Supporting Information

Amino Acid-Based Zwitterionic Polymer Surfaces Highly Resist Long-Term Bacterial Adhesion

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Experimental Section

Synthesis of SerMA, LysAA and OrnAA Monomers

The O-methacryloyl serine (SerMA), N-ε-methacryloyl lysine (LysAA) and N-δ-methacryloyl ornithine (OrnAA) monomers were synthesized using the method reported previously. [1, 2]

The amino acid (L-serine, L-lysine or L-ornithine, 100 mmol) was dissolved in 200 ml water at 90 °C. Then basic cupric carbonate (62.5 mmol) was added into the solution and stirred for 10 min. After filtering the insoluble residue, 100 ml of acetone was added into the solution followed by addition of 50 ml of 2 M aqueous KOH. After that, methacryloyl chloride (125 mmol) and 55 ml of 2 M aqueous KOH were added dropwise and simultaneously over 20 min at 0°C. The reaction was stirred overnight at room temperature. The blue precipitate was filtered and washed successively with water (50 ml × 2), ethanol (50 ml × 2), and diethyl ether (50 ml × 2). To remove the copper protection, 8-quinolinol (68.9 mmol) was added to a stirred suspension of the blue monomer-copper complex in 200 ml chloroform, followed by the addition of 200 ml water. After shaking overnight, the water phase was separated and concentrated to 20 ml. The final product in water was recrystallized from THF to get white powder. The structures of three monomers were confirmed by ^{1}H NMR (D_2O, 300 MHz).

^{1}H NMR of SerMA: δ= 6.09 (s, 1H, $C{=}CH_2$), 5.68 (s, 1H, $C{=}CH_2$), 4.53 (d, 2H, CH_2), 4.06 (t, 1H, CH), 1.85 (s; 3H, CH_3).

^{1}H NMR of LysAA: δ= 5.74 (s, 1H, $C{=}CH_2$), 5.50 (s, 1H, $C{=}CH_2$), 3.80 (t, 1H, CH), 3.34 (t, 2H, CH_2), 1.97 (s, 3H, CH_3), 1.75-2.00 (m, 2H, CH_2), 1.60-1.80 (m, 2H, CH_2), 1.40-1.60 (m, 2H, CH_2).

^{1}H NMR of OrnAA: δ= 5.75 (s, 1H, $C{=}CH_2$), 5.51 (s, 1H, $C{=}CH_2$), 3.82 (t, 1H, CH), 3.37 (t, 2H, CH_2), 1.97 (s, 3H, CH_3), 1.75-1.95 (m, 2H, CH_2), 1.60-1.80 (m, 2H, CH_2).

Synthesis of AspAA and GluAA Monomers

N^4-(2-methacrylamidoethyl) asparagine (AspAA) and N^5-(2-methacrylamidoethyl) glutamine (GluAA) were prepared through reaction of the corresponding amino acid (aspartic acid or glutamic acid) with N-(2-aminoethyl) methacrylamide hydrochloride (AEMAA·HCl).

AEMAA·HCl was synthesized with the method reported previously.[3] Ethylenediamine (7.5 mmol) was first dissolved in water (75 ml), adjusted to pH 8.5 by adding 3N HCl solution, and kept at 0 °C. Methacryloyl chloride (9 mmol), diluted in anhydrous chloroform (50 ml), was then added dropwise at 0 °C over 2 h. The reaction was carried out for another 2 h at 0 °C under stirring conditions. The aqueous layer was then separated and extracted with chloroform three times to remove the excessive methacryloyl chloride. Water was then removed under reduced pressure to yield white solid. The solid was washed with methanol repeatedly. After removing methanol, clear yellow oil of AEMAA·HCl was obtained. ^{1}H NMR (300 MHz, D_2O): δ= 5.76 (s, 1H, $C=CH_2$), 5.53 (s, 1H, $C=CH_2$), 3.60 (t, 2H, $CH_2–NH_2$), 3.21 (t, 2H, $CONH–CH_2$), 1.96 (s, 3H, CH_3-$C=CH_2$).

