# **Electronic Supplementary Information:**

# Molecular dynamics simulations and PRISM theory study of solutions of nanoparticles and triblock copolymers with solvophobic end blocks

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#### S.A. Cluster determination



**Figure S1.** Determination of connectivity criteria parameters. (a) and (c) B block centers of mass radial distribution function for  $B_6$ -b- $A_{12}$ -b- $B_6$  chains for volume fractions of  $\eta = 0.100$  (panel a), and 0.025 (panel c). The dashed line denotes a coordination threshold of 5.0*d*. (b) and (d) Nearest neighbor distributions for a coordination threshold of 5.0*d* for  $\eta = 0.100$  (panel a), and 0.025 (panel c). The dashed line denotes the number of nearest neighbors of 13 (panel b) and 8 (panel d).

Given the topological separation of solvophobic B blocks in BAB-BCP, we analyze the clustering of solvophobic ends. Two solvophobic ends are part of the same cluster if their centers of mass are below a coordination threshold of  $R_{\text{cut}} = 5.0d$  and if their number of nearest neighbors, i.e. the number of chains with B block centers of mass within the coordination threshold, is above a value of 8 for  $\eta = 0.025$  and 13 for  $\eta = 0.100$ . In Figures S1a and S1c we show the B block centers of mass radial distribution function,  $g_{\text{BB,COM}}(r)$  for *B*6 chains for  $\varepsilon_{\text{BB}} = 0.4$  and  $\varepsilon_{\text{BB}} = 1.3$  at volume fractions of  $\eta = 0.100$  and  $\eta = 0.025$ ,

respectively. Centers of mass radial distribution functions show that a coordination threshold of 5.0*d* captures the coordination hole for  $\varepsilon_{BB} = 0.4$ , where the system is fluid, as well as the first shell of neighbors (the first peak in  $g_{BB,COM}(r)$ ) for  $\varepsilon_{BB} = 1.3$ , where the micellar cores are formed for both volume fractions explored. In Figures S1b and S1d we show neighbor distributions for a coordination threshold of 5.0*d* for the same conditions shown in Figures S1a and S1c, respectively. In Figure S1b, the nearest neighbor distribution for fluid-like configurations at  $\varepsilon_{BB} = 0.4$  shows non-zero values up to a number of neighbors of 13, which is taken as the threshold for minimum number of neighbors for a pair of solvophobic ends to be considered to be part of the same cluster for  $\eta = 0.100$ . In Figure S1d, the nearest neighbor distributions for fluid-like configurations at  $\varepsilon_{BB} = 0.4$  shows non-zero values up to a number of neighbors of 8, which is taken as the threshold for minimum number of neighbors for a pair of solvophobic ends to be considered to be part of the same cluster for  $\eta = 0.100$ . In Figure S1d, the nearest neighbor distributions for fluid-like configurations at  $\varepsilon_{BB} = 0.4$  shows non-zero values up to a number of neighbors of 8, which is taken as the threshold for minimum number of neighbors for a pair of solvophobic ends to be considered to be part of the same cluster for  $\eta = 0.025$ .

The rationale behind the criteria stems from the necessity to differentiate between chains in fluidlike environments (with a small number of neighbors) and aggregated or micellar environments. The nearest neighbor distributions shown in Figures S1b and S1d show that the threshold number of neighbors determined form distributions at  $\varepsilon_{BB} = 0.4$  does is lower than the lowest non-zero value in the nearest neighbor distribution at high  $\varepsilon_{BB} = 1.3$ .

The parameters used for *B*6 chains we use for *B*3 and *B*9 chains, as the considerations explained above hold for the different polymers explored in this work.



### S.B. Identification of unimer-to-micelle solvophobicity

**Figure S2.** Identification of unimer-to-micelle transition solvophobicity. (a) individual (type I) and connected (type II) micellar core density,  $\rho_{clus}$ , as function of solvophobicity,  $\varepsilon_{BB}$ . (b) average number of solvophobic ends in a micellar core,  $\langle N_{clus} \rangle$ , as function of  $\varepsilon_{BB}$ . (c-g) distribution of number of solvophobic ends per micellar core,  $P(N_{clus})$ , at  $\varepsilon_{BB} = 0.8$  (panel c), 0.85 (panel d), 0.9 (panel e), 1.0 (panel f), and 1.2 (panel g).

