

Synthesis of Cationic Flocculant by Radiation-Induced Copolymerization of Methyl Chloride Salt of N,N-Dimethylaminoethyl Methacrylate with Acrylamide in Aqueous Solution

TOSHIMI OKADA, ISAO ISHIGAKI, TAKESHI SUWA, and SUEO MACHI, *Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Takasaki, Gunma, Japan 370-12*

Synopsis

The radiation-induced copolymerization of the methyl chloride salt of N,N-dimethylaminoethyl methacrylate (DMAEM-MC) with acrylamide (AAm) was used to prepare a cationic polymer flocculant. The polymerization rate increased with increasing dose rate, polymerization temperature, monomer concentration, and mole fraction of AAm in the monomer mixture. The molecular weight of the copolymer was also found to increase with monomer concentration and mole fraction of AAm, but at high concentration and fraction of AAm, intermolecular crosslinking tends to occur during the polymerization to form water-insoluble copolymer. A water-soluble copolymer having various molecular weights and cationic strengths can be synthesized by selecting suitable reaction conditions; i.e., this radiation process can provide a much higher molecular weight copolymer with a wide range of cationic strength. The flocculation effect was evaluated using sludge from wastewater of sugar manufacture. It was found that the radiation-polymerized copolymer DMAEM-MC-AAm has an excellent flocculation effect.

INTRODUCTION

Polyacrylamide is well known to be an effective flocculant for the separation of various suspensions from solution. The amount of polymer flocculant used for water treatment will largely increase year by year for minimizing or preventing public hazards. There are various types of polymer flocculant, i.e., nonionic, anionic, and cationic.

Cationic flocculants are very useful for the treatment of wastewater containing organic suspensions. Cationic flocculants can be prepared by the modifications of polyacrylamide or the copolymerization of acrylamide with comonomers having cationic electrolyte groups.^{1,2} Polyacrylamide is modified by the Mannich reaction or Hofman rearrangement to give cationic flocculant with relatively high molecular weight. However, the products from the Mannich reaction have amino groups which are so reactive as to crosslink with each other. In the Hofman rearrangement, the yield of cationic polymer is very low, and the main chain of the polymer is easily hydrolyzed by caustic alkali to give a lower molecular weight polymer.

On the other hand, cationic polymer flocculants such as polyimidazole, polydiallylamine, polyethylenimine, and condensation polymers such as aniline-formaldehyde, hexamethylenediamine-epichlorohydrin, and urea (or thio-urea)-ethylenediamine exist. However, one cannot expect these compounds

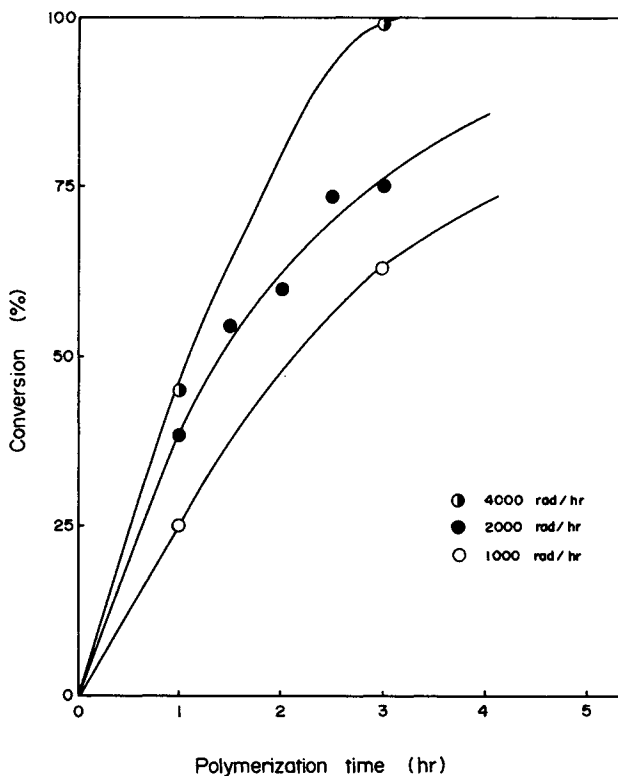


Fig. 1. Polymerization time-conversion curves at various dose rates. Monomer concentration, 2 mole/l.; monomer composition, DMAEM-MC:AAM = 3:7 (in moles); polymerization temperature, 28°C;

to have excellent flocculation effects since their molecular weights are not very high.

