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고분자 결합에 관한 연구(제 1 보). Anionic Polymer의 Graft Site 분포

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Studies of Graft Polymers (I). Graft Site Distribution of Anionic Polymer

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요 약. 고분자의 graft site 분포를 통계적 방법으로 구하고 그 이론치를 GPC를 사용한 실험에 의하여 증명하였다. 결과에 따르면 고분자의 metalation (Li^+ ion)은 통계이론에 따르고 anionic graft 반응결과는 homopolymer (side chain과 backbone 고분자) 및 graft site가 통계적으로 분포되어 있는 graft polymer로 구성되어 있다.

ABSTRACT. Graft site distribution of graft polymer was derived from a statistical model. Theoretical model was experimentally confirmed by preparing well defined graft polymer and using gel permeation chromatography (GPC). The results indicate that metalation of substrate polymer is statistically random process and anionic graft reaction products consist of ungrafted free side chain homopolymer; graft polymer with different number of graft chains and free backbone molecules when the average graft sites are small.

INTRODUCTION

Anionic graft copolymerization has recently received considerable attention and interest in this area appears to be increasing judging from the number of reports on the subject.[1~4]

Although anionic graft polymerization is suited for preparing well defined graft polymer by controlling the molecular weight of backbone molecules and average number of graft chains[6], the characterization of graft polymer is not a simple task. So far, attempts to evaluate the fluctuations in composition, i.e. graft sites distribution, were by fractionation and analysis of each fraction.

In this report, we present graft sites distribution of graft polymer derived from a statistical model and hope to provide a basis for characterizing highly branched polymer systems. Experimental confirmation of the statistical analysis was made by gel permeation chromatography (GPC). Also, characterization of grafting reaction product regarding molecular weight distribution and composition will be presented.

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THE GRAFT SITE DISTRIBUTION IN ANIONIC GRAFTING REACTION

A. Statistical Model. The first step involved in anionic graft copolymerization is the metalation of the backbone molecules. Normally, *n*-butyl or sec-butyl lithium is added in the presence of *NNN'N'*-tetramethylethylene diamine to the backbone molecules such as polystyrene or polybutadiene so that the graft sites are provided for subsequent side chain polymerization[6]. The amount of butyllithium is controlled to produce an average number of graft sites or graft chaines per backbone molecule. Although the average number of graft sites per backbone molecule is well controlled, the actual graft site distribution among backbone molecules is not known. Indeed, the experimental characterization of such graft copolymer is rather difficult. However, the conditions described here are suitable for statistical analysis of graft site distribution.

Now, let the probability of finding one alkyllithium ion(graft site) attached to backbone molecule be p. Among total AN alkyllithium ions in the system of anionic grafting reaction, The probability of finding n lithium ions attached to a particular backbone molecule and $AN-n$ lithium ions to all other backbone molecules is

$$f(n)=\frac{(AN)!}{n!(AN-n)!}p^n(1-p)^{AN-n} \qquad (1)$$

Where $f(n)$ is the probability of finding n alkyl lithium attached to a backbone molecule, A the average number of lithium ions per backbone molecule and N the number of backbone molecules. This is normal distribution. When n and AN are large, this approaches Gaussian distribution and when $p\rightarrow 0$, $N\rightarrow\infty$ and $A=$const, equation(1) approaches poisson distribution.

Since the total number of backbone molecules in the system is N, $p=\frac{1}{N}$

$$f(n)=\frac{(AN)!}{n!(AN-n)!}\left(\frac{1}{N}\right)^n\left(1-\frac{1}{N}\right)^{AN-n} \qquad (2)$$

Here, the position distribution of each molecule is statistically independent and any molecule among $AN-n$ will meet requirement. Also, the number of metalation sites available in the backbone molecules far exceeds the average number of lithium ion (A) in the system. In other words, the first metalation imposes no restrictions on subsequent metalation. The molecular weight distribution of the backbone molecules is assumed to be monodispersed or extremely narrow.

The average number of lithium ions or the average graft sites perbackbone molecule will be $A=n$. In the case of $A=1$, average one site per backbone molecule, equation(2) can simply be evaluated with the following results; 37% of the backbone chain molecules have no graft sites (no metalation), 37% one graft site, 18% two sites, 6% three sites and 1.5% four sites.

