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Anticoagulant Surface of 316 L Stainless Steel Modified by Surface-Initiated Atom Transfer Radical Polymerization

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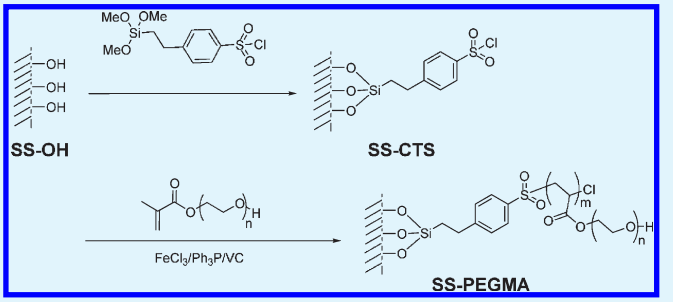
ABSTRACT: Polished 316 L stainless steel (SS) was first treated with air plasma to enhance surface hydrophilicity and was subsequently allowed to react with 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane to introduce an atom transfer radical polymerization (ATRP) initiator. Accordingly, the surface-initiated atom transfer radical polymerization of polyethylene glycol methacrylate (PEGMA) was carried out on the surface of the modified SS. The grafting progress was monitored by water contact angle measurements, X-ray photoelectron spectroscopy and atomic force microscopy. The polymer thickness as a function different polymerization times was characterized using a step profiler. The anticoagulative properties of the PEGMA modified SS surface were investigated. The results showed enhanced anticoagulative to acid-citrate-dextrose (ACD) blood after grafting PEGMA on the SS surface.



KEYWORDS: stainless steel, SI-ATRP, PEGMA, surface modification, biocompatibility, anticoagulant

INTRODUCTION

Tissue engineering materials are widely used in clinical therapy for coronary heart diseases, bone fracture, cardiac and vascular diseases, and so on.[1,2] Many of such materials are stainless steel (SS) based because of the excellent mechanical properties and chemical stability of SS.[3] However, the high rigidity of SS may have undesired effects on the organ; the corrosion of SS in the physiological environment may cause cytophathy; the direct contact of SS with blood may cause thrombus.[4] To reduce such problems, surface modification of SS was necessary for these applications.[5] These strategies are aimed at tailoring only the surface properties of material, to modify its biological activity, while preserving the bulk properties of the underlying support.[6] Different strategies have been applied to prepare well-defined surfaces, including painting, self-assembly, and grafting.[7] Among these strategies, polymer covered films showed some advanced features, especially with respect to their various and adjustable interference properties.[8] New strategies, such as "grafting to" and "grafting from", were developed to graft polymer chains on the surface via covalent bonding for the formation of a stable cover film.[9] Between these two methods, the "grafting from" strategy offered high theoretical grafting density because of the low steric hindrance and high mobility of small molecules.

The development of polymer chemistry in the field of living free radical polymerization provided the ability to control polymer structure and film thickness with high grafting density via the "grafting from" strategy. Typical living free radical polymerization techniques, such as stable free radical polymerization (SFRP),[10] atom transfer radical polymerization (ATRP),[11−13] and reversible addition−fragmentation chain transfer polymerization (RAFT),[14,15] have been developed for decades. Currently, these techniques have been well developed and widely used in developing new materials as well as in modifying solid surfaces because of their high functional group tolerance and mild experimental conditions.[16] The chain termination reactions in conventional free radical polymerization have been largely reduced in these living free radical polymerization techniques. The highest density, 0.8 polymer chain per nano square surface, was obtained via these strategies in the literature.[17] Among these "grafting from" techniques, ATRP was the most widely used because of its versatility in designing the grafted polymer chain. By introducing halogen containing groups on the solid surface, and then the subsequent ATRP of the monomer, high density polymer chains can be grafted onto the solid surface. This technique has been named surface-initiated ATRP (SI-ATRP).[18] In recent years, activators regenerated by electron transfer ATRP (AGET ATRP)[19] has been developed using of high oxidative state metal salts with levels as low as ppm. These high oxidative state metal salts allow easier handling in practical operation than normal ATRP, which used lower oxidized state metal salts. The AGET ATRP-based "grafting from" strategy also has been used in the modification of solid surfaces (such as silicon, metal, metal oxide, carbon, and polymers) with different shapes (such as plane, nanoparticles, tube, fiber, and film).[20−25] Furthermore, with the living characteristics of ATRP, the structure and length of the grafted polymer chain can be controlled and adjusted. Block, star, and hyperbranched polymer chains have been grafted from the