The copolymer of acrylamide with a quaternary ammonium salt of N,N-

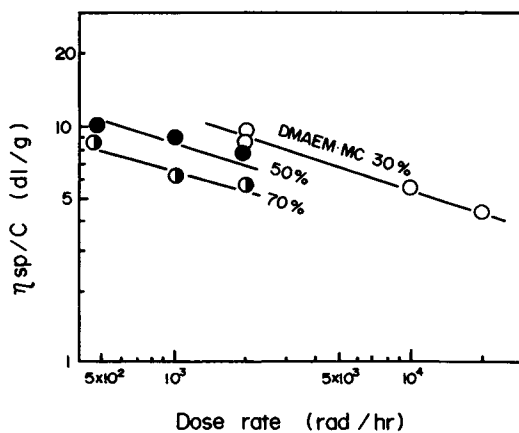


Fig. 2. Logarithmic plots of η_{sp}/c of copolymer vs. dose rate at various monomer compositions. Monomer concentration, 1 mole/l.; polymerization, 10 hr at 30°C.

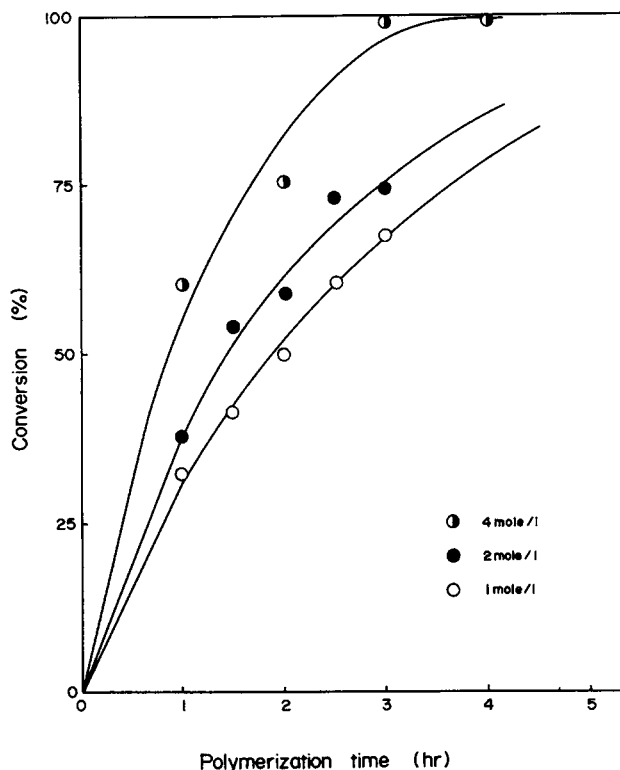


Fig. 3. Polymerization time-conversion curves at various monomer concentrations. Dose rate, 2000 rad/hr; monomer composition, DMAEM-MC:AAM = 3:7 (in moles); polymerization temperature, 28°C;

dimethylaminoethyl methacrylate is one of the most useful polymers as cationic flocculant. We studied the radiation-induced copolymerization of acrylamide with the methyl chloride salt of *N,N*-dimethylaminoethyl methacrylate in aqueous solution to prepare a cationic polymer flocculant and found that one can easily obtain cationic flocculants having relatively higher molecular weights and various cationic strengths. In the present study, the effects of dose rate, monomer concentration and composition, and polymerization temperature on the yield and molecular weight of the copolymer were investigated. The flocculation effect of the copolymer produced was also evaluated in comparison with that of commercial flocculants.

EXPERIMENTAL

Technical-grade acrylamide (Mitsubishi Chemical Industry Ltd.) was used without further purification. Technical-grade methyl chloride salt of *N,N*-dimethylaminoethyl methacrylate (Mitsubishi Rayon Co. Ltd.) was purified by washing with acetone followed by drying in vacuo before use.

