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# Effects of Cobalt-60 Gamma Radiation on Poly(vinyl alcohol) (III)

## Effects of Gamma Radiation on Water-Swollen Films and Aqueous Solutions

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Studies have been done on the effects of gamma irradiation both in air and *in vacuo* on aqueous solutions and water-swollen films of polyvinylalcohol (PVA). The radiation-induced changes were followed by the measurements of viscosity, sol fraction and degree of swelling. For the water-swollen films, remarkable differences were observed between the irradiation *in vacuo* and in air, but for the aqueous solutions of higher concentrations there were little differences between both cases. For the irradiation on water-swollen films in air the indirect effect of water was quantitatively discussed. It was found by a calculation that the energy absorbed by water was not completely but only 69% of it was used for the main chain fracture and that the energy dissipated per main chain fracture was about 36 eV. When the aqueous solutions were irradiated, those viscosities were increased with dose and finally a gel was formed in the similar manner observed in the case of vacuum-irradiation on the water-swollen films. The ratio of the number of fractures and crosslinked units,  $p_0/q_0$ , was increased with the weight fraction of the polymer; the value of  $p_0/q_0$  was 0.27, 0.39 and 0.55 at the weight fraction of 0.10, 0.20 and 0.25 respectively. The results obtained by the irradiation of the solutions containing 0.1 wt. fraction of polymer which had been stood for some period before irradiation showed that the sol fraction was decreased with standing time.

### 1. INTRODUCTION

In recent years a considerable number of investigations on the effects of high-energy radiation on high polymers have been reported. Generally these works have been carried out on polymers in the solid state, while for polymer-solvent systems only a few papers have been published. In the case of PVA-water system, experimental results have been published not only by us in II<sup>1)</sup> of this series but also by A. Charlesby<sup>2)</sup>, A. Danno<sup>3)</sup>, S. Okamura<sup>4)</sup> etc. According to these results, when PVA is irradiated in the solid state at room temperature, crosslinking does not occur to an extent that an insoluble gel is formed, independently of the presence or the absence of air. But, if water is present gel formation is observed. The following two factors may be mainly considered as the role played by water; 1) the action of the radicals produced by the radiolysis of water, and 2) the increase in mobility of chain segments by the presence of water. To elucidate the role played by water, it is necessary to obtain more sufficient data about the behavior of water dominating the effects of the irradiation on PVA.

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Accordingly, the present experiments were carried out on aqueous solutions and water-swollen films of PVA covering a more wide range of the polymer concentration with which the previous workers did not deal. The effects of air, concentration and mobility of chain segments, and also the differences in the effects of irradiation on the solutions and on the swollen films at the same concentration were studied.

## 2. EXPERIMENTAL

### 2. 1) Materials

Unfractionated and fractionated PVA were used in this experiment. The unfractionated PVA is the same one that was used in I<sup>7)</sup> and II. Its viscosity-average degree of polymerisation,  $P_v$ , is 1090 and its distribution curve of the degree of polymerisation is shown in I. The fractionated PVA was obtained by fractionating a commercial PVA from aqueous solutions by the slow addition of n-propanol.  $P_v$  of the fraction used in this experiment is 1990. Re-saponification of both PVA was performed, after which the excess of NaOH was completely extracted by methanol and no acetyl residue was detected.

### 2. 2) Preparation of swollen film and solution

The swollen films were prepared by the same method as described in I and II. The polymer was cast on the glass plate from 10 % aqueous solution to yield upon drying films of 0.03 to 0.08 mm thickness. The film was dried under vacuum at room temperature and preserved in a desiccator containing  $P_2O_5$ . The film was immersed in water at 30°C for two days till it achieved a swelling equilibrium, and was then cleared of the water from the surface. The aqueous solution for the irradiation was heated to eliminate the dissolved air from the solution, after the solution of a given concentration was prepared.

