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KINETIC STUDY ON REACTIONS BETWEEN POLYMER CHAIN-ENDS—II

REACTIONS BETWEEN CHLOROSULPHONYL-ENDED AND PRIMARY AMINO-ENDED POLYOXYETHYLENES FOLLOWED BY FLUOROMETRY

A. OKAMOTO, K. TOYOSHIMA and I. MITA
Institute of Interdisciplinary Research, Faculty of Engineering, University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153, Japan

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Abstract—Rates of the reaction of 1,5-naphthalenedisulphonyl dichloride, a bifunctional fluorescent reagent, with primary amino-ended polyoxyethylene were measured by fluorometry in dilute solution. The second-order rate constants obtained are equivalent to those for the reaction between polyoxyethylenes with chlorosulphonyl and primary amino groups as the reactive chain-ends respectively (polymer–polymer reaction). Rates of the reaction of 5-dimethylamino-1-naphthalenesulphonyl chloride, a monofunctional fluorescent reagent, with primary amino-ended polyoxyethylene were also measured as model (small molecule–polymer) reactions. In both cases the rates of reaction in cloroform (good solvent) are substantially independent of the degree of polymerization over the range of about 20 to 20,000. These and previous results show clearly that, if there is a "kinetic excluded volume effect", it is very small and Flory's principle of equal reactivity of a functional group holds. Recent theories of the kinetic excluded volume effect are discussed briefly.

INTRODUCTION

Our previous study on the reaction of living polystyrene with chloro-ended polystyrene showed that the rate of the reaction between polymer chain-ends is independent of the degree of polymerization in a good solvent, at least for degrees of polymerization up to 400 and the effect of the coil expansion is not detectable [1]. This does not conform to the theory of "kinetic excluded volume effect" for a polymer–polymer reaction in solution presented first by Morawetz [2, 3], but appears to confirm Flory's basic concept of the equal reactivity of a group in polymer chains [4].

The second-order rate constant for the reaction between polymer chain-ends is expected, according to the theories of Morawetz *et al.* [3] and Khokhlov [5], to decrease in proportion to -0.15 and -0.16 power of the degree of polymerization in a good solvent. These exponents can be established by careful experiments. Including the pioneering work by Cho *et al* [6], however, no experimental study has detected the kinetic excluded volume effect clearly [7, 8, 9]. In most of the experimental work, (i) the polymer concentration studied is not sufficiently low, (ii) the procedures to obtain the rate constants are not very simple or the reaction does not obey the simple bimolecular kinetics, and (iii) the experimental points are not numerous enough to show clearly the molecular weight dependence. Our previous study, however, has dealt not only with a simple S_N2 reaction between chain-end groups but with substantially monodisperse polymers in dilute solution and the results are unambiguous [1]. The only problem was that the experiments could not be carried out for polymers with degree of polymerization higher than 400, because the reaction system is too sensitive to traces of impurities to maintain the condition of dilute polymer concentration.

In this work a simple S_N2 reaction between reactive groups attached to each chain-end of polymers with a rather wide range of molecular weight is investigated by using the fluorescent kinetic probe method developed recently [10, 11]. The fluorescent kinetic method is a method which uses fluorescence of the product to follow reaction rates. As the fluorescence can be detected generally for very dilute solution, the method enables us to investigate the coupling reaction of polymers at a concentration where the theory of dilute polymer solution holds. Finally, recent theories of the kinetic excluded volume effect will be discussed briefly.

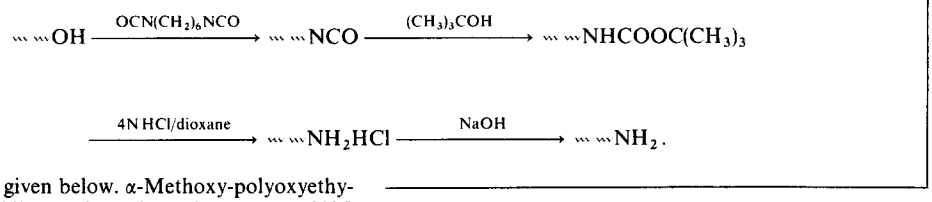
EXPERIMENTAL

Materials

1,5-Naphthalenedisulphonyl dichloride (NDSCl) was prepared by the reaction of disodium 1,5-naphthalenedisulphonate with phosphorus pentachloride [11]. 5-Dimethylamino-1-naphalenesulphonyl chloride (dasyl chloride; DNSCl) was obtained from Tokyo Kasei Co. and used without further purification. Chloroform was "Dotite Spectrosol" grade (from Wako Pure Chemical Industries Co.) and used as received.

