Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information for

Self-assembly of Model Short Triblock Amphiphiles in Dilute Solution

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1. Numerical implementation of the theory

In order to solve the molecular theory, the expressions for $\rho_{sol}(r)$, $P(\alpha,r)$ and $\rho_c(r)$ (eqs. 10, 11 and 13 in the main text) are substituted into the packing constraint (eq. 5 in the main text). The resulting equation is discretized in the *r* coordinate in layers of thickness δ, with δ = 0.2 nm. The layer *k* is defined as the planar region between *r* = (*k* – 1)δ and *r* = *k*δ (for a planar lamella) or the cylindrical or spherical shell enclosed by two cylinders or spheres of radii (*k* – 1)δ and *k*δ (for cylindrical fibers or spherical micelles, respectively). The size of the calculation box is given by *M*, which is the maximum value of *k*.

The discretized form of the packing constraint (eq. 5 in the main text) becomes:

$$\langle \phi_{sol}(k) \rangle + \sum_i \langle \phi_i(k) \rangle - 1 = 0 \qquad (0)$$

where $\langle \phi_i(k) \rangle$ is given by:

$$\langle \phi_i(k) \rangle = \langle n_i(k) \rangle v_i \qquad (0)$$

and $\langle n_i(k) \rangle$ is given by:

$$\langle n_i(k) \rangle = \sum_\alpha \sum_{k=1}^{M} \frac{G(k')}{G(k)} n_i(k;\alpha,k') P(k',\alpha) \rho_c(k') \qquad (0)$$

In eq. (0), *G*(*k*) is the volume element in layer *k* and hence for spherical micelles, *G*(*k*) = 4π(*k*-½)^2 δ^3; for cylindrical fibers, *G*(*k*) = 2π(*k*-½)δ^2 *L* (where *L* is the length of the fiber) and for planar lamellas, *G*(*k*) = 2δ*A* (where *A* is the area of the lamella). In this equation, $n_i(k;\alpha,k')$ is the number of segments that a chain with its center of mass in layer *k′* has in layer *k* when it is in conformation α.

The discretized probability density function, $P(k,\alpha)$, is given by:

$$P(\alpha,k) = q(k)^{-1} \exp\left(-\sum_{k'=1}^{M} \sum_i n_i(k';\alpha,k) \beta\pi(k') v_i - \sum_{k'=1}^{M} \sum_{k''=1}^{M} \sum_i \sum_j n_i(k';\alpha,k) \beta\varepsilon_{ij} \bar{g}_{ij}(k',k'') \langle n_j(k'') \rangle \right) \qquad (0)$$

where the coefficients $\bar{g}_{ij}(k',k'')$ are the discretized versions of the functions $g_{ij}(r',r'')$ and depend on the symmetry of the system (note that the factor G(r’’) in eq. 12 in the main text is adsorbed into $\bar{g}_{ij}(k',k'')$). The term $\varepsilon_{ij}\bar{g}_{ij}(k',k'')\langle n_j(k'') \rangle$ is therefore the effective attraction energy between a segment of type *i* in layer *k′* and all segments of type *j* in layer *k′′*.

In this work, we model the effective attraction potential between two segments separated by a distance *d* as:

$$u(d) = \begin{cases} -\left(\dfrac{a}{d}\right)^6 & \text{if } a < d < d_{cut-off} \\ 0 & \text{otherwise} \end{cases} \qquad (0)$$

where a is the segment length and $d_{\text{cut-off}}$ is a cut-off distance for the potential (we used 2.5δ in this work). Note that the potential is zero for $d < a$ because the minimum center-to-center distance between two segments is a.

We obtain the coefficients $\bar{g}_{ij}(k',k'')$ by integration of the potential function in eq. (0) in the proper symmetry. For planar lamellas, the coefficients are:

$$\bar{g}_{ij}(k',k'') = \int_{\delta(k''-1)}^{\delta k''} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}y \int_{-\infty}^{\infty} \mathrm{d}z \; u\left(\left[\left(x-\delta\left(k'-1/2\right)\right)^2 + y^2 + z^2\right]^{1/2}\right) \tag{0}$$

For cylindrical fibers, the coefficients are given by:

$$\bar{g}_{ij}(k',k'') = \int_{\delta(k''-1)}^{\delta k''} r \, \mathrm{d}r \int_{0}^{2\pi} \mathrm{d}\varphi \int_{-\infty}^{\infty} \mathrm{d}z \; u\left(\left[\left(r\cos\varphi-\delta\left(k'-1/2\right)\right)^2 + \left(r\sin\varphi\right)^2 + z^2\right]^{1/2}\right) \tag{0}$$

