

Effects of Gamma Radiation on Polymer in Solution. (I)

Poly(vinyl Acetate)

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When polyvinyl acetate (PVAc) was subjected to gamma radiation in various organic solvents at a concentration of 10 weight %, the polymer resulted in crosslinking in methanol and benzene, but in many other organic solvents degradation occurred predominantly. As the solvents became poorer, crosslinking was promoted at low concentrations but retarded at high concentrations of the polymer. The most optimum concentration for crosslinking of the polymer in methanol solution was about 20%, where it was found that degradation hardly ever occurred. When PVAc was irradiated in methanol-organic solvent mixtures, the rate of crosslinking was retarded as the solubility of the polymer in solution was raised. However, in methanol-water mixtures, no correlation was observed between the radiation-induced changes and the solubility, but the rate of crosslinking increased monotonically with increasing water content in the mixtures, which may indicate that water is a very effective solvent for crosslinking. The radiation-induced changes were very slight during irradiation at -50°C but relatively large at 70°C .

The minimum doses needed for gelation in the 10% benzene solutions were inversely proportional to the degree of polymerization of the initial polymer. It was directly confirmed that the density of crosslinked units was proportional to the radiation dose, and that crosslinks were formed not only from the main chain radicals (not end radicals), but also from the side chain radicals.

INTRODUCTION

Recent studies on the crosslinking and degradation of polymers in solution by ionizing radiations have shown that polymers undergo degradation or crosslinking upon irradiation in solution as well as in solid state, and that effects observed may widely depend on the concentrations and the character of polymers and solvents.

The mechanism of radiation-induced changes in solution are more complicated than that in solid state, since they may result from both a direct effect of radiation on the polymer and an indirect effect *via* the solvent.

One of our attempts to make the effects of radiation on the polymer in solution clearer consists in studying PVAc under various conditions. In this paper we will present some data on the effect of solvent, concentration, temperature and degree of polymerization on the radiation-induced degradation and crosslinking of the polymer in solution, will calculate the relative amount of de-

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gradation and crosslinking, and propose a mechanism of crosslinking.

EXPERIMENTAL

Materials

PVAc used in these experiments was prepared by the acetylation of polyvinyl alcohol (PVA). The original PVAc from which the PVA was obtained was prepared either by the polymerization of monomer in ethyl acetate at 60°C in the presence of benzoyl peroxide or by the bulk polymerization initiated by radiation at -78°C. The latter polymer was used only when the effect of the degree of polymerization on crosslinking was studied.

The PVAc was fractionated into seven fractions and the second fraction was used in most experiments reported here.

Irradiation Procedure

Irradiation was carried out at room temperature, except for the case where the temperature effect was investigated, using a 2000 Curies Co-60 at the Institute for Chemical Research, Kyoto University. The dose rate was in the vicinity of 1.8×10^6 r/hr. Glass tubes containing solutions or dry films were sealed *in vacuo* after heating under a reduced pressure to eliminate dissolved air and repeating evacuation in a nitrogen atmosphere, and then exposed to gamma radiation.

Analysis

The radiation-induced changes were followed by measurements of viscosity, sol fraction and degree of swelling of gel.

After irradiation, the solutions were poured into water or petroleum ether to precipitate the irradiated polymer. When a gel was formed, it was heated at 70°C for 16 hr. in a large excess of benzene to extract the sol part, then dried and weighed. Sol fraction was given by the following equation:

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

Limiting viscosity number, $[\eta]$, was determined in all cases in benzene solution at 30°C using an Ubbelohde viscometer. The viscosity-average degree of polymerization, \bar{P} , was calculated by the equation¹⁾:

$$[\eta] = 8.91 \times 10^{-3} \times \bar{P}^{0.62}$$

\bar{P} of PVA obtained by the alkaline hydrolysis of the irradiated PVAc was calculated by the following equation¹⁾:

$$[\eta] = 7.51 \times 10^{-3} \times \bar{P}^{0.64}$$

where $[\eta]$ is expressed in deciliters/gram.

RESULTS AND DISCUSSION

Irradiation in Various Solvents

In Fig. 1 are shown the results obtained by irradiation of PVAc in various

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solvents. \bar{P} of the polymer used was 1880 and the concentration of the polymer was 10 weight %. These are in good agreement with the results reported by A. Henglein²⁾. As can be seen from Fig. 1, change in $[\eta]$ with dose depends remarkably on the sort of solvent used. For example, in methanol and benzene the polymer results in crosslinking, while in other solvents degradation occurs predominantly.