Amino-ended polyoxyethylenes were prepared from commercially available polyoxyethylenes and α-methoxy-polyoxyethylenes having two or one hydroxyl group per chain respectively (from Aldrich Chemical Co. and Iwai

Chemicals Co.). First, isocyanato-ended polymers were prepared by the reaction of the polymers with a large excess of hexanediisocyanate [12, 13]. Since the direct conversion of the terminal isocyanato group to an amino group induces the side reaction of the isocyanato group with the resulting amino group, the former was first reacted with *t*-butyl alcohol to give the primary amino group protected by the *t*-butoxycarbonyl group [14]. Finally the protective group was removed to obtain the primary amino-ended polyoxyethylenes.



A typical example is given below. α-Methoxy-polyoxyethylene (20 g; $\bar{M}_n$ = 5300) was heated to dryness at 100°C under reduced pressure (15–20 mm Hg) with bubbling nitrogen for one hour and then dissolved in 30 ml of dry toluene. Hexanediisocyanate (15 ml) was added dropwise to the solution and then 2–3 mg of dibutyltin(IV) chloride as a catalyst was added followed by stirring for 2 hr at 60°C. The solution was mixed with 50 ml of distilled *t*-butyl alcohol and stirred for 1.5 hr at 65°C. Finally, 50 ml of 4 N HCl in dioxane was added dropwise to the solution with cooling in an ice bath to room temperature over half an hour. The polymer was precipitated from the solution with 2.5 l of diethyl ether. The polymer thus obtained was dissolved in 200 ml of chloroform followed by washing with aq. NaOH and then distilled water several times. After reprecipitating with diethyl ether and drying *in vacuo*, primary amino-ended polyoxyethylene was obtained (75% recovery). The amine content was determined by quantitative fluorescence analysis after converting the amino group to the fluorescent dansyl amide using dansyl chloride. Molecular weight and molecular weight distributionn of the polymer were measured with a gel permeation chromatograph (Toyo Soda HLC-802UR with columns of G5000PW and G3000PW) using a u.v. detector (365 nm). The characteristics of the polymers are listed in Table 1. The amino content at the chain-end is not quantitative, probably because the commercially available polyoxyethylenes do not always contain the expected quantity of hydroxyl groups. Another reason for the discrepancies may be hydrolysis of the urethane group between $[CH_2]_6$ and the POE chain.

Kinetic measurement

The reactions were followed by the increase in fluorescence intensity at the peak wavelength of the reaction products (340 nm for NDSCl; 500 nm for DNSCl), and the fluorescence measurements were performed without degassing by a JASCO FP-550 spectrofluorometer using a quartz cell with a cap. The fluorescence intensity was corrected by subtracting the value obtained in a blank solution without NDSCl or DNSCl. The final fluorescence intensity was measured after two days and was also corrected. The final fluorescence intensities thus obtained correlated well with the initial concentration of NDSCl or DNSCl and are independent of polymer samples. Second-order rate constants were calculated from the observed pseudo first-order rate constants for systems with excess amine.

RESULTS AND DISCUSSION

Model (small molecule–polymer) reactions

The reaction of primary amino-ended polyoxyethylene with 5-dimethylamino-1-naphthalenesulphonyl chloride (DNSCl) to form a sulphonamide in chloroform was studied as a model for small molecule–polymer reaction in a good solvent. The reactions were followed by fluorometry because the product is fluorescent while the reactants are not. We have confirmed that the reaction of butylamine with DNSCl is strictly second-order [10]. In another study on the effects of polymers on chemical reactions, we found that the presence of polyoxyethylene accelerates the reaction of the sulphonyl chloride with amines (small molecule–small molecule or small molecule–polymer reaction) because of two factors, *viz.* cosolvent effect of the polymer and coordination effect by the oxygen atoms in the polymer [15, 16]. The polymer cosolvent effect is, however, negligible at such a dilute polymer concentration as in the present experimental conditions (4×10^{-4} to 6×10^{-2} g/ml, see Tables 2 and 3) and the coordination effect alone should be observed. Table 2 lists the reaction conditions for the

