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Antimicrobial functionalization of poly(ethylene terephthalate) fabrics with waterborne *N*-halamine epoxides

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ABSTRACT: A water dispersible terpolymer of [2-(methacryloyloxy)ethyl]trimethylammonium chloride, glycidyl methacrylate and hydantoinyl acrylamide was synthesized and coated on poly(ethylene terephthalate) fabrics through a pad-dry-cure procedure. The coatings were rendered biocidal upon exposure to dilute household bleach solution. The halogenated fabrics exhibited great antimicrobial functionality with about six logs inactivation of *S. aureus* and *E. coli* O157:H7 within only two min of contact time. Moreover, the coatings were found to be very stable against repeated washings and UVA light exposure. It was shown that [2-(methacryloyloxy)ethyl]-trimethylammonium monomer is very useful in preparing waterborne *N*-halamines which can impart rechargeable, effective, and stable antimicrobial coatings to poly(ethylene terephthalate) fabrics. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43088.

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INTRODUCTION

Increasing threat of nosocomial infections and emergence of new drug-resistant bacteria necessitate developing robust, potent, durable, and stable antimicrobial materials for use in various applications, in particular for the medical industry. Antimicrobial modification of medical textiles such as gowns, gloves, bed sheets, drapes, lab coats, splash aprons, etc. is of critical interest, since bacteria can survive on the surfaces of these materials for days to months.[1] Moreover, infections on these surfaces can easily be transmitted through direct or indirect contact with the contaminated area. According to a clinical study, Methicillin-resistant *Staphylococcus aureus* (MRSA) was detected on 65% of gowns of nurses who had performed patient care activities on patients infected with MRSA. Furthermore, contamination occurred on 42% of gloves of personnel who touched contaminated surfaces, but had no direct contact with such patients.[2] Therefore, antimicrobial treatment of medical devices and textiles is necessary to combat bacterial infections. In this regard, various antimicrobials including quaternary ammonium salts, metals ions, and biguanides were developed and used to functionalize the surfaces of the aforementioned materials.

Simply known as halogen stabilizers, *N*-halamines are one of the most effective biocides among antimicrobial agents.[3] These contact active compounds inactive a broad spectrum of microorganisms including MRSA within minutes of contact time.[4] Transfer of oxidative halogen to cell membranes upon contact with pathogens results in cell lysis due to oxidation of thiol groups. Once the oxidative halogen is exhausted, it can be regenerated by simple exposure to a halogen source, such as household bleach. Various techniques including grafting,[5] blending,[6,7] coating,[8] or copolymerization[9,10] have been studied to incorporate *N*-halamine antimicrobial compounds. Several polymers including polyvinyl acetate,[11] polylactic acid,[12] polypropylene,[13] nylon,[14] polystyrene,[15] etc. have been rendered biocidal with *N*-halamines. *N*-halamine research has mainly focused on application on cotton surfaces, since cotton is widely used in the medical industry. On the other hand, poly(ethylene terephthalate) (PET) is also widely used for medical textiles; however, there have been limited studies concerning *N*-halamines on PET surfaces. For example, Liu *et al.* reported a surface thermoplastic semi-interpenetrating network of *N*-halamines on PET fabrics. Covalent bonding of *N*-halamine compounds through formaldehyde and siloxane groups on PET surfaces were achieved upon hydrolysis of the polymer with base by Lin *et al.*[16] and Ren *et al.*,[17] respectively. Ren *et al.* also studied thin film *N*-halamine coatings through admicellar polymerization on PET surfaces.[18] Lee *et al.* reported m-aramid coated PET fabrics through a pad-dry-cure procedure using dimethylacetamide as a

solvent.[19] Liu and Sun studied radical grafting of an allyl *N*-halamine monomer on PET surfaces.[20] Even though effective biocidal activities were obtained compared to other antimicrobials in these previous studies, slower inactivation rate was observed on PET surfaces as opposed to cotton, due to the more hydrophobic nature of PET. In this regard, it is desired to develop *N*-halamine coatings on PET fabrics with improved inactivation rate.

