

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

Poly (vinyl Methyl Ether)

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Polyvinylmethyl ether was 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.

INTRODUCTION

In previous articles, the effects of radiation have been investigated on polyvinyl alcohol in aqueous solution¹⁾ and polyvinyl acetate in various organic solutions²⁾. 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, polyvinylmethyl ether (PVME) was chosen as a polymer because of its very good solubility in many sorts of solvent such as water, carbon disulfide (CS₂) and almost of organic solvents except aliphatic hydrocarbons.

EXPERIMENTAL

Vinylmethyl ether purified in an ordinary way was bulk-polymerized at 0°C using boron trifluoride ether complex as a catalyst (0.02 g to 100 g monomer). The polymer obtained at 40% conversion of monomer was dried at 50°C and 10⁻² mm. Its appearance was tacky and light-brown. The viscosity-average degree of

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polymerization was 690 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 824000. 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 described²⁾.

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.

RESULTS

Viscosity Change of the 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.

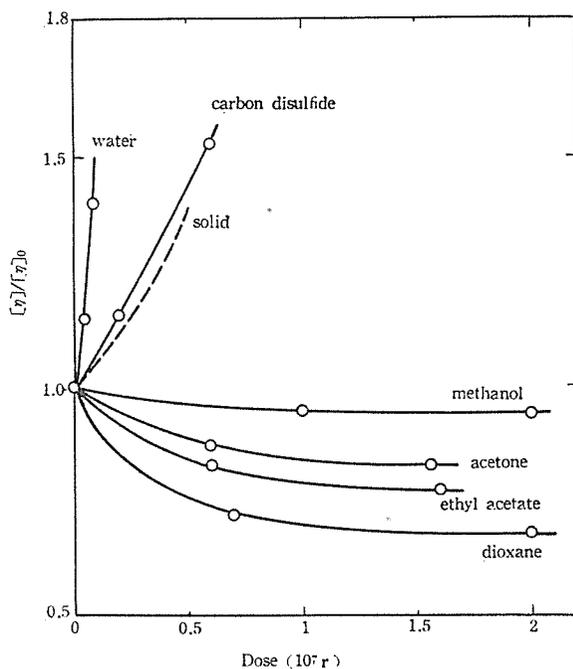


Fig. 1. Irradiation of PVME in various solvents at polymer concentration of 0.8 wt. %.

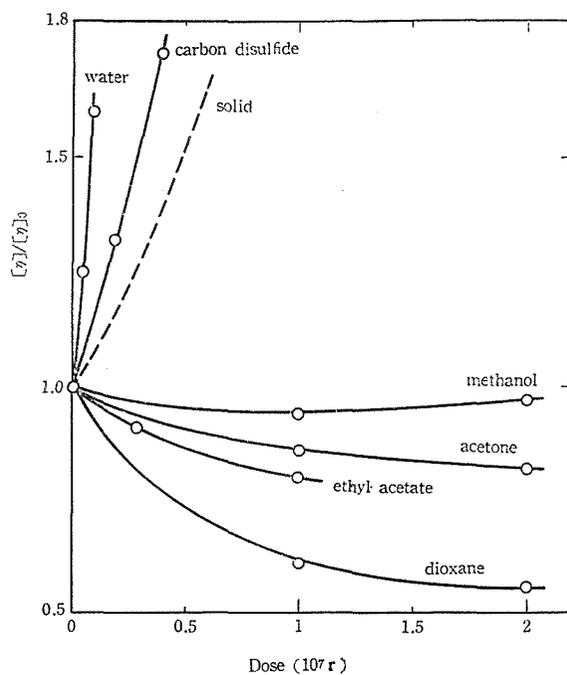


Fig. 2. Irradiation of PVME in various solvents at polymer concentration of 3.0 wt. %.

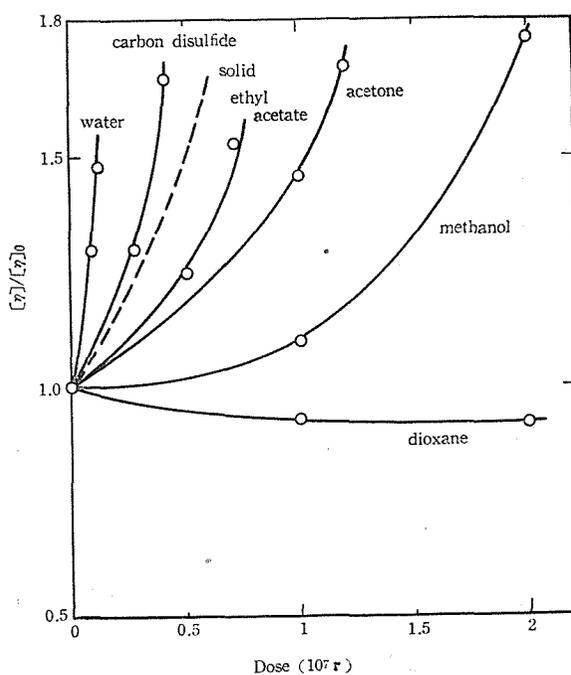


Fig. 3. Irradiation of PVME in various solvents at polymer concentration of 20 wt. %.

