Effects of Cobalt-60 Gamma Radiation on Poly (vinyl alcohol). II. Effects of Gamma Radiation on Water-Swollen Poly (vinyl alcohol) Films

By

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Poly (vinyl alcohol) films swollen in water or swollen with adsorbed water vapor were irradiated with the dose up to $3.2\times10^7 r$ in the presence of air. In these cases, gel formation occurred over a definite radiation dose. The active ends produced by main-chain fractures are assumed to be more capable of attacking other molecules at any point and joining to them, owing to the more mobile character of chains in the swollen films. On the assumption that the energy indirectly absorbed by the polymer depends on the water content in the swollen film, and that the free radicals produced from the water molecules do not directly contribute to the formation of linkage, theoretical calculation was performed for the case where the molecules are fractured by radiation and only a certain proportion **e** of the ends thus formed results in endinking and the remainder are stabilized and result in degradation. The experimental values of the radiation dose at gel point, the sol fraction, the average mole weight and the degree of swelling were compared with the theoretical relations. Assuning that the energy absorbed by the swollen film may entirely contribute to the polymer, we estimated the value of **e** at about 0.4 in the case of film swollen in water at 30°C.

Introduction

In the preceding paper, we pointed out that the random degradation of main-chain occurs dominantly by the irradiation on solid poly (vinyl alcohol) film, and we evaluated the energy required for fracture of a bond, E_d. In this paper, we will deal with the effects of irradiation on the water-swollen films. The effects of irradiation in the aqueous solution of rather low concentration range were investigated by Alexander,[1] Matsumoto,[2] Chitani[3] and Berkowich.[4] Among them, Matsumoto and others[2] pointed out that the experimental results on the changes of molecular weight with radiation dose, at above and under the critical condition for gel formation, can

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reasonably be explained by assuming the formation of endlinkage. But detailed mechanism of the reaction is not yet known. We, therefore, tried to proceed in this direction on the basis of the results previously obtained, and experimented with the PVA films swollen in water and swollen with adsorped water vapor.

Experimental Results

a. Effects of γ-irradiation in air on water-swollen poly (vinyl alcohol) films of fixed water content:

The fractionated PVA film, the one that was used in the preceding paper, was immersed in water at 30°C for 3 days till it achieved the swelling equilibrium, and then was cleared of the water attached to the surface and γ-irradiated at various doses in the glass tube sealed in air.

The degree of swelling (by weight) of the film before irradiation was 10.0 ± 0.5. With increasing dose there was observed the deswelling of the film and finally the formation of marked contracted gel at highest dose. The irradiated samples were dried in vacuo and weighed after the constant weight was achieved. Then the dried films were immersed in water at elevated temperature for ca. 16 hrs. to extract the soluble part. The insoluble part (get part) was then immersed in water at 30°C, and the degree of swelling of the gel was evaluated. The sol fraction, S, was calculated from the following definition:

$$\text{sol fraction,} \qquad S = 1 - \frac{\text{dried weight of gel after extraction}}{\text{dried weight of film before extraction}}.$$

The water soluble part (sol part) was dried, and then viscosity was measured in the aqueous solution. The viscosity-average degree of polymerization was calculated with the equation given before. These results are summarized in Table I.

Table I. Effects of γ-irradiation in air, on poly (vinyl alcohol) films swollen in water.

Radiation Dose (r)	Sol fraction S (%)	$[\eta]$, aq. solution of sol part	Visc.-av. deg. of polym. of sol part, P_η	Degree of swelling of gel
0	100	0.840	1590	—
5.1×10^5	100	0.705	1210	no gel
7.5 "	100	0.648	1060	no gel
1.11×10^6	98.4	0.688	1160	large
1.32 "	38.8	0.411	520	28.0
1.53 "	49.8	—	—	32.4
3.23 "	46.2	0.274	276	29.6
5.03 "	33.9	0.164	164	15.6
1.03×10^7	21.4	0.100	57	12.2
3.20 "	0	no sol	no sol	3.6

As is obvious from the Table, the dose required to produce a gel, R_g, was about $1\times10^6 r$. The sol fraction, the intrinsic viscosity and the degree of swelling of the gel decreased with increasing dose, and the sol fraction was zero at $3.2\times10^7 r$ in this experimental condition.

b. Effects of γ-irradiation in air on water-swollen poly (vinyl alcohol) films of various water contents:

The unfractionated PVA film, the one that was used in the preceding paper, was used. Films were allowed to remain in the vessels of different relative humidities for 5 days at room temperature, and were sealed into the glass tubes in air to be irradiated at a dose of $6.60\times10^6 r$.