Finally, for spherical micelles, the coefficients become:

$$\bar{g}_{ij}(k',k'') = \int_{\delta(k''-1)}^{\delta k''} r^2 \, \mathrm{d}r \int_{0}^{\pi} \sin\theta \, \mathrm{d}\theta \int_{0}^{2\pi} \mathrm{d}\varphi \; u\left(\left[\left(r\sin\theta\cos\varphi-\delta\left(k'-1/2\right)\right)^2 + \left(r\sin\theta\sin\varphi\right)^2 + \left(r\cos\theta\right)^2\right]^{1/2}\right) \tag{0}$$

2. Size of the calculation box

In our choice of coordinates, the origin (r = 0) corresponds to the center of the micelle, the axis of the fiber or the central plane of the lamella. The size of the calculation box is given by the cut-off distance $r_{\text{CM}}^{\text{max}}$, which is the maximum allowed distance between the center of mass of the amphiphile and the center of the aggregates. It is important to ensure that the structural and thermodynamic results of the calculation are the converged with respect to the choice of this parameter. For example in Figure S1, we show a condition where the chemical potential of the amphiphile converges with the size of the calculation box. We observed that convergence can be usually achieved when the number density of the amphiphiles close to the cut-off position is much lower than the number density of amphiphiles within the aggregate, because, in this condition, increasing the size of the calculation box does not alter the density profiles in the system. This condition is in general fulfilled when well-defined aggregates are formed, for example, Figure S2a shows results for a condition where the number density of the chains drops to almost zero near the end of the box and structural and thermodynamic convergence of the results is achieved with respect to the size of the box. On the other hand, for amphiphiles that are highly soluble (*e.g.* molecules containing long head blocks), there is a large density of amphiphiles close to $r_{\text{CM}}^{\text{max}}$ and thus we fail to converge the size of the calculation box (for example, for the conditions of Figure S2b)

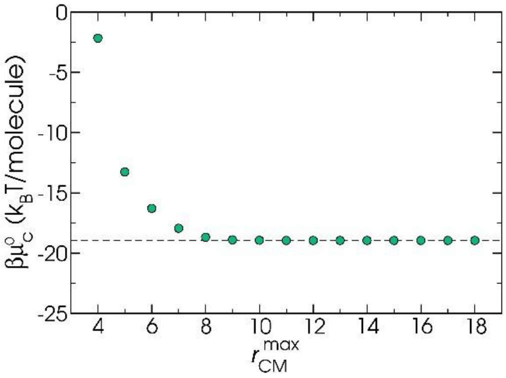

Figure S1. The chemical potential of an amphiphile molecule as a function of r_{CM}^{max}, which is the maximum allowed distance between the center of mass of the amphiphile and the center of the aggregates. Calculation parameters: lamellar aggregate; 7:0:8 tail:linker:head architecture; ε_{tail} = 3.0 k_BT.