### 2. 3) Irradiation

Irradiation was carried out in glass tubes at room temperature, using a Co-60 source of 2000 Curies at the Institute for Chemical Research, Kyoto University. The dose rate is  $2.1 \times 10^5$  r/hr. The glass tube containing the solution or swollen film was sealed in air at atmospheric pressure, or *in vacuo* after repeating evacuation in a nitrogen atmosphere. Irradiation was started one day after the tube was sealed.

### 2. 4) Measurements of viscosity, sol fraction and degree of swelling

After irradiation, water was added to the sample, and the sample was left to stand for a day at room temperature. Then the sample was heated on a boiling water bath. If the sample contains no gel part, it was readily dissolved in a few minutes, but otherwise it was heated for 16 hrs and the insoluble part (gel) was separated from the soluble part (sol) by a glass filter. Immediately after the separation, the swollen gel was weighed and then dried under vacuum. The degree of swelling was calculated by the following equation :

Degree of swelling (by weight) =  $\frac{\text{weight of the swollen gel}}{\text{weight of the dried gel}} - 1$  (at 100°C).

Sol fraction was given by the following equation:

$$\text{Sol fraction (\%)} = \left(1 - \frac{\text{weight of the dried gel}}{\text{weight of PVA used}}\right) \times 100.$$

$P_v$  of the sol part was calculated from the limiting viscosity number  $[\eta]$  measured in aqueous solution at 30°C by the following equation:

$$[\eta] = 7.51 \times 10^{-3} \times P_v^{0.64} \text{ (conc. in g/100 ml).}$$

### 3. RESULTS AND DISCUSSION

#### 3. 1) Irradiation in air on the water-swollen films

It seems very interesting to investigate the effects of irradiation on water-swollen films whose weight fraction of polymer can be changed in a very wide range. Particularly the range of high weight fraction of polymer is interesting, for it is very difficult to prepare PVA solution of very high concentration.

Irradiation was carried out in air on the water-swollen films of various water contents, which had been prepared from the unfractionated PVA with  $P_v$  of 1090.  $P_v$ , the probability of a fracture  $\alpha$  and other quantities are listed in Table 1.  $\alpha$  was calculated by the Sakurada-Okamura equation<sup>5)</sup> using  $m = [\eta]/[\eta]_0$ : where  $[\eta]$  and  $[\eta]_0$  was the limiting viscosity number before and after the degradation, respectively. To calculate  $\alpha$ , it was assumed that crosslinking was not occurred and that all ends of main chain fracture were stabilized. Therefore, the apparent probability of a fracture was thus obtained. As can be seen in Table 1, the main chain fracture is increased with increasing dose and at about  $4 \times 10^7$  r, a gel was formed. This is

Table 1. Effects of  $\gamma$ -irradiation in air on water-swollen films of PVA.

Concentration (wt. fraction)	Dose (r)	Sol fraction (%)	$[\eta]$ (100ml/g)	$P_v$	$\alpha$
non-irradiated PVA	—	—	0.655	1085	—
0.157	$5.4 \times 10^6$	100	0.360	429	0.0029
"	11.9 "	"	0.230	210	0.0075
"	38.0 "	"	0.158	117	0.02
0.193	5.4 "	"	0.390	480	0.0024
"	12.9 "	"	0.231	211	0.0074
"	13.5 "	"	0.223	200	0.0079
"	42.0 "	13	0.294*	308*	—
0.235	6.4 "	100	0.384	468	0.0024
"	7.1 "	"	0.379	459	0.0026
"	10.8 "	"	0.300	318	0.0044
"	12.9 "	"	0.261	287	0.0060
"	42.0 "	15	0.188*	153*	—
0.415	9.5 "	100	0.373	447	0.0027
"	11.9 "	"	0.322	355	0.0037

\*  $[\eta]$ ,  $P_v$  of sol part.