In a recent study, Kocer *et al.* developed a new acrylamide type *N*-halamine vinyl monomer, hydantoin acrylamide (HA), having a theoretical chlorine loading of 31 wt %.[21] This monomer was copolymerized with several vinyl monomers, and long-lasting functionality with almost instantaneous microbe inactivation was obtained on cotton surfaces.[22] These reactive copolymers were soluble in organic solvent mixtures, i.e., ethanol/water and ethanol/acetone; whereas, water dispersible/soluble polymers are advantageous in terms of industrial applications and environmental concerns. This paper reports the synthesis and application of such waterborne biocidal HA copolymers to impart antimicrobial functionality to PET fabrics. In this regard, a terpolymer of HA monomer with glycidyl methacrylate and [2-(methacryloyloxy)ethyl]trimethylammonium chloride was developed for the purpose of bonding with the surfaces and obtaining water dispersibility, respectively.

EXPERIMENTAL

Materials and Instrument

All starting chemicals were purchased from Aldrich Chemical Company, TCI America, or Alfa Aesar, and used as is. Desized, scoured woven PET fabric (five harness sateen) was obtained from Testfabrics. Clorox® brand household bleach was used for chlorination. Bacteria cultures of *Staphylococcus aureus* ATCC 6538 and *Escherichia coli* O157:H7 ATCC 43895 were purchased from American Type Culture Collection (Rockville, MD), and trypticase soy agar was obtained from Difco Laboratories.

Synthesis of the Copolymers

Hydantoinylacrylamide (HA) monomer was synthesized by a procedure outlined previously.[21] Similarly the copolymer poly(-hydantoinyl acrylamide-*co*-glycidyl methacrylate) (HA-*co*-GM) was prepared according to a previous study (Figure 1).[22]

Poly(hydantoinyl acrylamide-*co*-glycidyl methacrylate-*co*−2-(methacryloyloxy)ethyl trimethylammonium chloride) (HA-*co*-GM-*co*-METAC) copolymer was prepared by free radical polymerization. Briefly, 0.96 g (4 mmol) of HA, 0.58 g (4 mmol) of glycidyl methacrylate (GM), and 0.42 g (2 mmol) of 2-(methacryloyloxy)ethyl trimethylammonium chloride (METAC) were dissolved in 4 mL of anhydrous methanol in a 50 mL round-bottom flask reactor. Then, 0.02 g of the radical initiator azobisisobutyronitrile was added. The flask was equipped with a nitrogen inlet and a condenser. Nitrogen was bubbled through the solution for 15 min to remove dissolved oxygen. The polymerization was performed by stirring the mixture at 65°C for 60 min under nitrogen atmosphere (Figure 2). The copolymer poly(HA-*co*-GM-*co*-MATEC) formed a stable colloid in water when appropriate water was added to the polymer solution without isolation of the solid polymer.

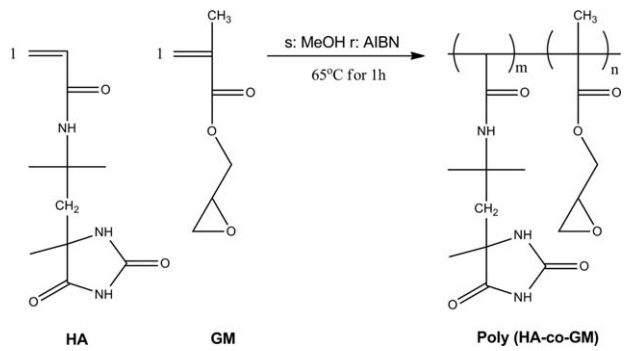

Figure 1. Synthesis of the copolymer poly (HA-*co*-GM).

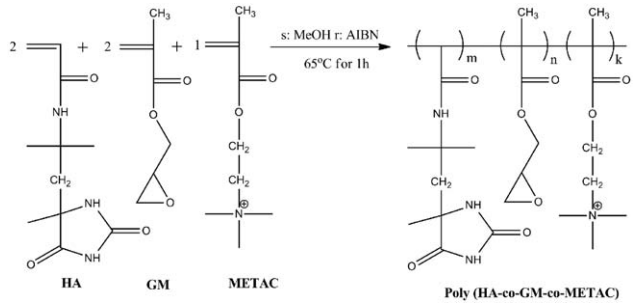

Figure 2. Synthesis of the copolymer poly(HA-*co*-GM-*co*-MATEC).