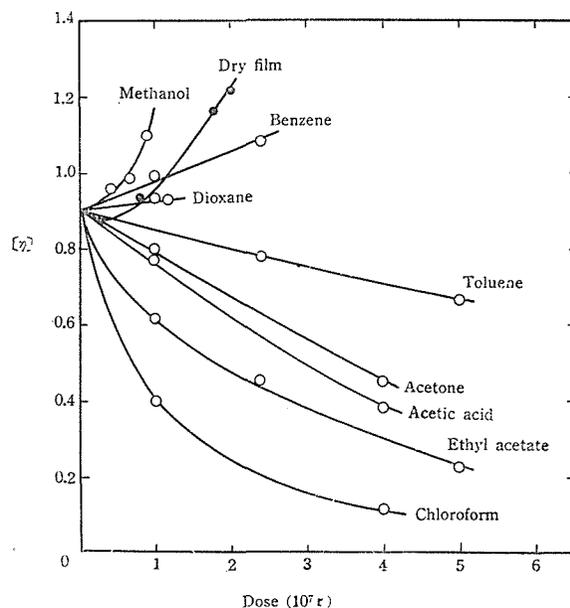


Fig. 1. Changes in the limiting viscosity number $[\eta]$ as a function of the radiation dose for PVAc irradiated in various solvents at the polymer concentration of 10 wt. %.

The following two factors may be considered as most important ones in solvent effects, *i.e.*, the solubility of the polymer in solvent and the sensitivity of solvent to radiation. In Table 1 are given these values, namely, polymer-solvent interaction constant³⁾, as a measure of solubility, and G_R -value⁴⁾ of free radicals produced by radiolysis of the solvent, as a measure of sensitivity. As evident from Table 1, the effect of solvent is parallel to neither the interaction

Table 1. G_R -value and interaction constant χ of the solvents.

Solvent	G_R (Chapiro)	χ
Methanol	15.0	0.575
Benzene	0.57~0.91	0.440
Dioxane	12.5	0.341
Toluene	2.0	0.530
Acetone	31.0	0.418
Acetic acid		0.326
Ethyl acetate	20.0	0.376
Chloroform	38	0.233

constant nor G_R -value, even if benzene, toluene and chloroform are excepted because of their peculiar behavior to radiation. As a conclusion, the effect of solvent can not be discussed only in terms of the solubility or the sensitivity, but should be interpreted taking into account other factors than these two.

Irradiation in Mixed Solvents

In order to clarify the relation between the radiation-induced changes in solution and the solubility or the sensitivity of solvent in detail, irradiation was carried out in mixed solvents which were prepared by a suitable combination of two different solvents.

Two sorts of mixed solvents were used in this experiment. One was prepared by mixing such a solvent as ethanol, hexane, xylene or chloroform with methanol by 10 weight %. In Table 2 are given the precipitation point, T_p , of solutions before irradiation, which can be regarded as a measure of the solubility of polymer, and G_R -value of mixed solvents calculated on assuming the additivity in G_R . These values indicate that by addition of one solvent to metha-

Table 2. Properties of mixed solvents.
(methanol : added solvent=9 : 1)

Added solvent	Precipitation points of solution	G_R
Ethanol	7.5°C	15.2
Hexane	4.5°C	14.7
Xylene	-4 °C	14.6
Carbon tetrachloride	-7 °C	15.2
Methanol	0 °C	15.0

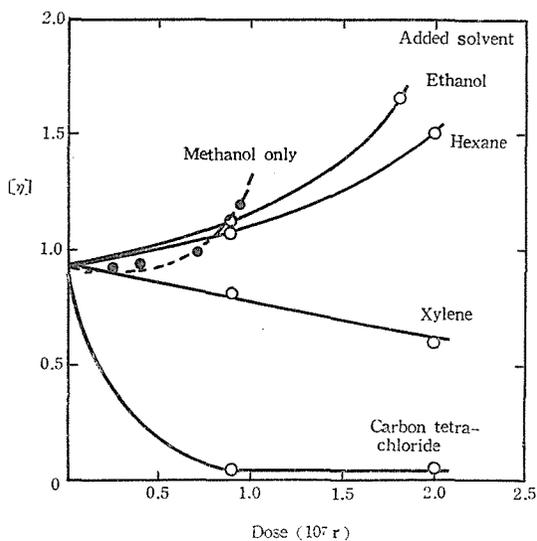


Fig. 2. Changes in the limiting viscosity number $[\eta]$ as a function of the radiation dose for PVAc irradiated in methanol-added solvent at the polymer concentration of 10%.

methanol : added solvent=9 : 1 (by weight)

not the solubility is considerably changed, while the G_R -value remains almost unchanged. The results obtained by irradiation at the polymer concentration of 10% are shown in Fig. 2. The following tendency is seen from these data; crosslinking is promoted as T_p is lowered, that is, as the solubility becomes larger, but it is not decisive since crosslinking occurs more readily in pure methanol than in a methanol-hexane or methanol-ethanol mixture, although the solubility of the polymer is smaller in these mixed solvents than in pure methanol.