Similar calculations can be extended to $A=2$, 5, 10 and 20 with the help of the help of the computer. In actual experimental conditions, N is in the order of 10^{20} molecules. However, $N=10^6$ was used in computation for convenience. We have found that the results were the same for all practical purposes when $n=10^4$, 10^5 or 10^6 and in case of $A=1$, the results are the same whether $N=10^6$ or the limiting value of $N\rightarrow\infty$. It should be pointed out here that the same results were obtained by poisson distribution.

The results presented in *Table* 1 are, therefore, valid for actual experimental conditions.

It is instructive to plot the results of *Table* 1 and such a plot is shown in *Fig.* 1.

The amount of the backbone molecules with no graft sites or no metalation decreases from 37% to 14% when the average number of graft sites per backbone molecule(A) is increased from

1 to 2. When A is 10, practically all the backbone molecules are metalated. As can be seen from *Fig.* 1, the graft sites distribution broadens with increasing A. For instance, when $A=1$, the graft sites are distributed between 0 and 5. When $A=10$, the graft sites are spread between 1 and 20, although about 67% of the total are clustered between 7 and 13 graft sites.

Table 1. Graft sites distribution.

$A=1$ n	$N=10^6$ $f(n)$	$A=2$ n	$N=10^6$ $f(n)$	$A=5$ n	$N=10^6$ $f(n)$	$A=10$ n	$N=10^6$ $f(n)$
0	0.3681	0	0.1355	0	0.0068	0	—
1	0.3681	1	0.2710	1	0.0338	1	0.0005
2	0.1841	2	0.2710	2	0.0845	2	0.0023
3	0.0614	3	0.1807	3	0.1402	3	0.0076
4	0.0153	4	0.0903	4	0.1761	4	0.0190
5	0.0031	5	0.0361	5	0.1761	5	0.0381
6	0.0005	6	0.0120	6	0.1467	6	0.0635
7	—	7	0.0034	7	0.1048	7	0.0907
8	—	8	0.0009	8	0.0655	8	0.1134
9	—	9	0.0002	9	0.0364	9	0.1260
10	—	10	—	10	0.0182	10	0.1260
				11	0.0083	11	0.1145
				12	0.0034	12	0.0954
				13	0.0013	13	0.0734
				14	0.0005	14	0.0524
				15	0.0002	15	0.0350

A=Average number of graft sites per backbone molecule
N=Number of backbone molecules in the system
n=Number of graft sites
$f(n)$=Probability of finding(n) graft sites per backbone molecule.

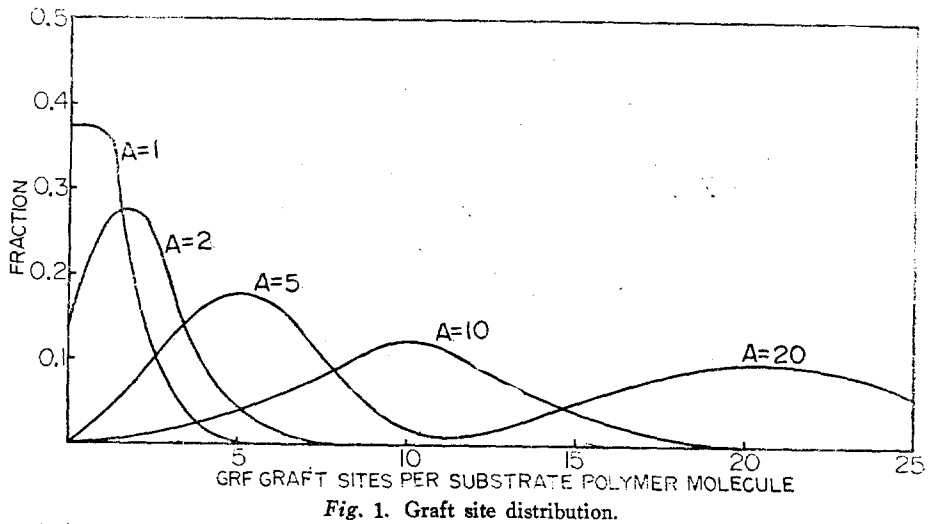

Fig. 1. Graft site distribution.

