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<tr>
<td>Author(s)</td>
<td>Ikada, Yoshito</td>
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Kyoto University
EFFECTS OF CATION SIZE ON POLARIZATION IN SOLUTION

1963

Marcelo Ibáñez
EFFECTS OF GAMMA RADIATION ON SOLUTIONS IN SOLUTION

1963

YOSHIRO IMADA

DEPARTMENT OF POLYMER CHEMISTRY
FACTORY OF ENGINEERING
RIKEN UNIVERSITY
The present studies have been carried out at Kyoto University under the direction of Professor Ichiro Sakurada in 1958~1962. Studies on the radiation effects of solutions of various polymers such as poly(vinyl alcohol), its derivative, poly(vinyl acetate), poly(vinyl methyl ether) and poly(acrylic acid) are involved in this dissertation. Irradiation was performed with gamma radiation from a Co-60 source of 2000 Curies at the Institute for Chemical Research, Kyoto University. All the papers were and shall be published in the Special Issues II, III and IV on Physical, Chemical and Biological Effects of Gamma Radiation in the Bulletin of the Institute for Chemical Research, Kyoto University, 32 (1961), 34 (1962) and 41 (1963).

The author should like to express his deep appreciation to Professor Ichiro Sakurada for his invaluable guidance and encouragement throughout the work and for introducing him to this field of science and directing his interest towards many of the problems discussed herein. Thanks are also tendered to Professors S. Kajita, A. Araki, Y. Sakaguchi and M. Konishi for their constant interest and numerous constructive comments in this work.
He is also pleased to thank Assistant Professor N. Iso, who has read portions of the manuscript and offered criticism and advice. Further he is greatly indebted to Professor S. Shimizu and stuffs of his laboratory for making the irradiation facilities available for these studies.

Yoshito Ikada

January, 1963

Department of Polymer Chemistry
Faculty of Engineering
Kyoto University
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Chapter I

GENERAL INTRODUCTION
Although an innumerable amount of study has been devoted on the action of radiation on polymer "in solid state", only comparatively little work has been carried out in the field of radiation chemistry of polymers "in solution". One of plausible reason for this lies in the fact that the processes taking place in solution under irradiation is much more complicated than that in solid state. When a polymer is irradiated in solution, the question always arises whether the effects produced are either due to the direct hits of radiation on the solute molecules or due to radicals produced in the solvent which then react with the solute. The first is referred to as direct effect and the second as indirect effect. In addition, there would be another factor such as solubility of individual chain segments, which seems to influence the rate of such reactions as crosslinking and deaccredation.

Until now, however, only a very few data were available for understanding the mechanism of process occurring in polymer solutions during irradiation. Moreover, earlier experiments were often conducted under very unsuitable conditions, and such influence as presence or absence of oxygen, was not appreciated fully enough, which often led to inconsistent results among different research groups.

The purpose of the present studies is to provide more detailed informations with respect to the effects of gamma radiation on various polymers in solution over a wide range of concentrations and to make clear the mechanism of radiation-induced reactions.
As can be easily expected, changes occurring in solution during irradiation depend strongly on the nature of solvents used. A large difference was observed in radiation effects particularly between aqueous and organic solutions. Results on aqueous solutions of poly(vinyl alcohol) will be described in Chapter II, and those on organic solutions of poly(vinyl acetate) in Chapter III. In order to understand this difference and the role of solvent in the radiolysis of polymer solutions, investigation was performed using poly(vinyl methyl ether) which can readily dissolve not only in water but also in many kinds of organic solvents. It will be clarified in Chapter IV that the crosslinking in aqueous solution is mainly caused by OH and H radicals produced as a result of radiolysis of water, whereas the crosslinking can be retarded by radicals produced from ordinary organic solvents.

In Chapters II and IV, the peculiar behavior is mentioned. On irradiation in vacuo of polymers in aqueous solution, no gel is formed by any dose, if the polymer concentrations are lower than a critical value. However, if the concentrations become slightly higher than this value, gelation occurs suddenly and the dose required for incipient gelation falls rapidly with increasing concentration. Then after reaching a minimum, the gelation dose increases again rather slowly. To devise an adequate theory to explain this peculiar curve of gelation dose with polymer concentration, it seems necessary to obtain much more knowledge concerning the crosslinking occurring in the
neighborhood of the critical concentration. Since the critical concentration is considered to show a marked dependence on the expansion of molecules in solution, two charged polymers are irradiated in aqueous solution. One is poly(vinyl alcohol) partially acetalized with glyoxylic acid (Chapter V) and the other is poly(acrylic acid) (Chapters VI and VII). The expansion of these polymers is adjusted by varying either the ionized carboxyl group content or the concentration of added salt. Furthermore, detailed study is carried out on an uncharged polymer, that is, poly(vinyl alcohol) with various degrees of polymerization (Chapter IV). It is concluded from these results that at the critical concentration every polymer molecule is just connected to every other within solution. The elucidation of the physical significance of the critical concentration enables us to interpret the peculiar behavior observed at the gelation occurring in aqueous solution. In addition to this, radius of polymer spheres can be also estimated using the data concerning the critical concentration (Chapters V, VII and IX). At the same time, effects of charge density on degradation of polyelectrolytes in solution are studied (Chapters V and VI). Chapter VIII is concerned with the effect of additives, in other words, the radiation protection and promotion. The irradiation effect of polymer solution below the critical concentration is studied. The results are given in Chapter VII for poly(acrylic acid) and in Chapter X for poly(vinyl alcohol). It is found that in vivo-molecular-crosslinked polymer, namely, micro-gel, can be formed at high doses. In Chapters II and
IX, the indirect effect is quantitatively discussed.

Undoubtedly, these studies on synthetic polymers and polyelectrolytes would render us a better understanding of the complicated feature of radiation chemistry. However far the way to go is, the final goal of this field of science is to get an understanding of the effects in biological systems. The author wishes to have been able to contribute something for this.
Chapter II

AQUOUS SOLUTIONS AND WATER-SWollen FILMS OF Poly(Vinyl Alcohol)


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

Effects of gamma radiation on water-swollen films and aqueous solutions
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, studies have been carried out not only in our laboratory\(^1\), but also by A. Charlesby\(^2\), A. Danno\(^3\), S. Okamura\(^4\) 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. However, if water is present, gel formation is observed. The following two factors may be mainly considered as those related to 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 accumulative data about the behavior of water during the effects of the irradiation on PVA.

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 by I. Sakutada et al7). Its viscosity-average degree of polymerisation, $P_v$, is 1090 and its distribution curve of the degree of polymerisation is shown elsewhere7). 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 HOH was completely extracted by methanol and no acetal residue was detected.

2.2) Preparation of swollen film and solution

The swollen films were prepared by the same method as described in the references1,7). 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. 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 immediately 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 10 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:

\[
\text{Degree of swelling (by weight)} = \frac{\text{weight of the swollen gel}}{\text{weight of the dried gel}} \times 100 \text{ (at 100°C)}
\]

Sol fraction was given by the following equation:

\[
\text{Sol fraction} = 1 - \frac{\text{weight of the dried gel}}{\text{weight of PVA used}} \times 100.
\]

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

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

3. Results and Discussion

3.1) Irradiation in air of the water-swollen films

It seems very interesting to investigate the effects of irradiation on water-swollen films, since water contents in films can be changed over wider ranges than those of solution.

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 Sakura (Ishihara equation) using
m = [\eta]/[\eta]_0$, where $[\eta]$ and $[\eta]_0$ are the limiting viscosity numbers before and after the degradation, respectively. To calculate $\alpha$, it was assumed that crosslinking did not occur and that all ends of main chain fracture were stabilized. As can be seen in Table 1, the main chain fracture is increased with

<table>
<thead>
<tr>
<th>Concentration (wt. fraction)</th>
<th>Dose (r)</th>
<th>Sol fraction (%)</th>
<th>$[\eta]$ (1 cm$^2$/dL)</th>
<th>$P_V$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>unirradiated PVA</td>
<td>—</td>
<td>—</td>
<td>0.655</td>
<td>1085</td>
<td>—</td>
</tr>
<tr>
<td>0.157</td>
<td>5.4x10$^5$</td>
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<td>0.360</td>
<td>429</td>
<td>0.295</td>
</tr>
<tr>
<td>0.193</td>
<td>11.9</td>
<td>—</td>
<td>0.230</td>
<td>210</td>
<td>0.047</td>
</tr>
<tr>
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<td>—</td>
<td>0.158</td>
<td>117</td>
<td>0.02</td>
</tr>
<tr>
<td>0.235</td>
<td>12.9</td>
<td>—</td>
<td>0.231</td>
<td>211</td>
<td>0.074</td>
</tr>
<tr>
<td>0.193</td>
<td>13.5</td>
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<td>0.223</td>
<td>200</td>
<td>0.079</td>
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<td>0.157</td>
<td>42.0</td>
<td>13</td>
<td>0.294$^*$</td>
<td>368$^*$</td>
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</tr>
<tr>
<td>0.415</td>
<td>6.4</td>
<td>100</td>
<td>0.384</td>
<td>468</td>
<td>0.0024</td>
</tr>
<tr>
<td>0.193</td>
<td>7.1</td>
<td>—</td>
<td>0.373</td>
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<td>0.261</td>
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<td>9.5</td>
<td>100</td>
<td>0.373</td>
<td>237</td>
<td>0.027</td>
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<tr>
<td>0.193</td>
<td>11.9</td>
<td>—</td>
<td>0.322</td>
<td>355</td>
<td>0.037</td>
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</table>

$^*$ $[\eta]$, $P_V$ of sol part.
increasing dose and at the dose of about $4 \times 10^7$ r, a gel was formed. This is in accord with the results obtained previously in our laboratory.\(^6\)

\(\alpha\) 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, hence the value of \(\alpha\) would become larger than those which would be obtained when only main chain fracture occurs.

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 \((C/C)\), 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 \(\alpha\) fraction of it is used, the total energy dissipated for fracture amounts to \(RAC + \alpha RA(1-C)\).

The number of main chain fracture per gram of swollen film is \(C\alpha/\mu_m\), where \(\mu\) is Avogadro's number and \(\mu_m\) is the molecular weight of the monomer unit.
Irradiability of a fracture against total dose for water-swollen films of \( \gamma \) irradiated in air.
To the energy dissipated per fracture, $E_d$, is given by,

$$E_d = \frac{\alpha M \kappa}{C \alpha / M} (1 - \kappa)$$  \hspace{1cm} (1)

or

$$\alpha = \frac{(\alpha M / E_d) \kappa}{C (\kappa / C + (1 - \kappa))}$$  \hspace{1cm} (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) also 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, $(\alpha M / E_d) \kappa / C (\kappa / C + (1 - \kappa))$ obtained from the initial slope was plotted against $1/C$ in Fig. 2. The corresponding values obtained in our laboratory\(^1\) are also plotted in Fig. 2. As shown in Fig. 2, a good straight line was obtained, from which $k = 0.09$, $\alpha = 36$ eV. were derived. This shows that not all the energy absorbed by water but only 0.9 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 36.7 eV. which was obtained in the case of irradiation on $\text{dr} \text{PVA}$ by I. Sakurada et al\(^7\).
Fig. 2 slopes of curves in Fig. 1 against reciprocal of concentration (wt. fraction) of polymer.

- point obtained in our laboratory
- point obtained in the present work
3.2) Irradiation in air of the aqueous solutions

Studies on the aqueous solutions so far published have dealt with solutions of rather low concentrations. In the present study, irradiation was carried out using aqueous solutions of comparatively high concentrations and the effects were compared with those of 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.

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

<table>
<thead>
<tr>
<th>Concentration (wt. fraction)</th>
<th>Dose (r)</th>
<th>Sol fraction (%)</th>
<th>[η] (10000/g)</th>
<th>Pv</th>
<th>Degree of swelling of gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>unirradiated PVA</td>
<td>--</td>
<td>--</td>
<td>0.655</td>
<td>1085</td>
<td>--</td>
</tr>
<tr>
<td>0.10</td>
<td>0.5×10⁶</td>
<td>100</td>
<td>0.224</td>
<td>1544</td>
<td>--</td>
</tr>
<tr>
<td>1.3</td>
<td>100</td>
<td>1.00</td>
<td>2385</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2.0</td>
<td>60</td>
<td>0.736</td>
<td>1292</td>
<td>80.3</td>
<td>--</td>
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<tr>
<td>3.3</td>
<td>35</td>
<td>0.312</td>
<td>522</td>
<td>47.5</td>
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<tr>
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<td>27</td>
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<td>490</td>
<td>43.2</td>
<td>--</td>
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<td>7.1</td>
<td>23</td>
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<td>313</td>
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<td>2110</td>
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</tr>
<tr>
<td>4.4</td>
<td>50</td>
<td>0.633</td>
<td>958</td>
<td>73.3</td>
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<tr>
<td>7.1</td>
<td>32</td>
<td>0.353</td>
<td>405</td>
<td>20.2</td>
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</table>
When the swollen films were irradiated in air, the \( P_v \) 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, \( P_v \) was increased consistently and a gel was formed. This phenomenon that \( P_v \) is increased with dose, finally resulting in gel formation, has been found in earlier studies\(^2,3,4\) on the effect of irradiation in vacuo on aqueous RNA solutions. It is also reported that polymer degrades always 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 using such a high concentrated solution as a gel structure was formed. Therefore, air would not be able to diffuse sufficiently into the solution, while 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 concerns 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 the solution is irradiated with the dose of \( R \), the energy actually used for the polymer
reactions will be reduced to $R_f(C)$, where $f(C)$ is a function of the weight fraction of polymer C, and is given, as in 3.1), by the following equation

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

Recently an empirical equation was deduced by A. Charlesby and W. R. Rimmer$^3$ 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:

$$S + \sqrt{S} = \frac{1}{q_o} + \frac{1}{q_o}R_f(C)u_1,$$

where $p_o$ and $q_o$ 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. From the intercept of the straight line obtained by plotting $\sqrt{S}$ against $1/R$, $p_o/q_o$ can be obtained, as if $f(C)$ is actually known, $p_o$ and $q_o$ 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. As the value

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<thead>
<tr>
<th>Concentration (wt. fraction)</th>
<th>$p_o/q_o$</th>
<th>$p_o \times 10^4$</th>
<th>$q_o \times 10^4$</th>
<th>Gelation dose (r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.77</td>
<td>3.1</td>
<td>0.5</td>
<td>1.7 x 10^5</td>
</tr>
<tr>
<td>0.20</td>
<td>0.39</td>
<td>2.7</td>
<td>0.5</td>
<td>4.2</td>
</tr>
<tr>
<td>0.25</td>
<td>0.55</td>
<td>2.5</td>
<td>0.1</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Fig. 3: Curves of $\sqrt[3]{s}$ against reciprocal of dose for aqueous solutions of IVA irradiated in air.
of k involved in the function \( f(C) \) was used, which had been obtained in 3.1).

As shown in Table 3, \( p \) is nearly independent of the weight fraction, while \( q \) 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 result suggests that increased stability brought about by the presence of water influences the crosslinking to some extent, but the degradation not so strongly.

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=1 was taken as the gel point.

3.3) Irradiation of water-swollen films at a fixed dose in air and in vacuo.

In this section, we investigated mainly the effect of oxygen. The water-swollen films prepared from the fractionated PHA with \( P_g \) of 1950 were irradiated in vacuo and in air at a fixed dose of \( 3.2 \times 10^3 \text{R} \). The results are shown in Table 4.

The sample used for irradiation in vacuo could be evacuated only up to \( 10^{-2} \text{mm Hg} \) because of the presence of water contained in the film, but in the case of the dry film, it was sealed after evacuation up to \( 10^{-3} \text{mm Hg} \) for 25 hrs. When irradiation in
Table 4. Effects of gamma-irradiation of water-swollen films of PVA in vacuo and in air. \( R=3.2 \times 10^6 \) r.

<table>
<thead>
<tr>
<th>Degree of swelling of films</th>
<th>Concentration (wt. fraction)</th>
<th>( [\eta] ) (100m1/g)</th>
<th>( P_V )</th>
<th>Sol fraction (%)</th>
<th>Degree of swelling of gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.8</td>
<td>0.095</td>
<td>0.722</td>
<td>1393</td>
<td>26.5</td>
<td>18.7</td>
</tr>
<tr>
<td>7.3</td>
<td>0.120</td>
<td>0.897</td>
<td>1766</td>
<td>31.6</td>
<td>23.5</td>
</tr>
<tr>
<td>3.8</td>
<td>0.208</td>
<td>1.135</td>
<td>2544</td>
<td>55.5</td>
<td>70.5</td>
</tr>
<tr>
<td>3.1</td>
<td>0.244</td>
<td>—</td>
<td>—</td>
<td>large</td>
<td>large</td>
</tr>
<tr>
<td>1.8</td>
<td>0.357</td>
<td>0.992</td>
<td>2063</td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>1.1</td>
<td>0.476</td>
<td>0.943</td>
<td>1903</td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>Dry film</td>
<td>1.00</td>
<td>0.810</td>
<td>1501</td>
<td>100</td>
<td>—</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Degree of swelling of films</th>
<th>Concentration (wt. fraction)</th>
<th>( [\eta] ) (100m1/g)</th>
<th>( P_V )</th>
<th>Sol fraction (%)</th>
<th>Degree of swelling of gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.8</td>
<td>0.095</td>
<td>0.593</td>
<td>922</td>
<td>35</td>
<td>26.9</td>
</tr>
<tr>
<td>7.3</td>
<td>0.120</td>
<td>0.578</td>
<td>886</td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>3.8</td>
<td>0.208</td>
<td>0.698</td>
<td>1190</td>
<td>&quot;</td>
<td>—</td>
</tr>
<tr>
<td>3.1</td>
<td>0.244</td>
<td>0.705</td>
<td>1209</td>
<td>&quot;</td>
<td>—</td>
</tr>
<tr>
<td>1.8</td>
<td>0.357</td>
<td>0.718</td>
<td>1243</td>
<td>&quot;</td>
<td>—</td>
</tr>
<tr>
<td>1.1</td>
<td>0.476</td>
<td>0.746</td>
<td>1320</td>
<td>&quot;</td>
<td>—</td>
</tr>
<tr>
<td>Dry film</td>
<td>1.00</td>
<td>0.798</td>
<td>1467</td>
<td>&quot;</td>
<td>—</td>
</tr>
</tbody>
</table>
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 unavoidably in a sealed tube.

In Fig. 4, $P_Y$ of sol part was plotted against the weight fraction of the polymer. It shows that there is a remarkable difference between irradiation in vacuo and in air. In the former case, $P_Y$ was decreased monotonically and gel was formed when $P_Y$ 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 about 23% for irradiation in vacuo and 10% for irradiation in air.

