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Effects of Gamma Radiation on Polymer in Solution. (VI) Radiation Protection and Promotion in Aqueous Solutions of Poly(Vinyl Alcohol).

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Effects of a number of additives have been measured for irradiation of deaerated and aerated aqueous solutions of poly(vinyl alcohol). Systems containing thiourea, methyl ethyl ketone, ethanol, $FeSO_4+0.8N$ H_2SO_4, $CuSO_4$ or KBr have been examined in detail and it was found that these additives modified the rate of crosslinking as well as degradation of polymers. On the contrary, methanol, K_2SO_4 or NaCl did not have any appreciable influence on polymer reactions, although their concentration was fairly high compared with that of the former additives. The various effects of additives could be explained mainly in terms of recombination process and radical transfer in the case of organic additives and electron transfer in the case of inorganic additives. The minimum number of additive molecules per initial polymer molecule required to affect the crosslinking were 0.08 (thiourea), 0.27 ($FeSO_4+0.8N$ H_2SO_4), 0.5 ($CuSO_4$), 3 (MEK), 10 (KBr) and 17 (ethanol). Discussion of the mechanism of radiation protection and promotion was given on the basis of these experimental results.

INTRODUCTION

In three earlier publications[1,2,3], we reported effects of expansion of polymer molecules on crosslinking and degradation of polyelectrolytes in aqueous solutions. The expansion of polyions was adjusted by varying ionizable group content or concentration of added salt (NaCl). It was then assumed that the added NaCl has no effect other than decreasing the expansion of polyions. However, the following possibility would not always be precluded that such ions as Na^+ and Cl^- would react with radicals produced from water and polymers by irradiation. In order to elucidate this problem, this study was started.

The main purpose of the present paper is to investigate widely the effect of additives on the crosslinking and degradation of polymers, in other words, the radiation protection and promotion. For this purpose, very small amounts of various inorganic and organic compounds were added to the aqueous solution to be irradiated, and the changes in the gelation dose and viscosity were measured.

EXPERIMENTAL

The polymer employed is a fractionated poly(vinyl alcohol) (PVA) with a viscosity-average degree of polymerization of 1618. The additives used include

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both organic and inorganic compounds. The former are thiourea, methyl ethyl ketone (MEK), ethanol and methanol, and the latter are NaCl, KBr, K_2SO_4, $FeSO_4 + 0.8N$ H_2SO_4 and $CuSO_4$.

Aqueous solutions of PVA containing one of these additives were irradiated in the presence and absence of air with Co-60 γ-rays. A dose rate of 1.45×10^5 r/hr was used and the temperature during irradiation was about 20°C. Degassing from solutions for irradiation was carried out by our usual method. Gel point was determined visually, and viscosities were measured in water at 30°C.

RESULTS

1) Irradiation in the Absence of Air

As is well known, irradiation of degassed aqueous solutions of PVA causes mainly the increase of viscosity, and finally the gelation of the system. Therefore, in the case of irradiation in the absence of air, the additives would have some effects on the crosslinking. Fig. 1 shows the change in gelation dose, when 0.4% solution of PVA was irradiated in the presence of various additives.
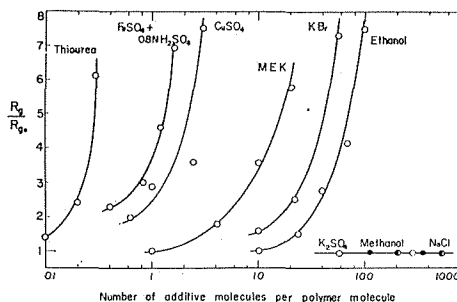

Fig. 1. Influence of various additives on gelation dose R_g for 0.4% aqueous solutions of PVA. R_{g0} is the gelation dose of aqueous solutions containing no additive.

It may be seen that NaCl, K_2SO_4 and methanol have no influence on the crosslinking reaction, even if their concentrations are relatively high. This result indicates also that the ions, which affect the polymer reaction, are not Na^+, K^+, SO_4^{--} and Cl^-, but Fe^{++}, Cu^{++} and Br^-. Charlesby and Alexander[1] also found that thiourea hinders the gelation very strongly.

