

Effects of Gamma Radiation on Polymer in Solution. (IV) Crosslinking and Degradation of Poly(Acrylic Acid) in Aqueous Solution.

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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 both 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, and both the gelation dose and the critical concentration for gel-formation increased as the degree of neutralization of polymers increased. The critical concentrations were 0.25, 0.30, 0.56 and 1.0 wt. %, for polymers with degrees of neutralization of 0, 5, 10 and 20%, respectively. When NaCl was added to the solution for irradiation so as 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 NaCl became higher than 0.01N, gel-formation was increasingly suppressed with increasing NaCl concentration. This fact demonstrates that there is an optimum expansion of polyion for crosslinking in aqueous solution. 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.

INTRODUCTION

Since the early demonstration by Charlesby and Alexander^{1,2)} that aqueous solutions of several polymers set to a continuous gel under irradiation with high energy radiations, the effects of radiation on polymers in aqueous solutions have received much attention in the literature. In our laboratory, also, a series of investigation was initiated to provide further informations about radiation effects on polymer solutions, and some of papers concerning the role of solvents playing at the irradiation of polymers in aqueous and organic solutions have already been published^{3,4)}.

As is well known, on irradiation of crosslink-type polymers in deaerated aqueous solutions, no gel is observed if the polymer concentration of solution is lower than a certain value which depends on such factors as the nature of polymer and its degree of polymerization. If the concentration becomes slightly higher than this value, however, gelation occurs suddenly and the dose required for incipient gelation falls rapidly with increasing concentration. Then, after

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reaching a minimum, the gelation dose increases again rather slowly.

Although various theories⁵⁾ have been proposed to explain this peculiar shape of the curve obtained by plotting gelation dose against polymer concentration, it seems to us that the conclusive explanation is not given yet. One possible reason for this is lack of available data. A satisfactory interpretation of the mechanism of crosslinking occurring in dilute aqueous solution could hardly be obtained in the absence of any knowledge regarding the physical significance of the critical concentration for gel-formation.

In the previous paper⁶⁾, radiation effects were studied on one of charged polymers, *i.e.*, poly(vinyl alcohol) partially acetalized with glyoxylic acid (PVAG) whose carboxyl group contents were ranged from 0 to 3.57 mol %. It was found that both the crosslinking and the degradation were strongly affected by the degree of expansion of the polyion, and it was concluded that the critical concentration corresponds to the concentration at which overlapping of polymer spheres just commences. In this case, however, as the polymer is regarded as a copolymer, it happened that change in chemical composition of the polymer accompanying acetalization reaction affected 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, poly(acrylic 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 the charge density can be controlled readily by addition of alkali such as NaOH without modification of side groups.

EXPERIMENTAL

Material. Purified acrylic acid was polymerized in 4.3 wt. % aqueous solution using 3×10^{-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 IR-45. The polymer was used without any treatment of fractionation for the following experiment. The viscosity-average degree of polymerization, calculated from an equation⁷⁾, $[\eta] = 6.52 \times 10^{-3} \bar{P}^{0.64}$ (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 $10^7 \Omega \text{cm}$, and NaCl (analytical grade) was used.

Irradiation procedures. The source of gamma-rays was Co-60 at the Institute for Chemical Research of Kyoto University. At the time the source was used, it was rated at 1.50×10^5 r/hr. Irradiation was carried out at room temperature both in the presence and in the absence of air. Elimination of air from the solution was made as follows. After glass ampules containing the solution for irradiation were connected with a vacuum line, successive shocking was given to the ampules under a reduced pressure in order to bubble out the dissolved

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 shaking. 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 ones.

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 sol fraction which occur at gel point. In the case of irradiation of solution, 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 the appearance of the irradiated solution which was taken out from the irradiation position at a few minute intervals.

