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Model Amphiphilic Polymer Conetworks in Water: Prediction of Their Ability for Oil Solubilization

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Appendix A. Lamellar Nanophase

Appendix A presents the derivation of closed-form expressions for the asymmetry ratios for the two nanophases in lamellae. This was attained by the analytical minimization of the three asymmetry-related Gibbs free energy components, i.e., the elastic Gibbs free energies in the core and in the shell, and the interfacial Gibbs free energy; the mixing Gibbs free energies in the core and in the shell, and the electrostatic Gibbs free energy in the shell are independent of the asymmetry ratios.

The left-hand-side part of Figure S1 shows the unit cell for an amphiphilic polymer conetwork (APCN) based on end-linked ABA triblock copolymers in the as-prepared state, swollen in a non-selective solvent, and, is, therefore, in the homogeneous, non-microphase separated state. Thus, this unit cell is highly symmetrical, having a cubic shape and bearing the cross-linking point in the center of the cube. The length of the edge of the cube is \( w_0 \). Upon transfer of the conetwork into the oil-water mixture, microphase separation into lamellae (for the considered case) takes place, with the cube being deformed into a rectangular parallelepiped, in a rather elongated shape so that the surface area of contact between the incompatible phases (interfacial area, in pink) be minimized. The oil-hydrophobic block nanophase (in red) is located in the middle of the unit cell, having a height \( h \) and a cross-sectional area equal to \( w \times w \) (\( w < w_0 \)), whereas the water-hydrophilic block nanophase (in blue) is located both above and below the hydrophobic nanophase, with the height of each hydrophilic portion being equal to \( l_2 \).

Volume balance in the hydrophobic nanophase implies that the volume of the lamellar core, \( V_{\text{core, lamellae}} \), is:

\[
V_{\text{core, lamellae}} = \frac{\beta \zeta}{\phi_{B\text{core}}} A^3
\]

(A1)

where \( A^3 \) is the volume of one monomer repeating unit.

On the other hand, geometry dictates that:

\[
V_{\text{core, lamellae}} = w^2 h
\]

(A2)
By combining equations (A1) and (A2), one obtains:

\[ w^2 = \frac{\beta \zeta}{\varphi_B^{\text{core}} h} A^3 \] (A3)

The interfacial area (in pink) in the unit cell, \( S_{\text{interfacial}}^{\text{lamella}} \), is:

\[ S_{\text{interfacial}}^{\text{lamella}} = 2w^2 \] (A4)

which takes into account the fact that the two square surfaces of the hydrophobic nanophase (hydrophobic blocks plus oil) within the unit cell come into contact with the two hydrophilic nanophases (hydrophilic blocks plus water), one above and the other below the hydrophobic one.

Using the result in equation (A3), equation (A4) becomes:

\[ S_{\text{interfacial}}^{\text{lamella}} = 2 \frac{\beta \zeta}{\varphi_B^{\text{core}} h} A^3 \] (A5)

**Figure S1.** Shape transformation and phase separation at the nanoscale upon transfer of the amphiphilic polymer conetwork from the non-selective solvent in the as-prepared state to the oil-water mixture in the final lamellar state.
The interfacial Gibbs free energy in the unit cell, $\Delta G_{\text{interfacial}}^{\text{lamella}}$, is equal to the product of the interfacial tension between the hydrophilic and hydrophobic nanophases, $\gamma$, times the interfacial area in the unit cell, $S_{\text{interfacial}}^{\text{lamella}}$:

$$\Delta G_{\text{interfacial}}^{\text{lamella}} = \gamma S_{\text{interfacial}}^{\text{lamella}} \quad (A6)$$

The interfacial tension, $\gamma$, is given by:

$$\gamma = \frac{kT}{A^2} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \quad (A7)$$

Substituting equations (A5) and (A7) into equation (A6) leads to:

$$\frac{\Delta G_{\text{interfacial}}^{\text{lamella}}}{kT} = 2 \frac{\beta \zeta A}{\varphi_B^{\text{core}}} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \quad (A8)$$

The elastic Gibbs free energy of the hydrophobic nanophase within the unit cell is:

$$\frac{\Delta G_{\text{elastic core}}^{\text{lamella}}}{kT} = \frac{\beta \zeta A}{4 \varphi_B^{\text{core}}} \left[ \frac{1}{2} \left( \frac{\alpha_{\text{lamella}}^{\text{elastic core}}}{\alpha_{\text{elastic core}}} \right)^2 + \frac{2}{\alpha_{\text{elastic core}}} \right] - 3 - \ln \left( \frac{\varphi_0}{\varphi_B^{\text{core}}} \right) \quad (A9)$$

where $\alpha_{\text{elastic core}}^{\text{lamella}}$ is the ratio of the stretched to unstretched heights of the lamellar core (also to be called the asymmetry ratio of the hydrophobic nanophase in lamellae), defined as:

$$\alpha_{\text{elastic core}}^{\text{lamella}} = \frac{h}{h_0} \quad (A10)$$

where $h$ is the height of the hydrophobic nanophase in the unit cell at swelling equilibrium, while $h_0$ is the height (length of the edge of the cube) at the state of conetwork preparation in the non-selective solvent, corresponding to the hydrophobic part of the unit cell.

Substitution of equation (A10) into equation (A9) gives:

$$\frac{\Delta G_{\text{elastic core}}^{\text{lamella}}}{kT} = \frac{\beta \zeta A}{4 \varphi_B^{\text{core}}} \left[ \left( \frac{\varphi_0}{\varphi_B^{\text{core}}} \right)^{2/3} \left( \left( \frac{h}{h_0} \right)^2 + 2 \frac{h_0}{h} \right) - 3 - \ln \left( \frac{\varphi_0}{\varphi_B^{\text{core}}} \right) \right] \quad (A11)$$

From simple geometrical considerations, $h_0$ can be estimated as:
\[ h_0 = w_0 \left( \frac{\zeta}{\zeta + \eta} \right)^{1/3} \]  \hspace{1cm} (A12)

Applying volume balance to the whole (cubic) unit cell in the as-prepared state, in a procedure analogous to that expressed in equations (A1) and (A2) for the hydrophobic nanophase in the unit cell, and combining, one can obtain an expression for \( w_0 \) as:

\[ w_0^3 = \frac{\beta(\zeta + \eta)}{\varphi_0} A^3 \]  \hspace{1cm} (A13)

Solving equation (A13) for \( w_0 \), and substituting the result in equation (A12), gives:

\[ h_0 = \left( \frac{\beta \zeta}{\varphi_0} \right)^{1/3} A \]  \hspace{1cm} (A14)

The elastic Gibbs free energy of the hydrophilic nanophase within the unit cell is:

\[ \frac{\Delta \text{G}_{\text{elastic}}^\text{lamella}}{kT} = \frac{\beta}{4} \left( \left( \frac{\varphi_0}{\varphi_A^\text{shell}} \right)^{2/3} \left[ \frac{\alpha_{\text{elastic, shell}}}{\alpha_{\text{elastic, shell}}}^2 + 2 \frac{\alpha_{\text{elastic, shell}}}{\alpha_{\text{elastic, shell}}} \right] - 3 - \ln \left( \frac{\varphi_0}{\varphi_A^\text{shell}} \right) \right) \]  \hspace{1cm} (A15)

where \( \alpha_{\text{elastic, shell}} \) is the ratio of the stretched to the unstretched heights of the lamellar shell (also to be called the asymmetry ratio of the hydrophilic nanophase in lamellae), defined as:

\[ \alpha_{\text{elastic, shell}} = \frac{l}{l_0} \]  \hspace{1cm} (A16)

where \( l/2 \) is the height of one of the two hydrophilic portions in the unit cell at swelling equilibrium, and \( l_0 \) is the height (length of the edge of the cube) at the state of conetwork preparation in the non-selective solvent corresponding to the hydrophilic part of the unit cell.

Substitution of equation (A16) into equation (A15) gives:

\[ \frac{\Delta \text{G}_{\text{elastic}}^\text{lamella}}{kT} = \frac{\beta}{4} \left( \left( \frac{\varphi_0}{\varphi_A^\text{shell}} \right)^{2/3} \left[ \left( \frac{l}{l_0} \right)^2 + 2 \frac{l}{l_0} \right] - 3 - \ln \left( \frac{\varphi_0}{\varphi_A^\text{shell}} \right) \right) \]  \hspace{1cm} (A17)

Applying simple geometrical considerations, \( l_0 \) can be estimated from:

\[ l_0 = w_0 \left( \frac{\eta}{\zeta + \eta} \right)^{1/3} \]  \hspace{1cm} (A18)
Solving equation \((A13)\) for \(w_0\), and substituting the result in equation \((A18)\), gives:

\[
l_0 = \left(\frac{\beta \eta}{\varphi_0}\right)^{1/3} A
\]

\((A19)\)

The ratio of the characteristic lengths of the two nanophases in lamellae, \(h\) and \(l\), can be related, via geometry, to the ratio of the volumes of the two nanophases:

\[
\frac{V_{\text{core}\_lamella}}{V_{\text{shell}\_lamella}} = \frac{w^2 h}{w^2 l} = \frac{h}{l}
\]

\((A20)\)

In analogy to equation \((A1)\), volume balance in the hydrophilic nanophase gives the volume of the lamellar shell in the unit cell:

\[
V_{\text{shell}\_lamella} = \frac{\beta \eta}{\varphi_A} A^3
\]

\((A21)\)

The ratio of the volumes of the two nanophases can also be calculated using the expressions provided in equations \((A1)\) and \((A21)\):

\[
\frac{V_{\text{core}\_lamella}}{V_{\text{shell}\_lamella}} = \frac{\frac{\beta \zeta A^3}{\varphi_B}}{\frac{\beta \eta A^3}{\varphi_A}} = \frac{\varphi_A^{\text{shell}} \zeta}{\varphi_B^{\text{core}} \eta}
\]

\((A22)\)

By combining equations \((A20)\) and \((A22)\), one obtains:

\[
\frac{h}{l} = \frac{\varphi_A^{\text{shell}} \zeta}{\varphi_B^{\text{core}} \eta}
\]

\((A23)\)

Solving equation \((A23)\) for \(l\) gives:

\[
l = h \frac{\eta \varphi_B^{\text{core}}}{\zeta \varphi_A^{\text{shell}}}
\]

\((A24)\)

Dividing both sides of equation \((A24)\) by \(l_0\) results in:

\[
\frac{l}{l_0} = \frac{h \eta \varphi_B^{\text{core}}}{l_0 \zeta \varphi_A^{\text{shell}}}
\]

\((A25)\)

In order to relate \(l_0\) with \(h_0\), we divide equation \((A19)\) by equation \((A14)\), yielding:
Using equation (A26) to substitute \( l_0 \) on the right-hand-side of equation (A25) gives:

\[
\frac{l}{l_0} = h \left( \frac{\eta}{\zeta} \right)^{2/3} \frac{\varphi_0^\text{core}}{\varphi_A^\text{shell}}
\]  

(A27)

Substitution of the result of equation (A27) into equation (A17) transforms the dependence on \( l \) of the elastic Gibbs free energy component in the shell to a dependence on \( h \):

\[
\frac{\Delta G^\text{lamella}_{\text{elastic shell}}}{kT} = \frac{\beta}{4} \left\{ \left( \frac{\varphi_0}{\varphi_A^\text{shell}} \right)^{2/3} \left[ \left( \frac{h}{h_0} \right)^2 \left( \frac{\eta}{\zeta} \right)^{4/3} \left( \frac{\varphi_0^\text{core}}{\varphi_A^\text{core}} \right)^2 + 2 \frac{h_0}{h} \left( \frac{\zeta}{\eta} \right)^{2/3} \frac{\varphi_A^\text{shell}}{\varphi_B^\text{core}} \right] - 3 \ln \left( \frac{\varphi_0}{\varphi_A^\text{shell}} \right) \right\}
\]

(A28)

At equilibrium, the total Gibbs free energy of the unit cell of the lamellar APCN is minimized:

\[
\Delta G^\text{lamella}_{\text{total}} = \Delta G^\text{lamella}_{\text{mixing core}} + \Delta G^\text{lamella}_{\text{elastic core}} + \Delta G^\text{lamella}_{\text{interfacial}} + \Delta G^\text{lamella}_{\text{mixing shell}} + \Delta G^\text{lamella}_{\text{elastic shell}} + \Delta G^\text{lamella}_{\text{electrostatic shell}} = \min
\]

(A29)

This happens when the first derivative of \( \Delta G^\text{lamella}_{\text{total}} \) with respect to \( h \) becomes equal to 0, and the second derivative with respect to \( h \) is positive. The former condition is equivalent to:

\[
\frac{\partial}{\partial h} \left( \Delta G^\text{lamella}_{\text{interfacial}} \right) + \frac{\partial}{\partial h} \left( \Delta G^\text{lamella}_{\text{elastic core}} \right) + \frac{\partial}{\partial h} \left( \Delta G^\text{lamella}_{\text{elastic shell}} \right) = 0
\]

(A30)

for which it has already been taken into account that the first derivatives of the three other Gibbs free energy components with respect to \( h \) are equal to 0.