The degree of swelling and the solubility of these irradiated films were measured at 30°C. Under the irradiation condition of this case, no gel was formed. This was confirmed by dissolution in hot water. Table II listed these results.

Table II. Effects of γ-irradiation in air, on poly (vinyl alcohol) films swollen with absorbed water vapor. ($R=6.60\times10^6 r$)

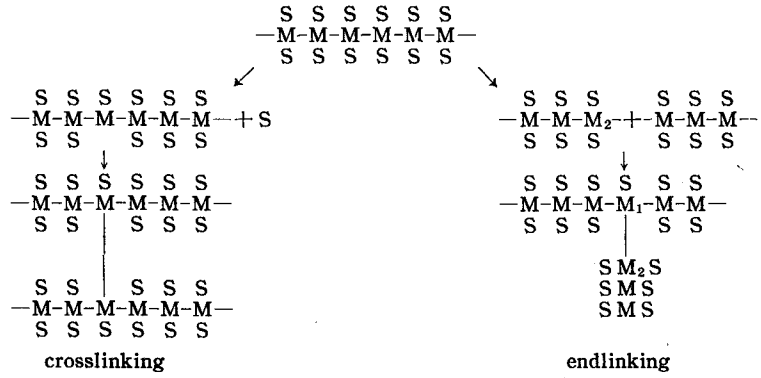
Water content (g/100g)	$[\eta]$ (100 cc/g)	$\bar{P}_\eta$	Deg. of swelling	Solubility	α
unirrad. PVA	0.658	1090	13.3	0.523	—
0	0.534	783	9.8	0.453	0.0013
4.9	0.536	787	6.3	0.379	0.0013
6.6	0.534	783	6.3	0.342	0.0013
14.1	0.520	751	6.6	0.378	0.0015
16.7	0.505	717	6.2	0.355	0.0018
26.2	0.451	601	4.3	0.205	0.0028
51.0	0.432	562	3.1	0.142	0.0034

The degree of swelling and the solubility were found to decrease with increasing water content, but the extents of changes were not so large. As compared with the case of 90% water content (i.e. case **a.**), the mobility of the chains is considered to be largely restricted in the film of low water content (i.e. case **b.**). In this case, therefore, the behaviors which do not largely differ from those in the solid PVA containing no water may be expected. The decrease in the degree of polymerization was slightly larger at higher water content.

Discussion of the Results

The process involving side-chain fracture and the formation of lateral links is referred to as *crosslinking*, and the alternative process whereby a molecule is linked to another via an active end group due to main-chain fracture is termed as *endlinking* by Charlesby.[5] One distinctive feature is that in the former all links are tetrafunctional,

whereas in the latter they are trifunctional. The processes of both cases are illustrated in the following figure.



In the case of crosslinking, the radiation-induced bond fractures occur in the main chain and result in a reduction in molecular weight. But if these occur in a side-chain as in the case of endlinking, there is no appreciable reduction in molecular weight.

As we pointed out, the main effect of radiation on PVA containing no water is the main-chain fracture. This fact supports the possibility of formation of endlinking. Further, in the water-swollen film we observed gel formation above a definite dose. With these experimental results, we suggest that when PVA is irradiated in the presence of water, both main-chain fracture and endlinking may occur by direct and indirect effects of radiation. Namely, the molecules are fractured and a certain proportion **e** of the end-groups thus formed is active and results in links.

In the case where water is not present, the direct actions of radiation to polymer are considered to be (i), (ii) and (iii) in the report I. But in the case where water is present, the indirect effect of the radicals is produced by the radiolysis of water:

$$H_2O \xrightarrow{\gamma\text{-ray}} H\cdot + OH\cdot$$

must be taken into account. Radicals thus formed behave just the same as those formed by direct action, and may produce the degraded and endlinked molecules.

