Effects of Gamma Radiation on Polymers in Solutions. (VIII)

Radiation Effects on Poly(Vinyl Alcohol) in Aqueous Solutions below Critical Concentration for Gel-Formations

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Aqueous solutions of poly(vinyl alcohol) (PVA) were irradiated in the absence of air with Co-60 γ-rays at very low concentrations such as 0.184, 0.100 and 0.06%. (The critical concentration for gel-formation of this solution was 0.22%). It was found that at small doses solution viscosity increased, but after reaching a maximum, decreased monotonically with increasing radiation dose. The increase in viscosity was attributed mainly to the formation of inter-molecular crosslinking, and the decrease in viscosity mainly to the intra-molecular crosslinking. The evidence for the formation of the intra-molecular crosslinking was obtained by various measurements such as turbidity, acetylation, swelling and X-ray diffractions. Infrared spectra of the irradiated PVA indicated that the OH groups of PVA disappeared partly during irradiation, while slight formation of carbonyl group was observed. The number of intra-molecular crosslinks was calculated using Flory-Rehner's and Einstein's equations.

INTRODUCTION

In the previous paper[1], we have investigated the gelation of poly (vinyl alcohol) (PVA) in aqueous solutions, and observed that, when polymer concentrations of the solutions to be irradiated were below a critical value, a macrogel, namely, an infinite network could not be formed by any dose. It was concluded that, at the critical concentration for gelation, all polymer spheres just begin to overlap with each other in the solution.

Then, if the solutions are irradiated below the critical concentration, how could the polymer be changed? This problem has been treated by a number of workers, such as Berkowitch et al.[2], Dieu[3], Desreux[4], Wippler[5], Danno[6] *etc.* However, all of them studied only briefly and, besides, their results were not always in agreement with each others.

In order to provide a more detailed picture of the radiation effect on polymer solutions below the critical concentration, a systematic study was carried out for thoroughly degassed aqueous solutions of PVA. The present paper is also concerned with various properties of the irradiated PVA thus obtained.

EXPERIMENTAL

1) Material

The PVA used here is the sample F-5, whose characteristics were described

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in the previous paper[1]. The limiting viscosity number $[\eta]$ and the viscosity-average degree of polymerization $\bar{P}$ are 0.800 and 1500, respectively.

2) Preparation of Aqueous Solutions and Irradiation Procedures

These are quite similar to those described previously[1], except the dose rate, which is approximately 1.33×10^5 r/hr in the present study. Irradiation was carried out in most cases at room temperature (about 20°C), with an exception of 85°C.

3) Viscosity Measurements

An Ubbelohde-type viscometer was used for the measurements in water at 30°C, unless otherwise specified.

4) Turbidity Measurements

Intensities of scattered lights in the direction of 90° from the incident light were measured at room temperature using a photoelectric turbidimeter. Experimental data were expressed by the value of relative turbidity τ, which was defined by the following equation :

$$\tau = 2.303 \log I_0/I_1 \tag{1}$$

where I_0 and I_1 are the intensities of light scattered from the solutions before and after irradiation, respectively.

5) Reaction of the Irradiated PVA with Alkali and Acid

NaOH or HCl was added to aqueous solutions of PVA, the final concentration being adjusted to 0.1 N, and the solutions thus obtained were heated on a boiling water bath for 3 hrs. The polymer concentration during the reaction was 0.1%.

6) Acetylations

Acetylation of PVA was carried out under a more severe condition than usual ones[7]. The reaction mixture containing one part of PVA, 20 parts of acetic anhydride and 40 parts of pyridine was sealed in tube under a nitrogen atmosphere, which were allowed to stand at 60°C for 3 hrs, and then rotated incessantly in an oil bath of 110°C for 15 or 30 hrs. The reactant was then poured into water and the acetylated PVA was separated and purified. The degree of acetylation was determined from the weight difference before and after the reaction.

7) Infrared Spectra Measurements

An AR-275-IIS type infrared spectrophotometer was used with a NaCl prism. Infrared spectra were measured using dry films of the PVA.

