Supplementary Information

Bacterial Adherence on Self-Assembled Films of Brush Polymers Bearing Zwitterionic Sulfobetaine Moieties

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GPC Analysis

For the synthesis of PECH-DMAPSm polymers, a PECH polymer was prepared in the first reaction step (Scheme 1). Its molecular weight was determined at 25.0 °C by gel permeation chromatography (GPC) analysis using a GPC system (model PL-GPC 210, Polymer Labs) calibrated with polystyrene standards; tetrahydrofuran (THF) was used as the eluent. The measured GPC data of the PECH polymer is illustrated in Fig. S1.



Fig. S1. GPC diagrams of a PECH polymer and polystyrene standards which were measured at 25.0 °C; THF was used as the eluent. A flow rate of 0.8 mL/min was employed.

NMR Spectroscopy Analysis

¹H and ¹³C NMR spectroscopy analyses were conducted for the polymer products obtained in the individual reaction steps (Scheme 1) using a Bruker NMR spectrometer with proton and carbon probes. For a representative example, the ¹H NMR spectrum of a PECH-DMAPS100 polymer is shown in Fig. S2.



Fig. S2. ¹H NMR spectrum of PECH-DMAPS100 which was measured in DMSO-*d*₆.

Determination of Surface Energy

The contact angle of a pure liquid on a solid can be expressed by the Young equation:^{S1}

$$\gamma_{\rm L}\cos\theta = \gamma_s - \gamma_{\rm SL} \tag{1}$$

where γ_L is the known surface tension of the liquid, θ is the contact angle, γ_{SL} is the solid/liquid interfacial energy. In order to obtain the solid surface free energy γ_s , γ_{SL} has to be determined. For surface energy calculation, Van Oss et al.^{S2} and van Oss and Good^{S3} developed an acid-base theory. The surface energy can be expressed by the sum of a Lifshitz-van der Waals apolar component γ_i^{LW} and a Lewis acid-base polar component γ_i^{AB} :

$$\gamma_{i} = \gamma_{i}^{LW} + \gamma_{i}^{AB} \tag{2}$$

The acid-base polar component $\gamma_i^{AB}\,\text{can}$ further be subdivided by using specific terms for an

electron donor (γ_i^-) and an electron acceptor ($\gamma_i^+)$ subcomponent:

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^- \gamma_i^+} \tag{3}$$

The solid/liquid interfacial energy is then given by the following equation:

$$\gamma_{\rm SL} = \gamma_{\rm S} + \gamma_{\rm L} - 2(\sqrt{\gamma_{\rm S}^{\rm LW}\gamma_{\rm L}^{\rm LW}} + \sqrt{\gamma_{\rm S}^{+}\gamma_{\rm L}^{-}} + \sqrt{\gamma_{\rm S}^{-}\gamma_{\rm L}^{+}}).$$
(4)

Combining the above equation with eq 1 (Young equation), a relation between the measured contact angle and the solid and liquid surface free energy terms can be obtained:

$$\gamma_{\rm SL} = \gamma_{\rm S} + \gamma_{\rm L} - 2(\sqrt{\gamma_{\rm S}^{\rm LW}\gamma_{\rm L}^{\rm LW}} + \sqrt{\gamma_{\rm S}^{\rm +}\gamma_{\rm L}^{-}} + \sqrt{\gamma_{\rm S}^{-}\gamma_{\rm L}^{\rm +}}).$$
(5)

In order to determine the surface free energy components (i.e., γ_{S}^{LW} , γ_{S}^{+} , and γ_{S}^{-}) of a solid, three equations are required at least. Thus, in the present study we have chosen three liquids with their surface tension components (γ_{L}^{LW} , γ_{L}^{+} , and γ_{L}^{-}) (Table 1) and used them for contact angle measurements.

Estimation of Gibbs Free Energy

We calculated the Gibbs free energy change ΔG_{adh} upon the adherence of bacteria onto a substrate in aqueous media, which is based on the interfacial tensions from bacteria/substrate, bacterial/water and substrate/water:^{S4}

$$\Delta G_{adh} = \gamma_{BS} - \gamma_{BW} - \gamma_{SW} \tag{6}$$

where B, S and W correspond to bacteria, solid substrates, and water, respectively. The interfacial tensions in eq 6 were calculated using the general form:

$$\gamma_{12} = (\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}})^2 + 2 \left[(\sqrt{\gamma_1^+} - \sqrt{\gamma_2^+}) (\sqrt{\gamma_1^-} - \sqrt{\gamma_2^-}) \right]$$
(7)

where 1 and 2 can refer to B, S and W.

All of the Lifshitz-van der Waals apolar terms and Lewis acid-base polar terms can be collected, so that an alternate way to represent the different contributions to the Gibbs free energy change upon adherence in aqueous media can be written.

Gibbs free energy change can be described as the sum of Lifshitz-van der Waals apolar term and Lewis acid-base polar term as shown in the flowing equation:

$$\Delta G_{adh} = \Delta G_{adh}^{LW} + \Delta G_{adh}^{AB}$$
(8)

Each Lifshitz-van der Waals apolar and Lewis acid-base terms can be derived by inserting eq 7 into eq 6. These terms are calculated according to the following equations:

$$\Delta G_{adh}^{LW} = (\sqrt{\gamma_B^{LW}} - \sqrt{\gamma_S^{LW}})^2 - (\sqrt{\gamma_B^{LW}} - \sqrt{\gamma_W^{LW}})^2 - (\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_W^{LW}})^2$$
(9)

$$\Delta G_{adh}^{AB} = 2 \left[\sqrt{\gamma_W^+} \left(\sqrt{\gamma_B^-} + \sqrt{\gamma_S^-} - \sqrt{\gamma_W^-} \right) + \sqrt{\gamma_W^-} \left(\sqrt{\gamma_B^+} + \sqrt{\gamma_S^+} - \sqrt{\gamma_W^+} \right) - \sqrt{\gamma_B^+ \gamma_S^-} - \sqrt{\gamma_B^- \gamma_S^+} \right]$$
(10)

References

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