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Kinetic Study of 1-Substituted Aziridines for Ring-Opening Polymerization Initiated with 3-Hydroxy-1-propane Sulfonic Acid Sultone

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ABSTRACT

Kinetics of the cationic polymerization of 1-substituted aziridines, such as 1-methoxycarbonylmethyl aziridine, 1-methoxycarbonylethyl aziridine, and 1-benzyl aziridine, initiated with 3-hydroxy-1-propane sulfonic acid sultone have been investigated, and the results are compared with the results of the polymerization of 1-β-cyanoethyl aziridine. The course of polymerization of 1-methoxycarbonylmethyl aziridine involved a termination reaction due to the reaction between the growing endgroup and the imino group in the polymer chain. On the other hand, the polymerizations of 1-methoxycarbonylethyl aziridine and 1-benzyl aziridine were terminated by a backbiting reaction with the formation of a piperadinium ring on the polymer end. The propagation and termination constants were obtained at different temperatures, and the enthalpies of activation (ΔH^*) and the entropies of activation (ΔS^*) for this polymerization were calculated.

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Recently, the ring-opening polymerization of 1-substituted aziridines with such cationic initiators as 3-hydroxyl-1-propane sulfonic acid sultone (PS), methyl tosylate, and methyl iodide was described [1]. The effects of 1-substituted groups on polymerization were very interesting in this polymerization. For example, in the polymerization of the lower basic monomer 1-β-cyanoethyl aziridine (CEA, pK_a 5.45 [2]), a high molecular weight polymer was produced, while the more basic monomer, 1-phenethyl aziridine (pK_a 7.36 [2]), could not produce a high molecular weight polymer. It was presumed that the termination reaction in this polymerization was markedly affected by the basicity of the monomer. The course of polymerization of CEA involved a propagation stage and a termination reaction due to the reaction between the growing chain and the imino groups in the polymer chain [1, 3]. The polymerization mechanism and the kinetics of CEA polymerization were reported in a previous paper [4], and the rate of polymerization of CEA is given by

$$\ln \frac{R_p}{[M][I]_0} = \ln k_p - k_t \int_0^t ([M_0] - [M])\, dt \qquad (1)$$

where R_p = rate of propagation

$[M]_0$ = concentration of the initial monomer

$[M]$ = concentration of the monomer

$[I]_0$ = concentration of the initial initiator

k_p = rate constant of propagation

k_t = rate constant of termination

Equation (1) has been used by others for the ring-opening polymerization of 3,3-bis(chloromethyl)oxetane [5] and 3,3-dimethyl thietane [6].

In this report, in order to explain the effects of 1-substituted groups in the aziridine ring for the polymerization of 1-substituted aziridine, a kinetic study of this polymerization was reported by using the following aziridines: 1-methoxycarbonylmethyl aziridine (MMA), 1-β-methoxycarbonylethyl aziridine (MEA), and 1-benzyl aziridine (BEA).

EXPERIMENTAL

Materials

MEA was synthesized from ethyleneimine and methyl acrylate as described by Yoshida [7]. It was purified by repeated distillation in a nitrogen atmosphere (MEA, bp 76°C/30 mmHg, NMR H_{cis} 1.16 ppm, H_{trans} 1.74 ppm).

MMA and BEA were synthesized from ethyleneimine and monochloroacetic acid methyl ester or benzyl chloride by Bestain [8] (MMA, by 48°C/6 mmHg, NMR H_{cis} 1.21 ppm, H_{trans} 1.8 ppm; BEA, bp 109°C/23 mmHg, NMR H_{cis} 1.24 ppm, H_{trans} 1.82 ppm in 10 wt% $CDCl_3$).

3-Hydroxy-1-propane sulfonic acid sultone (PS) and methyl tosylate, as initiators, were commercial reagents which were dried over P_2O_5 and purified by distillation.

Procedure

Polymerization was carried out in a sealed vessel. The monomer and an initial standard (o-dichlorobenzene for MMA, t-butylbenzene for MEA, and naphthalene for BEA) in acetonitrile were placed in a vessel and left in a thermostatic bath for 10 min. Then an initiator was added to this solution with a microsyringe. The rate of polymerization was measured by gas chromatography using an internal standard (Silicon Gum SE-30; 2 m; H_2 gas, 60 mL/min at 90°C). The amount of monomer was measured at appropriate intervals of time.