8) Swelling Measurements

Degrees of swelling were measured by immersing PVA films in water at 30°C for 48 hrs. Films (thickness ; 0.08 mm) were prepared by casting the polymer solution on glass plate and then dried over P_2O_5 at 20°C for 2 days. They were used for the swelling measurement without any heat treatment.

9) X-ray diffractions

X-ray diffraction patterns were obtained with nickel-filtered Cu Kα radiation (40 kV) using a flat film. The distance between the sample and camera was 2.9 cm, and the thickness of samples was about 0.2 mm.

RESULTS

1) Viscosity Change under Irradiation

1.1) Irradiation at 20°C Fig. 1 shows the change in $[\eta]$ occurring during irradiation of aqueous solutions of various polymer concentrations. Viscosities
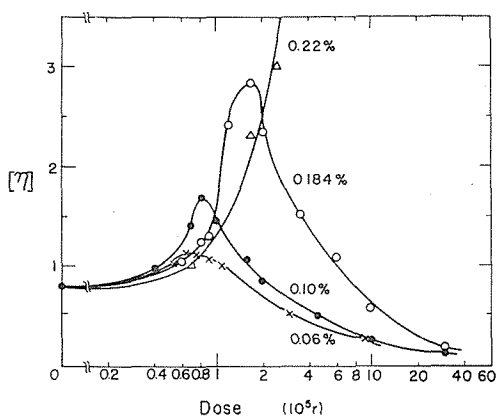

Fig. 1. Viscosity change of aqueous solutions of PVA irradiated at 20°C for various polymer concentrations. Viscosity was measured in water at 30°C.

of irradiated polymers were measured in water at 30°C. In the previous paper[1], the critical concentration of this polymer was found to be 0.22%. The solutions of lower concentrations than 0.22% became turbid upon irradiation and the value of $[\eta]$ decreased with increasing dose. Details of this phenomenon will be given later. Solutions irradiated with a dose of 3×10^6 r became light-brown.

Dieu[3,4] and Danno[6] obtained different results from ours in the range of small doses. Their results indicate that solution viscosity decreases at first with radiation dose, and after reaching a minimum, increases again. Thereafter, viscosity changes quite similarly to ours. The reason for the viscosity decrease observed in their cases may be that air was not thoroughly eliminated from the solutions for irradiation, hence causing the main-chain scission through HO$_2 \cdot$ until the dissolved air was completely exhausted.

Dieu[3] observed furthermore, that the maxima of curves in Fig. 1 disappeared when viscosity was measured in the mixed solvent of water and dioxane. He ascribed the increase in viscosity in water to association of several polymer spheres by hydrogen bonds, which would be destroyed by dioxane.

In order to examine his result, the viscosities were measured in the mixed solvent of water and n-propanol, since the latter is known to destroy the hydrogen bonds more powerfully than dioxane.
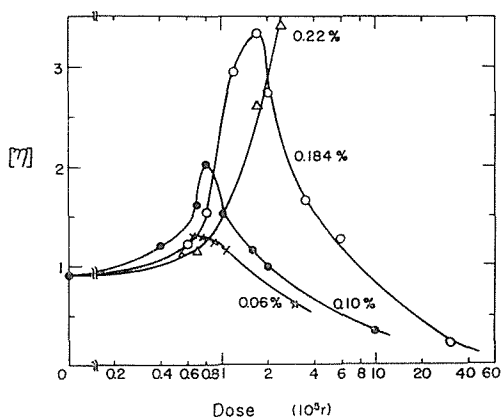
Fig. 2. Viscosity change of aqueous solutions of PVA irradiated at 20°C for various polymer concentrations. Viscosity was measured in mixed solvent of water and n-propanol (7:1) at 30°C.
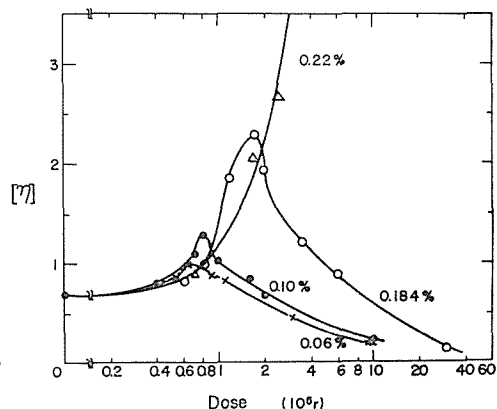
Fig. 3. Viscosity change of aqueous solutions of PVA irradiated at 20°C for various polymer concentrations. Viscosity was measured in water at 65°C.