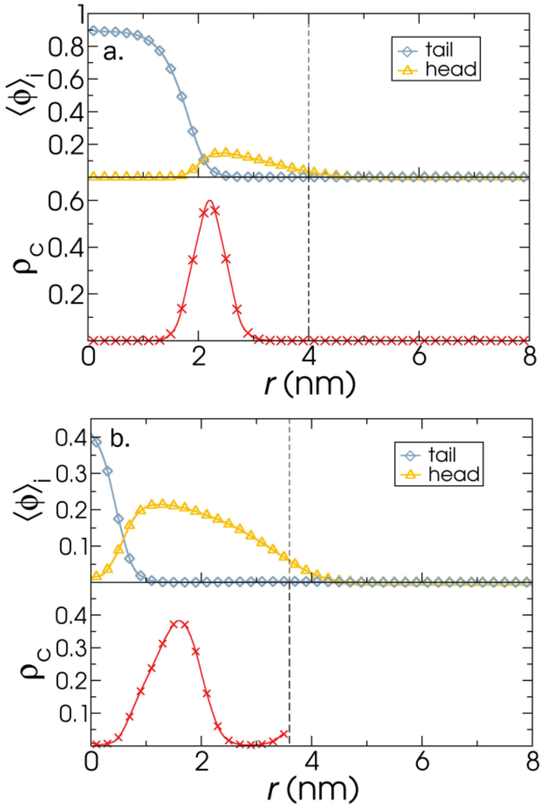

Figure S2. Volume fraction, $\langle\phi_i\rangle$ of tail and head segments and number density of chains (ρ_c. in units of chains·nm^{-3}) as a function of the distance to the center of the aggregate, *r*. Gray dashed lines indicate the maximum *r* at which the center of mass of the amphiphiles is allowed to be, r_{CM}^{max}. Plot (a) shows a typical case where the structure is well converged and hence the number density of amphiphiles (red line in the lower panel) at r_{CM}^{max} is close to zero. Plot (b) shows a case where the structure is not well converged and hence the number density of amphiphiles at r_{CM}^{max} is large. Our theory cannot make accurate predictions for the later cases. Calculation parameters: (a) micelar aggregate; 7:0:8 tail:linker:head architecture ; $\varepsilon_{tail} = 3.0\ k_BT$. (b) lamellar aggregate; 4:0:11 tail:linker:head architecture ; $\varepsilon_{tail} = 4.0\ k_BT$.

3. Molecular model

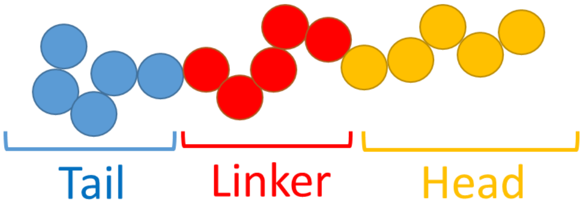

Figure S3. Schematic representation of the structure of a model surfactant. Blue, red and yellow beads represent tail, linker and head segments, respectively.

In this work, we are interested in studying the morphology behavior of triblock surfactants, which are linear chains formed by three blocks, each one with a different type of segment. Figure S3 shows a schematic diagram of the structure of a model surfactant. Blue, red and yellow beads represent tail, linker and head segments forming the hydrophilic terminal block, respectively. We use the same segment volume for the three types of segments, $v_i = 0.113$ nm^3, while the solvent molecular volume was set to that of water, $v_{sol} = 0.03$ nm^3. For simplicity, in this work we only consider linker-linker and tail-tail attractive interactions. Note that these are effective interactions, *i.e.* they model the difference between segment-segment and segment-solvent attractions. In other words, only two interaction parameters have to be set, ε_{tail} and ε_{linker}. Head segments do not effectively interact with each other, which means they are in a good solvent. The total number of segments forming the chain is fixed to 15.

The possible conformations of the chains are sampled with a representative set of 10^5 self-avoiding conformations for each position of the center of mass, which are randomly generated using the Rotational Isomeric State (RIS) model.[1,2] In the model, the length of each segment is fixed (we used 0.5 nm), as well as the angle between two consecutive segments (136°). Only three possible values of the dihedral torsion angle defined by four consecutive segments are allowed. These values are 0° (trans state), 120° and 240° (gauche states). A sequence of torsion-angles states defines a conformation.

4. Effect of the Size of the Set of Conformations

In order to check if 10^5 conformations (for each position of the center of mass of the amphiphiles) are sufficient to ensure that the set of conformations is representative, we repeated the calculations shown in Figure 1 in the main text using $4 \cdot 10^5$ conformations, see Figure S4. The coloured solid lines are the same curves shown in the main text and were calculated using 10^5 RIS conformations, while the black dashed lines were calculated using the enlarged set of $4 \cdot 10^5$ RIS conformations. In the plot, the three curves calculated with 4.10^5 conformations were shifted by exactly the same quantity, 1.39 k_BT. We conclude that enlarging the set of conformations shifts the chemical potential by a fixed quantity for all the cases. Since we are interested in differences of chemical potentials (and not their absolute values), all results presented in this work are converged with respect to the size of the set of conformations.

The number of conformations which guarantees representativeness strongly depends on the length of the chain. In this work we model short triblock amphiphiles represented by 15 segments, and 10^5 conformations were enough. In previous works which used the RIS method to model longer molecules, a larger set of conformations was needed, for instance, In reference 3 a set of $5{\cdot}10^5$ RIS conformations was used for grafted polyelectrolytes with a chain length of 50 segments/chain.