RESULTS

1) Irradiation of Deaerated Solution

1.1) In the absence of NaCl. Fig. 1 shows the concentration dependence of η_{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 solutions as a typical polyelectrolyte even in the case of a degree of

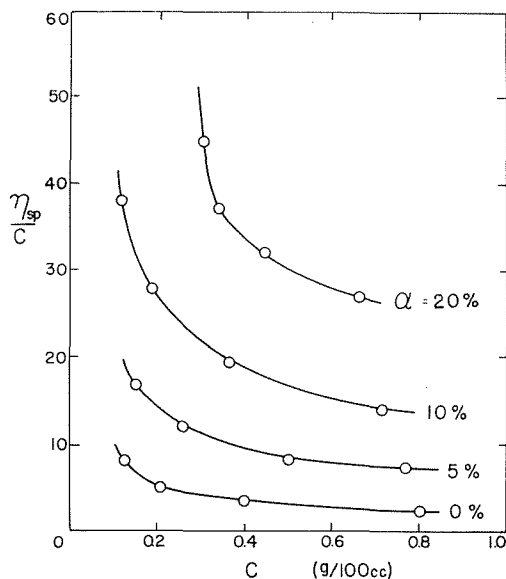


Fig. 1. Concentration dependence of the reduced viscosity in the absence of added salt for the unirradiated PAA with various degrees of neutralization α .

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 gelation dose. This is illustrated in Fig. 2, where gelation dose was plotted against 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 3~4%, the gel-formation seems to be virtually independent of the degree of neutralization. Alexander and Charlesby²⁾ have shown that the PAA does not exhibit crosslinking when its

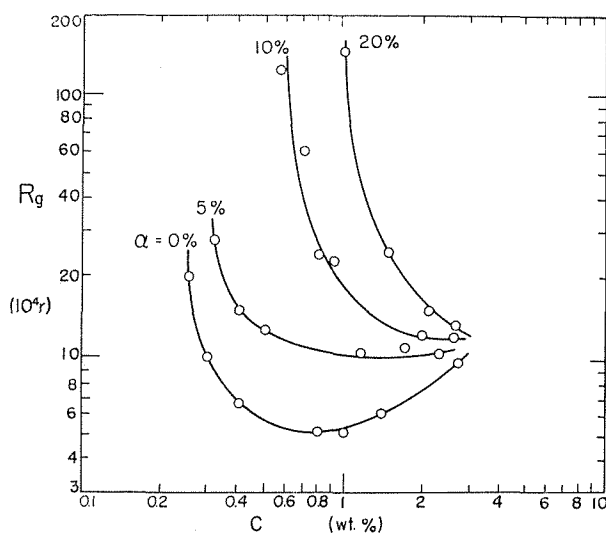


Fig. 2. Relation between the gelation dose R_g and the polymer concentration C for PAA with various degrees of neutralization α . PAA was irradiated in the salt-free solution.

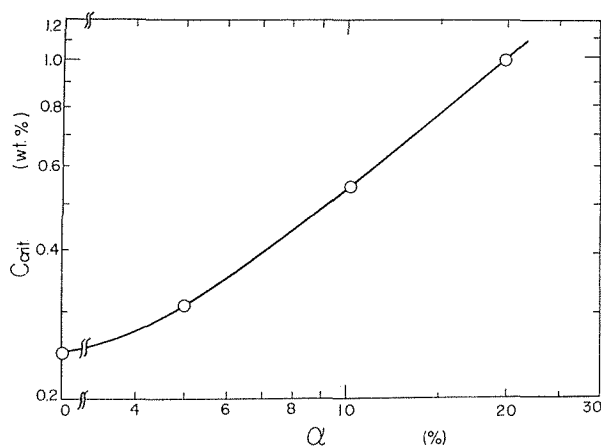


Fig. 3. Critical concentration C_{crit} for gel-formation of PAA with various degrees of neutralization α . PAA was irradiated in the salt-free solution.

degree of neutralization becomes higher than 10%. In our case, gel was formed even for the PAA 20% neutralized. 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.