Differentiation of equations (A8), (A11) and (A28) with respect to \( h \), and substitution into equation (A30), yields:

\[
\frac{\beta}{2} \left( \frac{\varphi_0}{\varphi_A^\text{shell}} \right)^{2/3} \left[ \frac{h}{h_0} \left( \frac{\eta}{\zeta} \right)^{4/3} \left( \frac{\varphi_0^\text{core}}{\varphi_A^\text{core}} \right)^2 - \frac{h_0}{h^2} \left( \frac{\zeta}{\eta} \right)^{2/3} \frac{\varphi_A^\text{shell}}{\varphi_B^\text{core}} \right] + \frac{\beta}{2} \left( \frac{\varphi_0}{\varphi_B^\text{core}} \right)^{2/3} \left( \frac{h}{h_0} \right)^2 \left( \frac{\zeta}{\eta} \right) - 2 \frac{\beta \chi_A}{\rho B^\text{core} h^2} \left( \frac{\chi_B}{\beta} \right)^{1/2} = 0
\]

(A31)

Equation (A31) can be written in the form of a simple cubic equation by multiplying throughout by \( h^2 \):

\[
h^3 \left[ \left( \frac{\varphi_0}{\varphi_A^\text{core}} \right)^{2/3} \left( \frac{\varphi_0^\text{core}}{\varphi_A^\text{core}} \right) \right] \left[ \frac{h}{h_0} \left( \frac{\eta}{\zeta} \right)^{4/3} \left( \frac{\varphi_0^\text{core}}{\varphi_A^\text{core}} \right)^2 + \frac{h_0}{h^2} \left( \frac{\zeta}{\eta} \right)^{2/3} \frac{1}{h_0} \right] - \left[ \left( \frac{\varphi_0}{\varphi_A^\text{core}} \right)^{2/3} \left( \frac{\varphi_A^\text{shell}}{\varphi_B^\text{core}} \right) \right] h_0 + \left( \frac{\varphi_0}{\varphi_B^\text{core}} \right)^{2/3} h_0 + \frac{4 \chi_A}{\rho B^\text{core} \beta} \left( \frac{\chi_B}{\beta} \right)^{1/2} = 0
\]

(A32)
Solving cubic equation (A32) for $h$ gives:

$$h = \left\{ \frac{\frac{4\zeta A}{\varphi_B \text{core}}(X_{AB})^{1/2} + h_0 \left( \frac{\varphi_0}{\varphi_B \text{core}} \right)^{2/3} + h_0 \left( \frac{\varphi_0}{\varphi_B \text{shell}} \right)^{2/3} \left( \frac{\varphi_B \text{core}}{\varphi_B \text{shell}} \right) }{1 + \frac{1}{h_0} \left( \frac{\varphi_0}{\varphi_B \text{core}} \right)^{2/3} + \left( \frac{\eta}{\xi} \right)^{4/3} \left( \frac{\varphi_B \text{shell}}{\varphi_B \text{core}} \right) } \right\}^{1/3} \quad (A33)$$

Applying the result of equation (A14) in equation (A33), and rearranging terms, leads to the asymmetry ratio in the hydrophobic nanophase for lamellae, $h/h_0$:

$$\frac{h}{h_0} = \left\{ \frac{1 + \left( \frac{\eta}{\xi} \right)^{4/3} \left( \frac{\varphi_B \text{shell}}{\varphi_B \text{core}} \right)^{8/3} + \frac{4\zeta^2}{\beta \varphi_B \text{core}} X_{AB}}{1 + \left( \frac{\eta}{\xi} \right)^{4/3} \left( \frac{\varphi_B \text{shell}}{\varphi_B \text{core}} \right)^{8/3}} \right\}^{1/3} \quad (A34)$$

Applying the result of equation (A34) in equation (A27) results in the expression for the asymmetry ratio in the hydrophilic nanophase in lamellae, $l/l_0$:

$$\frac{l}{l_0} = \left( \frac{\eta}{\xi} \right)^{2/3} \frac{\varphi_B \text{core}}{\varphi_B \text{shell}} \left\{ \frac{1 + \left( \frac{\eta}{\xi} \right)^{4/3} \left( \frac{\varphi_B \text{shell}}{\varphi_B \text{core}} \right)^{8/3} + \frac{4\zeta^2}{\beta \varphi_B \text{core}} X_{AB}}{1 + \left( \frac{\eta}{\xi} \right)^{4/3} \left( \frac{\varphi_B \text{shell}}{\varphi_B \text{core}} \right)^{8/3}} \right\}^{1/3} \quad (A35)$$

The equilibrium interfacial area for the lamellar unit cell, $S_{\text{lamella}}^{\text{interfacial}}$, can be calculated by substituting equations (A34) and (A14) into equation (A5):

$$S_{\text{lamella}}^{\text{interfacial}} = \frac{2\varphi_0^{1/3}(\beta \zeta)^{2/3} A^2}{\varphi_B \text{core} \left\{ \frac{1 + \left( \frac{\eta}{\xi} \right)^{4/3} \left( \frac{\varphi_A \text{shell}}{\varphi_B \text{core}} \right)^{8/3} + \frac{4\zeta^2}{\beta \varphi_B \text{core}} X_{AB}}{1 + \left( \frac{\eta}{\xi} \right)^{4/3} \left( \frac{\varphi_B \text{shell}}{\varphi_B \text{core}} \right)^{8/3}} \right\}^{1/3}} \quad (A36)$$
Appendix B. Cylindrical Nanophase

Appendix B presents the derivation of closed-form expressions for the asymmetry ratios for the two nanophases in cylinders. This was attained by the analytical minimization of the three asymmetry-related Gibbs free energy components, i.e., the elastic Gibbs free energies in the core and in the shell, and the interfacial Gibbs free energy; the mixing Gibbs free energies in the core and in the shell, and the electrostatic Gibbs free energy in the shell are independent of the asymmetry ratios.

The left-hand-side part of Figure S2 shows the unit cell for an amphiphilic polymer conetwork (APCN) based on end-linked ABA triblock copolymers in the as-prepared state, swollen in a non-selective solvent, and, is, therefore, in the homogeneous, non-microphase separated state. Thus, this unit cell is highly symmetrical, having a cubic shape and bearing the cross-linking point in the center of the cube. The length of the edge of the cube is $w_0$. Upon transfer of the conetwork into the oil-water mixture, microphase separation into cylinders (for the present case) takes place, with the cube being deformed into a hexagonal cylinder, in a rather compressed shape so that the surface area of contact between the incompatible phases (interfacial area, in pink) be minimized. The oil-hydrophobic block nanophase (in red) forms a cylinder, located in the central axis of the hexagonal unit cell, and having a height $H$ and a radius $r$, whereas the water-hydrophilic block nanophase (in blue) is located around the cylindrical hydrophobic core, and also having a height equal to $H$.

Figure S2. Shape transformation and phase separation at the nanoscale upon transfer of the amphiphilic polymer conetwork from the non-selective solvent in the as-prepared state to the oil-water mixture in the final cylindrical state.
Volume balance in the hydrophobic nanophase implies that the volume of the cylindrical core, $V_{\text{core cylinder}}$, is:

$$V_{\text{core cylinder}} = \frac{\beta \zeta}{\phi^\text{core}_B} A^3$$  \hspace{1cm} (B1)

where $A^3$ is the volume of one monomer repeating unit.

On the other hand, geometry dictates that:

$$V_{\text{core cylinder}} = \pi r^2 H$$  \hspace{1cm} (B2)

Upon combining equations (B1) and (B2), one obtains:

$$r = \left( \frac{\beta \zeta A^3}{\phi^\text{core}_B \pi H} \right)^{1/2}$$  \hspace{1cm} (B3)

The interfacial area (again in pink) in the unit cell, $S_{\text{interfacial cylinder}}$, is:

$$S_{\text{interfacial cylinder}} = 2\pi r H$$  \hspace{1cm} (B4)

which is the vertical outer lateral area of the hydrophobic (cylindrical) nanophase (hydrophobic blocks plus oil) within the unit cell which is in contact with the hydrophilic nanophase (hydrophilic blocks plus water).

Using the result in equation (B3), equation (B4) becomes:

$$S_{\text{interfacial cylinder}} = 2 \left( \frac{\pi H \beta \zeta A^3}{\phi^\text{core}_B} \right)^{1/2}$$  \hspace{1cm} (B5)

The interfacial Gibbs free energy in the unit cell, $\Delta G_{\text{interfacial cylinder}}$, is equal to the product of the interfacial tension between the hydrophilic and hydrophobic nanophases, $\gamma$, times the interfacial area in the unit cell, $S_{\text{interfacial cylinder}}$:

$$\Delta G_{\text{interfacial cylinder}} = \gamma S_{\text{interfacial cylinder}}$$  \hspace{1cm} (B6)

The interfacial tension, $\gamma$, is given by:
\[ \gamma = \frac{kT}{A^2} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \]  

(B7)

Substituting equations (B5) and (B7) into equation (B6) leads to:

\[ \frac{\Delta G_{\text{interfacial}}}{kT} = 2 \left( \frac{\pi \beta \zeta}{\varphi_B^{\text{core}}} \right)^{1/2} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \]  

(B8)

The elastic Gibbs free energy of the hydrophobic nanophase within the unit cell is:

\[ \frac{\Delta G_{\text{elastic}}}{kT} = \frac{2}{4} \left[ \left( \frac{\varphi_0}{\varphi_B^{\text{core}}} \right)^2 + \left( \frac{2}{\alpha_{\text{cylinder}}^{\text{elastic,core}}} \right) \right] - 3 - \ln \left( \frac{\varphi_0}{\varphi_B^{\text{core}}} \right) \]  

(B9)

where \( \alpha_{\text{cylinder}}^{\text{elastic,core}} \) is the ratio of the compressed to uncompressed heights of the cylindrical core (also to be called the asymmetry ratio of the hydrophobic nanophase in cylinders), defined as:

\[ \alpha_{\text{cylinder}}^{\text{elastic,core}} = \frac{H}{h_0} \]  

(B10)

where \( H \) is the height of the oil-swollen cylindrical core at swelling equilibrium, and \( h_0 \) is the height (length of the edge of the cube) at the state of conetwork preparation in the non-selective solvent, corresponding to the hydrophobic part of the unit cell.

Substitution of equation (B10) into equation (B9) gives:

\[ \frac{\Delta G_{\text{elastic}}}{kT} = \frac{2}{4} \left[ \left( \frac{\varphi_0}{\varphi_B^{\text{core}}} \right)^2 + 2 \left( \frac{h_0}{H} \right) \right] - 3 - \ln \left( \frac{\varphi_0}{\varphi_B^{\text{core}}} \right) \]  

(B11)

As in Appendix A, \( h_0 \) can also be estimated from simple geometrical considerations as:

\[ h_0 = w_0 \left( \frac{\zeta}{\zeta + \eta} \right)^{1/3} \]  

(B12)

Furthermore, applying volume balance to the whole (cubic) unit cell in the as-prepared state, in a procedure analogous to that expressed in equations (B1) and (A2) for the hydrophobic nanophase in the unit cell, and combining, one can obtain an expression for \( w_0 \) as:

\[ w_0^3 = \frac{B(\zeta + \eta)}{\varphi_0} A^3 \]  

(B13)
Solving equation (B13) for \( w_0 \), and substituting the result in equation (B12), gives:

\[
h_0 = \left( \frac{\beta \xi}{\varphi_0} \right)^{1/3} A
\]  

(B14)

The elastic Gibbs free energy of the hydrophilic nanophase within the unit cell is:

\[
\frac{\Delta G_{\text{hexagon parallelepiped}}^{\text{elastic shell}}}{kT} = \frac{\beta}{4} \left( \frac{\varphi_0}{\varphi_A^\text{shell}} \right)^{2/3} \left[ \frac{\alpha_{\text{hexagon parallelepiped}}^{\text{elastic shell}}}{\alpha_{\text{hexagon parallelepiped}}^{\text{elastic shell}}} + \frac{2}{\alpha_{\text{hexagon parallelepiped}}^{\text{elastic shell}}} \right] - 3 - \ln \left( \frac{\varphi_0}{\varphi_A^\text{shell}} \right)
\]  

(B15)

where \( \alpha_{\text{hexagon parallelepiped}}^{\text{elastic shell}} \) is the ratio of the compressed to uncompressed heights of the hexagonal shell (also to be called the asymmetry ratio of the hydrophilic nanophase in cylinders), defined as:

\[
\alpha_{\text{hexagon parallelepiped}}^{\text{elastic shell}} = \frac{H}{l_0}
\]  

(B16)

where \( H \) is the height of the water-swollen hexagonal shell at swelling equilibrium, and \( l_0 \) is the height (length of the edge of the cube) at the state of conetwork preparation in the non-selective solvent, corresponding to the hydrophilic part of the unit cell.

