Radiation-Induced Selective Main-chain Scission in Polyvinyl Alcohol

By Yutaka HIRANO*

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The overall effect of high energy radiation on organic substance is generally accepted to be the production of main-chain scission, with a corresponding decrease in the molecular weight and/or a crosslinking which finally forms an insoluble three-dimensional network structure.1-4) This behavior on irradiation has been correlated with the chemical structure of a repeating monomer unit in polymers and/or with their physicochemical properties just under irradiation.5-7) As a general rule, those polymers which have at least one hydrogen atom on every carbon atom become crosslinked, while those which have one quarternary carbon atom in a monomer unit are degraded.6)

Several papers8-10) have already been presented on the radiation-induced changes in polyvinyl alcohol. It is generally accepted that the irradiation of the polymer produces the main-chain scission and carbonyl group at the end of the chain fractured and/or in the main-chain.

This paper is concerned with the effect of such structural variations as head-to-head linkage on the radiation-induced main-chain scission of polyvinyl alcohol.

There are two types of chemical structures in the main-chain of polyvinyl alcohol.11) One is the regular, predominant head-to-tail structure, in which the monomer substituent OH occurs on alternate carbon atoms of the chain. Another is the anomalous structure in which a pair of substituents is situated on consecutive carbon atoms. The latter arises from the head-to-head addition of vinyl acetate, which gives a mother polymer for polyvinyl alcohol. This anomalous structure occurs on the average in every several tens of monomer units in the "usual" polymer.

Another paper12) has briefly suggested that the main-chain scission of polyvinyl alcohol on irradiation might occur at one part of this anomalous structure, i. e., the 1, 2-glycol structure. In the present investigation, polyvinyl alcohols which are different in the proportion of the 1, 2-glycol structure to the main-chain have been irradiated. A more complete picture of the experimental evidence for the selective main-chain scission at the special chemical structure in the polymer will be given here. The mechanism of the selective main-chain scission will also be discussed.

Experimental

The Preparation of Polyvinyl Alcohols for Irradiation Studies. — Vinyl acetate monomers, freshly distilled in a stream of nitrogen, were polymerized under various conditions, as is indicated in Table I. The resulting mixture of polymers and unreacted monomers was dissolved in benzene, from which the polymer was precipitated by the addition of an excess of petroleum ether. The polymers were then converted to polyvinyl alcohol by stirring, for 1 hr. at room temperature, a 3% solution of the polymer in methanol containing

TABLE I. PREPARATION AND PROPERTIES OF POLYVINYL ALCOHOLS STUDIED

Sample	Polymerization				P	δ*2
	AIBN %*1	Temp. °C	Time hr.	Conv. %		mol. %
A	—	—	—	—	149	0.0
B*3	3×10^{-2}	60	25	91	148	1.11
C	—	30	—	—	1460	1.17
D*4	—	60	—	50	1580	1.54
E	6×10^{-3}	140	2	23	1200	2.61
F	5×10^{-3}	170	2.5	26	890	2.81
G	2×10^{-3}	200	0.5	28	760	3.00
H	6.7% water-containing D-polymer					

*1 α-α' azobisisobutyronitrile
*2 1, 2-glycol structure content
*3 75% ethanol solution polymerization
*4 "usual" polymer, 20% methanol solution polymerization

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* Present address: Research Laboratory, Kurashiki Rayon Co., Ltd., Kurashiki, Okayama.

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0.05 mol. sodium hydroxide per liter. The precipitated product was dissolved in water containing a small amount of alkali in order to make the conversion more complete. After the solution had been left standing for 1 hr., polyvinyl alcohol was precipitated by pouring it into an excess of methanol. The product was purified by extraction with methanol, using a Soxhelt extractor. Then it was dried in a vacuum to a constant weight and stored in a desiccator over calcium chloride.

