)			
	Dose rate (r/hr)	Time of irrad. (hr)	Dose (r)	Decrease (%, wt.)	Dose rate (r/hr)	Time of irrad. (hr)	Dose (r)	Decrease (%, wt.)
In air	1.7×10^4	49.3	0.8×10^6	0.58	1.7×10^4	89.0	1.5×10^6	0.37
	″	338.0	5.7 ″	0.25	″	315.0	5.4 ″	—
	″	546.5	9.3 ″	0.34	″	722.0	1.23×10^7	0.59
	″	1106.0	1.88×10^7	0.55	1.7×10^4 6.8×10^4	312.0 225.0	2.06 ″	0.38
	6.8×10^4	654.5	4.45 ″	0.41	6.8×10^4	722.0	4.91 ″	0.61
In vacuo	1.7×10^4	49.3	0.8×10^6	0.49	1.7×10^4	89.0	1.5×10^6	0.35
	″	338.0	5.7 ″	0.45	″	315.0	5.4 ″	0.31
	″	546.5	9.3 ″	0.28	″	722.0	1.23×10^9	0.40
	″	1106.0	1.88×10^7	0.49	1.7×10^4 6.8×10^4	312.0 225.0	2.06 ″	0.61
	6.8×10^4	654.5	4.45×10^7	0.56	6.8×10^4	722.0	4.91 ″	0.63

As is obvious from this table, the decreases in weight were about 0.3~0.6% and almost independent of the radiation dose, and moreover, no remarkable differences were found between the result obtained in air and that obtained in vacuo. It is remarkable that the oxygen does not give its characteristic effects on the possibly dried poly (vinyl alcohol). The decrease in weight may be due to the evolution of hydrogen, water or both.

c. Degree of swelling and solubility: The irradiated films were allowed for 5 days in water at 30°C until equilibrium swelling was achieved. The degree of swelling was given by the ratio of the weight of swollen gel to that of the dried polymer after swelling. The solubility was expressed in fraction at 30°C as:

$$\frac{\text{(weight of dried polymer before swelling)} - \text{(that after swelling)}}{\begin{array}{c}\text{weight of dried polymer}\\ \text{before swelling}\end{array}}.$$

In Figs. 1 and 2, these changes were shown. Both decreased rapidly up to $1 \times 10^7 r$ radiation dose but above this they showed a slower decrease with dose; yet no marked difference was found between in air and in vacuo in either case.

In Table II comparison is made of the films after the irradiation and of those prepared from the solution of the irradiated polymers in respect of their swelling and solubility properties. As expected, with the films made of irradiated polymer by resolving, the swelling ratios and solubilities were much increased compared with the corresponding films after irradiation. This result
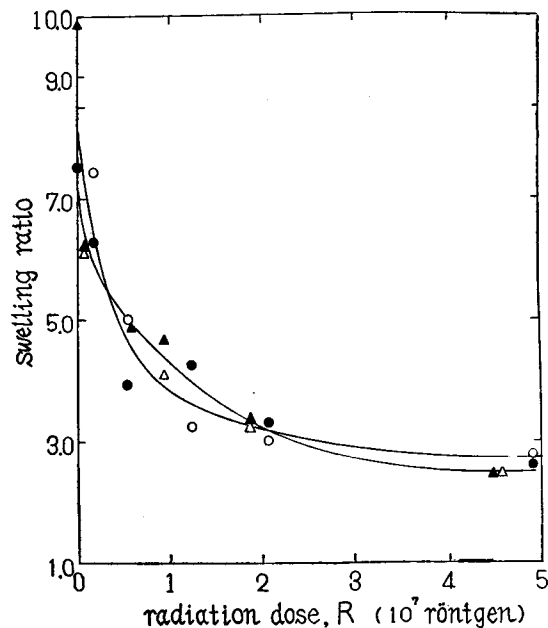

Fig. 1. Swelling ratio vs. radiation dose for irradiated poly (vinyl alcohol) films.
Fractionated PVA,
   irradiated in air (▲), in vacuo (△).
Unfractionated PVA,
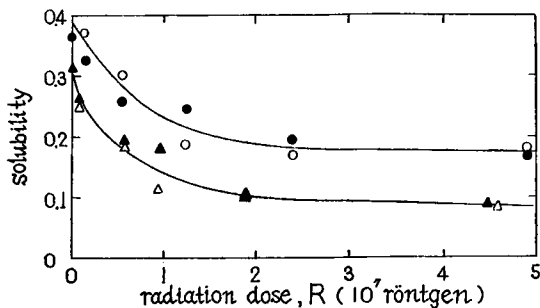   irradiated in air (●), in vacuo (○).