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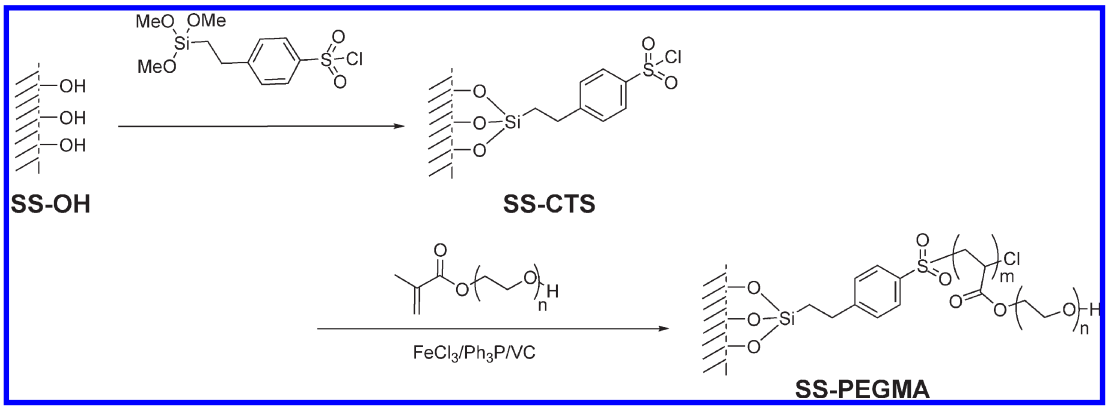
Scheme 1. Anchoring of CTS onto 316L SS and SI-ATRP Process of PEGMA



solid surface, which provided the surface with multiple functionalities for complex applications.[26]

However, modification of SS with polymer chains via the SI-ATRP technique has been rarely reported. Claes reported anchoring the poly(CPEA) by electrolysis followed by the use of SI-ATRP to modify an SS surface with polystyrene.[27] They found that the copper catalyst reacted with SS surface, which corroded the SS surface. The resulting rough surface precluded even thickness determination of the resulting polymer film. Fan et al. introduced an ATRP initiator onto the surface of TiO_2 covered 316 L SS surface for the SI-ATRP of PEGMA.[28] The results showed that the polymerization can be carried out without any free initiator or deactivator. Kang et al. reported a series of procedures to modify the stainless steel surface for multiple applications, such as reduction in protein adsorption[29] and the inhibition of biocorrosion.[30,31] Detailed SI-ATRP of MMA on the surface of cold roll steel, nickel, and SS was investigated by Zhu et al.[32] They used an iron-based catalyst system to avoid the possibility reaction between copper catalyst and these active metals.

In the current report, we selected the iron-based AGET ATRP strategy to conduct the SI-ATRP of polyethylene glycol methacrylate (PEGMA) on the 316 L SS surface. The polymerization behavior and morphology of the SS surface before and after polymerization was investigated. PEGMA is a well-known biocompatible polymer. The anticoagulantive properties of the resulting material were investigated. To the best of our knowledge, this should be the first report on the modification of SS via an iron-based AGET ATRP strategy.