RESULTS AND DISCUSSION

The bulk polymerization of 1-substituted aziridine was carried out with PS initiator at 30°C. The results are shown in Table 1. CEA and MMA could be polymerized with PS. They produced a white powdery polymer in high yield. A greasy polymer was obtained in the polymerization of BEA. An oily polymer was produced in the polymerization of MEA. The structures of the polymers obtained were confirmed by NMR spectra [1], and the molecular weight of each polymer was measured in chloroform by a molecular weight apparatus (Corona Model 117 vapor pressure osmometer).

Polymerization of MMA

The polymerization of MMA was carried out at several temperatures using PS in acetonitrile. The time-conversion curves of MMA are plotted in Fig. 1. On the basis of these, the polymerization of MMA proceeds in a manner similar to that of the polymerization mechanism for CEA. Figure 2 shows plots of $R_p/[M][I]_0$ against $\int_0^t ([M]_0 - [M])\,dt$ and gives a linear relationship as expected by Eq. (1). The polymerization of MMA with PS can be expressed by Eq. (1).

TABLE 1. Ring-Opening Polymerization of 1-Substituted Aziridines with 3-Hydroxy-1-propane Sulfonic Acid Sultone in Bulk (at 20°C for 24 h, monomer, 5 mmol; initiator, 2 mol% of monomer)

Monomer	Yield (%)	mp (°C)	η_{sp}/c^a	Mw[b]
1-β-Cyanoethyl aziridine	98	111-115	0.78	7000
1-Methoxycarbonyl-methyl aziridine	82	43-54	0.46	4000
1-β-Methoxycarbonyl-ethyl aziridine	72	-	-	
1-Benzyl aziridine	93	-	0.39	3100

[a] c = 0.5 g/100 mL DMF at 30°C.

[b] Measurements were made on a Corona Model 117 vapor pressure osmometer.

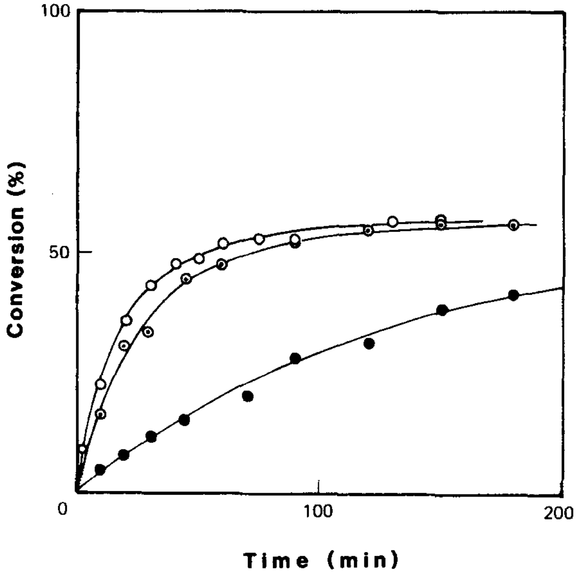


FIG. 1. The polymerization of MMA with PS at different temperatures. Monomer: 1 mol/L in acetonitrile. Initiator: 0.05 mol/L in acetonitrile. Temperature: (○) 61°C, (⊙) 50.5°C, (●) 30°C.