Substitution of equation (B16) into equation (B15) gives:

\[
\frac{\Delta G_{\text{elastic shell}}^{\text{hexagon parallelepiped}}}{kT} = \frac{\beta}{4} \left( \frac{\varphi_0}{\varphi_A^\text{shell}} \right)^{2/3} \left[ \left( \frac{H}{l_0} \right)^2 + 2 \frac{l_0}{H} \right] - 3 - \ln \left( \frac{\varphi_0}{\varphi_A^\text{shell}} \right)
\]  

(B17)

As in Appendix A, \( l_0 \) can also be estimated from simple geometrical considerations as:

\[
l_0 = w_0 \left( \frac{\eta}{\zeta+\eta} \right)^{1/3}
\]  

(B18)

Solving equation (B13) for \( w_0 \), and substituting the result in equation (B18), gives:

\[
l_0 = \left( \frac{\beta \eta}{\varphi_0} \right)^{1/3} A
\]  

(B19)

At equilibrium, the total Gibbs free energy of the unit cell of the cylindrical APCN is minimized:
\[ \Delta G_{\text{hexagonal cylinder}}^{\text{total}} = \Delta G_{\text{mixing core}}^{\text{cylinder}} + \Delta G_{\text{interfacial}}^{\text{cylinder}} + \Delta G_{\text{core}}^{\text{interface}} + \Delta G_{\text{hexagon parallelepiped}}^{\text{cylinder}} + \Delta G_{\text{elastic shell}}^{\text{hexagon parallelepiped}} + \Delta G_{\text{hexagon parallelepiped}}^{\text{hexagon parallelepiped}} = \min \] (B20)

This happens when the first derivative of \( \Delta G_{\text{hexagonal cylinder}}^{\text{total}} \) with respect to \( H \) becomes equal to 0, and the second derivative with respect to \( H \) is positive. The former condition is equivalent to:

\[
\frac{\partial}{\partial H} (\Delta G_{\text{cylinder}}^{\text{interfacial}}) + \frac{\partial}{\partial H} (\Delta G_{\text{cylinder}}^{\text{elastic core}}) + \frac{\partial}{\partial H} (\Delta G_{\text{hexagon parallelepiped}}^{\text{hexagon parallelepiped}}) = 0 \quad (B21)
\]

for which it has already been taken into account that the first derivatives of the three other Gibbs free energy components with respect to \( H \) are equal to 0.

Differentiation of equations (B8), (B11) and (B17) with respect to \( H \), and substitution into equation (B21), yields:

\[
\frac{\beta}{2} \left( \frac{\varphi_0}{\varphi_A^{\text{shell}}} \right)^{2/3} \left( \frac{H}{l_0^2} - \frac{l_0}{H^2} \right) + \frac{\beta}{2} \left( \frac{\varphi_0}{\varphi_B^{\text{core}}} \right)^{2/3} \left( \frac{H}{h_0^2} - \frac{h_0}{H^2} \right) + \left( \frac{\pi \beta \xi}{AH \varphi_B^{\text{core}}} \right)^{1/2} \left( \chi_{AB} / 6 \right)^{1/2} = 0 \quad (B22)
\]

Equation (B22) can be written in the form of a simple quadratic equation by multiplying throughout by \( H^2 \) and considering \( x = H^{3/2} \):

\[
\frac{\beta}{2} \varphi_0^{2/3} \left( \frac{1}{(\varphi_B^{\text{core}})^{3/2} h_0^2} + \frac{1}{(\varphi_A^{\text{shell}})^{3/2} l_0^2} \right) H^3 + \left( \frac{\pi \beta \xi}{AH \varphi_B^{\text{core}}} \right)^{1/2} \left( \chi_{AB} / 6 \right)^{1/2} H^{3/2} - \frac{\beta}{2} \varphi_0^{2/3} \left( \frac{h_0}{(\varphi_B^{\text{core}})^{3/2}} + \frac{l_0}{(\varphi_A^{\text{shell}})^{3/2}} \right) = 0 \quad (B23)
\]

Substituting \( h_0 \) and \( l_0 \) from equations (B14) and (B19), respectively, into equation (B23), and solving quadratic equation (B23) for \( H \) gives:

\[
H = \frac{\beta}{\varphi_0^{1/3} \chi_{AB}^{1/3}} \left[ \left( 1 + \frac{\beta^2/3 \varphi_0^{5/3} \lambda_{\varphi_B^{\text{core}}}^{\text{core}}} {\pi \chi_{AB}} \left( \frac{1}{(\varphi_B^{\text{core}})^{3/2}} + \frac{1}{(\varphi_A^{\text{shell}})^{3/2}} \right) \right)^{1/3} \left( \frac{\chi^{1/3}}{\varphi_B^{\text{core}}} + \left( \frac{\eta}{(\varphi_B^{\text{shell}})^{3/2}} \right)^{1/3} \right)^{1/2} \right]^{1/3}
\]

Applying the result of equation (B14) in equation (B24), leads to the asymmetry ratio in the hydrophobic nanophase for cylinders, \( H/h_0 \):
The expression for the asymmetry ratio in the hydrophilic nanophase in cylinders, $H/l_0$:

$$
\frac{H}{l_0} = \frac{1}{\beta^2/\phi_0^{5/4}} \left( \frac{\pi \chi_{AB}}{6 \phi_0^{5/4}} \right)^{1/3} \left[ 1 + \beta^2/3 \phi_0^{5/4} \phi_{\text{core}} B \pi \chi_{AB} \left( \frac{\phi_{\text{core}} B}{\phi_{\text{shell}} A} \right)^{1/3} \left( \frac{\chi}{\phi_{\text{core}} B} \right)^{1/3} \left( \frac{\eta_{\text{shell}} B}{\phi_{A}} \right)^{1/3} \right]^{1/3} - 1
$$

Applying the result of equation (B19) in equation (B24), results in the expression for the equilibrium interface area for the cylindrical unit cell, $S_{\text{cylinder}}$:

$$
S_{\text{cylinder}} = \frac{2}{\phi_0^{5/8}} \left( \frac{\pi \chi_{AB}}{6 \phi_0^{5/4}} \right)^{2/3} \left( \frac{\xi_{AB}}{6} \right)^{1/6} \left[ 1 + \beta^2/3 \phi_0^{5/4} \phi_{\text{core}} B \pi \chi_{AB} \left( \frac{\phi_{\text{core}} B}{\phi_{\text{shell}} A} \right)^{1/3} \left( \frac{\chi}{\phi_{\text{core}} B} \right)^{1/3} \left( \frac{\eta_{\text{shell}} B}{\phi_{A}} \right)^{1/3} \right]^{-1/3} A^{2/3}
$$
Appendix C. Gibbs Free Energy Components at the Energy Minima

i. Effect of mol fraction of the hydrophobic units

The preferred structure of the APCNs, in the simultaneous presence of water and oil, is that with the lower value of the minimized total Gibbs free energy among all structures considered. In turn, this value is determined from the contributions from all the Gibbs free energy components. However, some of these components contribute much more to the total Gibbs free energy than others, and they, therefore, have a more decisive role in the prevalence of the particular structure over the others. Table S1 lists the values of all Gibbs free energy components per chain, in $kT$ units, for APCNs with a constant degree of ionization of 0.02, and 0.10, 0.20, and 0.30 mol fractions of the hydrophobic units. In each case, the two structures with the lowest values of the minimized total Gibbs free energy were selected and presented in the table.

Examination of the Gibbs free energy components reveals that the prevalence of spheres for APCNs at a degree of ionization of 0.02 and with a 0.10 mol fraction of the hydrophobic units (top left quarter of Table S1) is mainly due to the more favorable (lower) value of the interfacial Gibbs free energy component and, to a lesser extent, due to the lower electrostatic Gibbs free energy in the shell component for spheres, whereas the Gibbs free energy of mixing in the core is the main component acting in the opposite direction, favoring cylinders. The interfacial Gibbs free energy and the electrostatic Gibbs free energy in the shell are more favorable for spheres due to the lower interfacial area per chain and lower polymer volume fraction in water for spheres, respectively. On the other hand, the Gibbs free energy of mixing in the core is more favorable for cylinders due to the lower polymer volume fraction in oil for cylinders.
Table S1. Values of all Gibbs free energy components per chain, in $kT$ units, and their differences between the two most prevalent structures, polymer volume fractions in water and oil, and interfacial area per chain for the structures with the lowest values of the minimized total Gibbs free energy for ionizable APCNs with a constant degree of ionization of 0.02, 0.10, 0.20, and 0.30 mol fractions of the hydrophobic units.

| 0.02 degree of ionization 0.10 hydrophobe mol fraction | $\Delta G$ for Spheres | $\Delta (\Delta G)$ | $\Delta G$ for Cylinders | 0.02 degree of ionization 0.20 hydrophobe mol fraction | $\Delta G$ for Spheres | $\Delta (\Delta G)$ | $\Delta G$ for Cylinders |
|--------------------------------------------------------|------------------------|---------------------|--------------------------|--------------------------------------------------------|------------------------|---------------------|--------------------------|
| Polymer volume fraction in water                       | 0.0070                 | ---                 | 0.0082                   | Polymer volume fraction in water                        | 0.0083                 | ---                 | 0.0089                   |
| Polymer volume fraction in oil                         | 0.6462                 | ---                 | 0.6000                   | Polymer volume fraction in oil                         | 0.6053                 | ---                 | 0.5450                   |
| Interfacial area per chain                             | 396.62                 | ---                 | 436.93                   | Interfacial area per chain                             | 657.68                 | ---                 | 659.15                   |
| Free energy of mixing in shell                         | -2374.47               | -0.25               | -2374.22                 | Free energy of mixing in shell                         | -2110.38               | +0.10               | -2110.28                 |
| Free energy of mixing in core                          | -196.63                | +10.18              | -206.81                  | Free energy of mixing in core                          | -411.42                | -23.14              | -434.56                  |
| Elastic free energy in shell                           | 107.80                 | -4.12               | 111.92                   | Elastic free energy in shell                           | 94.32                  | +5.15               | 99.47                    |
| Elastic free energy in core                            | -2.27                  | -0.99               | -1.28                    | Elastic free energy in core                            | -2.29                  | +0.18               | -2.11                    |
| Interfacial free energy                                | 228.99                 | -23.27              | 252.26                   | Interfacial free energy                                | 379.71                 | +0.85               | 380.56                   |
| Electrostatic free energy in shell                     | -766.09                | -13.06              | -753.03                  | Electrostatic free energy in shell                     | -668.52                | +5.45               | -663.07                  |
| Total free energy                                      | -3002.66               | -31.50              | -2971.16                 | Total free energy                                      | -2718.59               | -11.41              | -2730.00                 |

| 0.02 degree of ionization 0.20 hydrophobe mol fraction | $\Delta G$ for Cylinders | $\Delta (\Delta G)$ | $\Delta G$ for Lamellae | 0.02 degree of ionization 0.30 hydrophobe mol fraction | $\Delta G$ for Cylinders | $\Delta (\Delta G)$ | $\Delta G$ for Lamellae |
|--------------------------------------------------------|--------------------------|---------------------|--------------------------|--------------------------------------------------------|--------------------------|---------------------|--------------------------|
| Polymer volume fraction in water                        | 0.0089                   | ---                 | 0.2290                   | Polymer volume fraction in water                        | 0.0100                   | ---                 | 0.2310                   |
| Polymer volume fraction in oil                         | 0.5450                   | ---                 | 0.2210                   | Polymer volume fraction in oil                         | 0.5080                   | ---                 | 0.2360                   |
| Interfacial area per chain                             | 659.15                   | ---                 | 303.26                   | Interfacial area per chain                             | 830.90                   | ---                 | 297.12                   |
| Free energy of mixing in shell                         | -2110.28                 | -80.28              | -2030.00                 | Free energy of mixing in shell                         | -1846.27                 | +69.78              | -1776.49                 |
| Free energy of mixing in core                          | -434.56                  | +74.02              | -508.58                  | Free energy of mixing in core                          | -670.37                  | -89.85              | -760.22                  |
| Elastic free energy in shell                           | 99.47                    | +33.66              | 65.81                    | Elastic free energy in shell                           | 88.48                    | -32.11              | 56.37                    |
| Elastic free energy in core                            | -2.11                    | -6.61               | 4.50                     | Elastic free energy in core                            | -2.28                    | +12.99              | 10.71                    |
| Interfacial free energy                                | 380.56                   | +205.47             | 175.09                   | Interfacial free energy                                | 479.72                   | -308.18             | 171.54                   |
| Electrostatic free energy in shell                     | -663.07                  | -249.42             | -413.65                  | Electrostatic free energy in shell                     | -572.36                  | +210.27             | -362.09                  |
| Total free energy                                      | -2730.00                 | -23.17              | -2706.83                 | Total free energy                                      | -2523.08                 | -137.10             | -2660.18                 |