Next, more detailed experiments were carried out, varying both the polymer concentration and the amount of additives. The results for $CuSO_4$, KBr, thiourea and ethanol are shown in Figs. 2 and 3. In all cases, the gelation dose increased with decreasing polymer concentration, when the amount of additives was relatively large. This may be due to a fact that the number of additive molecules per polymer molecule increases as the polymer concentration decreases. From Figs. 1, 2 and 3, one can obtain Fig. 4, where relative gelation doses are plotted against the number of additive molecule. The data fall fairly well on straight lines, the slopes of which are nearly in accord with each other. Fig. 5 shows the change in viscosity of irradiated solution: irradiation was carried out using 0.4% solutions in the presence of KBr.
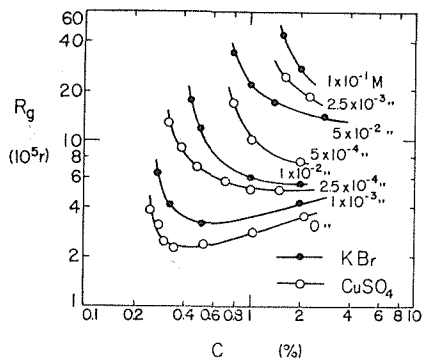
Fig. 2. Change in gelation dose R_g for PVA irradiated in aqueous solutions with various concentrations of polymer and additives.
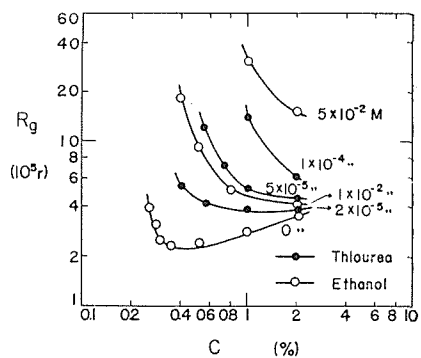
Fig. 3. Change in gelation dose R_g for PVA irradiated in aqueous solutions with various concentrations of polymer and additives.
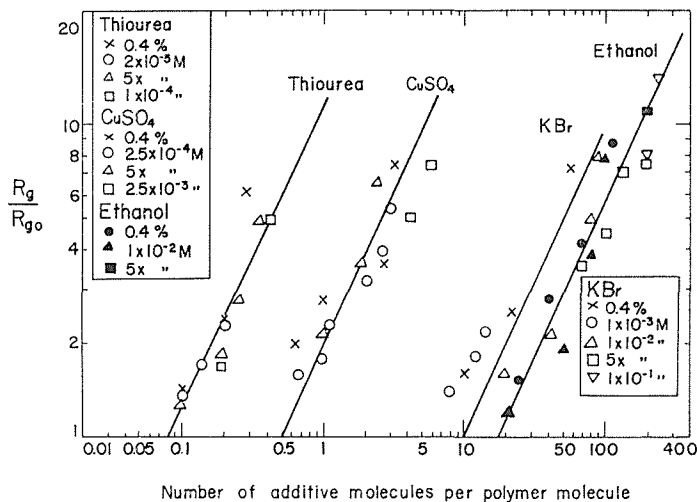

Fig. 4. Protection effect of various additives on crosslinking of aqueous solutions of PVA.
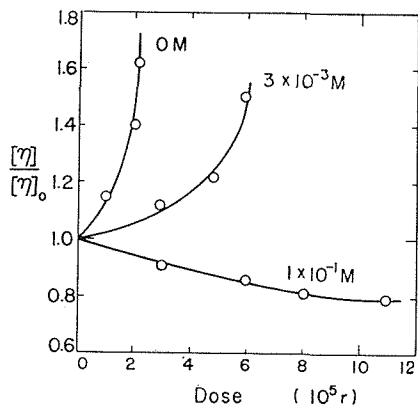

Fig. 5. Change in limiting viscosity number $[\eta]$ of PVA irradiated in 0.4% aqueous solutions containing KBr. $[\eta]_0$ is the limiting viscosity number of unirradiated PVA.