Fig. 2. Solubility vs. radiation dose for irradiated poly (vinyl alcohol) films. Designations are the same as in Fig. 1.

Table II. Swelling and solubility of the films prepared from
the solutions of irradiated poly (vinyl alcohol).

Radiation dose (r)	Films prepd. from solutions of irradiated PVA		Irradiated PVA films (references)	
	Degree of swelling	Solubility	Degree of swelling	Solubility
5.7×10^6	10.10	0.418	4.97	0.187
9.3 ″	9.06	0.393	4.67	0.182
3.25×10^7	11.80	0.515	3.79	0.152
3.44 ″	7.18	0.414	3.36	0.096

will be discussed later, but it may be due to the formation of branched molecule by irradiation.

d. Intrinsic viscosity and sol fraction: To examine whether gel is formed or not in the case of irradiation on solid PVA, the irradiated films were dissolved in water at elevated temperature. But no gel part was detected up to $5 \times 10^7 r$ radiation. Besides, one of us (I.S.) found lately that even at $5 \times 10^8 r$ radiation dose no gel part was formed. Therefore, it can be said that PVA, when irradiated in solid state containing no water, undergoes almost generally random degradation of the main-chains.

In the next place, we examined the after effects of the irradiation by making the measurement of intrinsic viscosities. Two cases followed: in the one the effects were presented in the solid state and in the other they were in the dissolved state after the irradiation was stopped. In Table III, these results were summarized. In either case, slight decrease in $[\eta]$, i.e. degradation of the chains, were recognized.

Table III. After effects of irradiation.

Condition of irradiation	Time of standing in air in solid state after irradiation was stopped. (day).	$[\eta]$	P_η
$R = 5.4 \times 10^7 \ r$ irrad. in vacuo	0	0.542	800
	4	0.524	760

Condition of irradiation	Time of standing in solution state for solutions prepared from irradiated films, (day).	$[\eta]$	P_η
$R = 4.9 \times 10^7 \ r$ irrad. in vacuo	0	0.306	330
	2	0.279	280
	3	0.279	280
	4	0.235	220
$R = 4.91 \times 10^7 \ r$ irrad. in air	0	0.291	300
	2	0.257	250

Taking these results into consideration, we measured the viscosities at 30°C in the following experiments immediately after the solutions were formed.

Viscosity-average degree of polymerization P_η was obtained with the equation:

$$[\eta] = 7.51 \times 10^{-7} P_\eta^{0.64} \quad (c \text{ in g/dl}).$$

In Tables IV and V, the changes of $[\eta]$ with radiation dose were shown. $[\eta]$ was rapidly decreased with radiation dose. This result indicates that the degradation of the main-chains occurred predominantly.

e. **Densities of the films:** The densities of the irradiated PVA films were measured by floating method in benzene-carbon tetrachloride mixture. As is obvious from Fig. 3, some decreases in density were found in the irradiated PVA. Estimated decrease in the degree of crystallization[9] using an equation for PVA was within about 10% at highest radiation dose (although changes in molecular structure must be taken into account in that case).

Fig. 3. Specific weight vs. radiation dose for irradiated unfractionated poly (vinyl alcohol) films. ● in are, ○ in vacuo.