EXPERIMENTAL SECTION

Materials. 316 L stainless steel (SS) with 0.5 mm thickness was purchased from Goodfellow Co. Ltd. containing Fe/Cr-18/Ni-10/Mo-3. It was cut to a size of 5 mm × 5 mm. 2-(4-Chlorosulfonylphenyl)ethyltrimethoxysilane (CTS) (50% in methylene chloride) was purchased from Meryer Chemical Co. Ltd., China, and was used directly. Tetrahydrofuran (analytical grade, Shanghai Chemical Regent Co. Ltd., China) was purified by standard procedures. Polyethylene glycol methacrylate (PEGMA, Mn~475 g/mol) was ordered from Aldrich and passed through a neutral Al_2O_3 column. Water was purified by a Millipore distillation apparatus. Other chemicals were ordered from Shanghai Chemical Regent Co. Ltd., China, and were used directly.

Surface Treatment of SS. The surface of the SS was polished sequentially with 600, 800, and 1200 mesh silicon carbide paper and W1 Al_2O_3 powder. The mirrorlike polished surface was further cleaned in an ultrasonic bath for 10 min sequentially with n-heptane, acetone, ethanol (anhydrous), and methanol (HPLC grade), until waster break-free surfaces were obtained. The SS samples were temporarily stored under methanol before treatment with the plasma.

Table 1. Water Contact Angles of 316L Stainless Steel before and after Surface Modification

	contact angle (deg)
SS−OH[a]	61 ± 2
SS−OH[b]	52 ± 2
SS-CTS	84 ± 3
SS-PEGMA	48 ± 2

[a] Bare SS. [b] Air-plasma-treated SS (150 W for 120 s).

Immobilization of Initiator. The SS was dried with a heat gun and was placed under plasma at 150 W for 120 s with air flow of 55 mL/min using a DT-03 plasma system from Suzhou China. Subsequently, the SS was transferred into a round-bottom flask, covered with THF (10 mL), and bubbled with argon for 15 min to eliminate air. CTS (0.1 mL) was added into the flask. The reaction mixture was sealed, placed in an ultrasonic bath for 30 s, and allowed to react for 24 h at 30 °C. The SS plate was carefully cleaned by ultrasonication with THF, acetone and methanol for 5 min with each solvent, and the SS plate was finally dried with a heat gun.

ATRP of PEGMA from Initiator-Functionalized SS Surface. In a typical ATRP grafting polymerization, PEGMA (1 mL, $M_n \approx 475$, 5 mmol), $FeCl_3$ (1.6 mg, 0.01 mmol), and PPh_3 (5.24 mg, 0.02 mmol) were added into a 5 mL ampule. The mixture was bubbled with Ar for 10 min. Afterward, four initiator-functionalized SS plates and Vitamin C (Vc, 3.6 mg, 0.02 mmol) were added into the ampule. The ampule was flame-sealed and placed into an oil bath, which was maintained at 60 °C. After 24 h, the ampule was opened. SS plates were taken out and washed with 5 mL of THF with the aid of an ultrasonic bath four times, for 5 min each time. The SS plates were finally dried under a vacuum for 24 h.

Characterization. The surface of the SS before and after polishing was examined using a Leica DM 4000 M microscope. Water contact angles were measured using a JC2000 contact angle determination system (Shanghai Zhongchen Co Ltd., China). The surface atomic compositions of the metal, metal-initiator and metal-g-PEGMA surface were measured using a KRATOS Analytical Ultra X-ray photoelectron spectroscopy (XPS) apparatus with Mg Ka source operating at 12 KV, 11 mA, and 2×10^{-8} Torr. The spectra were calibrated and referenced to C for 1 s at 248.6 eV. The thickness of the grafted polymer film was measured using an Alpha-step 500 profiler. AFM measurements were