To make some mathematical treatments, the following assumptions were made:

1. The radicals produced by the decomposition of water do not directly concern the formation of linking but bestow the energy to PVA.
2. The energy absorbed by PVA depends on the polymer concentration in the gel.
3. Effects of irradiation on polymers make no distinction between crystalline and amorphous regions, because the degree of crystallization is low in the present PVA.

4. A certain proportion **e** of the end-groups formed by the fracture of main-chains is active and results in end-links. The remainder of the radiation-induced breaks become stabilized and result in degradation.

For a radiation dose R, the energy absorbed per gram of swollen polymer is RA (where, $A=0.58\times10^{14}$ e.v.). If the fraction k of the energy absorbed is spent, the following expression is given from assumption 2:

$$\mathrm{k}RA = \mathrm{k}'RAc+\mathrm{k}''RA(1-c)\,, \tag{1}$$

where k′ and k″ are constant respectively and c is the polymer concentration (g/g). The number of the degrading fracture of the main-chains will be $\mathrm{k}RA/E_d$, and the number of the fractured ends be $\mathrm{k}RA/E_d$. Denoting the end result in endlinks as active ends and these result in degradation as inactive ends, then

$$\text{No. of active ends} = 2\mathrm{k}RA\mathbf{e}/E_d\,,$$
$$\text{No. of inactive ends} = [2\mathrm{k}RA(1-\mathbf{e})/E_d]+[2cN_L/M_n]\,,$$

where M_n is the mole weight of the unirradiated PVA, and $2cN_L/M_n$ is the number of the ends presented before irradiation. Further, expressing the probability of an end formed by the fracture forms an endlink by r, and that of an end is stable by i, then

$$\mathrm{r} = \frac{\mathrm{k}RAA\mathbf{e}/E_d}{cN_L/M_m}\,, \tag{2}$$

$$\mathrm{i} = \frac{\mathrm{k}RA(1-\mathbf{e})/E_d+cN_L/M_n}{cN_L/M_m}\,. \tag{3}$$

Charlesby[5] has made calculations for the case where the distribution before irradiation is an exponential type and the whole fractured ends result in endlinking.

Expanding his results to our model on the assumption that the original distribution is of exponential type, we calculated the radiation dose at gel point R_g, the sol fraction S, the number-average degree of polymerization P_n and the degree of swelling (by volume) Q_v as follows:

$$R_g = \frac{cN_LE_d}{\mathrm{k}AM_n(\mathbf{e}-1)}\,, \tag{4}$$

$$S = \left[\frac{\mathrm{k}RA(1-\mathbf{e})/E_d+cN_L/M_n}{3\mathrm{k}RA\mathbf{e}/E_d}\right]^2, \tag{5}$$

$$P_n = \frac{cN_L/M_m}{\mathrm{k}RA(1-2\mathbf{e})/E_d+cN_L/M_n} \quad \text{(before gel pt.)}\,, \tag{6}$$

$$P_n = \frac{M_n(4\mathbf{e}-1)}{2M_m\mathbf{e}} \quad \text{(at gel pt.)}\,, \tag{7}$$

$$P_n = \frac{3cN_L/M_m}{\mathrm{k}RA(10\mathbf{e}-1)/E_d+cN_L/M_n} \quad \text{(after gel pt.)}\,, \tag{8}$$

$$Q_v^{5/3} = \frac{(0.5-\mu)M_m(1+\sqrt{S})}{\rho v\mathrm{r}(1-\sqrt{S})^2}\,, \tag{9}$$

Q_v: swelling ratio by volume.

μ : interaction parameter,

v : mole volume of solvent.

ρ : density of polymer.