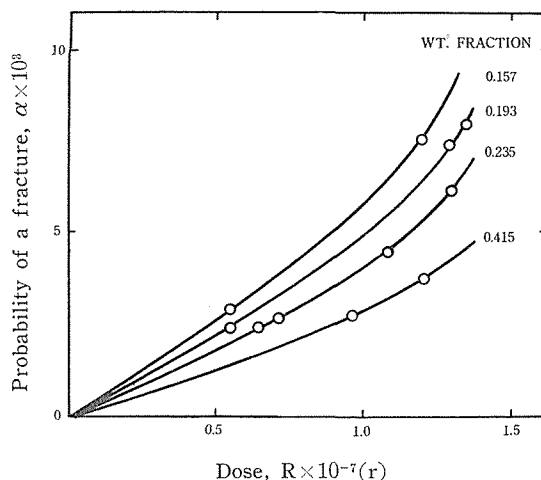


Fig. 1 Probability of a fracture against total dose for water-swollen films of PVA irradiated in air.

in accord with the results obtained previously in our laboratory<sup>6)</sup>.

$\alpha$  is plotted against dose  $R$  in Fig. 1, where it is seen that the relation between  $\alpha$  and  $R$  is linear at lower doses but deviates upward from the linearity at higher doses. This increase in  $\alpha$  at higher doses can be interpreted as follows; if in addition to main chain fracture some crosslinking occurs, the polymer molecules would become increasingly branched and their limiting viscosity number would fall increasingly below those of linear molecules of the same molecular weight and, therefore, the value of  $\alpha$  would become larger than those which would be obtained when only main chain fracture could occur.

Now, we will calculate how the indirect effect of water contributes to the main chain fracture. For a radiation dose  $R$  in roentgen unit, the energy absorbed per gram of swollen film is  $RA$  (where,  $A=0.58 \times 10^{14}$  eV.). Therefore, the energy absorbed directly by polymer in the swollen film is  $RAc$ , where  $c$  is the weight fraction of polymer (g/g), and similarly the energy absorbed by water is  $RA(1-c)$ . Provided that all  $RA(1-c)$  is not used for the degradation but that only fraction  $k$  of it is used, the energy transferred to polymer from water is  $kRA(1-c)$ . Therefore, the total energy given to polymer amounts to  $RAc+kRA(1-c)$ .

The number of main chain fracture per gram of swollen film is  $cN\alpha/M_m$ , where  $N$  is Avogadro's number and  $M_m$  is the molecular weight of the monomer unit.

So the energy dissipated per fracture,  $E_d$ , is given by,

$$E_d = \frac{RAc + kRA(1-c)}{cN\alpha/M_m} \quad (1)$$

or

$$\alpha = (RAM_m/E_dN) \{k/c + (1-k)\}. \quad (2)$$

Assuming that  $E_d$  is independent of the weight fraction of the polymer,  $k$  and  $E_d$  will be given by the slope and the intercept of the straight line obtained by plotting  $\alpha$  against  $1/c$  at a fixed dose.

Equation (2) indicates that a plot of  $\alpha$  against  $R$  should be a straight line, if  $c$  is constant. As mentioned above, the plots in Fig. 1 is linear only at low doses, possibly because of the formation of branched polymers. So,  $(AM_w/E_dN) \{k/c + (1-k)\}$  obtained from the initial slope was plotted against  $1/c$  (Fig. 2). The cor-

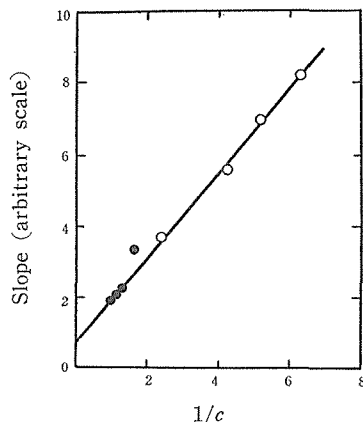


Fig. 2. Slopes of curves in Fig.1 against reciprocal of concentration (wt. fraction) of polymer.

