Supporting Information for "'A Versatile Method for the Distance-Dependent Structural Characterization of Interacting Soft Interfaces by Neutron Reflectometry"'

Samantha Micciulla,[†,‡] Yuri Gerelli,[‡] Richard A. Campbell,[‡] and Emanuel Schneck[*,†]

†*Max Planck Institute of Colloids and Interfaces, Potsdam, Germany*

‡*Institut Laue-Langevin, Grenoble, France*

E-mail: schneck@mpikg.mpg.de

Molecular structures

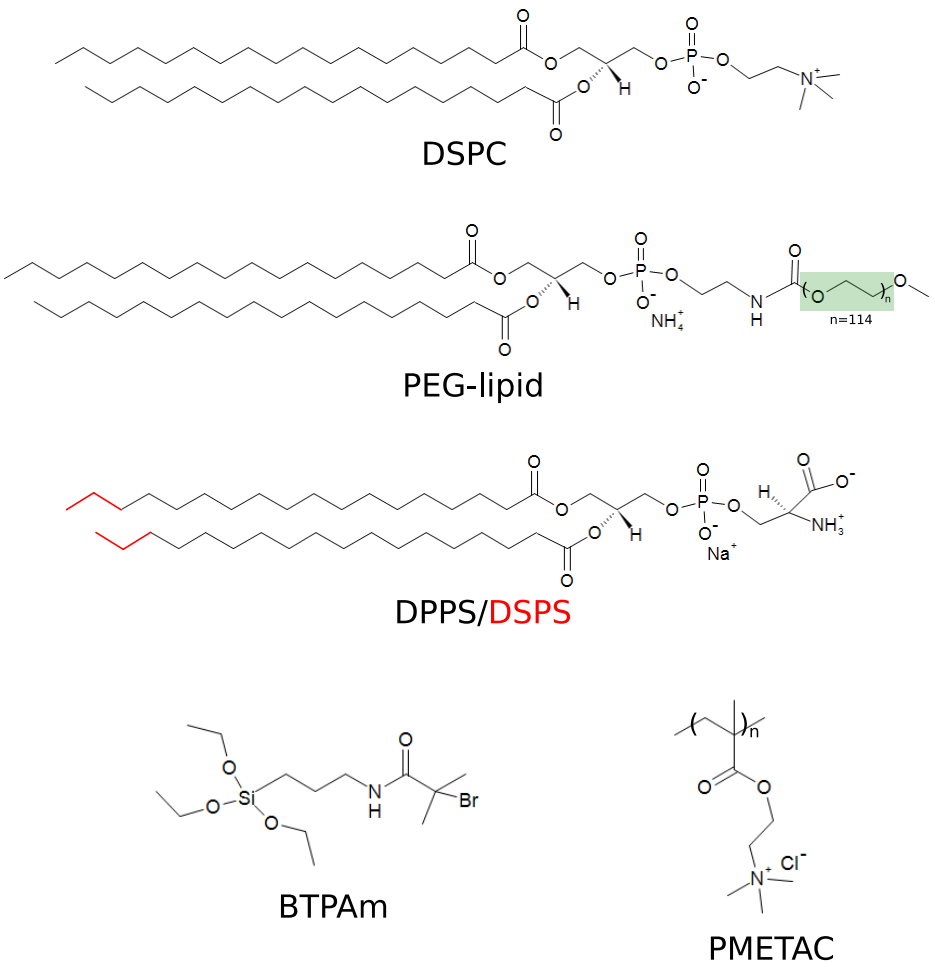

Figure S1: Chemical structures of phospholipids (DSPC, DSPS, and DPPS), PEG-lipid, silane (BTPAm) and polyelectrolyte (PMETAC) used for the preparation of lipid-anchored and solid-grafted polymer brushes.