Table 1. Characteristics of polymers

Polymer	$\bar{M}_n(\bar{DP}_n)$	$\bar{M}_w/\bar{M}_n$	No. of NH_2 groups/chain
POE(1)NH_2*	1000 (24)	2.3	0.22
POE(2)NH_2†	3000 (68)	2.7	0.01
POE(3)NH_2‡	4300 (98)	1.3	0.27
POE(4)NH_2†	5300 (120)	1.6	0.01
POE(5)NH_2†	8800 (200)	9.3	0.31
POE(6)NH_2*	10,000 (230)	2.6	0.73
POE(7)NH_2†	63,000 (1430)	2.2	0.10
POE(8)NH_2†	68,000 (1550)	1.1	0.30
POE(9)NH_2‡	915,000 (20,800)	9.6	1.28

* Prepared from α-methoxy-polyoxyethylene (from Aldrich Chemical Co.).

† Prepared from POE (from Aldrich Chemical Co.).

‡ Prepared from POE (from Iwai Chemicals Co.).

Table 2. Reaction conditions for small molecule–polymer reactions

Polymer	[DNSCl] (10^{-5} M)	[NH_2] (10^{-4} M)	[POE-NH_2] (g dl^{-1})
POE(1)NH_2	0.98	0.83	0.04
POE(1)NH_2	2.2	1.7	0.08
POE(2)NH_2	0.90	0.23	0.69
POE(3)NH_2	0.96	2.3	0.37
POE(4)NH_2	0.89	0.17	0.90
POE(5)NH_2	2.2	2.8	0.79
POE(5)NH_2	0.99	7.2	2.0
POE(6)NH_2	2.2	2.3	0.32
POE(7)NH_2	1.1	0.28	1.8
POE(7)NH_2	0.77	0.45	2.8
POE(7)NH_2	0.86	0.46	2.9
POE(9)NH_2	0.96	0.86	6.2

Table 3. Reaction conditions for polymer–polymer reactions

Polymer	[NDSCl] (10^{-5} M)	[NH_2] (10^{-4} M)	[POE-NH_2] (g dl^{-1})
POE(1)NH_2	0.97	0.83	0.04
POE(1)NH_2	0.97	1.6	0.07
POE(3)NH_2	1.0	1.9	0.30
POE(5)NH_2	0.99	2.5	0.71
POE(6)NH_2	0.97	0.39	0.05
POE(6)NH_2	0.99	3.0	0.41
POE(8)NH_2	1.0	0.85	1.9
POE(9)NH_2	1.0	0.85	6.1

model reaction in chloroform at 40°C. The values of the second-order rate constants, k_2^0, in Fig. 1 are about 7.5 times larger than that for the reaction of butylamine with DNSCl under the same conditions [10]. This acceleration may be due to the intramolecular coordination effect of the polyoxyethylene chain on the reaction site. The regression line from Fig. 1 gives the relation $k_2^0 \sim n^{-0.075}$ with correlation coefficient $r = 0.62$. Since Fig. 1 shows some scatter (or low value of r), it is better to conclude that the rate of the small molecule–polymer reaction is independent of the degree of polymerization as shown by a straight line in Fig. 1. This result is consistent with our previous work which showed that the rate of the reaction of living polystyrene with 1-chloropentane is independent of the degree of polymerization up to 400. These results are not unexpected, because there is no special reason why the chemical reaction between a small molecule and a polymer should be affected by the degree of polymerization, e.g. the propagation reaction in chain polymerization is always regarded as being independent of the degree of polymerization. Our results may be, however, the first data which showed experimentally that the chemical reaction of small molecules with high polymers with degree of polymerization up to 20,000 is independent of the degree of polymerization.