Coating and Chlorination Procedure

A 5 wt % poly(HA-*co*-GM-*co*-MATEC) aqueous dispersion was used to coat the fabrics. An acetone/water mixture (3:2 by weight) was used to coat 3 wt % poly(HA-*co*-GM), as this copolymer was not soluble or dispersible in water. The reason for using different concentrations for the coatings is to adjust to about the same chlorine loadings on the fabric surfaces. Since poly(HA-*co*-GM) copolymer has higher weight percentage of HA monomer in the copolymer structure, it also has higher number of N–H groups to be chlorinated resulting in higher chlorine loading for a fixed coating concentration.

PET fabrics were coated without any surface treatment. In this regard, the fabrics were immersed in the prepared coating solutions for 15 min, then padded through a laboratory wringer to remove excess solvents and obtain uniform coatings. The coated fabrics were cured at 165°C for 1 h, followed by washing with a 0.5 wt % detergent solution for 15 min at ambient temperature.

The fabrics were halogenated using commercial household bleach, Clorox®. A 10 wt % Clorox® solution at pH 7 was prepared using 6M HCl, and the coated fabrics were immersed in this solution for 1h at ambient temperature without stirring. The fabrics were then vigorously washed with tap water followed by rinsing with distilled water. Finally the fabrics were dried at 45°C for 1 h, so that the free chlorine on the surfaces was removed. The oxidative chlorine loadings were determined by conducting an iodometric/thiosulfate titration. The halogen amount was calculated using eq. 1 in which Cl^+ % is the weight percent of oxidative chlorine, N is the normality of the titrant in equiv/L, V is the volume of the titrant in L, and W is the weight of the PET sample in g.

$$Cl^{+}\% = \left(\frac{35.45 \times N \times V}{2 \times W}\right) \times 100 \quad (1)$$

Stability Testing

Washing stabilities of oxidative chlorine and the durabilities of the coatings were evaluated with a standard washing test according to AATCC Test Method 61. Fabric swatches in the size of 2.54 × 5.08 cm^2 were placed in a canister, then 150 mL of 0.15 wt % AATCC aqueous detergent solution was added along with 50 stainless steel balls. The loaded canisters were rotated at 49°C in a laboratory Launder-Ometer. Equivalents of 5, 10, 25, and 50 machine washes were performed. Three sets of experiments were conducted. In the first set, the chlorinated fabrics were washed and the remaining chlorine loadings were determined after a certain number of washing cycles. This set of experiments provided information about chlorine stabilities of the coatings. In the second set of samples, the fabrics were re-chlorinated and then titrated after a specified number of washing cycles. This set of experiments addressed the durabilities of the coatings. The third set of experiments was conducted to simulate real-life applications. In this experiment, the unchlorinated swatches were chlorinated during washings and titrated after the specified number of washing cycles. In this regard, 3 wt % Chlorox® was added to the washing solutions without any pH adjustment, so the swatches were chlorinated *in situ*.

An Accelerated Weathering Tester (The Q-panel Company) was used to evaluate the UVA light stabilities of the coatings. Two sets of experiments were conducted. In the first set of experiments, the stabilities of the oxidative chlorine were tested by exposing the halogenated swatches to UVA light (Type A, 315–400 nm) from 1 to 120 h. The remaining chlorine loadings were determined after specified times of exposure to analyze the chlorine stability, and rechlorinations were performed at one day exposure intervals to address the rechargeabilities of the coatings. In the second test of experiments, the unhalogenated swatches were chlorinated and titrated at one day exposure intervals to investigate if there was a photolytic decomposition taking place in the unchlorinated coatings.

Antimicrobial Efficacy Testing

The antimicrobial efficacies of the coatings were tested against *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* O157:H7 (ATCC 43895) using a "sandwich test". Briefly, a known concentration of bacteria were suspended in 100 μM phosphate buffer at pH 7, and 25 μL of this suspension were placed on the surface of a swatch having the size of 1 cm^2. Then, an identical swatch was placed on top, and a sterile weight was added to provide sufficient contact with the microorganisms. After a specified time of contact (2, 5, 10, and 30 min), the whole sandwich was immersed in 5 mL of 0.02N sodium thiosulfate solution and vortexed for 2 min. Vortexing provided the remaining oxidative chlorine to be quenched and transferred the bacteria from the surface to the solution. Dilutions were prepared from the vortexed solutions with 100 mM phosphate buffer solution at pH 7 and plated on trypticase soy agar plates. After incubation at 37°C for 24 h, the viable bacteria were enumerated to determine biocidal activity. The unchlorinated swatches serving as control samples were treated in the same manner.