- ..... result obtained in this paper.  
●..... result obtained in II.

responding values in the previous paper<sup>1)</sup> were also plotted in Fig. 2. As shown in Fig. 2, a good straight line was obtained, from which  $k=0.69$ ,  $E_d=36$  eV. was derived. This shows that not all the energy absorbed by water but only 69% of it was dissipated for main chain fracture. The value of 36 eV., *i. e.*, the energy dissipated per main chain fracture, is in accord with the value of 38.7 eV. which was obtained in I<sup>7)</sup> in the case of irradiation on dry PVA.

### 3. 2) Irradiation in air on the aqueous solutions

Studies on the aqueous solutions so far published have dealt with solutions of a rather low concentration. Therefore, irradiation was carried out on aqueous solutions of comparatively high concentrations and the effects were compared with those on the water-swollen films. The PVA used and the radiation condition are the same as described in 3. 1). The results are given in Table 2.

When the swollen films were irradiated in air, the  $P_g$  was decreased with increasing dose and abruptly a gel was formed at high doses. In the case of the solutions, on the contrary, as the dose was increased,  $P_g$  was increased consistently and a gel was formed. This phenomenon that  $P_g$  is increased with dose, finally resulting in gel formation, has been found in earlier studies on the effect of irradiation *in vacuo* on aqueous PVA solutions. It is also reported that polymer is degraded when the solution of a low concentration is irradiated in air. Notwithstanding that in our case the solution was irradiated in air, the result obtained was essentially the same as that obtained when irradiation is carried out *in vacuo*. This may well be due to the fact that irradiation was carried out on such a high concentrated solution as a gel structure was formed. Presumably air would not be able to

Table 2. Effects of  $\gamma$ -irradiation in air on aqueous solutions of PVA.

Concentration (wt. fraction)	Dose (r)	Sol fraction (%)	$[\eta]$ (100ml/g)	$P_v$	Degree of swelling of gel
Non-irradiated PVA	—	—	0.655	1085	—
0.10	$0.8 \times 10^6$	100	0.824	1544	—
"	1.3 "	100	1.06	2285	—
"	2.0 "	60	0.736	1292	80.3
"	3.3 "	35	0.412	522	47.5
"	3.5 "	27	0.390	480	43.2
"	7.1 "	23	0.300	318	25.1
"	8.0 "	23	0.289	300	22.6
0.20	1.5 "	100	0.797	1464	—
"	3.3 "	100	1.00	2100	—
"	4.6 "	50	0.603	946	73.6
"	4.9 "	44	0.655	1085	83.5
"	7.1 "	32	0.350	405	26.2
"	21.0 "	17	0.255	207	13.6
0.25	7.5 "	48	0.500	706	55.3
"	15.0 "	35	0.341	388	17.1

diffuse sufficiently into the interior of the solution, accordingly the oxygen has only affected the surface of the solution. In the case of the swollen films, it seems likely that air is able to diffuse more easily into the interior of the film because of its thin thickness. The effect of air is to be discussed in detail later.

The energy absorbed by the solution will be partly used for the reaction which concern neither with crosslinking nor degradation. So the energy actually used for crosslinking and degradation of polymer will be less than all the energy absorbed by the solution. Therefore when dose  $R$  is irradiated on the solution, the energy actually used for the polymer reactions will be reduced to  $Rf(c)$ , where  $f(c)$ , being a function of the weight fraction of polymer  $c$ , is given, as in 3. 1), by,

$$f(c) = c + k(1 - c)$$

Recently a theoretical equation was deduced by A. Charlesby and S.H. Pinner<sup>2)</sup> to calculate the ratio of degradation and crosslinking from the dose and the sol fraction  $S$ . The equation can be modified in our case as follows:

$$S + \sqrt{S} = p_0/q_0 + 1/q_0 Rf(c)u_1,$$

where  $p_0$  and  $q_0$  is the fracture density and the density of crosslinked units per unit dose respectively,  $R$  is the dose in roentgen unit and  $u_1$  is the initial number-average degree of polymerisation of PVA. Hence, from the intercept of the straight line obtained by plotting  $S + \sqrt{S}$  against  $1/R$ ,  $p_0/q_0$  can be obtained, and if  $f(c)$  is accurately known,  $p_0$  and  $q_0$  can be calculated separately.

