# Supplementary Information - Adsorption hierarchy of surfactants and polymers to a damaged hair model: effect of composition, order and polymer size

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## S1 Solid-liquid cell

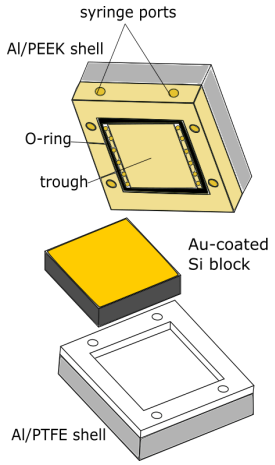


Fig. S1 Schematics of a solid-liquid cell used for the neutron reflectometry experiments. A 50*50*10 mm$^3$ block is drawn. The 80*50*10 mm$^3$ block was placed in a similar cell with one longer side. Tubes in the syringe ports connected the cell to a syringe pump and to the waste.

## S2 X-ray Photoelectron Spectroscopy (XPS)

XPS was performed to calculate the thiol ratio on the surface since it may not reflect the solution ratio[1], as mentioned in the main text. With XPS, the two sulphur species present in the system, i.e., the thiol and the sulphonate, can be separated since the binding energy of the first is $\approx$ 162 eV (2p orbital, bound to gold[2]) and the second one is $\approx$ 167 eV (reference value taken from the measurement of $Na_2SO_3$, 2p orbital of sulphur[3]). As PS has both sulphur species and MBT only the thiol moiety, a 50:50 ratio would give a sulphonate/thiol binding energy ratio of 0.5. The sample for XPS was prepared on a 1*1 cm$^2$ gold coated silicon chip using the same protocol described in the main text. The measurement was performed on two regions on the surface. In the range of binding energies for the 2p orbital of sulphur, four peaks were obtained, as shown in Figure S2. Corresponding results are in Table S1.

Table S1 XPS measurement of sulphur binding energies on two points of a 50:50 MBT:PS sample. The four peaks obtained in the region of sulphur 2p binding energies are indicated, separated according to the species they were attributed to

| Point 1 | Binding energy (eV) | Atomic % | Point 2 | Binding energy (eV) | Atomic % |
|---|---|---|---|---|---|
| S (thiol) | 162.6, 163.9 | 1.4 | S (thiol) | 162.4, 163.4 | 0.8 |
| $SO_3$ 2 | 168.6, 169.8 | 1.4 | $SO_3$ | 168.6, 169.3 | 0.6 |

Using the atomic percentage of each sulphur species listed in the table, ratios of 0.54 (Point 1) and 0.45 (Point 2) are calculated,

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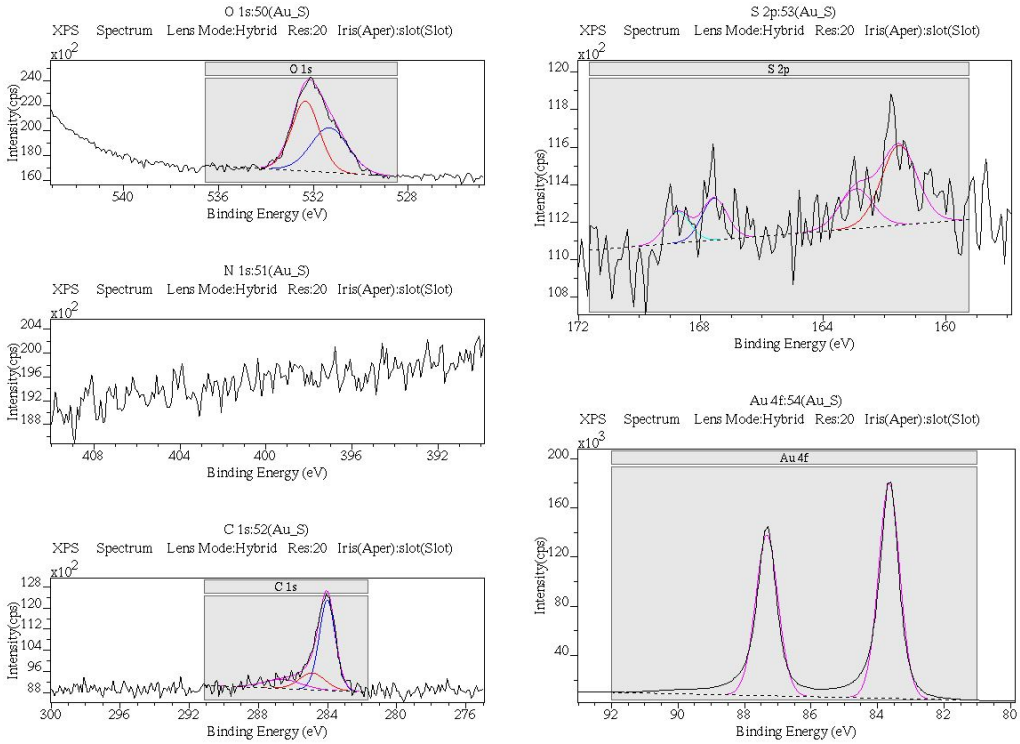



Fig. S2 XPS spectra of a 50:50 MBT:PS surface, with deconvoluted peaks. Analysed elements are: on the left, from the top, O, N, C (1s orbitals); on the right, S (2p - top) and Au (4f - bottom).

indicating that the MBT:PS ratio on the surface corresponds to the expected one.