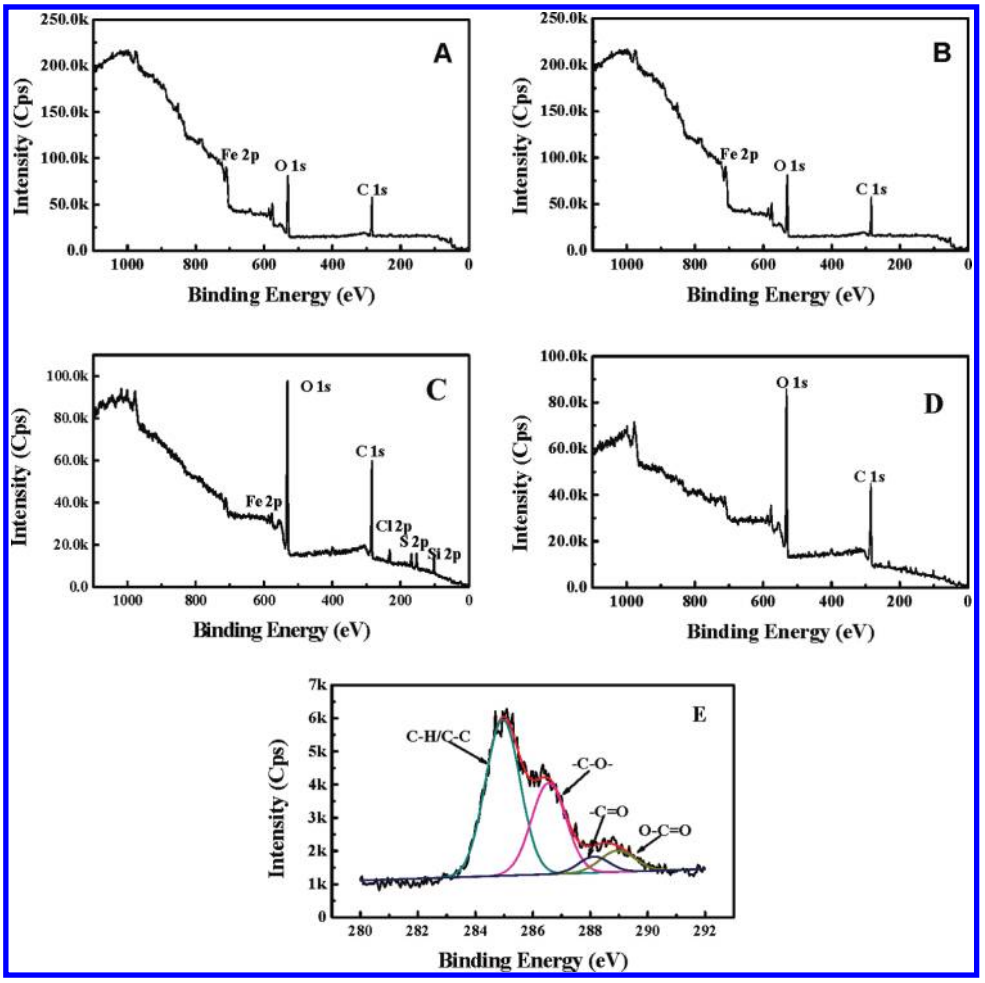


Figure 1. XPS survey spectra of (A) bare, (B) plasma-treated, (C) initiator, and (D, 48 h reaction) PEGMA grafted 316 L stainless steel surfaces. (E) High-resolution spectrum of the C 1s region of PEGMA-grafted 316 L stainless steel.

conducted using a MutiMode V machine. The anticoagulant properties were characterized using kinetic clotting time. The detailed method was performed as follows: Human whole blood (30 mL) from a healthy volunteer was collected and mixed with an aqueous solution containing anhydrous D-glucose (0.136 M), sodium citrate dihydrate (0.075 M) and citric acid monohydrate (0.0004 M) (ACD, 3 mL). Briefly, 100 μL of ACD blood was carefully added to the test samples surface, followed by the addition of 10 μL of calcium chloride solution (0.2 mol·L^{-1}). Thereafter, time was recorded. After 5, 10, 20, and 40 min, the surface of the test samples were individually rinsed slowly with distilled water. The resulting liquid was collected in a 96-well plate. The O.D. of the surplus extricate hemoglobin in the flowed liquid was measured in a spectrophotometer (Shimadzu UV-3150 UV−vis−NIR Spectrophotometer) at a wavelength of 545 nm.