$S + \sqrt{S}$  was plotted against  $1/R$  in Fig. 3, and the result obtained from these plots is given in Table 3. 0.69 was used for  $k$  involved in the function  $f(c)$ , which had been obtained in 3. 1).

Table 3. Radiation parameters and gelation doses for air-irradiated aqueous solutions of PVA.

Concentration (wt. fraction)	$p_0/q_0$	$p_0 \times 10^4$	$q_0 \times 10^4$	Gelation dose (r)
0.10	0.27	3.0	11.4	$1.0 \times 10^6$
0.20	0.39	2.7	6.8	4.2 "
0.25	0.55	2.5	4.4	6.0 "

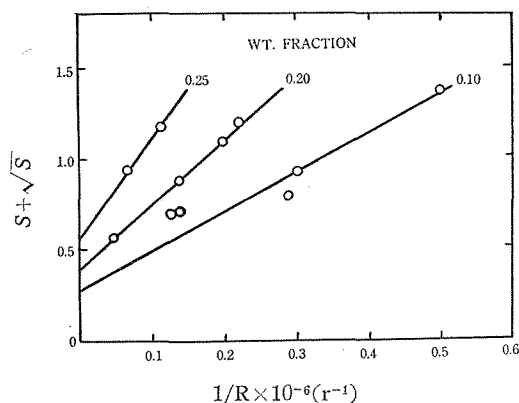


Fig. 3. Curves of  $S + \sqrt{S}$  against reciprocal of dose for aqueous solutions of PVA irradiated in air.  
 $S$  = sol fraction.

As shown in Table 3,  $p_0$  is nearly independent of the weight fraction, while  $q_0$  is remarkably decreased with increasing weight fraction of the polymer. This shows that the main chain fracture occurs independently of the weight fraction, but that the formation of crosslinking becomes difficult with increasing weight fraction.

The gelation dose is given in the last column of Table 3. It was obtained from the plot of the reciprocal of the degree of swelling against the dose. The dose at which the reciprocal of the degree of swelling = 0 was taken as the gel point.

### 3. 3) Irradiation at a fixed dose in air and *in vacuo* on the water-swollen films.

In this section, we investigated mainly the effect of oxygen. The water-swollen films prepared from the fractionated PVA with  $P_v$  of 1990 were irradiated *in vacuo* and in air at a fixed dose of  $3.2 \times 10^6$  r. The results were shown in Table 4.

The sample used for irradiation *in vacuo* could be evacuated up to  $10^{-3}$  mm Hg because of the presence of water which was contained in the film, but in the case of the dry film, it was sealed after evacuation up to  $10^{-6}$  mm Hg for 25 hrs. When irradiation is carried out in air, it is desirable to irradiate the sample in an open tube to supply air constantly, but in our case as the sample contained water, the irradiation was carried out in a sealed tube.

In Fig. 4,  $P_v$  of sol part was plotted against the weight fraction of the polymer.



Table 4. Effects of  $\gamma$ -irradiation *in vacuo* and in air on water-swollen films of PVA.  $R=3.2 \times 10^6 r$ .

<i>in vacuo</i>					
Degree of swelling of sample	Concentration (wt. fraction)	$[\eta]$ (100ml/g)	$P_v$	Sol fraction (%)	Degree of swelling of gel
10.8	0.095	0.722	1393	26.5	18.7
7.3	0.120	0.897	1760	31.6	25.5
3.8	0.208	1.135	2544	55.5	70.5
3.1	0.244	—	—	large	large
1.8	0.357	0.992	2063	100	—
1.1	0.476	0.943	1903	100	—
Dry film	1.00	0.810	1501	100	—

<i>in air</i>			
Sol fraction (%)	$[\eta]$ (100ml/g)	$P_v$	Degree of swelling of gel
35	0.593	922	26.9
100	0.578	886	—
"	0.698	1190	—
"	0.705	1209	—
"	0.718	1243	—
"	0.746	1320	—
"	0.798	1467	—