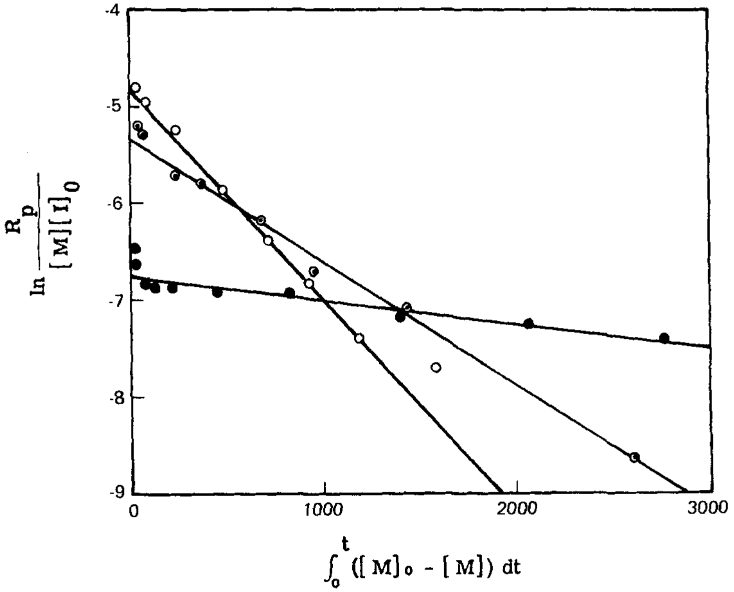
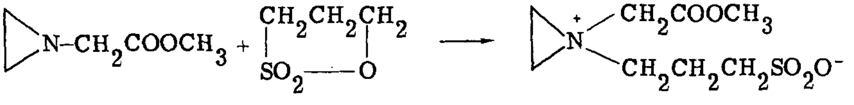
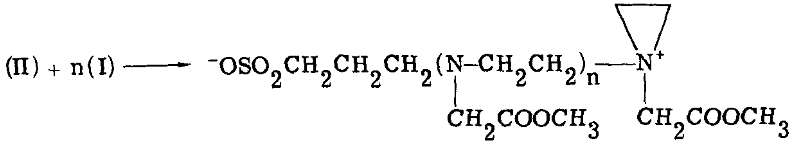


FIG. 2. The application of the experimental data (Fig. 1) to Eq. (1) and the effects of temperature: At 61°C (○): $k_p = 7.60 \times 10^{-3}$, $k_t = 17.4 \times 10^{-4}$. At 50.5°C (⊙): $k_p = 4.70 \times 10^{-3}$, $k_t = 9.86 \times 10^{-4}$. At 30°C (●): $k_p = 1.21 \times 10^{-3}$, $k_t = 2.45 \times 10^{-4}$.

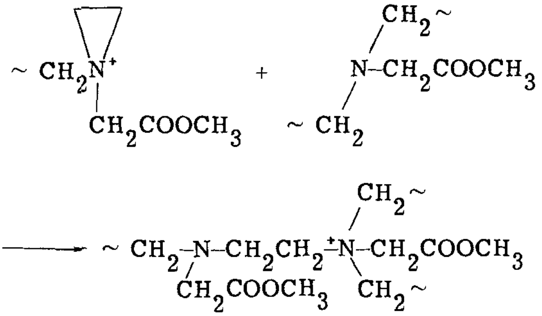
From these results we conclude that the polymerization of MMA is initiated by PS, and that the propagation and termination reactions proceed as shown in Eqs. (2), (3), and (5) in analogy with the polymerization of CEA:



(I) (II) (2)



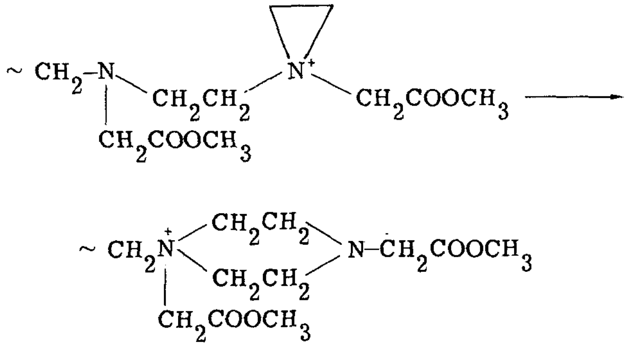
(3)



(4)

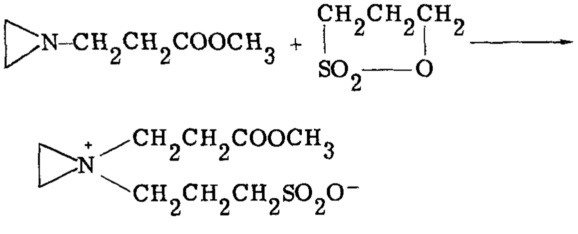
In the polymerization of MMA with PS, the values of k_p and k_t at different temperatures were obtained by the plots shown in Fig. 2.