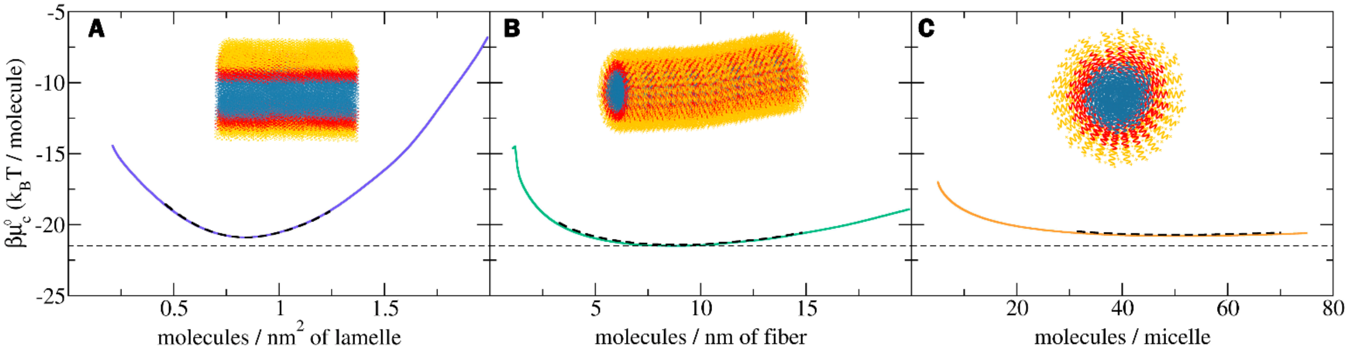

Figure S4. Chemical potential of an amphiphile molecule, $\mu^0{}_c$, within different types of supramolecular self-assembled structures: planar lamellas (b-i), cylindrical fibers (b-ii) and spherical micelles (b-iii) as a function of the total number of chains per micelle, the number of chains per unit length of fiber or the number of chains per unit area of lamella. In this calculation, the molecules have five tail segments, five linker segments and five head segments (5:5:5 architecture). For all cases, ε_{tail} = ε_{linker} = 3 k_BT/molecule. Coloured solid curves were calculated using a set of 10^5 conformations and black dashed curves were calculated using a set of $4{\cdot}10^5$ conformations.

4. Calculation of the radius of gyration

We describe in this section the strategy to calculate the radius of gyration of each block *k* for a given molecule in dilute solution, $\langle R_g^k \rangle$. First we calculate, for each conformation α*,* the energy associated with intramolecular interactions, $U(\alpha)$. Then, we calculate the radius of gyration of each block *k*, $R_g^k(\alpha)$, for each conformation α. Finally, we average the radii of gyration of all conformations for each block, weighting each conformation by the Boltzmann factor associated with the total internal energy of the chain $U(\alpha)$. Note that we explicitly consider intramolecular attractions between segment beads instead of treating interactions through a mean-field approximation because we are calculating the radii of gyration for isolated chains in solution.

The energy associated with intramolecular interactions is given by the sum of the pairwise attractions, given by:

$$U(\alpha) = -\frac{1}{2}\sum_{ij} \varepsilon_{ij} \left(\frac{a}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} \right)^6 \tag{0}$$

where ε_{ij} is the interaction parameter between segments *i* and *j* and $\mathbf{r}_i$ is the position of the segment *i* in real space. The sum is done over all the segments that form the chain. Note that repulsions are accounted for by the fact that all conformations are self-avoiding.

By definition, the radius of gyration of the block *k* for a chain in conformation α, $R_g^k(\alpha)$, is given by:

$$R_g^k = \sqrt{\frac{1}{2N_k^2}\sum_{i\in k}\sum_{j\in k}\left(\mathbf{r}_i - \mathbf{r}_j\right)^2} \tag{0}$$

where N_k is the number of segments forming the block *k* and the sum is done only over segments that form the block *k*.

Finally, the average radius of gyration of the block *k* is given by:

$$\left\langle R_g^k \right\rangle = \frac{\sum_\alpha \exp\left[-U(\alpha)\right] R_g^k(\alpha)}{\sum_\alpha \exp\left[-U(\alpha)\right]} \tag{0}$$