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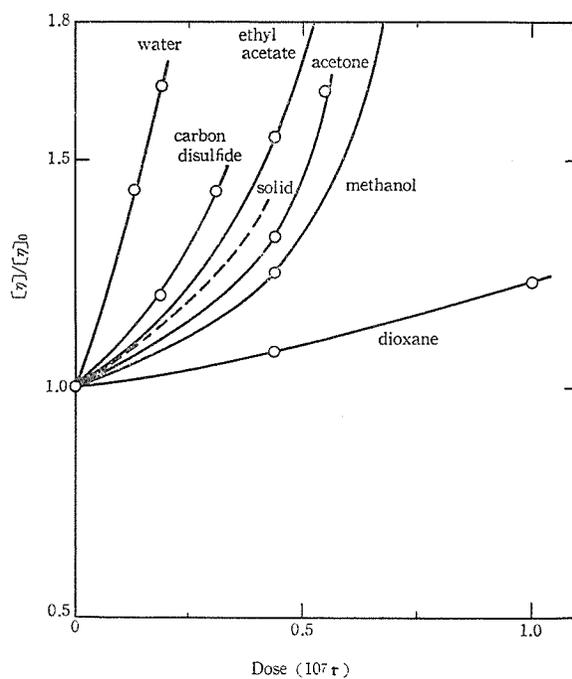


Fig. 4. Irradiation of PVME in various solvents at polymer concentration of 50 wt. %.

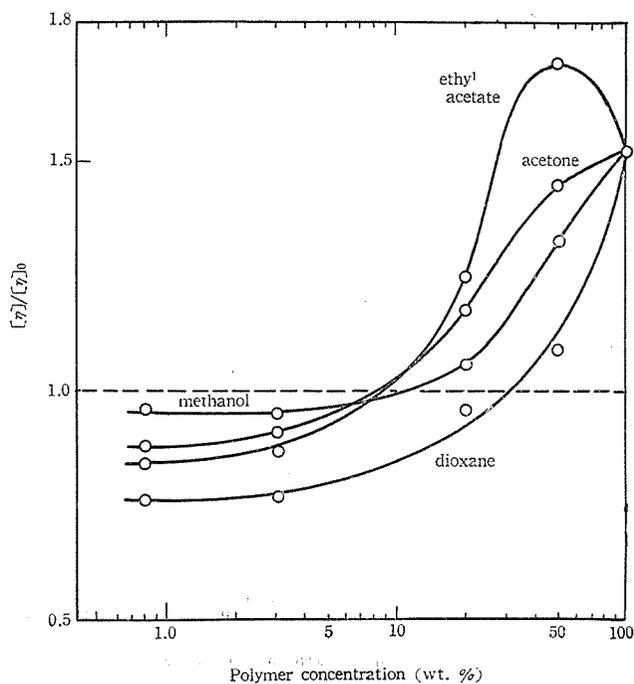


Fig. 5. Irradiation of PVME in various solvents at a dose of 5×10^6 r.

Plots of the viscosity changes $[\eta]/[\eta]_0$ against radiation dose for the irradiation at the concentration of 0.8, 3, 20 and 50 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 CS_2 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 pointing out 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 would 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 clearness of the irradiated solutions.

Gelation Dose Dependence on the Polymer Concentration

The doses for incipient gelation were determined for the 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.

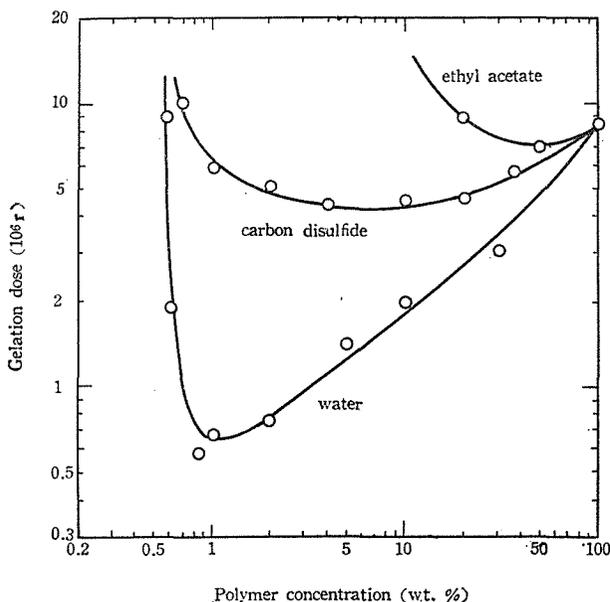


Fig. 6. Gelation dose as a function of polymer concentration for PVME irradiated in various solvents.