RESULTS AND DISCUSSION

FT-IR Characterization

Since the copolymer poly(HA-*co*-GM) has been characterized in our previous publication,[22] only the FT-IR spectrum of the copolymer poly(HA-*co*-GM-*co*-MATEC) and the monomers are shown in Figure 3. The bands at 1769, 1705, and 1645 cm^{-1}in the spectrum of the copolymer are due to the imide, the heterocyclic amide, and the acyclic amide groups of the comonomer

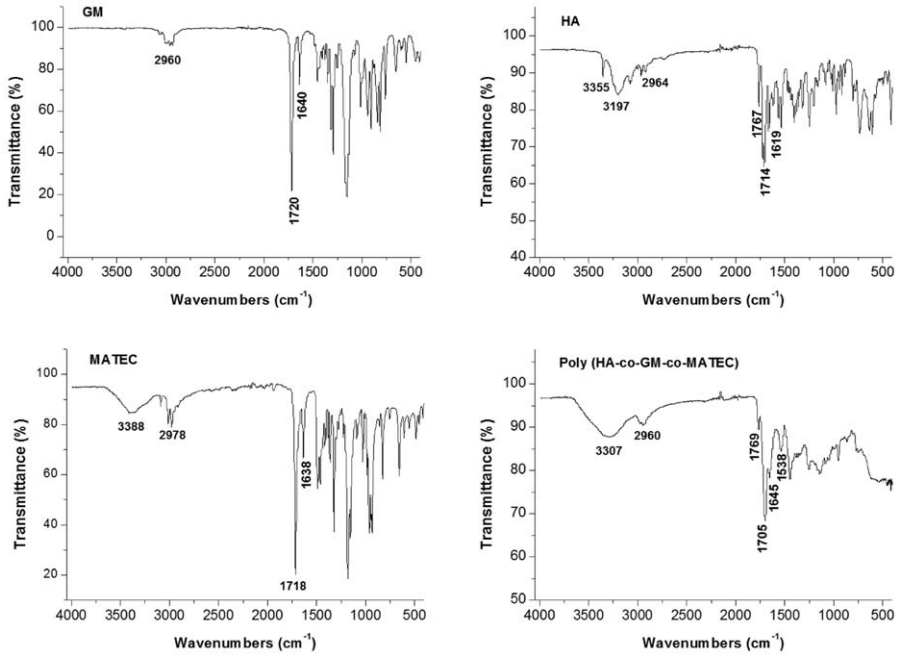

Figure 3. FT-IR spectra of the monomers and the copolymer.

Table I. Stability toward Washing of Coatings on PET (Cl^+ % Remaining)[a]

	Poly(HA-*co*-GM)			Poly(HA-*co*-GM-*co*-MATEC)		
NWC	A	B	C	A	B	C
0	0.18	0.18		0.19	0.19	
5	0.11	0.18	0.18	0.04	0.13	0.16
10	0.09	0.18	0.18	0.04	0.10	0.16
25	0.06	0.18	0.17	0.01	0.07	0.15
50	0.04	0.16	0.17	0.00	0.06	0.14

A: Chlorinated before washing, B: chlorinated before washing and then postchlorinated, C: *in situ* chlorinated; chlorinated during washings, NWC: number of machine washing cycles.
[a]The error in the measured Cl^+ weight percentage values was ±0.01.

HA, respectively. The ester carbonyl group stretching of GM at 1720 cm^{-1} and MATEC at 1718 cm^{-1}overlapped with the carbonyl stretching band of the heterocyclic amide group at around 1705 cm^{-1}. The vibrational stretching bands for the vinyl hydrogens of the monomers were obtained at around 1640, 1619, and 1638 cm^{-1} for the comonomer GM, HA, and MATEC, respectively. All of these vinyl stretching bands disappeared in the spectrum of poly(HA-*co*-GM-*co*-MATEC) signifying the copolymer formation. Moreover, CH, CH_2, and CH_3 deformation of the comonomers were observed as a broader band at around 2960 cm^{-1}in the spectrum of the copolymer.