As we describe in the main manuscript, we use the distribution of number of solvophobic ends,

 $P(N_{\text{clus}})$  as a way to determine the unimer-to-micelle transition solvophobicity. In Figure S2 we present results for *B*6 polymer at  $\eta = 0.025$ . As a function of  $\varepsilon_{\text{BB}}$  we identify type I and type II clusters, calculate the concentration of both types of cluster in Figure S2a, the average number of solvophobic ends in micellar cores in Figure S2b, and plot  $P(N_{\text{clus}})$  for different  $\varepsilon_{\text{BB}}$  in Figure S2c-g. The unimer-to-micelle transition conditions are identified as the condition where  $P(N_{\text{clus}})$  shows two distinct peaks: the unimer peak at the lowest  $N_{\text{clus}}$  values, and the micellar core peak. We note that the onset of distinction of the two peaks in  $P(N_{\text{clus}})$  occurs at the peak value of  $\rho_{\text{clus}}^{-1}$  vs.  $\varepsilon_{\text{BB}}$ , namely  $\varepsilon_{\text{BB}} = 0.9$ . This observation is presented here for *B*6 chains, but holds for *B*3 and *B*9 chains at the range of conditions we explore in this work.

#### S.C. Additional PRISM theory calculations at low solvophobicity for BAB-BCPs without NPs

As stated in the main manuscript, in Figure S3 we present the  $g_{\alpha\gamma}(r)$  results for BCP sequences and compositions analogous to Figure 2 but at lower solvophobicity  $\varepsilon_{BB}=0.1$  to demonstrate better agreement between PRISM and MD as  $\varepsilon_{BB}$  decreases.



**Figure S3.** Intermolecular correlation function,  $g_{\alpha\gamma}(r)$ , from MD simulations (symbols) and from PRISM theory (lines) at two volume fractions,  $\eta$ =0.100 (top) and  $\eta$ =0.025 (bottom), for **B<sub>3</sub>-b-A<sub>18</sub>-b-B<sub>3</sub>** (blue squares), **B<sub>6</sub>-b-A<sub>12</sub>-b-B<sub>6</sub>** (violet diamonds), and **B<sub>9</sub>-b-A<sub>6</sub>-b-B<sub>9</sub>** (black triangles). Each subsequent g(r) curve is shifted vertically by 0.8 for clarity purpose. All results are shown at constant solvophobicity  $\varepsilon_{\rm BB}$ =0.1.



**Figure S4.** Static A-A (top) and B-B (bottom) partial structure factors from PRISM theory (lines) are compared with the results from MD simulations with small simulation box (filled symbols) and large simulation box (open symbols). The results are shown for  $B_3$ -b-A<sub>18</sub>-b-B<sub>3</sub> (left),  $B_6$ -b-A<sub>12</sub>-b-B<sub>6</sub> (center), and  $B_9$ -b-A<sub>6</sub>-b-B<sub>9</sub> (right) at  $\varepsilon_{BB} = 0.45$  and  $\eta = 0.100$ .

In Figures S4 and S5 we illustrate the effect of simulation box size on agreement between PRISM and MD where we directly compare the S(k) from PRISM with results from two sets of MD simulations, one with smaller simulation box and one with larger simulation box (quadrupled number of chains). The error bar at lowest wave vector decreases dramatically as we go from small system to large system in MD, proving that the accuracy of low wave vector results in MD is heavily dependent on the system size.



**Figure S5.** Same as Figure S4 but at  $\eta = 0.025$ 

Figure S6 (next page) shows representative snapshots from MD simulations to illustrate that at low solvophobicity the structure is disordered.



