

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

Poly(vinyl Alcohol) Partially Acetalized with Glyoxylic Acid

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When polyvinyl alcohol (PVA) partially acetalized with glyoxylic acid (PVAG) was irradiated in air-free aqueous solution without added salt, gelation occurred more readily and the critical concentration for gel formation was reduced, as the degree of expansion of PVAG was increased. However, when NaCl was added to the solutions before irradiation so as to make the expansion of all PVAGs 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.

INTRODUCTION

The radiation chemistry of the polymer in solution, especially in aqueous solution, has been studied intensively by many workers¹⁾ 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 gelation 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 proposed²⁾. 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 partial-

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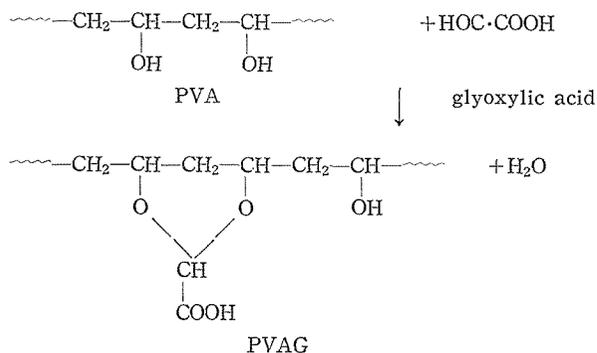
ly acetalized with glyoxylic acid (PVAG).

EXPERIMENTAL

Preparation of Sample

PVAG has first been prepared by A. Nakajima *et al*³⁾ 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 elsewhere³⁾.

The scheme of acetalization is:



The parent PVA used was an industrial product and had the degree of polymerization of 1618. 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 PVAG. It has been shown by I. Sakurada, M. Hosono and N. Ise⁴⁾, from potentiometric measurements, that PVAG is entirely analogous in its neutralization behavior to such a strong acid as HCl having pK of 2.4~2.6. 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 0.1 N 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.

Sample	B-1	B-2	B-3	B-4	B-5
Total carboxyl group content (mol %)	0.382	0.552	0.862	1.68	3.57
Dissociated carboxyl group content (mol %)	0.277	0.394	0.600	1.13	2.37

Preparation of Aqueous Solution and Irradiation Procedure

Solutions of lower polymer concentrations were prepared from the stock solu-

tions 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 Curies Co-60 source. The dose rate was about 1.55×10^5 r/hr. In the case of aerated solutions, they were irradiated in conical flasks without stopper under the same irradiation condition as described above.

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.

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.

RESULTS

Irradiation in the Absence of Added Electrolyte

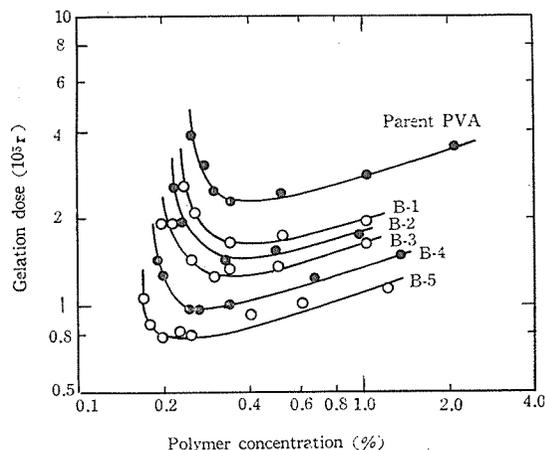


Fig. 1. Gelation dose-polymer concentration curves of PVAG irradiated in air-free aqueous solution.

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 curves¹⁾ generally observed when water-soluble vinyl polymers are irradiated in air-free 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 range of the carboxyl group content studied. This suggests