Next, irradiation was performed in methanol-water mixture in greater detail. It has been found by one of us that the solubility of PVAc in this mixed solvent is largest at water content of *ca.* 0.2²¹. Curves in Figs. 3 and 4, where the results obtained are given, show neither a maximum nor minimum point, but indicate a monotonic increase in the rate of crosslinking with increasing water content. The decrease in $[\eta]$ observed when the polymer was irradiated at the concentration of 1% may well be attributed to the formation of the intramolecular crosslinking. These facts suggest that the effect of solvent on crosslinking of polymer in solution can not be interpreted only in terms of the solubility of the polymer in solution.

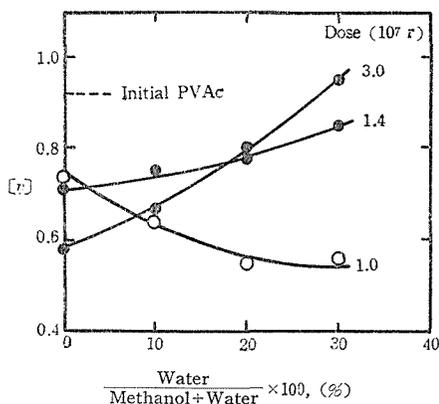


Fig. 3. Changes in the limiting viscosity number $[\eta]$ as a function of the water content (wt. %) in the mixed solvent for PVAc irradiated in methanol-water.

○.....irradiated in 1% solution
●.....irradiated in 5% solution

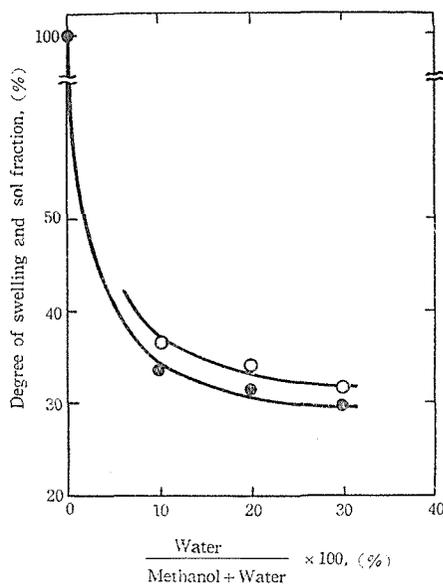


Fig. 4. Changes in the degree of swelling of gel in benzene and the sol fraction as a function of the water content in the mixed solvent for PVAc irradiated in methanol-water at the polymer concentration of 10% and dose of 2.0×10^7 r.

○.....degree of swelling of gel
●.....sol fraction (%)

A. Henglein has recently reported a result²¹ obviously different from ours, using PVAc with $[\eta]$ of 4.2 which is about ten times as large as ours. So, to confirm whether this discrepancy is due to the difference of materials used, branched PVAc with $[\eta]$ of 4.0 which was prepared by pearl polymerization

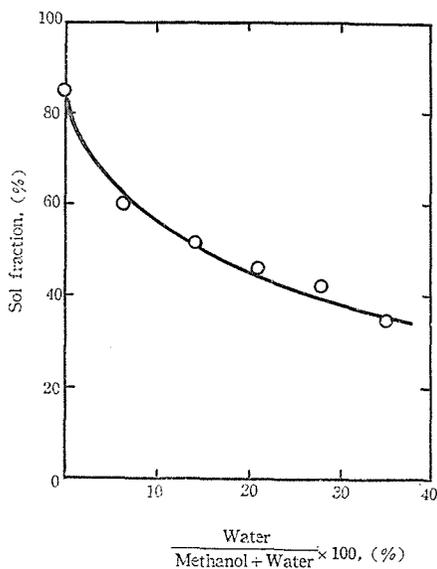


Fig. 5. Sol fractions as a function of the water content in the mixed solvent for PVAc irradiated in methanol-water at the polymer concentration of 5% and dose of 1.4×10^6 r.

$[\eta]$ of the unirradiated polymer is 4.0 in benzene at 30°C.

was irradiated under the same conditions as Henglein's. The result obtained here is, as shown in Fig. 5, exactly the same as those obtained above, but no maximum rate of crosslinking as Henglein has reported is observed. The reason for the discrepancy remains as yet unexplained, but our results suggest strongly that crosslinking is promoted directly by the radicals produced by radiolysis of water.

Concentration Dependence

It is well known that the effect of radiation on a polymer in solution depends on the concentration of the polymer as well as on the property of the solvent. The study on the concentration dependence may be necessary to disclose the function of solvent in the irradiation on polymer in solution. However, the analysis of the concentration dependence is very difficult, because the increase in concentration of polymer leads not only to the decrease in the relative amount of solvent to polymer molecule but also to the change in configuration, mobility and entanglement of polymer chains which are considered to have a large influence on the formation of crosslinking. In addition to these, it should be also taken into account that the extent of the attack of solvent radicals on polymers and the energy transfer between polymer and solvent may be changed with the concentration of polymer.