2) Irradiation in the Presence of Air

When air is sufficiently present in the solution to be irradiated, solution viscosities always decrease with radiation dose, indicating the occurrence of main-chain scission. In order to understand the mechanism of the radiation protection and promotion, it seems interesting to study how the degradation of polymer is affected by the presence of a very small amount of additives. The results obtained by irradiation of 0.4% aqueous solution containing various additives of 10^{-2}M are shown in Fig. 6. Evidently, the main-chain scission is in
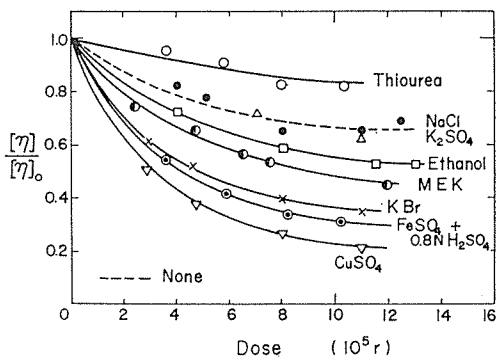

Fig. 6. Effect of additives on degradation of PVA in 0.4% aqueous solutions containing 10^{-2}M additives.

most cases accelerated by the presence of additives. The one exception is thiourea, which protects polymers against degradation considerably. As can be expected, the additives which do not affect the crosslinking, also show no influence on the degradation. In order to estimate the number of main-chain scission, the reciprocal of the degree of polymerization of the irradiated polymers was calculated from the results shown in Fig. 6 and plotted against the dose in Fig. 7. G-values for degradation calculated from the slopes of the staight lines
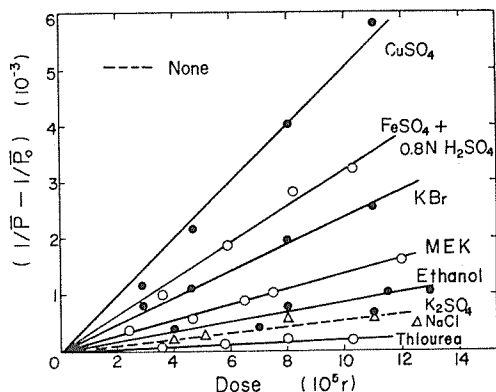

Fig. 7. Reciprocal of degree of polymerization $\bar{P}$ of PVA irradiated in 0.4% aqueous solution containing 10^{-2}M additives. $\bar{P}_0$ is the degree of polymerization of unirradiated PVA.

in Fig. 7 are given in Table 1. G_{d0} denotes the G-value in the case of the absence of any additives.

DISCUSSION

By extrapolation of R_g/R_{g0} to unity, one can obtain from Fig. 4 the minimum number of each additive molecule per polymer molecule required to affect gelation. The values are shown in Table 1, which indicates that there is no distinct correlation between the minimum amount of additives to affect the crosslinking

Table 1. Minimum numbers of additive molecules per polymer molecule to affect crosslinking, and G_d-values for degradation. (Additive$=10^{-2}$M)

Additives	Thiourea	FeSO$_4$	CuSO$_4$	MEK	KBr	Ethanol	K$_2$SO$_4$	NaCl	Methanol
Min. number	0.08	0.27	0.5	3	10	17	large	large	large
G_d/G_{d0}	0.39	6.0	9.5	2.6	4.5	1.6	1	1~1.5	1

and G_d-value for the degradation. In other words, the additive which protects the gelation more efficiently, does not necessarily retard or promote the degradation more strongly. It should also be noted that additives which promote the crosslinking could not be found out in our experiment.
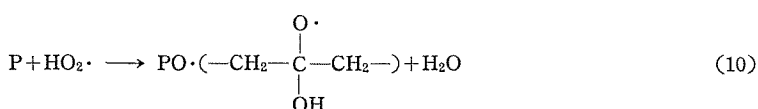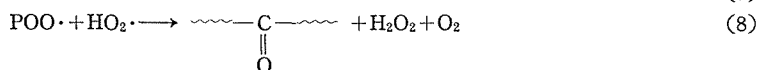
The results described above appear very complicated, suggesting that reaction schemes of each additives are different from each other. In the following, we will discuss the process occurring in the system in detail.

First of all, we will summarize briefly the mechanism of crosslinking and degradation occurring in the absence of additive.