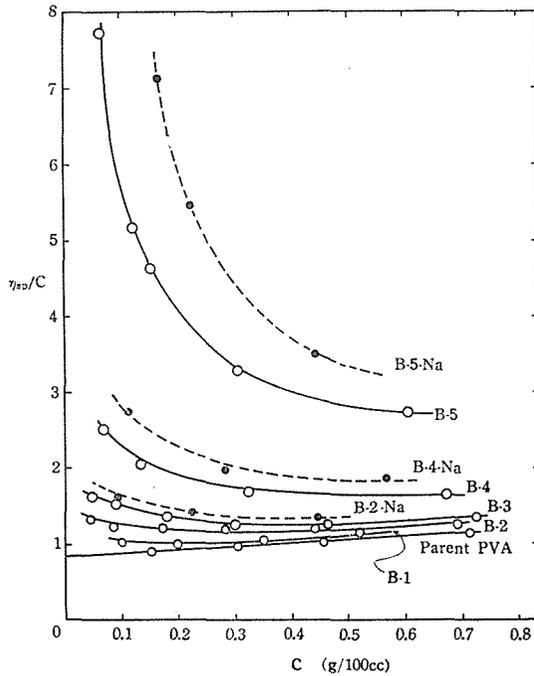


Fig. 2. Reduced viscosity-polymer concentration curves of PVAG in aqueous solution.

- , acid form (-COOH)
- , carboxyl groups are 100% neutralized (-COONa)

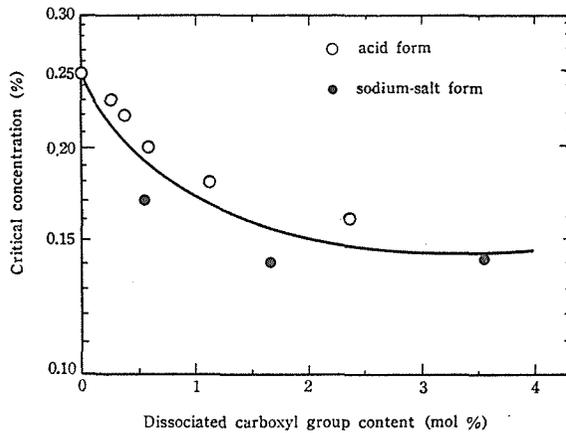


Fig. 3. Relation between the critical concentration and the dissociated carboxyl group content of PVAG.

that the crosslinking of the polymer in solution is closely related to the dimension or the expansion of the polymer molecules, since the PVAG is expanded more strongly with increasing carboxyl group contents as shown in Fig. 2, where reduced viscosities of unirradiated PVAG (acids and sodium-salts fully neutralized with NaOH) in aqueous solution are plotted against the polymer 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 polyelectrolyte even in the case of B-1 whose carboxyl group content is so 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 plotted.

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 N 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 0.2 N 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 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 cross-

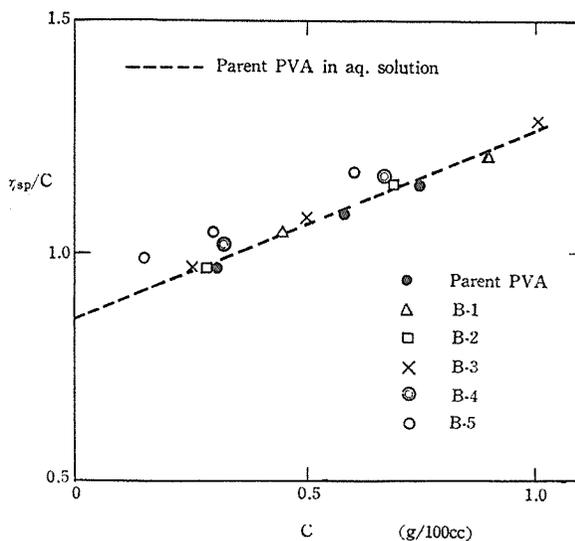


Fig. 4. Reduced viscosity-polymer concentration curves of PVAG in 0.2 N NaCl.

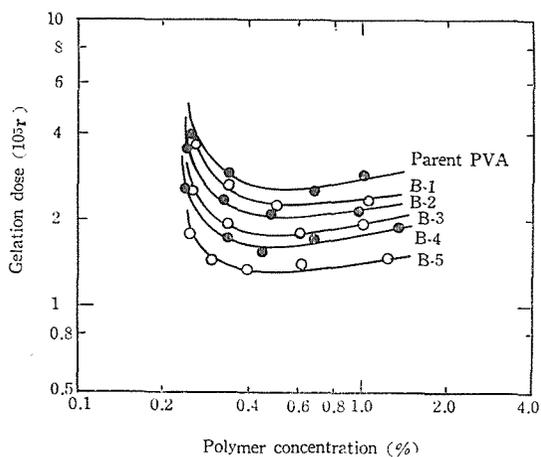


Fig. 5. Gelation dose-polymer concentration curves of PVAG irradiated in 0.2 N NaCl in the absence of air.

slinking 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 solution⁹⁾, the gelation dose was found to be decreased as the degree of acetylation was increased.