## References


1 J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chemical Reviews*, 2005, **105**, 1103–1170.

2 C. D. Bain, H. A. Biebuyck and G. M. Whitesides, *Langmuir*, 1989, **5**, 723–727.

3 D. Littlejohn and S.-G. Chang, *Journal of Electron Spectroscopy and Related Phenomena*, 1995, **71**, 47–50.


## S3 Sequence QCM3

Figure S3 shows the data for the third QCM experiment described in the main text. The data was tentatively fitted by applying either Voigt or Maxwell models in the software QTools, and Smartfit or Broadfit models using the software Dfind (both software are Biolin Scientific). In any case, the fitting did not appear reliable, especially from the introduction of chitosan on, probably due to the complexity of the sequence. As discussed qualitatively in the main text, SDS adsorption seems to cause a similar frequency shift each time (2 cmc, 20 cmc, 2 cmc after chitosan). The spreading between overtones and dissipation, though, increase along the sequence. It is also to be noted that, differently from what happens in Sequence QCM1, adsorption of the oligomer this time does not result in a clear frequency shift but instead causes an increased overtone spreading and dissipation shift. This is likely due to residual SDS (or dodecanol) that changed the surface properties and, consequently, the interactions with the species introduced after.

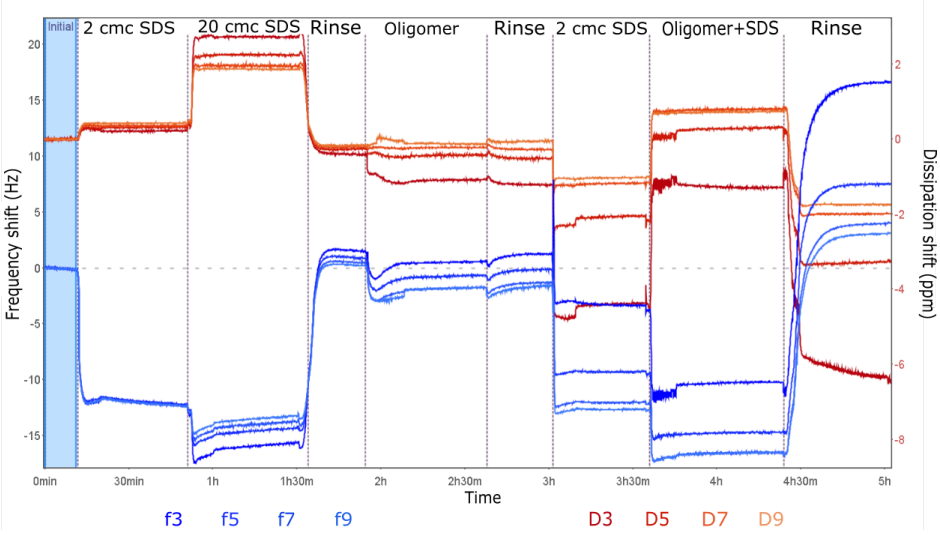
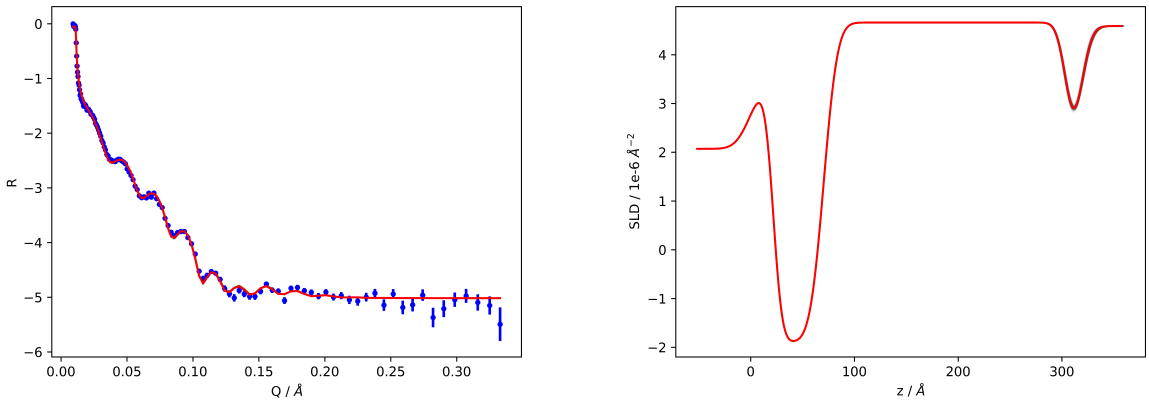