1 The difference was taken as ($\Delta G$ of prevailing structure) − ($\Delta G$ of competing structure).
For a 0.20 mol fraction of the hydrophobic units in the APCNs, cylinders are the dominant structure rather than spheres or lamellae. First, in comparison with spheres (top right quarter of Table S1), cylinders have a more favorable value of the Gibbs free energy of mixing in the core component due to the lower polymer volume fraction in oil for cylinders. In contrast, the electrostatic Gibbs free energy in the shell is more favorable for spheres due to the lower polymer volume fraction in water for spheres. The elastic Gibbs free energy in the shell is also more favorable for spheres due to the lower value of the isotropic deformation term, \[ \left( \frac{\varphi_s}{\varphi} \right)^{2/3} \], in the expression for the elastic Gibbs free energy in the shell for spheres. Second, in comparison with lamellae (bottom left quarter of Table S1), cylinders have a more favorable value of the electrostatic Gibbs free energy in the shell, and, to a lesser extent, a lower Gibbs free energy of mixing in the shell due to the lower polymer volume fraction in water for cylinders. In contrast, the interfacial Gibbs free energy and the Gibbs free energy of mixing in the core are more favorable for lamellae due to the much lower interfacial area per chain and lower polymer volume fraction in oil for lamellae, respectively.

For a 0.30 mol fraction of the hydrophobic units (bottom right quarter of Table S1) in the APCNs, lamellae represent the prevailing structure mainly due to the more favorable value of the interfacial Gibbs free energy component and, to a lesser extent, due to the lower Gibbs free energy of mixing in the core component, whereas the electrostatic Gibbs free energy in the shell and the Gibbs free energy of mixing in the shell are the main components acting in the opposite direction, favoring cylinders. The interfacial Gibbs free energy and the Gibbs free energy of mixing in the core are more favorable for lamellae due to the much lower interfacial area per chain and lower polymer volume fraction in oil for lamellae, respectively, while the electrostatic Gibbs free energy in the shell and the Gibbs free energy of mixing in the shell are more favorable for cylinders due to the lower polymer volume fraction in water for cylinders.
ii. Effect of degree of ionization of the hydrophilic units

Table S2 lists the values of all Gibbs free energy components per chain, in $kT$ units, at the total Gibbs free energy minimum for APCNs with a constant mol fraction of the hydrophobic units of 0.20 and degrees of ionization of 0.01, 0.02, 0.04, and 0.05. Similar to Table S1, in each case, the two structures with the lowest values of the minimized total Gibbs free energy were selected and presented in the table.

Examination of the Gibbs free energy components reveals that the prevalence of lamellae for APCNs with a 0.20 mol fraction of the hydrophobic units and at a degree of ionization of 0.01 (top left quarter of Table S2) is mainly due to the more favorable value of the interfacial Gibbs free energy component and, to a lesser extent, due to the lower Gibbs free energy of mixing in the core component for lamellae, whereas the electrostatic Gibbs free energy in the shell and the Gibbs free energy of mixing in the shell are the main components acting in the opposite direction, favoring cylinders. The interfacial Gibbs free energy and the Gibbs free energy of mixing in the core are more favorable for lamellae due to the much lower interfacial area per chain and lower polymer volume fraction in oil for lamellae, respectively, while the electrostatic Gibbs free energy in the shell and the Gibbs free energy of mixing in the shell are more favorable for cylinders due to the lower polymer volume fraction in water for cylinders.

For a degree of ionization of the hydrophilic units of 0.02 (top right quarter of Table S2) in the APCNs, cylinders are the dominant structure due to the more favorable value of the electrostatic Gibbs free energy in the shell component, and, to a lesser extent, due to the more favorable Gibbs free energy of mixing in the shell component for cylinders, whereas the interfacial Gibbs free energy and the Gibbs free energy of mixing in the core are the main components acting in the opposite direction, favoring lamellae. The electrostatic Gibbs free energy in the shell and the Gibbs free energy of mixing in the shell are more favorable for cylinders due to the lower polymer volume fraction in water for cylinders. On the other hand, the interfacial Gibbs free energy and the Gibbs free energy of mixing in the core are more favorable for lamellae due to the much lower interfacial area per chain and lower polymer volume fraction in oil for lamellae, respectively.
**Table S2.** Values of all Gibbs free energy components per chain, in $kT$ units, and their differences between the two most prevalent structures, polymer volume fractions in water and oil, and interfacial area per chain for the structures with the lowest values of the minimized total Gibbs free energy for ionizable APCNs with a constant mol fraction of the hydrophobic units of 0.20 and degrees of ionization of 0.01, 0.02, 0.04, and 0.05.

| 0.20 hydrophobe mol fraction | $\Delta G$ for Cylinders | $\Delta(\Delta G)^1$ | $\Delta G$ for Lamellae | 0.20 hydrophobe mol fraction | $\Delta G$ for Cylinders | $\Delta(\Delta G)^1$ | $\Delta G$ for Lamellae |
|-------------------------------|--------------------------|----------------------|-------------------------|-------------------------------|--------------------------|----------------------|-------------------------|
| 0.01 degree of ionization     |                          |                      |                          | 0.02 degree of ionization     |                          |                      |                          |
| Polymer volume fraction in water | 0.0100                  | ---                  | 0.2501                  | Polymer volume fraction in oil | 0.0089                  | ---                  | 0.2290                  |
| Interfacial area per chain    | 659.84                   | ---                  | 283.52                  | Interfacial area per chain    | 659.15                   | ---                  | 303.26                  |
| Free energy of mixing in shell | -2110.02                | +91.34               | -2018.68                | Free energy of mixing in shell | -2110.28                | -80.28               | -2030.00                |
| Free energy of mixing in core  | -434.56                  | -73.08               | -507.64                 | Free energy of mixing in core  | -434.56                  | +74.02               | -508.58                 |
| Elastic free energy in shell   | 90.20                    | -30.67               | 59.53                   | Elastic free energy in shell   | 99.47                    | +33.66               | 65.81                   |
| Elastic free energy in core    | -2.11                    | +7.17                | 5.06                    | Elastic free energy in core    | -2.11                    | -6.61                | 4.50                    |
| Interfacial free energy       | 380.96                   | -217.27              | 163.69                  | Interfacial free energy       | 380.56                   | +205.47              | 175.09                  |
| Electrostatic free energy in shell | -353.68                | +123.45              | -230.23                 | Electrostatic free energy in shell | -663.07                | -249.42              | -413.65                 |
| Total free energy             | -2429.21                 | -99.05               | -2528.26                | Total free energy             | -2730.00                 | -23.17               | -2706.83                |
| 0.04 degree of ionization     |                          |                      |                          | 0.05 degree of ionization     |                          |                      |                          |
| Polymer volume fraction in water | 0.0031                  | ---                  | 0.0036                  | Polymer volume fraction in oil | 0.0023                  | ---                  | 0.0027                  |
| Interfacial area per chain    | 657.68                   | ---                  | 646.61                  | Interfacial area per chain    | 657.68                   | ---                  | 641.48                  |
| Free energy of mixing in shell | -2111.43                | +0.11                | -2111.32                | Free energy of mixing in shell | -2111.513               | -0.007               | -2111.506               |
| Free energy of mixing in core  | -411.42                  | -23.84               | -435.26                 | Free energy of mixing in core  | -411.42                  | +25.23               | -436.65                 |
| Elastic free energy in shell   | 203.13                   | +4.90                | 208.03                  | Elastic free energy in shell   | 258.71                   | -3.22                | 261.93                  |
| Elastic free energy in core    | -2.29                    | +0.09                | -2.20                   | Elastic free energy in core    | -2.29                    | -0.05                | -2.24                   |
| Interfacial free energy       | 379.71                   | -6.39                | 373.32                  | Interfacial free energy       | 379.71                   | +9.35                | 370.36                  |
| Electrostatic free energy in shell | -1379.37               | +20.67               | -1358.70                | Electrostatic free energy in shell | -1743.18               | -32.41               | -1710.77                |
| Total free energy             | -3321.68                 | -4.45                | -3326.13                | Total free energy             | -3629.99                 | -1.12                | -3628.87                |

$^1$ The difference was taken as $(\Delta G$ of prevailing structure) $−$ $(\Delta G$ of competing structure).
For a degree of ionization of the hydrophilic units of 0.04 (bottom left quarter of Table S2) in the APCNs, cylinders still represent the prevailing structure mainly due to the more favorable value of the Gibbs free energy of mixing in the core component for cylinders, whereas the electrostatic Gibbs free energy in the shell is the main component acting in the opposite direction, favoring spheres. The Gibbs free energy of mixing in the core is more favorable for cylinders due to the lower polymer volume fraction in oil for cylinders, while the electrostatic Gibbs free energy in the shell is more favorable for spheres due to the lower polymer volume fraction in water for spheres.

For a degree of ionization of the hydrophilic units of 0.05 (bottom right quarter of Table S2) in the APCNs, spheres now dominate due to the more favorable value of the electrostatic Gibbs free energy in the shell component for spheres, whereas the Gibbs free energy of mixing in the core is the main component acting in the opposite direction, favoring cylinders. The electrostatic Gibbs free energy in the shell is more favorable for spheres due to the lower polymer volume fraction in water for spheres. On the other hand, the Gibbs free energy of mixing in the core is more favorable for cylinders due to the lower polymer volume fraction in oil for cylinders.
Appendix D. Extra Figures

a. Degrees of swelling and asymmetry ratios in water and oil

i. Effect of mol fraction of the hydrophobic units

Figure S3. Effect of the mol fraction of the hydrophobic units for APCNs with a degree of ionization of 0.10 on (a) the degree of swelling in water for the hydrophilic nanophase (b) the asymmetry ratio within the hydrophilic nanophase in water (c) the degree of swelling in oil for the hydrophobic nanophase and (d) on the asymmetry ratio within the hydrophobic nanophase in oil. The values used for the parameters were the same as those used in Figure 3, i.e., $\varphi_0 = 0.2$, $\beta = 20$, $\chi_{A\text{-water}} = 0.45$, $\chi_{B\text{-oil}} = 0.45$, $\chi_{A\text{-oil}} = 2.0$, $\chi_{B\text{-water}} = 2.0$, $\chi_{AB} = 2.0$, and $\eta + \zeta = 240$. 
Figure S4. Effect of the mol fraction of the hydrophobic units for APCNs with a degree of ionization of 0.08 on (a) the degree of swelling in water for the hydrophilic nanophase (b) the asymmetry ratio within the hydrophilic nanophase in water (c) the degree of swelling in oil for the hydrophobic nanophase and (d) on the asymmetry ratio within the hydrophobic nanophase in oil. The values used for the parameters were the same as those used in Figure 3, i.e., $\phi_0 = 0.2$, $\beta = 20$, $\chi_{A\text{-water}} = 0.45$, $\chi_{B\text{-oil}} = 0.45$, $\chi_{A\text{-oil}} = 2.0$, $\chi_{B\text{-water}} = 2.0$, $\chi_{AB} = 2.0$, and $\eta + \zeta = 240$. 
Figure S5. Effect of the mol fraction of the hydrophobic units for APCNs with a degree of ionization of 0.04 on (a) the degree of swelling in water for the hydrophilic nanophase (b) the asymmetry ratio within the hydrophilic nanophase in water (c) the degree of swelling in oil for the hydrophobic nanophase and (d) on the asymmetry ratio within the hydrophobic nanophase in oil. The values used for the parameters were the same as those used in Figure 3, i.e., $\phi_0 = 0.2$, $\beta = 20$, $\chi_{A,\text{water}} = 0.45$, $\chi_{B,\text{oil}} = 0.45$, $\chi_{A,\text{oil}} = 2.0$, $\chi_{B,\text{water}} = 2.0$, $\chi_{AB} = 2.0$, and $\eta + \zeta = 240$. 
ii. Effect of degree of ionization of the hydrophilic units