In Figs. 1, 2 and 3, S, P_n and Q_w were plotted against radiation dose R, for various **e**–values using the values of: $c=0.1$, $M_n=44\times1590=70000$, $E_d=38.7$, e.v.,

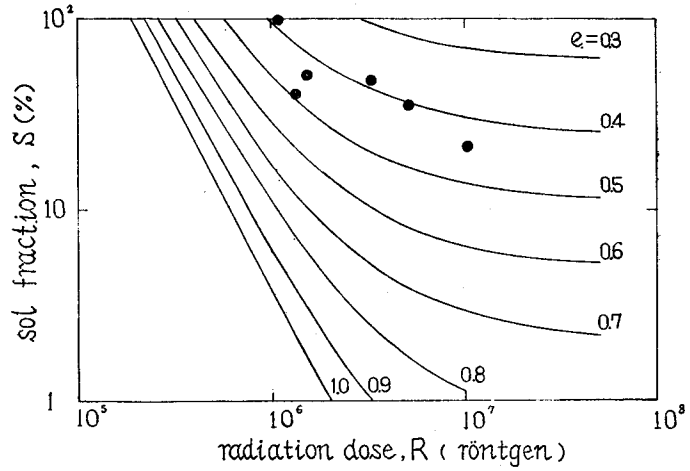


Fig. 1. Theoretical relationships between sol fraction S and radiation dose R, for various values of **e**.
Filled circles represent the experimental results.

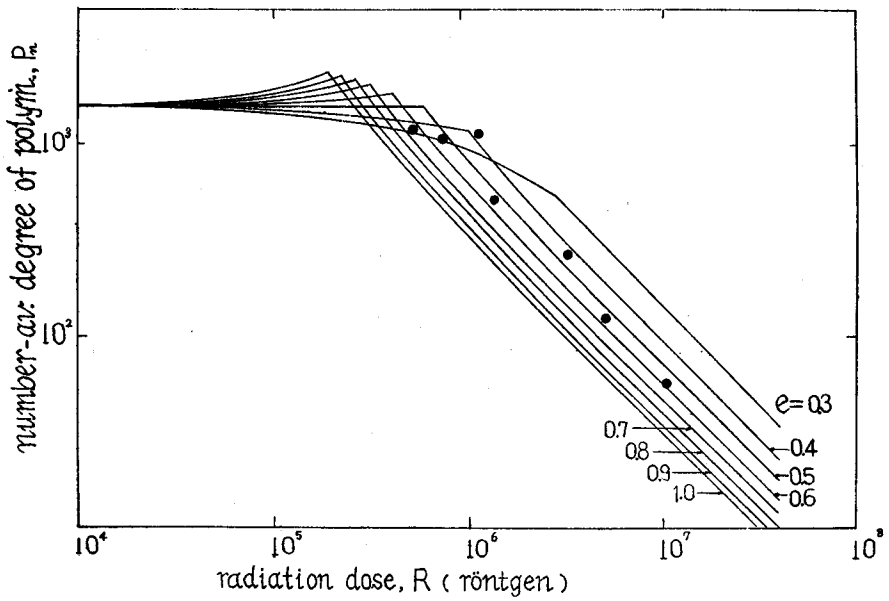


Fig. 2. Theoretical relationships between number-average degree of polymerization of sol part and radiation dose R, for various values of **e**.
Filled circles represent the experimental results.