Polymerizations of MEA and BEA were carried out in the same manner as for MMA. The time-conversion curves of the monomers MEA and BEA are plotted in Figs. 3 and 4. The polymerization rates of MEA and BEA have been examined by application of Eq. (1). However, the linear relationship in Eq. (1) could not be obtained exactly due to the termination reaction which forms the piperadium ring by the backbiting reaction on the polymer end for MEA and BEA [1]:



(5)

The polymerization of MEA was assumed to be initiated by zwitterion (III) which forms by an additional reaction of the monomer and PS:



(III)

(6)

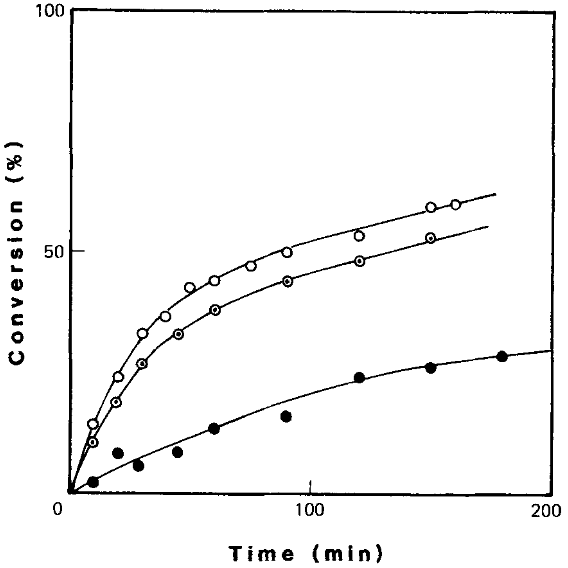


FIG. 3. The polymerization of MEA at different temperatures. Monomer: 1 mol/L in acetonitrile. Initiator: 0.05 mol/L in acetonitrile. Temperature: (○) 58°C, (⊙) 51°C, (●) 29°C.

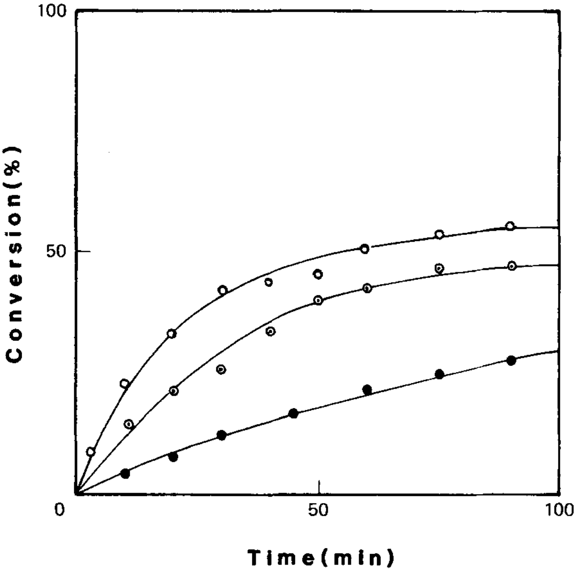


FIG. 4. The polymerization of BEA at different temperatures. Monomer: 1 mol/L in acetonitrile. Initiator: 0.3 mol/L in acetonitrile. Temperature: (○) 60°C, (⊙) 50°C, (●) 30°C.

After that, cationic polymerization occurred, and then the termination reaction was assumed to be as shown by Eq. (5).

On the basis of the results of CEA polymerization, the rate of initiation is given as

$$-d[I]/dt = k_i[I][M] \tag{7}$$

where [I] is the concentration of the initiator, [M] is the concentration of the monomer, and k_i is the rate constant of the initiation reaction. The rates of propagation R_p and termination are given by Eqs. (8) and (9), respectively:

$$R_p = -d[M]/dt = k_p[P^*][M] \tag{8}$$

$$-d[P^*]/dt = k_t[P^*] \tag{9}$$

where [P*] is the concentration of the growing chain.