Next, we will discuss the chemical mechanism of crosslinking and degradation.

a) Irradiation in vacuo

The phenomenon that $P_Y$ before gelation was increased with decreasing weight fraction, finally resulting in gel formation, may be interpreted as follows: with decreasing weight fraction, the concentration of $H^+$ and $HO^-$ produced by the radiolysis of water is increased, so the indirect effect is increased and hence crosslinking is promoted. It seems also very plausible that, as a result of the increase in mobility of chain segments
Fig. 4: Degree of polymerization $k_v$ of sol part against concentration for water-swollen films irradiated in vacuo and in air. 

$\alpha = 3.2 \times 10^{-1}$ cm.

$\circ$, $\bullet$ --- sol was not formed.
by penetration of water, the reactions between polymers may be promoted and increase the $I_v$. Probably both of these effects may influence the rate of crosslinking. Whether water promotes crosslinking mainly by behaving as a plasticizer, or the radicals produced by the radiolysis of water have large influence on crosslinking will be treated in the subsequent chapters.

b) Irradiation in air

In this case, $I_v$ was 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 is clear that oxygen influences degradation remarkably, but as it is probable that the amount of oxygen is constant at any weight fraction range, so the phenomenon that $I_v$ changes with the weight fraction, can not be interpreted by the action of oxygen only. However, with reference to the mechanism which was proposed by Phillips et al. in the study on the effects of irradiation on aqueous solutions of carbohydrates, the phenomenon can be explained qualitatively. According to their mechanism, the $\text{HC}_2^-$ which is produced by the reaction between oxygen and $H^-$ is considered to play a important role.

\[
\text{H}_2\text{O} \xrightarrow{\text{radiation}} H^- + \text{HC}_2^- \quad (1)
\]

\[
H^- + \text{O}_2 \xrightarrow{} \text{HC}_2^- \quad (2)
\]
The hydrogens of polymers will be abstracted by the direct action of radiation, or by the radicals produced from water, as follows:

\[
\text{H} - \text{CH}_2 - \text{C} - \text{OH} \xrightarrow{\text{radiation or H, H}_2} \text{H} - \text{CH}_2 - \text{C} - \text{OH} + \text{H}_2\text{O}, \text{H}_2 \quad (3)
\]

This polymer radicals may react with oxygen, and degrade via the following processes.

\[
\text{H} - \text{CH}_2 - \text{C} - \text{OH} + \text{O}_2 \rightarrow \text{H} - \text{CH}_2 - \text{C} - \text{OH} + \text{CO} \quad (4)
\]

\[
\text{H} - \text{CH}_2 - \text{C} - \text{OH} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{CO}_2 \quad (5)
\]

\[
\text{H} - \text{CH}_2 - \text{C} - \text{OH} \rightarrow \text{degradation} \quad (6)
\]

The polymer radicals, being able to crosslink, produced in the reaction (3) may be immediately attached to oxygen and degrade as indicated in the reactions (4), (5) and (6). An increase in the concentration of \( \text{H}_2\text{O}_2 \) 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 complete consumption of oxygen, the reactions (2) and (4) can no more occur and then crosslinking reaction begins.

3.4) Irradiation of aqueous solutions at a fixed dose in vacuo

In order to make clear the effect on RMA-water system over the entire weight fraction range, irradiation was carried out in vacuo using the aqueous solutions to cover the low weight fraction range which was not dealt with in the previous sections. The material used was the fractionated RMA with \( F_{\gamma} \) of 1950 and the radiation dose was \( 3.2 \times 10^6 \) 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 0.41 and 0.602 weight fraction became colored yellow to brown by irradiation. As the weight fraction was increased, \( F_{\gamma} \) was increased and finally a gel was formed at 0.603 wt. fraction. At higher concentrations than 0.603 wt. fraction, a slight increase in the weight fraction reduced suddenly the sol fraction from 100% to 0% and at 0.606 weight fraction no sol part was found. The gel formed by irradiation of the solution of 0.606-0.41 weight fraction floated freely in the solution which was essentially free from clots. At
Table 5. Effects of gamma-irradiation in vacuo of aqueous solutions of PVA. \( R = 3.2 \times 10^6 \) r

<table>
<thead>
<tr>
<th>Concentration (wt. fraction)</th>
<th>Sol fraction (%)</th>
<th>([\eta]) (100m1/g)</th>
<th>(E_V)</th>
<th>Degree of swelling of gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>unirradiated PVA</td>
<td>---</td>
<td>0.970</td>
<td>1966</td>
<td>---</td>
</tr>
<tr>
<td>0.001</td>
<td>13.0</td>
<td>0</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>0.002</td>
<td>&quot;</td>
<td>0.568</td>
<td>724</td>
<td>---</td>
</tr>
<tr>
<td>0.003</td>
<td>&quot;</td>
<td>0.555</td>
<td>1027</td>
<td>---</td>
</tr>
<tr>
<td>0.004</td>
<td>72.0</td>
<td>1.50</td>
<td>7930</td>
<td>large</td>
</tr>
<tr>
<td>0.006</td>
<td>0</td>
<td>0.54</td>
<td>---</td>
<td>22.5</td>
</tr>
<tr>
<td>0.010</td>
<td>0</td>
<td>0.55</td>
<td>---</td>
<td>24.3</td>
</tr>
<tr>
<td>0.030</td>
<td>10.5</td>
<td>0.466</td>
<td>630</td>
<td>27.6</td>
</tr>
<tr>
<td>0.061</td>
<td>34.0</td>
<td>0.420</td>
<td>538</td>
<td>20.1</td>
</tr>
<tr>
<td>0.102</td>
<td>42.0</td>
<td>0.527</td>
<td>795</td>
<td>18.7</td>
</tr>
<tr>
<td>0.124</td>
<td>60.3</td>
<td>0.543</td>
<td>804</td>
<td>23.4</td>
</tr>
<tr>
<td>0.152</td>
<td>85.1</td>
<td>0.560</td>
<td>843</td>
<td>43.2</td>
</tr>
</tbody>
</table>

The weight fraction of 0.03, a polymer fraction which did not take part in gel formation, whose amount was increased with increasing weight fraction of polymer until it reached to 100% at about 0.60 weight fraction. The result that at lower concentrations than 0.03 weight fraction no gel was formed and that at 0.001-0.01 weight fractions a gel was formed most readily, is in agreement with the results obtained by A. Charlebois\(^2\) and A. Danno\(^3\).

- 25-
Fig. 5: mol fraction $S$ against concentration for aqueous solutions of PVA irradiated in vacuo. Dose=$3.2 \times 10^4$ r.

- $\circ$ --- solution,
- $\bullet$ --- swollen film.
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 lower sol fraction than the solution at the same weight fraction. This may be attributed to the difference in crystallinity, which is higher for films than that of solutions. It is probable that crosslinks formed by radiation protect the crystalline parts, leading to the increase in sol fraction.

3.5) Irradiation of 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 periods before irradiation, 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
Fig. 7  Degree of polymerization $P_V$ against standing time before irradiation for higher concentrated aqueous solutions of PVA. Wt.fractiion=0.1, Dose=3.2x10^6 r.

Fig. 8  Sol fraction(?) and degree of swelling(?) against standing time before irradiation for higher concentrated aqueous solutions of PVA. Wt.fractiion=0.1, Dose=3.2x10^6 r.
Table 6. Effect of gamma-irradiation of higher concentrated aqueous solutions of PVA. Concentration (wt. fraction) of polymer = 0.10, R = 3.2 x 10^6r.

<table>
<thead>
<tr>
<th>Standing time before irradiation in days</th>
<th>0</th>
<th>0</th>
<th>1</th>
<th>4</th>
<th>10</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>sol fraction (%)</td>
<td>39.6</td>
<td>43.7</td>
<td>40.6</td>
<td>33.5</td>
<td>30.2</td>
<td>30.0</td>
</tr>
<tr>
<td>[η] (100cml/g)</td>
<td>0.540</td>
<td>0.590</td>
<td>0.560</td>
<td>0.525</td>
<td>0.703</td>
<td>0.703</td>
</tr>
<tr>
<td>ηV</td>
<td>797</td>
<td>820</td>
<td>843</td>
<td>1158</td>
<td>1203</td>
<td>1203</td>
</tr>
<tr>
<td>Degree of swelling of gel</td>
<td>28.1</td>
<td>30.6</td>
<td>21.4</td>
<td>17.5</td>
<td>17.2</td>
<td>20.7</td>
</tr>
</tbody>
</table>

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 decreased with the standing time, although the mobility of chain segment 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.

References

(1) I. Sakurada, A. Nakajima, and H. Aoki, Memoirs of the Faculty of Engineering, Kyoto Univ., 21, 94 (1959).


Chapter III

ORGANIC SOLUTIONS OF POLY(VINYL ACETATE)

40, 1 (1962)

Effects of Gamma Radiation on Polymer in Solution (I)
Poly(vinyl acetate)
1. 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 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 iVAc under various conditions. In this chapter we will report 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 degradation and crosslinking, and propose a mechanism of crosslinking.

2. Experimental

2.1) Materials

iVAc used in these experiment was prepared - the
acetylation of polyvinyl alcohol (PVA). The original PVA from which the PVA was obtained was prepared either by the polymerization of monomer in ethyl acetate at 80°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 cross-linking was studied.

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

2.2) Irradiation Procedure

Irradiation was carried out at room temperature, except for the case where the temperature effect was investigated. The dose rate was in the vicinity of 1.3 x 10^5 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.

2.3) 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 10 hr. in a large excess of benzene to extract the sol part, then dried and weighted. Sol fraction was given by the following equation:

\[
\text{Sol fraction, } S = 1 - \frac{\text{weight of dried gel}}{\text{weight of PVAc used}} \times 100, (\%)
\]

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, \(\tilde{M}\), was calculated by the equation\(^1\):

\[
[\eta] = 8.91 \times 10^{-3} \times \tilde{M}^{0.62}
\]

\(\tilde{M}\) of PVA obtained by the alkaline hydrolysis of the irradiated PVAc was calculated by the following equation\(^1\):

\[
[\eta] = 7.51 \times 10^{-3} \times \tilde{M}^{0.45}
\]

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

3. Results and Discussion

3.1) Irradiation in Various Solvents

In Fig. 1 are shown the results obtained by irradiation of PVAc in various solvents. \(\tilde{M}\) of the polymer used was 1.2 k and the concentration of the polymer was 1 weight %. These are in good agreement with the results reported by A. Engelm\(^2\). As can be seen from Fig. 1, change in \([\eta]\) with dose depends
Fig. 1 Changes in limiting viscosity number $[\eta]$ as a function of radiation dose for PVC irradiated in various solvents at the polymer concentration of 10 wt.
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.

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 constant $\mu$ of the solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$G_p$(Chloro)</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>15.0</td>
<td>0.575</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.57</td>
<td>0.440</td>
</tr>
<tr>
<td>Dioxane</td>
<td>12.5</td>
<td>0.341</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.5</td>
<td>0.530</td>
</tr>
<tr>
<td>Acetone</td>
<td>31.5</td>
<td>0.418</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.575</td>
<td>0.870</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>20.0</td>
<td>0.376</td>
</tr>
<tr>
<td>Chloroform</td>
<td>38</td>
<td>0.833</td>
</tr>
</tbody>
</table>

interaction constant$^3)$, as a measure of solubility, and $G_p$-value$^4)$ 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 constant nor $G_p$-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.

3.2) 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 more 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

Table 2. Properties of mixed solvents.

<table>
<thead>
<tr>
<th>Added solvent</th>
<th>Precipitation points of solution</th>
<th>( C_R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>7.5°C</td>
<td>15.2</td>
</tr>
<tr>
<td>Hexane</td>
<td>4.5°C</td>
<td>14.7</td>
</tr>
<tr>
<td>Xylene</td>
<td>-1 °C</td>
<td>14.6</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0 °C</td>
<td>15.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>0 °C</td>
<td>15.0</td>
</tr>
</tbody>
</table>

- 36 -
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 methanol 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 a 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. 0.5). Curves in Figs. 3 and 4, where the results obtained are given, show neither a maximum nor minimum, but indicate a monotonic increase in the rate of crosslinking with increasing water content. The decrease in $[\gamma]$ observed when the polymer was irradiated at the concentration of 1.5 molar will 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.

A. Denflein has recently reported a result\(^2\) obviously,
Fig. 2 Changes in limiting viscosity number \([\eta]\) as a function of radiation dose for \(\text{UV} \) irradiated in methanol-added solvent at the polymer concentration of 16 wt.%. Methanol:added solvent=9:1 (by weight).
Fig. 3 Changes in limiting viscosity number $[\eta]$ as a function of water content in mixed solvent for $\text{EVAc}$ irradiated in methanol-water.

- $\circ$ --- irradiated in 1% solution
- $\bullet$ --- irradiated in 5% solution
Fig. 4 Changes in degree of swelling of gel in benzene(o) and sol fraction(e) as a function of water content in mixed solvent for PV:c irradiated in methanol-water at the polymer concentration of 10 and dose of 2.0 x 10^6 r.
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 4.1 which was prepared by pearl polymerization 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.

3.3) 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 of 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
Fig. 5 Sol fractions S as a function of water content in mixed solvent for PVAir irradiated in methanol-water at the polymer concentration of 5% and dose of 1.4 x 10³ r. [η] of the unirradiated polymer is 4.6 in benzene at 30°C.
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 doses 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. For example, the critical concentration 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 $5 \times 10^7$ is given in Table 5.

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

<table>
<thead>
<tr>
<th>Solvent</th>
<th>[η] after irradiation</th>
<th>Gel fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0.032</td>
<td>100</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td></td>
<td>7.2</td>
</tr>
<tr>
<td>Dioxane</td>
<td></td>
<td>4.9</td>
</tr>
</tbody>
</table>

when the polymer was irradiated at the concentration of 10% in
Fig. 6 Dose for incipient gelation $R_g$ as a function of the polymer concentration for $\text{IVAsc}$ irradiated in methanol.
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, the polymer crosslinked almost completely in ethyl acetate and dioxane, but not in acetone though \( [\eta] \) was raised 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%.

3.4) 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 -50~70°C. T of PVAc used in this experiment was 155°C. It is obvious from Fig. 7 that the effect of temperature is not so large, compared with what has been observed at irradiation of various polymers in solid state\(^7\). A likely explanation for this is 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
Fig. 7 Changes in limiting viscosity number $[\eta]$ as a function of radiation dose for PVA irradiated in various solvents at a polymer concentration of 1.5% and irradiation temperatures of -46, 10, and 70°C.
Fig. 8 Changes in limiting viscosity number $[\eta]$ as a function of irradiation temperature for $\alpha$-VAc irradiated in various solvents at a polymer concentration of 10% and dose of $7.0 \times 10^{14}$. I, benzene; II, acetic acid; III, ethyl ethyl ketone; IV, ethyl acetate.
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 [7], which would be obtained when the polymer was irradiated with a dose of 7 x 10^6 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.

3.5) AFFECT 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 \( P \) were irradiated in 100% benzene solution. The degrees of polymerization of the polymer used in this experiment were 741 and 1,114 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 [7] plotted against the radiation dose are shown in Fig. 9, and the dose for incipient gelation, \( R_G \), are plotted against the \( P \) of polymer in Fig. 10.
Fig. 9 Changes in limiting viscosity number $[\eta]$ as a function of radiation dose for PVAc with various degrees of polymerization $f$. The polymers were irradiated in 10% benzene solution.
Fig. 10 Dose for incipient solution $R_g$ as a function of polymerization $\tau$ of initial $\text{VAc}$. Polymers were irradiated in 10$^3$ benzene solution.
It may be shown theoretically that if the density of crosslinked units, \( q \), is proportional to the radiation dose but independent of both \( r \) and the mobility of polymer, \( R_g \) should be inversely proportional to \( r \). It is seen from Fig. 10 that the product \( R_g \times r \) 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.

3.4) 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 Pinner\(^8\) and consists in the pursuit of the amount of gel produced during irradiation. Another was proposed by Kilb\(^9\), which consists in the pursuit of the changes in \([\eta]\). Kilb has dealt with the changes below the gel point, while Charlesby-INNER have dealt with the changes in gel 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 Stockmayer\(^1\). 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:

$$S + \sqrt{S} = \frac{p}{q_0} + \frac{1}{q_0} \cdot \frac{F_n}{R}$$

where $F_n$ is the number-average degree of polymerization, and $p$ and $q_0$ are 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 $2p_0/q_0 \approx 3.2$. 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 de-radiation scarcely occurs.
Fig. 11 Observed and theoretical limiting viscosity number ratios of irradiated to unirradiated NVLc in benzene, $[\eta]/[\eta]_0$ as a function of $R/R_g$, where $R_g$ is the dose for incipient gelation. Theoretical curves are given for several values of $2p_0/R_0$, the ratio of number of scissions to that of crosslinks.
Fig. 12 \( s + \sqrt{s} \) as a function of reciprocal of radiation dose for PVAc irradiated in 20\% methanol solution. S is sol fraction.
3.7) 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 partially 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 200 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 Todd\textsuperscript{13}) that $H_2$ and $CH_4$ but no $CH_3COOH$ were produced under irradiation of PVAc in solid state. Remembering this observation, we may represent the crosslinking processes as follows:
Fig. 15 Degrees of polymerization $F$ of IVAc and hydrolyzed \textit{IVA} as a function of radiation dose. IVAc was irradiated in \textit{CCl}_3 methanol solution.
(1) **Reactions between two side chains**

\[ \text{CH}_3 \rightarrow \text{CH}_2 + \text{H}_2, \quad \text{or} \quad \text{CH}_3 \rightarrow \text{CH}_2 + \text{CH}_4 \]

(2) **Reactions between a side chain and a main chain**

\[ \text{CH}_3 \rightarrow \text{CH}_2 + \text{CH}_3 \quad \text{or} \quad \text{CH}_3 \rightarrow \text{CH}_4 \]

(3) **Reactions between two main chains**

\[ \text{CH}_3 \rightarrow \text{CH}_3 + \text{H}_2 \]

\[ \text{CH}_3 \rightarrow \text{CH}_3 + \text{CH}_4 \]
Table 4. Limiting viscosity number and degree of polymerization of PVAc, $[\eta]_{AC}$, $\bar{\eta}_{AC}$ and of the hydrolyzed VA, $[\eta]_A$, $\bar{\eta}_A$, and number of crosslinks $K$ of PVAc irradiated in 260 methanol solution.