Polyvinyl alcohol containing no 1,2-glycol structure in the main-chain was obtained by the oxidation of "usual" polyvinyl alcohol with sodium periodate, which selectively attacks the 1,2-glycol structure.[13] "Usual" polyvinyl alcohol was dissolved in water in a 4% solution, and five times as much reagent as was consumed was added as an aqueous solution. The oxidation reaction was conducted at 30°C for 1 hr. with a constant stirring. It was thus established that all the 1,2-glycol structures in polymer are severed under these experimental conditions. The reaction mixture was then poured into an excess of cooled methanol. It was necessary to use cooled methanol for carrying out the precipitation without a substantial loss of the oxidized polymer, because the degree of polymerization of the oxidized polymer was very low. The precipitated polymer was filtered off and then washed well with cooled methanol until the filtrate did not show the presence of IO_3^- and IO_4^- ions any more. Most of the end groups of this oxidized polyvinyl alcohol are supposed to be of a chemical structure such as $-CH_2CHO$ judging from the analogous reaction between monomeric glycols and $NaIO_4$. For the reduction of this aldehyde-type end group to the alcohol-type, the oxidized polymer was treated with $NaBH_4$. A reagent (0.8 g.) was mixed with 100 cc. of the oxidized polymer solution containing 4 g. of polymer. After the solution had stood for 48 hr. while being occasionally stirred at room temperature, the reduced polymer was precipitated into methanol, cooled, and acidified with acetic acid. It was then filtered off and washed with methanol until no borate ions could be detected in the filtrate by flame reaction. Finally it was dried in a vacuum at room temperature.

The water-containing polyvinyl alcohol sample was prepared from the 30% aqueous solution of the polymer by moulding it into a rod-like shape, 3~4 m./m. in diameter and 7~8 cm. long. This water-containing sample was dried at room temperature over a long period of time to the desired extent of water concentration. The mole percent of the 1,2-glycol structure in various polymer samples was computed from the degree of degradation with sodium periodate by the use of Flory's method.[11] Table I lists the preparation and characterization data for the polymers.

The Irradiation of Samples. — Polymer samples (1.5~2.0 g.) were weighed in hard glass tubes for the irradiation in a Co-60 γ-ray source at the Japan Atomic Energy Research Institute. An ambient temperature of about 20°C was maintained during the irradiation.

Each tube containing a dry powder sample for the irradiation was evacuated to the pressure of 10^{-4} mmHg. In all casses, the vacuum was retained overnight, indicating that there was no significant amount of precipitant or solvent left in the polymer; then each tube was sealed under a vacuum. Each tube containing the water containing polymer was then sealed in the presence of air and irradiated.

Molecular Weight Measurement. — The solution viscosities of the irradiated polymer samples were measured in water at 30°C using an Ostwald-type viscometer. Three or four concentrations of each of the irradiated polymers were run, and the plots of both the viscosity number, η_{sp}/c, and the logarithmic viscosity number, $\ln(\eta_r/c)$, versus the concentration were extrapolated to zero concentration in order to determine their limiting viscosity number, $[\eta]$. The limiting viscosity numbers of polymers which are irradiated and subsequently oxidized with sodium periodate were obtained from the single-concentration viscosity data at a concentration sufficiently low to obviate the extrapolation of $\ln(\eta_r/c)$ to infinite dilution. Five times as much reagent as was consumed was added to a 10 cc. portion of the irradiated polymer solution containing around 0.13 g. of the polymer. After this mixture had stood for 30 min. at 30°C, the viscosities were measured. Polymer concentrations were computed from the known concentration of the initial aqueous solution and the total volume after the reagent was added. Molecular weights were computed from the following relationship;[14]

$$[\eta]=6.66\times10^{-4}M^{0.64}$$

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

Results and Discussion

The Irradiation of Water-containing Polyvinyl Alcohol. — The viscosity changes in the irradiated water-containing polyvinyl alcohol before and after oxidation with $NaIO_4$ are shown in Fig. 1. It is found that a sudden gel formation occurs in the irradiated polymer, although the molecular weight of the polymer decreases gradually during the initial period of irradiation. This behavior on irradiation is very similar to that of the irradiated polypropylene.[15] The minimum radiation dose necessary to produce a gel is estimated to be about 23 Mr.

On the other hand, the limiting viscosity number of the polymer which is irradiated and subsequently oxidized with $NaIO_4$ steadily increases with the radiation dose.