**Figure S6.** MD simulations snapshots for  $B_3$ -b-A<sub>18</sub>-b-B<sub>3</sub> (left),  $B_6$ -b-A<sub>12</sub>-b-B<sub>6</sub> (center), and  $B_9$ -b-A<sub>6</sub>-b-B<sub>9</sub> (right) at two volume fractions,  $\eta$ =0.100 (top two rows) and  $\eta$ =0.025 (bottom two rows). The results are shown for large and small simulation boxes at  $\varepsilon_{BB} = 0.45$ .

#### S.D. Additional MD results for BAB-BCPs without NPs

In this section, we include: a zoomed-in version of Figure 5a to highlight the high  $\varepsilon_{BB}$  behavior of  $\rho_{clus}^{II}$  in Figure S7, the end-to-end distance for *B*3, *B*6, and *B*9 polymers at  $\eta = 0.025$  in Figure S8, and high-resolution simulation renderings of *B*9 polymer at high  $\varepsilon_{BB}$  in Figure S9.



Figure S7. Type II cluster density for  $B_3$ -b- $A_{18}$ -b- $B_3$  chains at  $\eta = 0.100$  (zoomed in data from Figure 5a).



Figure S8. End-to-end distance distribution for chain conformations for  $B_3$ -b-A<sub>18</sub>-b-B<sub>3</sub> (a),  $B_6$ -b-A<sub>12</sub>-b-B<sub>6</sub> (b),  $B_9$ -b- $A_6$ -b-B<sub>9</sub> (c) from MD simulations at  $\eta$ =0.025.



**Figure S9.** MD simulation snapshots for  $B_9$ -b- $A_6$ -b- $B_9$  at high solvophobicity ( $\varepsilon_{BB}$ =0.94) at  $\eta$ =0.100 (left) and  $\eta$ =0.025 (right). Snapshots are shown from MD with small simulation box (top) and large simulation box (bottom).

#### S.E. Additional PRISM theory and MD simulation comparisons for BAB-BCPs without NPs

In this section, we present in Figure S10 micellization behavior for A6 and A3 polymer to compare results of ABA and BAB BCPs shown in main paper, and in Figure S11 S(k) for B3 chains calculated from PRISM theory analogous to results shown in Figures 6 and 7 in the main manuscript.



**Figure S10.** Micellization behavior for  $A_3$ -**b**- $B_{18}$ -**b**- $A_3$  chains (panels a and b) and  $A_6$ -**b**- $B_{12}$ -**b**- $A_6$  chains (panels c and d) at varying solvophobicity. Data are shown for two volume fractions,  $\eta = 0.100$  (panels a and c) and  $\eta = 0.025$  (panels b and d). Cluster density is shown in the top parts of each panel. Average number of chains in a micellar core is shown in the bottom parts of each panel.

For A3 and A6 polymers there is no distinction between type I and type II clusters as there is no

way for the type I micellar cores to be connected to form type II clusters; there is no possibility of bridges to form between micellar cores.



**Figure S11.** Static A-A (left) and B-B (center) partial structure factors for  $B_3$ -b-A<sub>18</sub>-b-B<sub>3</sub> chains at  $\eta$ =0.100 (a, b) and  $\eta$ =0.025 (d, e) from PRISM theory at range of low  $\varepsilon_{BB}$ . The snapshots from MD simulations at high  $\varepsilon_{BB}$  are also shown (c, f).

#### S.F. Additional PRISM theory calculations at low solvophobicity for BAB-BCPs with NPs

In this section, we present results that were not included in the main text for direct comparison of PRISM theory and MD simulations in real and reciprocal spaces. In Figure S12 we present direct comparison of intermolecular correlation function for B6 as in Figure 8 but at low NP affinity. Analogous results for B3 and B9 systems at various affinities are presented in Figures S13-S17. In Figures S18-S23 we present results for direct comparison of S(k) from PRISM and MD for B3, B6, B9 systems at various NP affinities and two volume fractions ( $\eta$ =0.1, 0.025).