<table>
<thead>
<tr>
<th>Dose ($10^6 \mu$)</th>
<th>$[\eta]_{AC}$</th>
<th>$\bar{\eta}_{AC}$</th>
<th>$[\eta]_A$</th>
<th>$\bar{\eta}_A$</th>
<th>$K_{1+2} \times 10^4$</th>
<th>$K_2 \times 10^4$</th>
<th>$(K_{1+2}+K_3) \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.934</td>
<td>1.14</td>
<td>0.51</td>
<td>1.17</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.2</td>
<td>1.03</td>
<td>2.15</td>
<td>0.972</td>
<td>2.60</td>
<td>0.30</td>
<td>0.11</td>
<td>0.47</td>
</tr>
<tr>
<td>2.4</td>
<td>1.23</td>
<td>2.74</td>
<td>1.178</td>
<td>2.96</td>
<td>0.51</td>
<td>1.80</td>
<td>2.11</td>
</tr>
<tr>
<td>3.7</td>
<td>3.92</td>
<td>3.54</td>
<td>1.195</td>
<td>2.75</td>
<td>1.64</td>
<td>1.69</td>
<td>2.93</td>
</tr>
<tr>
<td>5.7</td>
<td>2.90</td>
<td>6.51</td>
<td>1.17</td>
<td>3.98</td>
<td>1.73</td>
<td>2.3</td>
<td>4.71</td>
</tr>
</tbody>
</table>

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

$$K_{1+2} = (1/\bar{\eta}_A - 1/\bar{\eta}_{AC})$$  

for the total reactions of (1) and (2),

$$K_2 = (1/\bar{\eta}_0 - 1/\bar{\eta}_A)$$  

for the reaction (3)

where $\bar{\eta}_0$ is the number-average degree of polymerization of the unirradiated PVAc. $\bar{\eta}$ is the degree of polymerization which is calculated using the $[\eta] - F$ relation described above is number-average, for the relation was obtained by the osmotic pressure measurements of PVAc having the same molecular weight.
Fig. 14 Numbers of crosslinks per monomer unit as a function of radiation dose for $\cdot$VAc irradiated in 20% methanol solution.
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, \( K_{1+2+3} \), 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 9.6.

The gels obtained under irradiation with the dose of \( 2 \times 10^7 \) r completely dissolved in boiling water as a result of hydrolysis, but for the gels obtained with a dose higher than \( 3 \times 10^7 \) r, a water-insoluble part was observed even after severe hydrolysis.

4. 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 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 molecule. 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 are not in contact with each other and in the presence of oxygen and additives.

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Chapter IV

AQUEOUS AND ORGANIC SOLUTION OF POLY(VINYL METHYL ETHER)

40, 10 (1962)

Effects of Gamma Radiation on Polymer in Solution (II)

poly(vinyl methyl ether)
1. Introduction

In Chapters II and III, the effects of radiation have been investigated on polyvinyl alcohol in aqueous solution\(^1\) and polyvinyl acetate in various organic solutions\(^2\). The works were chiefly concerned with the crosslinking and the degradation of the polymer, and demonstrated that the changes induced by radiation on polymer in aqueous solution are different from those in non-aqueous solutions, and that the crosslinking reaction depends largely on the polymer concentration.

The present study is intended to supply informations with respect to the radiation effects on polymer in solution and especially to make clear the role of solvent at the irradiation of polymer in solution. For this purpose, polyvinyl-methyl ether (PVME) was chosen as a polymer because of its very good solubility in very sorts of solvent such as water, carbon disulfide (CS\(_2\)) and almost of organic solvents except aliphatic hydrocarbons.

2. Experimental

Vinylmethy ether purified in an ordinary way was bulk-polymerized at 60\(^\circ\)C using boron trifluoride ether complex as a catalyst (0.02\% to 10\% monomer). The polymer obtained at 40\% conversion of monomer was dried at 50\(^\circ\)C and 10\(^{-2}\)mm. Its appearance was tacky and light-brown. The viscosity-average
degree of polymerization was 60% and the degree of crystallization was nearly equal to zero. The polystyrene employed in the experiment shown in Fig. 7 was obtained by a bulk-polymerization at 70°C and the number-average molecular weight was 82,400. The solvents used for the irradiation were all of the analytical grade.

Irradiation was in all cases carried out in air-free solutions at room temperature. The preparation of the solution and the irradiation procedure were the same as previously described.

Viscosities of irradiated polymers were measured at 30°C in the same solvent that was used for the irradiation, since it was very difficult to separate irradiated polymers from the solution because of their good solubility and weak thermal resistance. The gel point was determined by visual inspection.

3. Results

3.1) Viscosity Change of Irradiated Polymer

The changes induced by radiation on polymer in solution have been found to be affected mainly by the following factors: (1) the sort of solvent, (2) the polymer concentration and (3) the atmosphere during irradiation. In our experiments, irradiation was carried out in the absence of air using various sorts of solvent over a wide range of the polymer concentration.
Aromatic and halogenated hydrocarbons were not used as a solvent because of their peculiar behavior in radiation chemistry. In this respect we will discuss in the part of General Discussion.

Plots of the viscosity changes $[\eta]/[\eta]_0$ against radiation dose for the irradiation at the concentration of 0.1, 3, 20 and 90 wt.% are shown in Figs. 1, 2, 3 and 4, respectively, where $[\eta]$ and $[\eta]_0$ represent the limiting viscosity numbers of irradiated and unirradiated polymers. The scale of abscissa of Fig. 4 is half that of other figures. These data show clearly that water and $\text{H}_2\text{O}$ favor the crosslinking remarkably, compared with other organic solvents. When the concentration became considerably high, viscosities were increased in all solvents. It is also worth noting that the order of solvent which was determined on the basis of the magnitude of viscosity change was partially revised with the increase in the concentration. In order to see these phenomena more clearly, viscosity changes which could be obtained under the irradiation at a dose of $5 \times 10^6 \text{r}$, were plotted against the concentration in Fig. 5. The possibility of formation of micro gel at low concentrations may be excluded because of the clearance of the irradiated solutions.

3.2) Gelation Dose Dependence on the Polymer Concentration

The doses for incipient gelation were determined for the
Fig. 1  Irradiation of PMMA in various solvents at polymer concentration of 0.8.
Fig. 2 Irradiation in various solvents at polymer concentration of 3.0%.
Fig. 3  Irradiation of $^{\alpha}$-W in various solvents at polymer concentration of 20..
Fig. 4 Irradiation of Ti in various solvents at polymer concentration of 90%.  

- 69 -
Fig. 5  Irradiation of PAN in various solvents at a dose of $5 \times 10^6 \text{r.}$
aqueous, CS$_2$ and ethyl acetate solutions. The results are shown in Fig. 6. The curve for water is quite similar to that of other polymers in aqueous solution and the curve for ethyl acetate to that of other polymers in organic solvents, whereas the curve for CS$_2$ is quite different from these two and lies between them. The aqueous and CS$_2$ solutions became turbid during the irradiation below critical concentrations.

Polystyrene also underwent gelation on irradiation in very dilute CS$_2$ solutions, as shown in Fig. 7.

4. Discussion of Results

In our preliminary experiments, it was found that the irradiation of PMMA in solid state in vacuo led to gel-formation with a $G$-value of crosslinking $= 1.84$, $q_\ast = 1.9 \times 10^{-1}$ and $p_\ast = 6.3 \times 10^{-1}$, where $p_\ast$ and $q_\ast$ are the density of the fracture and the crosslinked units per unit dose. It is seen clearly from these data that this polymer does not exhibit any peculiar behavior to radiation, and hence this can be regarded as a model material to study the role of solvent without any aid.

One of the most interesting observation in the present experiment is that of the irradiation in CS$_2$ where gelation occurs even at very low concentrations. The critical concentration for gel-formation ($C_{\text{crit.}}$) agrees with that for the aqueous solution. CS$_2$ seems to affect the crosslinking not via the solvent radicals, but act only as a diluent, because
Fig. 6 Gelation dose $R_g$ as a function of polymer concentration for $^{60}Co$ irradiated in various solvents.
Fig. 7 Gelation dose $R_g$ as a function of polymer concentration for polystyrene irradiated in vacuo in ethyl acetate and carbon disulfide. (No. av. mol. wt. of unirradiated polystyrene = 420000. Dose rate = 1.5 x $10^5$ r/hr.)
$G_R$-value of free radicals produced by the radiolysis is negligibly small as shown in Table 1. In other words, this solvent is extremely insensitive to radiation, compared with other organic solvents. Consequently, the gelation dose-concentration curve for \text{CS}_2 solution may be interpreted in terms of competition between the effect of dilution and that of mobility of the polymer. The former retards the crosslinking, but the latter favors it. From the discussion above mentioned and the finding that the gelation doses for aqueous solutions are considerably smaller than those for \text{CS}_2 solutions over a wide range of the concentration except near $C_{\text{crit}}$, the following important conclusion may be drawn: the promotion of crosslinking by water is attributed to the indirect effect of the reactive.

Table 1. Solvent power, $G_R$-value of free radicals and viscosity of solvent.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$[\eta]$</th>
<th>$G_R$-value$^a$</th>
<th>Viscosity of solvent(20°C) (centipoise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.169</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>0.291</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>0.393</td>
<td>15.0</td>
<td>0.593</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.336</td>
<td>31.2</td>
<td>0.331</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>0.400</td>
<td>19.9</td>
<td>0.349</td>
</tr>
<tr>
<td>Dioxane</td>
<td>0.353</td>
<td>12.5</td>
<td>1.26</td>
</tr>
</tbody>
</table>

$^a$) The values obtained by Harat, Chapiro et al. $G(Fe^{+++})=15.6$.
radicals formed by the radiolysis of water rather than to the increase in mobility of the macromolecule caused by the presence of water. On the physical meaning of $C_{\text{crit}}$, we will discuss in subsequent chapters.

In the case of other organic solvents, the results are different from those obtained at the irradiation in water and CS$_2$ especially at a lower concentration range, as seen in Figs. 1, 2 and 5. This may well be due to the difference of reactivities of radicals resulting from the radiolysis of these solvents. As well known, very reactive radicals such as $\cdot$OH and $\cdot$N$_2$ are produced from water; these radicals abstract hydrogen atoms from macromolecules to form macroradicals. Very few numbers of free radicals are produced from CS$_2$. On the contrary, the free radicals produced from other organic solvents seem to have little tendency to abstract hydrogen from macromolecules, but more likely to deactivate the macroradicals$^5$). As a consequence, degradation predominates over crosslinking at low concentrations where the fraction of solvent in the solution is sufficiently large, as shown in Fig. 5. The amount and reactivity of these radicals may be assumed to be practically identical, irrespectively of the sort of organic solvents except for the case of acetone. Therefore, it is very reasonable to decide that the difference of radiation-induced viscosity changes and the reversion of the order of organic solvent should be ascribed to the difference of solvation and mobility of the polymer. The former prevents both the comp-ro-recombination
which would protect the polymer from suffering main-chain 
scission, and the coupling reaction between two different 
macroradicals which would result in crosslinking; the latter 
promotes the coupling reaction. As a conclusion, the differ-
ence of radiation effects at low concentrations may be ascribed 
mainly to the difference of solvation, since it may be assumed 
that owing to a large number of the solvent molecules per 
macromolecule, deactivation takes place exclusively so as to 
make the effect of the mobility almost insignificant. If this 
is true, better solvents in which solvation occurs more 
strongly should favor the degradation more powerfully. One 
can see from Fig. 5 and Table 1 that this explanation is ac-
ceptable.

At higher concentrations, on the other hand, crosslinking 
predominates over de radiation owing to the decrease in the 
fraction of solvent in the solution. Then, a competition 
between deactivation and coupling of macroradicals, consequently 
the diffusive process may become rate-determining. This effect 
is more pronounced if the lifetime of the macroradicals is 
very short and the solution is highly viscous so as to limit 
the translational motion of the polymer chains. Thus, the 
mobility of macromolecule appears to play a more important 
role than the solvation. The mobility of polymer segment 
decreases with increasing viscosity of medium which is given 
in the fourth column of Table 1. Our results show that, as 
expected, crosslinking proceeds more readily in the solvent
of lower viscosity. One exception of this is seen in the case of acetone solution. The peculiarity was also observed at the irradiation of polyvinyl acetate in acetone solution. The possible explanation may be that acetone retards crosslinking more rapidly than other solvents because of its large $G_R$-value.

5. General Discussion on Role of Solvent

The present experiments and previous related ones$^{1,2}$ permit general conclusions to be drawn concerning the role of solvent at the irradiation of polymer in solution.

In general, the mechanism of crosslinking in solution is complicated because solvents possibly influence the radiation-induced reactions mainly via two independent effects. One is concerned with the attack of solvent radicals (we will call this "radical effect"); the other, with the change in mobility of the polymer, dilution and solvation due to the solvent ("solvent effect"). In addition, a large dependence of these effects on the nature of solvent makes the analysis of the results more difficult. In the case of the polymers which degrade under any conditions, the interpretation of the radiation-induced changes in solution is rather easy, because in this case only two factors are sufficient to be considered; namely, the attack of solvent radicals to the polymer and the cage-recombination prevention both of which accelerate the
degradation with decreasing concentration.

In order to make the discussion easier, it is convenient to classify the solvents into three groups.

(a) Solvent radicals have very strong reactivity

Water and halogenated hydrocarbons belong to this group, whose solutions have been investigated most extensively in the radiation chemistry of solution. The common feature is that the radicals are so reactive that "solvent effect" is almost overshadowed by "radical effect". \( \cdot H \) and \( \cdot CH \) favor crosslinking, while \( Cl\) and \( Cl_2 \) (formed by the reaction of \( H \) and \( O_2 \)) favor degradation. Therefore, with decreasing concentration, crosslinking occurs more readily in water in the absence of air, while in halogenated hydrocarbons the rate of degradation increases. However, when the aqueous solution becomes so dilute that a macromolecule can not interact with the others, gelation dose increases suddenly to a definite value.

(b) Radicals are not practically produced by radiolysis of solvent

The typical solvents belonging to this group are \( CS_2 \) and aromatic solvents. In this case, contrary to (a), "solvent effect" should be considered first of all as mentioned above.

The gelation dose-concentration curves obtained at the
irradiation of polystyrene solution are given in Fig. 7, which have the quite same shape as those obtained at the irradiation of PMMA (see Fig. 6). ( [7] of unirradiated polystyrene were 1.05 and 1.14, in CS₂ and ethyl acetate, respectively). It was also found in our experiments that CS₂ solution of rubber also sets to a continuous gel. These results indicate that on irradiation of vinyl polymers in such solvents that do not prevent the crosslinking reaction, gel-formation should always occur above the concentration where macromolecules just interfere with each other. In other words, if viscosities decrease under the irradiation in moderately concentrated solutions, the solvent radicals can be assumed to deactivate macroradicals. Concerning the aromatic solvent, many workers have carried out investigations to find that energy is transferred from the excited polymer to solvents so that the polymer is protected from radiation, and shows very slight crosslinking or degradation, which occurs almost independently of the concentration.

(c) Solvents have medium Gₚ-values

The interpretation of the radiation effects in this case becomes more difficult than the preceding, because "solvent effect" as well as "radical effect" should be taken into account.

The solvents mentioned in (a) and (b) show nearly the same effect independently of the sort of polymer, while those
belonging to this group which include almost of the ordinary organic solvents, exhibit different effects on different polymers. This suggests possibly that there is little difference among the reactivities of these solvent radicals, whose major role is to deactivate the macroradicals. Consequently, even in the moderately concentrated solutions, polymers show degradation. However, at considerably high concentrations, the effect of the mobility may become occasionally more important than that of deactivation and dilution. Therefore, in that case, the gelation dose-concentration curve has a minimum point as shown in the case of ethyl acetate solution.

The variation of the radiation effects with the variation of the organic solvents was discussed in detail in the part of Discussion of Results giving a satisfactory explanation so that the discussion in this respect will not be repeated here.

References

AQUEOUS SOLUTIONS OF POLY(VINYL ALCOHOL) PARTIALLY ACETALIZED WITH GLYOXYLIC ACID


Effects of Gamma Radiation on Polymer in Solution (III)

poly(vinyl alcohol) partially acetalized with glyoxylic acid
1. Introduction

The radiation chemistry of the polymer in solution, especially in aqueous solution, has been studied intensively by many workers\textsuperscript{1}) in the recent years. As well known, if the dose for incipient gelation is plotted against the polymer concentration, a peculiar curve is obtained, i.e., the relation dose decreases very sharply to a minimum then increases slowly. Until now, definite explanation has not been given for this remarkable change in behavior, although various theories have been proposed\textsuperscript{2}). The reason is that little or no information is available as to the mechanism of crosslinking of polymer in solution, especially, in the neighborhood of a critical concentration below which no macro gel is formed.

It is the main purpose of the work described here and the subsequent ones to investigate the gelation of dilute aqueous solutions of polymer and to elucidate the meaning of the critical concentration. To this end, a polyelectrolyte was chosen for a sample to be irradiated, since it can be expected that the dimension of the polymer molecule can be changed very easily with changes in ionizable group content of samples or added electrolyte concentration. The sample used in this investigation is a polyvinyl alcohol (PVA) derivative, that is, PVA partially acetalized with glyoxylic acid (PVAG).
C. Experimental

2.1) Preparation of Sample

PVAm has first been prepared by A. Nakajima et al. and the samples used in this investigation were prepared according to their method under the condition that neither decrease in chain length of the parent PVA nor the acetalization between different PVA molecules occurs during the reaction. The experimental details of acetalization employed in this work have been given elsewhere.

The scheme of acetalization is:

\[
\begin{align*}
\text{PVA} & \quad \text{glyoxalic acid} \\
\text{PVAG} & \quad \text{H}_2\text{O}
\end{align*}
\]

The parent PVA used was an industrial product and had the degree of polymerization of 1000. No attempt of fractionation was made in this work. The acetalized PVA was dialyzed against running water for a week and then was passed through an
Amberlite IR-120 and IR-45 column by turns. The aqueous solutions thus obtained, contained about 2 weight % of \( \text{PV} \). It has been shown by I. Sakurada, H. Hosono and N. Ise\(^4\), from potentiometric measurements, that \( \text{PV} \) is entirely analogous in its neutralization behavior to such a strong acid as HCl, having \( pK \) of 2.3~2.6. The solutions were stored in the dark and were used for all subsequent experiments. The total carboxyl group content of each sample was determined by titrations with 0.1M NaOH using phenolphthalein as an indicator, and the dissociated carboxyl group content was determined from the hydrogen ion concentration measured potentiometrically. They were summarized in Table 1.