Figure 2 illustrates schematically the main-chain scission and/or crosslinking of polyvinyl

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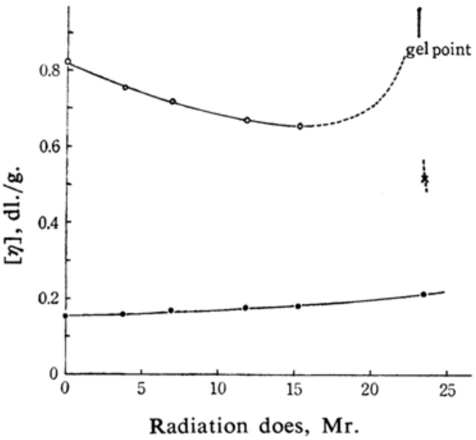

Fig. 1. Viscosity changes of irradiated water-containing polyvinyl alcohol ($\delta = 1.54$ mol.%) before and after oxidation with sodium periodate: Water content 6.7% (w/w). Intensity 4×10^4 r./hr. (○) before oxidation, (●) after oxidation, (×) viscosity of the soluble fraction (99.2%) of irradiated sample.

alcohol subjected to irradiation and/or chemical degradation with $NaIO_4$.

According to the theory of radiation-induced simultaneous degradation and crosslinking as developed by Saito,[16] the changes in the limiting viscosity number of the irradiated polymer are expressed as follows:

$$\eta(R)/\eta(0) = 1 + \{\alpha(\alpha+2)(\alpha+7)/6 - \alpha\lambda\}(cuR) + [\alpha(\alpha+1)\{(\alpha+2)(\alpha+3)(\alpha+7)(\alpha+14)/90 - (\alpha+2)(\alpha+7)\lambda/3 + \lambda^2\}](cuR)^2 + \cdots \quad (1)$$

where λ is ratio of the probability of the main-chain scission, r, and crosslinking, c, of monomer unit per unit of radiation dose; $\eta(0)$ and $\eta(R)$ are the limiting viscosity numbers of the polymer at zero dose and at radiation dose, R, respectively; u is a measure of the initial number average molecular weight, and α is the exponent of the relation between the viscosity and the molecular weight. This formula predicts that, if λ and α are the same in polymers, plots of $\eta(R)/\eta(0)$ versus uR of each of polymers can be superposed one upon the other by translation along the abscissa.

Provided that there are no differences in λ between the 1,3-glycol structure and the 1,2-glycol structure, the λ of *o*-PVA in Fig. 2 is equal to that of the "usual" PVA. Thus, *o*-*i*-PVA should decrease in viscosity with the radiation dose, since *i*-PVA decreases in viscosity during the initial period of irradiation. The treatment of this *o*-*i*-PVA with $NaIO_4$ might produce a further decrease in viscosity, if there exist 1,2-glycol structures formed by radiation-induced crosslinking. Furthermore, the degree of main-chain scission and crosslinking produced in this *o*-*i*-*o*-PVA is just the same as that in *i*-*o*-PVA, as is shown in Fig. 2.

The above-mentioned discussion leads us to the consideration that the viscosity of the "usual" PVA which is irradiated and subsequently oxidized with $NaIO_4$ should decrease with the radiation dose. This is inconsistent with the results shown in Fig. 1. The steady increase in the viscosity of irradiated and subsequently oxidized "usual" PVA would suggest that λ in a polymer which contains no 1,2-glycol structure is lower than that in a polymer which contains a 1,2-glycol structure in the main-chain. This discrepancy is considered to be partly due to the selective main-chain scission at a chemical structure such as a 1,2-glycol type on irradiation.

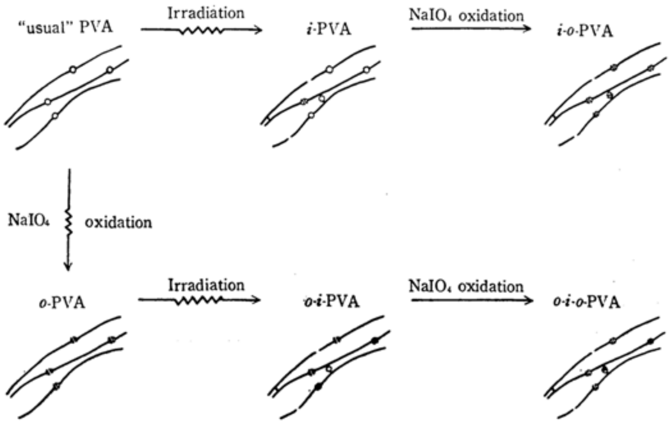

Fig. 2. Schematic main-chain scission and crosslinking of polyvinyl alcohol: —— 1,3-glycol structure, ○ 1,2-glycol structure.