The results are shown in Fig. 2, where curves have a similar shape to those in Fig. 1. Furthermore, viscosity measurements were carried out in pure water at an elevated temperature of 65°C, as the hydrogen bonds of PVA in aqueous solutions have been found to be easily broken especially at temperatures higher than 60°C[3].

Fig. 3, where the viscosities measured at 65°C were plotted against radiation dose, also indicates the same tendency as that shown in Figs. 1 and 2. We found that the viscosity of 100% acetylated PVA obtained from the irradiated PVA that gave the maximum $[\eta]$ is higher than that of 100% acetylated PVA from the unirradiated PVA. This finding, together with Figs. 1, 2 and 3, gives a strong evidence for the presence of polymer molecules bound together by primary-valence, in other words, for the formation of inter-molecular crosslinking by radiation.

1.2) Irradiation at 85°C Since the radiation effect on polymers in solutions is likely to depend on the state of solution, irradiation was carried out at an elevated temperature of 85°C, where the aqueous solutions of PVA may be more
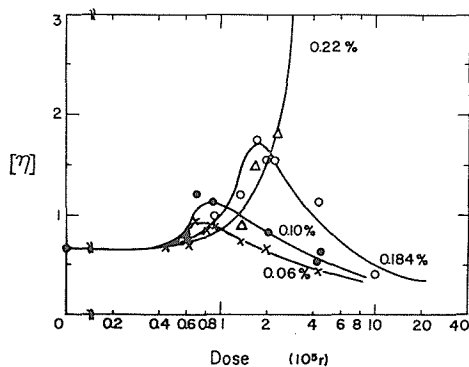
Fig. 4. Viscosity change of aqueous solutions of PVA irradiated at 85°C for various polymer concentrations. Viscosity was measured in water at 65°C.

stable than at room temperature. Viscosity changes are given in Fig. 4, which does not show qualitatively any features different from Fig. 1, indicating that the difference in the state of solution between 20° and 85°C does not essentially affect the radiation effects.

2) Turbidity of Irradiated Solutions

As described in 1), solutions became turbid when irradiated under certain conditions. The relative turbidity τ is plotted in Fig. 5 against the radiation dose for the solutions irradiated at 20°C. Comparison of Fig. 1 with Fig. 5 indicates
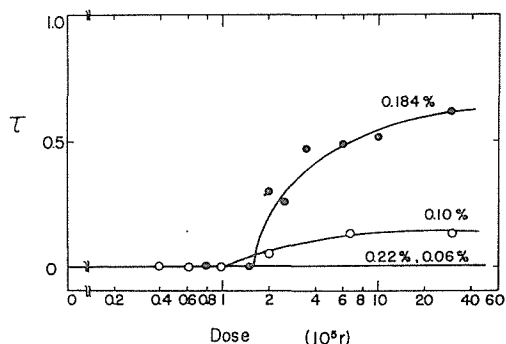

Fig. 5. Relative turbidity τ of aqueous solutions of PVA irradiated at 20°C for various polymer concentrations.

that the solutions become turbid, only when the solution viscosity begins to decrease with radiation dose. The solutions remain turbid after heating at 100°C.

It should be recalled here that aqueous solutions of poly(acrylic acid) were also found by us[9] to become turbid under irradiation *in vacuo* in the presence of NaCl. Then, it was concluded from the various measurements that the origin of turbidity should be attributed to the formation of intra-molecular crosslinking. These results suggest strongly that the intra-molecular crosslinking may be formed also in this present case. This suggestion will be justified by various experimental evidences described in the subsequent paragraphs.