At any rate, the decrease in the density indicates that the degradation of main-chains occurs in the crystalline regions equally as in the amorphous regions.
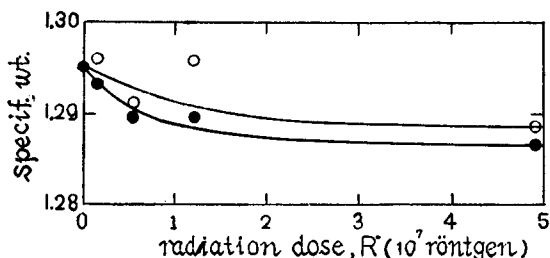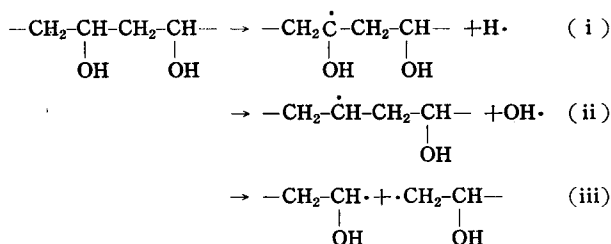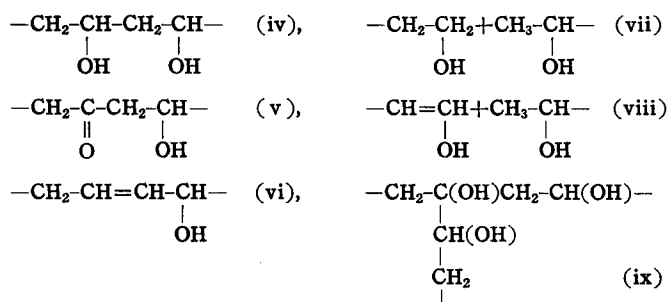
Discussion of the Results

From the foregoing results we can point out that the degree of polymerization, that of swelling and the solubility of irradiated PVA largely decreased with increasing radiation dose, though no gel formation was detected in our experimental conditions. Thus we conclude that, in the solid film containing no water, the PVA is dominantly degraded by random main-chain fracture throughout crystalline and amorphous regions, although a small amount of endlinking may occur in the latter region.

The mechanisms of degradation may be expressed as follows: independent of the presence or the absence of oxygen, abstraction of hydrogen radical as shown in (i), fracture of side chain as in (ii) or fracture of main-chain as in (iii) may occur.

$$-CH_2-CH-CH_2-CH- \rightarrow -CH_2\overset{\cdot}{C}-CH_2-CH- +H\cdot \qquad (\text{ i })$$
$$\qquad\ \ |\qquad\quad | \qquad\qquad\quad\ | \qquad\quad |$$
$$\qquad\ \ OH\qquad OH \qquad\qquad\ OH\qquad OH$$

$$\rightarrow -CH_2-\overset{\cdot}{C}H-CH_2-CH- +OH\cdot \quad (\text{ii})$$
$$\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\quad OH$$

$$\rightarrow -CH_2-CH\cdot + \cdot CH_2-CH- \qquad (\text{iii})$$
$$\qquad\qquad\quad | \qquad\qquad |$$
$$\qquad\qquad\quad OH \qquad\quad\ OH$$

Then accompanying the evolution of H_2, H_2O or both, formed from these radicals by chain transfer reaction and stabilization reaction, the chain of normal structure (iv), the chain containing carbonyl group (v), the chain containing double bond (vi), the degraded chains containing end groups as shown in (vii) and (viii), and the branched molecules as shown in (ix) formed by end-linking reaction may be produced.

$$-CH_2-CH-CH_2-CH- \quad (iv), \qquad -CH_2-CH_2+CH_3-CH- \quad (vii)$$
$$\qquad\; | \qquad\quad | \qquad\qquad\qquad\qquad\quad | \qquad\qquad |$$
$$\qquad\; OH \qquad OH \qquad\qquad\qquad\qquad OH \qquad\quad OH$$

$$-CH_2-C-CH_2-CH- \quad (v), \qquad -CH=CH+CH_3-CH- \quad (viii)$$
$$\qquad\;\; || \qquad\quad | \qquad\qquad\qquad\qquad\quad | \qquad\qquad |$$
$$\qquad\;\; O \qquad\;\; OH \qquad\qquad\qquad\qquad OH \qquad\quad OH$$

$$-CH_2-CH=CH-CH- \quad (vi), \qquad -CH_2-C(OH)CH_2-CH(OH)-$$
$$\qquad\qquad\qquad\; | \qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad OH \qquad\qquad\qquad\qquad\qquad\; CH(OH)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\; |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2 \qquad\qquad (ix)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\; |$$

In view of the result that the weight decrease in the irradiated sample is small, the mutual stabilizations between H· radicals or between H· and OH· radicals are considered to be small in percentage. As the chains are not mobile in the solid state, the polymer radicals formed, for example, by the reactions as in (i) and (ii), may immediately form stable molecules by stabilization reactions and a small per cent of them may form branched molecules by endlinking reaction, as shown in (ix).