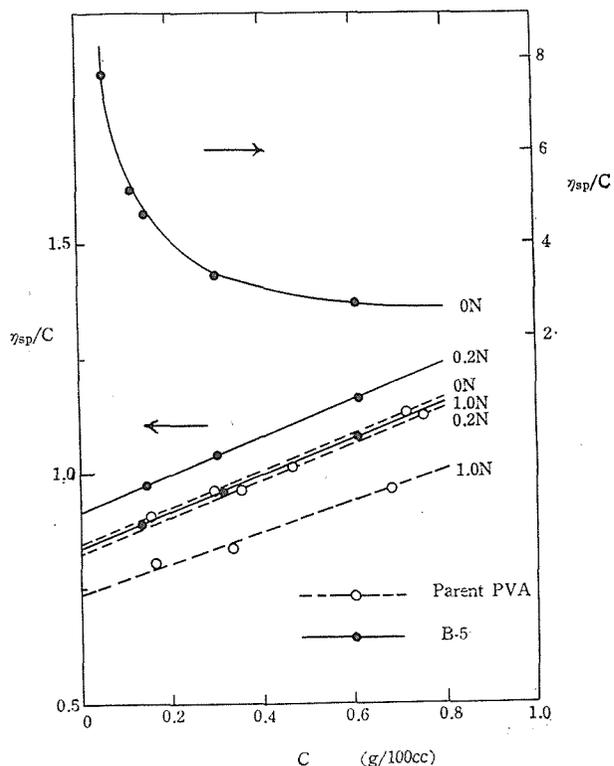


Fig. 6. Reduced viscosity-polymer concentration curves of parent PVA and B-5 in 0, 0.2 and 1.0 N NaCl.

Effect of Ionic Strength

Fig. 6 shows viscosities measure in 0, 0.2 and 1 N NaCl aqueous solutions, and Fig. 7 the results obtained on irradiation of these solutions. Samples used here were the parent PVA and B-5. It can be seen from Fig. 6 that viscosities of the parent PVA in 1 N 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.

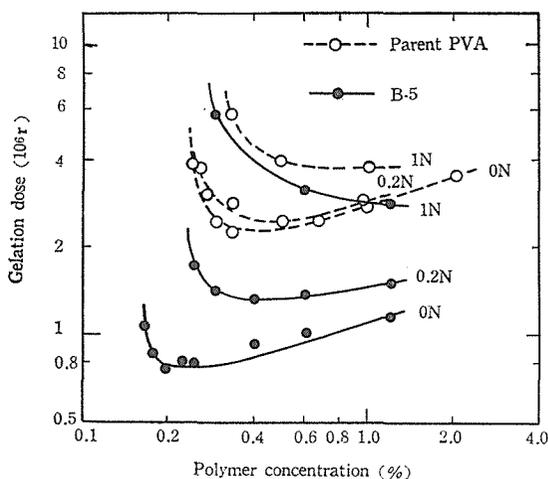


Fig. 7. Gelation dose-polymer concentration curves of parent PVA and B-5 irradiated in 0, 0.2 and 1.0 N NaCl in the absence of air.

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 0.2 N NaCl caused no change in gelation dose in the case of the parent PVA but caused a remarkable change for the B-5, may be considered to lend strong support for the 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.