3) Reaction of Irradiated PVA with NaOH or HCl

The values of $[\eta]$ measured before and after heating the PVA in alkaline

Table 1. Viscosity Change by the Reaction of Irradiated PVA with Alkali and Acid (Heating, 100°C, 3 hrs; Polymer Concentration=0.1%; Concentration of Solution during Irradiation=0.184%).

Dose (Mr)	Alkali or Acid concentration	30°	100°
0	0	0.803	0.80
0.40	1N–HCl	1.2	1.0
//	1N–NaOH	1.2	0.8
1.0	0	0.596	0.53
//	1N–HCl	0.53	0.58
//	1N–NaOH	0.56	0.41

and acidic aqueous solutions are given in Table 1. $[\eta]_{30°}$ and $[\eta]_{100°}$ denote the limiting viscosity number before and after heating, respectively. The PVA samples used for these reactions are the unirradiated and irradiated. The latter PVA was obtained by irradiation in 0.184% solution and used throughout in the experiments described hereafter.

As is evident from Table 1, the irradiated PVA undergoes no noticeable chemical changes by these treatments within experimental error, indicating that such bonds as ester, carbonyl and other weak ones which can be cleaved easily by alkali or acid, are not practically formed under irradiation.

4) Acetylation of Irradiated PVA

In order to ascertain whether all OH groups of the irradiated PVA can be acetylated, acetylation was carried out under a severe condition. The results of acetylation are shown in Table 2. Since there is no difference in the degree of acetylation between 15 hrs and 30 hrs, the acetylation reaction can be considered to have come to the end before 15 hrs. It is interesting to note that, in the case of samples 3, 4 and 5, the final products did not dissolve in the reaction system.

Table 2. Degree of Acetylation and Swelling of Acetylated PVA (Concentration of Solution during Irradiation=0.184%).

Sample	Dose (Mr)	$[\eta]$	Degree of Acetylation			Degree of Swelling in Acetone at 30°C
			Reaction time	15hr	30hr	
1	0	0.803		100.5	—	∞
2	0.08	1.22		101.0	—	∞
3	0.12	2.50		99.2	—	24.8
4	0.40	1.32		75.3	79.2	22.6
5	1.0	0.572		67.2	64.1	14.0

Table 2 indicates that all the OH groups cannot be acetylated in the case where $[\eta]$ of PVA decreases with radiation dose. The finding that the acetylated PVA's obtained from samples 3, 4 and 5 do not dissolve in good solvents such as dimethyl sulfoxide, chloroform, and acetone, but only swell in them, gives a strong support for the formation of intra-molecular crosslinking, namely, microgel particles. It cannot be concluded, however, only from this result that the intra-molecular crosslinking makes the OH groups less accessible to the acetylation reaction. The reason for this is that irradiation itself may have already changed some of OH groups into other ones such as not to be able to be acetylated.

5) Infrared Spectra

Whether the incomplete acetylation of the irradiated PVA should be attributed to steric hindrance due to the crosslinking, or to partial disappearance of OH groups by irradiation, may be elucidated to some extent by measurements of
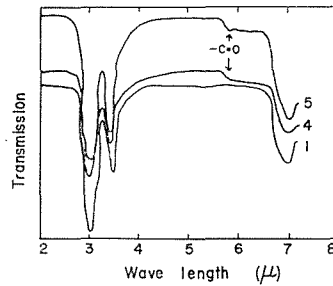
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Fig. 6. Infrared spectra of various PVA's. As for the number by curves, see Tab. 2.

infrared spectra of the irradiated PVA.

Fig. 6 shows the infrared spectra of the unirradiated and irradiated PVA in the wave length range where the obvious change of spectra was observed as a result of irradiation. Numbers 1, 4 and 5 in Fig. 6 correspond to the sample numbers in Table 2. It is seen from Fig. 6 that the absorption at 5.85μ (C=O group band) appears during irradiation, and fruthermore that the optical density at 3.0μ (OH group) decreases as the radiation dose increases. It suggests that the incomplete acetylation may be ascribed mainly to the disappearance of OH groups during irradiation.