Integration of Eq. (9) gives

$$-\ln [P^*] = k_t t + C \tag{10}$$

If the zwitterion as a propagation species [P*] is formed rapidly in good yield in Eq. (1) at t = 0, then [P*] is equal to the concentration of the initiator. Thus $C = -\ln [I]_0$. Equation 10 can be written as

$$-\ln [P^*] = k_t t - \ln [I]_0 \tag{11}$$

$$[P^*] = [I]_0 e^{-k_t t} \tag{12}$$

Combining Eqs. (8) and (12) gives

$$\ln \frac{R_p}{[M][I]_0} = \ln k_p - k_t \tag{13}$$

Here, R_p is obtained from the tangent at various points of the time-conversion curves.

Figures 5 and 6 show the data in Figs. 3 and 4 for the polymerization of MEA and BEA, and they give a linear relationship.

To make sure that the polymerization of BEA could be represented by Eq (13), the polymerization of BEA was carried out in chloroform with different amounts of methyltosylate as initiator at 50°C. The results are plotted in Fig. 7 by Eq. (13) which gives a linear relationship.

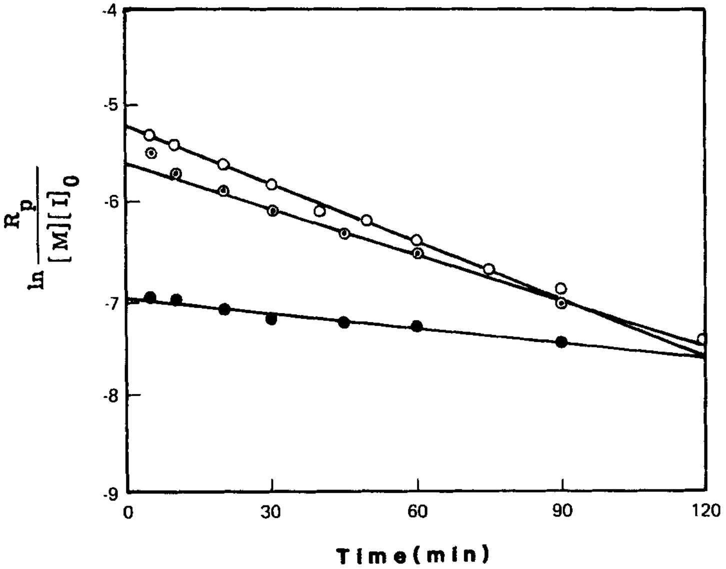


FIG. 5. The application of the experimental data (Fig. 3) to Eq. (13). At 58°C (○): $k_p = 5.57 \times 10^{-3}$, $k_t = 3.13 \times 10^{-4}$. At 51°C (⊙): $k_p = 3.70 \times 10^{-3}$, $k_t = 2.33 \times 10^{-4}$. At 20°C (●): $k_p = 0.96 \times 10^{-3}$, $k_t = 0.813 \times 10^{-4}$.

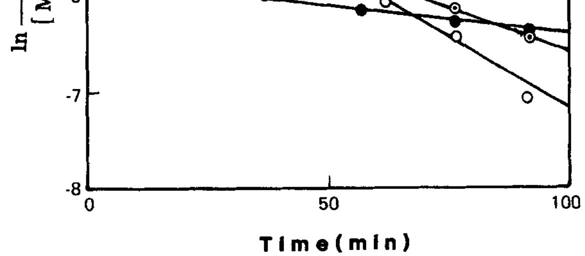


FIG. 6. The application of the experimental data (Fig. 4) to Eq. (13). At 60°C (○): $k_p = 16.1 \times 10^{-3}$, $k_t = 5.13 \times 10^{-4}$. At 50°C (⊙): $k_p = 9.28 \times 10^{-3}$, $k_t = 3.22 \times 10^{-4}$. At 30°C (●): $k_p = 2.93 \times 10^{-3}$, $k_t = 0.96 \times 10^{-4}$.