π-A isotherms

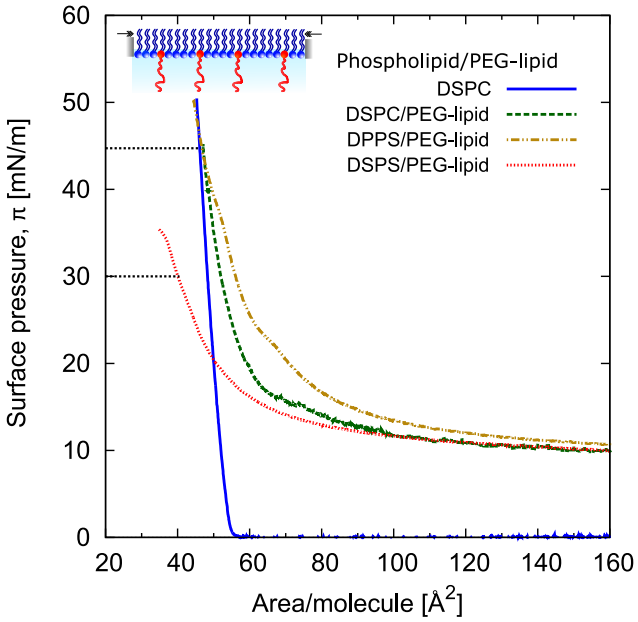

Figure S2: Surface pressure π *versus* area per molecule at the air/water interface for different phospholipid/PEG-lipid mixtures containing $90\%_{\mathrm{mol}}$ phospholipid (DSPC, DSPS, or DPPS) and $10\%_{\mathrm{mol}}$ PEG-lipid.

Comparison of PEG volume fraction profile with SCF theory

Within self-consistent-field (SCF) theory,[1] end-grafted neutral polymers in the brush regime assume parabolic profiles with height H_0^{SCF} and maximal volume fraction ϕ_0^{SCF} given as[2]

$$H_0^{SCF}(\sigma, N) = aN \left(\frac{8p\tau}{\pi^2}\right)^{1/3} \left(a^2\sigma\right)^{1/3} \tag{S1}$$

and

$$\phi_0^{SCF}(\sigma) = \frac{3}{2} \left(\frac{\pi^2}{8p\tau}\right)^{1/3} \left(a^2\sigma\right)^{2/3}, \tag{S2}$$

where σ is the brush grafting density, a is the linear dimension of a monomer and N is the polymerization degree. The reduced temperature τ is defined for polymers described by the Flory free energy and p the number of monomers in a persistent segment.

We calculate the equivalent parabolic parameter H_0 corresponding to the experimentally obtained parameter $\Lambda \approx 105$ Å of the stretched/compressed exponential description. Λ defines the decay of the distribution to 1/e. Applying this criterion to the profile of a parabolic brush with height H_0 yields $H_0 = \Lambda/\sqrt{1-e^{-1}} \approx 132$ Å. Equaling H_0 and H_0^{SCF} for $\sigma = 1.8 \times 10^{-3}$ Å^{-2}, $N = 114$, and $a = 4.1$ Å and solving for $p\tau$ then yields the estimate $p\tau \approx 0.9$.

Purely statistical parameter errors

Purely statistical errors corresponding to the 95% (two-sigma) confidence interval were calculated for the most relevant parameters from the diagonal elements of the parameter covariance matrix.[3] Note, however, that these estimates are valid only within the framework of a "perfect model" and typically largely underestimate the real parameter uncertainties which should also reflect uncertainties due to systematic errors.

- Lipid-anchored PEG brush at the air/water interface:

  $\delta D_{\mathrm{PEG}} = 0.05$ Å.

  $\delta\Lambda = 2$ Å.

  $\delta n = 0.05$.

  $\delta d_{\mathrm{dhc}} = 0.2$ Å.

  $\delta d_{\mathrm{hg}} = 0.4$ Å.

- Non-interacting PMETAC brush:

  $\delta\Lambda = 7$ Å.

  $\delta n = 0.04$.

- PMETAC/PEG brushes interacting at full hydration:

  $\delta d = 1$ Å.

  $\delta\delta_{wat/oil} = 1$ Å.

- PMETAC/PEG brushes interacting at dehydrating conditions:

  $\delta d = 1$ Å.

  $\delta\delta_{wat/oil} = 1$ Å.