Washing Stabilities

Washing stabilities of both poly(HA-*co*-GM) and poly(HA-*co*-GM-*co*-MATEC) were studied to analyze how incorporation of MATEC to the copolymer poly(HA-*co*-GM) affects the washing stabilities. The results are shown in Table I. In this table, column A represents remaining chlorine loadings of prechlorinated swatches, column B depicts chlorine loadings of pre- and postchlorinated swatches, and column C shows remaining chlorine loadings of *in situ* chlorinated (with 3 wt % Clorox®) swatches during washings. In this regard, oxidative chlorine stabilities could be analyzed from column A and the durabilities of the coatings could be evaluated from column B. Since dilute bleach is generally added during launderings especially for white apparels, column C is a better representation of real-life applications.

It was found that 3 wt % poly(HA-*co*-GM) and 5 wt % (HA-*co*-GM-*co*-MATEC) solution resulted in 0.18 and 0.19 wt % initial chlorine loadings on PET surfaces, respectively. As can be seen in Table I, even after 5 machine washing cycles, dramatic chlorine loss was observed for both coatings. It has been reported in a previous study that 0.05% Cl^+ is needed for effective biocidal activity.[23] Therefore, poly(HA-*co*-GM) coating was considered to be still antimicrobial, whereas poly(HA-*co*-GM-*co*-MATEC) coating lost its activity after five washing cycles. Nevertheless, when the swatches were rechlorinated after each of the washing cycles, most of the lost chlorine could be restored. For example, although all of the active chlorine was consumed after 50 machine washings for both copolymers, around 85 and 30% of the initial chlorine loadings could be reached upon rechlorination for poly(HA-*co*-GM) and poly(HA-*co*-GM-*co*-MATEC) coatings, respectively. This indicated that the loss in column A was mainly due to N—Cl bond dissociation rather than the coating being washed off from the surfaces. The durabilities of poly(HA-*co*-GM-*co*-MATEC) coatings were not comparable to poly(HA-*co*-GM), since the former coating was more hydrophilic due to its cationic group. On the other hand, when 3 wt % of bleach was introduced to washings for *in situ* chlorination, the durabilities and the stabilities of poly(HA-*co*-GM-*co*-MATEC) coatings were greatly improved. For instance, after 50 machine washings, 75% of the initial chlorine loading was found to be still on the surfaces. Although, poly(HA-*co*-GM-*co*-MATEC) terpolymer was water dispersible, the coatings on the PET surfaces were quite stable. It is thought that the improvement was due to in situ chlorination resulting in a more hydrophobic washing solution.

UVA Light Stabilities

UV-A light stabilities of the coatings were evaluated by exposing chlorinated and unchlorinated swatches to UVA light for up to 120 h. As can be seen in Table II, the oxidative chlorine amount

Table II. Stability toward UVA Light Exposure of Poly(HA-*co*-GM-*co*-MATEC) Coatings on PET (Cl^+ % Remaining)[a]

Time	Chlorinated	Unchlorinated
0	0.19	
1	0.18	
2	0.17	
3	0.16	
6	0.15	
12	0.13	
24	0.12	
24-Re	0.19	0.18
48	0.10	
48-Re	0.17	0.19
72	0.10	
72-Re	0.19	0.19
96	0.10	
96-Re	0.18	0.19
120	0.09	
120-Re	0.19	0.19

[a]The error in the measured Cl^+ weight percentage values was ±0.01. Re: Rechlorination.