Table 1. Carboxyl group content of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1-1</th>
<th>2-1</th>
<th>3-1</th>
<th>4-1</th>
<th>5-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total carboxyl group content(mol.)</td>
<td>0.382</td>
<td>0.552</td>
<td>0.602</td>
<td>1.05</td>
<td>3.57</td>
</tr>
<tr>
<td>Dissociated carboxyl group content(mol.)</td>
<td>0.277</td>
<td>0.394</td>
<td>0.600</td>
<td>1.15</td>
<td>2.57</td>
</tr>
</tbody>
</table>

2.2) Preparation of Aqueous Solution and Irradiation Procedure

Solutions of lower polymer concentrations were prepared from the stock solutions by successive dilution with freshly prepared conductivity water. The same water also was used in all other experiments. The added salt used in this investigation...
was analytical-grade sodium chloride.

Air-free solutions in which irradiation was performed in this study, except for the case mentioned specially, were prepared as follows. Successive shocks were given to the glass tubes containing the aqueous solution under a reduced pressure at 20°C to bubble out the gas dissolved in the solution. The glass tubes were sealed off after the dissolved air was considered to be eliminated completely. When the elimination of air was not sufficient enough, the experimental data were not very reproducible.

These sealed tubes were irradiated at 30°C with gamma-rays from a 2000 Curie Co-60 source. The dose rate was about 1.55 x 10^5 r/hr. In the case of aerated solutions, they were irradiated in conical flasks without stopper under the same irradiation condition as described above.

2.3) Solution Viscosities

Dilute solution viscosities of samples were measured in an Ubbelohde viscometer immersed in a water-bath at 30°C. The kinetic energy corrections were not employed.

2.4) Determination of Gel Points

The radiation-induced changes can be detected by a variety of physical and chemical measurements. For the purpose of
this work, however, it seems most relevant to determine the gel points at which networks are first formed and to plot the gelation doses as a function of the polymer concentration. The gel point could be easily and accurately determined by visual observation, as the gelation of the irradiated solution occurred quite abruptly.

3. Results

3.1) Irradiation in the Absence of Added Electrolyte

The gelation doses for PVAG of various carboxyl group contents irradiated in aqueous solutions without added salt are plotted against the polymer concentration in Fig. 1, which shows the peculiar curve1) generally observed when water-soluble vinyl polymers are irradiated in 10–150 dilute aqueous solutions. It is of interest to note that the gelation dose and the critical concentration for gelation are decreased markedly, as the carboxyl group content of PVAG are increased in the sense of the carboxyl group content studies. This suggests that the crosslinking of the polymer in solution is closely related to the dimension of the expansion of the polymer molecules, since the PVAG is known to be strongly with increasing carboxyl group content, as shown in Fig. 2, where reduced viscosities of unirradiated PVAG (acids and sodium-salts fully neutralized with NaCl) in aqueous solution are plotted against the polymer
Fig. 1  Gelation dose $R_g$ - polymer concentration curves of PVA irradiated in air-free aqueous solution.
Fig. 2 Reduced viscosity - polymer concentration curves of NaG in aqueous solution.
concentration. Fig. 2 shows that the reduced viscosities are increased with decreasing polymer concentration, particularly sharply in the range of low concentrations, indicating that the samples behave as typical polyelectrolytes even in the case of P-1 whose carboxyl group content is as low as 0.382 mol%. The relationship between the critical concentration and the dissociated carboxyl group content is shown in Fig. 3, where those of neutralized PVAG are also included.

3.3) Irradiation in the Presence of Added Electrolyte

The effects of the expansion of polymer molecule on crosslinking can be seen more clearly by adding a low-molecular-weight electrolyte such as NaCl, as it leads to suppression of the expansion of the polymer molecules. However, it should be taken for granted that the added salt does not react with the radicals produced from water and polymers.

Reduced viscosities of unirradiated PVAG in 0.2% NaCl are given in Fig. 4. The data lie nearly upon a straight line and can be extrapolated without difficulty to evaluate the intrinsic viscosity. Fig. 5 shows the results obtained on irradiation of PVAG in 0.4% NaCl. As can be seen from Figs. 4 and 5, gelation occurs more readily with increasing carboxyl group content, although all the PVAG have approximately the same intrinsic viscosity and hence the same expansion. However, change in gelation dose is considerably less than the
Fig. 3 Relation between critical concentration $C_c$ and dissociated carboxyl group content of CMS.
Fig. 4  Reduced viscosity - polymer concentration curves of EVAX in 0.21 bath.
Fig. 5 Gelation dose $R_g$ - polymer concentration curves of PVAG irradiated in 0.2 M NaCl in the absence of air.
case of solutions without NaCl. The most interesting finding in this experiment is that all the critical concentrations are equal to that of the parent PVA independently of the carboxyl group content of the samples. The slight enhancement of crosslinking with increasing carboxyl group content shown in Fig. 5 may part be due to the difference in the degree of acetalization, namely, to the difference in the side-chain structure among samples. However, in the case of partially acetylated PVA in aqueous solution\(^5\)), the gelation dose was found to be increased as the degree of acetylation was increased.

3.3) Effect of Ionic Strength

Fig. 6 shows viscosities measured in 0, 0.2, and 10 NaCl aqueous solutions, and Fig. 7 the results obtained on irradiation of these solutions. Samples used here were the parent PVA and P-E. It can be seen from Fig. 6 that viscosities of the parent PVA in 10 NaCl are lower than those in the absence of added salt. Further addition of salts in aqueous solutions of the parent PVA gave rise to a phase separation.

Fig. 7 shows that the gelation dose is increased in both cases as the expansion of polymer molecule is reduced. This behavior is quite similar to that shown in the above experiments. The fact that addition of 0.2N HCl caused no change in gelation dose in the case of the parent PVA but caused a remarkable change for the \(-5\), may be considered to lend strong support for the
Fig. 6 Reduced viscosity - polymer concentration curves of parent EVA and -5 in C, C.2 and 1. N NaCl.
Fig. 7 Gelation dose $R_g$ - polymer concentration curves of parent PVA and -5 irradiated in 0, 0.2 and 1.0 N NaCl in the absence of air.
above-stated assumption that NaCl does not react with radicals produced by the direct or indirect action of radiation but works only in the direction to suppress the dissociation of the carboxyl group. However, in order to make clearer the influence of the added salt on crosslinking and degradation of polymer in solution, further works should be carried out in more detail.

3.4) Irradiation in Aerated Solution

Degradation induced by radiation on PVAG in aerated aqueous solution in the presence and in the absence of added salt is shown in Fig. 8. Irradiation was performed in 0.3% solution with a dose of 40000eV. The degree of degradation is expressed as the percentage decrease in viscosity

$$\frac{\eta_p - \eta_p'}{\eta_p} \times 100, %$$

where $\eta_p$ and $\eta_p'$ are the specific viscosities of the solution before and after the irradiation, measured at 30°C and a polymer concentration of 0.3%. It is obvious from Fig. 8 that the rate of degradation becomes larger with increasing carboxyl group content when NaCl is absent. This tendency has been also recognized by R. Alexander et al.3,7) concerning the degradation of \( \text{Cl}_a \text{ar} \text{tic} \text{acid} \) and \( \text{poly} \text{meth} \text{a} \text{lic acid} \) in aerated aqueous solution. It must also be emphasized that there was no appreciable degradation when PVAG was irradiated in the presence of 1% NaCl.
Fig. 8 Decrease in viscosity versus carboxyl group content of \( \text{VAG} \) irradiated in 0.3% aerated aqueous solution with a dose of 40000R.

- \( \circ \) --- irradiated in the absence of added salt
- \( \bullet \) --- irradiated in the presence of 1 M \( \text{HCl} \)
4. Discussion

4.1) Critical Concentration and Expansion of Polymer

The result that there is a distinct shift toward lower critical concentration for gel-formation with increasing expansion of the sample is the most significant feature of this investigation. A likely explanation for this is as follows.

In order that crosslinks are formed among different polymer molecules, it is required that polymers should, at least, interact with each other. On the other hand, as the expansion of the polymer is increased, the probability of a polymer to overlap with other ones is increased and furthermore it becomes possible to form intermolecular crosslinking at lower concentration. Consequently gelation doses show a definite tendency to be decreased with increasing carboxyl group content of PVAG. However, it happens quite probably that the rate of crosslinking appears to be in to be decreased as the ionizable group content becomes considerably high, in other words, the effect of electrostatic repulsion between ions, which hinders the coupling of macroradicals, predominates over the effect of the expansion. This case has been, in fact, observed on the aqueous solution of polyacrylic acid by R. Alexander and A. Charlesby). We, also, have studied in this respect, and the details of this result will be described in Chapters VI and VII.
It may be concluded from the above considerations that the critical concentration corresponds to the concentration where the polymer molecules are just apart from others. This conclusion is also supported by the finding shown in Fig. 4 that when the PVAG with various carboxyl group contents were irradiated under the condition that the samples were same in their expansions, there was no difference in the critical concentration.

In order to explain the peculiar curve of gelation dose with polymer concentration shown in Figs. 1 and 5, the indirect effect should be taken into account in addition to the effect of the expansion of the polymer. The reason is that the curves will be obtained as a result of the interplay of these two effects, since the probability of interaction is increased with increasing polymer concentration, while the indirect effect is decreased.

Enhancement of degradation with increasing carboxyl group content in the case of the acrater solution without added salt may not be explained in terms of the expansion of the polymer molecule, for the expansion is thought to have little effect on degradation. It seems more likely that degradation is promoted as a result of prevention of macroradical-recombination owing to the electrostatic repulsion. This explanation can be also applied to the well-known fact that polyelectrolytes are degraded extraordinarily severely with very small doses in dilute aqueous solutions. (See Chapter VII).
4.2) **Calculation of extent of expansion**

It is, therefore, possible to calculate the expansion of polymers from the data of the critical concentration, on the basis of the conclusion that it corresponds to the concentration where the overlap of the polymer molecules commences. The values calculated thus can be compared with those calculated according to other methods such as viscosity or light scattering measurements.

Let us calculate the expansion from the date of the critical concentration and viscosities, assuming that the main-chain scission and the intramolecular crosslinking occurred to a negligible extent, and compare these two values. If a polymer molecule can be represented as a sphere, its effective volume, namely, the volume of solution available per particle is $V_{L} C_{C}$, where $V$ is the molecular weight of the polymer, $M_{L}$ is Avogadro's number and $C_{C}$ is the critical concentration expressed in $1/10^{6}$ cm. Therefore, the radius of the sphere $R$ can be given according to the equation:

$$\frac{4}{3} \pi R^3 = \frac{V_{L}}{M_{L}} C_{C}$$

where $0.74$ is the volume fraction for spheres in a closed packing array. The radii calculated from equation (1) are given as $R_0$ in Table 2. On the other hand, according to T. A. Orofino and T. J. Florio, the mean-square distance of a polyelectrolyte $\sqrt{\overline{h^2}}$ is:

- 99 -
Table 2. Expansion of PVAG calculated from the critical concentration and viscosity data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NaCl (g/l)</th>
<th>$C_C$(c)</th>
<th>$R_C$(A)</th>
<th>$R_E$(A)</th>
<th>$C_C$(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0.25</td>
<td>203</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Parent FVA</td>
<td>0.2</td>
<td>0.26</td>
<td>200</td>
<td>-</td>
<td>177 201</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.30</td>
<td>191</td>
<td>-</td>
<td>173 197</td>
</tr>
<tr>
<td>B-1</td>
<td>0</td>
<td>0.25</td>
<td>209</td>
<td>1.4</td>
<td>-</td>
</tr>
<tr>
<td>B-2</td>
<td>0</td>
<td>0.22</td>
<td>212</td>
<td>110</td>
<td>-</td>
</tr>
<tr>
<td>B-3</td>
<td>0</td>
<td>0.24</td>
<td>206</td>
<td>-</td>
<td>179 202</td>
</tr>
<tr>
<td>B-4</td>
<td>0</td>
<td>0.18</td>
<td>228</td>
<td>130</td>
<td>-</td>
</tr>
<tr>
<td>B-5</td>
<td>0</td>
<td>0.24</td>
<td>206</td>
<td>-</td>
<td>179 202</td>
</tr>
</tbody>
</table>

\[
\eta = 0.9 \times 10^{12} (\sqrt{M})^3
\]  

where $\eta$ is the intrinsic viscosity expressed in 100 cc/g. The values of $\sqrt{M}$ can be transformed into the radius of the
polymersphere R using the relationship introduced by J. J. Hermans and J. Overbeek:

\[ R^2 = \frac{5}{26} \frac{N A^2}{R^2} \left( 1 + \frac{\langle \vec{L}^2 \rangle}{N A^2} \right) \]  \hspace{1cm} (3)

where A and N are the length of a segment and the number of the segment in a molecule, respectively. The values calculated from the equation (2) and (3) are given as $R_{OP}$ in Table 2, where $R_{4C}$ and $R_{80}$ are values obtained on assuming $A = 40$ and $80 \, \text{Å}$, respectively. $R$ of polymers in salt-free solutions was calculated from the Einstein equation assuming $R_{sp}/c$ at the critical concentration to be [7], because theories to estimate the expansion of the polymer in finite dilute solution only from the viscosity data have not been established.

As can be seen from Table 2, $R_{4C}$ are very close to $R_{C}$, while $R_{80}$ are too small. The latter discrepancy may be attributed chiefly to the very rough approximation made for the calculation of $R_{sp}$. Furthermore, it should be pointed out that $R_{C}$ are not necessarily in accord with $R_{B}$ or $R_{OP}$, since the effective volume of the polymer sphere may very depending on the property of the polymer solution to be considered.

References

(2) A. Charlesby, Comparative effects of Radiation (edited by M. Burton et al) p.253 (1960)
(3) A. Nakajima, S. Ishida and I. Sakurada, Chemistry of High Polymers, Japan, 14, 259 (1957)
(4) I. Sakurada, N. Hosono and N. Ise, Memoirs of the Faculty of Engineering, Kyoto Univ., 52, 402 (1957)
Chapter VI

CROSSLINKING AND DEGRADATION OF POLY(ACRYLIC ACID) IN AQUEOUS SOLUTION


Effects of Gamma Radiation on Polymer in Solution (IV)

Crosslinking and Degradation of poly(acrylic acid) in aqueous solution
1. Introduction

In Chapter V, radiation effects were studied on one of charged polymers, i.e., polyvinyl alcohol partially acetalized with glyoxylic acid (PAG) whose carboxyl group contents were ranged from 0 to 3.57 mol%. It was found that both the crosslinking and the degradation are strongly affected by the degree of expansion of the polymer and it was concluded that the critical concentration corresponds to the concentration at which overlapping of polymer coils just commences. In this case, as the polymer is regarded as a copolymer, it was possible that change in chemical composition of the polymer accompanying acetalization reaction might affect the crosslinking, especially when the carboxyl group content was considerably high. Thus, it was not desirable to use this polymer for studying the effect of expansion over a wide range of charge density. In the present work, therefore, polyacrylic acid (PAA) was chosen for the sample to be irradiated. This polyelectrolyte, which is a weak polyacid, has an advantage for the purpose above described because of the possibility that the charge density can be controlled readily by addition of alkali such as NaOH without modification of side groups.
2. Experimental

2.1) Material

The PAA sample was prepared by polymerization of monomer in 4.5 wt.% aqueous solution using $3 \times 10^{-3}$ mol/l of potassium persulphate at 50°C for 17 hrs. The conversion of monomer to polymer was about 80%. Purification of the polymer was done by dialyzing against running water for a week and thereafter passing several times through a cylinder filled with a cation exchange resin, Amberlite IR-120, and an anion-exchange resin, Amberlite IRA-45. The polymer was used for the following experiment without any treatment of fractionation. The viscosity-average degree of polymerization, calculated from an equation\(^1\), $[\eta] = 6.52 \times 10^{-2} \, M^{0.64}$ (in 2N NaOH, at 25°C), was approximately 5700. Partially neutralized PAA was prepared by ionizing the carboxyl group by addition of appropriate amounts of NaOH. Water used in all the experiments was conductivity water of about $10^7 \Omega$ cm, and NaCl (analytical grade) was used.

2.2) Irradiation Procedure

At the time the Co-60 source was used, it was rated at $1.50 \times 10^5$ r/min. Irradiation was carried out at room temperature both in the presence and in the absence of air.
Evacuation and injection of nitrogen gas into the vacuum line was carried out repeatedly until further bubbling-out was not observed at any violent shocking. Finally the ampules were sealed off. It seemed that our method was more effective for degassing than the usual one which requires repeated processes of freezing and evacuation. When our method was adopted, results were found to be much more reproducible, compared with the other case.

2.3) Measurements of Viscosity and Gelation dose

Solution viscosities were measured at 30°C in an Ubbelohde-type viscometer, on diluting the solutions in this viscometer.

The gelation dose is generally determined from the sudden changes in viscosity, degree of swelling or amount of solid fraction which occur at gel point. In the case of irradiation of solutions, the appearance of irradiated solution changes abruptly as a result of incipient gelation, so that the gelation dose can be determined easily and very precisely by visual observation. In this experiment, gel points were determined by inspection of appearance of the irradiated solution which was taken out from the irradiation position at a few minute intervals.
3. Results

3.1) Irradiation of Deoxygenated Solution

3.1.1) In the Absence of NaCl

Fig. 1 shows the concentration dependence of \( \frac{\lambda_{sp}}{c} \) for unirradiated PAA with various degrees of neutralization of 0, 5, 10 and 20. It can be seen from the shape of curves that PAA behaves in dilute aqueous solution as a typical poly-electrolyte even in the case of a degree of neutralization = 0. When these aqueous solutions containing no air were irradiated with gamma-rays, gelation occurred if the solution for irradiation was not extraordinarily dilute.

The most convenient measure of following the crosslinking in the present case may be by the use of the gelation dose. This is illustrated in Fig. 2, where gelation doses were plotted against the polymer concentration. An interesting feature of Fig. 2 is that the critical concentration shifts towards higher concentration as the degree of neutralization increases.

It should be furthermore noted that beyond a certain polymer concentration of 3 \( \sim \) 4\%, the gel formation seems to be virtually independent of the degree of neutralization. Alexander and Charlesby\(^2\) have shown that the PAA does not exhibit crosslinking when its degree of neutralization becomes higher than 10\%. In our case, gel was formed even for the PAA 20\% neutralized.
Fig. 1 Concentration dependence of reduced viscosity in the absence of added salt for unirradiated PAA with various degrees of neutralization $\alpha$. 
Fig. 2 Relation between gelation dose $R_g$ and polymer concentration $C$ for PAA with various degrees of neutralization $\alpha$. PAA was irradiated in salt-free solution.
This discrepancy may be due to the difference of the degree of polymerization of samples used or to the degree of elimination of dissolved air. The critical concentration is shown in Fig. 3 as a function of the degree of neutralization.