So, we will only give experimental results here. The dose for incipient gelation are plotted against the concentrations of polymer in Fig. 6 when the polymer was irradiated in methanol solution. This curve is similar to that obtained for other polymers in organic solvents, but distinctly different from that of the aqueous solution of a polymer⁽⁹⁾. For example, the critical concentration

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below which no gel is formed, is higher by about one order than that of the aqueous solutions. Next, considering that even if degradations occurred at lower concentrations the polymer might crosslink at higher concentrations, we irradiated the polymer at a concentration of 40% in acetone, ethyl acetate or dioxane solution. The result obtained by irradiation at a dose of 5×10^7 r is given in Table 3. When the polymer was irradiated at the concentration of 10% in these solvents, $[\eta]$ was scarcely changed in dioxane, but dropped to about 50% and 30% of the initial value in acetone and ethyl acetate, respectively (see Fig. 1). On the other hand, polymer crosslinked almost completely in ethyl acetate and dioxane, but not in acetone though $[\eta]$ was risen slightly, when irradiated at a high concentration, as shown in Table 3. These results indicate that when solvent becomes poorer, crosslinking is promoted at the concentration of 10%, but is retarded at 40%.

Table 3. Radiation effects on PVAc irradiated in 40% solution at a dose of 5.0×10^7 r.

Solvent	$[\eta]$ after irradiation	Sol fraction (%)
Acetone	0.632	100
Ethyl acetate	—	7.2
Dioxane	—	4.9

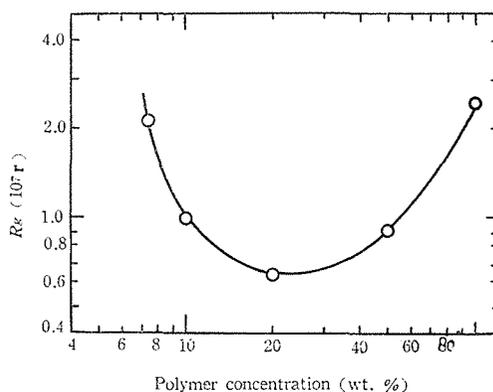


Fig. 6. Dose for incipient gelation R_g as a function of the polymer concentration for PVAc irradiated in methanol.

Effect of Temperature

The effect of temperature on the crosslinking and degradation of polymer has been investigated extensively with regard to the irradiation in solid state, but there are only few experiments ever published on the effect of temperature on the radiation effect of a solution.

In Fig. 7 are shown the results obtained by irradiation of PVAc in organic solvents at the concentration of 10% in a temperature range of $-50 \sim 70^\circ\text{C}$. \bar{P} of PVAc used in this experiment was 1385. It is obvious from Fig. 8 that the effect of temperature is not so large, compared with what has been observed at irradiation of various polymers in solid state⁷⁾. A likely explanation for this is

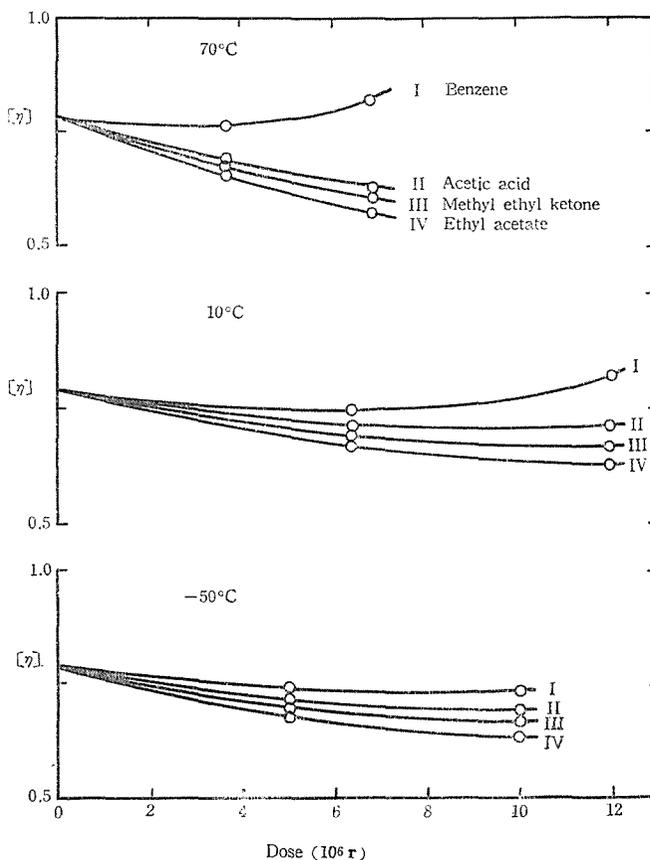


Fig. 7. Changes in the limiting viscosity number $[\eta]$ as a function of the radiation dose for PVAc irradiated in various solvents at a polymer concentration of 10% and irradiation temperatures of -50 , 10 and 70°C .