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The Irradiation of Polyvinyl Alcohols Which are Different in the Proportion of the 1, 2-Glycol Structure. — Figure 3 illustrates the results of the irradiation of "usual" polyvinyl alcohol as the reciprocal degree of the polymerization versus the radiation dose, R. A monotonous decrease in the molecular weight, but no gel formation, was observed for this dry specimen up to 130 Mr., which is in contrast with water-containing specimen. The main-chain scission process is predominant and does not depend on the radiation intensity in the range covered. No color has been detected in any irradiated specimens in a vacuum in contrast with the yellow coloration which appears upon irradiation in air.

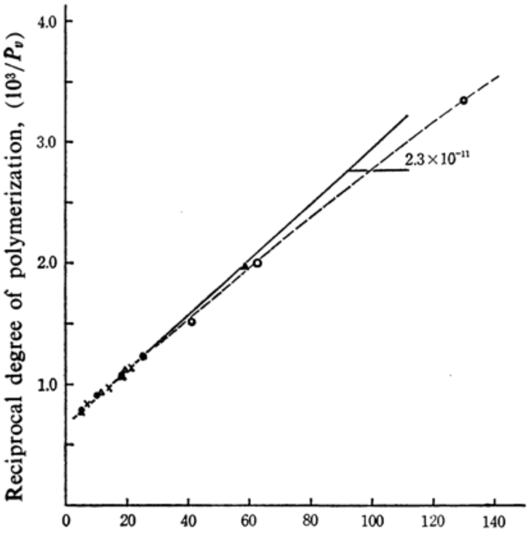

Fig. 3. Changes in the reciprocal degree of polymerization of irradiated polyvinyl alcohol ($\delta=1.54$ mol.%) with radiation dose: (×) 10^6 r./hr., (●) 6.4×10^5 r./hr., (△) 5.8×10^5 r./hr., (○) 2.8×10^4 r./hr.

Similar plots for the various polyvinyl alcohols which are different in the proportion of the 1, 2-glycol structure in the main-chain are shown in Figs. 4 and 5. The linearity of the curves obtained shows that the number of the main-chain scission produced is proportional to the radiation dose.

Pure random radiation-induced main-chain scission of the polymer reduces the initial molecular weight distribution to the most probable one and, then, predicts linear plots between $1/P_v$ and R. The relation is:[1]

$$(1/P_v) = (1/P_{v_1}) + w(KNE_d)^{-1}(R_2 - R_1) \quad (2)$$

where P_{v_1} and P_{v_2} are the viscosity average degree of polymerization of the polymer at radiation doses R_1 and R_2 ($R_1 < R_2$) respectively, N is Avogadro's number, E_d is the average energy absorbed in eV. per main-chain scission produced, 1 r.$=5.81\times10^{13}$ eV./g., w is the molecular weight of structural unit, and K is the ratio of the viscosity average degree of polymerization to the number average one, which is given by $K=\{\Gamma(\alpha+2)\}^{1/\alpha}$.

For polyvinyl alcohol with $w=44$ and $\alpha=0.64$, we may, therefore, calculate $E_d=2.32\times10^{-9}$ eV./slope for various specimens from Figs. 4