3.1.2) In the presence of NaCl

As can be seen from Fig. 1, the expansion of polyelectrolyte in dilute aqueous solutions increases generally with increasing degree of neutralization because of increasing coulombic repulsion between ionized groups. It is also well known that when neutral low-molecular-weight salt is added to the polyelectrolyte solution, its expansion decreases with increasing ionic strength. In order to see in more detail how the expansion of polyelectrolyte influences the crosslinking reaction, the following experiment was carried out using NaCl as an added salt and FAA in acid form as a sample for irradiation. Thereby, if NaCl might influence radiolysis of water and formation of polymer radicals, interpretation of results obtained would be much complicated. In this respect, however, our succeeding experiment 3) clarified that these effects of NaCl are unnecessary to be taken into account, and that NaCl affects the crosslinking only through the action to reduce the expansion of polymer coil.

Fig. 4 shows the solution viscosities of unirradiated FAA in the presence of various concentrations of NaCl. As is
Fig. 3  Critical concentration $C_{\text{crit.}}$ for gel-formation of PAA with various degrees of neutralization $\alpha$. PAA was irradiated in salt-free solution.
Fig. 4 Concentration dependence of reduced viscosity in the presence of various amounts of NaCl for unirradiated PAA in acid form.
seen from Fig. 4, addition of 0.1 M NaCl was sufficient to make the viscosity behavior of this PAA quite similar to that of uncharged polymers. The gelation dose for PAA irradiated in the presence of C to 0.4 M NaCl is plotted in Fig. 5 against the polymer concentration. It is of particular interest to point out that gel can be formed more easily by the presence of NaCl unless NaCl concentration is higher than 0.01 M. Influence of NaCl on the critical concentration is shown in Fig. 5, which indicates clearly that gel-formation occurs more readily at first, with increasing NaCl concentration, whereas beyond the NaCl concentration of 0.01 M, the formation is retarded as the concentration increases.

3.2) Irradiation of Aerated Solution

3.2.1) In the Absence of NaCl

Concerning irradiation of polyelectrolyte in aerated aqueous solution, a number of papers have been already published. It was found in all cases that the polymers having ionized groups degrade in the presence of air with rather small doses and more readily as the degree of neutralization increases. In the present work, therefore, the study on aerated solution was done briefly only for comparison with the results on irradiation of deaerated solution.
Fi. 5 Relation between the gelation dose $R_g$ and polymer concentration $C$ for PAA with various amounts of added salt. PAA was irradiated in acid form.
Fig. 6 Critical concentration $C_{\text{crit.}}$ for gel-formation of PAN in acid form irradiated with various amounts of sodium $\text{NaCl}$. 
Fig. 7 shows the percentage decrease in viscosity induced under irradiation of 0.3% solution at a dose of $2 \times 10^4 \mu r$. The viscosity of solution is found to be lowered under irradiation, and the decrease in viscosity become larger as the degree of neutralization increases.

3.2.2) In the Presence of NaCl

In this case, the result is apparently simple. The effect of NaCl on the degradation is shown in Fig. 8 for FAA irradiated at a dose of $2 \times 10^4 \mu r$ in 0.3% acetic aqueous solution. It can be seen that degradation is suppressed strongly when NaCl is added to the solution for irradiation. Indeed, degradation occurred only to a negligible extent when NaCl concentration was as high as 0.15.

4. Discussion

4.1) On the Crosslinking

When the mechanism involved in radiation-induced crosslinking of polyelectrolyte in aqueous solutions is to be discussed, it should be taken into account that there are electrostatic repulsions between the ionized groups fixed not only on the same molecule but also on the different ones. The reason is that the repulsion will affect the crosslinking mainly through
Degradation of PAA with various degrees of neutralization α under irradiation in the presence of air, in 0.3N aqueous solution and at a dose of 2 × 10^6 r. Viscosities were measured in the absence of added salt (•) and in 2 N HCl (○).
Fig. 8  Degradation of PAA in acid form with various amounts of added salt under irradiation in the presence of air, in aqueous solution and at a dose of $2 \times 10^4$ r.
the following two factors. One is related to prevention by the repulsive force of combination of polymer radicals which would otherwise lead to the formation of inter- or intramolecular crosslinking. Another factor is to extend the polymer chain, thereby causing the crosslinking to occur more readily. With these two competing effects in mind, we will discuss the experimental results above described.

The result shown in Fig. 3 is apparently inconsistent with that of PVAG in the previous chapter, which is again shown in Fig. 9 (i.e., 3 in Chapter V). The curve of i. 9 indicates that, as the charge density of polymer ions increase from 0 to $3.37 \text{ mol} \%$, the critical concentration decrease, while in the case of IAA the critical concentration steadily increases with the degree of neutralization. The apparent inconsistency is not, however, surprising if one recalls that some amounts of the carboxyl groups in the polymer are existing in ionized form in aqueous solution even in the unneutralized state. This can be, also, expected from the viscosity behavior shown in Fig. 1. Fig. 11 shows the critical concentration for 1-formation of IAA plotted against the actually ionized carboxyl group content in place of the degree of neutralization. The ionized carboxyl group content was determined from the measurements of pH of their solutions. For instance, the carboxyl group content = $3.37 + 1 \%$ corresponds to the degree of neutralization = 0.6. Paying attention to the difference of charge density, one can see from Figs. 9 and 11 that, as
Fig. 9  Critical concentration $C_{\text{crit.}}$ for gel-formation of polyvinyl alcohol partially acetalized with $\text{HOAc}$lic acid irradiated in the salt-free solution, varying carboxyl group content: (○) in acid form, (●) in sodium-salt form.
Fig. 10 A modified plot of critical concentration $C_{\text{crit}}$, for gel-formation of PMA with various degrees of neutralization irradiated in the salt-free solution as a function of actually dissociated carboxyl group content.
the content of ionized group increases, the critical concentration decreases at first, but after reaching a minimum which lies in the vicinity of 3~4 ol L, it begins to increase. The presence of the minimum strongly suggests the interplay of two competing effects influencing crosslinking reaction. This may be also suggested by Fig. 5. Since these phenomena have been observed only in the crosslinking of polyelectrolytes, it appears likely that the two competing effects may be arising from the repulsion between the ionized groups. When the repulsion force works between the adjacent groups belonging to the same molecule, it happens that the chain is more extended. In this case, the rate of crosslinking would increase with attendant lowering of the critical concentration, since possibility of the polymer segment of different chains to be in contact with each other increases with increasing extension. On the contrary, the repulsion between the ionized groups belonging to the different chains would lead to prevention of combination of the polymer radicals, consequently, to suppression of the rate of crosslinking. Now, if these are true the behaviors shown in Figs. 6, 9 and 10 can be explained as follows.

In a range of lower ionized carbon group contents, the effect of the increase in size will overshadow that of prevention of radical combination. Therefore, at first, the critical concentration may become lower with increasing charge density as is seen in Fig. 5. However, when the ionized group
content becomes high enough not to be able to neglect the repulsion between the groups of different polymers, the critical concentration increases with increasing carboxyl group content as is shown in Fig. 10.

The minimum of the curve in Fig. 6 can be explained in the similar way, because addition of neutral salt to solutions has an effect opposite to that of addition of NaCl. In other words, addition of NaCl causes the ionization to decrease and hence reduces the expansion of solution. As the concentration of NaCl increases, the repulsion preventing the radical combination decreases, so that the reaction may occur more readily. If the NaCl concentration becomes higher than 0.01N, the critical concentration increases steadily, since the effect of decreasing size of polymer coils may become a dominant factor. It is of interest to note that inter-molecular-crosslinked polymer was formed when solutions containing NaCl above 0.1N were irradiated below a critical concentration. In this respect, details will be presented in the subsequent chapter.

4.2) On the Degradation

Inspection of Figs. 7 and 8 shows that the degradation became increasingly more efficient as the charge density of polymer chain increases. This fact has also been found by other workers\(^*\) on the degradation of polyelectrolyte in dilute aqueous solution. Several theories have been proposed
to account for these results. Among them, we will discuss the following three theories.

(1). This theory assumes that C-C bonds of main-chain become liable to scission as a result of the presence of charged side groups. It is probable that electron density in the C-C bond will be varied by the electric charge present near—o, and also that the O— bond will be strained owing to the repulsion between adjacent groups. However, it is very dangerous to accept this theory without any doubt, since the tendency above described was also observed in the case of PVA whose structure is given by:

\[
\left( -CH_2 - CH - CH_2 - CH_2 - \right)_n
\]

In this case, the O— bond of the main-chain is fairly distant from the ionized carboxyl group. Therefore it seems inaccesible that the bonding force of this bond will be affected strongly by the presence of the carboxyl group.

(2). The second theory regards the increase in size of polymer coil as the most important factor. With increasing charge density, the expansion of polymer increases and hence the local concentration of the segment within the domain of a polymer
coil will become lower. This leads to an increase in the relative amount of water molecules available per polymer segment, thus, to an increase in the indirect effect. As a conclusion, increasing charge density results in the increase in the indirect effect, which causes the degradation to occur more rapidly. This theory seems more acceptable than the first. However, large dependence of degradation on the charge density observed at the irradiation of PAA and PVAG in U.S. solutions is not favorable for this theory. In such a relatively high concentration as 0.3%, the amount of water per segment may be considered to be almost independent of the charge density.

(3). This theory is related to the electrostatic repulsion between ionized groups belonging to the same molecule. It is generally accepted that radicals produced as a result of main-chain scission partly recombine at once as if the change never occurred. If the radical recombination is prevented to some extent, the over-all extent of degradation will become lower. It seems very probable that the repulsion force will prevent the polymer radicals to recombine. If this scheme is correct, the polymer may undergo degradation more effectively with increasing charge density, as is shown in Fig. 7. This theory also can account for the fact that the dose to attain a noticeable change on polyelectrolytes is usually found to be remarkably small compared with the uncharged polymers.\(^4,6\)
References

Chapter VII

Intra-molecular crosslinking of poly(acrylic acid) in dilute aqueous solution


Effects of Gamma Radiation on polymer in solution (V)

Intra-molecular crosslinking of poly(acrylic acid) in dilute aqueous solution
1. Introduction

Effects of ionized group content and added salt on cross-linking of polyacrylic acid (PAA) in aqueous solutions, described in Chapter VI\(^1\), may be summarized in \(\text{eq. 1}\). These two variables are put together in eq. 1 in such a fashion that the expansion of polymer increases in the rightward direction of abscissa. Assuming that, in the left-hand region from the minimum of the curve, the effect of varying size of polymer predominates over the effect of repulsion, while in the opposite region the effect of repulsion prevails, one was able to explain the change in the critical concentration. Obviously, properties of the continuous gel produced by irradiation of solutions above a critical concentration may be independent of whether formation of the gel is influenced by either effect. On the other hand, below the critical concentration reactions induced by irradiation of dilute solutions may be possibly influenced by these two competing effects. When solutions are irradiated below the critical concentration, as is well known, a continuous gel is never formed, but either a micro-gel-formation\(^2,3\) or degradation takes place. In the case of polyelectrolytes, it may be expected that, if the repulsion is sufficiently strong, polymers exhibit no micro-gel-formation, but only degradation.

The present work was undertaken to find out what reactions are occurring under irradiation of dilute solutions below the
Fig. 1 Influence of charge density of PAA on critical concentration $C_{\text{crit}}$ for gel-formation.
critical concentration and to confirm the above supposition that crosslinking of polyelectrolyte is influenced by two competing effects, that is, repulsion and variation in size.

2. Experimental

PAA samples used, irradiation procedure and methods of viscosity measurements were quite the same as described in the previous chapter. When it was necessary to remove the added salt from the irradiated solutions, they were passed through two columns filled with a cation-exchange resin, Amberlite IRA-120, and an anion-exchange resin, Amberlite IRA-400.

The relative turbidity of solutions observed during irradiation was estimated from an equation \( \tau = 2.3 \log \frac{I_1}{I_0} \), where \( I_0 \) and \( I_1 \) are the intensities of the light scattered in a direction of 90° with the direction of an incident ray for the solution before and after irradiation, respectively. The intensity was measured at a polymer concentration of 0.1% by means of an electrophotometer.

Potentiometric titrations were performed at room temperature with a type pH meter (manufactured at Horiba Instruments Inc., Kyoto). The solution to be titrated was stirred on a magnetic stirrer, the stirrer being stopped for each reading. Each titration was made with a period of a few minutes between successive readings, as the pH became constant almost instantaneously after the addition of a base, 0.01N NaOH.
3. Results

It has been found in the studies on polyvinyl methyl ether\(^4\) that irradiation of this polymer in aqueous solutions below the critical concentration does not lead to formation of a continuous gel, but makes the solutions turbid. This suggests the plausible transformation of molecular configuration in solutions due to formation of intra-molecular crosslinkings by irradiation. It is of interest to see whether the intra-molecular crosslinking can be formed in the PAA solutions where intra-molecular repulsive force exists.

3.1) Occurrence of Turbidity under Irradiation

When the ionic strength of solutions exceeded a certain value, the solutions became turbid under irradiation. The solutions before irradiation were, of course, transparent independently of the presence and the absence of NaCl. The relative turbidity of solutions of PAA irradiated in acid form at a polymer concentration of 0.1 wt.% in the absence of air is shown in Fig. 2. The ionic strength was adjusted by addition of appropriate amounts of NaCl. The turbidity was measured without removing from the irradiated solution the NaCl which was present during irradiation, because the presence of NaCl seemed to affect the turbidity not at all, or only very slightly. If a sufficient amount of air was dissolved in the
Fig. 2 Relative turbidity $\tau$ of irradiated solution as a function of radiation dose for PAA irradiated in the absence of air and in 0.1 M solution varying amount of added NaCl.
solutions to be irradiated, turbidity did not occur, however large a dose was used. From Fig. 2, the relative turbidity appears to approach an upper limit as the irradiation proceeds.

To demonstrate the relation between ionic strength and turbidity, initial slopes of the curves in Fig. 2 were plotted against NaCl concentration in Fig. 3. It is of particular interest to note that the minimum concentration of NaCl needed for the incipient occurrence of turbidity agrees exactly with the NaCl concentration corresponding to the minimum critical concentration which Fig. 1 shows. It is clear that solutions become turbid only when irradiated at NaCl concentrations above 0.01M. This finding affords a support to the expectation above mentioned that either of two different reactions would occur preferentially, in each range of NaCl concentration below and above 0.01M.

3.2) Viscosimetric Behavior of the Irradiated Polymer

Occurrence of the turbidity may be attributed mainly either to aggregation of polymers or to more tightly coiled configuration of polymers. The latter may be brought about by the formation of intramolecular crosslinking unless the solvent power remains constant during irradiation. The transformation of the molecular configuration is expected to affect necessarily hydrodynamic properties such as solution viscosity. Fig. 4 shows the intrinsic viscosities measured
Initial slopes of curves in Fig. 2

(Arbitrary unit)

Fig. 3  Effect of NaCl on turbidity occurring during irradiation.
Fig. 4 Changes in limiting viscosity number $[\eta]$ during irradiation of C.I. solution under various conditions (a)~(d): for the conditions see the text.
in C.1N NaCl of various PAA's obtained on irradiation under the following conditions; (a) in aerated salt-free solution, (b) in aerated C.1N NaCl solution, (c) in deaerated salt-free solution, (d) in deaerated C.1N NaCl solution. As can be seen from Fig. 4, the intrinsic viscosity decreases with radiation dose in all cases regardless of the irradiation conditions. The presence of air and the absence of NaCl in solutions for irradiation caused the intrinsic viscosity to fall more rapidly. Among the four different cases (a) to (d), occurrence of turbidity was observed only when radiation was exposed to deaerated C.1 NaCl solution, i.e., the case (d). Furthermore, in this case, solution viscosities decreased most slowly. If the viscosity-drop can be assumed to be owing to main-chain scission, the reciprocal of degree of polymerization should increase linearly with increasing radiation dose. The results are shown in Fig. 5, where it is seen that in the cases (a), (b) and (c) where the solution remained transparent during irradiation, a linearity was observed. On the other hand, in the case (d) where the irradiated solutions became turbid, the curve was found not to be linear, which implies occurrence of a reaction different from the main-chain scission. It is probably the intra-molecular crosslinking.

In order to ascertain the formation of intra-molecular-crosslinked polymer, viscoelastic behaviors were examined for the polymers obtained under the same condition as above described except the radiation dose. Irradiation time was
Fig. 5  Reciprocal of degree of polymerization $\frac{1}{P}$ as a function of radiation dose for IAA irradiated under various conditions.
controlled in such a way that all the limiting viscosity numbers of these polymers in 0.1 M NaCl are exactly identical. For simplicity, these polymers were designated according to the irradiation condition as follows: PA-a, irradiated at 5.0 x 10^4 r in aerated salt-free solution; PA-b, at 1.1 x 10^5 r in aerated 0.1 M NaCl solution; PA-c, at 1.2 x 10^5 r in aerated salt-free solution; PA-D, at 3.0 x 10^5 r in deaerated salt-free solution; PA-A-d, at 3.0 x 10^5 r in deaerated 0.1 M NaCl solution. As noted above, only in the case of PA-D, the solution became turbid under irradiation. Plots of the reduced viscosity against the polymer concentration are given in Fig. 6. It is evident that the reduced viscosities of PA-a, -b and -c in the absence of added salt rise very sharply at lower polymer concentrations similarly to those of PAA before irradiation. At the same time, for the PA-c, the reduced viscosities increase only very slightly even at the considerably low concentration.

3.3) Potentiometric Behavior of the Irradiated Polymer

Solution properties of the irradiated PAA were, further, examined by means of a potentiometric titration. Fig. 7 shows titration curves for the various irradiated PAA polymers. The polymers studied here are the unirradiated PAA, PA-b and PA-D. The titration was carried out at a 0.1 M concentration of polymer with CaCl_2 in the absence of added salt. Plots of pH as a function of log \( \frac{1-\alpha}{\alpha} \), being on a modified
Concentration dependence of reduced viscosity for irradiated IAA: for the irradiation condition see the text. Viscosity was measured in the absence of added salt (O, a) and in the presence of 0.1 M NaI (a, e, t).
Fig. 7  Titration curves and Henderson–esselbach plots for unirradiated PAA(●), LAA-b(x), and LIA-c(●): for the irradiation and measurement conditions see the text.
Henderson-Hasselbalch equation, \[ \text{pH} = \text{pK}_a + \text{n log} \left( \frac{1 - \alpha}{\alpha} \right), \]
where \( \alpha \) is the degree of neutralization, \( n \) is a constant and \( \text{pK}_a \) is the average ionization constant, are also shown for these titrations. As can be seen from Fig. 7, the pH of PAA-d are clearly higher than those of the unirradiated PAA and -A-b, both of which are virtually identical. In every case, Henderson-Hasselbalch plots of the data give straight lines in the range of \( \alpha > 0.5 \). The intercepts and the slopes of these straight lines indicate that \( \text{pK}_a \) and \( n \) of both the unirradiated PAA and PAA-b are 7.0 and 2.4, respectively; and \( \text{pK}_a \) and \( n \) of PAA-d are 7.7 and 1.9, respectively. Evidently, there is noticeable difference in \( \text{pK}_a \) between PAA-d and PAA-b or the unirradiated PAA.