1.2) In the presence of NaCl. As can be seen from Fig. 1, the expansion of polyion 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 polyion influences the crosslinking reaction, the following experiment was carried out using NaCl as an added salt and unneutralized PAA 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 experiment⁸⁾ 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 PAA in the presence of

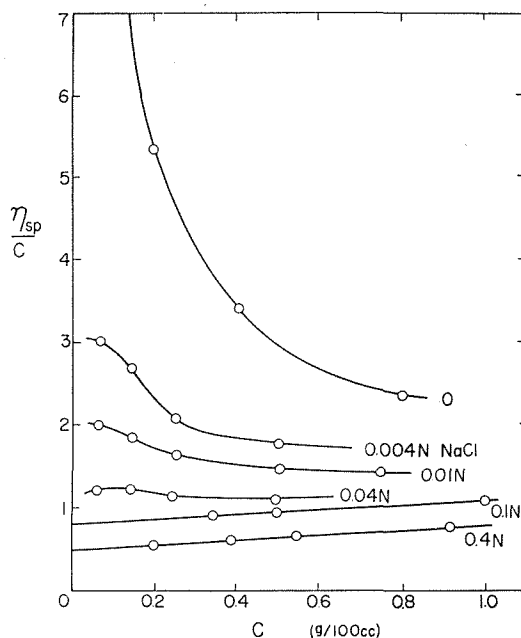


Fig. 4. Concentration dependence of the reduced viscosity in the presence of the various amounts of NaCl for the unirradiated PAA in acid form.

various concentrations of NaCl. As is seen from Fig. 4, addition of 0.1N 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 0 to 0.4N NaCl is plotted in Fig. 5 against the polymer concentration. It is of

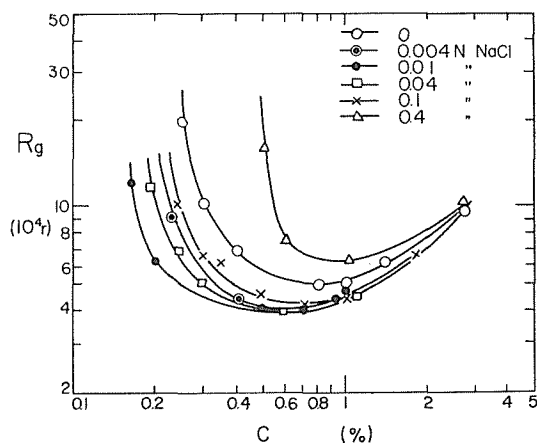


Fig. 5. Relation between the gelation dose R_g and the polymer concentration C for PAA with various amounts of added NaCl. PAA was irradiated in acid form.

particular interest to point out that gel can be formed more easily by the presence of NaCl unless the NaCl concentration is higher than 0.01N. Influence of NaCl on the critical concentration is shown in Fig. 6, which indicates clearly that gel-formation occurs more readily, at first, with increasing NaCl concentration, whereas beyond a NaCl concentration of 0.01N, the formation is retarded as the concentration increases.

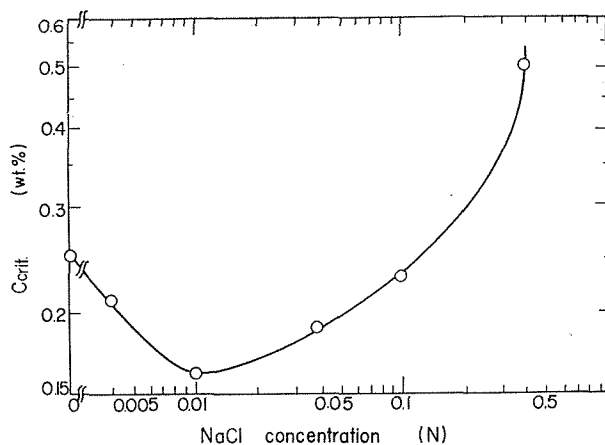


Fig. 6. Critical concentration $C_{crit.}$ for gel-formation of PAA in acid form irradiated with various amounts of added NaCl.