6) Swelling of Films of Irradiated PVA in Water

In order to obtain knowledge concerning the crystalizability of the irradiated PVA molecule, the degree of swelling in water was measured using films prepared from the irradiated PVA. The results obtained at 30°C are given in Table 3, which shows the increasing degree of swelling with radiation dose. The most

Table 3. Degree of Swelling in Water at 30°C of Films of Irradiated PVA (Concentration of Solution during Irradiation=0.184%).

Sample	Dose (Mr)	$[\eta]$	Degree of Swelling (in wt.)
1	0	0.803	5.85
4	0.40	1.32	52.1
5	1.0	0.572	∞*
6	0	0.583	7.69

* Apparent degree of swelling.

interesting feature is that the film of sample 5 was so fragile, especially when immersed in wate at 30°C, that the degree of swelling could not be determined by our method. For comparison, the degree of swelling of an unirradiated PVA was also given in Table 3, whose $[\eta]$ is approximately equal to that of sample 5. Comparison of the degree of swelling of film 5 with that of film 6 shows clearly that the crystalizability of the film 5 is lower than that of unirradiated, ordinary PVA (No. 6), demonstrating the presence of intra-molecular crosslinking in the sample 5.

7) X-ray Diffraction Patterns

Photographs of the unirradiated and irradiated PVA are shown in Figs. 7 and 8. Sharpness of rings of the irradiated PVA is obviously weaker than that of the unirradiated PVA. This indicates that the former is less crystalizable than the latter, in agreement with the result of swelling measurements. As shown in Table 4, the plane distances of these two different films were identical within experimental error.
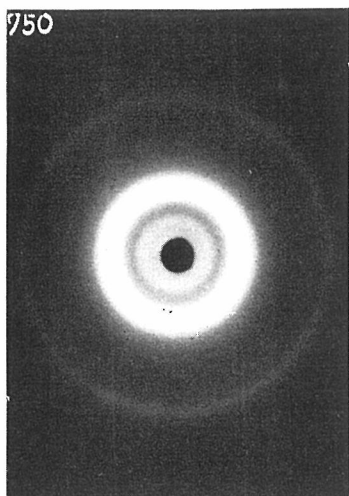

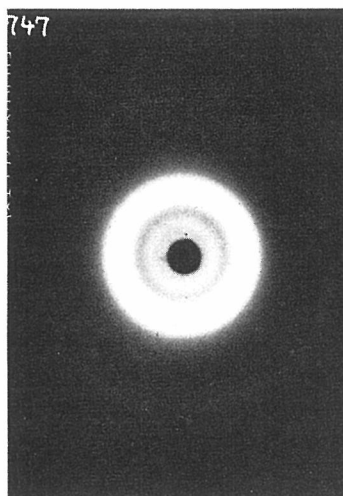Fig. 7. X-ray diffraction pattern of unirradiated PVA.

Fig. 8. X-ray diffraction pattern of irradiated PVA. Irradiation was carried out in 0.184% aqueous solution at 20°C.

Table 4. Plane Distance (Å) of Crystalline Part of PVA (Concentration of Solution during Irradiation=0.184%, Dose=1×10^6 r).

Sample	A_1	$A_{3,4}$	A_5	A_6	A_7	I_1	I_2
unirradiated[a]	7.71	4.51	3.86	3.21	2.74	2.41	2.20
irradiated[b]	7.68	4.52	3.86		2.75		2.21

a), b); heat-treated at 180°C for 15 mins.

DISCUSSION

1) Inter- and Intra-Molecular Crosslinking

In the previous paper[1], it was assumed that the polymer molecules distributed "uniformly" —from the statistical viewpoint— in the solutions, so that one was led to a hypothesis of the closed packing of the molecules. However, the local deviation from this uniformity may be possible due to the Brownian motion, which would give rise to the collisions of the molecules.

