

Supporting information for Polymer Chemistry manuscript:

Patterning of individual *Staphylococcus aureus* bacteria onto photogenerated polymeric surface structures

Marta Palacios-Cuesta^a, Aitziber L. Cortajarena^b, Olga García^{a*} and Juan Rodríguez-Hernández^{a*}.

^a Department of Chemistry and Properties of Polymers, Instituto de Ciencia y Tecnología de Polímeros, (ICTP-CSIC), Juan de la Cierva 3, 28006-Madrid, Spain.

* To whom correspondence should be addressed. E-mail: ogarcia@ictp.csic.es and rodriguez@ictp.csic.es

^b Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), Cantoblanco, 28049 Madrid, Spain & CNB-CSIC-IMDEA Nanociencia Associated Unit "Unidad de Nanobiotechnología".

Synthesis of the block copolymers

2.1. Polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) diblock copolymers

The diblock copolymers have been prepared by ATRP in two steps:

Synthesis of a polystyrene (PS) macroinitiator by ATRP. All polymerizations were performed in Schlenk flasks previously flamed and dried under vacuum. ATRP was carried out using the following stoichiometry [M]:[I]:[CuBr]:[L] = 250:1:1:2, where M = styrene, I = initiator (PhEBr) and L = ligand (bipy). The reactants were added under N₂. The reaction mixtures were then degassed by three freeze-pump-thaw cycles and placed in a thermostated oil bath at 110°C. After the polymerization, the mixtures were cooled to room temperature; the contents were diluted with dichloromethane (CH₂Cl₂) and passed through a neutral alumina column to remove the copper salt. After evaporation, the polymers were precipitated in ethanol, filtered, washed and dried under vacuum.

*Synthesis of PS-*b*-PtBA by ATRP.* The macroinitiator PS-Br and 5mL of degassed acetone were added to the mixture ([M]:[I]:[CuBr]:[L] = 400:1:1:1). Acetone enhanced the solubility of the CuBr/PMDETA complex. The *t*BA polymerizations were carried out at 65°C.

*Hydrolysis of the PtBA block in the PS-*b*-PtBA copolymers.* Copolymers were first dissolved in CH₂Cl₂. Trifluoroacetic acid (TFA) was then added (10 equivalent to *t*-butyl ester units), and the

mixture was stirred at room temperature for 3 days. The deprotected polymers precipitated in the reaction media, were filtered and washed with CH₂Cl₂ and finally dried under vacuum.

2.2. Polystyrene-*b*-poly(L-glutamic acid) PS-*b*-PGA

The synthesis of these diblock copolymers was carried out in several steps.¹ First, styrene was polymerized by atom transfer radical polymerization (ATRP). By tuning adequately the conversion to values lower than 40% a large percentage of end-brominated polystyrene groups should be obtained. The end-terminal bromo group was easily modified into an amine function by reaction with 1,4-diaminoethane². The amine modified PS was employed, in turn, as macroinitiator for the ring-opening polymerization of γ -benzylester-L-glutamate N-carboxyanhydride. Finally, deprotection under basic conditions (KOH/H₂O/THF) lead to the amphiphilic PS-*b*-PGA diblock copolymers. The block copolymers have been characterized by ¹H NMR spectroscopy and GPC both to evaluate the integrity of the structure and to determine the chemical composition.

2.3. Polystyrene-*b*-poly[poly(ethylene glycol) methyl ether methacrylate] PS-*b*-PEGMA

The amphiphilic block copolymer polystyrene-*b*-poly[poly(ethylene glycol) methyl ether methacrylate] (PS₄₀-*b*-P(PEGMA300)₄₈) (copolymer is labeled with the degree of polymerization of each block) and poly(2,3,4,5,6-pentafluorostyrene) (P5FS₂₁) were synthesized via atom transfer radical polymerization (ATRP) as previously reported.^{3,4}

Illustrative images of the immobilization of bacterial cells onto PS-*b*-PGA and PS-*b*-PEGMA block copolymer films.

¹ Dimitrov, I.; Schlaad, H., Chem. Comm. 2003, 2944-2945.

² Babin, J.; Leroy, C.; Lecommandoux, S.; Borsali, R.; Gnanou, Y.; Taton, D., Chem. Comm. 2005, 1993-1995.

³ Muñoz-Bonilla, A.; Ibarboure, E.; Papon E.; Rodriguez-Hernandez, J. 2009 J. Polym. Sci. Part A: Polym. Chem. 47(9): 2262-2271.

⁴ Muñoz-Bonilla, A., Van Herk, A. M.; Heuts P. A. 2010 Macromolecules 43(6): 2721-2731.

(PS/PGA)

(PS/PEGMA)

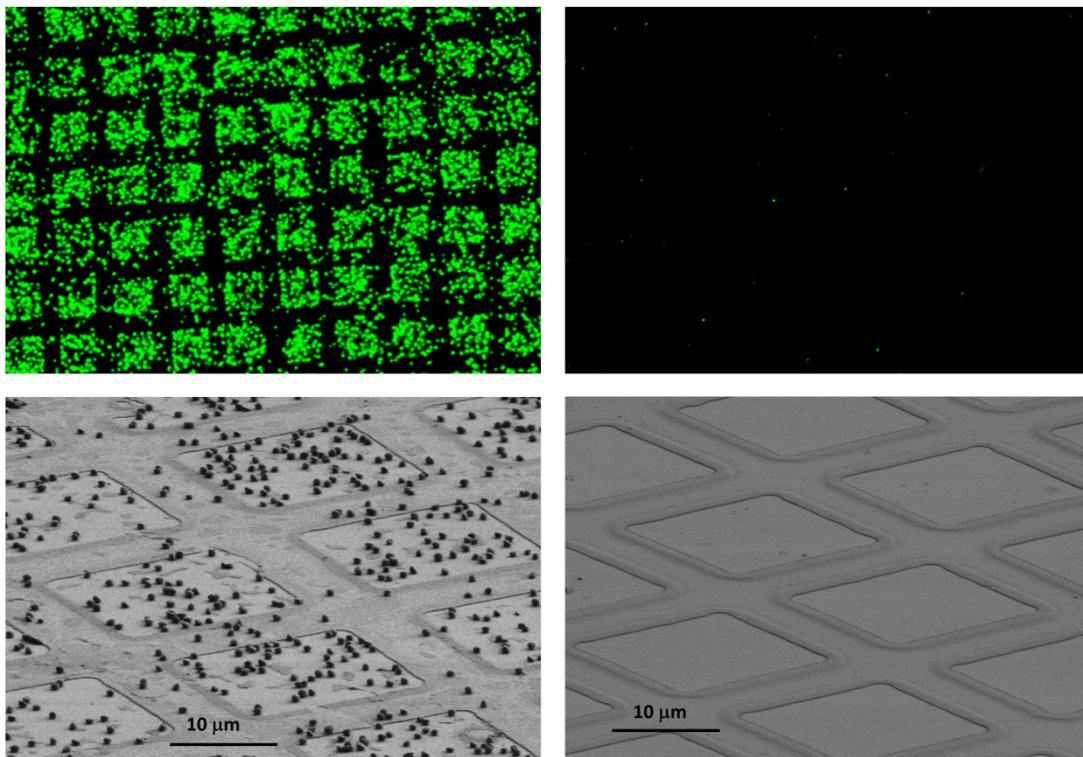


Figure S1. Comparative bacterial adhesion between hydrophilic charged (PS-*b*-PGA) and uncharged (PS-*b*-PEGMA) block polymer surfaces. Up: fluorescence images of the surface upon bacterial immobilization. Down: Scanning electron microscopy images of the resulting surfaces.