It shows that there is a remarkable difference between irradiation *in vacuo* and in air. In the former case,  $P_v$  was increased with decreasing weight fraction up to gel point, while in the latter case,  $P_v$  was decreased monotonously and gel was formed when  $P_v$  was decreased suddenly. This may be explained as due to the formation of branched polymers, eventually resulting in the formation of network structure, as mentioned in 3. 1). The maximum concentration for gelation was

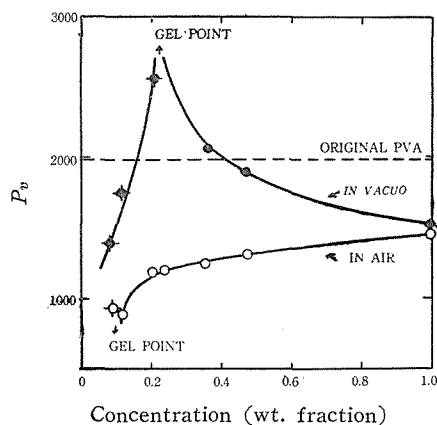


Fig. 4. Degree of polymerisation of sol part against concentration for water-swollen films irradiated *in vacuo* and in air.  $R=3.2 \times 10^6 r$

○, ●..... no gel was formed.

about 23% for irradiation *in vacuo* and 10% for irradiation in air.

Now we will discuss the chemical mechanism of crosslinking and degradation.

a) Irradiation *in vacuo*

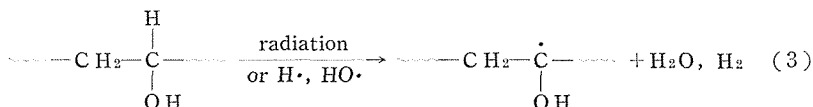
The phenomena that  $P_v$  of the sol part is increased with decreasing weight fraction, finally resulting in gel formation, may be interpreted as follows; with decreasing weight fraction, the concentration of  $H\cdot$  and  $HO\cdot$  produced by the radiolysis of water is increased, so the indirect effect is increased and crosslinking is promoted. Moreover it seems also very plausible that, as a result of the increase in mobility of chain segments by penetration of water, the reactions between polymers may be promoted and increase the  $P_v$  of the sol part. Probably both of these effects may concern. Whether water promotes crosslinking mainly by behaving as a plasticizer, or the radicals produced by the radiolysis of water have large influence on crosslinking is now studied in our laboratory. Up to this time it has been simply considered that  $H\cdot$  and  $HO\cdot$  promote crosslinking, but the possibility should be also noticed that these radicals, on the contrary, may suppress crosslinking by deactivating polymer radicals or may participate in the degradation of the polymer.

b) Irradiation in air

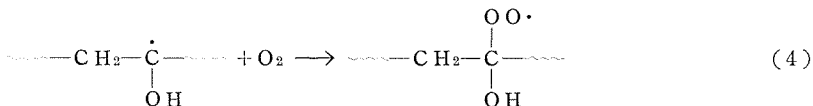
In this case,  $P_v$  is decreased with decreasing weight fraction of the polymer. If degradation is due to only the direct effect of the polymer, it should occur independently of the weight fraction of the polymer. It seems unlikely that the increase in mobility of chain segments may promote degradation. Apparently oxygen influences degradation remarkably, but as it may be assumed that the amount of oxygen is constant at any weight fraction range, so the phenomena that  $P_v$  changes with the weight fraction, can not be interpreted by the action of oxygen only. But by the mechanism which was proposed by Phillips *et al.*<sup>9)</sup> in their study on the effects of irradiation on aqueous solutions of carbonhydrates, the phenomena can be explained qualitatively. According to their mechanism, the  $HO_2\cdot$  which is produced by the reaction between oxygen and  $H\cdot$  is considered to play a important role.