**Figure S12.** Intermolecular correlation function,  $g_{\alpha\gamma}(r)$ , for *B*<sub>6</sub>-*b*-*A***<sub>12</sub>-<b>***b*-*B*<sub>6</sub> chains with symmetric low nanoparticle affinity  $\varepsilon_{AC} = \varepsilon_{BC} = 0.25$ . Results are shown from MD simulations (symbols) and from PRISM theory (lines) at two volume fractions,  $\eta = 0.100$  and  $\eta = 0.025$ , and two nanoparticle contents,  $\phi_C = 0.10$  and  $\phi_C = 0.25$ , Each subsequent g(r) curve is shifted vertically by 0.8 for clarity purpose. All results are shown at constant  $\varepsilon_{BB} = 0.45$ .



Figure S13. Same as Figure S12 but for  $B_3$ -b- $A_{18}$ -b- $B_3$  chains with symmetric low nanoparticle affinity  $\varepsilon_{AC} = \varepsilon_{BC} = 0.25$ .



**Figure S14.** Same as Figure S12 but for  $B_3$ -b- $A_{18}$ -b- $B_3$  chains with symmetric intermediate nanoparticle affinity  $\varepsilon_{AC} = \varepsilon_{BC} = 0.5$ .



**Figure S15.** Same as Figure S12 but for  $B_3$ -b- $A_{18}$ -b- $B_3$  chains with symmetric high nanoparticle affinity  $\varepsilon_{AC} = \varepsilon_{BC} = 1.0$ . Comparison for  $\eta = 0.025$  and  $\phi_C = 0.25$  is not shown because at these parameters PRISM does not converge to a numerical solution.



**Figure S16.** Same as Figure S12 but for  $B_9$ -*b*- $A_6$ -*b*- $B_9$  chains with symmetric low nanoparticle affinity  $\epsilon_{AC} = \epsilon_{BC} = 0.25$ .



**Figure S17.** Same as Figure S12 but for  $B_9$ -*b*- $A_6$ -*b*- $B_9$  chains with symmetric intermediate nanoparticle affinity  $\epsilon_{AC} = \epsilon_{BC} = 0.5$ .



**Figure S18.** Static A-A (top), B-B (center), and C-C (bottom) partial structure factors from PRISM (lines) and MD (symbols) for  $B_6$ -b- $A_{12}$ -b- $B_6$  chains at  $\eta = 0.100$  and  $\varepsilon_{BB} = 0.45$ . Results are shown for two nanoparticle volume fractions,  $\phi_C = 0.10$  (dashed lines, squares) and  $\phi_C = 0.25$  (solid lines, triangles). In the left and right panels two symmetric nanoparticle affinities are shown,  $\varepsilon_{AC} = \varepsilon_{BC} = 0.25$ ; 0.50 correspondingly.



**Figure S19.** Same as Figure S18 but at  $\eta = 0.100$ .



**Figure S20.** Static A-A (top), B-B (center), and C-C (bottom) partial structure factors from PRISM (lines) and MD (symbols) for  $B_3$ -b- $A_{18}$ -b- $B_3$  chains at  $\eta = 0.100$  and  $\varepsilon_{BB} = 0.45$ . Results are shown for two nanoparticle volume fractions,  $\phi_C = 0.10$  (dashed lines, squares) and  $\phi_C = 0.25$  (dotted lines, triangles). Results for various symmetric and asymmetric affinities are shown, where  $\varepsilon_{AC}$  and  $\varepsilon_{BC}$  are 0.25 or 0.50.



Figure S21. Same as Figure 20 but for  $B_3$ -b- $A_{18}$ -b- $B_3$  chains at  $\eta = 0.025$ .



Figure S22. Same as Figure 20 but for  $B_9$ -b- $A_6$ -b- $B_9$  chains at  $\eta = 0.100$ .



Figure S23. Same as Figure 20 but for  $B_9$ -b- $A_6$ -b- $B_9$  chains at  $\eta = 0.025$ .