RESULT AND DISCUSSION

Surface-Initiated ATRP of PEGMA on SS. Atom transfer radical polymerization (ATRP) has been proven to be an effective route to graft polymer chains on a solid surface, including stainless steel (SS).[26] Here, the surface of SS was functionalized with polyethylene glycol methacrylate (PEGMA) via activators regenerated by electron transfer ATRP (AGET ATRP) according to Scheme 1. First, the SS surface was polished stepwise with sand paper and Al_2O_3 until it attained a mirror like appearance. It was further exposed to air plasma for 120 s at 150 W to increase the amount of OH groups on the surface. Then, the SS was allowed to react with 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CTS) to immobilize the ATRP initiator group on the surface. 2-(4-Chlorosulfonylphenyl)ethyltrimethoxysilane (CTS) was selected as the functional agent because it contains the alkyltrialkoxysilane group, which serves as coupling point, and the chlorosulfonyl group, which serves as the ATRP initiator.[33] With this agent, the process was simplified from three steps to two, as compared with the normally used route, which included an additional step the step to convert reactive groups (−NH_2 or −OH) to halogen. The current route should be more effective compared with the normal route in reducing possibilities for

Table 2. Surface Atomic Compositions (wt %) of 316L Stainless Steel before and after Surface Modification via XPS

	C	O	S	Si	Cl	Fe
SS−OH[a]	43.8	50.7	0	0	0	5.5
SS−OH[b]	43.2	51.1	0	0	0	5.7
SS-CTS	42.3	38.4	8.5	5.2	4.2	1.4
SS-PEGMA	45.7	52.4	0	0	1.9	0

[a] Bare SS. [b] Air-plasma-treated SS (150 W for 120 s).

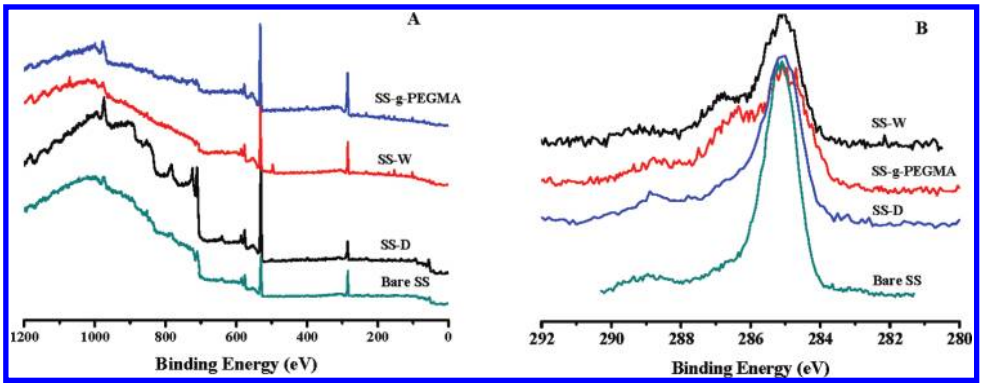


Figure 2. XPS spectra of SS samples after different treatment processes. (A) Full scan; (B) high-resolution XPS spectra of the C 1s region. Bare-SS, bare SS sample; SS-D, bare SS dipping in PEGMA solution for 24 h followed by washing with water under ultrasonic; SS-W, PEGMA-grafted SS washing with 5 wt % sodium dodecyl benzene sulfonate solution for 2 h under ultrasonic followed by washing under ultrasonic with water, THF, acetone, and methanol for 5 min with each solvent; SS-g-PEGMA, PEGMA grafted SS.

hydrolysis of moisture sensitive silane groups during the introduction of ATRP initiator groups.