Figure S6. Effect of the degree of ionization of the hydrophilic units for APCNs with a 0.10 mol fraction of the hydrophobic units on (a) the degree of swelling in water for the hydrophilic nanophase (b) the asymmetry ratio within the hydrophilic nanophase in water (c) the degree of swelling in oil for the hydrophobic nanophase and (d) the asymmetry ratio within the hydrophobic nanophase in oil. The values used for the parameters were the same as those used in Figure 3, i.e., $\varphi_0 = 0.2$, $\beta = 20$, $\chi_{A\text{-}water} = 0.45$, $\chi_{B\text{-}oil} = 0.45$, $\chi_{A\text{-}oil} = 2.0$, $\chi_{B\text{-}water} = 2.0$, $\chi_{AB} = 2.0$, and $\eta + \zeta = 240$. 
Figure S7. Effect of the degree of ionization of the hydrophilic units for APCNs with a 0.40 mol fraction of the hydrophobic units on (a) the degree of swelling in water for the hydrophilic nanophase (b) the asymmetry ratio within the hydrophilic nanophase in water (c) the degree of swelling in oil for the hydrophobic nanophase and (d) the asymmetry ratio within the hydrophobic nanophase in oil. The values used for the parameters were the same as those used in Figure 3, i.e., $\phi_0 = 0.2$, $\beta = 20$, $\chi_{A\text{-water}} = 0.45$, $\chi_{B\text{-oil}} = 2.0$, $\chi_{A\text{-oil}} = 0.45$, $\chi_{B\text{-water}} = 2.0$, $\chi_{AB} = 2.0$, and $\eta + \zeta = 240$. 
**Figure S8.** Effect of the degree of ionization of the hydrophilic units for APCNs with a 0.70 mol fraction of the hydrophobic units on (a) the degree of swelling in water for the hydrophilic nanophase (b) the asymmetry ratio within the hydrophilic nanophase in water (c) the degree of swelling in oil for the hydrophobic nanophase and (d) the asymmetry ratio within the hydrophobic nanophase in oil. The values used for the parameters were the same as those used in Figure 3, i.e., $\phi_0 = 0.2$, $\beta = 20$, $\chi_{A\text{-water}} = 0.45$, $\chi_{B\text{-water}} = 0.45$, $\chi_{A\text{-oil}} = 2.0$, $\chi_{B\text{-oil}} = 2.0$, $\chi_{AB} = 2.0$, and $\eta + \zeta = 240$. 

\[ \text{degree of ionization} \]

\[ \text{degree of swelling in water} \]

\[ \text{degree of swelling in oil} \]

\[ \text{asymmetry ratio in water} \]

\[ \text{asymmetry ratio in oil} \]
b. Characteristic lengths of anisotropic morphologies

i. Effect of mol fraction of the hydrophobic units

**Figure S9.** Effect of the mol fraction of the hydrophobic units on the characteristic lengths of lamellae for APCNs with a degree of ionization of 0.04. The values used for the parameters were the same as those used in Figure 3, *i.e.*, $\phi_0 = 0.2$, $\beta = 20$, $\chi_{A\text{-water}} = 0.45$, $\chi_{B\text{-oil}} = 0.45$, $\chi_{A\text{-oil}} = 2.0$, $\chi_{B\text{-water}} = 2.0$, $\chi_{AB} = 2.0$, and $\eta+\zeta = 240$.

**Figure S10.** Effect of the mol fraction of the hydrophobic units on the characteristic lengths of cylinders for APCNs with a degree of ionization of 0.08. The values used for the parameters were the same as those used in Figure 3, *i.e.*, $\phi_0 = 0.2$, $\beta = 20$, $\chi_{A\text{-water}} = 0.45$, $\chi_{B\text{-oil}} = 0.45$, $\chi_{A\text{-oil}} = 2.0$, $\chi_{B\text{-water}} = 2.0$, $\chi_{AB} = 2.0$, and $\eta+\zeta = 240$. 
ii. Effect of degree of ionization of the hydrophilic units

Figure S11. Effect of the degree of ionization of the hydrophilic units on the characteristic lengths of lamellae for APCNs with a 0.70 mol fraction of the hydrophobic units. The values used for the parameters were the same as those used in Figure 3, i.e., $\varphi_0 = 0.2, \beta = 20, \chi_{A\text{-water}} = 0.45, \chi_{B\text{-oil}} = 0.45, \chi_{A\text{-oil}} = 2.0, \chi_{B\text{-water}} = 2.0, \chi_{AB} = 2.0$, and $\eta + \zeta = 240$.

Figure S12. Effect of the degree of ionization of the hydrophilic units on the characteristic lengths of cylinders for APCNs with a 0.40 mol fraction of the hydrophobic units. The values used for the parameters were the same as those used in Figure 3, i.e., $\varphi_0 = 0.2, \beta = 20, \chi_{A\text{-water}} = 0.45, \chi_{B\text{-oil}} = 0.45, \chi_{A\text{-oil}} = 2.0, \chi_{B\text{-water}} = 2.0, \chi_{AB} = 2.0$, and $\eta + \zeta = 240$. 
Oil solubilization capacities

i. Effect of mol fraction of the hydrophobic units

**Figure S13.** Effect of the mol fraction of the hydrophobic units on the oil solubilization capacity for APCNs with a degree of ionization of 0.10. The values used for the parameters were the same as those used in Figure 3, *i.e.*, $\phi_0 = 0.2$, $\beta = 20$, $\chi_A$-water = 0.45, $\chi_B$-oil = 0.45, $\chi_A$-oil = 2.0, $\chi_B$-water = 2.0, $\chi_{AB} = 2.0$, and $\eta + \zeta = 240$.

**Figure S14.** Effect of the mol fraction of the hydrophobic units on the oil solubilization capacity for APCNs with a degree of ionization of 0.08. The values used for the parameters were the same as those used in Figure 3, *i.e.*, $\phi_0 = 0.2$, $\beta = 20$, $\chi_A$-water = 0.45, $\chi_B$-oil = 0.45, $\chi_A$-oil = 2.0, $\chi_B$-water = 2.0, $\chi_{AB} = 2.0$, and $\eta + \zeta = 240$. 

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Figure S15. Effect of the mol fraction of the hydrophobic units on the oil solubilization capacity for APCNs with a degree of ionization of 0.04. The values used for the parameters were the same as those used in Figure 3, i.e., $\phi_0 = 0.2$, $\beta = 20$, $\chi_{A-$water$} = 0.45$, $\chi_{B-$oil$} = 0.45$, $\chi_{A-$oil$} = 2.0$, $\chi_{B-$water$} = 2.0$, $\chi_{AB} = 2.0$, and $\eta+\zeta = 240$.

ii. Effect of degree of ionization of the hydrophilic units

Figure S16. Effect of the degree of ionization of the hydrophilic units on the oil solubilization capacity for APCNs with a 0.10 mol fraction of the hydrophobic units. The values used for the parameters were the same as those used in Figure 3, i.e., $\phi_0 = 0.2$, $\beta = 20$, $\chi_{A-$water$} = 0.45$, $\chi_{B-$oil$} = 0.45$, $\chi_{A-$oil$} = 2.0$, $\chi_{B-$water$} = 2.0$, $\chi_{AB} = 2.0$, and $\eta+\zeta = 240$. 
Figure S17. Effect of the degree of ionization of the hydrophilic units on the oil solubilization capacity for APCNs with a 0.40 mol fraction of the hydrophobic units. The values used for the parameters were the same as those used in Figure 3, i.e., φ₀ = 0.2, β = 20, χ_A-water = 0.45, χ_B-oil = 0.45, χ_A-oil = 2.0, χ_B-water = 2.0, χ_AB = 2.0, and η + ζ = 240.

Figure S18. Effect of the degree of ionization of the hydrophilic units on the oil solubilization capacity for APCNs with a 0.70 mol fraction of the hydrophobic units. The values used for the parameters were the same as those used in Figure 3, i.e., φ₀ = 0.2, β = 20, χ_A-water = 0.45, χ_B-oil = 0.45, χ_A-oil = 2.0, χ_B-water = 2.0, χ_AB = 2.0, and η + ζ = 240.

iii. Correlation of degrees of swelling in water and oil solubilization capacity

The oil solubilization capacity was defined as:

\[ S.C. = \frac{\zeta \varphi_A^{\text{shell}}}{\eta \varphi_B^{\text{core}} \varphi_A^{\text{shell}}} \]  \hspace{1cm} (24)
For a constant mol fraction of the hydrophobic units, the $\frac{\zeta}{\eta}$ ratio is constant. Furthermore, for a 0.10 mol fraction of the hydrophobic units, where spheres prevail, the degree of swelling in oil for the hydrophobic nanophase is not affected by changes in the degree of ionization (see Figure S6(c)). As a result, the $\frac{1 - \varphi_B^{core}}{\varphi_B^{core}}$ term is constant. Finally, for a 0.10 mol fraction of the hydrophobic units, the degree of swelling in water for the hydrophilic nanophase is very high, implying that the $1 - \varphi_A^{shell}$ term is very close to 1.

It follows that:

$$S \cdot C \propto \varphi_A^{shell}$$  \hspace{1cm} (D1)

$$\Rightarrow S \cdot C \propto \frac{1}{D S_A^{shell}}$$  \hspace{1cm} (D2)
Appendix E. Approximate Analytical Solutions

In this Appendix, we derive approximate analytical expressions for the degrees of swelling, using the two dominant, equilibrium-determining first derivatives, with respect to the polymer volume fraction of the Gibbs free energy components as those were identified from the value of the numerically calculated derivatives, listed in Table S3 below. This was done for the three ordered morphologies, i.e., spheres, cylinders, and lamellae, plus unimers in oil. The calculations were performed in the middle of the area where each morphology prevails in the phase diagram.

| Table S3. | First derivatives of all Gibbs free energy components for the prevailing morphologies for ionizable conetworks based on end-linked amphiphilic ABA triblock copolymers in an oil-water mixture. |
|-----------|--------------------------------------------------------------------------------------------------|
| **Spheres** | **Cylinders** |
|  | **hydrophobic mol fraction = 0.10** | **hydrophobic mol fraction = 0.40** |  |
|  | **degree of ionization = 0.10** | **degree of ionization = 0.08** |  |
| $\varphi_A^{\text{shell}} = 6.92 \times 10^{-4}$ | $\varphi_B^{\text{core}} = 0.646$ | $\varphi_A^{\text{shell}} = 0.0019$ | $\varphi_B^{\text{core}} = 0.476$
| $\frac{\partial \Delta G}{\partial \varphi_A^{\text{shell}}} = 0$ | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = 235.58$ | $\frac{\partial \Delta G}{\partial \varphi_A^{\text{shell}}} = 0$ | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = 578.5$
| $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = 124.98$ | 0 | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = 1350$ | 0
| $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = 624226.6$ | 0 | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = 121250$ | 0
| $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = -624386.4$ | 0 | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = -136575$ | 28
| $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = -34.82$ | 0 | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = -1314.7$ | -0.8
|  |  |  |  |
| **Lamellae** | **Unimers in Oil** |
|  | **hydrophobic mol fraction = 0.70** | **hydrophobic mol fraction = 0.99** |  |
|  | **degree of ionization = 0.04** | **degree of ionization = 0.05** |  |
| $\varphi_A^{\text{shell}} = 0.1896$ | $\varphi_B^{\text{core}} = 0.2541$ | $\varphi = 0.0583$
| $\frac{\partial \Delta G}{\partial \varphi_A^{\text{shell}}} = 0$ | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = 0$ | $\frac{\partial \Delta G}{\partial \varphi} = 0$
| $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = 178$ | 0 | 0
| $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = 303.5$ | 0 | 0
| $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = 198.05$ | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = -313.6$ | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = -304.39$
| $\frac{\partial \Delta G}{\partial \varphi_A^{\text{shell}}} = -346.65$ | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = 142.65$ | 0
| $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = -333.5$ | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = -351$ | 0
| $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = -0.6$ | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = 3.05$ | $\frac{\partial \Delta G}{\partial \varphi_B^{\text{core}}} = -0.02$
i. Hydrophilic nanophase of spheres:

In the case of the hydrophilic nanophase of spheres, Table S3 shows that the dominant first derivatives are those of the electrostatic Gibbs free energy in the shell and the elastic Gibbs free energy in the shell:

$$\frac{\partial}{\partial \chi_A^\text{ext}} (\Delta G_{\text{electrostatic shell}}^{\text{spheres}}) + \frac{\partial}{\partial \chi_A^\text{ext}} (\Delta G_{\text{elastic shell}}^{\text{spheres}}) \approx 0$$  \hspace{1cm} (E1)