At $A=20$, only about 57% of the total have between 17 and 23 graft sites and graft sites distribution between 6 and 38.

B. Experimental Proof of Graft Site Distribution. In order to obtain experimental evidence on graft site distribution, we have taken two approaches. First, attempt was made to prepare average one and two graft sites samples with sufficiently long side chains and to analyze for ungrafted portion of backbone molecules. Since 37% of backbone molecules for aver age one site and 14 % for average two sites case have no graft sites, these can be analyzed by gel permeation chromatography. The following model substance-styrene graft polymer shown in *Table* 2 were prepared for this purpose.

In anionic grafting reaction, the actual composition of the sample will differ from the intended one. Thus, the intended average one graft site per backbone molecule would result in average graft site less than one. This would depend, of course, on grafting efficiency which varies according to number of graft sites and side chain length. The site distribution for fractional average site is shown in *Table* 3.

As can be seen, the ungrafted portion of backbone molecules increases with decrease in A value. The GPC chromatograms of sample O, P, and O are shown in *Fig.* 2. These chromatograms show that a considerable portion of backbone molecules remain with no graft sites attached. In fact, the ungrafted portion in these cases turned out to be 47 weight percent and 29 weight percent respectively according to the extrapolation as shown, Now, the GPC chromatogram represents the mixture of backbone molecules, ungrafted free polystyrene, and molecules having different number of side chains according to graft site distribution. The second GPC peak, then, consists of free backbone molecules and ungrafted polystyrene. Thus, in case $A=0.6$ for sample P (the graft efficiency is about 60 percent when side chain molecular weight exceeds 50,000: see *Table* 4, 55 % of backbone molecules are free and corresponds to 19 weight percent of total sample. 40 percent of the styrene is not grafted to the backbone molecules and remain as homopolymer. This corresponds to 26 weight percent of the total sample. The second GPC peak of *Fig.* 2 (*a*) is 47 weight percent of total sample in excellent agreement with the value calculated in this manner. Similarly, when $A=1.4$ for sample Q (see *Table* 2), the free backbone molecules correspond to 8.6

Table 2. Styrene-styrene graft samples (intended composition).

Sample	Average graft sites	Backbone MW	Each side chain MW
O	0	50,000	0
P	1	50,000	100,000
Q	2	50,000	50,000
R	5	50,000	20,000
S	10	50,000	10,000

Table 3. Graft site distribution for fractional A values.

$N=10^6$ n	$A=0.6$ $f(n)$	$A=0.7$ $f(n)$	$A=0.8$ $f(n)$	$A=0.9$ $f(n)$	$A=1.4$ $f(n)$	$A=1.6$ $f(n)$
0	0.55	0.50	0.45	0.41	.25	.20
1	0.33	0.35	0.36	0.37	.35	.32
2	0.10	0.12	0.14	0.16	.24	.26
3	0.02	0.03	0.04	0.05	.11	.13
4	—	0.01	0.01	0.01	.04	.06