- Global parameters:

  $\delta D_{PME} = 0.6$ Å. $\delta D_{PEG} = 0.9$ Å.(at water/oil interface)

Reversibility

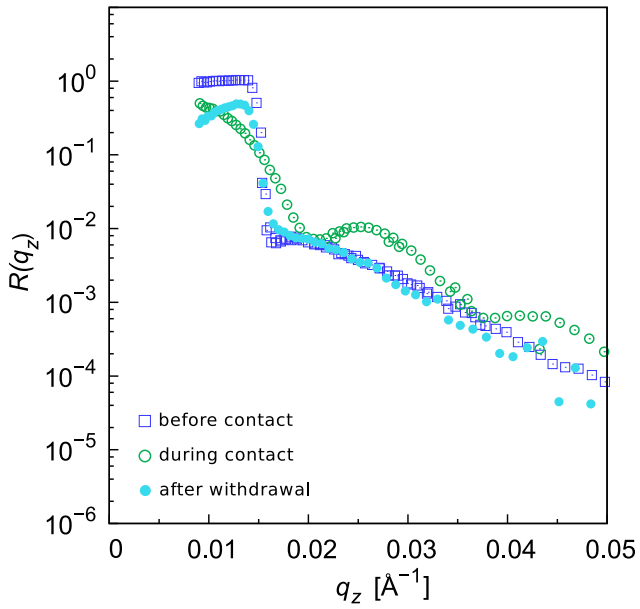

Figure S3: Reflectivity data of end-grafted PMETAC brush on a silicon substrate before (open squares) and during (open circles) contact with the lipid-anchored PEG brush. After the experiment, the PEG brush was withdrawn from the PMETAC brush by injecting excess D_2O into the sample cell (filled circles). The key features of the reflectivity curve of the non-interacting PMETAC brush are recovered, while the deformation of the curve at low q_z can be attributed due to beam attenuation by residual oil traces on the wall of the sample cell.

Structural characterization of other mixed phospholipid/lipopolyme monolayers

NR was used to structurally characterize phospholipid/lipopolymer monolayers differing from the one presented in the main text either in the mol percentage of PEG lipids ($f = 0.01$ instead of $f = 0.1$) or in the polymer chain length ($N_{PEG} = 17$ instead of $N_{PEG} = 114$). The surface pressure was π= 45 mN/m. The required amount of solution was calculated on the basis of Langmuir isotherms (Fig. S4).

High chain length ($N_{PEG} = 114$), low grafting density ($f = 0.01$) (from A to D in Fig. S5): Alkyl chains and head groups are described by slabs. Their thickness and

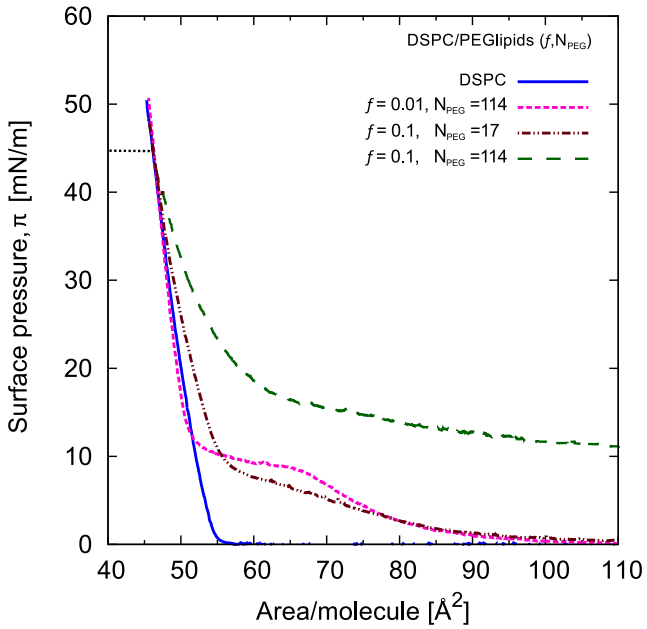

Figure S4: Surface pressure π *versus* area per molecule at the air/water interface for different phospholipid:lipopolymer mixtures investigated by neutron reflectometry.

SLDs corresponding to the best-matching parameters are summarized in Table S1. The PEG chains are described with a stretched/compressed exponential (eq. 4 in the main text) with characteristic length Λ and exponent n. To obtained a robust description of the experimental data, it was necessary to constrain the amount of polymer to D_{PEG}=1.60 Å calculated from eq. 4 in the main text, and the characteristic length Λ= 47 Å considering the relation $\Lambda = H\sqrt{1-e^{-1}} \approx 0.8\ H_0$. The parameter H_0 was estimated from eq. S1 according to SCF theory for $p\tau \approx 0.9$.