Differentiation of equations (T1.6) and (T1.9) with respect to $\chi_A^\text{ext}$, and substitution of the resulting partial derivatives into equation (E1), yields:

$$\beta \eta \frac{1}{\chi_A^\text{ext}} - \frac{\beta}{2} \frac{\phi_0^{2/3}}{\chi_A^{2/3}} + \frac{\beta}{4} \chi_A^\text{ext} \approx 0$$  \hspace{1cm} (E2)

Rearranging terms leads to the approximate analytical solution for the hydrophilic nanophase of spheres:

$$\frac{\eta + \frac{1}{4}}{\chi_A^\text{ext}^{2/3}} \approx \frac{\phi_0^{2/3}}{2 \chi_A^{2/3}}$$  \hspace{1cm} (E3)

$$\Rightarrow \chi_A^\text{ext}^{2/3} \approx \frac{\phi_0^{2/3}}{\eta + \frac{1}{4}}$$  \hspace{1cm} (E4)

$$\Rightarrow \chi_A^\text{ext} \approx \frac{\phi_0}{(2 \eta + \frac{1}{2})^{3/2}}$$  \hspace{1cm} (E5)

Thus, the polymer volume fraction in the hydrophilic nanophase of spheres, $\chi_A^\text{ext}$, decreases as the $\frac{3}{2}$-power of the product of the degree of ionization of the hydrophilic units times the number of hydrophilic units in one arm in the unit cell, with the latter being proportional to 1 minus the mol fraction of the hydrophobic units. This would imply that the degree of swelling in water for the hydrophilic nanophase (which is the inverse of the corresponding polymer volume fraction) increases as the $\frac{3}{2}$-power of the product of the degree of ionization of the hydrophilic units times the number of hydrophilic units in one arm in the unit cell:

$$DS_{\text{shell}} \sim (\eta^{1/2})^{3/2}$$  \hspace{1cm} (E6)
These dependencies justify the trends in Figures 6(b) (points in top-left corner) and (c) (points in top-right corner), which illustrate the effect of the mol fraction of the hydrophobic units and that of the degree of ionization of the hydrophilic units on the degrees of swelling in water for the hydrophilic nanophase, respectively.

ii. **Hydrophobic nanophase of spheres:**

In the case of the hydrophobic nanophase of spheres, Table S3 suggests that the dominant first derivatives are those of the Gibbs free energy of mixing in the core and the interfacial Gibbs free energy:

$$\frac{\partial}{\partial \phi_B^{\text{core}}} (\Delta G_{\text{mixing,core}}^{\text{spheres}}) + \frac{\partial}{\partial \phi_B^{\text{core}}} (\Delta G_{\text{interfacial}}^{\text{spheres}}) \approx 0$$  \hspace{1cm} (E7)

Differentiation of equations (T1.3) and (T1.15) with respect to $\phi_B^{\text{core}}$, and substitution of the resulting partial derivatives into equation (E7), yields:

$$-\beta \zeta \left[ \chi_{B-oil} + \frac{1}{(\phi_B^{\text{core}})^2} \ln(1 - \phi_B^{\text{core}}) + \frac{1}{\phi_B^{\text{core}}} \right] + (4\pi)^{1/3} \left( \frac{x_{AB}}{6} \right)^{1/2} \left( 3\beta \zeta \right)^{2/3} \left[ \frac{-2}{3(\phi_B^{\text{core}})^{7/3}} \right] \approx 0$$  \hspace{1cm} (E8)

Applying a Taylor’s series expansion to the second term in brackets in equation (E8) for $\phi_B^{\text{core}} \ll 1$ leads to:

$$(\beta \zeta)^{1/3} \left[ \chi_{B-oil} - \frac{1}{\phi_B^{\text{core}}} - \frac{1}{2} - \frac{\phi_B^{\text{core}}}{3} - \frac{\phi_B^{\text{core}}}{2} \right] + (4\pi)^{1/3} \left( \frac{x_{AB}}{6} \right)^{1/2} \frac{2}{3(\phi_B^{\text{core}})^{7/3}} \approx 0$$  \hspace{1cm} (E9)

Considering the fact that the higher-order term $\left( \frac{\phi_B^{\text{core}}}{2} \right)^2$ is much smaller than the immediately lower-order term, $\frac{\phi_B^{\text{core}}}{3}$, equation (E9) simplifies to:

$$(\beta \zeta)^{1/3} \left( \chi_{B-oil} - \frac{1}{2} - \frac{\phi_B^{\text{core}}}{3} \right) + (4\pi)^{1/3} \left( \frac{x_{AB}}{6} \right)^{1/2} \frac{2}{3(\phi_B^{\text{core}})^{7/3}} \approx 0$$  \hspace{1cm} (E10)

Rearranging terms leads to:

$$(\beta \zeta)^{1/3} (\phi_B^{\text{core}})^{5/3} \left( \chi_{B-oil} - \frac{1}{2} - \frac{\phi_B^{\text{core}}}{3} \right) + \frac{2}{3} (36\pi)^{1/3} \left( \frac{x_{AB}}{6} \right)^{1/2} \approx 0$$  \hspace{1cm} (E11)
\[
\phi_B^{\text{core}} \approx \left( \chi_{B-\text{oil}} - \frac{1}{2} \right) \left( \phi_B^{\text{core}} \right)^{5/3} - \frac{1}{3} \left( \phi_B^{\text{core}} \right)^{8/3} + \frac{2}{3} \left( \frac{36\pi}{\beta\zeta} \right)^{1/3} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \approx 0
\] (E12)

\[
\phi_B^{\text{core}}^{9/3} - 3 \left( \chi_{B-\text{oil}} - \frac{1}{2} \right) \left( \phi_B^{\text{core}} \right)^{5/3} - 2 \left( \frac{36\pi}{\beta\zeta} \right)^{1/3} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \approx 0
\] (E13)

To enable an analytical solution to equation (E13), we approximate the \(\frac{5}{3}\) power of \(\phi_B^{\text{core}}\) with its \(\frac{4}{3}\) power: \(\phi_B^{\text{core}}^{5/3} \approx \phi_B^{\text{core}}^{4/3}\).

Setting \(x = \left( \phi_B^{\text{core}} \right)^{4/3}\), \(A = -3 \left( \chi_{B-\text{oil}} - \frac{1}{2} \right)\), and \(B = -2 \left( \frac{36\pi}{\beta\zeta} \right)^{1/3} \left( \frac{\chi_{AB}}{6} \right)^{1/2}\), we obtain:

\[x^2 + Ax + B \approx 0\] (E14)

Solving quadratic equation (E14) gives:

\[x \approx -A \pm \sqrt{A^2 - 4B} = \frac{1}{2} \left[ 3 \left( \chi_{B-\text{oil}} - \frac{1}{2} \right) \pm \sqrt{9 \left( \chi_{B-\text{oil}} - \frac{1}{2} \right)^2 + 8 \left( \frac{36\pi}{\beta\zeta} \right)^{1/3} \left( \frac{\chi_{AB}}{6} \right)^{1/2}} \right]\] (E15)

Rearranging terms results in:

\[\phi_B^{\text{core}}^{4/3} \approx \frac{1}{2} \left[ 3 \left( \chi_{B-\text{oil}} - \frac{1}{2} \right) \pm \sqrt{9 \left( \chi_{B-\text{oil}} - \frac{1}{2} \right)^2 + 8 \left( \frac{36\pi}{\beta\zeta} \right)^{1/3} \left( \frac{\chi_{AB}}{6} \right)^{1/2}} \right]\] (E16)

\[\Rightarrow \phi_B^{\text{core}}^{4/3} \approx \frac{3}{2} \left( \chi_{B-\text{oil}} - \frac{1}{2} \right) \left[ 1 \pm \sqrt{1 + \frac{8}{9} \left( \frac{36\pi}{\beta\zeta} \right)^{1/3} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \frac{1}{\left( \chi_{B-\text{oil}} - \frac{1}{2} \right)^2}} \right] \] (E17)

\[\Rightarrow \phi_B^{\text{core}} \approx \left\{ \frac{3}{2} \left( \chi_{B-\text{oil}} - \frac{1}{2} \right) \left[ 1 \pm \sqrt{1 + \frac{8}{9} \left( \frac{36\pi}{\beta\zeta} \right)^{1/3} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \frac{1}{\left( \chi_{B-\text{oil}} - \frac{1}{2} \right)^2}} \right] \right\}^{3/4} \] (E18)

Since \(\left( \chi_{B-\text{oil}} - \frac{1}{2} \right) < 0\), choosing the negative root leads to the approximate analytical solution for the hydrophobic nanophase of spheres:

\[\phi_B^{\text{core}} \approx \left\{ \frac{3}{2} \left( \chi_{B-\text{oil}} - \frac{1}{2} \right) \left[ 1 - \sqrt{1 + \frac{8}{9} \left( \frac{36\pi}{\beta\zeta} \right)^{1/3} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \frac{1}{\left( \chi_{B-\text{oil}} - \frac{1}{2} \right)^2}} \right] \right\}^{3/4} \] (E19)
Equation (E19) suggests that an increase in the number of hydrophobic units, $\zeta$, leads to a reduction in the polymer volume fraction in the hydrophobic nanophase and, consequently, to an increase in the degree of swelling in oil for the hydrophobic spherical nanophase ($D_{core}$ is the inverse of $\varphi_B^{core}$). This is reflected in Figure 6(e) (points in the bottom-left corner) which displays the effect of the mol fraction of the hydrophobic units on the degree of swelling in oil for the hydrophobic nanophase.

As the first derivative of the electrostatic Gibbs free energy in the hydrophilic nanophase with respect to the polymer volume fraction in oil was zero, the degree of ionization of the hydrophobic units does not appear at all in the calculation of the polymer volume fraction in the hydrophobic nanophase, and this ultimately results in a degree of swelling in oil which is totally independent of the degree of ionization, consistent with the results for spheres in Figure 6(f) (points in bottom of this figure), which illustrates the effect of the degree of ionization of the hydrophilic units on the degree of swelling in oil for the hydrophobic nanophase.

iii. Hydrophilic nanophase of cylinders:

In the case of the hydrophilic nanophase of cylinders, Table S3 indicates that the dominant first derivatives are those of the electrostatic Gibbs free energy in the shell and the elastic Gibbs free energy in the shell, as was also the case for the hydrophilic nanophase of spheres:

$$\frac{\partial}{\partial \varphi_A^{shell}} (\Delta G_{cylinders}^{electrostatic,shell}) + \frac{\partial}{\partial \varphi_A^{shell}} (\Delta G_{cylinders}^{elastic,shell}) \approx 0 \quad (E20)$$

Considering for simplicity that the asymmetry ratio in the hydrophilic nanophase of cylinders, $\frac{H}{l_0}$, is approximately constant (Figures 8(a) – (c) show that the $\frac{H}{l_0}$ values range only between 0.67 and 0.75), differentiation of equations (T1.6) and (T1.11) with respect to $\varphi_A^{shell}$, and substitution of the resulting partial derivatives into equation (E20), yields:

$$\beta \eta_1 \frac{1}{\varphi_A^{shell}} - \frac{\beta}{6} \left( \frac{H}{l_0} \right)^2 + 2 \frac{l_0}{H} \left( \frac{\varphi_0}{\varphi_A^{shell}} \right)^{2/3} + \frac{\beta}{4 \varphi_A^{shell}} \varphi_A^{shell} \approx 0 \quad (E21)$$

Rearranging terms leads to the approximate analytical solution for the hydrophilic nanophase of cylinders:
\[
\frac{\eta^{\frac{1}{2}}}{\varphi_A^{\text{shell}}} \approx \left[ \left( \frac{H}{l_0} \right)^2 + 2 \frac{l_0}{H} \right] \frac{\varphi_0^{2/3}}{6(\varphi_A^{\text{shell}})^{5/3}} \]  
(E22)

\[\Rightarrow \left( \varphi_A^{\text{shell}} \right)^{2/3} \approx \left[ \left( \frac{H}{l_0} \right)^2 + 2 \frac{l_0}{H} \right] \frac{\varphi_0^{2/3}}{6\eta^{1/2}} \]  
(E23)

\[\Rightarrow \varphi_A^{\text{shell}} \approx \left[ \left( \frac{H}{l_0} \right)^2 + 2 \frac{l_0}{H} \right]^{3/2} \frac{\varphi_0}{3(2\eta^{1/2})^2} \]  
(E24)