#### S.G. Additional MD results for BAB-BCPs with NPs

In this section, we present in Figures S24-S26 the micellization behavior of *B*3 and *B*6 polymer at  $\eta = 0.10$  and  $\phi_C = 0.1$ , analogous to results shown in Figure 9. We also show in Figure S27 simulation renderings for *B*9 polymer at  $\eta = 0.025$ ,  $\phi_C = 0.1$  for the whole range of  $\varepsilon_{AC}$  and  $\varepsilon_{BC}$ .



**Figure S24.** Micellization behavior for  $B_6$ -b- $A_{12}$ -b- $B_6$  chains and nanoparticles as  $\eta = 0.100$ , nanoparticle loading of  $\phi_C = 0.10$ , and nanoparticle affinity to the solvophobic block  $\varepsilon_{BC} = 0.5$  as a function of solvophobicity,  $\varepsilon_{BB}$ . Panel a shows results for  $\varepsilon_{AC} = 0.25$ . Panel b shows results for  $\varepsilon_{AC} = 0.50$ . Panel c shows results for  $\varepsilon_{AC} = 1.00$ . Plots from top to bottom show: cluster concentration,  $\rho_{clus}$ , for type I (individual micellar cores, open triangles) and type II (connected micellar cores, filled circles) clusters; average number of solvophobic ends in a micellar core,  $\langle N_{clus} \rangle$ ; nanoparticle uptake,  $f_{tot}$ ; average number of nanoparticles in A-rich region (red circles), B-rich region (green triangles), and A-B interface (black squares); fraction of loops (magenta circles), bridges (cyan triangles), and free ends (grey squares).



**Figure S25.** Micellization behavior for  $B_3$ -b- $A_{18}$ -b- $B_3$  chains and nanoparticles as  $\eta = 0.100$ , nanoparticle loading of  $\phi_C = 0.10$ , and nanoparticle affinity to the solvophilic block  $\varepsilon_{AC} = 0.5$  as a function of solvophobicity,  $\varepsilon_{BB}$ . Panel a shows results for  $\varepsilon_{BC} = 0.25$ . Panel b shows results for  $\varepsilon_{BC} = 0.50$ . Panel c shows results for  $\varepsilon_{BC} = 1.00$ . Plots from top to bottom follow Figure S24.



Figure S26. Same as Figure S24 for *B*<sub>3</sub>-*b*-*A*<sub>18</sub>-*b*-*B*<sub>3</sub> chains.



**Figure S27.** Snapshots for  $B_9$ -b- $A_6$ -b- $B_9$  chains at  $\varepsilon_{BB} = 1.0$ ,  $\eta = 0.025$ , and  $\phi_C = 0.1$  with NPs at different affinities,  $\varepsilon_{AC}$ ,  $\varepsilon_{BC}$ .

#### S.H. Additional PRISM theory and MD simulation comparisons for BAB-BCPs with NPs

In this section, we present: results analogous to those from Figure 11 but at intermediate NP affinity (Figure S28), and results analogous to those from Figure 12 but at low NP affinity (Figure S29).



**Figure S28.** Static A-A (a) and B-B (b) partial structure factors for  $B_6$ -b- $A_{12}$ -b- $B_6$  at  $\eta$ =0.100 from PRISM theory at a range of low  $\varepsilon_{BB}$  with nanoparticle concentration of  $\phi_C$ =0.1. Results are analogous to Figure 11 but for intermediate symmetric nanoparticle affinity,  $\varepsilon_{AC} = \varepsilon_{BC} = 0.5$ . (c) Type I and type II cluster density,  $\rho_{clus}$ , as function of  $\varepsilon_{BB}$ . Corresponding snapshots from MD simulations at high  $\varepsilon_{BB}$  are also shown: full simulation box snapshot without NPs shown for clarity (left), and detail on a micellar core (right).