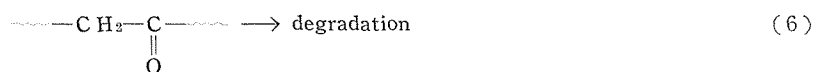
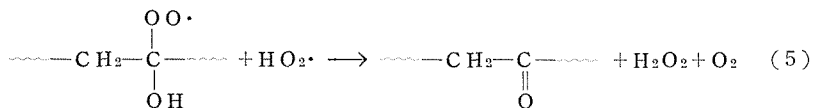


The hydrogens of polymers will be abstracted by the direct action of radiation, or by the radicals produced from water, as follows:



This polymer radicals may react with oxygen, and are degraded *via* the following processes.





The polymer radicals, being able to crosslink, produced in the reaction (3) may be immediately attacked by oxygen and be degraded as indicated in the reactions (4), (5) and (6). An increase in the concentration of  $\text{HO}_2 \cdot$  with decreasing weight fraction of the polymer leads to an increase in the main chain fracture.

Now, as degradation proceeds considerably, the amounts of polymer radicals may be increased and hence the probability of formation of branched polymers will become higher and finally a network may be formed. It may be also taken into account that as a result of consumption of oxygen, the reactions (2) and (4) can no more occur and then crosslinking reaction begins.

### 3. 4) Irradiation at a fixed dose *in vacuo* on aqueous solutions

In order to make clear the effect on PVA-water system over the entire weight fraction range, irradiation was carried out *in vacuo* on the aqueous solutions covering the low weight fraction range which was not dealt with in the previous sections.

The material used was the fractionated PVA with  $P_v$  of 1990 and the radiation dose was  $3.2 \times 10^6 \text{r}$ . The effects of irradiation are given in Table 5. Sol fraction is plotted against the weight fraction of polymer in Fig. 5.

The solutions of 0.001 and 0.002 weight fraction become colored yellow to brown by irradiation and no polymeric substance was detected after the irradiated solution was evaporated to dryness. As the weight fraction was increased,  $P_v$  was increased and finally a gel was formed at 0.003 wt. fraction. At a higher concentration than 0.003 wt. fraction, a slight increase in the weight fraction reduced suddenly the sol

Table 5. Effects of  $\gamma$ -irradiation *in vacuo* on aqueous solutions of PVA.  $R=3.2 \times 10^6 \text{r}$

Concentration (wt. fraction)	Sol fraction (%)	$[\eta]$ (100ml/g)	$P_v$	Degree of swelling of gel
non-irradiated PVA	—	0.970	1990	—
0.001	100	0	—	—
0.002	"	0.508	724	—
0.003	"	0.635	1027	—
0.004	72.0	1.50	3930	large
0.006	0	—	—	22.5
0.010	0	—	—	24.3
0.030	18.5	0.466	630	27.6
0.061	34.0	0.420	538	20.1
0.102	42.0	0.527	795	18.7
0.124	60.3	0.543	804	23.4
0.152	85.1	0.560	843	43.2

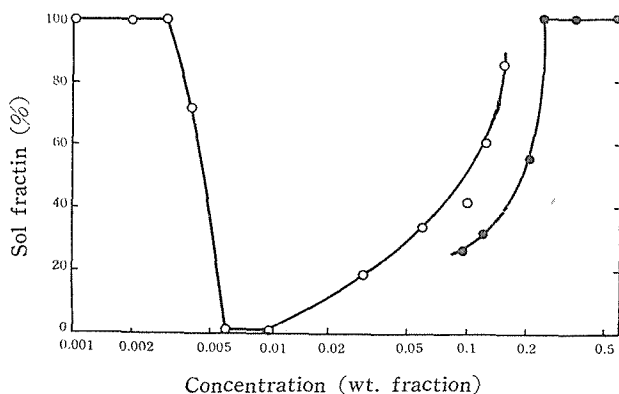


Fig. 5. Sol fraction against concentration for aqueous solutions of PVA irradiated *in vacuo*.  $R=3.2 \times 10^6$ r.