Low chain length (N_{PEG} = 17), high grafting density (f = 0.1) (from E to panel H in Fig. S5): As in the previous cases, alkyl chains and head groups are described by slabs (Table S1) and the PEG profile is described with a stretched/compressed exponential, where the amount of polymer D_{PEG} =2.40 Å and characteristic length Λ= 15 Å were fixed to the calculated values from theoretical prediction.

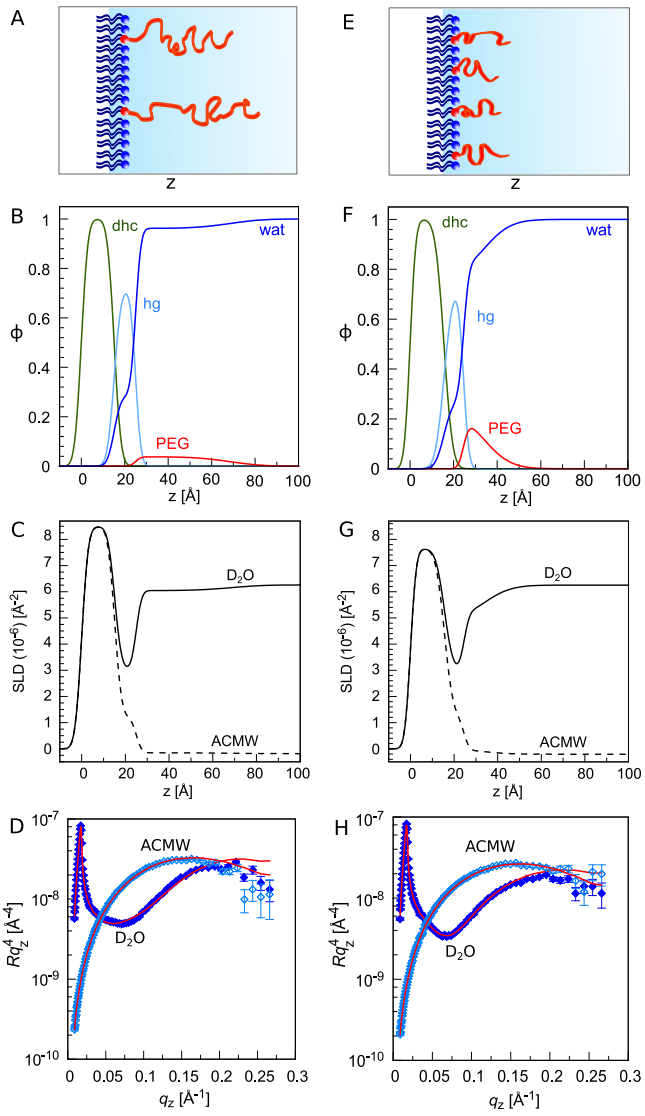

Figure S5: (A and E) Schematic representations of the phospholipid:lipopolymer monolayers, dDSPC:PEG-lipid, characterized at the air/water interface by neutron reflectometry. The monolayers differ from those presented in the main text either in the grafting density ($f = 0.01$ instead of $f = 0.1$, panel A) or in the polymer chain length ($N_{PEG} = 17$ instead of $N_{PEG} = 114$, panel E). (B and F) Best-matching volume fraction distribution according to the solid lines in the reflectivity data. (C and G) SLD profiles in D_2O and ACMW contrast. (D and H) Experimental reflectivities (data points) and simulated curves corresponding to the best-matching model parameters (solid lines).

Table S1: Thicknesses d, SLDs of alkyl chains ρ_{dhc} and stretching/compression exponent n obtained from the reflectivity fits in Fig. S5.

	d_{dhc} [Å]	ρ_{dhc} [Å^{-2}]	d_{hg} [Å]	n
$f = 0.01$, $N_{PEG} = 114$	15.1	$8.48\times(10^{-6})$	9.9	2.0
$f = 0.1$, $N_{PEG} = 17$	15.5	$7.63\times(10^{-6})$	9.0	0.9

References

(1) Milner, S.; Witten, T.; Cates, M. *Macromolecules* **1988**, *21*, 2610–2619.

(2) Schneck, E.; Schollier, A.; Halperin, A.; Moulin, M.; Haertlein, M.; Sferrazza, M.; Fragneto, G. *Langmuir* **2013**, *29*, 14178–14187.

(3) Bevington, P.; Robinson, D. Data reduction and error analysis for the physical sciences. 2003.