An aqueous solution of the monomers in a glass ampoule was degassed by repeated (usually more than four times) freezing and thawing under vacuum. The ampoule was then sealed under vacuum and subjected to γ -ray irradiation from Co 60 in a temperature-controlled bath. After the irradiation, the reaction

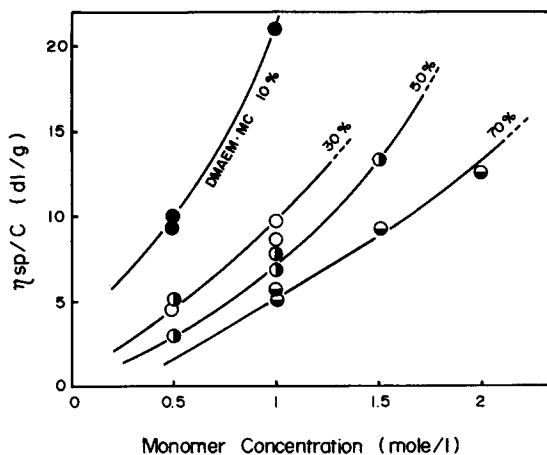


Fig. 4. Effect of monomer concentration on η_{sp}/c of copolymer at various monomer compositions. Dose rate, 2000 rad/hr; polymerization, 10 hr at 30°C.

mixture was taken out and poured into excess acetone to precipitate the polymer. The polymer was then powdered in a large amount of acetone using a homogenizer (Tokyo Nihonseiki Seisakusho Co. Ltd.), filtered, washed with acetone, and dried at room temperature for 24 hr under vacuum.

The reduced viscosity η_{sp}/c of the polymer at a concentration of 0.5 g/dl was measured in 1N NaNO₃ aqueous solution at 30°C using an Ubbelohde viscometer. It is difficult to determine the intrinsic viscosity of the copolymer, since polymer containing quaternary ammonium salt dissociates in aqueous solution. In this study, therefore, the η_{sp}/c of the polymer was mainly used as a measure of molecular weight.

The copolymer composition was determined by colloidal titration.³ A 0.5% aqueous solution of the polymer was titrated with potassium poly(vinyl sulfate) using toluidine blue as an indicator. Dosimetry was carried out using cobalt glass.

The flocculation effect of the copolymer was determined as follows. The sludge obtained from wastewater of sugar manufacture was used. The prescribed amount of polymer solution was added to the suspension of sludge, and then the suspension was stirred at 150 rpm for 2 min and at 50 rpm for 3 min. The mixture thus obtained was filtrated using a Nutsch funnel under reduced pressure of 400 mm Hg. The volume of the filtrate for 10 sec was measured.

RESULTS AND DISCUSSION

The relationship of polymer conversion against polymerization time at various dose rates is shown in Figure 1. The polymerization rate increased with dose rate. From the logarithmic plots, the dose rate exponent of the polymerization rate was found to be 0.8. This result suggests that the termination reaction of two propagating polymer radicals is depressed because the reaction medium becomes highly viscous as the polymerization proceeds. Collison et al.⁴ and Schulz et al.⁵ found that the dose rate exponent of the polymerization rate at a lower dose rate is slightly higher than 0.5 for the radiation polymerization of acrylamide in aqueous solution. On the other hand, η_{sp}/c of the polymer formed

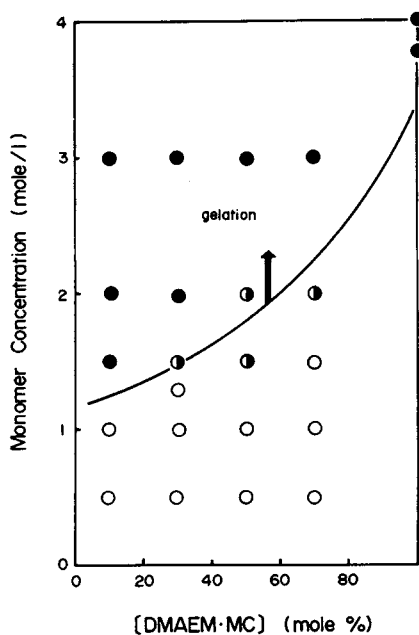


Fig. 5. Effects of monomer concentration and composition on copolymer solubility in water: (O) water soluble; (◐) partially insoluble in water; (●) water insoluble; dose rate, 2000 rad/hr; polymerization, 10 hr at 28°C; polymer conversion, 100%.