Boc-L-aspartic acid *α-tert*-butyl ester or boc-L-glutamic acid *α-tert*-butyl ester (6.9 mmol) was dissolved in 20 ml dichloromethane. To activate the carboxylic acid group, CDI (7.6 mmol) was added slowly. After stirring for 1 h, AEMAA·HCl (8.8 mmol, dissolved in 5 ml DMF) and triethylamine (17.7 mmol) were added dropwise, and stirred overnight at room temperature. The resulting solution was then purified by extraction with water, 0.1 M HCl, and brine three times each. The solvent was removed to obtain the white solid. To remove the protection groups, the white solid was dissolved in a mixed solution of 4 ml CF_3COOH and 4 ml CH_2Cl_2 and stirred for 24 hours. The final product (AspAA or GluAA) was obtained by precipitating the resulting solution in diethyl ether.

^{1}H NMR of AspAA: δ= 5.76 (s, 1H, $C=CH_2$), 5.52 (s, 1H, $C=CH_2$), 4.33 (t, H, CH), 3.45 (m, 4H, CH_2CH_2), 3.02 (d, 2H, CH_2), 1.99 (s, 3H, CH_3).

^{1}H NMR of GluAA: δ=5.68 (s, 1H, $C=CH_2$), 5.46 (s, 1H, $CH=CH_2$), 3.95 (t, 1H, CH), 3.38 (m, 4H, CH_2CH_2), 2.44 (m, 2H, CH_2), 2.19 (m, 2H, CH_2), 1.92 (s, 3H, CH_3).

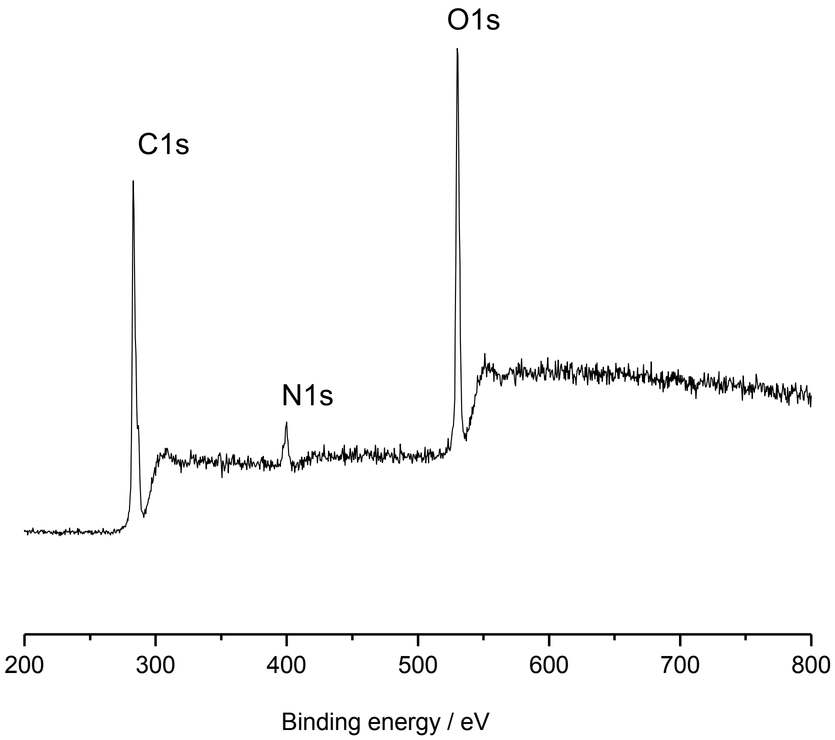

Figure S1. XPS spectrum of the pSerMA-grafted surface

Reference:

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3. Chan, G. Y.; Jhingran, A. G.; Kambouris, P. A.; Looney, M. G.; Solomon, D. H. Approaches to the Controlled Formation of Network Polymers: 1. Synthesis and Evaluation of Monomers with Vinyl Differentiation. *Polymer* **1998,** *39* (23), 5781-5787.