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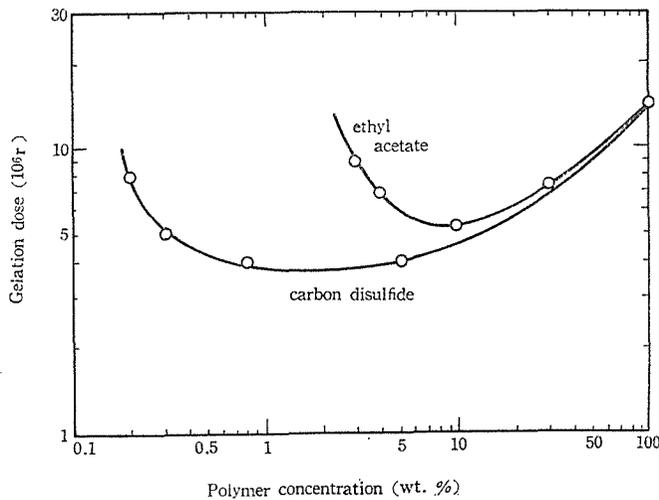


Fig. 7. Gelation dose as a function of polymer concentration for polystyrene irradiated *in vacuo* in ethyl acetate and carbon disulfide. (No. av. M. W. of unirradiated polystyrene=824000. Dose rate= 1.50×10^6 r/hr.)

DISCUSSION OF RESULTS

In our preliminary experiments, it was found that the irradiation of PVME in solid state *in vacuo* led to gel formation with a G -value of crosslinking=1.64, $q_0=1.9 \times 10^{-4}$ and $p_0=0.31 \times 10^{-4}$, where p_0 and q_0 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 may be regarded as a model material to study the role of solvent.

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 (Ccrit.) lies very near to that for the aqueous solution. CS_2 seems to affect the crosslinking not *via* the solvent radicals, but act only as a diluent, because 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 CS_2 solution is determined as a result 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 CS_2 solutions over a wide range of the concentration except near Ccrit., the following important conclusion may be drawn: the promotion of crosslinking by water is attributed to the indirect effect of the reactive 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 Ccrit., we will discuss in subsequent papers.

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 6. 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 $\text{OH}\cdot$ and $\text{H}\cdot$ 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 seems to have little tendency to abstract hydrogen from macromolecules, but more likely to deactivate the macroradicals⁹. 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 equal except for the case of acetone. Therefore, it is very reasonable that the difference of radiation-induced viscosity changes and the reversion of the order of organic solvent should be interpreted in terms of the difference of solvation and mobility of the polymer. The former prevents both the cage-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 difference 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 acceptable.

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

Solvent	$[\eta]_0$	G_R -value ^{a)}	Viscosity of solvent (20°C) (centipoise)
Water	0.169		
Carbon disulfide	0.291	0.52	
Methanol	0.393	15.0	0.593
Acetone	0.396	31.2	0.331
Ethyl acetate	0.400	19.9	0.449
Dioxane	0.453	12.5	1.26

^{a)} The values obtained by Magat, Chapiro *et al.* $G(\text{Fe}^{+++})=15.6$.

At higher concentrations, on the other hand, crosslinking predominates over degradation 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 life time 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 proceed 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.

GENERAL DISCUSSION ON THE 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 of the possibility of solvent having influence on 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 make 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 the solvent effect is almost overshadowed by the radical effect. $H\cdot$ and $OH\cdot$ favor crosslinking, while $Cl\cdot$ and $HO_2\cdot$ (formed by the reaction of $H\cdot$ 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, as the aqueous solution becomes so dilute that a macromolecule can not interact with the others, the gelation dose increases suddenly to a infinite 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), the 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 obtain-

ed at the irradiation of PVME (see Fig. 6). ($[\eta]_0$ of unirradiated polystyrene were 1.85 and 1.14, in CS_2 and ethyl acetate, respectively.) It was also found in our experiments that CS_2 solution of rubber also set 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 contact 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 G_x -values**

The interpretation of the radiation effects in this case becomes more difficult than the proceedings, because the solvent effect as well as the 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. The gelation dose-concentration curve has a minimum point in that case, 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.

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REFERENCES

- (1) I. Sakurada and Y. Ikada, *This Bulletin*, 39, 99 (1961).
- (2) I. Sakurada and Y. Ikada, *This Bulletin*, 40, 1 (1962).
- (3) A. Henglein, *J. Phys. Chem.*, 63, 1852 (1959).