Effect of degree of polymerization on polymer–polymer reactions

Polymer–polymer reactions were studied in detail for the reaction of 1,5-naphthalenedisulphonyl dichloride (NDSCl), a bifunctional fluorescent reagent, with primary amino-ended polyoxyethylenes in chloroform. The reaction consists of two steps represented thus

$$\sim\sim NH_2 + ClO_2S{-}C_{10}H_6{-}SO_2Cl \xrightarrow{\text{fast}} \sim\sim NHSO_2{-}C_{10}H_6{-}SO_2Cl \quad (1)$$

and

$$\sim\sim NH_2 + \sim\sim NHSO_2{-}C_{10}H_6{-}SO_2Cl \xrightarrow{\text{slow}} \sim\sim NHSO_2{-}C_{10}H_6{-}SO_2NH\sim\sim . \quad (2)$$

In our previous paper, we confirmed that the disulphonamide or the final reaction product of NDSCl with butylamine is fluorescent while the reactants and the intermediate monosulphonamide are not [11]. The kinetics of the reaction can therefore be followed by fluorescence measurements. Further it was confirmed that the rate of the reaction of the second sulphonyl chloride with amine is slower by *ca.* one order than the first and the second step is rate-determining

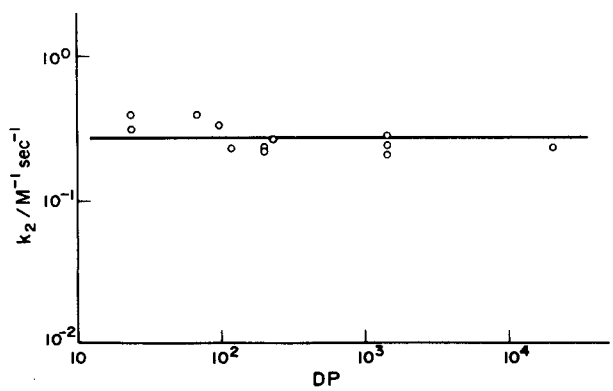


Fig. 1. Effect of DP on the second-order rate constant for the reaction of primary amino-ended polyoxyethylene with dansyl chloride in chloroform at 40°C.

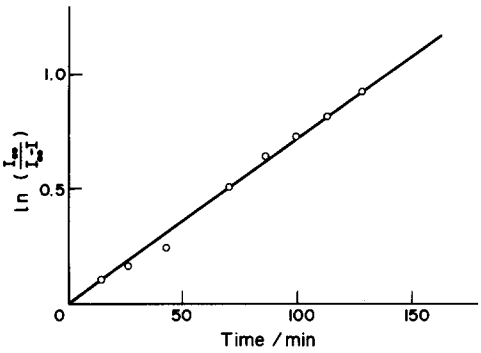


Fig. 2. Pseudo first-order plots of the reaction of NDSCl with a large excess of POE(9)NH_2 in chloroform at 40°C.

[11]. Consequently the rate of the reaction of NDSCl with the primary amino-ended polyoxyethylene detected by fluorometry corresponds to that of the polymer–polymer reaction between a sulphonyl chloride-ended polyoxyethylene and a primary amino-ended polyoxyethylene.

Figure 2 shows the pseudo first-order plots for the reaction of NDSCl with a large excess of the primary amino-ended polyoxyethylene in chloroform at 40°C. The plot gives a straight line passing through the origin. This indicates that the rate of the reaction of the first sulphonyl chloride with amine is more than one order faster than that of the second. When the rate of the reaction of the first sulphonyl chloride with amine is not much faster than that of the second, e.g. less than one order, the pseudo first-order plot is not linear but it is curved in the initial stage of the reaction [11]. The reaction of the first sulphonyl chloride with amine may be accelerated preferentially by the intramolecular coordination effect of the polyoxyethylene chain.