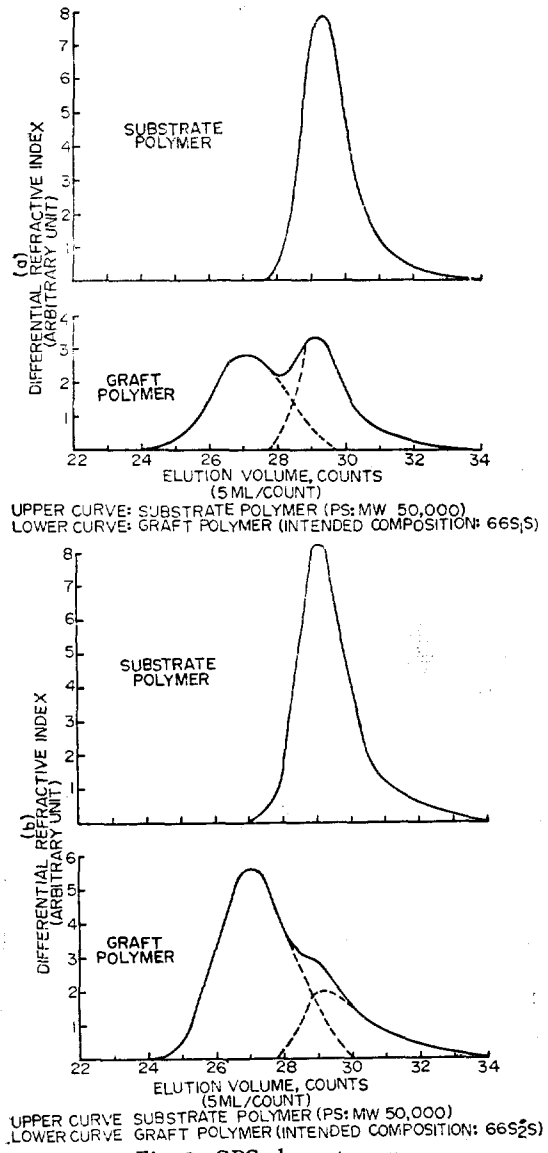

Fig. 2. GPC chromatogram.

weight percent, and free polystyrene, resulting from side chain polymerization, 20 weight percent of total sample. This is in good agreement with the value (29 percent) of *Fig.* 2 (*b*) considering the uncertainty involved in extrapolation procedure. These experimental results, then, support the graft site distribution derived from statistical model.

Another experimental evidence for graft site distribution was obtained by fractionating styrene butadiene graft copolymer with GPC and analyzing styrene content of each fraction by ultraviolet spectroscopy. Using a proper side chain length, the number of graft chains in each fraction was determined. These results show also the graft site distribution and support the calculations presented in section **A**. The details on determination of number of graft chains in styrene–butadiene graft copolymer are presented in the following section.

COMPOSITION OF ANIONIC GRAFTING REACTION PRODUCT

The metalation of backbone molecules (narrow molecular weight distribution) such as polybutadiene or polystyrene is a statistical phenomenon as has been discussed previously. In characterizing anionic graft copolymer, it is rather important to understand the details of anionic grafting reaction. Although the average degree of grafting and average side chain length can be controlled resonably well by adjusting the amount of metalation and subsequent side chain polymerization, the grafting reaction or metalation of backbone molecules is not a clean-cut reaction. In other words, grafting efficiency is not 100 percent. Thus, a certain percentage of anion catalyst remains in solution unattached to backbone molecules and polymerizes during side chain polymerization to form free homopolymer. The grafting reaction product, then, consists of free backbone molecules (when average degree of grafting (A) is greater than 5, there is no free backbone molecules according to calculations and judging from the molecular weight of second GPC peak, (see *Fig.* 3), free polystyrene and graft polymer with different numbers of graft chains. Since there is no free backbone molecules in the sample when *A* is greater than 5, overall composition can be evaluated by

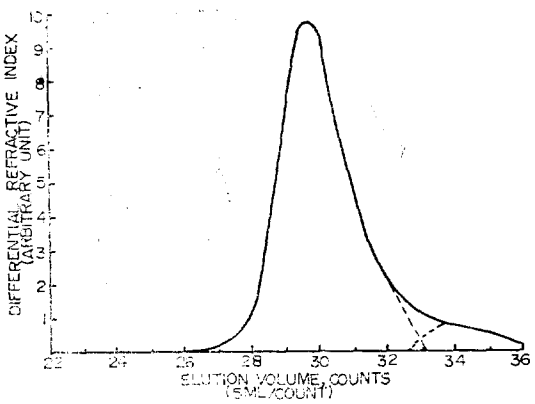

Fig. 3. GPC chromatogram: $64S_{9.3}S$.

determining the amount of free polystyrene from the GPC curve and the total amount of styrene used for side chain polymerization. If graft efficiency is 90 percent, *A* value and percentage of side chain polymer are 10 percent less. *Table* 4 presents the actual composition of gtraf polymer determined in this manner from GPC curve. Typical representative GPC curve are shown in *Fig.* 3. All the rest of the samples have similar characteristics except that peak positions are different.

The calculation of grafting effciency was based on the number of milimoles of free polystyrene formed during the side chain polymerization. The number average molecular weight of free polystyrene was used in estimating the number of free anions in solution. Actual composition of the sample was calculated in the following manner. The weight percent of side chain polymers was estimated based on the amount of free polystyrene and the amount of styrene used for side chain polymerization. The number of average graft sites was determined from grafting efficiency. The actual overall composition presented in *Table* 4 is true representation of the grafting reaction products. A significant decrease in graft efficiency is noticed as the side chain length is increased. As will be shown later, the side chain length is increased. As will be shown later, the side chain length distribution is non-uniform and this must reflect the different rate of polymerization among the side chains.