2) Irradiation of Aerated Solution

2.1) **In the absence of NaCl.** Concerning irradiation of polyelectrolytes in aerated aqueous solution, several studies have been already carried out⁹⁻¹⁴, especially with an aim to obtain an understanding of the effects of radiation on living systems. 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 to compare with the results of deaerated solution.

Fig. 7 shows the percentage decrease in viscosity induced under irradiation of 0.3% solution at a dose of 2×10^4 r. The viscosity of solution was found to be lowered under irradiation, and the decrease in viscosity became larger as the degree of neutralization increased.

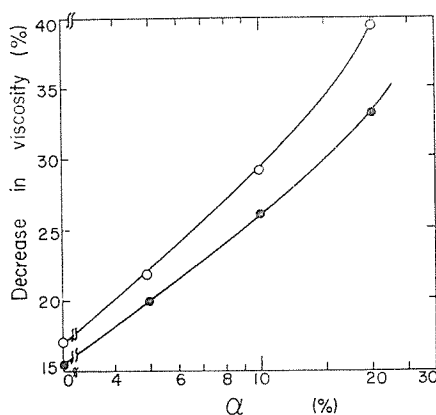


Fig. 7. Degradation of PAA with various degrees of neutralization α under irradiation in the presence of air, in 0.3% aqueous solutions and at a dose of 2×10^4 r. Viscosities were measured in the absence of added salt (○) and in 2N NaOH solution (●).

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 PAA irradiated at a dose of 2×10^4 r in 0.3% aerated 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 0.4N.

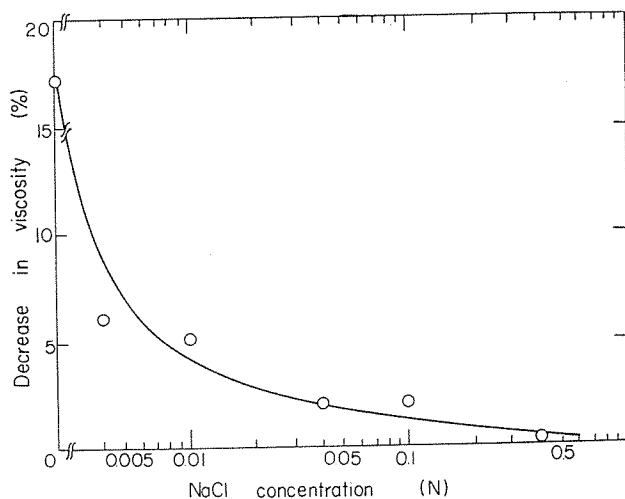


Fig. 8. Degradation of PAA in acid form with various amounts of added salt under irradiation in the presence of air, in 0.3% aqueous solution and at a dose of 2×10^4 r.

DISCUSSION

On the Crosslinking. When the mechanism involved in radiation-induced crosslinking of polyelectrolyte in aqueous solutions is to be discussed, it should be always 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 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 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 work⁽⁶⁾ which is again shown in Fig. 9 (Fig. 3 in the original paper). The curve of Fig. 9 indicates that, as the charge density of polymer ions increases