**Figure S29.** Static A-A (a) and B-B (b) partial structure factors for  $B_9$ -b- $A_6$ -b- $B_9$  chains at  $\eta = 0.025$  from PRISM theory at range of low  $\varepsilon_{BB}$  with nanoparticle concentration of  $\phi_C=0.1$ . Results are analogous to Figure 12 but for low symmetric nanoparticle affinity,  $\varepsilon_{AC} = \varepsilon_{BC} = 0.5$  (c) Type I and type II cluster density,  $\rho_{clus}$ , as function of  $\varepsilon_{BB}$ . Corresponding snapshots from MD simulations at high  $\varepsilon_{BB}$  are also shown: full simulation box snapshot with NPs (left) and without NPs (right).

# S.I. Illustration of how to map our generic implicit solvent bead-spring polymer model to specific polymer and solvents chemistries

Here we show how one could map our generic implicit solvent model for symmetric BAPB-BCP,  $B_6$ -b- $A_{12}$ -b- $B_6$ , to a specific amphiphilic block copolymer solution. We choose one specific system of PSb-PEO-b-PS (poly(styrene)-block-poly(ethylene oxide)-block-poly(styrene)) in THF-water mixture. PEO is relatively more hydrophilic than PS, and while THF and water are good solvents for PEO, only THF is a good solvent for PS (due to its hydrophobicity). In this scenario having the BCP initially in THF and gradually adding water would be equivalent to making the solvent gradually poor for PS, i.e. increasing solvophobicity of PS block.

First, we equate the size of a single polymer B bead to the Kuhn segment length of PS ( $\Box$  = 1.8nm), which corresponds to 9.5 PS repeat units<sup>1</sup>. 12 B block beads thus correspond to 12 x 9.5 = 114 PS repeat units. Since the size of the A polymer bead and B polymer bead is the same, we then calculate the number of PEO repeat units that fit in a 1.8nm size bead. To calculate this, we assume ideal chain scaling (N ~ R<sup>0.5</sup>) and use the relationship 6.7 x (1.8 / 1.1)<sup>2</sup> = 17.9 repeat units, where 1.1nm is the Kuhn segment length of PEO, and 6.7 is the number of PEO repeat units in the Kuhn segment. Therefore, 12 A beads corresponds to 17.9 x 12 = 216 PEO repeat units. Thus, roughly a  $B_6$ -b- $A_{12}$ -b- $B_6$  chain corresponds to PS<sub>57</sub>-b-PEO<sub>216</sub>-b-PS<sub>57</sub>.

Next, we map the solvophobicity (Lennard Jones potential strength),  $\varepsilon_{BB}$ , to solvent composition in the mixture of THF and water. To tie  $\varepsilon_{BB}$  to solvents we use the Hildebrand solubility theory, specifically we use the Hildebrand-Scott equation<sup>2</sup> that relates Hildebrand solubility parameters to the solvophobic block (PS)-solvent Flory interaction parameter,  $\chi_{PS-S}$ , as

$$\chi_{PS-S} = \frac{\left(v_{m,PS}v_{m,S}\right)^{0.5} \left(\delta_{PS} - \delta_{S}\right)^{2}}{RT} , \qquad \forall \text{MERGEFORMAT S3}$$

where  $v_{m,X}$  is the molar volume of species *X*, with *X* being either the polymer (*PS*) or the solvent (*S*),  $\delta_X$  is the Hildebrand solubility parameter for species *X*, *R* is the ideal gas constant, and *T* is the absolute temperature. For a water(W)-THF(T) solvent mixture the interaction parameter for PS-solvent mixture becomes

$$\chi_{PS-S} = \frac{\left(v_{m,PS} \left[yv_{m,W}^{-1} + (1-y)v_{m,T}^{-1}\right]^{-1}\right)^{0.5} \left(\delta_{PS} - \left[y\delta_{W} + (1-y)\delta_{T}\right]\right)^{2}}{RT}, \text{ MERGEFORMAT S4}$$

where y is the volume fraction of water in the solvent mixture. The molar volume and solubility parameters for water and THF are explicitly stated. We then equate the interaction parameter with the formal definition by Flory for a solvophobic polymer, B, and solvent,  $\chi_{BS}$ , as

