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Supporting Information

Mussel-inspired coatings with tunable wettability, for enhanced antibacterial efficiency and reduced bacterial adhesion

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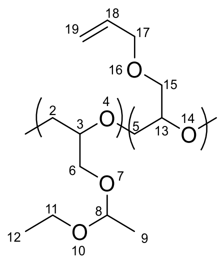
1. Synthetic approach

1.1 Synthesis of MI-dPG

The dendritic polyglycerol (dPG) with Mn=12.000 g·mol^{-1} and Mw=16.000 g·mol^{-1} was polymerized by a one-step ring-opening anionic polymerization (ROAP) as described in earlier publications.[1, 2] Amine-functionalized dPG (dPG-NH_2) was prepared according to previously published procedures of our group.[3] 800 mg dPG-NH_2 (4 mmol) were dissolved in a mixture of MeOH and pH 4.8 2-(N-morpholino)ethanesulfonic acid (MES, 0.1 M) buffer (25 ml, 1v/1v). After addition of 1.11 g 3, 4-dihydroxyhydrocinnamic acid (DHHA, 6 mmol) and 0.93 g 1-ethyl-3-(3-dimethyl-aminopropyl) carbodiimid (EDC, 6 mmol), the solution was stirred for 16 h at room temperature. After removal of the solvent in vacuum, the final residue was dialyzed in MeOH for 4 days. For higher stability and better storage 37% HCl was added before drying the MI-dPG. ^{1}H NMR (500 MHz; CD3OD): δ = 6.68-6.53 (m, Ar); 4.21-3.02 (m, PG-backbone); 2.75 (m, $COCH_2\underline{CH_2}C$); 2.52 (m, $CO\underline{CH_2}CH_2C$) ppm.

1.2 Synthesis of amine-functionalized linear polyglycerol (lPG-NH_2)

EEGE-*b*-AGE block-copolymer synthesis. The synthesis was performed under the exclusion of air (i.e., argon atmosphere) and moisture, according to an adjusted version of the method published by Gervais et al.[2] EEGE monomer (19.2 ml, 18.43 g, 126.10 mmol) and triisobutylaluminium (1.8 ml, 1.41 mg, 7.13 mmol) were respectively added to a magnetically stirred solution of tetraoctylammonium bromide (543.0 mg, 0.99 mmol) in toluene (140 ml), and the resulting mixture was stirred for 4 hours at 0 °C. Subsequently, the AGE monomer (1.7 ml, 1.60 g, 14.02 mmol) and another equivalent of triisobutylaluminium were added. The mixture was then stirred for 16 hours, during which it warmed up to room temperature. Subsequently, the reaction was quenched with EtOH. The crude product was obtained as a light gray-brown oil upon removal of the solvent under reduced pressure. Next, the crude mixture was redissolved in diethylether and centrifuged at 4000 rpm for 15 min, after which the supernatant was isolated and evaporated under reduced pressure. The pure product was obtained as a highly viscous white-gray oil (20.0 g, 0.95 mmol, > 99%), and was characterized by means of ^{1}H and ^{13}C NMR spectroscopy and GPC (DMF was used as mobile phase).

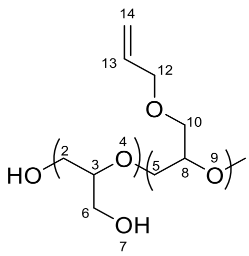


^{1}H NMR [500 MHz, δ(ppm), $CDCl_3$]: 5.85 (**18**; m, 11 ^{1}H, *H_2C=C**H**-R-*), 5.24 (**19**; d, 13 ^{1}H, ***H_2**C=CH-R-*), 5.11 (**19**; d, 13 ^{1}H, ***H_2**C=CH-R-*), 4.68-4.65 (**8**; q, 140 ^{1}H, *CH_3C**H**(OR-)$_2$*), 3.95 (**17**; d, 28 ^{1}H, *H_2C=CCH**O**-*), 3.65-3.4 (**2, 3, 5, 6, 13, 15, 6** and **11**; m, 1100 ^{1}H, *-RC**H**OR* and *-RC**H_2**OR*), 1.26 (**9**; dd, 455 ^{1}H, *-C**H_3***), 1.17 (**12**; t, 435 ^{1}H, *-C**H_3***).