Next, we will analyse the changes in molecular weight distribution in irradiated PVA on the assumption that the random degradation of the main-chains is dominated by radiation on the solid PVA.

The random degradation of polymer chain was formerly discussed by Sakurada and Okamura[10] and Matsumoto[11], to whom we shall refer as we proceed to analyse our results.

(a) Degradation of the fractionated PVA :

When the initial distribution of the degree of polymerization is uniform, the distribution after random degradation was formulated with α, the probability of a fracture between two adjacent monomer units, as a parameter[10]. α is equal to s/N, where s is the number of fracture per polymer chain and N is the degree of poly-merization. Expressing the intrinsic viscosity before and after the degradation by $[\eta]$ and $[\eta]'$ respectively, we can give the degradation coefficient m by the expression : $m=[\eta]/[\eta]'$,

$$1/m = \frac{1}{s^{n+1}}\{(s+2)(n+1,\,s)!-(n+2,\,s)!\}+e^{-s}, \qquad (1)$$

where n is the value of power in the equation $[\eta]=KP^n$. As n was found to be 0.64 for PVA in aqueous solution at 30°C, m can be evaluated from Eq. (1) for

various values of α. The curve (a) in Fig. 5 expresses the relation in case the initial degree of polymerization is 1540. α-values obtained from observed m using this curve were listed in Table IV.

Table IV. Fracture probability α calculated from the intrinsic viscosity of fractionated PVA ($P=1540$) after irradiation.

Dose (r)		0	0.8×10^6	5.7×10^6	9.3×10^6	1.88×10^7	4.45×10^7
In air	$[\eta]$	0.822	0.740	0.667	0.592	0.477	0.347
	P	1540	1300	1110	920	660	400
	m_{obs}	1.00	1.11	1.23	1.39	1.72	2.37
	α	0	0.00028	0.00060	0.00103	0.00193	0.0038
In vacuo	$[\eta]$	0.822	0.795	0.667	0.610	0.477	0.300
	P	1540	1360	1110	960	660	320
	m_{obs}	1.00	1.08	1.23	1.35	1.72	2.74
	α	0	0.0002	0.0006	0.00093	0.0093	0.0050

(b) Degradation of the unfractionated PVA:

If the weight distribution, W_P, of the polymer before degradation is expressed by

$$W_P = \varphi(N), \tag{2}$$

then that of the polymer after degradation is to be given by the following equation:[10]

$$W_P' = e^{-\alpha P}\varphi(P) + 2\alpha e^{-\alpha P} \cdot P \int_{P+1}^{\infty} \frac{\varphi(N)}{N} dN$$

$$+ \alpha^2 e^{-\alpha P} \cdot P \int_{P+1}^{\infty} \varphi(N) dN - \alpha^2 e^{-\alpha P} \cdot P^2 \int_{P+1}^{\infty} \frac{\varphi(N)}{N} dN. \tag{3}$$

The weight-distribution of the unfractionated PVA used in the present work was experimentally checked and given by the open circles along the curve F in Fig. 4. It shows two peaks. A shape similar to this distribution curve was also found in our previous work[12].

After a few trials, it was found that this experimental curve could be formulated so as to represent the distribution in low mole weight range by a function $\beta^2 e^{-\beta N}$ (Schulz's distribution) and that in high mole weight range by the Gaussian function $(1/\sqrt{2\pi}\cdot\sigma)\exp[1-(N-\bar{P}_2)^2/2\sigma^2]$, where β is a constant, and σ is the standard deviation and $\bar{P}_2$ is the most probable degree of polymerization in the Gaussian function. Noting that $\int_0^{\infty} W_P dN = 1$, and expressing the integrated weight of the Schulz's distribution in the total weight ($=1$) by f, we can give W_P by the following equation:

$$W_P = f\beta^2 e^{-\beta N} N + (1-f) \frac{1}{\sqrt{2\pi}\cdot\sigma} e^{-\frac{(N-\bar{P}_2)^2}{2\sigma^2}}. \tag{4}$$

From the experimental data, the following values were obtained.