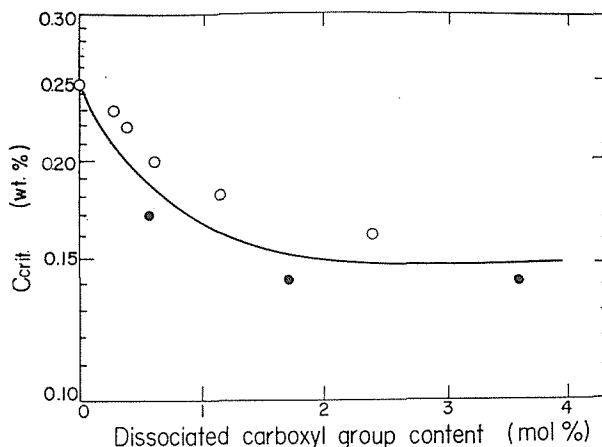


Fig. 9. Critical concentration C_{crit} for gel-formation of poly(vinyl alcohol) partially acetalized with glyoxylic acid irradiated in salt-free solution, varying the carboxyl group content: (○) in acid form; (●) in sodium-salt form.

from 0 to 3.57 mol%, the critical concentration decreases, while in the case of PAA 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 ionized in aqueous solution even in the unneutralized state. This can be, also, expected from the viscosity behavior shown in Fig. 1. Fig. 10 shows the critical concentration for gel-formation of PAA 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 = 3.47 mol% corresponds to the degree of neutralization = 0%. Paying attention to the difference of charge density, one can see from Figs. 9 and 10 that, as 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 mol%, it

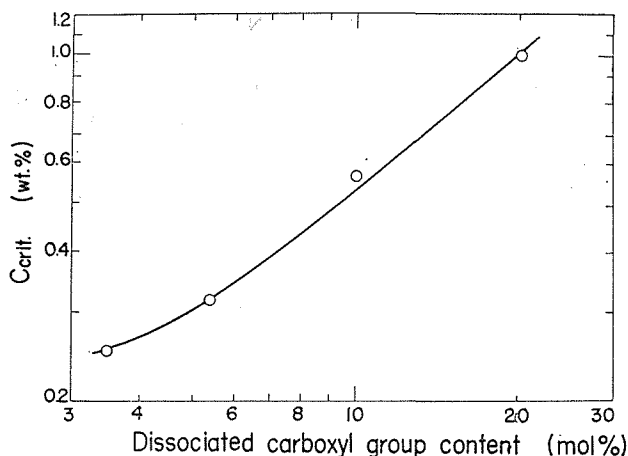


Fig. 10. A modified plot of critical concentration $C_{crit.}$ for gel-formation of PAA with various degrees of neutralization α irradiated in the salt-free solution as a function of actually dissociated carboxyl group content.

begins to increase. The presence of the minimum strongly suggests the interplay of two competing effect influencing crosslinking reaction. This may be also suggested by Fig. 6. Since these phenomena have been observed only in the crosslinking of polyelectrolytes, it appears likely that the two competing factors may come into effect 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 expansion. 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.

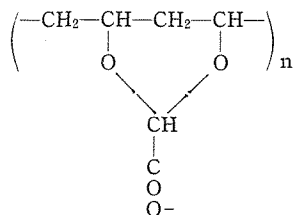
In a range of lower ionized carboxyl group contents, the effect of the increase in size may overshadow that of prevention of radical combination. Therefore, at first, the critical concentration may become lower with increasing charge density as is seen in Fig. 9. However, when the ionized group content 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 NaOH. In other words, addition of NaCl causes the ionization to decrease and hence reduces the expansion of polyion. As the concentration of NaCl increases, the repulsion preventing the radical combination decreases, so that the gelation 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 intra-molecular-crosslinked polymer was formed when solutions containing NaCl above 0.01N were irradiated below a critical concentration. In this respect, details will be presented in the subsequent paper.

On the degradation. Inspection of Figs. 7 and 8 shows that the degradation becomes increasingly more efficient as the charge density of polymer chain increases. This fact was also found by other workers^{9,11,13,14)} 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-by, and also that the C-C 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 PVAG whose structure is given by :



In this case, the C-C bond of the main-chain is fairly distant from the ionized carboxyl group. Therefore it seems uniplausible 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 polyion 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 0.3% 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 by some way, over-all extent of degradation will become larger naturally. It seems very probable that the repulsive 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^{9,11)}.

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