The compositions of graft polymers shown in *Table* 4 were derived from the amount of ungrafted free polystyrene in anionic grafting reaction product. Harada *et al.*[4] reported that

Table 4.

Sample[a] intended composit.	Ungrafted free polystyrene(Mn)	Wt. of free PS (mg/5mg)	Free PS No. of mmoles	AlK Li added mmoles	Graft eff. (%)	Actual composition
$66S_1S$						
$66S_2S$			Backbone molecules and side chain PS overlap			
$50S_5S$	24,600	0.692	0.23×10^{-4}	1.25×10^{-4}	78.5	$42S_{3.9}S$
$66S_5S$	19,300	0.582	0.30×10^{-4}	1.7×10^{-4}	87.4	$62S_{4.3}S$
$83S_5S$	34,000	1.44	0.425×10^{-4}	0.85×10^{-4}	50.0	$76S_{2.5}S$
$66S_{10}S$	9,700	0.291	0.30×10^{-4}	3.4×10^{-4}	91.2	$64S_{9.1}S$
$34S_5B$	12,000	0.209	0.17×10^{-4}	1.65×10^{-4}	89.7	$31S_{4.5}B$
$50S_5B$	19,000	0.652	0.342×10^{-4}	1.25×10^{-4}	72.7	$43S_{3.6}B$
$34S_{10}B$	8,400	0.105	0.125×10^{-4}	3.3×10^{-4}	96.2	$33S_{9.6}B$
$50S_{10}B$	12,600	0.287	0.226×10^{-4}	2.5×10^{-4}	91.0	$47S_{9.1}B$
$34S_{15}B$	6,400	0.113	0.176×10^{-4}	4.95×10^{-4}	90.4	$33S_{14.5}B$
$50S_{15}B$	9,900	0.191	0.193×10^{-4}	3.75×10^{-4}	94.8	$48S_{14.2}B$

[a] $66S_1S$ means that the side chain and the backbone molecules are 66 and 34 weight percent respectively and *A* is one.

free polystyrene and side chain polymer are essentially the same based on their viscosity measurement of free polystyrene, and grafted polystyrene obtained by oxidizing the butadiene backbone molecules. It would be, therefore, convincing to obtain experimental evidence that the second GPC peak indeed consists entirely of ungrafted free polystyrene formed during side chain polymerization. Also, as briefly mentioned in previous section, we shall present details of experimental results in determining number of graft chains in styrene-butadiene graft copolymers. It should be noted here that compositional analysis of styrene-butadiene graft copolymer can be rigorously made by GPC fractionation and analysis of each fraction regarding butadiene and styrene contents.

Employing analytical GPC unit for fractionation, 5 m*l* fractions were collected and optical density of each fraction at 260 nm was measured with DK-A UV spectrophotometer to determine styrene content as suggested by Runyon *et al.*[5] Quantitative interpretation of the results was rendered by the following procedure. Optical density of styrene (OD_s) is converted to GPC refractometer response scale. The styrene contribution of GPC response curve (RI_s) is

$$RI_s = OD_s \cdot F \qquad (3)$$

The conversion factor F is determined by the ratio of OD_s in GPC chart scale to GPC RI_s obtained from known polystyrene samples. The OD_s plot was obtained by measuring optical density of fractionated polystyrene standard and constructing the curve in GPC scale. The conversion factor F turned out to be 7.7 in this case. Having determined the styrene content of each fraction, the remaining GPC response curve is converted to polybutadiene concentration as follows. The RI_s is subtracted from the midpoint of each 5 m*l* fraction GPC curve. This corresponds to butadiene contribution. (For the fraction at peak position, the area average point instead of midpoint should be taken).

Since refractive indices of styrene and butadieneare different, the GPC response of butadiene contribution should be multiplied by 1.37. Then the RI_s and corrected RI_B are directly proportional to the weight contents of styrene and butadiene in the 5 m*l* fraction.

