The isotopic effect in self-assembly of amphiphilic block copolymers: the role of hydrogen bonds

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Supplementary material

Numerical method

The numerical solution of the minimization of the free energy functional is obtained by discretization of the radial coordinate into parallel spherical layers of thickness δ. Define the ith spherical layer as the region between $(i-1)\delta \le r < i\delta$. The packing constraint in discrete form for layer i becomes

$$\frac{N}{V(i)}\underset{\alpha}{\Re} P(\alpha)v_{eo}(\alpha,i) + \frac{N}{V(i)}\underset{\alpha}{\Re} P(\alpha)v_{po}(\alpha,i) + \phi_w(i) = 1 \qquad \text{(S1)}$$

V(i) is the volume of the spherical layer between *(i-1)δ* and *iδ*.
The pdf of the pluronic chain is given by

$$P(\alpha) = \frac{V(\alpha,i)}{q} {}_{i=1}^{i_{MAX}} \exp\{-\beta\pi(i)[v_{eo}(\alpha,i) + v_{po}(\alpha,i)]$$

$$-2[n_{eo}(\alpha,i)\ln(1-x_{eo}(i)) + n_{po}(\alpha,i)\ln(1-x_{po}(i))] \qquad \text{(S2)}$$

$$-[\frac{\chi_{eo-w}}{v_w}v_{eo}(\alpha,i)\phi_w(i) + \frac{\chi_{po-w}}{v_w}v_{po}(\alpha,i)\phi_w(i) + \frac{\chi_{eo-po}}{v_w}v_{eo}(\alpha,i)\langle\phi_{po}(i)\rangle + \frac{\chi_{eo-po}}{v_w}v_{po}(\alpha,i)\langle\phi_{eo}(i)\rangle]\}$$

The volume fraction of water is

$$\phi_w(i) = \exp[\beta\mu_w - \beta\pi(i)v_w - \chi_{eo-w}\langle\phi_{eo}(i)\rangle - \chi_{po-w}\langle\phi_{po}(i)\rangle - 2(\ln x_w(i) - \ln 2\rho_w(i)v_w - \beta\Delta F_w)] \quad \text{(S3)}$$

The fractions of different hydrogen bonds are

$$\ln x_w(i) - \ln(1-x_w(i)) - \beta\Delta F_w = \ln[1 - x_w(i) - \frac{x_{eo}(i)\rho_{eo}(i)}{\rho_w(i)} - \frac{x_{po}(i)\rho_{po}(i)}{\rho_w(i)}] + \ln 2\rho_w(i)v_w \quad \text{(S4)}$$

$$\ln x_{eo}(i) - \ln(1-x_{eo}(i)) - \beta\Delta F_{eo} = \ln[1 - x_w(i) - \frac{x_{eo}(i)\rho_{eo}(i)}{\rho_w(i)} - \frac{x_{po}(i)\rho_{po}(i)}{\rho_w(i)}] + \ln 2\rho_w(i)v_w \quad \text{(S5)}$$

$$\ln x_{po}(i) - \ln(1-x_{po}(i)) - \beta\Delta F_{po} = \ln[1 - x_w(i) - \frac{x_{eo}(i)\rho_{eo}(i)}{\rho_w(i)} - \frac{x_{po}(i)\rho_{po}(i)}{\rho_w(i)}] + \ln 2\rho_w(i)v_w \quad \text{(S6)}$$

Substituting eqs (S2)-(S6) into the constraint eq. (S1) results in a set of coupled nonlinear equations for the lateral pressure fields and that together with the self-consistent equations for the average volume fractions of the PEO and PPO, Eq (2) in the text, are solved by standard numerical methods.

The chain model that we employ to generate the chain conformations is a three-state RIS model. We generate one configuration with the middle point at the position of r=0, and then translate it for 10 times with different random positions within $r \quad [0,R](R = i_{\max}\delta)$. The total number of configurations is 10^6 for all the calculations. The spherical layer thickness is $\delta = 0.2nm$. Each EO segment and PO segment occupies three layers due to $r_{eo} = 0.25nm$ and $r_{po} = 0.28nm$.

Free energy for mixed solvents

In the case of mixtures of solvent we need to consider all the possible combinations of hydrogen bond pairs, as well as the fact that when D_2O and H_2O are mixed there is isotope exchange and we also find HDO molecules. Therefore, the total free energy will include all the appropriate mixing terms, the different hydrogen bond pairs possibilities as well as the vdw type of interactions between the different types of solvents and the different types of polymer segments. The generalization of the free energy for the case of solvent mixtures is then given by

$$\beta F_{hb} = \int_0^R 4\pi r^2 2\rho_{eo}(r)[x_{eoh}(r)\ln x_{eoh}(r) + x_{eod}(r)\ln x_{eod}(r) - x_{eoh}(r)\beta\Delta F_{eoh}$$

$$-x_{eod}(r)\beta\Delta F_{eod} + (1 - x_{eoh}(r) - x_{eod}(r))\ln(1 - x_{eoh}(r) - x_{eod}(r))]dr$$

$$+\int_0^R 4\pi r^2 2\rho_{po}(r)[x_{poh}(r)\ln x_{poh}(r) + x_{pod}(r)\ln x_{pod}(r) - x_{poh}(r)\beta\Delta F_{poh}$$

$$-x_{pod}(r)\beta\Delta F_{pod} + (1 - x_{poh}(r) - x_{pod}(r))\ln(1 - x_{poh}(r) - x_{pod}(r))]dr$$