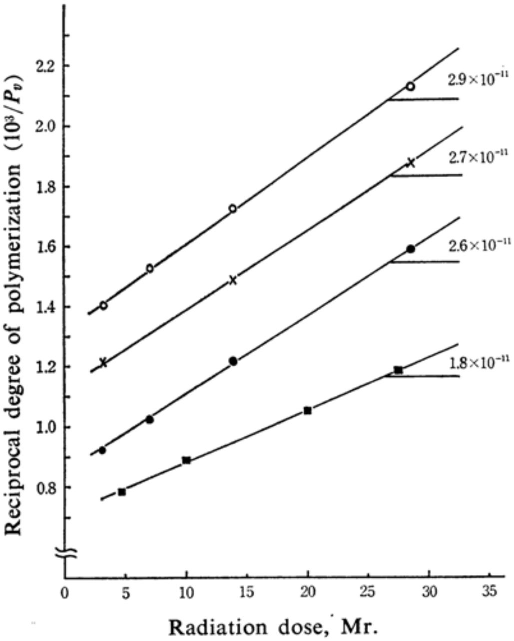

Fig. 4. Changes in the reciprocal degree of polymerization of polyvinyl alcohol samples with radiation dose: 1,2-glycol structure content, (○) 3.00, (×) 2.81, (●) 2.61, (■) 1.17 mol.%. Intensity 6.4×10^5 r./hr.

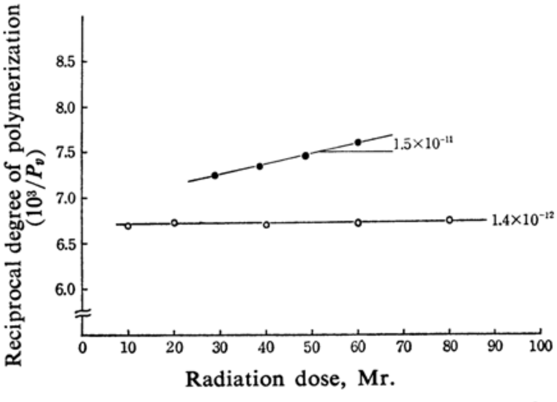

Fig. 5. Changes in the reciprocal degree of polymerization of polyvinyl alcohol samples with radiation dose: 1,2-glycol structure content, (○) 0.00, (●) 1.11 mol.%. Intensity 6.4×10^5 r./hr.

TABLE II. VARIATION IN E_d AND G_d WITH 1,2-GLYCOL STRUCTURE CONTENT

δ, mol. %	E_d, eV.	G_d
0.0	1670	0.06
1.11	154	0.65
1.17	128	0.78
1.54	100	1.00
2.61	88	1.13
2.81	85	1.17
3.00	79	1.26

and 5. In Table II the results are given as a function of the 1,2-glycol structure content, δ, in the polymer chain. The difference in G value for main-chain scission between $\delta=0$ mol.% specimen and $\delta=1.11$ mol.% one, which have nearly identical original degrees of polymerization, is beyond the range of experimental error. This fact definitely shows the predominant radiation-induced main-chain scission at a special part, such as the 1,2-glycol structure in the polymer chain.

Since it is not unreasonable to assume that the 1,2-glycol structures are distributed at random throughout the polymer, the molecular weight distribution of the irradiated polymer will approximate the most probable distribution, even if only these anomalous structures are selectively fractured on irradiation. This selectivity will, however, reduce the number of these structures on irradiation. Consequently, the average absorbed energy needed to produce a main-chain fracture varies as a function of the radiation dose and must increase gradually with an increase in the radiation dose. The departure from the linear relation between $1/P_v$ and R at high radiation doses in Fig. 3 may be ascribed to this specificity.

The Mechanism of Radiation-Induced Main-chain Scission.—A rapid approach to a certain value of G_d was observed with the increase in the 1,2-glycol content in the polymer chain (Table II and Fig. 6). It may, therefore, be suggested that a transfer of energy occurs from the 1,3-glycol structure to the 1,2-glycol structure along the polymer chain and that the latter part suffers a sacrificial damage. On the basis of the random distribution of the 1,2-glycol structure in the polymer chain, it is possible to deduce, from the G_d dependence on δ, the range of energy transfer offered by the 1,2-glycol structure. For this purpose let M represent the 1,3-glycol structure, I, the 1,2-glycol structure, and n, the number of units as a measure of the maximum range of energy transfer from M to I.