$$\chi_{BS} = z \Big[ -\varepsilon_{BS} + 0.5 \left( \varepsilon_{BB} + \varepsilon_{SS} \right) \Big], \qquad \forall \text{MERGEFORMAT S5}$$

with  $\varepsilon_{ij}$  being the Lennard Jones interaction strength used in the present work, and z being the coordination number. Since we treat our solvent mixture implicitly, the only non-zero interaction parameter in equation S5 is  $\varepsilon_{BB}$ . Setting  $\chi_{BS}$  and  $\chi_{PS-S}$  equal results in

$$\varepsilon_{BB} = \frac{2}{z} \frac{\left( v_{m,PS} \left[ y v_{m,W}^{-1} + (1-y) v_{m,T}^{-1} \right]^{-1} \right)^{0.5} \left( \delta_{PS} - \left[ y \delta_{W} + (1-y) \delta_{T} \right] \right)^{2}}{RT} \quad \land * \text{ MERGEFORMAT S6}$$

The following figure shows the value of  $\varepsilon_{BB}$  that corresponds to a solvent mixture composition y.



**Figure S30.** Mapping model solvophobicity  $\varepsilon_{BB}$  for a PS<sub>57</sub>-*b*-PEO<sub>216</sub>-*b*-PS<sub>57</sub> block copolymer in a water-THF mixture as function of the water volume fraction, *y*. Different possible values of the coordination number, *z*, are shown for comparison.

The different lines shown correspond to possible values of the coordination number, z; in principle, one can obtain z from the first peak in the B-B radial distribution function. For illustration of the effect of z on the above mapping we show the data for z=10 to 16. This shows that  $PS_{57}$ -b-PEO<sub>216</sub>-b-PS<sub>57</sub> solution with the solvent composition ranging from pure THF to increasing volume fraction of water in THF-water mixture corresponds to our model copolymer going through a staged increase in solvophobicity in the simulations.

Disclaimer: This passage above is also present in the supplementary information for another paper entitled "Molecular dynamics simulations and PRISM theory study of solutions of nanoparticles and triblock copolymers with solvophobic end blocks" which at the time of writing this note was under review at the Journal of Chemical and Engineering Data. We are not able to refer to that paper here as we do not have a citation at the moment.

#### S.J. Protocol for parameter space screening with PRISM theory

As an example, we present a protocol that one could use to address the question: "For a given block copolymer, what nanoparticle design and nanoparticle concentration leads to microphase separated states or avoids macrophase separation at high solvophobicity?"

Step 1) define the *parameter space* to explore (for example, increasing values of NP affinity to A and B block and increasing values of NP concentration in the solution)

Step 2) for each value in the *parameter space*, do the following:

- a. perform PRISM calculations and calculate S(k) with increasing solvophobicity ( $\varepsilon_{BB}$ )
- b. identify tendency either to micro- or macro-phase separate according to the following criteria:

- if microphase ( $k^* \neq 0$ ) peak grows with  $\varepsilon_{BB}$  more strongly than the macrophase ( $k \rightarrow 0$ ) peak, then conclude that the system has a tendency to microphase separate at high  $\varepsilon_{BB}$ 

- if microphase peak is absent or the macrophase peak grows more strongly with  $\varepsilon_{BB}$  than the microphase peak does, then conclude that the system has a tendency to macrophase separate at high  $\varepsilon_{BB}$ 

Step 3) based on step 2 results, mark the "critical" values in *parameter space* that would answer the design question "For a given block copolymer, what nanoparticle design and nanoparticle concentration leads to microphase separated states or avoids macrophase separation at high solvophobicity?". These "critical" values in the *parameter space* are just predictions based on PRISM theory.

Step 4) run MD simulations near and at the "critical" values of *parameter space* 

- a) test/validate PRISM predictions
- b) obtain more detailed structural information than PRISM theory provides

We note that the above protocol would work only at conditions where micro- and macro-phase peaks are distinguishable and present in the structure factors, for example, at higher total volume fractions ( $\eta = 0.100$ ).

## References

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