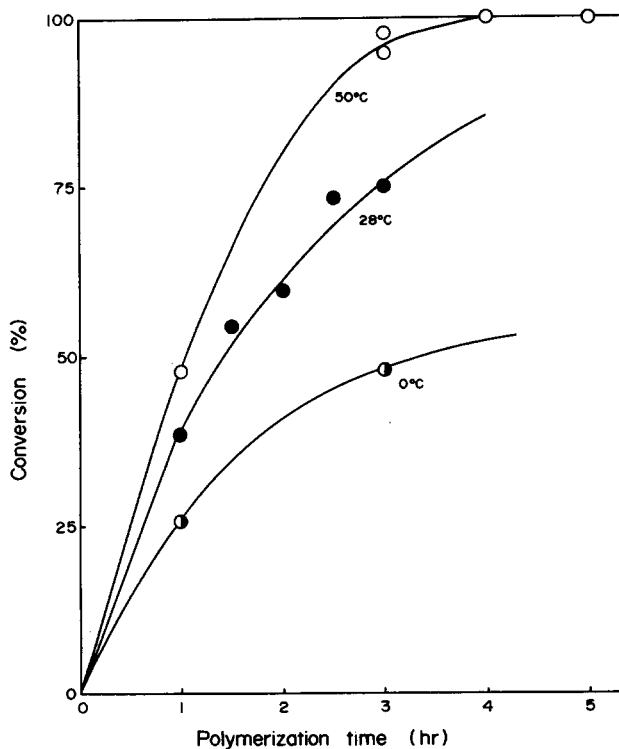


Fig. 6. Polymerization time-conversion curves at various polymerization temperatures. Monomer concentration, 2 mole/l.; monomer composition, DMAEM-MC:AAM = 3:7 (in moles); dose rate, 2000 rad/hr.

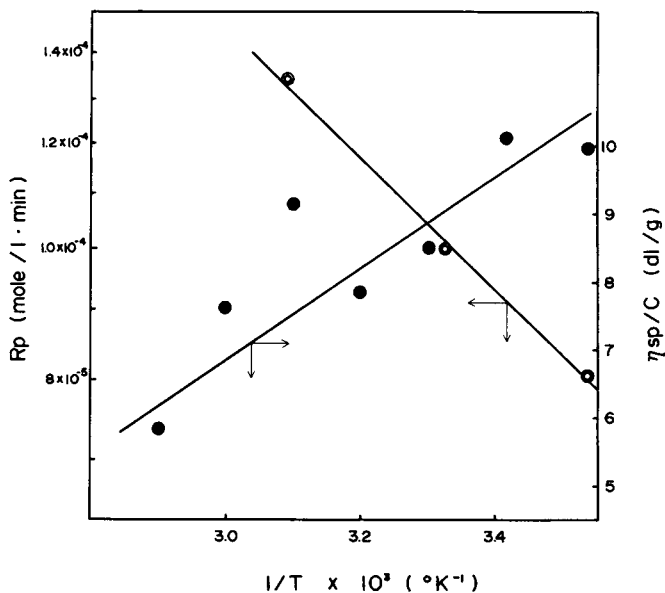


Fig. 7. Arrhenius plots for copolymerization of DMAEM-MC with AAm. Dose rate, 2000 rad/hr; monomer concentration, 1 mole/l.; monomer composition, DMAEM-MC:AAm = 3:7 (in moles).

is found to decrease with increasing dose rate and mole fraction of the methyl chloride salt of *N,N*-dimethylaminoethyl methacrylate (DMAEM-MC) in the monomer mixture, as shown in Figure 2.

Figure 3 shows the yield-polymerization time curves obtained at various monomer concentrations and a constant dose rate. The polymerization rate determined from these curves was proportional to the 1.3th power of the monomer concentration. Wada et al.,⁶ studying the radiation-induced polymerization of methyl iodide salt of *N,N*-dimethylaminoethyl methacrylate in aqueous solution, found that the polymerization rate is proportional to the first power of monomer concentration in the range of 0.1 to 0.5 mole/l. On the other

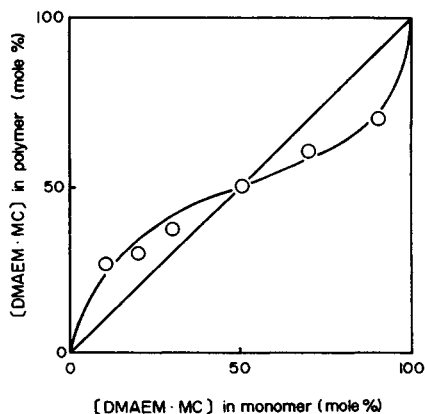


Fig. 8. Relationship between compositions of monomer and copolymer. Dose rate, 2000 rad/hr; monomer concentration, 2 mole/l.; polymerization temperature, 30°C; polymer conversion, 6–11%.