The surface-initiated AGET ATRP of PEGMA was conducted using $FeBr_3/PPh_3$/VC as a catalyst. As shown in the literature, SS 316 L contains iron and nickel, which would significantly affect the efficiency of the normally used copper-based ATRP catalyst system because of the exchange reaction between iron or nickel and copper.[34] Furthermore, this reaction also showed corrosive effects on the surface of SS. By using an iron-based catalyst system, the surface-initiated ATRP of methyl methacrylate (MMA), N,N′-dimethylaminoethyl methacrylate (DMAEMA), oligo-ethylene glycol methyl methacrylate (OEGMA) and 2,2,2-trifluoroethyl methacrylate (TFEMA) on the active iron, nickel and stainless steel surface were successfully conducted by Zhu et al.[32] However, the use of oxidatively sensitive Fe(II) in the catalyst system increased the operative difficulty. Thus, we selected the stable ion Fe(III) as the catalyst and Vc as the reducing agent for the AGET ATRP technique to perform the surface-initiated ATRP of PEGMA, which is the first report of such technique using for grafting polymer on the SS surface.

The water contact angles of SS surface before and after these modifications are summarized in Table 1. The water contact angle for the SS surface after polishing was 61 ± 2°. It was reduced to 52 ± 2° after plasma irradiation because of the increased number of OH groups on the surface. The water contact angle subsequently increased to 84 ± 2° after anchoring CTS because of the introduction of a hydrophobic sulfonyl group. The value decreased to 48 ± 2° after grafting the hydrophilic PEGMA polymer chain onto the SS surface. This value is in agreement with that reported in the literature, 44° for the water contact angle of a PEGMA surface.[32,26−37] The water contact angle variations with different treatment steps reflected the change of surface component. The value of the water contact angle was determined using 3 samples and 4 times for each sample on different areas, the maximum difference for each surface was 3°, which implies the surface of these samples was almost uniform.

To further confirm the modification process, the surface elemental composition was characterized via X-ray photoelectron spectroscopy (XPS). The results are summarized in Figure 1 and Table 2. The XPS spectra of bare SS (Figure 1A) and plasma treated SS (Figure 1B) are highly similar. C, O and Fe are observed on the surface of SS. High concentrations of O and C on the surface should result from the large amount of O containing groups adsorbed on the surface of SS. This high O concentration did not significantly change, even after the treatment with air plasma. This lack of change may result from the small mass of H atom relative to that of O atom. However, after the introduction of CTS on the SS surface, signals due to Si, S and Cl were also observed in the XPS spectrum (Figure 1C). Simultaneously, the elemental distribution on the SS surface changed. However, the elementary distribution of Si, S, Cl, C, and O was different than that of CTS, which should be because the surface film of CTS was very thin (lower than the XPS detection limit, e.g., 8−10 nm[9]). Additionally, the possibility of cross-linking reactions between CTS through the hydrolysis of alkyltrialkoxysilane groups during the anchoring process and the high concentrations of C and O on the SS surface made it difficult to accurately estimate the structure of the SS surface. However, the observation of S, Si and Cl signals implies that the anchoring of CTS on SS surface was successful. After grafting the PEGMA polymer chain, signals due to Fe, Si, and S decreased to an undetectable level in the XPS spectrum (Figure 1D), suggesting that there was polymer film grafted on the SS surface and that the thickness of the polymer film was greater than the detection limit of XPS (8−10 nm[9]). The oxygen concentration significantly increased after grafting (Table 2), additionally confirming that the PEGMA chain grafted onto the SS surface. However, because of the high oxygen adsorption ability of PEGMA,[38] the concentrations of C and O in the XPS results differed from the theoretical values (C 53.0% and O 35.6%). High-resolution C data in XPS spectra of grafted samples (Figure 1E) were in good agreement with those of PEGMA, which confirmed the introduction of the surface polymer chain structure. Thus, the surface-initiated ATRP of PEGMA on the surface of SS was successfully conducted under the current conditions.