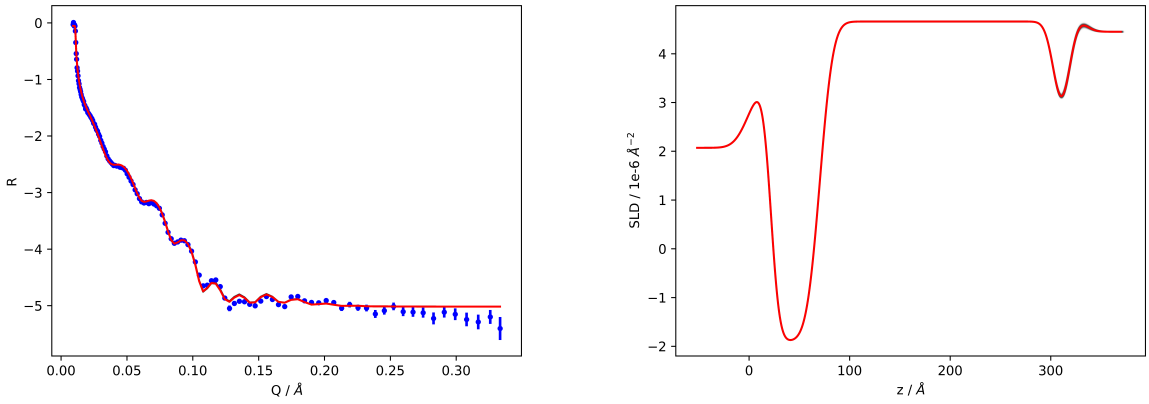

Fig. S3 QCM-D data for adsorption on 50:50 MBT:PS (Sequence QCM3 in main text). The adsorption sequence is indicated on the graph. Frequency shifts are shown in blue and dissipation in red, for the overtones specified in the legend.

## S4 Neutron Reflectometry data collected on INTER (Sequence NR1)



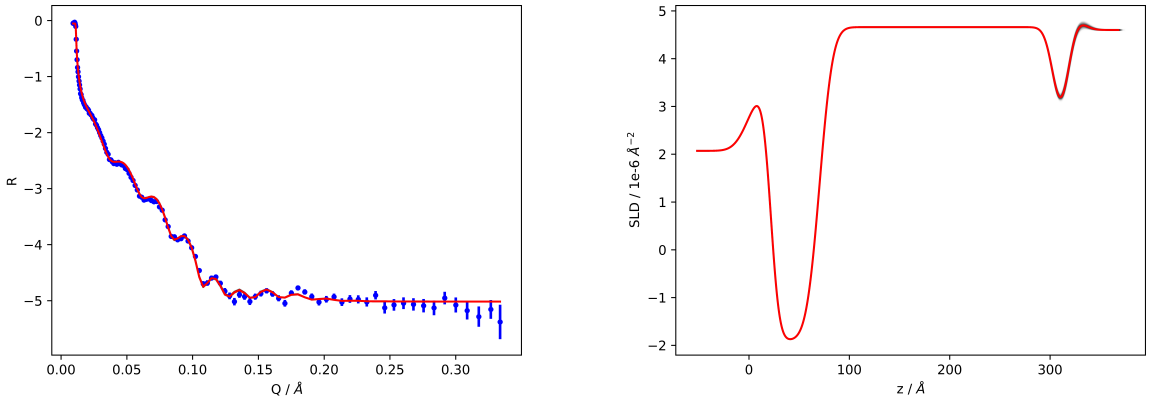

(a) (b)

Fig. S4 Fitting of NR data (blue dots) of 50:50 MBT:PS in GCMW and 100 mM NaCl. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.



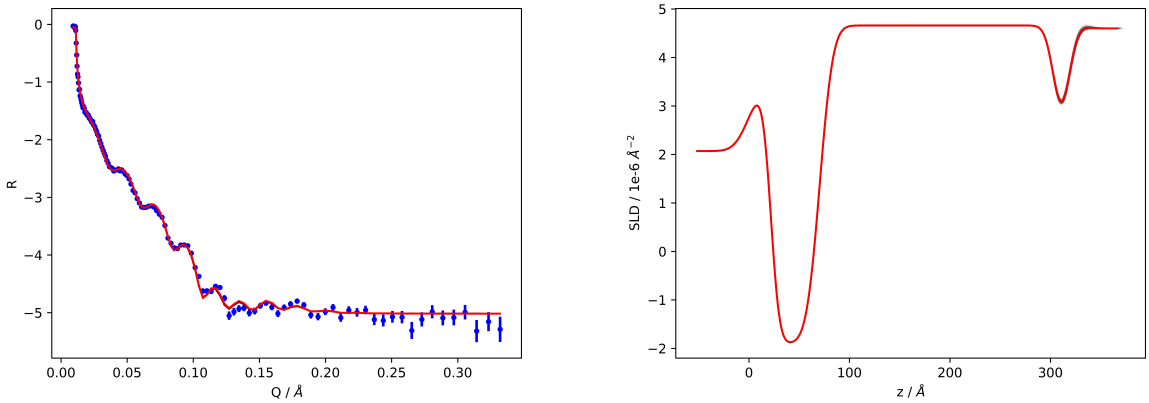

(a) (b)

Fig. S5 Fitting of NR data (blue dots) of 50:50 MBT:PS in the presence of 2 cmc d-SDS in GCMW and 100 mM NaCl. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.