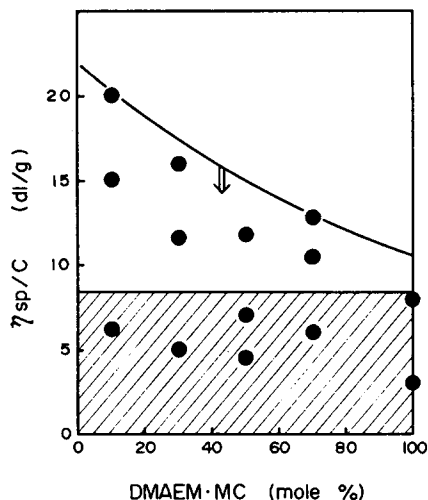


Fig. 9. Region of η_{sp}/c -DMAEM-MC fraction of copolymer obtained by radiation and commercially available: (●) obtained by radiation process; (◻) commercially available.

hand, it is well known that the polymerization rate for radical polymerization can be represented by the equation

$$R_p = k_p k_t^{1/2} R_i^{1/2} [M] \quad (1)$$

where k_p and k_t are the rate constants of propagation and termination, and R_i and $[M]$ are the rate of initiation reaction and monomer concentration, respectively. If the initiating radicals are generated only from the solvent and the rate of initiation reaction is independent of monomer concentration, the polymerization rate is proportional to the first power of monomer concentration. In the

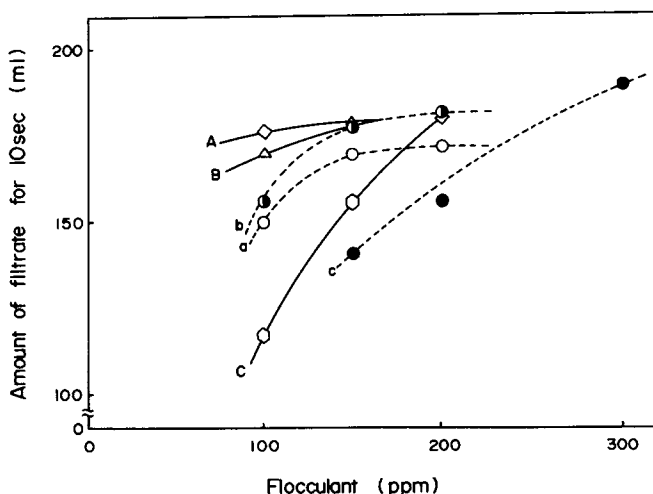


Fig. 10. Relation between amount of filtrate and concentration of various flocculants. Sample sludge from wastewater of sugar manufacture. Flocculants (\diamond) (Δ), and (\circ), radiation products; flocculants (\circ), (\bullet), and (\bullet), commercial products. $[\eta]$ (dl/g) and DMAEM-MC (mole-%): A, 11.7 and 36.9, respectively; B, 8.7 and 42.6; C, 6.2 and 34.0; a, 4.5-5 and 100; b, 7-8 and 30; c, 7-8 and 10-15.

present system, however, the monomer concentration was relatively high so that initiating radicals are formed to some extent from the monomer, i.e., R_i in eq. (1) may be represented as follows:

$$R_i = \Phi_m[M] + \Phi_s[H_2O] \quad (2)$$

where Φ is the G value for the radical formation. Schulz et al.⁵ found that the polymerization rate was proportional to $[M]^{1.33}$ for the polymerization of acrylamide at a monomer concentration of 0.1 to 0.8 mole/l.