The relative probability of some configurations about a given M will be considered to be a function of the mole fraction of the 1,2-glycol structure, δ in the polymer chain. The probability of such a configuration when none of I is present within its n nearest neighbors on either side of M will be given as $(1-\delta)^{2n}$. In this configuration M can not lose its energy by transferring it to I and consequently, will be fractured with the probability of bond rupture per unit radiation dose, r_{13}. On the other hand, the probability of such a configuration when one or more I's are in existence within its n nearest neighbors on either side is equal to $1-(1-\delta)^{2n}$. In this case the energy transfer will occur from a given M to I. M will be protected against the bond ruputure by I. The released energy from M, however, will migrate and be "trapped" in one of the nearest neighboring I's. Therefore, this will give rise to a bond rupture of I, the probability of which is r_{12}. In other words, the 1,2-glycol structure may serve as an "energy sink" and draw off energy from the 1,3-glycol structure and dissipate it with the subsequent, sacrificial bond rupture. Thus, the total number of main-chain scissions, dS, produced with the radiation dose, dR, will be given by the equation:

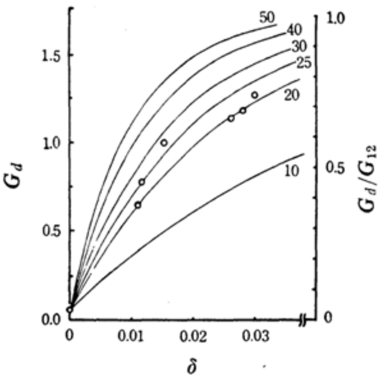

Fig. 6. G value for the main-chain scission plotted against the mole fraction of 1,2-glycol structure. Figures on the curve are the numbers of the monomer units in which the transfer of absorbed energy occurs.

$$dS=N(1-\delta)(1-\delta)^{2n}r_{13}dR+N(1-\delta)\times\{1-(1-\delta)^{2n}\}r_{12}dR+N\delta r_{12}dR \quad (3)$$

where N is the total number of units in the irradiated system.

By rewriting Eq. 3, we obtain:

$$(1/N)(dS/dR)=r=r_{12}-(r_{12}-r_{13})(1-\delta)^{2n+1} \quad (4)$$

The term on the left-hand side of Eq. 4 indicates the average probability for the main-chain scission of the polymer during irradiation. Thus, we obtain, by the use of the G_d value:

$$(G_d/G_{12})=1-\{1-(G_{13}/G_{12})\}(1-\delta)^{2n+1} \quad (5)$$

As $G_{13}=0.06$, G_{12} was evaluated as about 1.7 from Fig. 5 by the extrapolation of experimental results to $\delta=100$ mol.%.

A plot of (G_d/G_{12}) versus δ is shown in Fig. 6, along with the calculated curves for several values of n. It may be seen in the figure that the experimental points, although scattered, lie between two curves for which n is 20 and 25. For $n=20$, it is estimated that the range of energy transfer is about 60 Å along the zigzag chain of the polymer.

The phenyl group is known to have a protecting effect against radiation-induced changes in various co-polymer systems.[17-20] The energy transfer process is also postulated, and a value of $n=1\sim6$ for its range is estimated. The evaluated value, $n=20$, for polyvinyl alcohol is quite large. However, a transfer of energy over distances of 50 Å or more is estimated in scintilater systems.[21,22]

Summary

Polyvinyl alcohols which are different in the mole fraction of the head-to-head structure, in which two of –OH substituents are situated on consecutive carbon atoms, have been irradiated with Co-60 gamma rays in a vacuum at room temperature in order to investigate the effect of this anomalous structure on the radiation-induced main-chain scission of the polymer. The selective main-chain scission in polyvinyl alcohol has been observed at such positions as the head-to-head structure. The average absorbed energy necessary to produce a main-chain scission, i. e., E_d, is about 1700 eV. for polyvinyl alcohol containing no head-to-head structure, while E_d is 100 eV. for polyvinyl alcohol containing a 1.54 mol.% head-to-head structure. A rapid increase up to a certain value in G_d, the number of chain scissions produced per 100 eV. of energy absorbed by the polymer, has been observed with the increase in the head-to-head structure content in the polymer chain. Thus, it has been postulated that there is a transfer of radiation energy from the head-to-tail structure to the head-to-head structure. An estimation has been made on the range of energy transfer from the G_d dependency on the concentration of the head-to-head structure.

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Department of Applied Physics
Faculty of Engineering
The University of Tokyo
Hongo, Tokyo

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