Compositional analysis of the sample (intended composition $50S_{10}B$) has been made in such a manner and the results are presented in *Table* 5. The figures are in arbitrary unit. It is clear from columns 4 and 5 that the relative concentration of styrene and butadiene changes as the molecular separation occurs in GPC.

The number of graft chains in each fraction was evaluated from the following equation, since the molecular weights of backbone and side chain molecules are known.

$$\frac{RI_s}{RI_B} = \frac{nM_G}{M_B} \quad \text{or} \quad n = \frac{RI_s}{RI_B} \cdot \frac{M_B}{M_G} \qquad (4)$$

The number average molecular weight of free polystyrene obtained from second GPC peak was used as M_G since the molecular weights of free and grafted polystyrene are the same[4]. The mode of GPC fractionation is shown in *Fig.* 4. M_B was taken to be 100,000.

The average overall comopsition can also be

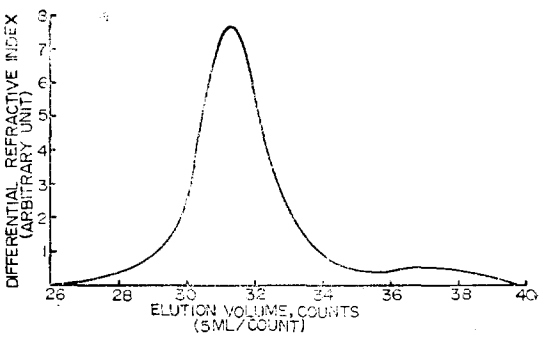

Fig. 4. Mode of GPC fractionation $47S_{9.1}B$.

Table. 5. Compositional analysis of graft copolymer sample (intended composition $50S_{10}B$, *Fig.* 4).

Fraction	*O. D.* 260nm	Total *RI*	RI_s	RI_R	No. of graft chains	Wt. eraction(%) of backbone mol
5	0.05704	0.55	0.4392	0.1518	23.1	3.0
6	0.15439	1.87	1.1888	0.8921	9.7	17.0
7	0.29420	3.78	2.2653	2.0751	8.7	39.3
8	0.17069	2.30	1.3143	1.3504	7.7	25.6
9	0.04993	0.80	0.3845	0.5692	5.4	10.8
10	0.01701	0.31	0.1310	0.2452	4.2	4.6
11	0.01416	0.14	0.1090	0.0424	—	—
12	0.03417	0.22	0.2631	—	—	—
13	0.03261	0.22	0.2511	—	—	—

estimated from the results of *Table* 5. The overall average sites are calculated from $\Sigma nf(n)$ of each fraction. Also, total amount of styrene content in graft copolymer can be obtained by summing up all the styrene contents and dividing by the total amount of graft copolymer. The overall composition thus obtained turned out to be $52S_{8.5}B$. This is in good agreement with the results of *Table* 4 considering the experimental error involved. This agreement in the result, then, supports the conclusion of Harada *et al.*[4] regarding the similarity of free polystyrene and side chain polymer molecules in styrene-butadienegraft copolymer.

It is clear from the compositional analysis presented in the table that the graft site distributions do exist and the results here are in excellent accord with the calculated value of *Table* 1. These experimental results show that more than 70 percent of the sample consists of molecules having graft chains between 7 and 10 for $A=9.1$. In addition, these results provide a convincing evidence that the second GPC peak indeed consists entirely of polystyrene homopolymer formed during side chain polymerization and represents the side chain length distribution of styrenebutadiene graft copolymer.

CONCLUSION

1. The following conclusions can be drawn from these results: Metalation of substrate polymer molecule in anionic grafting reactions is statistically random process.

2. Anionic graft reaction products consist of ungrafted free side chain homopolymer, graft polymer with different number of graft chains and free backbone molecules when the average graft sites are small.

3. The side chains have non-uniform length distribution.

4. Compositional analysis of styrene-butadiene graft copolymer shows that the ungrafted free polystyrene appears to have the same molecular weight and distribution as the side chain polymer

EXPERIMENTAL

Experimental procedure has been published elsewhere.[6]

The Water's GPC Model 200A and DK-A UV spectrophometer were empolyed using freshly distilled tetrahydrofuran as the solvent.

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