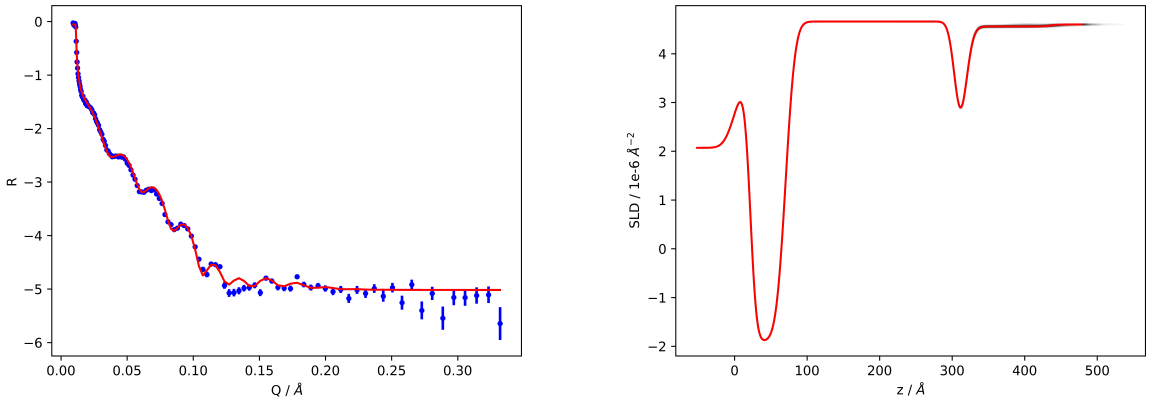

(a) (b)

Fig. S6 Fitting of NR data (blue dots) of 50:50 MBT:PS in the presence of 20 cmc d-SDS in GCMW and 100 mM NaCl. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.



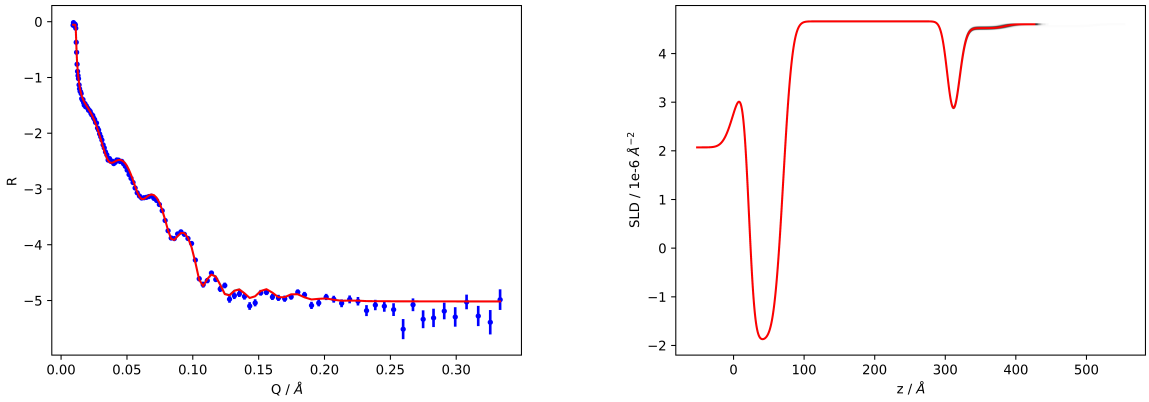

(a) (b)

Fig. S7 Fitting of NR data (blue dots) of 50:50 MBT:PS rinsed with GCMW and 100 mM NaCl after adsorption of d-SDS. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.