Table 3 lists the reaction conditions for the polymer–polymer reaction in chloroform at 40°C. The values of the second-order rate constants, k_2 (Fig. 2), are about 25 times larger than that for the reaction of butylamine with the second chlorosulphonyl group in NDSCl ($k_2^2 = 4.8 \times 10^{-2}\ M^{-1}\ sec^{-1}$ in chloroform at 40°C [11]). To examine the kinetic excluded volume effect, the solution of the reactive polymers must be so dilute that only binary interactions need to be considered, or else the forced interpenetration of the polymeric chain should be taken into account [6]. Because the fluorescent kinetic probe method allows the coupling reaction to be followed by fluorometry for very low concentrations (10^{-5} to 10^{-7} M), the rate of the reaction of such polymers with degree of polymerization up to 20,000 could be obtained in substantially dilute polymer solution (at worst 6.1 g/dl for POE(9)NH_2, see Table 3). Although the regression line from Fig. 3 gives the relation $k_2 \sim n^{0.070}$ with the correlation coefficient 0.68, it may not mean a tendency for greater rates at higher molecular weight because of the low value of r. So we prefer to say that the rate of polymer–polymer reaction over a wide range of degree of polymerization is constant in chloroform, a good solvent. This confirms the previous result obtained for the reaction of living polystyrene with chloro-ended polystyrene showing that the rate of the polymer–polymer reaction is independent of the degree of polymerization up to 400 [1]. Although the molecular weight distributions of polymers used here are not as sharp as those in the previous study, it does not matter because the conclusion is the independence of the reaction rate of the molecular weight of the polymer. Our results for two different kinds of reactions show clearly that the kinetic excluded volume effect is not detectable for the reaction between polymer chain-ends; in other words, the polymer–polymer reaction is independent (or strictly, independent within experimental error) of the degree of polymerization at least for reaction between polymer chain-ends.

Discussion of theories

Several theories have been presented on the kinetic excluded volume effect. The first, advanced by Morawetz *et al.* [3], is based on the equivalent sphere model, in which the polymer coils are represented as spheres with a volume $v_e = (4\pi/3)R_e^3$ containing a uniform density of chain segments and the reactive group is given the same probability of being located at any position within the equivalent sphere. The excluded volume effect is taken into account by the repulsive potential proportional to the overlapping volume of the two spheres. In this model, the probability of the reaction is also proportional to the overlapped volume. The theory shows that the ratio of the second-order rate constant k_2 for the reactive group

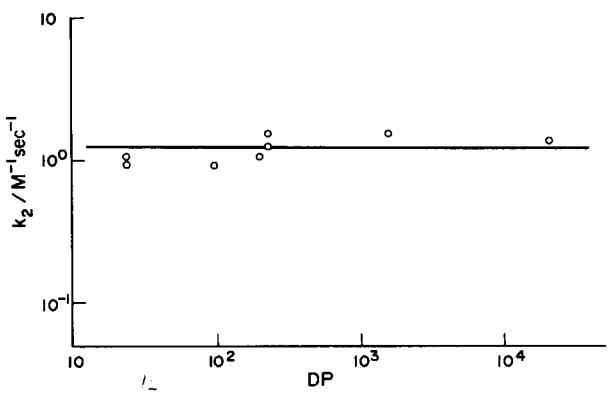


Fig. 3. Effect of DP on the second-order rate constant for the reaction of primary amino-ended polyoxyethylene with chlorosulphonyl-ended polyoxyethylene in chloroform at 40°C.

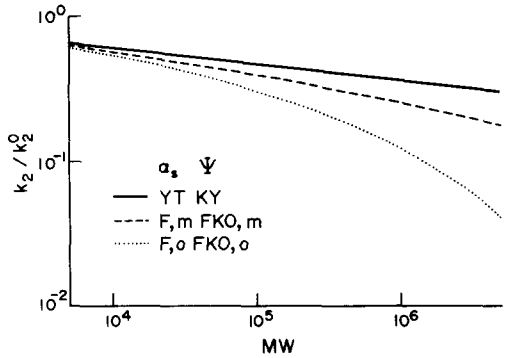


Fig. 4. Molecular weight dependence of k_2/k_2^0 based on Eqn (3) with three combinations of theoretical values of Ψ and α_s.

attached to any position on the polymer chain to k_2^0 for the reaction of low molecular weight model (or k_2 at the theta point) becomes inversely proportional to the 0.27 power of the chain length for a long chain in a good solvent. In the following discussion we will show that the kinetic excluded volume effect can be expressed consisely by the interpenetrating function Ψ, which is familiar in the theory of the second virial coefficient of dilute polymer solutions [17]. For polymer spheres with volume v_e and molecular weight M, the second virial coefficient is represented by $A_2 = 3\sqrt{\pi}N_A v_e \Psi/M^2$, whereas for rigid spheres with volume v'_e and molecular weight M, $A_2 = 4N_A v'_e/M^2$. Collating v_e with v'_e, one can readily consider that each polymer sphere is interpenetrable by the fraction of $1 - (3\sqrt{\pi}/4)\Psi$ and is completely interpenetrable at the theta pont at which Ψ vanishes. Assuming that the probability of finding a reactive group is independent of segment location, we obtain