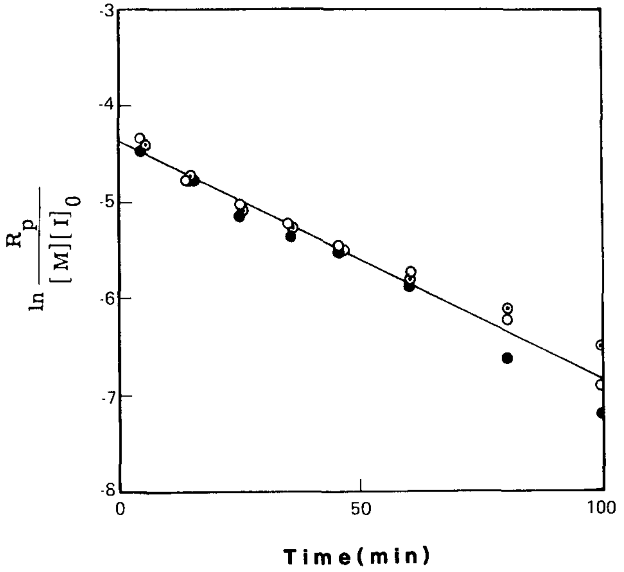


FIG. 7. The effects on the initiator concentration of the polymerization of BEA in chloroform at 50°C and the application of the data to Eq. (13). Monomer: 1 mol/L in chloroform. Initiator: Methyl tosylate, (○) 0.025 mol/L, (⊙) 0.05 mol/L, (●) 0.01 mol/L.

The polymerization of BEA could be expressed by Eq. (13). From these results it seems appropriate to consider that the polymerization of MEA and BEA proceeds by way of the schemes shown by Eqs. (3), (4), and (6).

This difference in the cause of the polymerization mechanism for 1-substituted aziridines of 1-substituted groups can probably be explained by the basicity of the monomer and the different sizes of the 1-substituted groups.

According to Eq. (14), as shown by Eyring, the enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) for the propagation and termination reactions were determined by plotting $\ln(k_p/T)$ or $\ln(k_t/T)$ against $1/T$ (Fig. 8):

$$\ln(k/T) = \ln \frac{k}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{R} \frac{1}{T} \qquad (14)$$

where, $k = k_p$ or k_t, k = the Boltzmann constant, and
h = the Planck constant.

The values for ΔH^* and ΔS^* are summarized in Table 2 by Eq. (14).

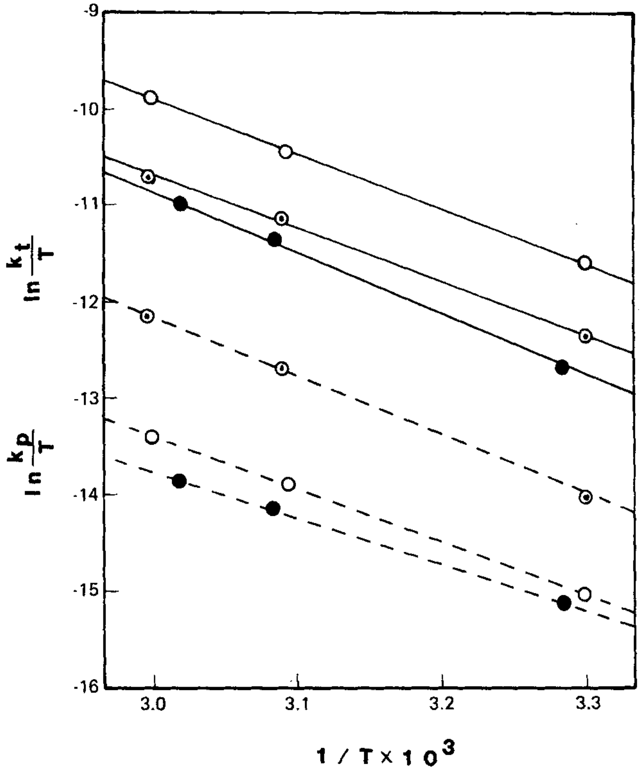


FIG. 8. The determination of ΔH_p*, ΔH_t*, ΔS_p*, and ΔS_t* according to Eq. (14). (—) ln (k_p/T), (- -) ln (k_t/T), (○) BEA, (⊙) MMA, (●) MEA.

TABLE 2. The Thermodynamic Parameters of 1-Substituted Aziridines for Ring-Opening Polymerization

Monomer	ΔH_p* (kcal/mol)	ΔH_t* (kcal/mol)	ΔS_p* (eu)	ΔS_t* (eu)
1-Methoxycarbonyl methylaziridine	11.6	11.4	-33.7	-37.1
1-β-Methoxycarbonyl ethylaziridine	11.6	8.62	-33.9	-48.7
1-Benzylaziridine	10.8	10.5	-34.6	-38.4

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