Therefore, in the initial stage of irradiation, the formation of inter-molecular crosslinking is quite possible. Really, the increase in viscosity observed in Figs.

1~4, supports this expectation. Further irradiation may make the local density of the polymer molecules in solutions higher, since each polymer will be integrated into large molecules by the inter-molecular crosslinking. When irradiation proceeds to some extent, the distance from one to adjacent polymer spheres becomes so large that the intra-molecular crosslinking occurs much more preferentially than the inter-molecular crosslinking. Therefore, at higher doses, viscosities begin to decrease as shown in Figs. 1~4, as a result of formation of the intra-molecular crosslinking, which was already ascertained by various results described above.

We will try to calculate the average number of initial molecule contained in a molecule of the final product, to which further inter-molecular crosslinking can occur no more, or only negligibly by any high dose. Let us assume here that the $[\eta]\text{-}\bar{P}$ relationship obtained by Nakajima and Furutachi[10] for PVA can be applied in this case and that the degree of polymerization calculated from the relationship is number-average. Then, we can obtain the numbers of initial molecule contained in a molecule of the final product, since the numbers can be taken to be equal to $\bar{P}_{max}/P_0$, where $\bar{P}_{max}$ and P_0 are the degrees of polymerization calculated from $[\eta]_{max}$ and $[\eta]$ of the initial PVA, respectively. The values obtained are given in the last column of Table 5. When the concentration of the solution for irradiation approaches to zero, the ratio perhaps approaches 1. Namely, in this case, the inter-molecular crosslinking may not be formed at all.

Table 5. Number of Primary Molecules Contained in a Final Molecule (Irradiation Temperature=20°C).

Concentration (%)	$[\eta]_{max}$	$\bar{P}_{max}$	Number of primary molecule $(=\bar{P}_{max}/P_0)$
0.22	∞	∞	∞
0.184	2.82	25000	17
0.100	1.68	6000	4
0.06	1.10	2500	1.67

The decrease in $[\eta]_{max}$ with decreasing polymer concentration may be due to the fact that as the solution becomes more dilute, the polymer molecules will be more apart from each others and hence it will be more difficult to form crosslinks.

2) Structures of Intra-Molecular-Crosslinked PVA

Figs. 1~4 indicate that the intra-molecular crosslinks reduce the size of polymer coils. This tendency was also found by Kuhn and Balmer[11] who used tetraphthalaldehyde as a crosslinking agent to crosslink PVA in dilute aqueous solutions.

It would be interesting to estimate the degree of swelling and hence the degree of polymerization between two crosslinked points $\bar{P}_c$, from $[\eta]$ of the intra-molecular-crosslinked PVA, in other words, micro-gels. Calculated values for

Table 6. Degree of Swelling of Micro-Gel and Number of Intra-Molecular-Crosslinks (Concentration of Solution during Irradiation=0.184%).

Dose (Mr)	$[\eta]$	P	Degree of swelling (in vol.)	$\bar{P}_c$	υ
0.17	2.82	25000	—	—	—
0.20	2.34	//	93.5	11900	1.05
0.40	1.32	//	52.8	11100	1.13
0.60	1.10	//	44.0	10690	1.17
1.0	0.572	//	22.8	8330	1.50
3.0	0.191	//	7.6	3030	4.1

the micro-gel obtained under irradiation of 0.184% solutions were listed in Table 6. The degree of swelling and $\bar{P}_c$ were calculated using Einstein's formula and Flory-Rehner's equation for swelling[12]. As the interaction-constant μ, which is necessary for the calculation of $\bar{P}_c$, a value of 0.494 was used which was obtained by Nakajima and Furutachi[10]. The numbers of intra-molecular-crosslinks $v(=\bar{P}/2\bar{P}_c)$ are also given in the last column. It is interesting to point out that such large decreases in viscosity, solubility, acetylability and sharpness of X-ray diffraction pattern, are caused by so relatively small amounts of the intra-molecular crosslinks.

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