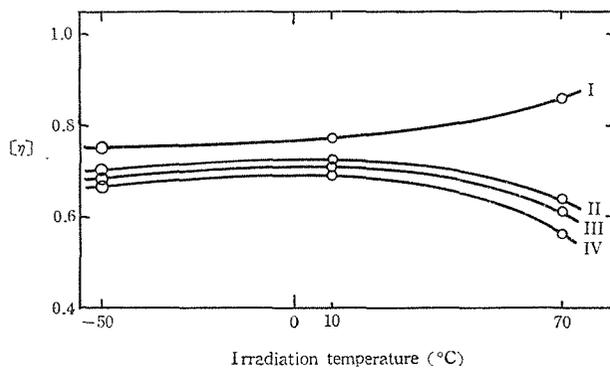


Fig. 8. Changes in the limiting viscosity number $[\eta]$ as a function of the irradiation temperature for PVAc irradiated in various solvents at a polymer concentration of 10% and dose of $7.0 \times 10^6 \text{r}$. I, benzene; II, acetic acid; III, methyl ethyl ketone; IV, ethyl acetate.

that the flexibility of polymer in solid state increases with increasing temperature, particularly at the temperature above the glass transition point, whereas the mobility of polymer in solution will be affected very slightly by temperature. It is of interest that the radiation-induced changes are relatively small at -50°C . The effect of freezing which occurred in the case of benzene and acetic acid solutions at -50°C was not reflected on radiation effects at all. The values of $[\eta]$, which would be obtained when the polymer was irradiated with a dose of $7 \times 10^6 \text{r}$, were read from Fig. 7 and plotted against the irradiation temperature in Fig. 8. It shows that degradation is slightly enhanced as the irradiation temperature rises, except for the case of benzene solutions.

Effect of Degree of Polymerization

It may be expected that as the degree of polymerization of polymer increases the viscosity of solution increases, resulting in the reduction of the mobility of polymer segments. In order to examine whether this change in viscosity of solution affects the crosslinking, polymers with various \bar{P} were irradiated in 10% benzene solution. The degrees of polymerization of the polymer used in this experiment were 741 and 1814 whereby polymers were prepared by the polymerization using a catalyst, and 5323 and 19700 whereby polymers were prepared by the radiation-initiated polymerization. The change in $[\eta]$ plotted against the radiation dose are shown in Fig. 9, and the dose for incipient gelation, R_g , are plotted against the \bar{P} of polymer in Fig. 10.

It may be shown theoretically that if the density of crosslinked units, q_0 , is proportional to the radiation dose but independent of \bar{P} and the mobility of poly-

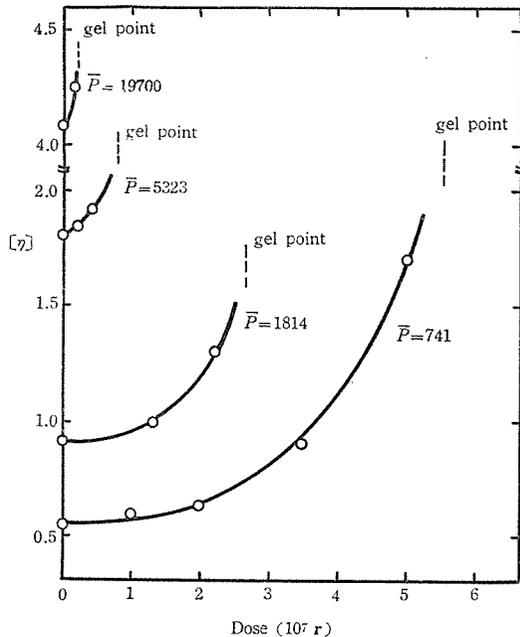


Fig. 9. Changes in the limiting viscosity number $[\eta]$ as a function of the radiation dose for PVAc with various degrees of polymerization \bar{P} . The polymers were irradiated in 10% benzene solution.

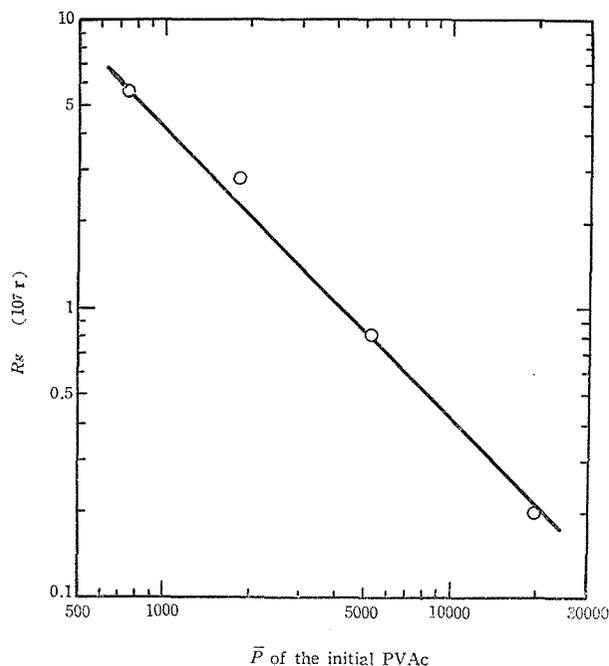


Fig. 10. Dose for incipient gelation R_g as a function of the degree of polymerization \bar{P} of the initial PVAc. The polymers were irradiated in 10% benzene solution.

mer, R_g should be inversely proportional to \bar{P} . It is seen from Fig. 10 that the product $R_g \times \bar{P}$ is constant within the experimental error, as theoretically predicted. From this result, it can be concluded that the increase in viscosity of solution caused by increasing the degree of polymerization does not affect the density of crosslinked units in the polymer in solution.