$$\beta = 0.004, \quad \sigma = 165, \quad \bar{P}_2 = 1500, \quad f = 0.478.$$

The curve F in Fig. 4 is the calculated curve with these values. Inserting equation (4) in (3) W'_P is

$$W'_P = f(\alpha-\beta)^2 e^{-(\alpha+\beta)P} \cdot P + e^{-\alpha P}(1-f) \frac{1}{\sqrt{2\pi} \cdot \sigma} e^{-\frac{(P-\bar{P}_2)^2}{2\sigma^2}}$$

$$+ (2-\alpha P)\alpha e^{-\alpha P} \cdot P(1-f) \int_{P+1}^{\infty} \frac{1}{N} \frac{1}{\sqrt{2\pi} \cdot \sigma} e^{-\frac{(N-\bar{P}_2)^2}{2\sigma^2}} dN$$

$$+ \alpha^2 e^{-\alpha P} \cdot P(1-f) \int_{P+1}^{\infty} \frac{1}{\sqrt{2\pi} \cdot \sigma} e^{-\frac{(N-\bar{P}_2)^2}{2\sigma^2}} dN \ . \tag{5}$$

The distribution curves for $\alpha=0.05 \sim 0.0005$ were calculated by Eq. (5) and shown by the curves A~E in Fig. 4. From these curves, the degradation coefficient m was estimated.

$$m = \frac{[\eta]}{[\eta]'} = \frac{\sum P_i^n W_p \Delta P}{\sum P_i^n W_p' \Delta P} . \tag{6}$$

For the unfractionated PVA used in this work, theoretical values of m obtained from Eq. (6) were plotted against α by curve (b) in Fig. 5. By the use of
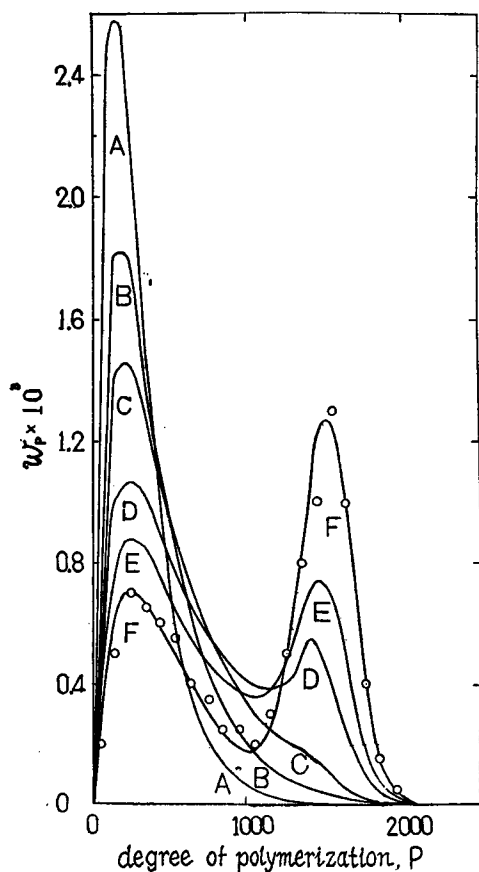

Fig. 4. Changes of the weight distribution curve by main-chain fracture as a function of α. The open circles represent the experimental values for the unfractionated poly (vinyl alcohol) used.
A: $\alpha=0.005$, D: $\alpha=0.001$
B: $\alpha=0.003$, E: $\alpha=0.0005$
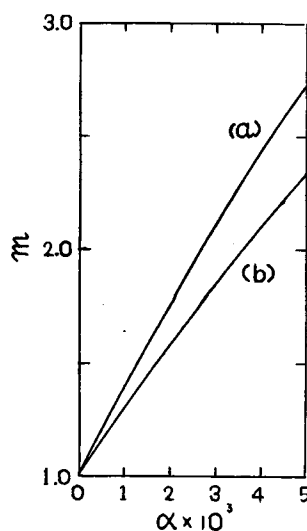C: $\alpha=0.002$, F: $\alpha=0$ (original PVA).

Fig. 5. Fracture coefficient, m, calculated as a function of fracture probability α, for
(a) fractionated PVA (P=1540),
(b) unfractionated PVA (P=1090),

this curve, α was found from the observed m value, as shown in Table V,

Table V. Fracture probability α calculated from the intrinsic viscosity
of unfractionated PVA ($P=1090$) after irradiation.