Denote the PVA molecule by the symbol of P, and the PVA radical produced as a result of hydrogen abstraction from a main-chain by the symbol of P·, then the radiolysis of aqueous solutions of PVA may be described in terms of the following equations,

$$H_2O \longrightarrow H\cdot,\ HO\cdot,\ H_2,\ H_2O_2 \tag{1}$$
$$P \longrightarrow P\cdot + H\cdot \tag{2}$$
$$P + H\cdot \longrightarrow P\cdot + H_2 \tag{3}$$
$$P + OH\cdot \longrightarrow P\cdot + H_2O \tag{4}$$
$$P\cdot + P\cdot \longrightarrow P-P\ (crosslinking) \tag{5}$$

When air is present, the expected reaction is assumed to be[8],

$$H\cdot + O_2 \longrightarrow HO_2\cdot \tag{6}$$
$$P\cdot + O_2 \longrightarrow POO\cdot \tag{7}$$
$$POO\cdot + HO_2\cdot \longrightarrow \sim\!\!\sim\!\!-C-\!\!\sim\!\!\sim\ +H_2O_2+O_2 \tag{8}$$
$$\overset{\|}{O}$$

$$\sim\!\!\sim\!\!-\underset{\overset{\|}{O}}{C}-\!\!\sim\!\!\sim\ \longrightarrow degradation \tag{9}$$

$$P + HO_2\cdot \longrightarrow PO\cdot(-CH_2-\overset{\overset{O\cdot}{|}}{\underset{|}{C}}-CH_2-)+H_2O \tag{10}$$
$$\underset{OH}{}$$

$$\text{~~~}-CH_2-\overset{\overset{\displaystyle O\cdot}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2-\text{~~~} \longrightarrow \text{~~~}-CH_2-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{C}}+\cdot CH_2-\text{~~~} \quad \text{(degradation)} \quad (11)$$
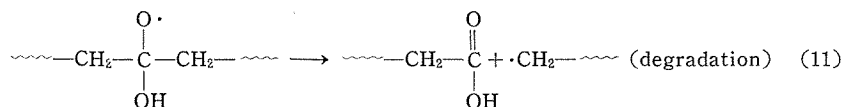
It has been found that the amount of P· produced by the reaction (2) is very small, compared with that produced by the reactions (3) and (4). The rate of reaction (7) is generally considered to be much higher than that of (5).

1) Organic Additives

1.1) Thiourea. It is well known that very low amounts of thiourea protect many materials against damage by radiation. This compound may exist in solutions partly in an enol form, $HN:C(NH_2)SH$ (hereafter abbreviated as RSH), and it has been found that the sulfur linkage is particularly reactive towards free radicals. Thus, the radical transfer may occur readily between thiourea and radicals:

$$P\cdot + RSH \longrightarrow P + RS\cdot \qquad\qquad (12)$$
$$H\cdot + RSH \longrightarrow H_2 + RS\cdot \qquad\qquad (13)$$
$$HO\cdot + RSH \longrightarrow H_2O + RS\cdot \qquad\qquad (14)$$
$$HO_2\cdot + RSH \longrightarrow H_2O_2 + RS\cdot \qquad\qquad (15)$$

It is also likely that radical recombination occurs between RS· and other radicals as follows,

$$P\cdot + RS\cdot \longrightarrow RSH \qquad\qquad (16)$$
$$POO\cdot + RS\cdot \longrightarrow POOSR \qquad\qquad (17)$$

From the reactions (12)~(17), the protective property of thiourea against the crosslinking and degradation is quite understandable. In this connection, Charlesby and Kopp[5] found using labelled thiourea that the thiourea molecule, or at least part of it, combined with the polymer molecule.

1.2) MEK and ethanol. These compounds were found to hinder the gelation, and to promote the degradation to some extent. For simplicity, we will denote these additives by RH. Similarly to thiourea, RH may attack the radicals, though more mildly than thiourea. The recombination with R· is also quite probable. Thus, the crosslinking may hardly occur owing to the following reaction.

$$H\cdot + RH \longrightarrow R\cdot + H_2 \qquad\qquad (18)$$
$$HO\cdot + RH \longrightarrow R\cdot + H_2O \qquad\qquad (19)$$
$$P\cdot + RH \longrightarrow R\cdot + P \qquad\qquad (20)$$
$$P\cdot + R\cdot \longrightarrow PR \qquad\qquad (21)$$

It should be emphasized that R· produced from ordinary organic compound is too unreactive to abstract hydrogen from polymer molecules. The fact that methanol does not practically affect the crosslinking, may be ascribed to the lower G_R-value of radical-formation than the other organic additives[6].