$$+\int_0^R 4\pi r^2 2\rho_{h2o}(r)[x_{hh}(r)\ln x_{hh}(r) + x_{hd}(r)\ln x_{hd}(r) - x_{hh}(r)\beta\Delta F_{hh}$$

$$-x_{hd}(r)\beta\Delta F_{hd} + (1 - x_{hh}(r) - x_{hd}(r))\ln(1 - x_{hh}(r) - x_{hd}(r))]dr$$

$$+\int_0^R 4\pi r^2 2\rho_{d2o}(r)[x_{dh}(r)\ln x_{dh}(r) + x_{dd}(r)\ln x_{dd}(r) - x_{dh}(r)\beta\Delta F_{dh}$$

$$-x_{dd}(r)\beta\Delta F_{dd} + (1 - x_{dh}(r) - x_{dd}(r))\ln(1 - x_{dh}(r) - x_{dd}(r))]dr$$

$$+\int_0^R 4\pi r^2 2\rho_{h2o}(r)(1 - x_{hh}(r) - \frac{x_{eoh}(r)\rho_{eo}(r)}{\rho_{h2o}(r)} - \frac{x_{poh}(r)\rho_{po}(r)}{\rho_{h2o}(r)} - \frac{x_{dh}(r)\rho_{d2o}(r)}{\rho_{h2o}(r)})$$

$$\propto\ln(1 - x_{hh}(r) - \frac{x_{eoh}(r)\rho_{eo}(r)}{\rho_{h2o}(r)} - \frac{x_{poh}(r)\rho_{po}(r)}{\rho_{h2o}(r)} - \frac{x_{dh}(r)\rho_{d2o}(r)}{\rho_{h2o}(r)})dr$$

$$+\int_0^R 4\pi r^2 2\rho_{d2o}(r)(1-x_{dd}(r)-\frac{x_{eod}(r)\rho_{eo}(r)}{\rho_{d2o}(r)}-\frac{x_{pod}(r)\rho_{po}(r)}{\rho_{d2o}(r)}-\frac{x_{hd}(r)\rho_{h2o}(r)}{\rho_{d2o}(r)})$$

$$\times\ln(1-x_{dd}(r)-\frac{x_{eod}(r)\rho_{eo}(r)}{\rho_{d2o}(r)}-\frac{x_{pod}(r)\rho_{po}(r)}{\rho_{d2o}(r)}-\frac{x_{hd}(r)\rho_{h2o}(r)}{\rho_{d2o}(r)})dr$$

$$-\int_0^R 4\pi r^2(2\rho_{eo}(r)x_{eoh}(r)+2\rho_{po}(r)x_{poh}(r)+2\rho_{h2o}(r)x_{hh}(r)+2\rho_{d2o}(r)x_{dh}(r))\ln\frac{2\rho_{h2o}(r)v_w}{e}dr$$

$$-\int_0^R 4\pi r^2(2\rho_{eo}(r)x_{eod}(r)+2\rho_{po}(r)x_{pod}(r)+2\rho_{h2o}(r)x_{hd}(r)+2\rho_{d2o}(r)x_{dd}(r))\ln\frac{2\rho_{d2o}(r)v_w}{e}dr$$

$$+\int_0^R 4\pi r^2\beta\pi(r)(\phi_{eo}(r)+\phi_{po}(r)+\phi_{h2o}(r)+\phi_{d2o}(r))dr \quad +\int_0^R 4\pi r^2\beta\lambda(\phi_{h2o}(r)-\phi_{d2o}(r))dr$$

where $x_{eoh}(r)$ is the fraction of eo-h hydrogen bonds at r, $x_{eod}(r)$ is the fraction of eo-d hydrogen bonds at r, $x_{poh}(r)$ is the fraction of po-h hydrogen bonds at r, $x_{pod}(r)$ is the fraction of po-d hydrogen bonds at r, $x_{hh}(r)$ is the fraction of oh-h hydrogen bonds at r, $x_{hd}(r)$ is the fraction of oh-d hydrogen bonds at r, $x_{dh}(r)$ is the fraction of od-h hydrogen bonds at r and $x_{dd}(r)$ is the fraction of od-d hydrogen bonds at r.

Note that the free energy explicitly considers the fact that in mixtures of D_2O and H_2O there is proton-deutereum exchange and therefore one needs to explicitly include DHO, which

Parameters:

$$\Delta F_{eoh}=\Delta E_{eoh}-\Delta S_{eoh}=\frac{2000}{T}+\ln(\frac{1-\cos(\pi/8.35)}{2})$$

$$\Delta F_{eoh}=\Delta F_{poh}=\Delta F_{eod}=\Delta F_{pod}$$

$$\Delta F_{hh}=\Delta E_{hh}-\Delta S_{hh}=\frac{1800}{T}+\ln(\frac{1-\cos(\pi/4.75)}{2})$$

$$\Delta F_{dd}=\Delta E_{hh}\times 1.05-\Delta S_{hh}=\frac{1800}{T}\times 1.05+\ln(\frac{1-\cos(\pi/4.75)}{2})$$

$$\Delta F_{dh}=\Delta E_{hh}\times 1.02-\Delta S_{hh}=\frac{1800}{T}\times 1.02+\ln(\frac{1-\cos(\pi/4.75)}{2})$$

$$\Delta F_{hd}=\Delta F_{dh}$$