

*Selectivity in Radiation-Induced Crosslinking
and Scission of Polyvinyl Alcohol (PVA)*

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The chemical structure of radiation-induced crosslinking of PVA irradiated in aqueous solution was supposed to be of 1,2-glycol type and/or α -oxy ketone type¹⁾.

We studied the mechanism of scission and/or crosslinking of irradiated PVA. The samples were either dry or swollen with water, when irradiated.

We found a certain selectivity in scission and crosslinking in PVA. The samples were exposed to radiation from a cobalt-60 gamma source in air or in vacuo up to 10^8 rad. at several temperatures and intensities.

We observed the influence of oxidation by periodic acid (HIO_4) upon the limiting viscosity number of irradiated PVA and, in particular, its variation with radiation dose.

In our experiments, the limiting viscosity number of PVA decreased with the increase in radiation dose. As shown in Fig. 1, there is a difference in the results between dry samples and swollen ones.

It should be noted that the limiting viscosity number after oxidation of dry samples is quite independent of radiation dose and agrees with the value of the sample, oxidized but not irradiated. But swollen samples show a different behavior of the limiting viscosity number after oxidation which definitely increases with radiation dose.

These results are inconsistent with the assumption of random scission and crosslinking, on which current theories^{2,3)} are based.

We are forced to conclude as follows: Only special types of bonds such as of 1,2-glycol type which exists initially in usual samples⁴⁾, can be fractured selectively, in either dry or swollen samples. Also, bonds formed by crosslinking in dry samples are definitely of the special types that are susceptible to oxidation by periodic acid. But in swollen samples we have at least two kinds of bonds formed by crosslinking, one susceptible and one not susceptible to oxidation.

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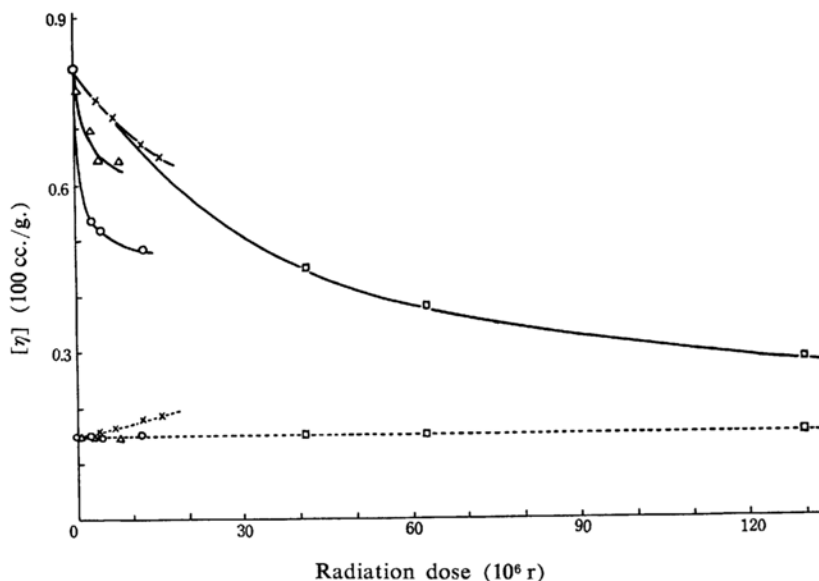


Fig. 1. The changes in the limiting viscosity number of irradiated PVA before and after oxidation by HIO_4 , plotted against radiation dose: Full lines show the results before oxidation and dotted lines after oxidation by HIO_4 .

- \triangle Dry powder, irradiated in air at 95°C and 1×10^5 r/hr. and aged for 9 months.
- \circ Dry powder, irradiated in air at room temperature and 3×10^4 r/hr. and aged for 1.9 years.
- \square Dry powder, irradiated in vacuo at room temperature and 2.9×10^4 r./hr. and aged for 1.1 years.
- \times Monofilament containing 6.7% water by weight, irradiated in air at room temperature and 4×10^4 r/hr.

Detailed results will be presented in a forthcoming paper.

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