Thus, similar to spheres, the polymer volume fraction in the hydrophilic nanophase of cylinders, \(\varphi_A^{\text{shell}}\), also decreases as the \(\frac{3}{2}\) power of the product of the degree of ionization of the hydrophilic units times the number of hydrophilic units in one arm in the unit cell, with the latter being proportional to 1 minus the mol fraction of the hydrophobic units. This would imply that the degree of swelling in water for the hydrophilic nanophase (which is the inverse of the corresponding polymer volume fraction) of cylinders increases as the \(\frac{3}{2}\) power of the product of the degree of ionization of the hydrophilic units times the number of hydrophilic units in one arm in the unit cell (equation (E6)). These predicted trends in the degrees of swelling in water for the hydrophilic cylindrical nanophase are confirmed in Figures 6(b) (top-left points, just below those for spheres) and (c) (top-right points, just below those for spheres), which illustrate the effect of the mol fraction of the hydrophobic units and that of the degree of ionization of the hydrophilic units on the degrees of swelling in water for the hydrophilic nanophase, respectively. Comparing equation (E24) with equation (E5), these are very similar, with the only difference between them being the term \(\left[ \left( \frac{H}{l_0} \right)^2 + 2 \frac{l_0}{H} \right]^{3/2} \) in the former equation, capturing the effect of asymmetry in the hydrophilic nanophase of cylinders. Using an average value of 0.71 for the asymmetry ratio in the hydrophilic nanophase of cylinders, the value of the above term was calculated to be 1.165, implying that a sphere to cylinder transition is accompanied by an abrupt reduction of the \(DS_{\text{shell}}\) value by 14% \(\left(= 1 - \frac{1}{1.165} \right)\).
iv. Hydrophobic nanophase of cylinders:

In the case of the hydrophobic nanophase of cylinders, Table S3 shows that the dominant first derivatives are those of the Gibbs free energy of mixing in the core and the interfacial Gibbs free energy, as was also the case for the hydrophobic nanophase of spheres:

\[
\frac{\partial}{\partial \phi_{B}^{\text{core}}} (\Delta G_{\text{mixing, core}}^{\text{cylinders}}) + \frac{\partial}{\partial \phi_{B}^{\text{core}}} (\Delta G_{\text{interfacial}}^{\text{cylinders}}) \approx 0
\]  

(E25)

Considering for simplicity that the asymmetry ratio in the hydrophobic nanophase of cylinders, \( \frac{H}{h_0} \), is approximately constant (Figures 8(d) – (f) show that the \( \frac{H}{h_0} \) values range from 0.65 to 1.16), differentiation of equations (T1.3) and (T1.16) with respect to \( \phi_{B}^{\text{core}} \), and substitution of the resulting partial derivatives into equation (E25), yields:

\[-\beta \zeta \left[ \chi_{B-\text{oil}} + \frac{1}{(\phi_{B}^{\text{core}})^2} \ln(1 - \phi_{B}^{\text{core}}) + \frac{1}{\phi_{B}^{\text{core}}} \right] - \left( \frac{\pi H}{h_0} \right)^{1/2} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \frac{1}{\phi_{o}^{1/6} (\phi_{B}^{\text{core}})^{3/2}} \approx 0 \]  

(E26)

Applying a Taylor’s series expansion to the second term in brackets in equation (E26) for \( \phi_{B}^{\text{core}} \ll 1 \) leads to:

\[ (\beta \zeta)^{1/3} \left( \chi_{B-\text{oil}} - \frac{1}{2} \frac{\phi_{B}^{\text{core}}}{3} - \frac{(\phi_{B}^{\text{core}})^2}{2} + \frac{1}{\phi_{B}^{\text{core}}} \right) + \left( \frac{\pi H}{h_0} \right)^{1/2} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \frac{1}{\phi_{o}^{1/6} (\phi_{B}^{\text{core}})^{3/2}} \approx 0 \]  

(E27)

Considering that the higher-order term \( \left( \frac{\phi_{B}^{\text{core}}}{3} \right)^2 \) is much smaller than the immediately lower-order term, \( \frac{\phi_{B}^{\text{core}}}{3} \), equation (E27) simplifies to:

\[ (\beta \zeta)^{1/3} \left( \chi_{B-\text{oil}} - \frac{1}{2} \frac{\phi_{B}^{\text{core}}}{3} \right) + \left( \frac{\pi H}{h_0} \right)^{1/2} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \frac{1}{\phi_{o}^{1/6} (\phi_{B}^{\text{core}})^{3/2}} \approx 0 \]  

(E28)

Rearranging terms leads to:

\[ (\beta \zeta)^{1/3} \left( \phi_{B}^{\text{core}} \right)^{3/2} \left( \chi_{B-\text{oil}} - \frac{1}{2} \frac{\phi_{B}^{\text{core}}}{3} \right) + \left( \frac{\pi H}{h_0} \right)^{1/2} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \frac{1}{\phi_{o}^{1/6}} \approx 0 \]  

(E29)

\[ \Rightarrow \left( \chi_{B-\text{oil}} - \frac{1}{2} \right) \left( \phi_{B}^{\text{core}} \right)^{3/2} - \frac{1}{3} \left( \phi_{B}^{\text{core}} \right)^{3/2} + \left( \frac{\pi H}{h_0} \right)^{1/2} \left( \frac{\chi_{AB}}{6} \right)^{1/2} \frac{1}{(\beta \zeta)^{1/3} \phi_{o}^{1/6}} \approx 0 \]  

(E30)
To enable an analytical solution to equation (E31), we approximate the \( \frac{5}{4} \)-power of \( \varphi_B^{\text{core}} \) with its \( \frac{3}{2} \)-power: \( \varphi_B^{\text{core}} \approx (\varphi_B^{\text{core}})^{5/4} \).

Setting \( x = (\varphi_B^{\text{core}})^{5/4} \), \( A = -3 \left( \chi_{B-oil} - \frac{1}{2} \right) \), and \( B = -3 \left( \frac{\pi H}{h_0} \right)^{1/2} \left( \frac{X_{AB}}{6} \right)^{1/2} \frac{1}{(\beta\zeta)^{1/3} \varphi_0^{1/6}} \), we obtain:

\[
x^2 + Ax + B \approx 0
\]

Solving quadratic equation (E32) gives:

\[
x \approx \frac{-A \pm \sqrt{A^2 - 4B}}{2}
\]

Rearranging terms results in:

\[
(\varphi_B^{\text{core}})^{5/4} \approx \frac{1}{2} \left[ 3 \left( \chi_{B-oil} - \frac{1}{2} \right) \pm \sqrt{9 \left( \chi_{B-oil} - \frac{1}{2} \right)^2 + 12 \left( \frac{\pi H}{h_0} \right)^{1/2} \left( \frac{X_{AB}}{6} \right)^{1/2} \frac{1}{(\beta\zeta)^{1/3} \varphi_0^{1/6}}} \right]
\]

Given that \( \left( \chi_{B-oil} - \frac{1}{2} \right) < 0 \), choosing the negative root leads to the approximate analytical solution for the hydrophobic nanophase of cylinders:
\[ \varphi_{B}^{\text{core}} \approx \left\{ \frac{3}{2} \left( \chi_{B-oil} - \frac{1}{2} \right) \left[ 1 - \sqrt{1 + \frac{4}{3} \left( \frac{\pi H}{h_0} \right)^{1/2} \left( \chi_{AB} \right)^{1/2} \frac{1}{\beta \zeta} \frac{1}{\varphi_0^{1/6} \left( \chi_{B-oil} - \frac{1}{2} \right)^{1/2}} \right] \right\}^{4/5} \]  

(E37)

Equation (E37) suggests that an increase in the number of hydrophobic units, \( \zeta \), leads to a reduction in the polymer volume fraction in the hydrophobic nanophase, and, consequently, to an increase in the degree of swelling in oil for the hydrophobic cylindrical nanophase (\( DS_{\text{core}} \) is the inverse of \( \varphi_{B}^{\text{core}} \)). This is reflected in Figure 6(e) (points in the lower part of the figure in the range of hydrophobic mol fraction from 0.20 to 0.60), which displays the effect of the mol fraction of the hydrophobic units on the degree of swelling in oil for the hydrophobic nanophase.

As the first derivative of the electrostatic Gibbs free energy in the hydrophilic nanophase with respect to the polymer volume fraction in oil was zero, the degree of ionization of the hydrophilic units does not appear at all in the calculation of the polymer volume fraction in the hydrophobic nanophase of cylinders. This would imply that the degree of swelling in oil should be independent of the degree of ionization of the hydrophilic units. However, Figure 6(f) (points in the lower part of the figure, just above those for spheres, in the degree of ionization range from 0.02 to 0.10) shows a slight increase in the degree of swelling in oil for the hydrophobic nanophase of cylinders as the degree of ionization of the hydrophilic units increases. This apparently counterintuitive result can be attributed to the asymmetry ratio of the hydrophobic nanophase in cylinders, \( \frac{H}{h_0} \), which slightly varies (decreases) with the degree of ionization of the hydrophilic units (Figure 8(f)), thereby indirectly correlating the degree of swelling in oil for the hydrophobic nanophase of cylinders to the degree of ionization of the hydrophilic units in the aqueous nanophase of cylinders.

v. Hydrophilic nanophase of lamellae:

Similar to the hydrophilic nanophase of spheres and cylinders, in the hydrophilic nanophase of lamellae too, Table S3 shows that the dominant first derivatives are those of the electrostatic Gibbs free energy in the shell and the elastic Gibbs free energy in the shell:

\[ \frac{\partial}{\partial \varphi_{A}^{\text{shell}}} (\Delta G_{\text{electrostatic,shell}}^{\text{lamellae}}) + \frac{\partial}{\partial \varphi_{A}^{\text{shell}}} (\Delta G_{\text{elastic,shell}}^{\text{lamellae}}) \approx 0 \]  

(E38)
Considering for simplicity that the asymmetry ratio in the hydrophilic nanophase of lamellae, \( \frac{l}{l_0} \), is approximately constant (Figures 8(a) – (c); although nearly independent of the degree of ionization, the \( \frac{l}{l_0} \) values are strongly dependent on hydrophobe content; overall range of values from 1.28 to 4.06), differentiation of equations (T1.6) and (T1.13) with respect to \( \varphi_A^{shell} \), and substitution of the resulting partial derivatives into equation (E38), yields:

\[
\beta \eta \frac{1}{\varphi_A^{shell}} - \frac{\beta}{6} \left[ \left( \frac{l}{l_0} \right)^2 + 2 \frac{l_0}{l} \right] \varphi_0^{2/3} + \frac{\beta}{4 \varphi_A^{shell}} \approx 0
\]

(E39)

Rearranging terms leads to the approximate analytical solution for the hydrophilic nanophase of lamellae:

\[
\frac{\eta + \frac{1}{\varphi_A^{shell}}} {\varphi_A^{shell}} \approx \left[ \left( \frac{l}{l_0} \right)^2 + 2 \frac{l_0}{l} \right] \frac{\varphi_0^{2/3}} {6(\varphi_A^{shell})^{5/3}}
\]

(E40)

\[
\Rightarrow \left( \varphi_A^{shell} \right)^{2/3} \approx \left[ \left( \frac{l}{l_0} \right)^2 + 2 \frac{l_0}{l} \right] \frac{\varphi_0^{2/3}} {6\eta + \frac{1}{\varphi_A^{shell}}}
\]

(E41)

\[
\Rightarrow \varphi_A^{shell} \approx \left[ \left( \frac{l}{l_0} \right)^2 + 2 \frac{l_0}{l} \right] \frac{3}{2(\eta + \frac{1}{\varphi_A^{shell}})} \varphi_0
\]

(E42)

Thus, similar to spheres and cylinders, the polymer volume fraction in the hydrophilic nanophase of lamellae, \( \varphi_A^{shell} \), also decreases as the \( \frac{3}{2} \)-power of the product of the degree of ionization of the hydrophilic units times the number of hydrophilic units in one arm in the unit cell, with the latter being proportional to 1 minus the mol fraction of the hydrophobic units. This would imply that the degree of swelling in water for the hydrophilic nanophase of lamellae (which is the inverse of the corresponding polymer volume fraction) increases as the \( \frac{3}{2} \)-power of the product of the degree of ionization of the hydrophilic units times the number of hydrophilic units in one arm in the unit cell (equation (E6)). This predicted dependence of the degrees of swelling in water for the hydrophilic nanophase of lamellae on the degree of ionization of the hydrophilic units is qualitatively confirmed in Figure 6(c) (points with degree of swelling values just below 10, whole range of degree of ionization, from 0.001 to 0.10).
However, Figure 6(b) shows that the above predicted dependence of the degrees of swelling in water for the hydrophilic nanophase on the mol fraction of the hydrophobic units is not qualitatively confirmed for all values of the degree of ionization considered. In particular, for degrees of ionization from 0.001 to 0.03, the degrees of swelling in water slightly increase with the mol fraction of the hydrophobic units (behavior opposite to that predicted), while, for degrees of ionization of 0.04 and higher, the degrees of swelling in water present a shallow minimum, as the content in hydrophobic units increases (see Figures S19(a) and (b)). This counterintuitive behavior can be attributed to the great variation of the asymmetry ratio in the hydrophilic nanophase of lamellae, $\frac{l}{l_0}$, with the mol fraction of the hydrophobic units (Figure 8(b), whereas our approximate analytical solution assumed a constant value of the asymmetry ratio).