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 40000 r. The degree of degradation is expressed as the percentage decrease in viscosity

$$\frac{\eta_{sp} - \eta'_{sp}}{\eta_{sp}} \times 100, \%$$

where η_{sp} and η'_{sp} are the specific viscosities of the solution before and after the

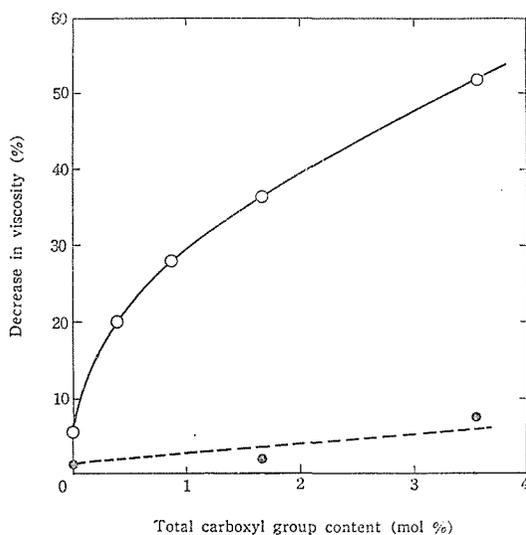


Fig. 8. Decrease in viscosity *versus* carboxyl group content of PVAG irradiated in 0.3 % aerated aqueous solution with a dose of 40000 r.

- , irradiated in the absence of added salt
- , irradiated in the presence of 1 N NaCl

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 P. Alexander *et al*.^(6,7) concerning the degradation of polyacrylic acid and polymethacrylic 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 N NaCl.

DISCUSSION

Critical Concentration and Expansion of Polymer

The result that there is a distinct trend 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 crosslink 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 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 which favors the crosslinking. This case has been, in fact, observed on the

aqueous solution of polyacrylic acid by P. Alexander and A. Charlesby⁹⁾. We, also, have been studying in this respect, and the details of this result will be published in the subsequent papers.

It may be concluded from the above considerations that the critical concentration corresponds to the concentration where the polymer molecules are first 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 aerated 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.

Calculation of Extent of Expansion

It is, therefore, possible to calculate the expansion of polyions 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 data 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 $100 M/N_L C_c$, where M is the molecular-weight of the polymer, N_L is Avogadro's number and C_c is the critical concentration expressed in g/100 cc. Therefore, the radius of the sphere R can be given according to the equation:

$$\frac{4\pi}{3} R^3 \times \frac{1}{0.74} = 100 M/N_L C_c \quad (1)$$

where 0.74 is the volume fraction for spheres in a closed packing array. The radii calculated from equation (1) are given as R_c in Table 2. On the other hand, according to T. A. Orofino and P. J. Flory⁸⁾, the end-to-end distance of a polyelectrolyte $\sqrt{\bar{h}^2}$ is:

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

Sample	NaCl (N)	$C_c(\%)$	$R_c(\text{Å})$	$R_E(\text{Å})$	$R_{OF}(\text{Å})$	
					R_{40}	R_{80}
Parent PVA	0	0.25	203	99	—	—
	0.2	0.26	200	—	177	201
	1.0	0.30	191	—	173	197
B-1	0	0.23	209	104	—	—
	0.2	0.25	203	—	179	202
B-2	0	0.22	212	110	—	—
	0.2	0.24	206	—	179	202
B-3	0	0.20	219	114	—	—
	0.2	0.24	206	—	179	202
B-4	0	0.18	228	130	—	—
	0.2	0.24	207	—	180	203
B-5	0	0.16	239	172	—	—
	0.2	0.24	208	—	183	208
	1.0	0.28	198	—	178	202

$$[\eta] = 0.9 \times 10^{21} \frac{(\sqrt{\bar{h}^2})^3}{M} \quad (2)$$

where $[\eta]$ is the intrinsic viscosity expressed in 100 cc/g. The values of $\sqrt{\bar{h}^2}$ can be transformed into the radius of the polymer sphere R using the relationship introduced by J. J. Hermans and J. Overbeek⁹⁾:

$$R^2 = \frac{5}{36} NA^2 \left(1 + \frac{(\sqrt{\bar{h}^2})^2}{NA^2} \right) \quad (3)$$

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 equations (2) and (3) are given as R_{OF} in Table 2, where R_{40} and R_{80} are values obtained on assuming $A=40$ and 80 Å, respectively. R of polymers in salt-free solutions was calculated from the Einstein equation assuming η_{sp}/c at the critical concentration to be $[\eta]$, 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_{80} are very close to R_c , while R_E are too small. The latter discrepancy may be attributed chiefly to the very rough approximation made for the calculation of R_E . Furthermore, it should be pointed out that R_c are not necessary in accord with R_E or R_{OF} , since the effective volume of the polymer sphere may vary depending on the property of the polymer solution to be considered.

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