4. Discussion

The significant difference in viscometric behaviors between the PAA-d and the PAA-\( a \), -b and -c may be attributed undoubtedly to the difference in chain structure. The content of carbonyl groups seen to \( v_{\text{CO}} \), if so, only to a negligible extent under irradiation in the radiation dose range investigated here. An examination of Fig. 5 reveals that curves of PAA-\( a \), -b and -c are approximately identical and have the shape characteristic to the linear PAA. From this observation and Fig. 5, it may be concluded that the viscosities' dips of these polymers shown in Fig. 4 may be attributed to the main-chain scission.
Furthermore, the fact that the reduced viscosity of PAA-d is always much lower than that of the PAA-a, -b and -c may be regarded as an evidence showing that in the case of PAA-d there is restrictive force upon extensions of the polymer coil. This restrictive force is supposed to be caused to the intramolecular crosslinking formed under irradiation. As a conclusion, the occurrence of turbidity in solutions can be attributed to the formation of the intramolecular-crosslinked polymer, namely, the micro-gel particle.

A further confirmatory evidence for the existence of the micro-gel particle can be given by the result shown in Fig. 7 that the average ionization constant of the PAA-d is noticeably higher than that of the PAA-b. This difference may be explained as follows. Since the concentration of ionizable carboxyl groups in a volume element is higher with the crosslinked than the linear polymers, suppression of ionization of COOH caused by COO⁻ becomes larger with the crosslinked polymers, and hence the hydrogen ion concentration decreases in the solution of the crosslinked polymer, leading to the larger ionization constant for the crosslinked polymer.

Although the formation of the intramolecular crosslinking was clarified only in the case of the PAA-d which was obtained on irradiation of 0.1M NaCl solution, it seems quite reasonable to expect that the intramolecular crosslinking can be formed if the NaCl concentration of solutions is higher than 0.1M. The reason for this is that, in this concentration range, the
solutions became turbid under irradiation similarly to the case of the PAA-d. Thus, it can be concluded that the reaction actually taking place under irradiation of the deaerated solution below the critical concentration depends on whether NaCl concentration is below or above C.CN. One is the main-chain scission and the other is the intra-molecular crosslinking.

The result shown in Fig. 1 could be explained in Chapter VI reasonably on the basis of the following assumption. In a low ionic strength range below C.CN, NaCl, the repulsion, which prevents the radical combination, may influence the crosslinking most significantly. On the other hand, when the NaCl concentration becomes higher than C.CN, the diminution of polyelectrolyte with increasing ionic strength may become more important than the effect of repulsion. This assumption is strongly supported by the conclusion above cited. The result that the degradation occurs exclusively in the NaCl concentration range below C.CN may be explained as being due to the repulsion which prevents the formation of crosslinking and would be most important in this range. Similarly, the result that the formation of intra-molecular crosslinking becomes possible in the range above C.CN NaCl may be explained in terms of the remarkable decrease in repulsion which is observed in this range. Increasing rate of the crosslinking with higher ionic strength may be due to the well-known fact that higher ionic strength leads to more tightly coiled configuration, so that the intra-molecular crosslinking can
be formed more efficiently.

It may be unavoidably necessary for the micro-gel-formation that polymer coils are only partially in contact with each other in the solution or not at all. Therefore, the maximum concentration, below which the micro-gel-formation becomes possible, may correspond to a concentration, at which polymers begin to interfere each other, if deaggregation does not occur and the repulsion force is not so intense as to prevent the radical recombination. Such conditions may be satisfied only in the case of the solution containing NaCl above 0.1M. Also, in this case, the maximum concentration for micro-gel-formation may just agree with the critical concentration for (macro-) gel-formation. If this is true, it will be possible to estimate the expansion of polymer from the value of critical concentration on the assumption of closed packing array, as described in Chapter V5). The radii of PAA in 0.1M and 0.3M NaCl shown in Fig. 1 are given in Table 1. The radius in the third column is calculated using the data of the critical concentration for gel-formation, and the radius in the last column is the hydrodynamic effective radius calculated from Einstein's formula. Obviously, there is nearly two times difference between the radii calculated from the two different methods. The similar result was also obtained in the study on rVAG5). This difference is not surprising if one considers the physical meanings of these two radii. In this respect, detailed discussion will be presented in the subsequent chapter.
Table 1
Expansions of Polyion Calculated Using the Crosslinking Data and Einstein's Formula.

<table>
<thead>
<tr>
<th>Conc. of solution</th>
<th>Initial [η] of the solution</th>
<th>Radius of IAA from the critical conc.</th>
<th>Radius of IAA from Einstein's formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M</td>
<td>0.30</td>
<td>374 Å</td>
<td>173 Å</td>
</tr>
<tr>
<td>0.4 M</td>
<td>0.50</td>
<td>300 Å</td>
<td>148 Å</td>
</tr>
</tbody>
</table>
Hitherto, the decrease in viscosity observed during irradiation of dilute aqueous solutions has often been attributed to the formation of the intra-molecular crosslinking, of course, except the case where the main-chain scission undoubtedly occurs. However, there has been no direct support for the existence of these intra-molecular crosslinkings. The decrease in viscosity is only a necessary, but not sufficient evidence for the crosslinking. In order to examine the formation of this crosslinking, it seems most promising to determine the molecular weight change during irradiation. In the aqueous systems, however, it is known to be rather difficult to determine the absolute value of molecular weight by means of light scattering or osmotic pressure measurement. Recently Sieu and Besieux$^{2,3}$ have studied the change in sedimentation constant and intrinsic viscosity occurring during irradiation of polyvinyl alcohol (PVA) in dilute aqueous solutions. They found that, in higher dose range, the viscosity of irradiated PVA decreased with dose, whereas the sedimentation constant increased, demonstrating the formation of more spherical molecular clusters, or, micelle-like particles. It seems to us that this is an only study which gave the strong evidence for the intra-molecular crosslinking under irradiation. In our case, the existence of the intra-molecular crosslinking could be confirmed by determination of the viscosity of the potential electrostatic titration, by taking advantage of electrostatic property of ionized groups among a cluster chain.
References

Chapter VII

EFFECTS OF ADDITIVES


Effects of Gamma Radiation on Polymer in Solution (VI)
Radiation protection and promotion in aqueous solutions of poly(vinyl alcohol)
l. Introduction

In three earlier chapters\(^1\,^2\,^3\), we reported effects of expansion of polymer molecules or crosslinking and de-crosslinking of electrolytes in aqueous solution. The expansion of polymers was adjusted by varying ionizable group content or concentration of added salt(salts). It was then assumed that the added salt has no effect other than decreasing the expansion of polymers. However, the following possibility would not always be precluded that such ions as \(\text{Ca}^+\) and \(\text{Cl}^-\) 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 vividly the effect of additives on the crosslinking and de-crosslinking of polymers, in other words, the radiation protection and reactivation. 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 solution were and viscosity were measured.

2. Experimental procedure

The polymer employed is a fractionated copolymer of vinyl alcohol (v.1 alcohol) (v.1A) with a viscosity-average degree of polymerization of 1,600. The additives used include both inorganic and organic compounds: the former are thiourea, methyl ethyl ketone (m.e.k.), cyanhydrin and
methanol, and the latter are NaCl, KI, FeC₄, FeC₅ + C₆, K₂SC₄, and CuSC₄.

Aqueous solutions of IVA containing one of these additives were irradiated in the presence and absence of air with 60-Co-γ-rays. A dose rate of 1.5 x 10⁻⁵ r/h was used and the temperature during irradiation was about 20°C. Separation 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.

3. Results

3.1) Irradiation in the absence of air

As is well known, irradiation of acetic acid aqueous solutions of IVA 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 solution dose, when 0.1% solution of IVA was irradiated in the presence of various additives. It may be seen that NaCl, FeC₄, and methanol have no influence on the crosslinking reaction, even if their concentrations are relatively high. The result indicates also that the ions, which affect the polymer reaction, are not Fe⁺, K⁺, SO₄⁻² and Cl⁻, but Cu⁺⁺, Cu⁴⁺ and Cr⁻. Charles also found that thiourea hinders the solution most strongly.
Number of additive molecules per polymer molecule

1.1 Influence of various additives on gelation dose $R_g$ for 0.4% aqueous solutions of LVA. $R_g$ is the gelation dose of aqueous solution containing no additive.
Next, more detailed experiments were carried out, varying both the polymer concentration and the amount of additives. The results for Cu(C₂H₅)₂Br, 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. 7, where relative gelation doses are plotted against the number of additive molecules per polymer 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 0.5 M solutions in the presence of Cu(C₂H₅)₂Br.

3.2) 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 10⁻⁵ M are shown in Fig. 6.
Fig. 2 Change in gelation dose $R_g$ for IVA irradiated in aqueous solutions with various concentrations of polymer and additives.
Fig. 3 Change in gelation dose $R_g$ for EVA irradiated in aqueous solutions with various concentrations of polymer and additives.
Thiourea
- 0.4x 10^{-5}
- 2 x 10^{-5}
- 5 x 10^{-5}
- 1 x 10^{-5}
- CuC\(_4\)
- C\(_{\text{Br}}\)
- 2.5 x 10^{-5}
- 5 x 10^{-5}
- 0.5 x 10^{-5}

Ethanol
- C\(_{\text{Br}}\)
- 1 x 10^{-5}
- 5 x 10^{-5}
- 0.5 x 10^{-5}
- 1 x 10^{-5}
- 5 x 10^{-5}
- 1 x 10^{-1}

Number of additive molecules per polymer molecule

Figure 4 Protection effect of various additives on cross-linking of aqueous solutions of EVA.
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.
Fig. 6  Effect of additives on degradation of PVA in 0.45 aqueous solutions containing $10^{-2}$ additives.
Evidently, the main-chain scission is in 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 cross-linking, 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 straight lines in Fig. 7 are given in Table 1. G_{do} denotes the G-value in the case of the absence of any additives.

4. Discussion

By extrapolation of 1/(n/n_{do}) to unity, one can obtain from Fig. 6 the minimum number of each additive molecules 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 cross-linking and G_{do}-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 cross-linking could not be found out in our experiment.

The results described above appear very complicated,
Fig. 7 Reciprocal of degree of polymerization $\frac{1}{P}$ of 4VA irradiated in 0.05 aqueous solution containing $10^{-7}$ additives. $P_0$ is the degree of polymerization of unirradiated 4VA.
Table 1

Minimum Numbers of Additive Molecules per Polymer Molecule to Affect Crosslinking, and \( G_d \)-values for Degradation (additive = \( 10^{-2}\)M)

<table>
<thead>
<tr>
<th>Additives</th>
<th>Thiourea</th>
<th>FeSO(_4)</th>
<th>CuSO(_4)</th>
<th>MnK</th>
<th>KBr</th>
<th>Ethanol</th>
<th>( K_2SO_4 )</th>
<th>NaCl</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min. Number</td>
<td>0.08</td>
<td>0.27</td>
<td>0.5</td>
<td>3</td>
<td>10</td>
<td>17</td>
<td>large</td>
<td>large</td>
<td>large</td>
</tr>
<tr>
<td>( G_d/G_{do} )</td>
<td>0.39</td>
<td>6.0</td>
<td>9.5</td>
<td>2.6</td>
<td>4.5</td>
<td>1.6</td>
<td>1</td>
<td>1</td>
<td>1.5</td>
</tr>
</tbody>
</table>
suggesting that reaction schemes of each additive 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.

\[ \text{H}_2\text{C} \rightarrow \text{H}^*, \text{C} = \text{O}, \text{H}_2, \text{H}_2\text{O}_2 \] (1)
\[ \text{P} \rightarrow \text{P}^* + \text{H}^* \] (2)
\[ \text{P} + \text{H}^* \rightarrow \text{P}^* + \text{H}_2 \] (3)
\[ \text{P} + \text{C} = \text{O} \rightarrow \text{P}^* + \text{C} = \text{O} \] (4)
\[ \text{P}^* + \cdot \rightarrow \text{P} + \text{P} \text{ (crosslinking)} \] (5)

When air is present, the expected reaction is assumed to be \[^3\text{O}_2\]

\[ \text{H}^* + \text{O}_2 \rightarrow \text{HO}_2^* \] (6)
\[ \text{P}^* + \text{O}_2 \rightarrow \text{PO}_2^* \] (7)
\[ \text{PO}_2^* + \text{H}_2\text{O}_2 \rightarrow \text{C} = \text{O} + \text{H}_2\text{O}_2 + \text{O}_2 \] (8)
\[ \text{C} = \text{O} \rightarrow \text{degradation} \] (9)
\[ \text{P} + \text{HO}_2^* \rightarrow \text{IC} \cdot (\cdot \text{H}_2^- + \text{H}_2^-) + \text{H}_2\text{O} \] (10)
\[ \text{C} \cdot \text{CH}_2 - \text{C} \rightarrow \cdot \text{CH}_2 - \text{C} + \cdot \text{CH}_2 - \text{C} \text{ (degradation)} \] (11)
It has been found that the amount of $F^-$ produced by the reaction (2) is very small, compared with that produced by the reactions (5) and (4). The rate of reaction (7) is generally considered to be much higher than that of (5).

4.1) Organic additives

4.1.1) Thiourea

It is well known that very low amount of thiourea protects many materials against damage by radiation. This compound may exist in solutions partly in an enol form, $H_2:C(NH_2)OH$ (hereafter abbreviated as $RSH$), and it has been found that the sulfur linkage is particularly reactive toward free radicals. Thus, the radical transfer may occur readily between thiourea and radicals:

\begin{align}
    P^* + RSH & \rightarrow P + RSH^* \quad (12) \\
    H^* + " & \rightarrow H_2 + " \quad (13) \\
    HO^* + " & \rightarrow H_2O + " \quad (14) \\
    CO_2^* + " & \rightarrow H_2CO_2 + " \quad (15)
\end{align}

It is also likely that radical recombination occurs between $RSH^*$ and other radicals as follows,

\begin{align}
    P^* + RSH^* & \rightarrow PSH \quad (16) \\
    COO^* + " & \rightarrow COOSR \quad (17)
\end{align}

From the reactions (12)~(17), the protective property of thiourea against the cross-linking 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.

4.1.2) HMK 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 weakly than thiourea. The recombination of R• with R• is also quite probable. Thus, the crosslinking may here also occur as a result of the following reaction.

\[
\begin{align*}
H^\cdot + RH & \rightarrow R^\cdot + H_2 \\
HO^\cdot + H & \rightarrow R^\cdot + H_2O \\
P^\cdot + H & \rightarrow R^\cdot + P \\
P^\cdot + R^\cdot & \rightarrow PR
\end{align*}
\]

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 \( k \)-value of radical-formation than the other organic additives.6

It is rather difficult to explain the result that very low quantity of HMK and ethanol accelerates 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 does not take place entirely.

4.2) Inorganic additives

As has been intensively studied, results obtained here can be explained rather easily in terms of electron transfer, which is usually observed for oxidation and reduction.

4.2.1) FeSO₄ + C₆H₆S₆₄⁺

This system is known as Fricke's solution. When air is absent in the solution to be irradiated, the mechanism may be written:

\[ \text{OH}^- + \text{Fe}^{++} \rightarrow \text{Fe}^{+++} + \text{H}_2\text{O}^- \]  \hspace{1cm} (22)

\[ \text{H}^- + \text{Fe}^{++} + \text{H}^+ \rightarrow \text{Fe}^{+++} + \text{H}_2 \]  \hspace{1cm} (23)

Further, presumably Fe⁺⁺ attacks \( \cdot \text{OH} \) by a reaction such as

\[ \text{Fe}^{++} + \text{H}^+ \rightarrow \text{Fe}^{+++} + \text{H}_2 \]  \hspace{1cm} (24)

Clearly, the reactions (22)~(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 HOO⁺ and this peroxodic acid can be assumed to be fairly stable in the aqueous solutions, then the ferrous ions reduce this product.
\[
\text{ROOH} + \text{Fe}^{++} \rightarrow \text{RO}^- + \text{Cu}^- + \text{Fe}^{+++}
\]  
\begin{align*}
\text{The RO}^- \text{ would give rise to the degradation through reaction (11)}
\end{align*}

4.2.2) KBr

As is well-known, Br\(^-\) is a reducing agent, as powerful as Fe\(^{++}\).
\[
\begin{align*}
\text{OH}^- + \text{Br}^- & \rightarrow \text{OH}^- + \text{Br}^- \\
\text{H}^- + \text{Br}^- & \rightarrow \text{H}^+ + \text{Br}^-
\end{align*}
\]
Hence, the rate of reactions (2) and (3) 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\(^{++}\).
\[
\text{ROOH} + \text{Br}^- \rightarrow \text{RO}^- + \text{H}^- + \text{Br}^-
\]  

4.2.3) Cu\(_{2}\)O

\(\text{Cu}^{++}\), a powerful oxidizing agent, reacts with \(\text{H}^-\) to become \(\text{Cu}^+\), which further reacts with \(\text{OH}^-\).
\[
\begin{align*}
\text{H}^- + \text{Cu}^{++} & \rightarrow \text{H}^+ + \text{Cu}^+ \\
\text{OH}^- + \text{Cu}^+ & \rightarrow \text{OH}^- + \text{Cu}^{++}
\end{align*}
\]
The reason for the most striking decrease in viscosity of solution irradiated in the presence of air and \(\text{CuSO}_4\), \(\text{CuO}\), be that \(\text{ROOH}\) is perhaps attached to both \(\text{Cu}^{++}\) and \(\text{Cu}^+\) with the mechanism,
\[
\text{ROOH} + \text{Cu}^{++} \rightarrow \text{ROO}^- + \text{Cu}^+ + \text{H}^+
\]
Finally, it must be noted that in the reaction schemes described above, no energy transfer in any case 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.