○... solution, ●... swollen film.

fraction from 100% to 0% and at 0.006 weight fraction no sol part was found. The gel formed by irradiation of the solution of 0.006~0.01 weight fraction floated freely in the solution which was essentially free from polymers. At the weight fraction of 0.03, a polymer fraction which did not take part in gel appeared, whose amount was increased with increasing weight fraction of polymer until it reached to 100% at about 0.20 weight fraction. The result that at concentrations less than 0.003 weight fraction no gel is formed and that at 0.006~0.01 weight fractions a gel is formed most readily, is in agreement with the results obtained by A. Charlesby<sup>23</sup> and A. Danno<sup>24</sup>.

Fig. 5, in which the results obtained for the water-swollen films were compared with that for the solutions, shows that the swollen film has less sol fraction than the solution at the same weight fraction.

### 3. 5) Irradiation on higher concentrated aqueous solutions

It is well known that a gel structure connected by hydrogen bonds is formed on standing a higher concentrated aqueous solution of PVA at room temperature and that the viscosity of the solution increases with the standing time. Therefore, if irradiation is carried out on solutions which have been stood for some period after preparation, the standing effect will be reflected upon the effects of irradiation.

The PVA used and radiation condition are the same as described in 3. 3) and 3. 4). The weight fraction of polymer in the solution was 0.10. This solution did not flow after standing for a day after preparation. Irradiation was carried out at four times, namely immediately after preparation of the solution; one day, four days and ten days after preparation. The temperature of irradiation and standing was 20°C. Table 6, Figs. 6 and 7 show the results.

As can be seen in Fig. 6, sol fraction and degree of swelling were decreased slightly with the standing time. It is quite likely that the polymer segments are arranged by the hydrogen bonds in the solution during standing so as to favor crosslinking. Accordingly sol fraction and degree of swelling of the gel would be

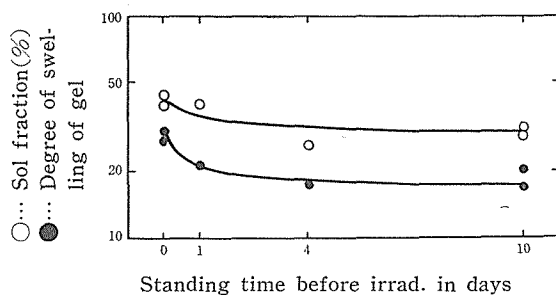


Fig. 6. Sol fraction and degree of swelling against standing time before irradiation for higher concentrated aqueous solutions of PVA. Concentration (wt. fraction)=0.10,  $R=3.2 \times 10^6 r$ .

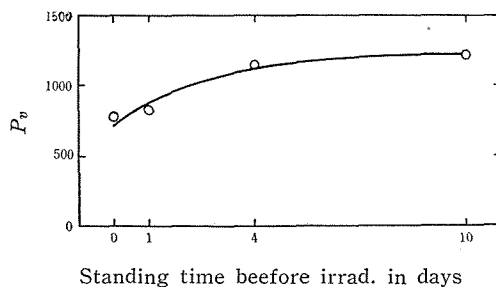


Fig. 7. Degree of polymerisation against standing time before irradiation for higher concentrated aqueous solutions of PVA. Concentration (wt. fraction) =0.10,  $R=3.2 \times 10^6 r$ .

Table 6. Effect of  $\gamma$ -irradiation on higher concentrated aqueous solutions of PVA. Concentration (wt. fraction) of polymer=0.10,  $R=3.2 \times 10^6 r$ .

Standing time before irradiation in days	0	0	1	4	10	10
Sol fraction (%)	39.6	43.7	40.6	26.5	30.2	30.0
$[\eta]$ (100ml/g)	0.540	0.550	0.560	0.685	0.703	0.703
$P_v$	797	820	843	1158	1203	1203
Degree of swelling of gel	28.1	30.6	21.4	17.5	17.2	20.7

decreased with the standing time, although the mobility of chain segments were reduced by the gel formation. The results answer the expectation but the effect of standing on the irradiation effect is not so remarkable as expected from the viscosity change occurred during standing.

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