Ratio of Number of Scissions to Crosslinks

A number of methods have been presented to calculate the relative amount of crosslinking and degradation. Among them, the following two methods are well known. One was suggested by Charlesby and Pinner⁸⁾ and consists in the pursuit of the amount of gel produced during irradiation. Another was proposed by Kilb⁹⁾, which consists in the pursuit of the changes in $[\eta]$. Kilb has dealt with the changes below the gel point, while Charlesby-Pinner have dealt with the changes in sol fraction after some gel has been formed. Kilb calculated the changes in $[\eta]$, combining his theory that $[\eta]$ of the branched polymer was smaller than that of the linear polymer, with the molecular weight distribution function given by Stockmayer¹⁰⁾. However, as it has been reported^{11,12)} that in the case of PVAc the magnitude of $[\eta]$ of the branched polymer is really equal to that of the linear polymer if $[\eta]$ is measured in a good solvent as benzene, we derived a revised equation only using the distribution function given by Stockmayer, without any consideration for the effect of branching on $[\eta]$. We will call it Stockmayer's equation, which is not shown here because of its complexity.

Charlesby derived the following equation relating the sol fraction S to the radiation dose R for the most probable molecular weight distribution ;

$$S + \sqrt{S} = p_0/q_0 + 1/q_0 \bar{P}_n R$$

where \bar{P}_n is the number-average degree of polymerization, and p_0 and q_0 is the density of the fracture and crosslinked units per unit dose, respectively. Accordingly, the ratio of the number of scissions to crosslinks amounts to $2p_0/q_0$. Plots of $[\eta]/[\eta]_0$ versus R/R_g for data obtained by the irradiation of PVAc in 10% methanol solution, together with the theoretical curves, are shown in Fig. 11, where $[\eta]_0$ and $[\eta]$ are the limiting viscosity numbers of the initial and irradiated polymer. Comparison of the experimental results with theory yields $2p_0/q_0 \sim 3.2$. The changes in viscosity and sol fraction at the irradiation in 20% methanol solution are shown in Figs. 11 and 12. The ratio is about zero when calculated by Stockmayer's equation and 0.52 by Charlesby's. These two values may be regarded as identical within the experimental error, indicating that degradation scarcely occurs.

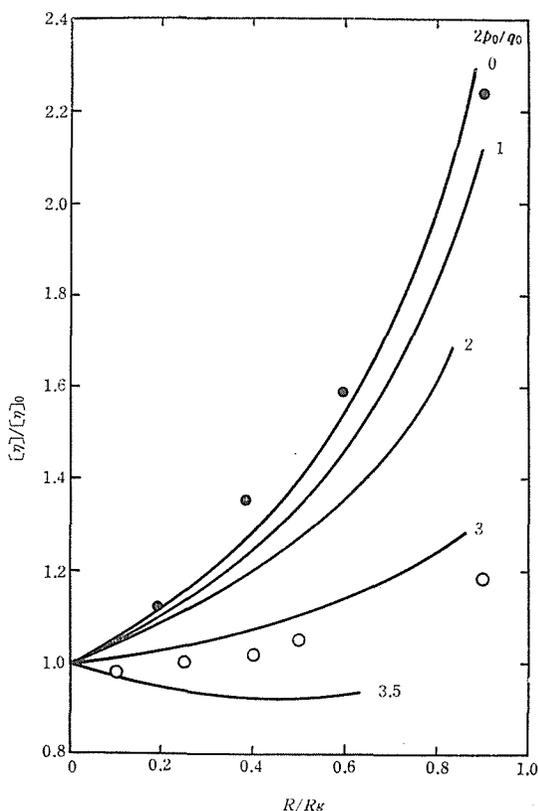


Fig. 11. Observed and theoretical limiting viscosity number ratios of irradiated to unirradiated PVAc in benzene, $[\eta]/[\eta]_0$, as a function of R/R_g , where R_g is the dose for incipient gelation.

The theoretical curves are given for several values of $2p_0/q_0$, the ratio of the number of scissions to that of crosslinks.