References

7) See, for example, A. O. Allen, The Radiation Chemistry of Water and Aqueous Solutions (Van Nostrand, 1961)
9) H. Fricke and S. Horse, Phil. Mag. Z, 129 (1929)
Chapter II

EFFECTS OF DEGREE OF POLYMERIZATION ON CROSSLINKING OF POLYVINYL ALCOHOL IN AQUEOUS SOLUTION
1. Introduction

During the course of a continuing program of study concerning the radiation-induced crosslinking of polymers in aqueous solution\(^1,^2,^3,^4\), it was found to be very likely that the critical concentration for cross-linking corresponds to the polymer concentration where the polymer coils just begin to be in contact with each other. If this is true, the size of the polymer coil will be able to be calculated easily using the data concerning the crosslinking in solutions. In the previous works\(^2,^4\), the expansion of polyelectrolytes was calculated briefly for various charge densities and added salt concentrations. In the case of polyelectrolytes, however, the quantitative treatment of experimental results was not easy, since the crosslinking was largely influenced by the electrostatic repulsive forces arising from the ionized side groups.

The present work is an extension of previous investigations, with attention being focussed in the effect of size of polymer coil on the crosslinking in dilute aqueous solutions. The sample used here is polyvinyl alcohol (PVA) with various degrees of polymerization from 65 to 19700. In addition to the estimation of the radius of polymer sphere, the contribution of water to the crosslinking of polymer was quantitatively discussed.
2. Experimental

2.1) Material

Initial degrees of polymerization and limiting viscosity numbers of PVA used are shown in Table 1. The preparative method of original polyvinyl acetate (PVAc) is also tabulated there. Samples I, S, L and F were obtained by re-saponification of fractionated linear PVAc, and samples N and R by fractionation of PVA. The degree of saponification was in all cases approximately 100%. The polymers obtained were purified several times by precipitation from aqueous solutions with methanol or acetone and by extraction by methanol in a Soxhlet extractor for 8 hrs. After drying under vacuum at 50°C, they were stored over P2O5.

The degree of polymerization \( \bar{M} \) was calculated from the equation: 
\[
[\eta] = 7.51 \times 10^{-3} \times M_0^{0.84} \quad \text{(in water, 30°C)}
\]
except for samples of I-1 and S-2. For these two samples, the equation could not be used, since \( \bar{M} \) of these polymers were too high for the equation to be applied. Therefore, they were estimated indirectly assuming that \( \bar{M} \) of these samples were precisely equal to those of PVAc, which was obtained by acetylation of these PVA. The value of \( \bar{M} \) of these acetylated PVA was calculated from the following equation: 
\[
[\gamma] = 3.91 \times 10^{-2} \times F^{0.62} \quad \text{(in acetone, 30°C)}
\]
Table 1. Characteristic of Samples and Polymerization Condition of Original PVAc

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{H}_2\text{O}$</th>
<th>$r$</th>
<th>Solvent</th>
<th>Monomer conc. (%)</th>
<th>Initiator conc. (%)</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I - 1</td>
<td>2.7</td>
<td>19700</td>
<td>Bulk</td>
<td></td>
<td>- ray</td>
<td>-78</td>
</tr>
<tr>
<td>I - 2</td>
<td>1.9</td>
<td>1500</td>
<td>&quot;</td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>N - 1</td>
<td>1.88</td>
<td>4000</td>
<td>Commercial product</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I - 8</td>
<td>1.06</td>
<td>2350</td>
<td>Bulk</td>
<td>ALBN</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>F - 5</td>
<td>0.86</td>
<td>1500</td>
<td>Ethyl acetate</td>
<td>CC</td>
<td>BPO</td>
<td>0.05</td>
</tr>
<tr>
<td>N - 2</td>
<td>0.380</td>
<td>470</td>
<td>Commercial product</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H - 3</td>
<td>0.212</td>
<td>190</td>
<td>Ethanol</td>
<td>30</td>
<td>BPO</td>
<td>0.1</td>
</tr>
<tr>
<td>H - 5</td>
<td>0.128</td>
<td>86</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>H - 6</td>
<td>0.094</td>
<td>60</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
2. Irradiation Procedure and Determination of Gel Point

They are nearly similar to those described previously\(^3\). The temperature during irradiation was about 30°C and the dose rate was 1.45 x 10^5 r/hr. All solutions before irradiation were quite transparent. Irradiation was carried out in the absence of air in all cases.

3. Results and Discussion

3.1) Effects of Degree of Polymerization and Concentration on Gelation

Minimum doses needed for incipient gelation, i.e., gelation doses, are plotted in Fig. 1 against the polymer concentration for the samples having various initial degrees of polymerization. Evidently, all the curves in Fig. 1 have the similar shape to those found out when a number of polymers were irradiated in aqueous solutions; beyond a certain concentration gelation abruptly occurs, and the gelation dose decreases very sharply with the concentration and then after reaching a minimum it increases again rather slowly. The critical concentration, below which gel cannot be formed however large a dose is used, seems to be somewhat ambiguous from the shape of curves in Fig. 1. However, they could be determined very definitely, since the solutions never exhibited
Fig- 1 Influence of polymer concentration \( C \) and degree of polymerization on relation dose \( R_g \) for \( \gamma \)VA irradiated in deaerated aqueous solutions. The number in parentheses represents the initial degree of polymerization.
relation when irradiated at the concentrations of only 0.01% lower than the critical concentration. At such low concentrations the irradiated solutions were clear, irrespectively of the degree of polymerization of the samples used, indicating the formation of intra-molecular crosslinking.

The critical concentration as a function of degree of polymerization and limiting viscosity number of unirradiated PVA is shown in Figs. 2 and 3, respectively. The dependence appears in either case to be linear as a first approximation. The observed deviation from the linearity may be due to the difference of the degree of fractionation rather than to the difference in the polymerization condition under which the original PVA was prepared. The relatively large deviation of plots for 1-5 sample may be ascribed to its being roughly fractionated because of final fraction.

The linear relation observed in Fig. 3 can be given by

$$C_{\text{crit.}}[\eta]^{0.35} = C$$

where $C_{\text{crit.}}$ is the critical concentration for gel-formation and the polymer concentration is expressed in g/100cc unit.

Now, we will discuss briefly the equation (1). Similarly to the treatment in the previous papers\textsuperscript{2,3}, we will regard the polymer coil in dilute solutions as a sphere. On assuming that these spheres exist in solutions in the close-packed structure, the average distance $\frac{1}{12}$ between two molecular centers at a polymer concentration $C$ and for a molecular weight
Fig. 2 Relation between critical concentration $C_{\text{crit}}$ for gel-formation and initial rate of polymerization.
Fig. 3  Relation between critical concentration $C_{\text{crit.}}$ for gel-formation and initial limiting viscosity number $[\eta]$. 
The limiting viscosity number \([\eta]\) may be regarded as a measure of the ratio of the effective hydrodynamic volume \(V_e\) (\(V_e \propto R_h^3\)) of the polymer to its molecular weight; that is,

\[
[\eta] \propto \frac{3}{N}
\]

(4)

And the \([\eta]-M\) relation for PVA in aqueous solutions has been determined as

\[
[\eta] \propto M^{0.55} \quad (5)
\]

Then, by combining (1), (3), (4) and (5), we find that

\[
R_C \propto M^{0.7} \quad (6)
\]

\[
R_h \propto M^{0.55} \quad (7)
\]

Both equations indicate that the radius is nearly proportional to the square root of the molecular weight.
3.2) Dimension of PVA Molecule in Aqueous Solution

If it can be taken for granted that the main-chain scission occurs to a negligible extent during irradiation, the radius of PVA in solution can be evaluated from the equation (3). The possibility of scission is, now, supposed to be quite negligible because the dose used here are much smaller by a factor of several tens than those required to degrade solid PVA detectably. Furthermore, the facts that, in the present case, air is eliminated completely from the solution, and that the rise observed in the curves in Fig. 1 is in all cases very sharp, may provide also a support for the absence of the scission. H. A. Gies (8), also, concluded that degradation did not occur, based on the viscosity change of PVA solutions irradiated under the same condition as ours.

By rewriting (3), we obtain

$$R_C = 10.9 \sqrt{\frac{E}{D_{\text{crit.}}}}.$$  (9)

where $R_C$ is expressed in Å.

Figure 4 is a double logarithmic plot of the radius of the polymer sphere calculated from equation (9) against degree of polymerization. For comparison, radius of gyration $\sqrt{\bar{M}}$, and hydrodynamic effective radius $R_H$ were also plotted. As can be seen from Fig. 4, $R_C$ would be said to have about the same order of magnitude as that of $R_H$ and $\sqrt{\bar{M}}$.  

- 173 -
Fig. 4  Radius of polymer sphere calculated from the data of crosslinking and viscosity.
3.3) Mechanism of Crosslinking in Solutions

The radius of polymer sphere calculated by regarding the critical concentration as the minimum concentration, at which overlapping of polymer coils begins, was nearly proportional to the hydrodynamic radius. This fact may give a certain evidence for the assumption concerning the significance of the critical concentration. It is probably because the meaning of the critical concentration has not been made clear that a satisfactory explanation has not been given concerning the mechanism of crosslinking in dilute solutions up to date.

If the critical concentration can be regarded as the minimum concentration of overlapping as described above, the anomalous concentration dependence on crosslinking observed in Fig. 1 can be explained by the following simple mechanism. We will treat, in the present chapter, mainly the crosslinking occurring in the concentration range above \( C_{\text{crit}} \), and the details as to the crosslinking below \( C_{\text{crit}} \) will be presented in the subsequent chapter.

When the crosslinking mechanism in aqueous solutions is concerned, the indirect effect due to water should be taken into account, first of all. However, as the concentration of the solutions become relatively low, contact or overlap of polymer coils may become a more important factor for crosslinking than the indirect effect. In Fig. 5 a schematic representation of the relative location of each polymer
Fig. 5  Relative location of polymer spheres in solutions.
sphere in solution is given. When the concentration is so low that the sphere cannot interfere each other as is illustrated in Fig. 5(a), the formation of three-dimensional network gel will be impossible undoubtedly. In the case of a moderately concentrated solution as is shown in Fig. 5(b), where all polymer spheres just are in contact with each other in the solution, a continuous macro-gel can be formed. The concentration at this point corresponds to $C_{\text{crit}}$.

As the solution becomes more highly concentrated as shown in Fig. 5(c), the effect of overlapping will be less important than the indirect effect as far as the concentration dependence in concern, because the inter-molecular crosslinking can occur readily in this case. The influence of this overlapping on the crosslinking in solutions is shown qualitatively by a curve (a) in Fig. 6. For convenience, we used the gelation dose as a measure of the rate of crosslinking.

Next, we will consider by what type of reactions the crosslink is formed. We have found, in the previous studies on the radiation-induced crosslinking of various polymers, that $H^-$ and $OH^-$ produced by the action of radiation on water play an important role in the crosslinking reaction. Basically, the crosslinking may be formed partly by coupling of two polymer radicals which are produced as a result of hydrogen abstraction from the polymer chain by $H^-$ and $OH^-$. The reaction scheme is then:
Fig. 6  Schematic representation of concentration dependence of the overlapping effect (a) and the indirect effect (b). (c) represents the resultant effect of these two factors.
\[
\begin{align*}
H_2O & \xrightarrow{\text{radiation}} H^+ + OH^- \quad (16) \\
1 + 1 & \rightarrow 1 + 1 \quad (11) \\
P + OH^- & \rightarrow P + H_2O \quad (12) \\
P + P' & \rightarrow P - P' \quad (13)
\end{align*}
\]

where \( P \) represents the polymer molecule. In addition to these reactions, the crosslinking may be partly formed by the reaction of \( P \) produced from polymers by the direct action of radiation:

\[
\begin{align*}
P & \xrightarrow{\text{radiation}} P' \quad (14) \\
P' + P' & \rightarrow P - P' \quad (15)
\end{align*}
\]

The formation of crosslinking through the reactions (10) to (13) is generally called "indirect effect", and that through (14) and (15) "direct effect". Obviously, the indirect effect depends on the polymer concentration, while the direct effect does not. It has been generally accepted that in dilute solutions the direct effect is almost negligible compared with the indirect effect. The concentration dependence on the indirect effect will be shown qualitatively by a curve (b) in Fig. 1. The steady increase of the gelation dose with increasing polymer concentration is due to the increasing amount of \( H^+ \) and \( OH^- \) per polymer molecule.

Combining these two curves of (a) and (b), one can obtain a curve quite similar to those in Fig. 1. This indicates that the crosslinking in aqueous solutions is strongly influenced by the degree of overlapping of the polymer coil in the neighborhood of \( C_{\text{crit}} \).
solution it depends exclusively on the indirect effect. It is, of course, very likely that, besides these two effects, there may be a few factors influencing the concentration dependence on crosslinking. Main factors among them may be the mobility of polymer segments and the dimension of polymer coils. However, these concentration dependence is supposed to be negligible compared with that of the indirect effect, except for the high concentration range.

3.4) Indirect Effect

Although it is very important to estimate the indirect effect quantitatively, only few attempts\(^9,11\) have been done probably because of the uncertainty of the mechanism of reactions which are closely related to the indirect effect. In order to avoid difficulties in calculation, we will discuss here, the crosslinking, occurring in the concentration range relatively higher than the \(C_{\text{crit.}}\), since near the \(C_{\text{crit.}}\) such factors as the degree of overlapping should be taken into account. We shall make the assumptions: (1) polymer coils "drain through" each other so that the segment distribution is uniform, (2) the formation of intramolecular crosslinking can be neglected, (3) the energy absorbed directly by the polymer molecule is completely used for the crosslinking and (4) the energy transfer does not occur.

Let \(c\) be the polymer concentration expressed in weight %.
and $R$ the radiation dose in roentgen unit. Then, for 100 gram
of the solution, the energy absorbed by the polymer is $RAc$ and
the energy absorbed by water is $W(100 - c)$. $A$ is the conver-
sion factor from roentgen unit to e.v. ($A = 0.58 \times 10^{14}$ e.v./r). It seems very plausible that the energy absorbed in water, i.e., $W(100 - c)$ is used for the cross-
linking not completely, but only partly. Then, the total energy
actually dissipated for the crosslinking is given by

$$ E = RAc + W(100 - c) \tag{10} $$

where $k$ is assumed tentatively to be independent of $c$.

The first term in the right side of the equation (10) is
related to the direct effect, and the second term to the
indirect effect. The number of polymer molecules which are
present in 100 gram of the solution, is $cR/\ell$, so that the
energy per polymer molecule is

$$ \xi = \frac{RAc + W(100 - c)}{cR/\ell} \tag{17} $$

Therefore, if we define the energy required for the formation
of a crosslink as $\xi$, the number of crosslinks per polymer
molecule is

$$ \delta = \frac{RAc + W(100 - c)}{cR/\ell} \tag{18} $$

According to the theories proposed by E. H. Stokoe,\(^{12}\) and
A. Charlebois,\(^{13}\), the incipient gelation occurs when there is
one crosslink per two initial molecules and when they have
initially a uniform molecular weight distribution;
that is
\[ \bar{g} = 0.5 \]  \hspace{1cm} (19)

Thus, if the gelation dose is denoted by \( N_g \), we find that
\[ \frac{1}{R_g} = 2AN/2c (100k/c + 1 - k) \]  \hspace{1cm} (20)
or,
\[ \frac{1}{R_g} = AN_c/5CN_c G_c (100k/c + 1 - k) \]  \hspace{1cm} (21)

where \( N_0 \) is the molecular weight of the monomer unit and \( G_c \) is the G-value for crosslinking, in other words, the number of crosslinks formed per 100 e.V. of energy. The equation (21) indicates that \( R_g \) is inversely proportional to \( T \) of the samples, if \( c = \text{const.} \) As can be seen from Fig. 7, which is a double logarithmic plot of \( R_g \) at the 1.0 % solution against \( T \), the relation \( R_g \propto 1/T \) is obtained as expected.

Furthermore, according to the equation (21), the plot of \( 1/R_g T \) against \( 1/c \) should give a straight line. By applying this equation to the data in Fig. 1, we obtain a straight line shown in Fig. 8 in good agreement with the theory.

From these results, the above assumption that \( k \) is independent of \( c \), is found to be true. The slope and the intercept of this straight line show that \( G_c = 6.2, x_c = 10 \) e.V. and \( k = 0.055 \).

We shall define the fraction of indirect effect \( f_{\text{in.}} \) such as,
\[ f_{\text{in.}} = \frac{\text{indirect effect}}{\text{direct effect} + \text{indirect effect}} \]  \hspace{1cm} (22)
Fig. 7 Influence of initial degree of polymerization on gel-formation of PVA irradiated in 0.1 M solutions.
Fig. 8 Plot of $1/R_g$ against $1/C$ for various PVA.
Fig. 9 Dependence of indirect effect on polymer concentration.
Then, we obtain

\[ f_{in.} = \frac{k(100 - c)}{c + k(100 - c)} \]  

(23)

By substituting \( k = 0.055 \) into the equation (23), and plotting \( f_{in.} \) against the polymer concentration according to the equation (23), we obtained a curve shown in Fig. 9. It indicates clearly that the indirect effect is very important in the low concentration range, while in the highly concentrated solution the direct effect becomes more prominent.

Hitherto, this feature generally observed pertaining to the crosslinking and degradation in aqueous solution has been described only qualitatively.

References

Chapter X

RADIATION EFFECT OF POLY(VINYL ALCOHOL) IN AqUACOS SOLUTION. DOES CRITICAL CONSIDERATION FOR CR-FORMATION
1. Introduction

In the previous chapter, we have investigated the solution 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 so-called, 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 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 Berkovich et al.\(^1\), Dieu\(^2\), Honl\(^3\), and others\(^4\), etc. However, all of them studied only briefly, and, besides, their results were not always in agreement with each other's.

In order to provide a 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.

2. Experimental

2.1) Material

The PVA used here is the sample -5, whose characteristics
was described in the previous chapter. The limiting viscosity number \([\eta]\) and the viscosity-average degree of polymerization \(\bar{\eta}\) are 0.800 and 1500, respectively.

2.2) Preparation of aqueous solutions and irradiation procedures

These are quite similar to those described previously, except the dose rate, which is approximately \(1.33 \times 10^5\) r/hr in the present study. Irradiation was carried out in most cases at room temperature (about 25°C), with an exception of 35°C.

2.3) Viscosity measurements

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

2.4) 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 \(\tau\), which was defined by the following equation;

\[ \tau = 2.303 \log \frac{I_0}{I_1} \]

where \(I_0\) and \(I_1\) are the intensities of light scattered from the solutions before and after irradiation, respectively.
2.5) Reaction of the irradiated IVA with alkali and acid

NaOH or HCl was added to aqueous solutions of IVA, the final concentration being adjusted to 0.1N, and the solutions thus obtained were heated on a boiling water bath for 5 hrs. The polymer concentration during the reaction was 0.1M.

2.6) Acetylations

Acetylation of IVA was carried out under a more severe condition than usual ones. The reaction mixture containing one part of IVA, 20 parts of acetic anhydride and 40 parts of pyridine was sealed in tubes 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 IVA was separated and purified. The degree of acetylation was determined from the weight change before and after the reaction.