^{13}C NMR [125.7 MHz, δ(ppm), $CDCl_3$]: 134.84 (**18**; *H_2C=**C**HR-*), 116.58 (**19**; *-RCH=**C**H_2*), 99.79 (**8**; *CH_3**C**H(OR-)$_2$*), 79-60 and 50.46 (**2**, **3**, **5**, **6**, **11**, **13**, and **15**; *-RCH$_2$O-*), 72.20 (**17**; *-R**C**H$_2$O-,* as shown by combining NOSY and COSY), 19.75 (**12**; *H_3**C**R-*), 15.26 (**9**; ***C**H_3C(OR-)$_2$*)

GPC [THF]**:** Monomodal size distribution with: M_n= 2.11*10^4 Da, M_w= 2.32*10^4 Da, M_w/M_n= 1.10.

Acetal deprotection of the EEGE-*b*-AGE block-copolymer. To a magnetically stirred solution of the EEGE-*b*-AGE block-copolymer (20 g, 0.86 mmol) in EtOH (100 ml), concentrated HCl-solution (10 ml, 37% in H_2O) was added. The resulting reaction mixture was stirred for 19 hours at room temperature, after which NaOH-solution (1M) was added until a neutral pH was reached. The crude product was obtained upon evaporation of the solvent under reduced pressure. The crude product was then redissolved in MeOH and purified by dialysis in MeOH (dialysis tubing with a molecular cutoff of 2 kDa was used). The pure product was obtained as a white oil (9 g, 0.73 mmol, 85%), upon the removal of the solvent under reduced pressure. Finally, the product was characterized by means of ^{1}H and ^{13}C NMR spectroscopy. Molecular size and weight distribution were analyzed by means of GPC.

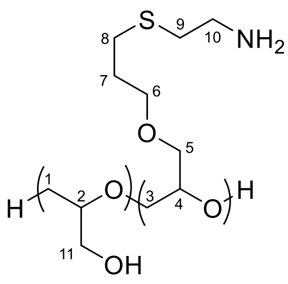


^{1}H NMR [500 MHz, δ(ppm), CD_3OD]: 5.91 (**13**; m, 11 ^{1}H, *H_2C=C**H**-R-*), 5.29 (**14**; d, 11 ^{1}H, ***H_2**C=CH-R-*), 5.17 (**14**; d, 11 ^{1}H, ***H_2**C=CH-R-*), 4.0 (**12**; d, 22 ^{1}H, -OC**H_2**CH=CH_2, as shown by COSY), 3.75-3.45 (**2, 3, 5, 6, 8,** and **10**; m, 805 ^{1}H, *-RC**H**OR* and *-RC**H_2**OR*).

^{13}C NMR [125.7 MHz, δ(ppm), $CDCl_3$]: 134.85 (**13**, *H_2C=**C**HR-*), 115.60 (**14**, *H_2C=CHR*), 80.18, 69.19, and 61.23 (**2, 3, 5, 6, 8,** and **10**; *HO**C**H_2R-*), 72.19 (**12**; *-R**C**HO-*, as shown by combining NOSY and COSY).

GPC [DMF]: Monomodal size distribution with: M_n= 1.03*10^4 Da, M_w= 1.26*10^4 Da, M_w/M_n= 1.23.