- irradiated in 10% methanol solution
- irradiated in 20% methanol solution

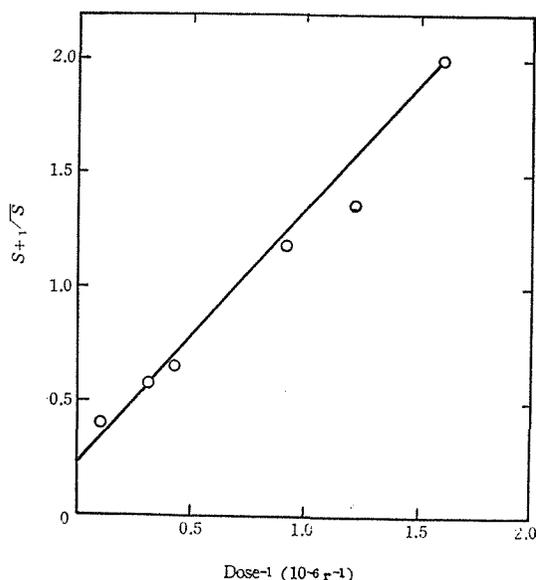


Fig. 12. $S + \sqrt{S}$ as a function of the reciprocal of the radiation dose for PVAc irradiated in 20% methanol solution. S is the sol fraction.

Mechanism of Crosslinking

At present, very little information is known concerning the mechanism of crosslinking, although many detailed studies have been done on the crosslinking of polymer. In the case of PVAc, fortunately, the mechanism of crosslinking can be pursued rather easily since these crosslinks can be partly hydrolyzed. As the calculation of the number of crosslinks becomes difficult if degradation occurs simultaneously with crosslinking, we will discuss the mechanism of crosslinking using the results obtained by irradiation in 20% methanol solutions where it was found in the above experiment that the main chain scissions occur only to a negligible extent. The degree of polymerization of the irradiated PVAc, \bar{P}_{Ac} , and that of PVA obtained by hydrolysis of the irradiated PVAc, \bar{P}_A , are shown in Table 4 and Fig. 13.

It was demonstrated by Todd¹³⁾ that H_2 and CH_4 but no CH_3COOH were produced under irradiation of PVAc in solid state. Remembering this observation,

Table 4. Limiting viscosity number and degree of polymerization of PVAc, $[\eta]_{Ac}$, \bar{P}_{Ac} and of the hydrolyzed PVA, $[\eta]_A$, \bar{P}_A , and number of crosslinks K of PVAc irradiated in 20% methanol solution.

Dose (10 ⁶ r)	$[\eta]_{Ac}$	\bar{P}_{Ac}	$[\eta]_A$	\bar{P}_A	$K_{1+2} \times 10^4$	$K_3 \times 10^4$	$(K_{1+2} + K_3) \times 10^4$
0	0.934	1814	0.910	1814	0	0	0
1.2	1.041	2155	0.972	2000	0.36	0.11	0.87
2.4	1.261	2944	1.178	2696	0.31	1.80	2.11
3.7	1.492	3864	1.195	2756	1.04	1.89	2.93
5.7	2.090	6651	1.287	3094	1.73	2.28	4.01

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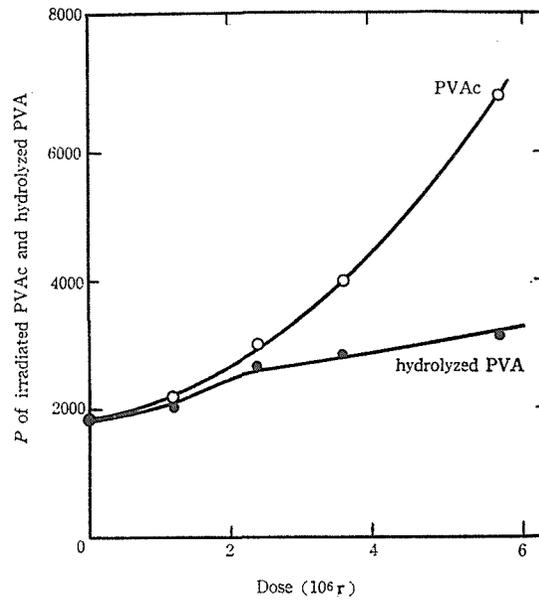
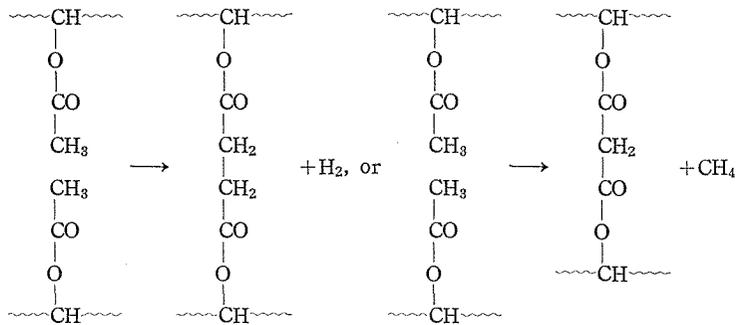