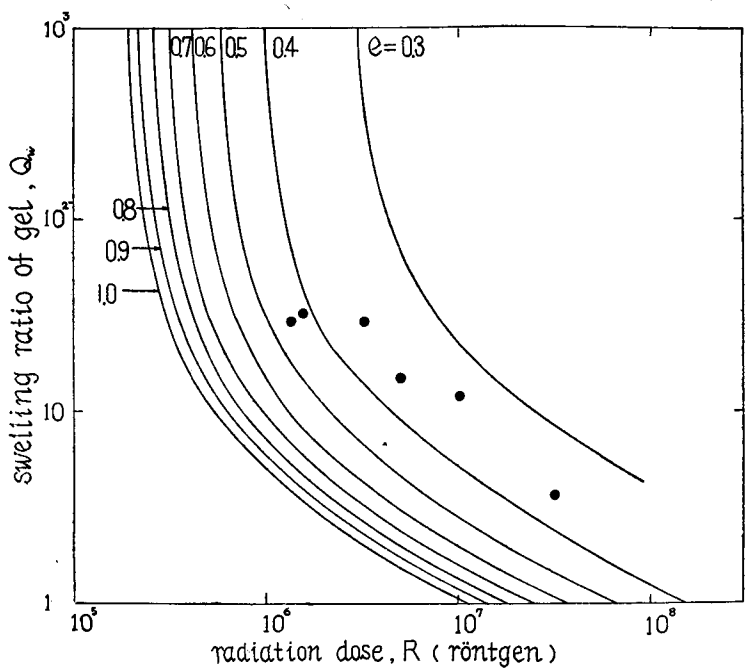


Fig. 3. Theoretical relationships between degree of swelling of gel part Q_W and radiation dose R, for various values of **e**. Filled circles represent the experimental results.

$\rho_s=0.9957$, $\rho=1.269$, $v=18.08$, $\mu=0.494$, assuming k=1. When k varies, these theoretical curves are only moved horizontally.

These theoretical curves were obtained by assuming the exponential distribution for polymers before and after irradiation, as mentioned above. On the other hand, the fractionated PVA was used for the present experiments. But it is well known that the degradation that occurs at random along a chain rapidly converts the distribution, whatever its initial pattern, to an exponential type. Accordingly, we can discuss our experimental results with these theoretical curves. In our experiments, the degrees of polymerization were given by the viscosity-average values, but they may be displaced by the number-average values, for the initial PVA was a fractionated sample. The experimental values were plotted by the filled circles in Figs. 1~3.

The **e** values estimated from these three independent quantities showed good agreement. In the case of k=1, **e**=0.4~0.5 was found. k=1 means that all the energy absorbed by the water-swollen film is ultimately consumed to the degradation of PVA chains. Thus, **e**=0.4~0.5 means that 40–50% of the ends formed by main-chain fracture results in the endlinks and the remainder are stabilized and result in the degradation. There is no experimental ground that k is 1, but much smaller value

than 1 seems to be improbable, and k somewhat smaller than 1 may be considered to be reasonable.

In the next place, we consider the results on the experiments where the definite dose was irradiated on the water-swollen PVA of different water contents. For this case, **e** values were calculated from viscosity data by equation (6) in which equation (1) was inserted on the assumption that $k'=1$ and for the values of k'' of 1 and 0.85. The results are shown in Table III.

Table III. **e**-values calculated for the water-swollen poly (vinyl alcohol) films of different water contents. ($R=6.60\times10^6 r$)

PVA conc. (g/g)	**e**	
	$k''=1$	$k''=0.85$
0.590	0.034	0.004
0.738	−0.03	−0.05
0.833	0.062	0.051
0.859	0.082	0.077
0.934	0.085	0.076
0.951	0.081	0.079
1.000	0.056	0.056

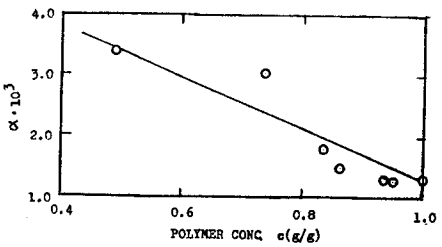


Fig. 4. Probability of main-chain fracture, α, vs. polymer concentration for PVA films irradiated at different water contents.

In this table the sample corresponds to $c=1$ and represents the result of irradiation on the solid film containing no water, as obtained in the preceding paper. The **e**-values shown in Table III are much smaller than those in the case of $c=0.1$. These results show that only less than 10% of the ends degraded by the irradiation can concern the formation of endlinks, and, moreover, the **e** does not change with concentration in this concentration range. Such behaviors are considered to be due to the lack of mobility of the chains in the low water content sample. Therefore, we may further assume for simplicity that in these samples the main-chain fractures occurred dominantly. In Fig. 4, the probability of a fracture α calculated with the assumption shown in the report I, was plotted against the polymer concentration c for the samples in Table II. A linear relation was found between them. This supports the assumption given by the equation (1). Further, as R is constant in the experiments of Table II, the energy consumed for the main-chain fracture per molecule will be increased with decreasing polymer concentration c. This means that, if the **e** is assumed to be constant, the numer of endlinking may be increased with decreasing polymer concentration c. Additional experimental results will be reported later.

Acknowledgment

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