It is rather difficult to explain the result that very small amounts of MEK and ethanol accelerate the viscosity decrease observed under irradiation in the presence of air. One of the plausible explanation for this is that these compounds may completely inhibit the crosslinking, the probability of which could not be negligible even under irradiation in the presence of air. Naturally, it

follows that the viscosity of irradiated solution decreases more sharply when the crosslinking takes place no more.

2) Inorganic Additives

As the radiation chemistry of aqueous solutions containing inorganic compounds has been intensively studied[7], results obtained here can be explained rather easily in terms of electron transfer, which is usually observed for oxidation and reduction.

2.1) $FeSO_4+0.8N\ H_2SO_4$. This system is known as Fricke's solution[9]. When air is absent in the solution to be irradiated, the mechanism may be written :

$$OH\cdot+Fe^{++} \longrightarrow Fe^{+++}+OH^- \tag{22}$$

$$H\cdot+Fe^{++}+H^+ \longrightarrow Fe^{+++}+H_2 \tag{23}$$

Further, presumably Fe^{++} attacks $P\cdot$ by a reaction such as

$$P\cdot+Fe^{++}+H^+ \longrightarrow Fe^{+++}+P \tag{24}$$

Clearly, the reactions $(22)\sim(24)$ lead to the prevention of crosslinking. On the other hand, it is not understandable to us why the presence of so small amounts of ferrous ions causes such a large decrease in the solution viscosity under irradiation in the presence of air. If irradiation of polymers in aerated aqueous solutions produces considerable amounts of POOH and this peroxidic acid can be assumed to be fairly stable in the aqueous solutions, then the ferrous ions reduce this product.

$$POOH+Fe^{++} \longrightarrow PO\cdot+OH^-+Fe^{+++} \tag{25}$$
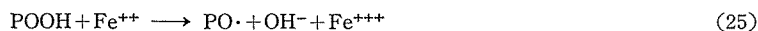
The $PO\cdot$ would give rise to the degradation through reaction (11).

2.2) KBr. As is well known, Br^- is a reducing agent, as powerful as Fe^{++}.

$$OH\cdot+Br^- \longrightarrow OH^-+Br \tag{26}$$

$$H\cdot+Br \longrightarrow H^++Br^- \tag{27}$$

Hence, the rate of reactions (3) and (4) would be remarkably lowered, so that the crosslinking is prevented. The process occurring under irradiation in the presence of air may be similar to that supposed in the case of Fe^{++}

$$POOH+Br^- \longrightarrow PO\cdot+OH^-+Br \tag{28}$$

2.3) $CuSO_4$. Cu^{++}, a powerful oxidizing agent, reacts with $H\cdot$ to become Cu^+, which further reacts with $OH\cdot$

$$H\cdot+Cu^{++} \longrightarrow H^++Cu^+ \tag{29}$$

$$OH\cdot+Cu^+ \longrightarrow OH^-+Cu^{++} \tag{30}$$

The reason for the most striking decrease in viscosity of solution irradiated in the presence of air and $CuSO_4$, may be that POOH is perhaps attacked by both Cu^{++} and Cu^+ with the mechanism,

$$POOH+Cu^{++} \longrightarrow POO\cdot+Cu^++H^+ \tag{31}$$

$$POOH+Cu^+ \longrightarrow PO\cdot+OH^-+Cu^{++} \tag{32}$$
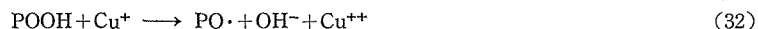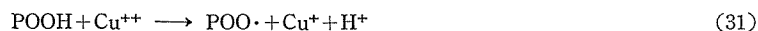
Finally, it must be noted that in the reaction schemes described above, no energy transfer in any cases between species and no occurrence of main-chain scission in the case of irradiation of degassed solutions were assumed even if

additives are present. The latter assumption, being opened to criticisms, will be discussed in the future.

ACKNOWLEDGMENT

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