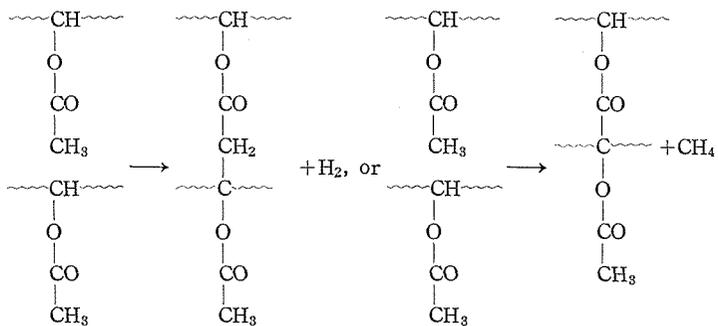
Fig. 13. Degrees of polymerization \bar{P}_n of PVAc and its hydrolyzed PVA as a function of the γ -radiation dose. PVAc was irradiated in 20% methanol solution.

we may represent the crosslinking processes as follows :

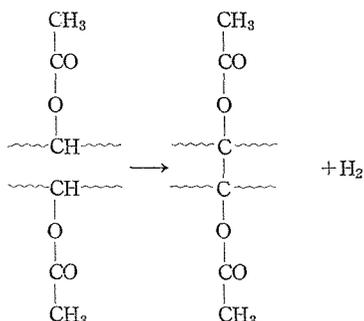
(1) reactions between two side chains



(2) reactions between a side chain and a main chain



(3) reactions between two main chains



The crosslinks formed by the reactions (1) and (2) can be cleaved by hydrolysis, but those formed by the reaction (3) can not be cleaved. Therefore, the number of crosslinks per monomer unit can be calculated by the following equations;

$$\begin{aligned}
 K_{1+2} &= (1/\bar{P}_A - 1/\bar{P}_{Ac}), \text{ for the total reactions of (1) and (2),} \\
 K_3 &= (1/\bar{P}_0 - 1/\bar{P}_A), \text{ for the reaction (3)}
 \end{aligned}$$

where \bar{P}_0 is the number-average degree of polymerization of the unirradiated PVAc. By the way, the degree of polymerization which is calculated using the $[\eta]-\bar{P}$ relation described above is number-average, for the relation was obtained by the osmotic pressure measurements of PVAc having the same molecular weight distribution as ours. The calculated values are given in Table 4 and Fig. 14, which show that crosslinks are formed not only *via* main chains, but also *via* side chains. As is seen in Fig. 14, the curve for the total numbers of crosslinks, $K_{1+2} + K_3$ is approximately a straight line. This means that the density of crosslinked units is proportional to the radiation dose and that the G -value for crosslink is 9.0. The gels obtained under irradiation with the dose of 2×10^7 r completely dissolved in boiling water as a result of hydrolysis, but for

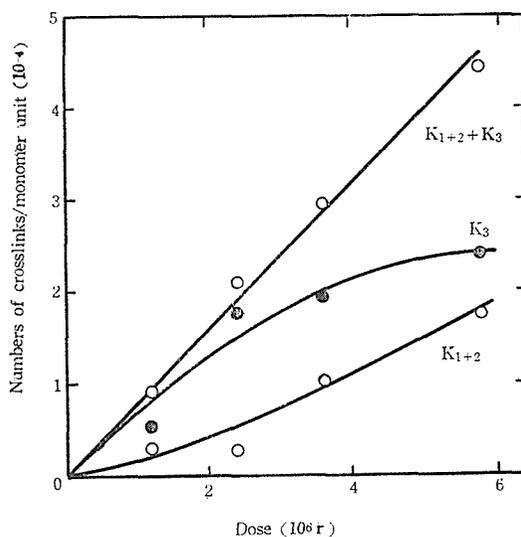


Fig. 14. Numbers of crosslinks per monomer unit as a function of the radiation dose for PVAc irradiated in 20% methanol solution.

the gels obtained with a dose higher than 3×10^7 r, a water-insoluble part was observed even after severe hydrolysis.

CONCLUSION

From our data it is concluded that various factors should be taken into account to explain the irradiation effect of polymer in solution. However, the temperature effect is very slight and the dependence of \bar{P} on radiation effects is similar to that of the irradiation in solid state. The fact that the radiation-induced changes depend largely on the concentration of the polymer and on the properties of the solvent used is undoubtedly strong evidence for the indirect effect, but it is not reasonable to conclude that the indirect effect is entirely due to the attack of solvent radicals to the polymer molecules. Results obtained above also suggest that in order to make the effect of the solvent clearer it is necessary to irradiate the polymer in more various solvents and over a wider range of concentrations of the polymer. It seems very dangerous to draw some conclusions from irradiation experiments at only one fixed concentration. Many available data may be obtained by the experiments which were not carried out here, for example, the irradiation in a so dilute solution that polymer molecules do not interact each other and in the presence of oxygen and additives.

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