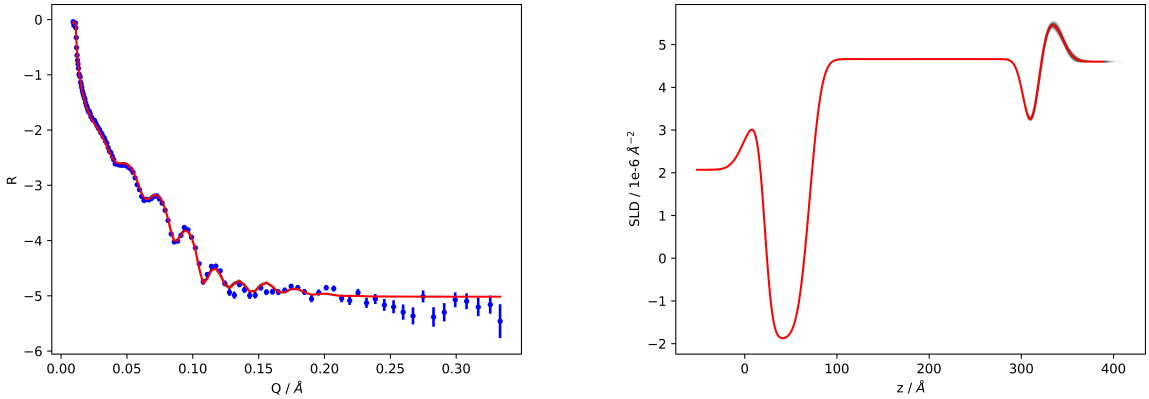

(a) (b)

Fig. S8 Fitting of NR data (blue dots) of 50:50 MBT:PS in the presence of 100 ppm chitosan polymer in GCMW and 100 mM NaCl (pH 4). The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.



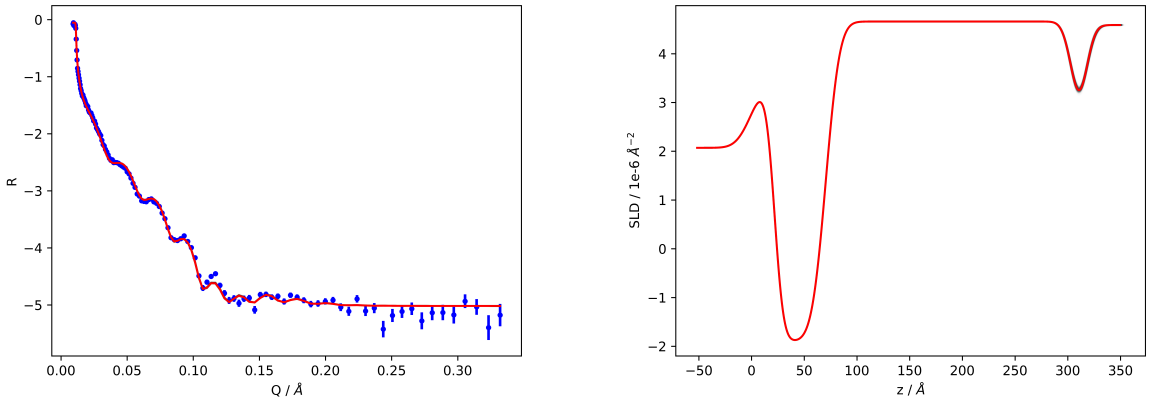

(a) (b)

Fig. S9 Fitting of NR data (blue dots) of 50:50 MBT:PS rinsed with GCMW and 100 mM NaCl after adsorption of the polymer. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.




(a) (b)

Fig. S10 Fitting of NR data (blue dots) of 50:50 MBT:PS in the presence of 20 cmc d-SDS in GCMW and 100 mM NaCl, after adsorption of polymer and rinsing. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.

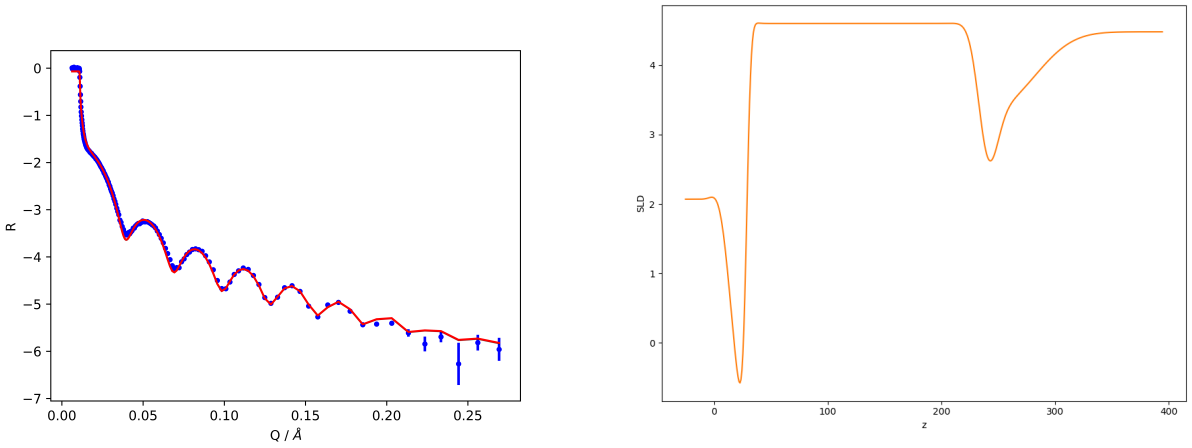



(a) (b)

Fig. S11 Fitting of NR data (blue dots) of 50:50 MBT:PS rinsed with GCMW and 100 mM NaCl at the end of the adsorption sequence. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.