Thiol-ene click chemistry of lPG-*b*-AGE and cysteamine. To a magnetically stirred solution of the lPG-*b*-AGE block-copolymer (2.5 g, 0.20 mmol) in H_2O/EtOH (100 ml, 1:1), cysteamine hydrochloride (1.5 g, 13.6 mmol, 5 equivalents respectively to the allyl-double bonds of the AGE-block) and 2-hydroxy-1-(4-(2-hydroxyethyl) phenyl) -2-methylpropan-1-one (600 mg, 2.7 mmol) were added. The resulting reaction mixture was irradiated with UV-light (1 h). Subsequently, the product was purified by dialysis in H_2O (3x), followed by the removal of the solvent by freeze-drying. The product was obtained as a yellow oil. The purified product was characterized with the help of ^{1}H and ^{13}C NMR spectroscopies, and GPC.



^{1}H NMR [500 MHz, δ(ppm), D_2O]: 4.0-3.4 (**1**, **2**, **3**, **4**, **5**, **6**, and **11**; 827 ,m, ^{1}H, *-RC**H**₂OR)*, 3.18 (**10**; s, 15 ^{1}H, *-RC**H**₂NH₂*), 2.83 (**9**; s, 13 ^{1}H, *-RSC**H**₂R-*), 2.63 (**8**; s, 12 ^{1}H, *-RC**H**₂SR-*), 1.86 (**7**; s, 12 ^{1}H, *-RC**H**₂R-*).

^{13}C NMR [125.7 MHz, δ(ppm), D_2O]: 79.97, 69.90, 69.16, 68.90, 60.89 (**1**, **2**, **3**, **4**, **5**, **6,** and **11;** *-R**C**H₂O-*), 38.57 (**10**; *-RCH₂NH₂*), 28.66 (**9**; *-RS**C**H₂R-*), 28.37 (**8**; *-R**C**H₂SR-*), 27.56 (**7;** *-R**C**H₂R-*).

GPC [H_2O]: Monomodal size distribution with: Mn= 1.13*10^4 Da, Mw= 1.49*10^4 Da, Mw/Mn= 1.32

2. X-ray photoelectron spectroscopy (XPS)

The samples with different wettability coatings for XPS test were prepared on the surface of naturally oxidized silicon wafer (SiO_2). The surface compositions were determined by XPS using a Kratos Axis Ultra DLD spectrometer equipped with a monochromatized Al Kα X-ray source at an analyzer pass energy of 80 eV for survey spectra. High-resolution core-level spectra were recorded in FAT (fixed analyzer transmission) mode at pass energy of 20 eV for O 1s, N 1s, C 1s and Ag 3d orbitals. The electron emission angle was 60° and the source-to-analyzer angle was 60°. The binding energy scale of the instrument was calibrated following a Kratos analytical procedure that uses ISO 15472 binding energy data. Spectra were recorded by setting the instrument to the hybrid lens mode and the slot mode providing approximately a 300 x 700 µm^2 analysis area using charge neutralization. All XPS spectra were processed with the UNIFIT program (version 2017). The highly resolved Ag 3d core level spectra were acquired using a pass energy of 20 eV and fitted with doublets of fixed separation of 6 eV, an area ratio of Ag3d$_{5/2}$: Ag3d$_{3/2}$ = 2:1, and equal FWHMs for Ag3d$_{5/2}$ and Ag3d$_{3/2}$. The FWHM of the Ag3d doublets was fixed for both doublets. For the curve fitting of the high-resolution Ag 3d spectrum a Gaussian/Lorentzian sum function peak shape model was used (G/L = 0.27 constrained) with an asymmetry of −0.16 (constrained) for Ag^0 and 0 for Ag$^+$ (constrained) in combination with a Shirley background. After peak fitting of the C 1s spectra, all the spectra were calibrated in reference to the C–C aliphatic C1s component at a binding energy of 285.0 eV.