The adhesion force for the grafted PEGMA on the SS substrate was an important factor for future application. It was examined by washing with surfactant solution under ultrasonic bath. The PEGMA grafted SS was dipped into 5 wt % sodium dodecyl benzene sulfonate solution for 2 h under ultrasonic followed by washing under ultrasonic with water, THF, acetone and methanol for 5 min with each solvent, and finally dried with heat gun. The treated sample was labeled as SS-W. For contrast, the bare SS was dipped into PEGMA monomer for 24 h followed by washing with 5 mL THF under the aid of ultrasonic bath for four times, 5 min for each time. The treated sample was labeled

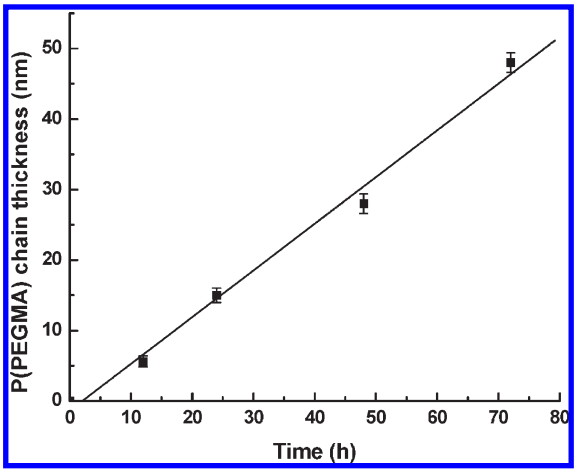


Figure 3. Thickness versus polymerization time in the SI-ATRP grafting of PEGMA from stainless steel substrate in solution at 60 °C. [PEGMA]/[$FeCl_3$]/[PPh_3]/[Vc] = 300/1/2/2. PEGMA/THF = 1/1 (v/v).

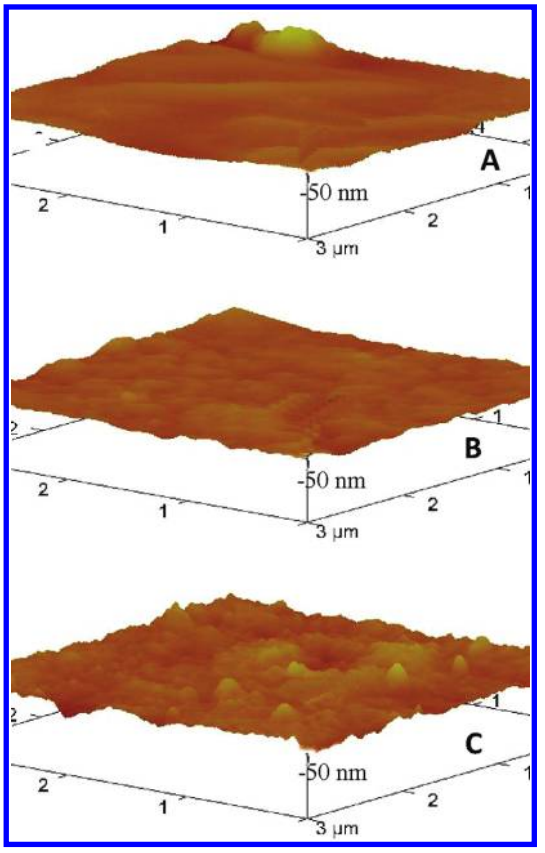


Figure 4. AFM images of (A) bare and (B, C) PEGMA-grafted with different time ((B) 48 and (C) 72 h) stainless steel surface.

as SS-D. The surface chemical composition of these two samples was characterized by XPS. The results were showed in Figure 2 along with bare SS and PEGMA grafted SS (SS-g-PEGMA). The results showed that the XPS spectra of SS-W and SS-g-PEGMA were almost same, which implied that the PEGMA chains linked on the surface of SS is strong enough for the exchange effect of sodium dodecyl benzene sulfonate under ultrasonic. Very similar

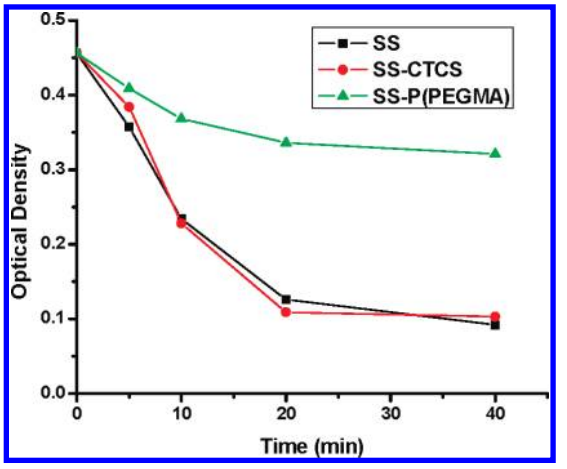


Figure 5. Relationship between time and optical density value for ACD blood solution measured at 540 nm.