$$k_2/k_2^0 = (1 - 3\sqrt{\pi}\Psi/4)^2. \tag{3}$$

Figure 4 shows the molecular weight dependence of k_2/k_2^0 calculated according to Eqn 3 by using the relation $z = 0.0053\,M^{1/2}$ obtained experimentally by Berry for PS in toluene [18] and three sets of approximate theories of Ψ and α_s: (i) the original Flory–Krigbaum–Orofino theory and the original Flory theory, (ii) the modified Flory–Krigbaum–Orofino theory and the modified Flory theory, and (iii) the Kurata–Yamakawa theory and the Yamakawa–Tanaka theory. Since the combination (iii) have been shown to be best [17], k_2/k_2^0 seems inversely proportional to the 0.10 power of the chain length for usual polymer–polymer reactions in a good solvent.

In Eqn 3, k_2/k_2^0 is expressed by the familiar and more reliable function, Ψ, and the value of the exponent -0.10 seems reasonable as compared with the large value of -0.27 estimated by Morawetz *et al.* Although the present model gives the average value of k_2/k_2^0 with respect to the location of the reactive groups, it is clear that the kinetic excluded volume effect does not greatly reduce the rate of polymer–polymer reactions.

More elaborate theories by Iwata *et al.* [19] and Kozlov [20] are based on the Gaussian chain model in which the probability of finding each reactive group is expressed by the Gaussian distribution with respect to the centre of mass of the polymer coil. According to their theories, k_2/k_2^0 for the reaction between polymer molecules each having only one reactive group at the ith segment is expressed as

$$k_2/k_2^0 = \frac{4}{\sqrt{\pi}}\int_0^\infty \exp\left\{-t^2 - 3^{1.5}\cdot\bar{z} \times \exp\left(-\frac{\langle s_i^2\rangle}{\langle s^2\rangle}t^2\right)\right\} t^2\,dt. \tag{4}$$

where $\langle s_i^2\rangle$ is the mean-square distance from the centre of mass to the ith segment. Since $\langle s_i^2\rangle$ takes the maximum value at $i = 0$ or n (the number of segments in the chain) and the minimum value at $i = n/2$, k_2/k_2^0, which depends on the location of the reactive group, is larger for the end segment than the middle segment. These authors gave some illustrations for the i dependence of the rate constants but did not give any idea of the n dependence. Therefore we calculated numerically the molecular weight dependence of k_2/k_2^0 for polymer–polymer reactions in a good solvent for two extreme cases with the relation $z = 0.0053\,M^{1/2}$ for PS in toluene and the Yamakawa–Tanaka theory of α_s: the reaction between the chain-ends of polymers and that between the central segments (Fig. 5). Figure 5 shows that k_2/k_2^0 for usual polymer–polymer reactions in a good solvent is inversely proportional to the 0.07th power of the chain length for the chain ends, but the exponent is as large as -0.35 for the central reactive groups at large M.

Our experimental results show that the molecular weight dependence of the rate of the reactions between polymer chain-ends in a good solvent is smaller than 0.07th power or independent of the chain length. Theories with approximation of higher order may make the exponent smaller. The kinetic excluded volume effect might not be, however, so small for the reactions between reactive groups at the middle of polymer chains.

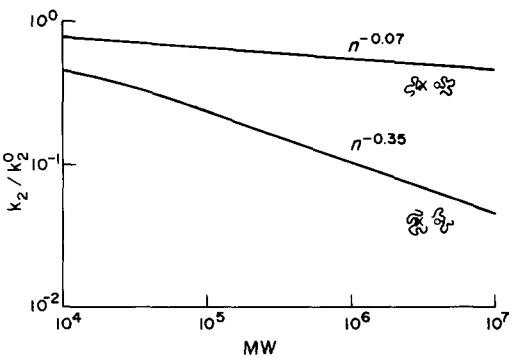


Fig. 5. Molecular weight dependence of k_2/k_2^0 based on Eqn (4) with Yamakawa-Tanaka theory of α_s.

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