Table III. Biocidal Efficacies of the Coated PET Fabrics

Samples	Contact time (min)	Bacterial reduction (log)	
		S. aureus[a]	*E. coli* O157:H7[b]
Control	30	0.92	0.39
Coated fabric Cl^+ % = 0.19	2	5.98	6.52
	5	5.98	6.52
	10	5.98	6.52
	30	5.98	6.52

[a] The inoculum concentrations was 5.98 logs.
[b] The inoculum concentrations was 6.52 logs.

progressively diminished till 24 h. On the other hand, after 24 h of exposure, the fabrics retained 0.12 wt % chlorine which was enough to perform reasonable antimicrobial activities.[23] When 24 h exposed swatches were rechlorinated, they could be loaded to their initial chlorine loadings. Further rechlorinations performed at 24 h UVA exposure intervals revealed that the chlorine loss was due to chlorine dissociation from the surfaces. Moreover, the unchlorinated swatches were loaded with around the initial chlorine level when they were chlorinated after certain times of UVA exposure. This result indicated that unlike from previous *N*-halamine studies,[21,22,24] there was no significant photolytic decomposition taking place in the coating.

It is speculated that this improved result is related to base material fabric composition. Most of the previous studies focused on cellulose base materials and photocatalytic decomposition was reported in all of these studies.[24–26] Additionally, in our previous study, poly (HA-*co*-GM) copolymer was coated on cotton fabrics and around 25% decomposition was observed upon 72 h exposure to UVA light.[22] Even though similar copolymer structure was used in this study, there was almost no decomposition on PET fabrics. Therefore, it is thought that decomposition of ether bonds might be contributing photolytic decomposition of *N*-halamines on cellulose materials. On the other hand, with more UVA resistant ester bonds, PET fabrics may not adversely affect the UVA light stabilities of *N*-halamine coatings. Further studies are needed to explain the exact mechanisms resulting in this difference.

Biocidal Efficacies

Antibacterial efficacies of the coatings are shown in Table III. The chlorinated and unchlorinated (control) samples were challenged with *S. aureus* and *E. coli* O157:H7 for contact times of 2–30 min. The control samples did not exhibit significant biocidal activity. It has been reported in various studies that the limited inactivation obtained for the unchlorinated swatches is due to adhesion of the microorganisms to the fabric surfaces. On the other hand, the swatches having 0.19 wt % oxidative chlorine loading inactivated all of the Gram-positive (*S. aureus*) and Gram-negative (*E. coli* O157:H7) bacteria (around 6 logs) within only 2 min of contact time. This is a superior antimicrobial activity on PET surfaces in the *N*-halamine literature. Although comparable inactivation rates on cellulose surfaces were observed in previous studies, it took longer times for complete inactivation on PET surfaces for the same *N*-halamine coatings. This difference is due to the hydrophobic nature of PET surfaces. Increasing surface hydrophobicity resulted in slower inactivation by making poorer contact with microorganisms. In this regard, the faster inactivation obtained in this study could be due to the existence of cationic trimethyl ammonium chloride groups imparting some hydrophilicity to the PET surfaces. In addition to effective biocidal activity, it is expected that all of the coating to be biocompatible, as previous in vitro cell viability test have suggested that *N*-halamine coatings with about the same chlorine loadings provide sufficient cytocompatibility to mammalian cells.[27,28]

CONCLUSIONS

[2-(methacryloyloxy)ethyl]trimethylammonium chloride was used to provide water dispersibility for a hydantoinyl acrylamide-*co*-glycidyl methacrylate polymer. The synthesized terpolymer, poly(-hydantoinyl acrylamide-*co*-glycidyl methacrylate-*co*-[2-(methacryloyloxy)ethyl]trimethylammonium) was coated on PET fabric and rendered biocidal upon halogenation with household bleach. It was found that introducing dilute bleach to the washing process greatly improved the stabilities, such that the fabrics possessed adequate chlorine loadings for effective antimicrobial activities. Even though the wash fastness of the coatings was not comparable to poly(hydantoinyl acrylamide-*co*-glycidyl methacrylate) coatings, the coating exhibited acceptable stabilities and durabilities for industrial applications. UVA light stabilities of the coatings were remarkable in that no significant photolytic decomposition was observed. The fabrics were challenged with *S. aureus* and *E. coli* O157:H7, and around six logs of both bacteria were completely inactivated within only 2 min of contact time. Even though comparable antimicrobial efficacies were reported with various *N*-halamines on cellulose based materials, this study was the first to report such rapid inactivation on PET fabrics. It was concluded that the incorporation of the cationic monomer to the polymer structure resulted in rapid inactivation by increasing the surface hydrophilicity.

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