## S5 Neutron Reflectometry data collected on D17 (Sequence NR2)

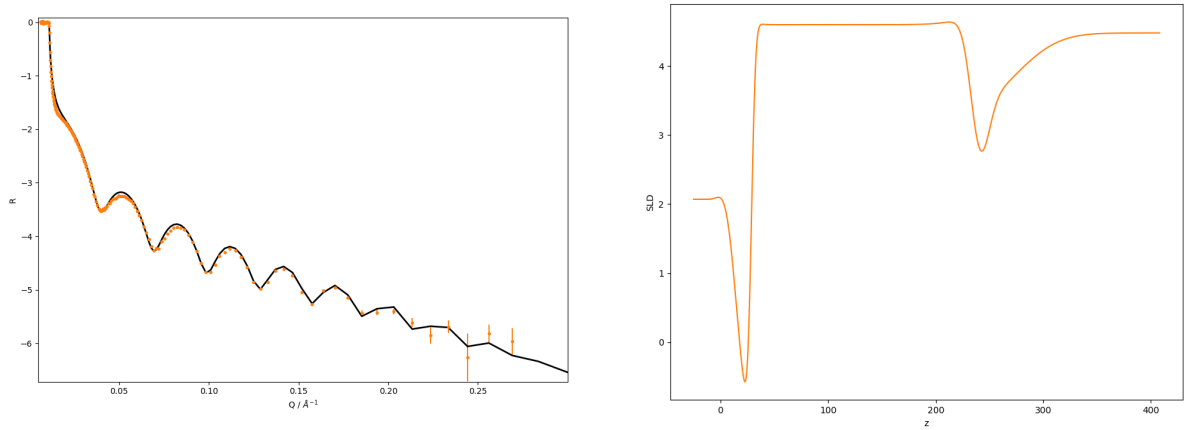
Note on the fitting model: as mentioned in the main text, the possibility of using different fitting approaches was considered but discarded. However, to test the applied standard slab model, fitting using a mixed area model was performed. Results are in Figure S12: the data was fitted simulating that two structures form the system, i.e., 1 - the thiol layer in contact with the adsorbed chitosan, and 2 - the thiol layer in bulk solution.




(a) (b)

Fig. S12 NR data (blue dots) of 50:50 MBT:PS in the presence of 100 ppm chitosan oligomer in GCMW and 100 mM NaCl, fitted with a mixed area model. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile of structure 1.

The SLD of the adsorbed chitosan layer was set to 3.2*$10^{-6}$ $Å^{-2}$ (dry chitosan), but this is an approximation (applied to reduce the number of fitting parameters and consequently the correlations between them) since the aggregates are likely hydrated. The fitted scaling factors of the two structures are 0.34 and 0.51, so that the region of total reflection at very low Q is underestimated. If the scaling factors are manually set, adjusting that of structure 2 to have a total of 1 (i.e., 0.34 and 0.66), the best fit curve does not follow well the maxima of the NR fringes, and converges to a high roughness value that affects the gold/thiol interface (Figure S13).



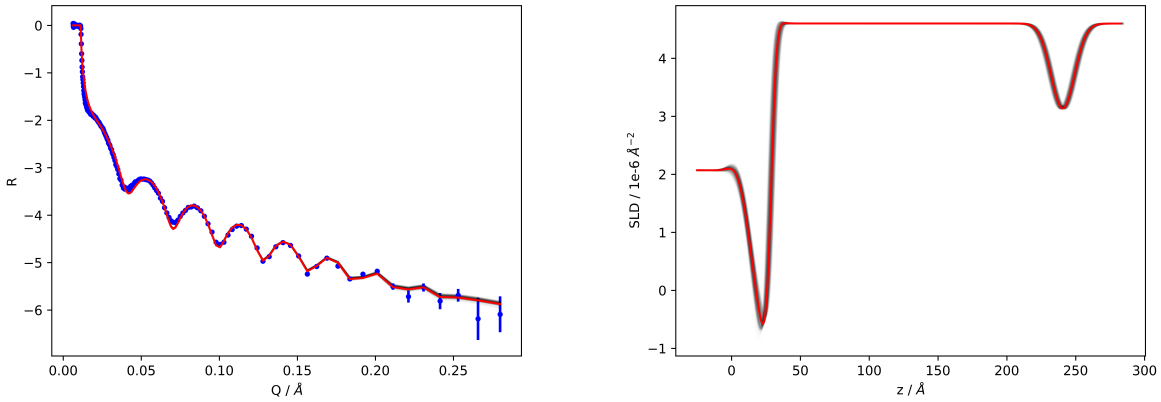

(a) (b)

Fig. S13 NR data (orange dots) of 50:50 MBT:PS in the presence of 100 ppm chitosan oligomer in GCMW and 100 mM NaCl, fitted with a mixed area model. a) Fitted curve (black line), b) SLD profile of structure 1.