XPS spectra of bare SS and SS-D confirmed that the adsorbed PEGMA on SS surface can be removed by washing with THF under ultrasonic.

Kinetics of Surface-Initiated AGET ATRP of PEGMA and Surface Morphology. The polymer film thickness as a function of polymerization time was monitored by the step profiler. The results are shown in Figure 3. The thickness of the polymer film increased with the polymerization time. It reached a thickness of approximately 50 nm after 72 h polymerization. Zhu et al. reported that a thickness of only 6.4 nm of PMMA film can be grafted onto the SS surface using the "adding free initiator" ATRP strategy, while the maximum thickness of PMMA film can be increased to 20 nm or even 40 nm on the surface of cold rolled steel,[32] whereas, by using the "adding deactivator" strategy, a PMMA film with a thickness of 80 nm was obtained in 80 min. Similar results were observed in the current system. With the AGET ATRP approach, no obvious polymer film can be observed on the surface of SS by using the "adding free initiator" strategy because of monomer depletion in the solution as well as termination between surface and solution radicals. Thus, the "adding free initiator" strategy in grafting PEGMA on SS surface by AGET ATRP proceeded with very low efficiency.

The surface morphology of the SS surface before and after grafting was characterized by AFM. The results are shown in Figure 4. The surface morphology was significantly different before and after grafting the PEGMA polymer chain. The SS surface was relatively smooth before grafting but became rough after grafting PEGMA. The rms roughness for the bare polished SS, SS with grafted PEGMA for 48 and 72 h were (0.5 ± 0.1) nm, (2.2 ± 0.2) nm, and (3.9 ± 0.6) nm, respectively. The rms roughness increased with polymerization time or the polymer film thickness. Similar results were found by Voccia et al. when grafting a PCL chain on an SS surface. The reason should be due to the motivation and entanglement of the polymer chains.[37]

Anticoagulative Effects of SS Surface before and after Modification. PEGMA-based polymer materials have been widely used as biorelated materials because of their high biocompatibility.[39−41] Here, PEGMA was grafted onto the surface of SS to enhance its anticoagulative properties. Thus, the anticoagulant properties of the SS surface before and after grafting were characterized. The results are shown in Figure 5. For the bare SS surface, the O.D. of ACD blood was reduced to 0.1 after

approximately 20 min of contact with the surface. Similar results were observed in the case of a CTS modified SS surface. However, after grafting PEGMA chains onto the SS surface, the O.D. value of ACD blood still remained at a relatively high value (approximately 0.35) even after 40 min of contact. Thus, the anticoagulative properties of the SS surface were significantly enhanced by grafting the PEGMA chain, which would help to improve its biological applications. Further investigation of such techniques toward the modification of SS-based tissue engineering materials was undertaken in our lab.

CONCLUSION

The iron-mediated surface-initiated activators regenerated by electron transfer ATRP (AGET ATRP) method was used to introduce polyethylene glycol methacrylate (PEGMA) on 316 L stainless surface and was successfully carried out under catalysis by $FeBr_3/PPh_3$/VC. The water contact angle was reduced to approximately 48 degrees, and high-resolution carbon X-ray photoelectron spectroscopy (XPS) spectrum of the SS surface with PEGMA confirmed the successful grafting of PEGMA onto the SS surface. The thickness of PEGMA film increased linearly with polymerization time up to approximately 50 nm. The morphology of the SS surface was significantly altered after grafting. The anticoagulative properties toward ACD blood were enhanced after the PEGMA modification of SS relative to those of the bare SS, e.g., a high O.D. value was observed even after 40 min of contact with modified SS, whereas low O.D. values were observed after only 20 min of contact for bare SS.

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