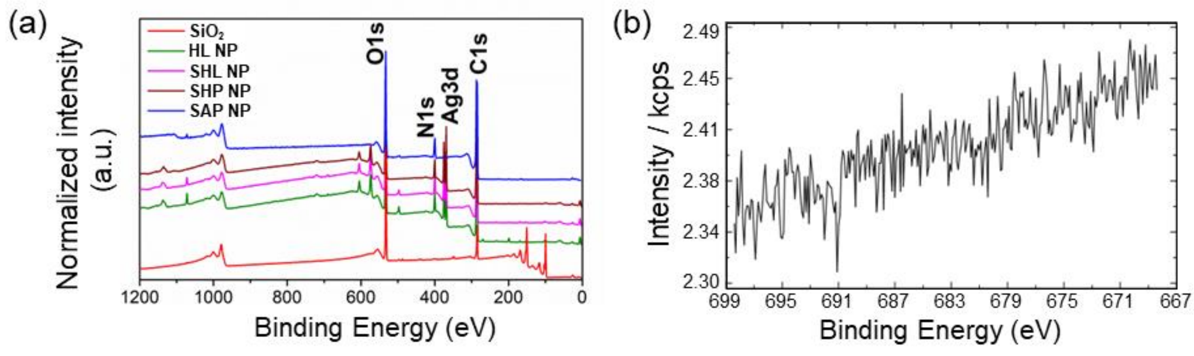


Figure S1. XPS survey spectra of SiO_2, SHL NP, HL NP, SHP NP and SAP NP surfaces (a). Highly-resolved Ag 3d XPS spectra of the substrate of SiO_2 surface (b).

Table S1. Elemental composition of the polymer-coated surfaces measured by XPS analysis

Surface	Relative molar ratio of element in the analyzed surface layer (at %)			
	C	N	O	Ag
SiO_2	31.1	1.0	31.5	-
SAP NP	66	5.6	21.6	2.9
SHP NP	67.1	5.9	21.6	2.6
SHL NP	67	6.6	23.7	2.6
HL NP	66.7	6.7	24	2.5

Table S2. Interpretation of the fitted components in the highly resolved Ag 3d XPS spectra.

Surface	Spectrum	Binding energy	Interpretation	Relat. Area	Abs. Area [cps*eV]
SAP NP	Ag3d	368.2	Ag (I)	0.29	5128
		368.8	Ag (0)	0.71	12426
SHP NP	Ag3d	368.5	Ag (I)	0.30	4821
		369.1	Ag (0)	0.70	11406
SHL NP	Ag3d	368.5	Ag (I)	0.28	4142
		368.9	Ag (0)	0.72	10635
HL NP	Ag3d	368.5	Ag (I)	0.31	4755
		369.0	Ag (0)	0.69	10790

3. Scanning electron microscope (SEM)

The surface morphology of the coatings were analyzed by a field emission scanning electron microscope (FE-SEM, Hitachi SU8030, Japan) at an accelerating voltage of 10 kV, a current of 10 µA and a working distance (WD) of around 8.3 mm. The samples were dried under high vacuum and coated with a 8-10 nm gold layer by using a sputter coater (Emscope SC 500, Quorum Technologies, UK) for 20 s at 30 mA, 10-1 Torr (1.3 mbar) in a argon atmosphere.

4. Statistics

All data in this study were presented in the mean ± SD (Standard Deviation). Independent t-test computing with Origin 9 was used to compare bacteria counts on the different surfaces.

Notes and references

1. L. Yu, Y. Hou, C. Cheng, C. Schlaich, P.-L. M. Noeske, Q. Wei and R. Haag, *ACS Appl. Mater. Interfaces*, 2017, **9**, 44281-44292.
2. C. Schlaich, L. Yu, L. Cuellar Camacho, Q. Wei and R. Haag, *Polym. Chem.*, 2016, **7**, 7446-7454.
3. L. Yu, C. Cheng, Q. Ran, C. Schlaich, P.-L. M. Noeske, W. Li, Q. Wei and R. Haag, *ACS Appl. Mater. Interfaces*, 2017, **9**, 6624-6633.