Figure 4 shows the relationship between the reduced viscosity of copolymer at 100% polymer conversion and the monomer concentration at various monomer compositions. It can be seen that η_{sp}/c of the copolymer increases as the monomer concentration and mole fraction of acrylamide (AAM) in the monomer mixture increase. However, the water-insoluble copolymer is also formed at a higher monomer concentration. Figure 5 shows the region where the water-soluble copolymer can be obtained at a polymer conversion up to 100%. This indicates that the monomer concentration at which the water-insoluble copolymer is formed increases with increasing mole fraction of DMAEM-MC in the monomer mixture. This finding may be explained as follows. Acrylamide gives a relatively high molecular weight polymer which becomes easily insoluble in water due to intermolecular crosslinking formed by the imidation of two amide groups. Intermolecular crosslinking of polyacrylamide seems to occur not only by the imidation but also by the branching of the polymer chain. The polymer chain is presumably branched by the chain transfer reaction of propagating radicals or the effect of γ -ray irradiation of the formed polymer to create new radicals (initiating points) on carbon atoms at the α position in the AAm unit of the polymer. It has been reported that the hydrogen atom bound to the tertiary carbon atom is easily drawn out as compared with those bound to the secondary and primary carbon atoms.⁷ Therefore, the region of monomer concentration which gives the water-soluble polymer increased with decreasing mole fraction of AAm in the monomer mixture.

Figure 6 shows the polymer yield-time curves at various temperatures from 0° to 50°C. Arrhenius plots of the polymerization rates determined from these curves are shown in Figure 7. The overall activation energy for this copolymerization system was estimated to be approximately 2.0 kcal/mole. In general, the overall activation energy of radical polymerization is given by

$$E_a = (E_i/2) + [E_p - (E_t/2)] \quad (3)$$

where E_i , E_p , and E_t are the activation energies of the initiation, propagation, and termination reactions, respectively. In the radiation-induced polymerization, E_i is considered to be approximately zero. The E_p values for radical polymerization are known to be of the order of 6 to 8 kcal/mol.⁸ The value of $E_a = 2.0$ indicates that E_t is about 8 to 12 kcal/mole. This large value of E_t is presumably due to the diffusion barrier of the propagating chains.

Although the relationship between η_{sp}/c of the copolymer and the polymerization temperature ($1/T$) is somewhat scattered as seen in Figure 7, η_{sp}/c tends to decrease with increasing temperature. This is so because the temperature dependences of the termination and chain transfer reactions are larger than that of the propagation reaction.

Figure 8 shows monomer-copolymer composition curves at a constant dose

rate of 2×10^3 rads/hr and polymerization temperature of 30°C. The copolymerization was stopped below 11% polymer conversion, since the monomer composition may vary as the reaction proceeds at a high conversion. From the curve, the monomer reactivity ratios were found to be $r_1 = 0.35$ and $r_2 = 0.4$ using the Lewis-Mayo method (M_1 , DMAEM-MC; M_2 , AAm).

In this copolymerization system, as mentioned above, the reduced viscosity (molecular weight) of copolymer was found to be dependent on dose rate, polymerization temperature, and concentration and composition of the monomer. The solubility of the copolymer in water was affected by the concentration and composition of the monomer. However, a water-soluble copolymer of various molecular weights and cationic strengths can be synthesized by selecting suitable reaction conditions. Figure 9 shows the region of solution viscosity and cationic strength of the copolymer obtained at 100% conversion by the radiation-induced copolymerization of DMAEM-MC-AAm in comparison with that of commercially available flocculants. It can be seen that the radiation process provides a much higher molecular weight flocculant at a wide range of cationic strength. The possible reason for the higher molecular weight polymer obtainable by radiation may be that radiation polymerization occurs at a lower temperature than conventional polymerization by free-radical initiator.

In order to evaluate the flocculation effect of the copolymer formed by the radiation process, the filtration rate of sludge from wastewater of sugar manufacture was measured. The relationship between filtration rate and amount of flocculant added is shown in Figure 10 for the copolymers together with commercial flocculants. The filtration rate increased with the amount of flocculant and leveled off above 150 ppm for some flocculants, A, B, and a. In the cases of A and B, a large filtration rate was obtained at a relatively small amount of copolymer. These results indicate that the flocculation effect is largely affected not only by molecular weight but also by the cationic strength of the flocculant; i.e., the larger the molecular weight and the higher the cationic strength, the higher the rate of filtration. In conclusion, the results suggest that the radiation-polymerized copolymer DMAEM-MC-AAm has excellent flocculation effect.

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