Figure S19. (a) Dependence of the degree of swelling of the hydrophilic nanophase in water for lamellae on the mol fraction of the hydrophobic units for different degrees of ionization (0.001-0.10 = 0.1-10%) of the hydrophilic units. (b) Magnification of the 0.04-0.10 (4-10%) degree of ionization region of (a). The values of the parameters used here were also the same as those used in Figure 3, and, in particular, $\varphi_0 = 0.2$, $\beta = 20$, $\chi_{A\text{-water}} = 0.45$, $\chi_{B\text{-oil}} = 0.45$, $\chi_{AB} = 2.0$, and $\eta + \tilde{c} = 240$.

Given equation (E42), the degrees of swelling in water for the hydrophilic nanophase of lamellae can be calculated as:

$$\text{DS}_{\text{lamellae}}^{\text{shell}} = \left[ \frac{3}{\left( \frac{l}{l_0} \right)^3 + 2\frac{l_0}{l}} \right]^{3/2} \left( \frac{2\eta + \frac{1}{2}}{\varphi_0} \right)^{3/2} $$ (E43)

For low degrees of ionization ($\iota = 0.001 - 0.03$), when the hydrophobe mol fraction increases, the asymmetry ratio for the hydrophilic nanophase of lamellae, $\frac{l}{l_0}$, decreases, whereas the asymmetry
ratio term, \( \left[ \frac{3}{(\frac{l}{l_0})^2 + 2\frac{l_0}{T}} \right]^{3/2} \), increases much faster than the hydrophilic term, \( \left( 2\eta + \frac{1}{2} \right)^{3/2} \), decreases.

As a result, the degrees of swelling in water of lamellae increase with the mol fraction of the hydrophobic units. On the other hand, for degrees of ionization of 0.04 and higher, when the hydrophobe mol fraction increases, a shallow minimum is observed for the degree of swelling in water for lamellae. This is due to the fact that, as the hydrophobe content increases, the hydrophilic term, \( \left( 2\eta + \frac{1}{2} \right)^{3/2} \), initially prevails, leading to a small reduction in \( D_{S_{\text{shell}}} \) (\( \eta \) decreases), whereas for even higher hydrophobe contents, the asymmetry ratio term, \( \left[ \frac{3}{(\frac{l}{l_0})^2 + 2\frac{l_0}{T}} \right]^{3/2} \), takes over.

In summary, under conditions that do not favor swelling in water, i.e., low degrees of ionization and high mol fractions of the hydrophobic units, the asymmetry ratio term is the dominant one resulting in a swelling behavior opposite to the one normally anticipated.

Comparing equation (E42) for lamellae with equation (E24) for cylinders, these are essentially identical, each bearing the corresponding asymmetry ratio term, \( \left[ \frac{3}{(\frac{l}{l_0})^2 + 2\frac{l_0}{T}} \right]^{3/2} \) and \( \left[ \frac{3}{(\frac{H}{l_0})^2 + 2\frac{l_0}{T}} \right]^{3/2} \), respectively. Considering these two expressions, the reduction factor of the \( D_{S_{\text{shell}}} \) value upon a cylinder to lamella transition may be calculated as the ratio of the former divided by the latter.

vi. Hydrophobic nanophase of lamellae:

In the case of the hydrophobic nanophase of lamellae, Table S3 shows that the dominant first derivatives are those of the Gibbs free energy of mixing in the core and the interfacial Gibbs free energy, as was also the case for the hydrophobic nanophases of spheres and cylinders:

\[
\frac{\partial}{\partial \varphi_B} (\Delta G_{\text{mixing, core}}) + \frac{\partial}{\partial \varphi_B} (\Delta G_{\text{interfacial}}) \approx 0 \tag{E44}
\]

Considering for simplicity that the asymmetry ratio in the hydrophobic nanophase of lamellae, \( \frac{h}{h_0} \), is approximately constant (Figures 8(d) – (f); although nearly independent of the degree of ionization, the \( \frac{h}{h_0} \) values are strongly dependent on hydrophobe content; overall range of values
from 1.75 to 4.26), differentiation of equations (T1.3) and (T1.17) with respect to \( \varphi_{B}^{core} \), and substitution of the resulting partial derivatives into equation (E44), yields:

\[
-\beta \zeta \left[ X_{B-oil} + \frac{1}{(\varphi_{B}^{core})^2} \ln(1 - \varphi_{B}^{core}) + \frac{1}{\varphi_{B}^{core}} \right] - 2 \frac{h_0}{\gamma} \left( \frac{X_{AB}}{6} \right)^{1/2} \left[ (\beta \zeta)^2 \varphi_0 \right]^{1/3} \frac{1}{(\varphi_{B}^{core})^2} \approx 0 \quad (E45)
\]

Applying a Taylor’s series expansion to the second term in brackets in equation (E45) for \( \varphi_{B}^{core} \ll 1 \) leads to:

\[
(\beta \zeta)^{1/3} \left[ X_{B-oil} - \frac{1}{2} \varphi_{B}^{core} \right] - 2 \frac{h_0}{\gamma} \left( \frac{X_{AB}}{6} \right)^{1/2} \varphi_0 \frac{1}{3} \frac{1}{(\varphi_{B}^{core})^2} \approx 0 \quad (E46)
\]

Considering that the higher-order term \( \left( \varphi_{B}^{core} \right)^2 \) is much smaller than the immediately lower-order term, \( \varphi_{B}^{core} \), equation (E46) simplifies to:

\[
(\beta \zeta)^{1/3} \left( X_{B-oil} - \frac{1}{2} \varphi_{B}^{core} \right) + 2 \frac{h_0}{\gamma} \left( \frac{X_{AB}}{6} \right)^{1/2} \varphi_0 \frac{1}{3} \approx 0 \quad (E47)
\]

Rearranging terms leads to:

\[
(\beta \zeta)^{1/3} \left( \varphi_{B}^{core} \right)^2 \left( X_{B-oil} - \frac{1}{2} \varphi_{B}^{core} \right) + 2 \frac{h_0}{\gamma} \left( \frac{X_{AB}}{6} \right)^{1/2} \left[ \frac{\varphi_0}{(\beta \zeta)} \right]^{1/3} \approx 0 \quad (E48)
\]

\[
\Rightarrow \left( X_{B-oil} - \frac{1}{2} \right) \left( \varphi_{B}^{core} \right)^2 - \frac{1}{3} (\varphi_{B}^{core})^3 + 2 \frac{h_0}{\gamma} \left( \frac{X_{AB}}{6} \right)^{1/2} \left[ \frac{\varphi_0}{(\beta \zeta)} \right]^{1/3} \approx 0 \quad (E49)
\]

\[
\Rightarrow (\varphi_{B}^{core})^3 - 3 \left( X_{B-oil} - \frac{1}{2} \right) \left( \varphi_{B}^{core} \right)^2 - 6 \frac{h_0}{\gamma} \left( \frac{X_{AB}}{6} \right)^{1/2} \left[ \frac{\varphi_0}{(\beta \zeta)} \right]^{1/3} \approx 0 \quad (E50)
\]

Setting \( x = \varphi_{B}^{core} \), \( A = -3 \left( X_{B-oil} - \frac{1}{2} \right) \), and \( B = -6 \frac{h_0}{\gamma} \left( \frac{X_{AB}}{6} \right)^{1/2} \left[ \frac{\varphi_0}{(\beta \zeta)} \right]^{1/3} \), we obtain:

\[
x^3 + Ax^2 + B \approx 0 \quad (E51)
\]

Solving cubic equation (E51) gives: \(^1\)

\[
x \approx \sqrt[3]{\left( \frac{-A^3}{27} - \frac{B}{2} \right) + \sqrt{\left( \frac{-A^3}{27} - \frac{B}{2} \right)^2 + \left( \frac{-A^2}{9} \right)^3} + \frac{3}{2} \left[ \frac{-A^2}{27} - \frac{B}{2} \right] - \sqrt{\left( \frac{-A^3}{27} - \frac{B}{2} \right)^2 + \left( \frac{-A^2}{9} \right)^3} - \frac{A}{3} \quad (E52)
\]
Setting \(-\frac{A^3}{27} = e, \left(-\frac{A^2}{9}\right)^3 = f\), and \(\frac{A}{3} = g\) results in:

\[
x = \varphi_{B\text{core}}^c \cong 3 \sqrt{\left(\frac{e - \frac{B}{2}\right)}{2}} + \sqrt{\left(\frac{e - \frac{B}{2}\right)^2 + f} + 3 \sqrt{\left(\frac{e - \frac{B}{2}}{2}\right) - \sqrt{\left(\frac{e - \frac{B}{2}\right)^2 + f - g}}}
\] (E53)

Equation (E53) can be used to calculate various values of \(\varphi_{B\text{core}}^c\) for the range of values of \(\zeta\) for which lamellae prevail. The various values of \(\zeta\) were used to calculate the corresponding values of \(B\), which also appear in Table S4. For the calculations, constant values of \(e\), \(f\), and \(g\) were employed since the value of \(A\) was constant for the present system.

Table S4. Calculation of the polymer volume fraction in the hydrophobic nanophase for 0.40, 0.50, 0.60, and 0.70 mol fractions of the hydrophobic units and a constant value of the asymmetry ratio in the hydrophobic nanophase of lamellae.

| \(\zeta\) | \(B\left(\frac{\eta}{\eta_0} = 3.005\right)\) | \(A\) | \(e\) | \(f\) | \(g\) | \(x = \varphi_{B\text{core}}^c\) | \(DS_{\text{core}}\) |
|---|---|---|---|---|---|---|---|
| 96 | -0.054 | 0.15 | -1.2500 \times 10^{-4} | -1.5625 \times 10^{-8} | 0.050 | 0.3340 | 2.9939 |
| 120 | -0.050 | | | | | 0.3246 | 3.0809 |
| 144 | -0.047 | | | | | 0.3172 | 3.1528 |
| 168 | -0.045 | | | | | 0.3121 | 3.2044 |

Table S4 suggests that an increase in the value of \(\zeta\), and, therefore, in the mol fraction of the hydrophobic units, leads to a reduction in the polymer volume fraction in the hydrophobic nanophase and, consequently, to an increase in the degree of swelling in oil for the hydrophobic nanophase of lamellae (\(DS_{\text{core}}\) is the inverse of \(\varphi_{B\text{core}}^c\)). However, Figure 6(e) shows that the degrees of swelling in oil slightly decrease with the mol fraction of the hydrophobic units (behavior opposite to that predicted). As in the case of the hydrophilic nanophase of lamellae, this counterintuitive behavior of the degrees of swelling in oil of lamellae may again be attributed to the asymmetry ratio term. Since the swelling in oil is somewhat lower than that in water, in the present region of the phase diagram, the asymmetry ratio term is the dominant factor for the whole range of degrees of ionization considered (Figure S20).
**Figure S20.** Dependence of the degree of swelling of the hydrophobic nanophase in oil of lamellae and that of the asymmetry ratio within the hydrophobic nanophase in oil of lamellae on the mol fraction of the hydrophobic units for a 0.04 degree of ionization of the hydrophilic units. The values of the parameters used here were also the same as those used in Figure 3, and, in particular, $\phi_0 = 0.2$, $\beta = 20$, $\chi_{A-\text{water}} = 0.45$, $\chi_{B-\text{oil}} = 0.45$, $\chi_{AB} = 2.0$, and $\eta + \zeta = 240$.

As the first derivative of the electrostatic Gibbs free energy in the hydrophilic nanophase with respect to the polymer volume fraction in oil was zero, the degree of ionization of the hydrophilic units does not appear at all in the calculation of the polymer volume fraction in the hydrophobic nanophase of lamellae. This would imply that the degree of swelling in oil of lamellae should be independent of the degree of ionization of the hydrophilic units. However, Figure 6(f) shows a slight increase in the degree of swelling in oil for the hydrophobic nanophase of lamellae as the degree of ionization of the hydrophilic units increases. This apparently counterintuitive result is attributed to the asymmetry ratio of the hydrophobic nanophase in lamellae, $\frac{h}{h_0}$, which slightly varies (decreases) with the degree of ionization of the hydrophilic units (Figure 8(f)), thereby indirectly correlating the degree of swelling in oil for the hydrophobic nanophase to the degree of ionization of the hydrophilic units in the aqueous nanophase.

**Reference**

1. Spiegel, M. R. *Mathematical Handbook of Formulas and Tables*; McGraw-Hill, Inc.: NY, USA, 1968; p 32.