Dose (r)		0	1.5×10^6	5.4×10^6	1.23×10^7	2.06×10^7	4.81×10^7
In air	$[\eta]$	0.658	0.622	0.521	0.447	0.428	0.291
	P	1090	990	750	590	550	300
	m_{obs}	1.00	1.06	1.26	1.47	1.54	2.26
	α	0	0.0002	0.00085	0.0016	0.0018	0.0048
In vacuo	$[\eta]$	0.658	0.622	0.542	0.466	0.433	0.306
	P	1090	990	800	630	560	330
	m_{obs}	1.00	1.06	1.21	1.41	1.52	2.15
	α	0	0.0002	0.0007	0.00014	0.0018	0.0043

Now, if we assume that the rate of degradation is proportional to the number of
bond which is not fractured, then

$$\frac{d\alpha}{dt} = k(1 - \alpha)$$

or,
$$t = -\frac{1}{k} \ln(1 - \alpha). \qquad (7)$$

If this assumption holds true $-\ln(1-\alpha)$ must be linear against time t or against
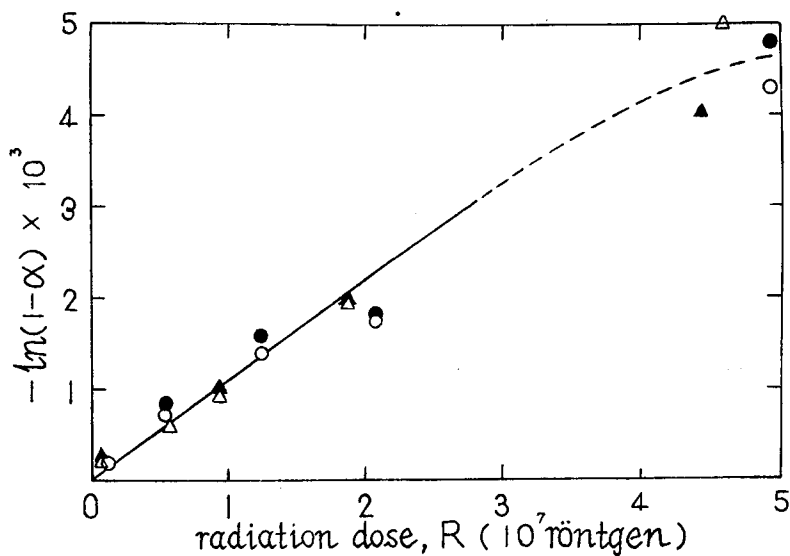radiation dose R. In Fig. 6, experimental results were plotted. A straight line was

Fig. 6. Fracture probability α plotted against radiation R.
Fractionated PVA irradiated in air ($\blacktriangle$), in vacuo ($\triangle$).
Unfractionated PVA irradiated in air ($\bullet$), in vacuo ($\bigcirc$).

obtained independently of whether the presence or the absence of oxygen throughout the unfractionated and fractionated samples, excepting the region of the high doses. Some deviations at high doses are considered to result from the discontinuity of the irradiation.

Next, we calculate the energy E_d, required to degrade a bond in the main-chain. For a radiation dose $1r$, the energy absorbed per gram of PVA is A ($=0.58 \times 10^{14}$ e.v.), and the number of bond degraded per gram of PVA is $N_L \alpha / M_m$, where N_L is Avogadro's number and M_m is the mole weight of the monomer. E_d was obtained as 38.7 e.v., from the slope of the curve in Fig. 6, using the equation;

$$E_d = \frac{RAM_m}{N_L \alpha}. \qquad (8)$$

From this value, G–value was obtained as 2.5. This value is about the same as that for poly(methyl methacrylate)[13] and poly(tert-butyl methacrylate) which belong to the degradation-type.

From the foregoing results, we conclude that in the solid film, poly (viny alcohol) is dominantly degraded by random main-chain fracture throughout the crystalline and amorphous regions, and in this case, the presence of oxygen does not exhibit any characteristic effects on the properties at least here concerned.

Reasonable conclusions were obtained both from the fractionated sample and from the unfractionated one by assuming random degradation of the main-chains. The possibility of the formation of branched molecules, especially in the amorphous regions, may not be denied from the behaviors of the swelling and solubility curves. This problem, however, will be discussed further in the following paper.[14]

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