5. Extrapolation to long amphiphiles

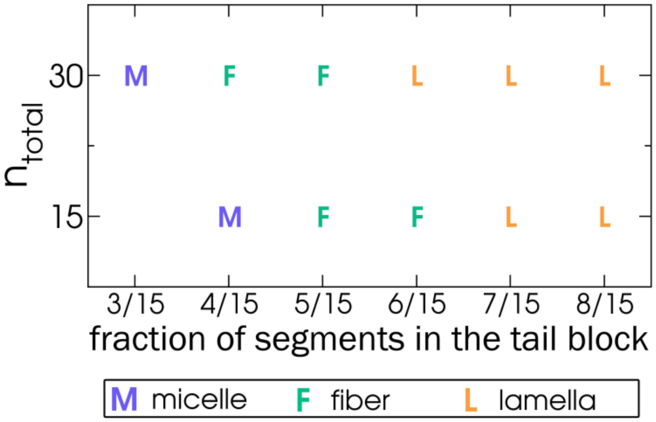

Figure S5. Morphology diagram as a function of the total number of segments, n_{total}, and the fraction of segments in the tail block for a fixed fraction of segments in the linker block of 4/15. Calculation parameters: $\varepsilon_{\text{linker}} = \varepsilon_{\text{tail}} = 3\ k_BT$. The calculations using n_{total}=30 were performed with $5{\cdot}10^5$ RIS conformations for each position of the center of mass.

Figure S5 shows the morphology diagram for n_{total} = 15 (lower row) or 30 (upper row) as a function of the fraction of segments in the tail block. The number of segments in the linker block was 4 for n_{total} = 15 and 8 for n_{total} = 30 (*i.e.* in both cases the fraction of segments in the linker block was 4/15). Increasing the length of the chain stabilizes the lamella, but the order of the transition (M → F → L) and widths of the regions of stability for each morphology are similar for both values of n_{total}. Therefore, Figure S5 suggests that the trends observed for short amphiphiles can be qualitatively extrapolated to longer neutral triblock molecules.

6. List of symbols used in the molecular theory

Symbol	*Definition*
α	Label the amphiphile conformation (spatial distribution of chain segments).
β	Inverse temperature, $(k_BT)^{-1}$.
δ	Discretization step, we used δ = 0.2 nm.
ε_{ij}	Van der Waals parameter for the attractive interaction between segments of types *i* and *j*.
$\varepsilon_{\text{linker/tail}}$	Van der Waals parameter for the attractive interaction between linker/tail segments.
κ	Lagrange multiplier associated with the restriction on the integral of the number density of chains. It is equal to μ_c^o.

$\lambda(r)$	Multiplied by $\beta\rho_c(r)G(r)$ gives the Lagrange multiplier associated with the normalization of $P(\alpha,r)$ at *r*.
μ_c^o	Standard chemical potential of a chain within an isolated aggregate fixed on the space.
$\pi(r)$	Position-dependent osmotic pressure. Multiplied by $\beta G(r)$ gives the Lagrange multiplier associated with the packing constraint.
$\rho_i(r)$	Number density of species *i* at position *r.* (*i* = *sol* for solvent or *c* for chains)
$\langle\phi_i(r)\rangle$	Volume fraction of *i* at position *r*. (*i*= tail, head or linker for each type of segment; sol for solvent)
A	Area of the lamella.
F	Total free energy of an aggregate of N_c amphiphiles.
$g_{ij}(r,r')$	Function that accounts for the geometric dependence of the interaction between segments of types *i* and *j*.
$G(r)dr$	Volume element at a distance *r* from the center of the micelle, the axis of the cylindrical fiber or the central plane of the planar lamella.
k_B	Boltzmann‘s constant.
L	Length of the fiber.
$n_i(r;\alpha,r')dr$	Number of segments of type *i* that a chain in conformation α at position *r′* has in the spherical, cylindrical or planar region between *r* and *r* + d*r.*
$\langle n_i(r)\rangle$	Average number density of segments of type *i* at position *r*.
$N_i(r)dr$	Number of segments of type *i* between *r* and d*r*.
N_c	Total number of amphiphiles within an aggregate.
$P(\alpha,r)$	Probability of having a chain in conformation α when its center of mass is at position *r*.
$q(r)$	Single-chain partition function at position *r*
T	Temperature.
$U(\alpha)$	Energy associated with intramolecular interactions of a chain in conformation α.
v_i	Volume of a segment of type *i* or a solvent molecule (*i*= tail, head or linker for each type of segement; sol for solvent)

7. References

1 P. Flory and M. Volkenstein, *Statistical mechanics of chain molecules*, Wiley Online Library, 1969.
2 M. Rubinstein and R. H. Colby, *Polymer physics*, Oxford University Press New York, 2003, vol. 23.
3 M. Tagliazucchi, M. Olvera de la Cruz and I. Szleifer, *Proc. Natl. Acad. Sci. USA*, 2010, **107**, 5300–5305.