2.7) Infrared spectral measurements

An A-15/11 type infrared spectrophotometer was used with a NaCl prism. Infrared spectra were measured using dry films of the IVA.
2.6) 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 glassplate and then dried over P_2O_5 at 20°C for 2 days. They were used for the swelling measurement without any heat treatment.

2.7) X-ray diffractions

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

3. Results

3.1) Viscosity change under irradiation

3.1.1) Irradiation at 20°C

Fig. 1 shows the change in [γ] occurring during irradiation of aqueous solutions of various polymer concentrations. Viscosities of irradiated polymers were measured in water at 30°C. In the previous chapter, the critical concentration of this polymer was found to be 0.1%.

The solutions of lower concentrations
Fig. 1 Viscosity change of aqueous solution of PVA irradiated at 20°C. Viscosities were measured in water at 30°C.
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 \times 10^4 \text{r} became light-brown.

Dieu\textsuperscript{2, 3}) and Danno\textsuperscript{5}) 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 chain scission through HO\textsubscript{2} until the dissolved
air was completely exhausted.

Dieu\textsuperscript{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 \textit{n}-propanol, since the latter is
thought to destroy the hydrogen bonds more powerfully than dioxane.
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\degree, as
the hydrogen bonds of PVA in aqueous solutions have been found
to be easily broken especially at temperatures higher than 60\degree.\textsuperscript{7})
Fig. 2 Viscosity change of aqueous solution of rVA irradiated at 20°C. Viscosities were measured in a mixed solvent of water and $n$-propanol (7:1) at 30°C.
Fig. 3, where the viscosities measured at 85°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 [17] 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 intermolecular crosslinking by radiation.

3.1.2) 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 solution of PVA may be more 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°C and 85°C does not essentially affect the radiation effects.

3.2) Turbidity of irradiated solutions

As described in 3.1), solutions became turbid when irradiated under certain conditions. The relative turbidity \( T \) is plotted in Fig. 5 against the radiation dose for the solutions irradiated
Fig. 3  Viscosity change of aqueous solution of EVA irradiated at 20°C.  Viscosities were measured in water at 65°C.
Fig. 4  Viscosity change of aqueous solution of NA irradiated at 65°C. Viscosities were measured in water at 65°C.
Fig. 5 Relative turbidity $\tau$ of aqueous solutions of PVA irradiated at 20°C.
at 20°C. Comparison of Fig. 1 with Fig. 5 indicates 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 polyacrylic acid were also found by us\(^5\) 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 intramolecular crosslinking. These results suggest strongly that the intramolecular crosslinking may be formed also in this present case. This suggestion will be justified by various experimental evidences described in the subsequent paragraphs.

3.3) Reaction of the irradiated PVA with NaOH or HCl

The values of \([\eta]\) measured before and after heating the PVA in alkaline and acidic aqueous solutions are given in Table 1. \([\eta]_{30^\circ}\) and \([\eta]_{100^\circ}\) 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 0.134% 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
Table 1

Viscosity Change by the Reaction of Irradiated PVA with Alkali and Acid. (Heating, 100°C, 3 hrs; Polymer Concentration = 0.18; Concentration of Solution during Irradiation = 0.18%)

<table>
<thead>
<tr>
<th>Dose (Mr)</th>
<th>Alkali or Acid concentration</th>
<th>([\eta]_{30^\circ})</th>
<th>([\eta]_{100^\circ})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.865</td>
<td>0.86</td>
</tr>
<tr>
<td>0.4C</td>
<td>1N - HCl</td>
<td>1.2</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>1N - NaOH</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>1.0</td>
<td>0</td>
<td>0.596</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>1N - HCl</td>
<td>0.53</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>1N - NaOH</td>
<td>0.56</td>
<td>0.31</td>
</tr>
</tbody>
</table>

and other weak ones which can be cleaved easily by alkali or acid, are not practically formed under irradiation.

3.4) Acetylation of the 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 EVA
(Concentration of Solution during Irradiation=0.184,)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose(μr)</th>
<th>Degree of Acetylation</th>
<th>Degree of Swelling in Acetone at 30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Reaction time 15hr 30hr</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.303</td>
<td>100.5</td>
</tr>
<tr>
<td>2</td>
<td>0.16</td>
<td>1.22</td>
<td>101.6</td>
</tr>
<tr>
<td>3</td>
<td>0.12</td>
<td>2.50</td>
<td>99.2</td>
</tr>
<tr>
<td>4</td>
<td>0.46</td>
<td>1.32</td>
<td>75.3</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>0.572</td>
<td>67.2 64.1 14.1</td>
</tr>
</tbody>
</table>

Table 2 indicates that all the OH groups cannot be acetylated in the case where [η] of EVA decreases with radiation dose. The finding that the acetylated EVA's obtained from samples 3, 4 and 5 do not dissolve in dimethyl sulfoxide, chloroform, and acetone, but only swell in them, gives a strong support for the formation of intra-molecular crosslinking, namely, micro-cl 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.

3.5 Infrared spectra

whether the incomplete acetylation of the irradiated EVA
should be attributed to steric hindrance due to the crosslinking, or to partial disappearance of CH groups by irradiation, may be elucidated to some extent by measurements of infrared spectra of the irradiated PVA. Fig. 6 shows the infrared spectra of the unirradiated and irradiated PVA in the wavelength 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 5.05 μ (C = O group band) appears during irradiation, and furthermore that the optical density at 3.65 μ (CH group) decreases as the radiation dose increases. It suggests that the incomplete acetylation may be ascribed mainly to the disappearance of CH groups during irradiation.

3.6) Swelling of the irradiated PVA in water

In order to obtain knowledge concerning the crystallizability 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 interesting feature is that the film of sample 5 was so fragile especially when immersed in water at 30°C that the degree of swelling could not be determined by our method. For comparison, in Table 3 the degree of swelling of an unirradiated PVA was also given, whose [%] is approximately equal to that of sample 5.
Fig. 6  Infrared spectra of various FVA. For the number of curves, see chap. 2.
Table 3
Degree of Swelling (in wt.) in water at 30°C of Irradiated PVA (Concentration of Solution during Irradiation = 0.184%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose (ir)</th>
<th>[η]</th>
<th>Degree of Swelling</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.803</td>
<td>5.85</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>1.32</td>
<td>52.1</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>0.572</td>
<td>0.0 *</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0.583</td>
<td>7.69</td>
</tr>
</tbody>
</table>

* Apparent Degree of Swelling

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 cross-linking in the sample 5.

3.7) α-2θ, diffraction patterns

Photographs of the unirradiated and irradiated PVA are show 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 show in Table 4, the plane distances of these two different films were
Fig. 7 X-ray diffraction photograph of unirradiated PVA.

Fig. 8 X-ray diffraction photograph of irradiated PVA.

Irradiation was carried out in 0.1M aqueous solution at 1 x 10^6 r and 20°C.
identical within experimental error.

Table 4

Plane Distance (Å) of Crystalline Part of PVA
(Concentration of solution during irradiation = 0.164 g/L,
Dose = 1 x 10^6 r)

<table>
<thead>
<tr>
<th>Sample</th>
<th>A1</th>
<th>A2,4</th>
<th>A5</th>
<th>A0</th>
<th>A7</th>
<th>I1</th>
<th>I2</th>
</tr>
</thead>
<tbody>
<tr>
<td>unirradiateda)</td>
<td>7.71</td>
<td>4.51</td>
<td>3.86</td>
<td>5.21</td>
<td>2.74</td>
<td>2.41</td>
<td>2.20</td>
</tr>
<tr>
<td>irradiatedb)</td>
<td>7.65</td>
<td>4.52</td>
<td>3.86</td>
<td></td>
<td>2.75</td>
<td>2.21</td>
<td></td>
</tr>
</tbody>
</table>

a), b); heat-treated at 120°C for 15 mins.

4. Discussion

4.1) Inter- and intra-molecular crosslinking.

In the preceding chapters, 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 close 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 larger 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. 1-3, as a result of formation of the intra-molecular crosslinking, which was already ascertained by various results described in 3).

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 $[\eta] - T$ relationship obtained by Nakajima and Furutachi\(^3\) 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 number-average numbers of initial molecule contained in a molecule of the final product, since the numbers can be taken to be equal to $\frac{T_{\text{max}}}{T_0}$, where $T_{\text{max}}$ and $T_0$ are the degrees of polymerization calculated from $[\eta]_{\text{max}}$ 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.

Table 5

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

<table>
<thead>
<tr>
<th>Concentration(%)</th>
<th>$[\eta]_{\text{max}}$</th>
<th>$\Phi_{\text{max}}$</th>
<th>Number of primary molecule ($=\frac{[\eta]<em>{\text{max}}}{\Phi</em>{\text{max}}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.22</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
</tr>
<tr>
<td>0.184</td>
<td>2.82</td>
<td>25000</td>
<td>17</td>
</tr>
<tr>
<td>0.100</td>
<td>1.00</td>
<td>6000</td>
<td>4</td>
</tr>
<tr>
<td>0.06</td>
<td>1.10</td>
<td>2500</td>
<td>1.67</td>
</tr>
</tbody>
</table>

The decrease in $[\eta]_{\text{max}}$ 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.

4.2) Structures of the intra-molecular-crosslinked PVA

Figs. 1-4 indicate evidently that the intra-molecular crosslinks reduce the size of polymer coils. This tendency was also found by Huhn and Balmer 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 \( T_c \), from \([\eta]\) of the intra-molecular-crosslinked EVA, in other words, micro-gels. Calculated values for the micro-gel obtained under irradiation of 0.134, solutions were listed in Table 6. The degree of swelling and \( T_c \) were calculated using Table 6

<table>
<thead>
<tr>
<th>Dose (Mr)</th>
<th>([\eta])</th>
<th>(T)</th>
<th>Dep. swell. (in vol.)</th>
<th>(T_c)</th>
<th>(V_{BP})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17</td>
<td>2.82</td>
<td>25000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>2.52</td>
<td></td>
<td>93.5</td>
<td>11000</td>
<td>1.15</td>
</tr>
<tr>
<td>0.40</td>
<td>1.32</td>
<td></td>
<td>52.3</td>
<td>11100</td>
<td>1.13</td>
</tr>
<tr>
<td>0.60</td>
<td>1.10</td>
<td></td>
<td>34.6</td>
<td>10690</td>
<td>1.17</td>
</tr>
<tr>
<td>1.0</td>
<td>0.972</td>
<td></td>
<td>22.8</td>
<td>8330</td>
<td>1.50</td>
</tr>
<tr>
<td>3.0</td>
<td>0.191</td>
<td></td>
<td>7.6</td>
<td>3030</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Einstein's formula and Florey-Hilchler's equation for swelling. As the interaction constant \( \mu \), which is necessary for the calculation of \( T_c \), a value of 0.893 was used which was obtained by Nakajima and Furutachi. The numbers of intra-molecular-crosslinks \( V_{BP} (= \frac{T}{2T_c}) \) 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.

References

4) C. Wipper, Nuclonics, 14, 68 (1960).
6) I. Sakurada and M. Fujikawa, Chemistry of High Polymer (Japan), 2, 143 (1945).
7) I. Sakurada and S. Tsuchiya, unpublished data.
9) A. Nakajima and S. Furutachi, Chemistry of High Polymer (Japan), 8, 460 (1949).
Chapter I: Historical background of the radiation chemistry of polymer solutions was briefly written, and the outline of this dissertation was given.

Chapter II: Studies have been done on the effects of gamma radiation 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, sorption 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 of water-swollen films in air the indirect effect of water was quantitatively discussed. It was found by a calculation that the energy observed by water was not completely, but only 0.9 of it was used for the main chain fracture and that the energy dissociated per main chain fracture was about 30 eV. When the aqueous solutions were irradiated, these viscosities increased with dose and finally a gel was formed in the similar manner observed in the case of vacuum-irradiation of the water-swollen films. The ratio of the number of fractures and crosslinked units, \( p_c/q_c \), increased with the weight fraction the polymer; the value of \( p_c/q_c \) was 0.27, 0.39 and 0.55 at the weight fraction of 0.10, 0.30 and 0.55, respectively.
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 decreased with standing time.

Chapter III: When poly(vinyl 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 retarded 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.

Chapter IV: Poly(vinylmethyl ether) degraded more easily in better solvents when irradiated in dilute air-free organic solutions except in carbon disulfide, but in higher concentrated solutions crosslinking proceeded more readily in solvents of lower viscosity. Gel was formed even at concentrations below 1 weight % in carbon disulfide; the critical concentration for gel-formation was nearly equal to that of an aqueous solution. The critical concentration in the case of polystyrene in carbon disulfide solution was about 0.15 wt. %.

On the basis of the observed results, a role of solvent at the irradiation of polymer in solution was discussed in considerable detail, and it was found that the mechanism of radiation-induced reactions could be satisfactorily explained in terms of (1) formation or deactivation of macroradicals by the solvent radicals, and (2) change in the rate of the coupling or the cage-recombination reactions caused by the increase in mobility, dilution and solvation of polymers due to the solvent.

Chapter V: When poly(vinyl alcohol) (PVA) partially acetalized with glyoxallic acid (PVAG) was irradiated in air-free aqueous
solution without added salt, gelation occurred more readily and the critical concentration for gel-formation reduced, as the degree of expansion of PVAG increased. However, when NaCl was added to the solutions before irradiation so as to make the expansion of all PVAG's equal to that of parent PVA, the critical concentrations were practically identical to the value of parent PVA, independently of their carboxyl group contents. Further addition of the salt to solutions led to the increase in gelation dose. It was concluded from these results that the critical concentration corresponds to the concentration at which the overlap of a polymer with other ones commences. Based on this conclusion, the expansion of the polymer molecule was calculated and compared with that calculated from the viscosity data. These two showed a considerable good agreement. When PVAG was irradiated in aerated aqueous solution without added salt, degradation was promoted with increasing carboxyl group content, while in the case of solutions containing added salts degradation occurred scarcely.

Chapter VI : Dilute aqueous solutions of poly(acrylic acid) in acid form and in sodium-salt form have been irradiated with gamma rays from a Co-60 source in the presence and in the absence of air. Changes in gelation dose and viscosity have been measured. On irradiation in the absence of air, gel-formation was observed. Both the gelation dose and the
critical concentration for gel-formation increased as the degree of neutralization of samples increased. The critical concentrations were 0.25, 0.32, 0.50 and 1.0 wt.%, for samples with the degree of neutralization of 0, 5, 10 and 20%, respectively. When BaCl₂ was added to the solution for irradiation to diminish the ionization of carboxyl groups, gelation occurred more readily with increasing NaCl concentration, if the NaCl concentration was relatively low. However, as the concentration of BaCl₂ became higher than 0.01 M, gel-formation was increasingly suppressed with increasing NaCl concentration. This fact demonstrates that there is an optimum expansion of polyelectrolyte for crosslinking in aqueous solutions. On irradiation in the presence of air, the polymer appeared to degrade exclusively. The higher the degree of neutralization, the higher the degree of degradation. If, however, NaCl was present sufficiently in the solution for irradiation, degradation did not occur practically.

Chapter VII: The previous work has shown that gelation of poly(acrylic acid) in solution occurs most readily in acid form in the presence of 0.015 NaCl. The present investigation has been carried out to elucidate in more detail the mechanism of crosslinking occurring in these concentration ranges. The experiment was done under the nearly same condition as described in the previous chapter. Irradiation of the deaerated solutions below the critical concentration led to main-chain
scission when NaCl concentration of solutions to be irradiated was lower than 0.01N. However, in the case of the solution containing NaCl above 0.01N, the solutions became turbid on irradiation. Detailed studies on properties of the turbid solutions have revealed that the origin of turbidity can be attributed to the formation of intra-molecular crosslinking, namely, the micro-gel particles. The shape of the reduced viscosity-concentration curve for the micro-gel was somewhat different from those of linear poly(acrylic acid) polymers. The reduced viscosities of the intra-molecular-crosslinked polymer were considerably lower than those of the linear polymer over the polymer concentration range studied; and the increase in the reduced viscosity usually observed at the lower concentration was very slight in the case of intra-molecular-crosslinked polymer. The pH values of the intra-molecular-crosslinked polymer were higher than those of the linear polymer. The present study confirms the conclusion in the previous chapter that the crosslinking of polyelectrolyte in aqueous solutions can be explained in terms of both the change in expansion and the repulsion due to ionized groups.

Chapter VIII: Effects of a number of additives have been measured for deaerated and aerated aqueous solutions of PVA. Systems containing thiourea, methyl ethyl ketone, ethanol, FeSO₄ + 0.8N H₂SO₄, CuSO₄ or KBr have been examined in detail and it was found that these additives modified the rate of crosslinking.
ing as well as degradation of polymers. On the contrary, methanol, \( K_2\text{SO}_4 \) or \( \text{NaCl} \) 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 (\( \text{FeSO}_4 + 0.88 \text{H}_2\text{SO}_4 \)), 0.5 (\( \text{CuSO}_4 \)), 3 (\( \text{MnO}_2 \)), 10 (KBr) and 17 (ethanol). Discussion of the mechanism of radiation protection and promotion was given on the basis of these experimental results.

Chapter IX: Dilute aqueous solutions of poly(vinyl alcohol)

having various degrees of polymerization from 30 to 1000 were exposed to gamma radiation in the absence of air and the crosslinking mechanism was examined in detail. It was found from the results that the critical concentration for gel-formation \( C_{\text{crit}} \) can be written by the following equation:

\[
C_{\text{crit}} \cdot [\eta]^{0.62} = \text{const.}
\]

where \([\eta]\) is the limiting viscosity number of unirradiated samples. The assumption that at the critical concentration the polymer spheres just begin to overlap with each other and array in the order of closed packing could give a satisfactory
account of the experimental results. Namely, the radius of polymer sphere calculated on the basis of the above assumption was almost proportional to the hydrodynamic effective radius calculated from the Einstein formula and radius of gyration. The rapid rise of gelation dose usually observed near the critical concentration may be due to slight change in the degree of overlapping of polymer coils. The gelation dose at a fixed concentration was inversely proportional to the degree of polymerization of samples used. $G$-value for crosslinking was found to be 6.2. The indirect effect via water was quantitatively discussed and it was found that only 5.5% of radiation energy absorbed directly by water was actually dissipated for the formation of crosslinking.

Chapter X: Aqueous solutions of poly(vinyl alcohol) (PVA) were irradiated in the absence of air with Co-60 $\gamma$-rays at very low concentrations such as 0.154, 0.166 and 0.167 (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, 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 inter-molecular crosslinks was calculated using Flory-Rehner's and Hinsberg's equation.