The application of a simple slab model that describes the hydrated adsorbed layer on average (shown below in Figure S15) gives a better fit (by eye and chi2). A mixed area model, in this case, should not be applied due to the fact that the coherence volume of the neutron beam is larger than the aggregate size (which, evaluating from the AFM data presented in the main text, are several tens of nm).

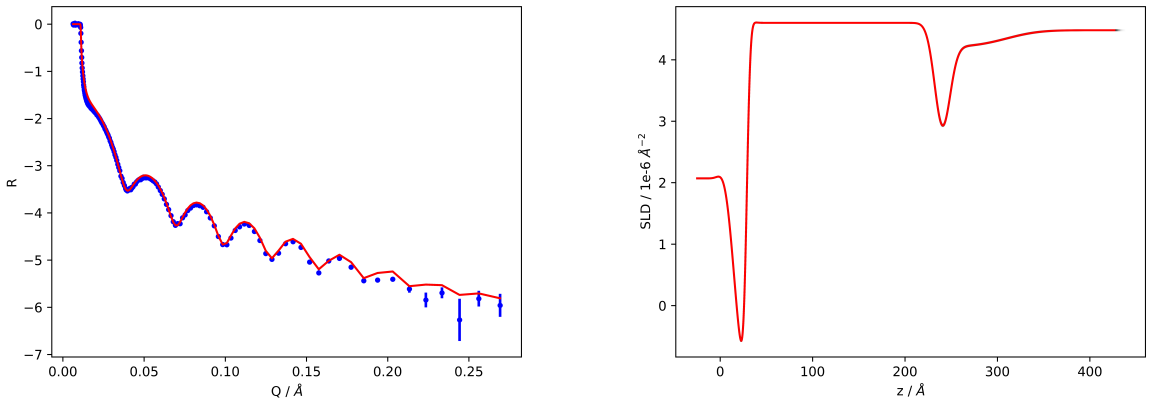
Even if the criterion of aggregates larger than the coherence volume of the beam was met, such approach has other drawbacks. Firstly,

the larger number of fitting parameters increases the uncertainty on the fitted values. Secondly, the application of such mixed area model on the other steps in the two adsorption sequences (consider, e.g., chitosan polymer, introduced after exposure of the surface to SDS) would mostly require some assumption on the composition of the different areas. Finally, such approach would prevent a direct comparison of different SLD profiles, that would not represent anymore the sample *globally* (the adsorbed aggregates have variable coverage, reflected in variable scaling factors).



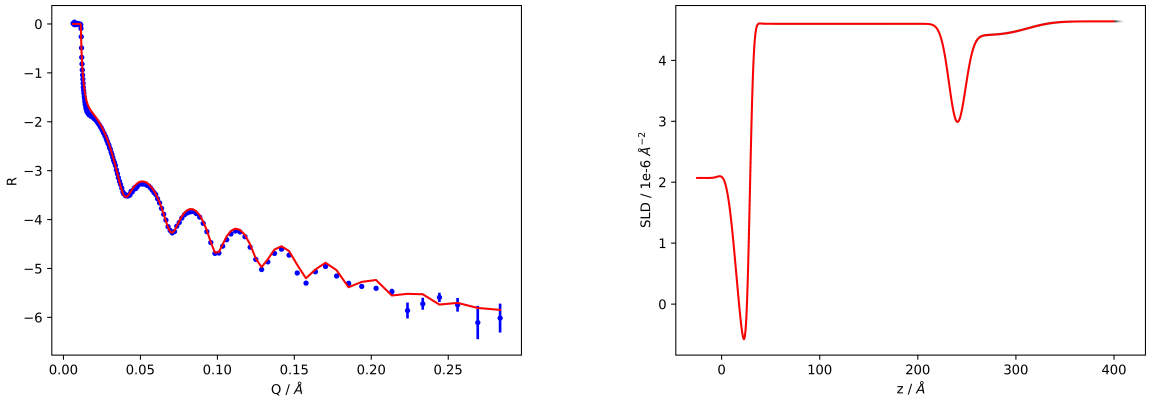

(a) (b)

Fig. S14 Fitting of NR data (blue dots) of 50:50 MBT:PS in GCMW and 100 mM NaCl. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.



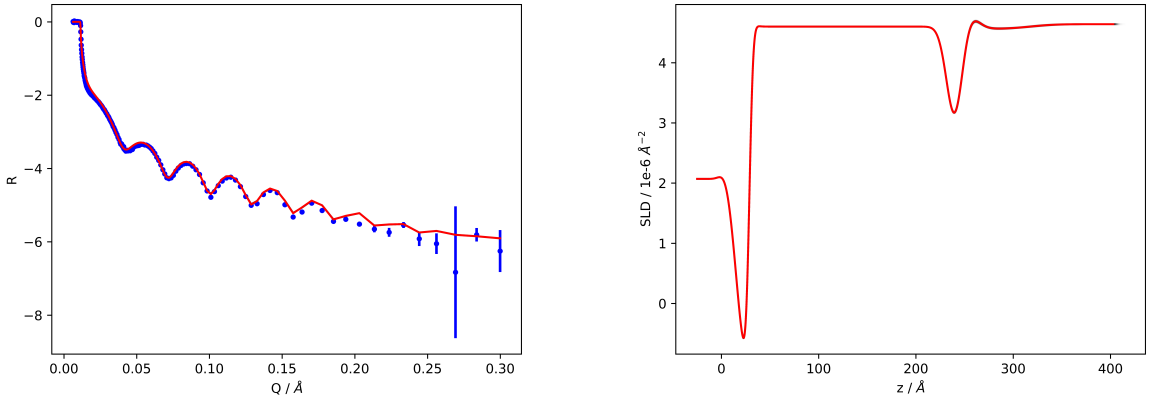

(a) (b)

Fig. S15 Fitting of NR data (blue dots) of 50:50 MBT:PS in the presence of 100 ppm chitosan oligomer in GCMW and 100 mM NaCl. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.



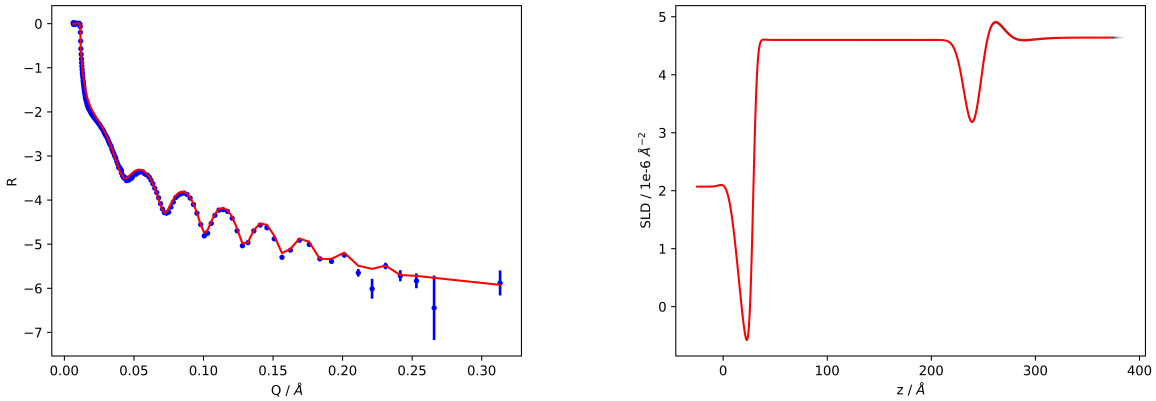

(a) (b)

Fig. S16 Fitting of NR data (blue dots) of 50:50 MBT:PS rinsed with GCMW and 100 mM NaCl after adsorption of chitosan oligomer. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.



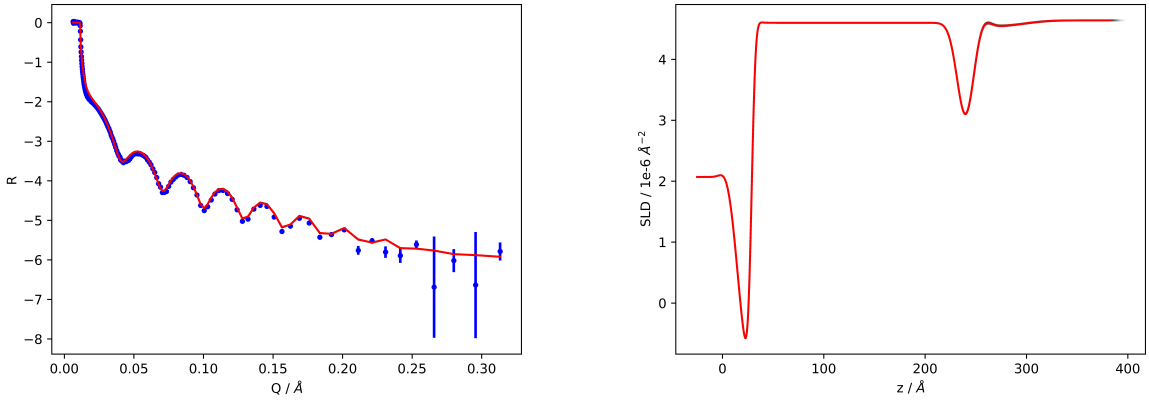

(a) (b)

Fig. S17 Fitting of NR data (blue dots) of 50:50 MBT:PS in the presence of 2 cmc d-SDS in GCMW and 100 mM NaCl. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.




(a) (b)

Fig. S18 Fitting of NR data (blue dots) of 50:50 MBT:PS in the presence of 20 cmc d-SDS and 100 ppm chitosan oligomer in GCMW and 100 mM NaCl. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.




(a) (b)

Fig. S19 Fitting of NR data (blue dots) of 50:50 MBT:PS rinsed with GCMW and 100 mM NaCl at the end of the adsorption sequence. The shadowed part indicates the range of possible solutions. a) Fitted curve (red) b) SLD profile.